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Toxicity of building materials

Edited by F. Pacheco-Torgal, S. Jalali and A. Fucic

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Toxicity of building materials

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Introduction: types of potentially toxic building materials

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The construction industry is one of the largest and most active sectors in the world and in the next decades will keep on growing at a very fast pace. For instance, China will need 40 billion square meters of combined residential and commercial floor space over the next 20 years – equivalent to adding one New York every two years (Pacheco-Torgal and Jalali, 2011). Buildings have high energy consumption and account for a significant part of carbon dioxide emissions. Since 1930 more than 100,000 new chemical compounds have been developed, and insufficient information exists for health assessments of 95% of chemicals that are used to a significant extent in construction products (Pacheco-Torgal and Jalali, 2011). Moreover, many buildings currently suffer from problems related to excessive moisture with mold formation, or present low humidity levels, giving rise to respiratory diseases. A recent investigation (Fisk *et al.*, 2011) shows that improving indoor environmental quality in the stock of US office buildings would generate a potential annual economic benefit of approximately \$20 billion. So it is rather obvious that the indoor air quality must be put in the center of eco-efficient building design.

Many books have been written about building materials, covering their physical and mechanical properties and more recently their durability. But the focus has now shifted to their environmental performance, in order to answer the question of how building materials can contribute to the eco-efficiency of the construction industry. Reducing the toxicity of building materials is part of the ‘greening’ process, and avoiding the use of materials that release pollutants is one of the principles of eco-efficient construction. Indoor pollutants include volatile organic compounds (VOC), formaldehyde, semi-volatile organic compounds (SVOC), radon, NO_x, asbestos and nanoparticles. Homes contain a large amount of chemicals and heavy metals that either contaminate indoor air or pollute tap water, thus causing several health-related problems such as asthma, itchiness, burning eyes, skin irritations or rashes, nose and throat irritation, nausea, headaches, dizziness, fatigue, reproductive impairment, disruption of the endocrine system,

cancer, impaired child development and birth defects, and immune system suppression. However, and contrary to general belief, buildings usually contain many toxic materials, some of which even comply with legal regulations. For instance, the threshold for lead in drinking water was reduced from 300 µg/l in the 1970s to 50 µg/l in the 1980s and 25 µg/l in the 1990s and will be reduced again to just 10 µg/l from 25 December 2013. The reason for that long delay has much to do with the fact that the replacement of lead pipes just in Europe would cost around 200,000 million euros. Recent recommendations towards the reduction of indoor air exchange rate to minimize energy consumption contribute to increasing the effects of hazardous substances on human health. Ironically, this means that the economic savings in energy bills will be offset by much more expensive medical bills.

On 9 March 2011 the European Union approved Regulation (EU) 305/2011, the Construction Products Regulation (CPR), that replaced Directive 89/106/EEC, already amended by Directive 1993/68/EEC, known as the Construction Products Directive (CPD). The new CPR was published in the *Official Journal of the European Union* (OJEU) on 4 April 2011. In accordance with Article 68, the CPR entered into force on 24 April, the 20th day following its publication in the OJEU. This includes Articles 1 and 2, 29 to 35, 39 to 55, 64, 67 and 68, and Annex IV. However, Articles 3 to 28, 36 to 38, 56 to 63, 65 and 66, as well as Annexes I, II, III and V, shall apply from 1 July 2013. This means that only by 1 July 2013 will the CPR will be fully enforced without the requirement for any national legislation. Being a Regulation means that it *'shall have general application. It shall be binding in its entirety and directly applicable in all Member States'* while the CPD was *'binding, as to the result to be achieved, upon each Member State to which it is addressed, but shall leave to the national authorities the choice of form and methods'*. This also means that the UK, Ireland and Sweden will then lose their 'opt-out' clause employed under the CPD period.

When comparing the basic requirements of the CPR and CPD, one can see that the CPR has a new requirement, no. 7 (Sustainable use of natural resources), and also that no. 3 (Hygiene, health and the environment) and no. 4 (Safety and accessibility in use) have been refined. This means that a new and more environmentally friendly approach will determine the manufacture of construction products. A crucial aspect of the new regulation relates to the information regarding hazardous substances. While the CPD considered only a very limited range of dangerous substances, e.g. formaldehyde and pentachlorophenol, the CPR links this subject to Regulation (EC) No. 1907/2006 (Registration, Evaluation, Authorisation and Restriction of Chemicals – REACH Regulation). The introduction of the CPR states that *'the specific need for information on the content of hazardous substances in construction products should be further investigated'*. Besides, Article 67 mentions that *'By 25 April 2014, the Commission shall*

assess the specific need for information on the content of hazardous substances in construction products and consider the possible extension of the information obligation provided for in Article 6(5) to other substances’.

Toxicity aspects have been a field outside the boundaries of the construction industry, with its practitioners belonging to the realm of health professionals. That is why architects, civil engineers and other professionals involved in the construction industry have so little knowledge about this area. This means that a new approach to building materials is needed that is capable of solving this complex problem – a more integrative approach that is capable of joining the best efforts of construction practitioners and health specialists. Bringing together important contributions from several international experts from very different specialties, this book is intended to fill the aforementioned gap by analyzing several aspects related to the toxicity of building materials.

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The main health hazards from building materials

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Abstract: Social awareness of the need to preserve natural resources and energy efficiency politics has enabled a framework for the definition of sustainable building which can be realized by the introduction of new building materials and technologies. However, in some cases the use of new building materials and technologies can create microenvironments that may represent a complex radiochemical setting that could pose a potential threat to the health of its occupants. This chapter gives an overview of the health risks related to (a) increased indoor radioactivity due to new methodologies that enable increased use of industrial waste as building materials (fly ash) and the increased use of granite or zircon, (b) emissions of nanoparticles used in building materials, (c) emissions of concrete additives, and (d) chemical agents in finishing coatings and furnishing.

Key words: health risk, indoor environment, ionizing radiation, nanoparticle, volatile organic compound, complex exposure, healthy building certificate.

1.1 Introduction

The outdoor and indoor living environment, occupational exposure and lifestyle may have diverse effects on human health depending on age and gender. Segments of living conditions may be modified on an individual basis, such as diet, smoking or drinking habits, while the major contaminants in air, food or water can only be improved through political will, economic conditions and public awareness which is largely based on the educational level of the parties involved. Development of sustainable buildings is a significant step forward, from both economic and ecological viewpoints, though the microenvironment created in such living surroundings may present a complex radiochemical setting that could pose a potential threat to the health of its occupants. As the modern lifestyle involves spending the majority of time indoors (70–80%) (Farrow *et al.*, 1997), indoor air quality significantly contributes to overall public health.

The construction sector is rapidly developing and over the past two decades many new materials and technologies that improve the economy and energy efficiency of buildings have been introduced. Although reliable data on the health effects of volatile organic compounds, formaldehyde, asbestos and flame retardants have been collected, legislation and control of their application and emissions remain unsatisfactory. Small children and

pregnant women deserve special concern, as foetuses and small children have specific metabolism, bioaccumulation and elimination of xenobiotics. Knowledge of the health effects of dangerous gases, particles and fibres that may be emitted at room temperature from certain building furnishing materials and construction products containing radionuclides that increase indoor exposure to ionizing radiation, has to be applied by all parties involved in construction of buildings and available to their occupants. Xenobiotics in indoor air may be irritants, immunodisturbing agents, endocrine disruptors and/or carcinogens. Their mechanisms interact and overlap, provoking various diseases based on genomic and non-genomic mechanisms which are both age- and gender-specific.

1.2 Radiation

Exposure to ionizing radiation is one of the basic mechanisms of evolution. However, the nuclear weapons industry and testing, nuclear war and nuclear accidents have increased ionizing radiation in the living environment to levels to which life on Earth has not adapted during evolution.

For decades, exposure to radiation was associated with genome damage and cancer development. Recent research on the mechanisms by which ionizing radiation may increase health risk has also been focused on cardiovascular diseases and immunological disturbances. There are special cases of very complex mechanisms involved in the biological effects of radioactive isotopes which may not only be a source of radiation but, as heavy metals, such as uranium, can express also hormonal, oestrogen-like activity.

In addition to naturally occurring radon, which may be present in high concentrations in some areas depending on geological characteristics and the soil, radioisotopes from fly ash, certain granites and zirconium minerals are major sources of exposure to ionizing radiation in the indoor environment.

Indoor exposure to radon is correlated with an increased risk of lung cancer, with an excess relative risk of 10% per 100 Bq m⁻³ (Fucic *et al.*, 2010). Causality between radon exposure and lung cancer is known for uranium miners (Vacquier *et al.*, 2011). Genome damage caused by densely ionizing radiation of radon represents a complex interaction of DNA damage and repair capacity that can be exhausted during tissue regeneration of lung cells. Such new mechanisms explain disturbance of cell division control beyond the threshold dose rate (Madas and Balásházy, 2011). Other biological mechanisms may also appear after exposure to radon (alpha particles), such as the bystander effect (in which unirradiated cells exhibit irradiated effects as a result of signals received from nearby irradiated cells) and adaptive response (when exposure to low doses of ionizing radiation

can make cells more resistant to later radiation exposure). These mechanisms result in different lung cancer aetiology between uranium miners and residential, low-dose exposures (Balásházy *et al.*, 2009). At the individual level, the risk of radon-induced lung cancer is much higher among current cigarette smokers than among lifelong non-smokers. This was illustrated in a pooled analysis of European residential radon studies (Darby *et al.*, 2005). For lifelong non-smokers, it was estimated that living in a home with an indoor radon concentration of 0, 100 or 800 Bq m⁻³ was associated with a risk of lung cancer death (at the age of 75) of 4, 5 or 10 per 1000 persons, respectively. However, for cigarette smokers, each of these risks is substantially greater, namely 100, 120 and 220 per 1000 persons. For former smokers, the radon-related risks are substantially lower than for those who continue to smoke, though they remain considerably higher than the risks for lifelong non-smokers. This confirms the cost-effectiveness of indoor radon control of future policies, especially if complemented with policies for smoking reduction (Groves-Kirkby *et al.*, 2011). It should be pointed out that cigarettes are not only a major source of numerous chemical agents, the majority of which are carcinogens, but also of radioactivity, as cigarettes also contain polonium and radioactive lead (Desideri *et al.*, 2007). Additionally, the risk of combined exposure to smoking and indoor radon is gender-specific (Truta-Popa *et al.*, 2010). There are also inter-individual differences in radiosensitivity to radon, since for carriers of certain types of the detoxification enzyme glutathione-S-transferase, the risk of lung cancer is three times higher (Bonner *et al.*, 2006).

Regulation and control of radon levels in occupational and living environments has been ongoing for several decades and reflects the knowledge to date. The current opinion given by international bodies such as ICRP, WHO and IAEA agrees on an upper limit for residential indoor radon of 200–300 Bq m⁻³, which will be incorporated in their new documents in a short time (Bochicchio, 2011). However, the control of indoor radon levels and recommended remediation pertain to naturally occurring indoor radon, while there is no regulation that would control the incorporation of fly ash in concrete which may also significantly increase indoor radon levels.

Children are of special concern (Fucic *et al.*, 2008; Holland *et al.*, 2011) as they are more radiosensitive due to the higher cell division rate and underdeveloped xenobiotic elimination system. For this reason, radon-caused genome damage is especially dangerous in children (Bilban and Vaupotič, 2001). As radon is nine times heavier than air, small children who breathe air closer to the floor and at a higher frequency per body mass than adults (Gratas-Delamarche *et al.*, 1993) are more exposed than adults. It could be thus suggested that recommendations for radon level in kindergartens and schools should be lower than in other buildings and the general population should be educated in how to protect children at home.

Fly ash as a by-product of thermal plants concentrates radionuclides such as uranium (^{235}U , ^{238}U), radium (^{226}Ra), thorium (^{232}Th), lead (^{210}Pb), polonium (^{210}Po) and potassium (^{40}K) by a factor of 20 to 25 compared to levels in the original peat (European Commission, RP-112, 1999). Globally, about 280 million tonnes of coal ash is produced annually, of which 40 million tonnes is used in the production of bricks, cement, road stabilizers, road fill, and asphalt mix (UNSCEAR, 2006). From such sources, individual doses of radiation exposure to the general public can be about 100 μSv per year (Menon *et al.*, 2003). Cement is successfully replaced with fly ash in concrete in the range from 10% to 80%. As fly ash is a hazardous waste containing toxic metals and radionuclides, its use as a construction material is encouraged as a form of waste management. Thus, fly ash has become a zero-cost raw building material that would otherwise require special waste management (Nisnevich *et al.*, 2008) due to its physical and chemical characteristics. Similarly, the use of red mud, bauxite and clay additives should be strictly controlled from a radiation protection aspect due to the possible ^{226}Ra and ^{232}Th activity, especially when applied in the brick industry (Somlai *et al.*, 2008).

Health effects related to exposure to uranium and thorium from fly ash are much more complex than in the case of indoor radon. As a heavy metal, uranium is a source of ionizing radiation, is highly toxic, teratogenic and embryotoxic, and has affinity to oestrogen receptors (endocrine disruption) (Bosque *et al.*, 1993; Raymond-Whish *et al.*, 2007).

Exposure to thorium is associated with pancreatic and lung cancer and respiratory diseases (Polednak *et al.*, 1983). As it is a heavy metal, it can accumulate in bones and may cause bone cancer (Rosemann *et al.*, 2006; Ottaviani and Jaffe, 2009). Like uranium, thorium probably has affinity for oestrogen receptors, although this biological mechanism has not been investigated. However, as both lung and pancreatic cancer are oestrogen related (Fucic *et al.*, 2010) such mechanism could be involved.

The emission of radionuclides from concrete depends on its ageing; however, studies have not been conducted regarding the emission of their decay products, especially thoron in concretes where 70% of cement is replaced with fly ash (Chambers *et al.*, 2011; Ramachandran, 2010).

A special concern is building waste which in the future will contain more radionuclides than ever before. It must also be stressed that in addition to radioactive isotopes, fly ash contains a number of other contaminants, mostly heavy metals. Emissions from ageing and microcracking concrete containing radioactive fly ash represent a mixture of radioisotopes, meaning that their biological effects also depend on their interaction. Current knowledge on the emissions of radionuclides from concrete is available from monitoring and experiments on concrete materials in nuclear facilities (Deissmann *et al.*, 2006).

Zircon (zirconium silicate) is a mineral often used as an opacifier and pigment in the production of ceramic tiles. Its high level of radioactivity is due to its specific crystal structure, which incorporates radium (^{226}Ra and ^{228}Ra), uranium and thorium. Radiation emissions from ceramic tiles are specific, as radon is locked up in the tile by a glass-like matrix during the vitrification process (Xinwei, 2004), making gamma radiation the basic radiation type. Fashion and floor heating systems have increased the coverage of floors in living rooms with tiles and granite, which can significantly increase exposure to ionizing radiation compared with just decades ago when tiles were typically applied only in kitchens and bathrooms. As the radioactivity of zircon and granite vary according to geological origin, in order to control levels of exposure, activities in the future should be focused on control of their radiation emissions and limitation of the upper mass of zircon in porcelain/ceramics and granite used in indoor ambient (Selby, 2007). As in the case of indoor radon, small children and toddlers are more exposed to radiation from tiles and granite by playing on the floor.

The biological effects of radiation, like other xenobiotics, should never be estimated alone without investigating their possible interaction at the level of different biological pathways. Of course, it is also important to stress that in indoor environments sources of non-ionizing radiation are also present, such as microwave ovens, cellphones and computers, whose effects should not be neglected.

1.3 Chemical carcinogens and endocrine disruptors

Humans are exposed to hundreds of chemicals in food, water and air. Some of these chemicals are transplacental and may cause significant health risks which can be expressed later in life. Indoor air, especially in new buildings due to emissions from walls and floors, may represent a mixture of chemicals. Risk assessment of possible health effects of such mixtures is required and should include assessment of their mechanisms as toxic, carcinogenic and endocrinic either individually or as a consequence of their interactions. The majority of cancer types are related to the levels of oestrogen receptor disturbances, and thus the biological effects of chemical agents are gender-related. As lung cancer is the most frequent cancer type that could be expected from indoor air exposure, it is important to know that lung cancer differs between women and men in levels of oestrogen receptors, and this also has an impact on therapy selection and the survival prognosis (Fucic *et al.*, 2010).

Chemical compounds in indoor air differ in the range of their preferential biological effects. New methods in xenobiotics research have dramatically changed our insight into the pathways involved in carcinogenesis. For example, formaldehyde was long described as a chemical that could cause

irritation and nasopharyngeal cancer by inducing cell division. However, it was recently shown that formaldehyde also has an impact on signalling pathways related to cancer, inflammatory response and endocrine system regulation (Rager *et al.*, 2011; Goldstein, 2011; Nielsen and Wolkoff, 2010). This also indicates that age differences in the biological response could be expected, as disturbance of the immunological system of an adult man could significantly differ from that in a small child whose immunological system is underdeveloped. Similar differences can be expected at the excretion level due to differences in metabolism and the rate of elimination between adults and children in whom, up to two years of age, the kidneys do not have the same clearance as in adults.

Volatile organic compounds (VOC) are a large group of chemicals used in finishing and furnishing. This is also a group of chemicals which is supported by the largest number of investigations on health effects. The highest levels of VOCs are present in new buildings and those with poor ventilation (Nielsen *et al.*, 2007). The timing of measurements of VOCs in buildings is of major significance, as the highest levels of emissions are present during the first few months after finishing and furnishing, though this can exceed more than a year (Xu *et al.*, 2009). As new flats and buildings are expected to be occupied by young couples, the most exposed subpopulation is therefore at the same time the most susceptible, i.e. pregnant women and children.

According to estimations the VOCs with highest indoor concentrations are toluene, xylene, styrene and 1,2,4-trimethylbenzene (Delgado-Saborit *et al.*, 2011). Despite general awareness of the need for efficient control of indoor air emissions, the unstandardized approach to their measurements and the fact that health effects have to be interpreted as a consequence of complex radiochemical exposure and not based solely on summarizing the causality of health effects of each agent make legislation articulation difficult. This indicates the need for serious remodelling of the current evaluation system. An additional problem is that the available data on health risks concerning exposure to the majority of VOCs are related to occupational exposure and experimental models with substantially higher concentrations than in the case of indoor air in residential buildings. It can be hypothesized that lower doses may cause different health effects than those described for high doses.

Toluene, benzene and xylene exposures have been associated with asthma, especially in children (Hulin *et al.*, 2010; Arif and Shah, 2007). In animal models toluene in low concentrations causes very complex airway inflammatory responses by modulating neuroimmune crosstalk (Shwe *et al.*, 2007). Toluene and benzene are usually present in indoor air as a mixture. Investigation of their effect showed that they act synergistically. After *in vitro* exposure to toluene the induced DNA damage was repaired within

24 h after the treatment; however, after exposure to a mixture of toluene and benzene an increase in the cytotoxic effect and DNA damage was detected without any further repair (Pariselli *et al.*, 2009). Benzene, as a known hematotoxicant and carcinogen, is shown to have more severe effects on those subjects with certain polymorphisms of immune genes (Shen *et al.*, 2011). However, it is interesting that as a transplacental agent it causes gender-related differences in liver metabolism in animal models (Badham *et al.*, 2010).

Styrene levels in indoor air, similar to benzene, toluene, ethylbenzene and xylenes, can originate from building material emissions and from cigarette smoke (Chambers *et al.*, 2011). As for other VOCs, the majority of data on styrene is available for males, due to the fact that most studies are performed on workers in industry. Therefore, there are insufficient data on effects of styrene on women, pregnant women and children. According to the Final Report on the Carcinogens Background Document for Styrene of the National Toxicology Program (2008), lymphohematopoietic and pancreatic cancers are associated with exposure to styrene. The same report summarizes a large number of studies on animal and cell models showing that styrene metabolites (styrene-7,8-oxide and 4-vinylphenol) are genotoxic. In experiments much higher doses are applied than those to which occupants can be exposed in buildings. Such high doses of styrene vapours can cause also eye and respiratory tract irritation and CNS depression. Sublethal doses are associated with maternal toxicity, foetotoxicity, skeletal and kidney abnormalities, decreases in birth weight and developmental delays. There are also studies outlining endocrine effects of styrene. In animal models styrene significantly decreases testosterone levels in male mice, thus pointing out the importance of investigating its possible effects on boys during prepuberty and puberty (Takao *et al.*, 2000).

It is also important to incorporate calculations of the transgenerational effects of VOCs in risk assessment. Very commonly glycol ether, 1-methoxy-2-propanol is shown in animal models to have an impact on three subsequent generations with regard to sex ratio, foetal loss and birth weight reduction after parental exposure (Lemazurier *et al.*, 2005).

The constant increase in respiratory problems such as asthma, allergy and rhinitis cannot be explained only by the genetic predisposition of sensitive subpopulations (Pearce and Douwes, 2006). According to recent findings, oestrogen seems to have a strong promoting effect on asthma, which explains its higher prevalence in adult women (Tantisira *et al.*, 2008; Shah *et al.*, 2010; Chen *et al.*, 2008). As a large number of VOCs are xenoestrogens, this may explain the described mechanisms in asthma etiology relating to exposure to VOCs.

Increased interest in the use of wood as a building material basically will not reduce indoor exposure to different chemicals. On the contrary, since

current agents for wood preservation are characterized by much deeper penetration into the wood structure than preceding compounds, they cause emissions over longer periods of time. An example is chromated copper arsenate (CCA) which is used as a potent wood preserver. Its application enables wood to last up to 40 years, making wood building material a new item of special waste if specific procedures for its detoxification are not conducted (McLean and Beveridge, 2001). This chemical agent represents a health risk, especially for small children and pregnant women, as the chromate VI present in CCA is toxic for the foetus, while arsenic has a strong impact on oestrogen receptors (Danielsson *et al.*, 1982; Apostoli and Catalani, 2011; Chatterjee and Chatterji, 2010; Bae-Jump *et al.*, 2008). Despite the fact that the US EPA prohibited its application for residential uses in 2003, due to the longevity of wood preserved with this chemical it will be present in living environments for decades. The US EPA has proposed alternatives for CCA such as copper azole, cyproconazole or crioconazole; however, all these compounds contain azoles which are aromatase inhibitors, i.e. endocrine disruptors that decrease the levels of oestrogen in living organisms and which are already in use as fungicides and in the treatment of breast cancer (Furet *et al.*, 1993; Trosken *et al.*, 2004).

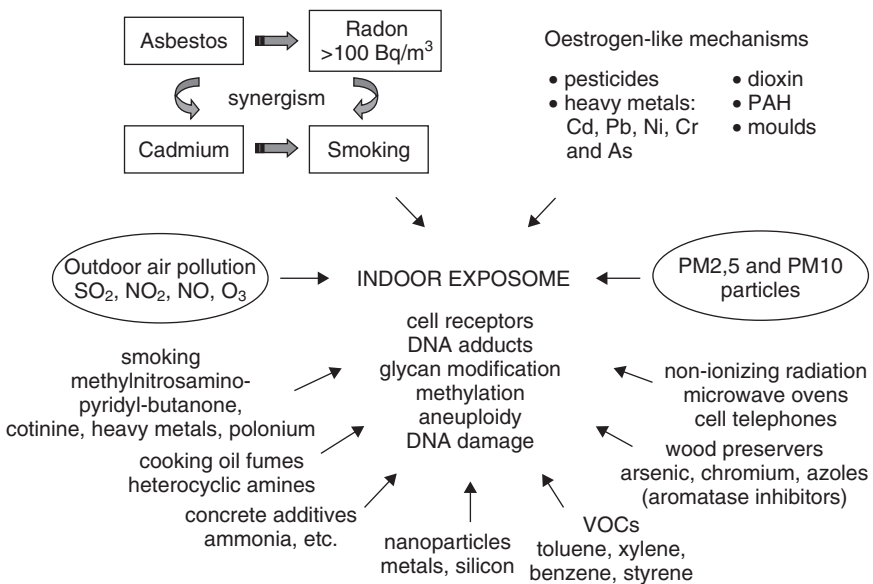
Tight-fitting windows and doors made of plastics may increase indoor humidity, creating excellent conditions for mould growth. In addition to causing respiratory problems, exposure to moulds should be evaluated with regard to its complex impact on endocrine imbalance. Mould produces various mycotoxins, some of which are also endocrine disruptors such as ochratoxin, zearalenone and aflatoxin (Jennings-Gee *et al.*, 2010; Tuomi *et al.*, 2000; Storvik *et al.*, 2011). Currently, there is insufficient research being performed on the levels of zearalenone, known to have oestrogen-like activity in buildings, despite the fact that the fungus *Fusarium* which produces it is one of the most common mould species in damp buildings (Saremi and Okhovvat, 2006; Jarvis and Miller, 2005; Daisey *et al.*, 2003). The mechanisms of endocrine disruption related to exposure to mould may be seen in the gender differences in the development of asthma caused by moulds (Meyer *et al.*, 2005). On the other hand, moulds are eliminated from the indoor environment using agents that are aromatase inhibitors, which disturb the synthesis of oestrogen in mould cell membranes, thereby halting their growth (Zarn *et al.*, 2003), though the same effect may also be caused in exposed humans.

Ammonia may cause respiratory problems, especially in vulnerable sub-populations such as those suffering from asthma. As a concrete additive in new residential buildings, it was shown that ammonia levels remained high during the entire first year after building was finished (Jarnstrom *et al.*, 2006). The levels of ammonia measured in such buildings (0.11 ppm) are recommended for preliminary remediation actions according to the US

Environmental Protection Agency (US EPA, 2003). The possibility of elimination of ammonia levels in indoor air by extra drying of concrete to which urea-based antifreeze substances are added is rarely applied (Bai *et al.*, 2006; Tuomainen *et al.*, 2003).

Flame retardants responsible for saving numerous human lives could be the cause of increased sterility of men and the incidence of testicular cancer in the Western world. Recently, one possible source of reproductive diseases in men is suggested to be the flame retardants tris(1,3-dichloro-2-propyl) phosphate (TDCPP) and triphenyl phosphate (TPP) (Meeker and Stapleton, 2010).

Data on the interaction of xenobiotics and effects of their mixtures are insufficient, as the basic scientific approach of the twentieth century was reductionism in which the causality between a single agent and disease was investigated. Currently, the approach taken is based on complexity which is possible with the introduction of new software and methods for multi-parametric analysis. The well-known synergism described for smoking, polyvinyl chloride and asbestos (Fucic *et al.*, 1990; National Toxicology Program: Asbestos, Report on Carcinogens, 2005) will soon be incorporated into large systems-biology schemes. Figure 1.1 presents known biological effects and health risks related to indoor environment exposure. The exposure of indoor air is a complex radiochemical system that soon will be



1.1 Known biological effects and health risks related to indoor environment exposure.

evaluated as a real-time module, thus allowing an estimation of the health risk according to age, gender and metabolic characteristics, with the option of introducing new data.

Exposure of the general population to a low-quality indoor environment in low-income countries is related to increased health risks; however, the sources of indoor air contamination differ from those in developed countries. Application of lead-based paints, asbestos, cooking over an open fire, poor ventilation and insecticides, combined with poor diet and hygiene, can be recognized as contributing to the increased number of respiratory diseases, cancer and inflammations. Heavy air pollution in such countries and the free market in building materials which are prohibited in the Western world will remain an issue in the coming decades, as the world economy unfortunately still exploits these markets as a relevant source of profit.

1.4 Nanoparticles

Due to their size and chemical content, the biological effects of nanoparticles (NP) should be evaluated as both physical and chemical agents. Alongside their complex physicochemical properties the different shape and size of NPs play a significant role in their toxic potency (Borm *et al.*, 2006). The main difference between natural and man-made NPs is in their chemical composition, unique surface chemistry and geometrical forms. Unlike natural NPs, which are mostly crystals or spheroids, artificial NPs may additionally have net and tube forms (Pacheco-Torgal and Jalali, 2011).

The health effects of NPs are more pronounced than fine particles with regard to the equivalent mass concentration. In evaluating the health risks of NPs their aggregation must also be considered as these vary in relation to their physicochemical properties (Soto *et al.*, 2005). Contrary to the controlled transport of metal ions in living organisms, there is no such mechanism for metal oxides NPs and they can enter the cell according to their solubility. Additionally, due to their large surface area, NPs adsorb heavy metals, polyaromatic hydrocarbons, quinolines, etc., and facilitate their incorporation in organisms, which is especially dangerous for the brain as NPs easily cross the blood–brain barrier (Kahru *et al.*, 2008).

There is no specific biomarker for measuring the level of exposure or effect of NPs on living organisms. Due to their dual nature as both physical and chemical agents, investigation of health effects after exposure to NPs is very demanding and requires investigation by multidisciplinary teams. Additionally, as certain NPs are metals which can also act as endocrine disruptors (metal oestrogens, e.g. aluminium) this makes elucidating their interaction with the living organism an even more challenging task.

Nanoparticles can be inhaled or ingested, while some cross the skin and placenta (Wu *et al.*, 2009, Vega-Villa *et al.*, 2008). When inhaled they can

enter the systemic circulation via the lungs and also enter the brain (Oberdörster *et al.*, 2004; Elder *et al.*, 2006; Rückerl *et al.*, 2007; Ferin *et al.*, 1992; Nemmar *et al.*, 2001). However, it is unknown how and by which dynamic NPs are eliminated from the body and whether there are age and gender differences in this process. The difference in the bioaccumulation of NPs in children can vary, as small children breathe more air than adults per body mass, and their lungs are still developing. Nanoparticles translocate to different organs after intake, though the time of translocation between organs is still not known (El-Ansary and Al-Daihan, 2009). However, the ability of NPs to enter different organs from the gastrointestinal tract has already been applied in pharmaceutical practice (El-Ansary and Al-Daihan, 2009; Balbus *et al.*, 2007). Different and conflicting results in the investigation of the distribution of NPs in mammals can be explained by the different experimental models applied, exposure measurements and types of NPs that can significantly change the biological response (Brown *et al.*, 2002; Mills *et al.*, 2006; Nemmar *et al.*, 2001). The ability of NPs to adsorb proteins, which will be used in new generations of drugs, shows that NPs may disturb signalling via receptors. This is of special concern if they are present during prenatal and postnatal development.

Pulmonary diseases related to inhaled nanoparticles seem to include reactive oxygen species (ROS) via the Fenton/Haber-Weiss reaction, deviations in mitochondrial function, inflammation and activation of cell death receptor pathways (Coultas and Strasser, 2000). The iron ion seems to play a critical role in these mechanisms. Genome damage caused by ROS produced by NPs is similar to that described for some chemicals and radiation.

Especially disturbing is the fact that NPs are transplacental agents (Oberdörster *et al.*, 2004; Hagens *et al.*, 2007), which may disturb brain development in the foetus (Takahashi *et al.*, 2010) by altering blood–brain integrity (Lockman *et al.*, 2004).

The most frequently applied NPs in building technology are TiO_2 , Al_2O_3 , Fe_2O_3 and SiO_2 (Pacheco-Torgal and Jalali, 2011). However, many new types of NPs are introduced each year following the needs of advanced technologies in building construction and aimed especially towards a better standard of living for occupants (Granqvist *et al.*, 2007).

Although silicosis (Thomas and Kelley, 2010) is a well-known disease related to exposure to silica fibres, the health risks related to silica NPs are unknown. Recent results show that long nanotubes have the same inflammatory effect as asbestos (Donaldson *et al.*, 2010). Similar in structure, nanocrystalline silica (SiO_2) has a more detrimental effect on the lungs than amorphous silica (Soto *et al.*, 2005). Available experimental studies show that silica NPs have specific routes of bioaccumulation. It has been shown that they may even cause production of ROS in the brain at very low levels,

changes in proinflammatory gene activity, genome damage and immunologic disturbances (Choi *et al.*, 2010; Grassian *et al.*, 2007; Gong *et al.*, 2010). Silica NPs in sizes from 20 nm to 80 nm, which are used as cement additives, cause cytotoxicity and oxidative stress in hepatic cells (Ye *et al.*, 2010). It is also interesting to note that NPs used in cancer radiotherapy enhance the effects of ionizing radiation (Berbeco *et al.*, 2010; Hamoudehm *et al.*, 2008). Experiments show that silica-based NPs increase production of ROS when they enter the brain, causing inflammation at very low concentrations (Choi *et al.*, 2010).

Titanium dioxide is frequently used in the production of paints, paper, and plastics, welding rod-coating material and cosmetics, as it was thought to have low toxicity (Hext *et al.*, 2005). Recent studies on rat lungs demonstrated that exposure to TiO_2 can produce differential pulmonary effects, based upon their composition and crystal structure (Warheit *et al.*, 2007). Due to the formation of ROS and inflammation, TiO_2 may cause genome damage and gene function disturbances. As a transplacental agent in animal models it causes genome damage in the foetus of exposed dams (Dunford *et al.*, 1997; Trouiller *et al.*, 2009; Halappanavar *et al.*, 2011). The significance of animal models in investigating the transdermal effect of TiO_2 is shown in a study in which TiO_2 did not penetrate through isolated porcine skin, but after 60 days of exposure through the skin of the ear in animals TiO_2 NPs were detected in the liver and brain. The most significant pathological changes were observed in skin and liver (Wu *et al.*, 2009). It has also been shown that the pulmonary toxicity of TiO_2 depends additionally on the changes of pH in the exposed tissues. Disturbances of pH differ and are related to a combination of TiO_2 particle size and concentration, and thus pH varies in range from 3.7 to 5.3 for NP sizes of 3–20 nm and at concentrations from 0.1 to 10 mg/mL (Li *et al.*, 2007).

Aluminium is a widely used toxic agent with several major pathways of carcinogenesis which likely include an impact on oestrogen receptors in the body. For Al_2O_3 NPs it has been shown that in addition to producing ROS they also disturb cell division and have a specific impact on genes involved in carcinogenesis (Dey *et al.*, 2008).

There is no evidence to date as to how the ageing process of buildings influences the emission of NPs into the air. The European Construction Industry Federation performed an evaluation of safety issues concerning the use of NPs in construction. The conclusion of this evaluation was that (a) the marketing and application of NPs will grow; (b) information on NP composition is generally lacking; and (c) as health risks for workers involved in building and for consumers are unknown, a precautionary approach is suggested (van Broekhuizen and van Broekhuizen, 2009).

Silica NPs and carbon nanotubes have been introduced in the production of cement mortars and NPs (Jo *et al.*, 2007; Nazari *et al.*, 2010; Morsy and

Aglan, 2007), in particular because they increase their quality when a higher percentage of fly ash is used (which also contains NPs) (Gilmour *et al.*, 2004; Chaipanich *et al.*, 2010). Application of NPs in concrete production clearly shows the need for precautionary measures, as they allow for more extensive use of fly ash which in turn increases the radioactivity of concrete. Consequently, a redefinition of building waste disposal is needed, as such building materials demand special handling similar to that required for asbestos or lead.

1.5 Conclusion and future trends

The development of building technologies is closely connected with the energy-saving demands of a growing population, significant waste issues and an economy that is attempting to be self-sustainable in balancing profit, social trends such as fashion, the need for a higher standard of living, and raising awareness of the irreversible destruction of nature. In such a social and economic environment, the construction sector is incorporating new technologies and materials which have brought a significant improvement in meeting all these demands but while also producing a new complex indoor radiochemical environment.

Living organisms have their own robustness of systems and pathways (repair, signalling adaptation, etc.) developed during evolution, which buffer the effects of variations in environmental conditions. By producing artificial microclimates in buildings which have practically no communication or exchange with the atmosphere (in the Western world very often exclusively via ventilation) the limits of achieving living homeostasis are exceeded. The health risks of indoor air cannot be analysed if isolated from other factors such as smoking habits, application of biocides, cleaning agents, air fresheners, candles, scented sticks (Singer *et al.*, 2006), occupational exposure of occupants, and the quality of the diet.

A decrease of environmental exposure to known carcinogens such as lead or asbestos in developing countries did not slow the increase in cancer incidence in adults and children. This can be attributed to the constant introduction of new xenobiotics. However, due to the long latency period for the development of some cancer types, such as mesothelioma caused by asbestos, elimination of agents from the living environment will show a reduction of cancer incidence only in the coming decades (Marinaccio *et al.*, 2012).

Studies evaluating the use of fly ash in the production of concrete and light concrete agree that such technology is favourable for both economic and environmental reasons. However, these technologies should be accompanied by adequate radiation protection measurements, such as regular radioactivity measurements of fly ash for each new delivery from thermal

plants, as radioactivity varies among coal sources (Nisnevich *et al.*, 2008; Kovler, 2009; Cevik *et al.*, 2007; Turhan *et al.*, 2011). Leaching of metals from concrete with a high percentage of fly ash is a matter for future research.

VOC levels could be controlled by issuing building use permits only after their levels due to the evaporation and ventilation processes in finished buildings drop to below those associated with health risks. However, data on the levels of VOCs in children and evaluations of their susceptibility are anecdotal and should be done in future (Adgate *et al.*, 2004; Delfino *et al.*, 2003). Tight-fitting windows decrease air exchange rates and lower the dilution of indoor air mass with ambient air, thus additionally increasing VOC levels. This phenomenon makes homes more isolated from the natural environment than ever before in human history. In the near future temperature, humidity, ion composition and the smell of indoor air may become a custom-made product, delivered to consumers via ventilation systems.

Nanoparticle measurement standardization must also be defined in the future, as this will enable the introduction of dose–response curves and possible threshold values for exposures related to health risks. As TiO₂ NPs are shown to increase accumulation of cadmium and other pollutants (Sun *et al.*, 2007; Zhang *et al.*, 2007) in the body, it is of great significance that the biological microenvironments in which NPs change their charge and other physicochemical properties be explored (Navarro *et al.*, 2008). It could be suggested that biomonitoring of the population exposed to NPs should follow the knowledge and experience of the pharmaceutical industry, as the potency of NPs is recognized in drug production.

Human society is not able to follow large amounts of scientific data and options aimed at improving living environments. This is why strong efforts should be made towards ensuring the interdisciplinarity, education of policymakers and more dynamic incorporation of available knowledge into the legislation.

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Plastic materials: polyvinyl chloride (PVC)

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Abstract: PVC is a ‘contested’ versatile material used in the construction industry. There is always a controversy about whether or not there are significant health risks associated with its use, because a number of toxic additives are involved, and hence there remains the question of whether the health risks of the use of PVC outweigh its many benefits. In the text, the applications of PVC in construction are reviewed and health concerns are briefly summarized. A brief discussion of the replacement possibilities is presented.

Key words: PVC, VCM, plasticizers, additives, safety.

2.1 Introduction

Polyvinyl chloride (PVC), or vinyl for short, or using the IUPAC name ‘chloroethane’ or ‘poly(chloroethanediyl)’, with 57% of mass by chlorine, is an ‘infrastructure thermoplastic’ material. PVC is one of the most important plastic materials used worldwide in various phases of the construction industry, such as pipes, fittings and gutters, window profiles and doors, ceiling tiles, various furniture and upholstery applications, coatings for electrical cables, etc., mainly because of its economy, in addition to its durability and ease of assembly. PVC is also a much used ‘commodity plastic’ in our everyday life, e.g. in clothing, synthetic leather, car seat covers, inflatable structures, etc. PVC with its predicted annual production of around 40 million tons (Ebner, 2009) is second only to polyethylene (PE), the number one commodity plastic. The global market for PVC is expected to continue to grow at about 3–5% per year, with the strongest demand predicted to be in Asia, e.g., China and India, and the EU representing about a fifth of the world market.

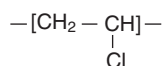
2.2 Polyvinyl chloride (PVC – CAS number: 9002-86-2)

PVC is a ‘contested’ versatile material, that is, there is a controversy about whether or not there are significant risks to human health associated with its use. Over its life cycle, a number of by-products and additives, most of which are known to be human toxicants, are involved with PVC materials and hence there remains the question of whether the health risks of PVC

use outweigh its many benefits. Controversy extends to both research findings and their interpretation, as well as to the regulatory policy. Green certifying boards have already been asked to award credit for buildings that reduce or eliminate PVC use. Government regulations for the use of PVC in the US and EU have been focused mostly on medical and consumer products, but not on building materials. While this review certainly will not intend to resolve these controversies, it is intended to outline the science relevant to understanding them for the use of PVC as a building material.

2.2.1 Production, structure and properties of PVC

PVC, with chemical formula C_2H_3Cl , is a vinyl polymer composed of repeating vinyl groups (ethenyls), having one hydrogen atom replaced by chlorine on alternate carbon atoms per repeat unit:



PVC production and processing consists of five major steps (Titow, 1984):

1. Ethylene (C_2H_4) and chlorine gas production
2. Vinyl chloride monomer (VCM) production
3. Polymerization of VCM into polymer
4. Formulation of polymer product with additives
5. Direct molding or end product processing.

VCM is polymerized into the polymer product by an exothermic free-radical reaction at 40–70°C in the liquid state under pressure (in batch reactors) with continual mixing of the ‘suspension’ to obtain a uniform particle size. After degassing, stripping, centrifuging and drying of the resulting slurry, it is sieved to obtain the powdered ‘suspension PVC’ product with sizes of 120–150 μm . There are other production methods for PVC as well, e.g. the ‘emulsion’ technique, which produces smaller sizes (e.g., 10 μm). Suspension and emulsion type PVCs have somewhat different properties and are used for different applications, suspension being the more commonly used. Normally, any PVC product is expected to have less than 1 ppm (parts per million) of monomer (VCM) content left unreacted:



PVC is a white, amorphous, odorless powder, which is stable under normal temperatures and pressures up to 70–80°C, after which it begins to decompose with evolution of hydrochloric acid (HCl) gas and discoloration (yellowing).

PVC was first made in 1872 by the German chemist Eugen Baumann, who did not apply for any patent. In 1912, the German chemist Fritz Klatte working for Greisheim-Electron, Germany, decided to try to react acetylene with HCl (which apparently produced the monomer VCM), and he left the product on the shelf, where it apparently polymerized over time by sunlight. Hence Klatte was the first inventor to receive a patent for PVC (in 1913), using mercuric chloride as a catalyst; this patent expired in 1925. This original method was widely used during the 1930s and 1940s, but has since been superseded by more economical advanced processes, at least in the Western hemisphere.

The importance of PVC and its use was not realized until 1926 when Waldo Semon, an American chemist working at B.F. Goodrich, invented PVC independently. Semon quickly understood that this new material would have a big potential to produce brand-new objects, and he first produced a shower curtain. Semon and B.F. Goodrich immediately patented PVC for the USA (Semon, 1926a, 1926b). Later, Semon tried to produce golf balls and shoe heels from PVC. A great many new uses for this wonderful waterproof material then followed, and PVC was a real success in the world.

Being a thermoplastic, PVC softens if heated and hardens as it cools; and it can be processed by the use of any conventional plastics processing techniques, such as extrusion (specifically for complex-shaped extrusion profiling for housing materials), calendering (wide films and sheets such as agricultural films and PVC leather), injection and blow molding (except injection molding, because its melt viscosity is high). PVC materials have rather low densities, hence they offer relatively low material costs on a volume basis and hence are cost-effective. PVC is one of the major low-cost, high-volume commodity resins used today due to its economy and the excellent chemical and mechanical properties it provides.

Two main types of PVC resins are produced and processed:

1. Rigid PVC resins (unmodified PVC, uPVC), which have considerable strength and hardness; they are processed mainly by extrusion or molding to make pipes and conduits, fittings, window profiles, roof tiles, fences and various rigid automotive parts. Rigid PVC sheets can be welded easily to produce tanks, trays and troughs.
2. Flexible PVC resins, which contain various additives, mainly plasticizers, usually in high proportions to make them soft and flexible and heat and UV stable.

When plasticizers are added, flexible plasticized PVC (pPVC) is obtained with rubber-like elasticity, high tensile and fatigue strengths, which can be used specifically for industrial hoses, gaskets, elastic automotive parts and electrical cable covers, where elasticity is a must. pPVC also finds applications in film and sheets, flooring, shower curtains and synthetic leather products. In the 1970s pPVC was often used to make 'vinyl car tops', and it was also used to make vinyl records. PVC-based materials also have a key role in the production of medical and clinical devices; however, similar arguments are arising with regard to its safety issues (Latini *et al.*, 2010). Table 2.1 summarizes some characteristics of PVC.

PVC can be mixed mechanically with various substances rather easily, hence it has the 'ease of formulation' characteristics, because of the existing

Table 2.1 Some characteristics of (rigid) uPVC

Density (at 25°C)	0.5–1.45 g/cm ³
Specific gravity	1.3–1.7
Hardness durometer	R 90–115
Tensile strength	30–65 MPa (flexible: 7–25 MPa)
Tensile (Young's) modulus	2–4 × 10 ² MPa
Tensile elongation	20–190%
Compressive strength	50–90 MPa
Fatigue strength	17 MPa (after application of repeated stress by 10 ⁷ times)
Impact strength (notched)	2–6 kJ/m ²
Service temperatures	–13°C (min.) to 70–80°C (max.)
<i>T_g</i> (glass transition temperature)	80°C
<i>T_m</i> (melting temperature)	240°C (decomposes)
Ignition temperature	455°C (inherently fire retardant)
Coefficient of thermal expansion (linear)	5 × 10 ^{–5} mm/mm°C
Resistance to acids (dilute/concentrated), alcohols, bases, aliphatic hydrocarbons, mineral oil	Excellent
UV resistance	Good
Water absorption (24 h)	0.04–0.4
Resistance to vegetable oil and oxidizing agents	Good
Resistance to aldehydes, esters, aromatic and halogenated hydrocarbons, ketones	Limited (poor)
Resistance to oxidation by atmospheric oxygen	Excellent (Durable)
Mechanical stability	Excellent (very low creep deformation) (Makino, 1998)
Dimensional accuracy for molded PVC products	High
Secondary processability (in welding, high-frequency bonding and vacuum forming, as well as 'on-site workability' properties)	Excellent

polar groups (chlorine). Mainly plasticizers and various additives and modifiers are used in PVC formulations to design the required physical properties of end products, such as improved flexibility, elasticity, impact resistance, anti-fouling, prevention of microbial growth, anti-misting, improved fire retardance, etc. The same polarity of chlorine also contributes to its ease of coloring, printing and adhesion. PVC is used in various decorative applications in buildings such as wall coverings and floorings by taking full advantage of its superior printability and ease of colorability with desired patterns and weatherability characteristics (Patrick, 2005).

2.3 Building applications of polyvinyl chloride (PVC)

Globally, over 50% of processed PVC is currently being used in construction, in products such as pipes, wiring, siding, flooring and wallpaper. As a building material, PVC provides economy, and ease of installation and replacement compared to more traditional building materials (e.g., wood, concrete, even clay) (Thornton, 2002).

2.3.1 PVC pipes

Because of its inherent water resistance, PVC is used to make raincoats and shower curtains and, of course, especially water pipes. PVC is extensively used for municipal water supply/sewage pipes, spouts, etc., since its mechanical properties such as tensile strength and tensile modulus are better than those of other general-purpose olefin plastics, and it is robust and durable. Home plumbing systems have different types of piping materials for different types of use, e.g., domestic water supply, waste drainage, appliances, irrigation and so on. PVC as a rigid plastic is used preferably in sanitary waste lines, vent pipes and drain traps for both residential and commercial applications. PVC rigid pipe can be easily cut (with a hacksaw or tubing cutter) and fitted, and it is often used to repair sections of broken old cast iron waste pipes. Its sections can be joined together mechanically (using plastic pressure fittings for later removal) or permanently (using the special chemical solvent) (Fig. 2.1).

PVC pipes are expected to last for a significantly long time (predicted to be up to or in excess of 100 years) under normal conditions, reducing both maintenance costs and environmental impact (Makino, 1998).

Global annual demand for plastic pipe, most of which is made of PVC, is predicted to reach 20.3 Mt (million tons) by 2015 with an annual increase of about 7% and with continued strong prospects in developing nations, particularly in China, which already accounted for 30% of the overall profits for plastic pipe between 2007 and 2012 (Anon., 2011c). In fact, generally increasing demand for PVC piping in China is primarily driven by



2.1 PVC pipe and fittings.

expansion in construction expenditures, as well as by the advances in consumer spending; and it would be good to remember that in 2005 China had already passed the US to become the largest consumer of PVC in the world (Anon., 2007a).

2.3.2 PVC profiles

Window and door profiles are other demanding applications for rigid PVC (uPVC), because of the high level of product performance required. uPVC profiles are used for window frames, doors, conservatories, fascias, skirting boards, architraves, soffits, guttering, rainwater systems, fences and decking, etc. PVC offers for all such applications a lightweight, maintenance-free and cost-effective alternative in a range of colors with an esthetic wood-grain finish, if needed, in addition to effective heat and sound insulation characteristics, so that it has already displaced traditional materials such as wood, steel and aluminum that had long been in use (Table 2.2). PVC window profiles are expected to last for more than 40 years under normal conditions, reducing both maintenance costs and environmental impact appreciably. As seen from Table 2.2, uPVC has the lowest values of k (and hence the highest values of R), meaning that it is a much more effective thermal insulator than aluminum, steel and wood.

Table 2.2 Some heat insulation characteristics of selected profile materials

Material	Conductivity (k) value	Insulative (R) values
uPVC	0.21(as a reference, for a perfect insulator, polyurethane foam insulation board, $k = 0.17$)	4.80
Wood (dry)	0.33	3.03
Aluminum (6061)	1160.00	0.00086
Aluminum (5052)	960.00	0.00104

Thermal insulation is characterized by the thermal conductivity (also referred to as the k value), which is the level of the speed at which heat travels through a material through conduction: the lower the k value, the better the thermal insulation. The reciprocal of k is R , which is frequently used to describe the performance of insulation materials: therefore, the higher the R value, the better is the insulation quality.

Impact strength is one of the key requirements in plastic profiles, and it is being improved by using certain additives in rather small quantities in PVC profiles, such as chlorinated polyethylene (CPE) and/or certain acrylic rubber-like compounds. In addition, nano-sized (precipitated) calcium carbonate (CaCO_3) particles are being applied to provide larger surface areas to improve their interactions with the PVC matrix.

2.3.3 PVC flooring and tiles

PVC flooring (or PVC floor coverings, vinyl–polyvinyl floors and tiles) is of great interest for residential uses such as in garages, basements, wetrooms, kitchens – almost anywhere where a durable floor is needed. PVC has been a popular flooring material in North America for over 40 years, replacing traditional linoleum (or lino) floor coverings (made from renewable materials such as linseed oil, pine rosin, cork dust, wood flour and mineral fillers). PVC tiles and floors can withstand the toughest environmental and heavy loading conditions, and their commercial and industrial grades are available for use in places such as offices and other heavy traffic areas (for both pedestrians and vehicles), sports areas, hospitals, etc. PVC floors provide waterproof and soundproof solutions. They are almost a natural choice in buildings with large floor spaces, such as schools, offices and public buildings, where durability and low maintenance are vital. PVC anti-slip mats are available. Vinyl flooring also offers an affordable and effective solution for places where sensitive electrical and computer equipment is installed and static charges are a big problem, with its additional ‘antistatic’ grades.

Most PVC floors are created through a process known as ‘plastisol spread coating’. For this, the plasticizers are first combined with PVC powder to produce a liquid paste or ‘plastisol’ which is then applied in several layers, that is, the floor is composed of a foam core and a decorative and clear protective wear layer is built up on top. PVC floorings are predicted to last for at least 10 and up to 30 years.

PVC floorings should be elastic enough to provide flexibility and damping, and the material usually contains certain chemicals as additives to provide these properties. Plasticizers, mainly phthalate plasticizers, such as diisononyl phthalate (DINP) with 5–16 wt% and butyl benzyl phthalate (BBP) with 1.6–5 wt%, as well as others, have been used to help flexibilize the system. In addition, various organotin compounds, e.g. dibutyl tin (DBT) and tributyl tin (TBT) with concentrations of 38–560 ppm and 128–18,000 ppb, respectively, have been used as heat stabilizers (Allsop *et al.*, 2000). Most of these compounds are toxic and can leach or emit from the system to the surroundings, which has drawn particular concern. A more detailed account of these additives will be given in Section 2.4.

2.3.4 PVC siding

PVC (or vinyl or uPVC weatherboard) siding is a plastic cladding for the house, used for weatherproofing, insulation and decoration, externally. PVC siding has been the most commonly installed exterior cladding for residential construction in the US and Canada since the late 1950s. It is an engineered product with the possibility of a range of colors and finishes, used as an alternative to traditional sidings such as wood, aluminum and fiber cement.

Approximately 80% of PVC siding’s weight is PVC resin, the rest being composed of additives that are needed for properties like color, opacity, gloss, impact resistance, flexibility, and durability for the system. Within these additives, small amounts of various plasticizers may be used to flexibilize the system, together with a number of stabilizers such as lead compounds. Additionally, vinyl sidings can release toxic fumes when they burn (e.g., in the case of fire), particularly dioxins. All of these raise considerable health concerns and will be discussed in more detail in Section 2.4.

2.3.5 Other PVC applications in construction

PVC liners

PVC liners use the advantage of combining good chemical resistance and good physical properties, along with their ease of heat or radiofrequency (RF) weldabilities. There are a number of applications of PVC liners, mostly

as geo-membranes, such as in landfill liners, secondary waste containment liners, pond liners (for both hazardous and non-hazardous compounds), and liners for artificial lagoons, among others.

In addition to a number of such practical and important applications, flexible PVC liner systems that are used to insulate city potable water tanks have been shown to extend the life of these tanks considerably (Anon., 2008).

Geo-fabrics or geotextiles, which may be considered as another version of PVC liners, are systems associated with permeable fabrics which, when used in the soil, have the ability to separate, filter, reinforce, protect, or drain.

PVC wire and cable insulation (coatings)

pPVC is commonly used as an insulator on electric wires and cables to provide electrical insulation, where again health considerations related inherently to PVC as well as to the plasticizers and other additives used are under discussion.

Others

Tarpaulins are large sheets of strong, flexible, waterproof material, for which a cloth such as canvas is coated with plastic or latex. Commonly, the material used for tarpaulin systems is composed simply of outer sheet layers of PVC with the fabric layer inside.

Several other examples of the uses of PVC can be given: blinds, wall-papers, vinyl-backed carpets, fences and roofing membranes to reflect solar energy, mainly for the outside of the house. Vinyl (PVC) roof membranes have been used in commercial construction for over 40 years in the US and for even longer in Europe.

PVC is also used as a composite in portable electronic accessories or housings. Through a specific fusion process, PVC can also gain ‘cleaning by absorption’ properties to absorb dust particles and bacteria.

2.4 Health and safety concerns and polyvinyl chloride (PVC)

Two large and overlapping categories are generally used to classify chemicals that threaten human health:

1. Persistent bio-accumulative and toxic chemicals (PTBs)
2. Chemicals that mimic or block the action of hormones, also called endocrine disruptors (ECDs).

PTBs are of particular concern for human health, because they do not break down quickly in the environment (that is, they persist and can become widely dispersed over long distances by wind and water). And finally they become concentrated in tissues as they move up the food chain.

Persistent organic pollutants (POPs) are a common term, essentially synonymous with PTBs. The single international treaty attempting to limit the use of 10 specified chemicals primarily pesticides, is known as the POPs Treaty. Dioxins, to be discussed below, are perhaps the best known of the PTBs.

While ECDs are usually exogenous man-made industrial chemical products or by-products, occasionally they are also found in some plants and herbs. ECDs imitate or block the hormones of normal human physiologic regulation. The concept of ECDs is relatively recent, dating back to 1991. The term was first used to describe industrial chemicals found in the environment that appear to disturb the development and function of hormonal systems by participants in the Wingspread Consensus Conference in Wisconsin, USA, in 1991 (Anon., 1991). ECD is an important toxicological concept, but many still believe that evidence for ECDs causing disease in humans is contested. Several reviews of this topic are available, e.g. Tausch *et al.* (2000) and Diamanti-Kandarakis (2009).

PVC is a sturdy, versatile, relatively low-cost material well adapted to use as a building and construction material. The use of PVC is complicated somewhat due to some of its properties being associated with possible toxicity. By-products that can be hazardous to human health are formed throughout the lifecycle of PVC, from its manufacture right through to its use and eventual disposal. These concerns have led some nations to limit or even completely ban the use of PVC. PVC manufacture and use is a contentious issue in the US and the EU, in particular. Environmental health advocates argue for severe limits to PVC use; while others, primarily in the chemical and building industries, support its use.

Health effects attributed mainly to PVC and related chemicals found in building materials include:

- Neuro-developmental problems including learning disabilities and autism
- A number of reproductive developmental problems including anatomic abnormalities such as hypospadias
- Altered male/female birth sex ratios at birth
- Preterm birth, early puberty and menstrual disorders
- A variety of cancers
- Impaired immune functions mainly connected to disorders such as asthma.

The question is how strong are these associations and how was the evidence developed.

2.4.1 Health and safety concerns related to the inherent chemistry of PVC

PVC is an organochlorine chemical (which is a carbon-based organic chemical with one or more chlorine atoms), which exhibits a number of important attributes shared by the class. Over three-quarters of about 40 million tons of chlorine produced annually is used in the production of more than 11,000 different organochlorine chemicals, including plastics (i.e., PVC), various pesticides, chemical intermediates, etc., and thousands of additional organochlorines are formed as by-products (during manufacture, use, and disposal of organochlorine-containing products).

There are three main characteristics of organochlorines that help to make them particularly troublesome, and have to be considered:

1. Chlorination changes the chemical stability of organic chemicals, making many organochlorines highly persistent in the environment. Even dilute discharges of such substances can accumulate in the environment over time, reaching measurable levels in air, water, and sediments. Persistent substances are transported long distances through the atmosphere and can be distributed globally, accumulating even in the remote regions of the Canadian and European Arctic, the rainforests of South America, and the Pacific islands.
2. Many organochlorines are strongly lipophilic – that is, they are highly soluble in fats (but not in water), so they preferably can accumulate in fatty tissues. In addition, these fat-soluble substances that resist degradation (and excretion) can magnify in concentration as they move up the food chain; organochlorine body burdens in carnivores are typically millions of times greater than the levels found in ambient air, soil, and sediments. Hence the human population, at the apex of the food chain, is bound to be particularly contaminated,
3. Finally, organochlorines tend to be considerably more toxic and more carcinogenic than their non-chlorinated analogs. It has long been known that some organochlorine chemicals produce a variety of adverse health impacts, including cancer, organ damage, and damage to reproductive systems, with neurological and immunological toxicity, in particular during sensitive periods of fetal and infant development. Within the several hundred organochlorines that have undergone toxicological testing to date, all organochlorines examined have been found to cause one or more of a wide variety of adverse health effects, often at very low doses. A large number of organochlorines are endocrine disrupters

(ECDs) that can mimic or otherwise interfere with hormone action, raising the possibility of severe long-term effects on reproduction, development and behavior.

In addition, when PVC is burned, some chlorines are easily released (which is the reason why PVC is not flammable and has inherent flame retarding properties, because chlorines react with radicals produced during the process, hence inhibiting the process), producing toxic hydrochloric acid (HCl) fumes. When hydrogen chloride gas enters the lungs, it becomes an extremely caustic acid that can result in internal chemical burns in a person who inhales it. This acid smoke is so potent that it can even kill a person inside a house fire, hence it will be the main danger when a PVC compound is combusted.

Combustion of PVC produces not only smoke of toxic acidic HCl gas and lead (the latter from stabilizers), but it can also produce dioxin-like products in the gas phase. Dioxin is an organic chemical with a pair of benzene rings, two oxygen and four chlorine atoms (the well-known DDT and dioxin share several characteristics chemically, primarily that both are toxic even in very small quantities). Dioxin and dioxin-like compounds (DLC) are among the products of burning of PVC, e.g. from incineration of waste PVC in domestic garbage or from house fires, as well as by-products of various other industrial processes. They are commonly regarded as highly toxic compounds and POPs, although their toxicity is not agreed by the whole scientific community. Dioxin was used through the infamous 'Agent Orange' by the US armed forces during the Vietnam War.

Within the dioxins, there are:

- Polychlorinated dibenzo-p-dioxins (PCDDs), known simply as dioxins. There are 35 PCDDs, and seven of them are specifically very toxic.
- Polychlorinated dibenzofurans (PCDFs), or simply furans. There are 75 PCDFs, and 10 of them have highly toxic dioxin-like properties.
- Polychlorinated biphenyls (PCBs), which have dioxin-like properties.
- Finally, there is dioxin itself, the basic chemical unit of the more complex dioxins. This simple compound is not persistent and has no PCDD-like toxicity.

The Greenpeace group has advocated the complete phase-out of PVC globally because according to their claim dioxin is produced as a by-product during vinyl chloride monomer (VCM) production, as well as from the incineration of waste PVC in domestic garbage and through landfill and home fires. The lifecycle of PVC begins with the manufacture of VCM gas. VCM, the monomer, which is toxic (see below), is then polymerized into the polymer PVC and then formulated with a number of different additives into final products.

2.4.2 Health and safety concerns related to the VCM and additives

The conversion of PVC into more useful final materials requires the incorporation of a number of different additives, i.e., additives that serve as plasticizers needed to flexibilize the system, heat and UV stabilizers for stabilization, fillers either to improve mechanical and physical properties or to make the system more cost-effective, flame-retardants to improve flammability characteristics, biocides for sterilization and to add anti-microbial properties, pigments, etc. These additives and other processing aids are physically mixed into the PVC matrix, but they are not chemically bound. Table 2.3 presents additives used in PVC, their functions and substance classes used.

Table 2.3 Examples of additives and their functions in PVC

Additive	Function	Substance classes used
Plasticizers	Protection of elasticity	Phthalate esters: Di(2-ethylhexyl) phthalate (DEHP) Di-isononyl phthalate (DINP) Dibutyl phthalate (DBP) Benzylbutyl phthalate (BBP) Di-isodecyl phthalate (DIDP) Di- <i>n</i> -octyl phthalate (DNOP) Di-isopentyl phthalate (DIPP) Other plasticizers: Adipic acid esters, e.g. di(2-ethylhexyl) adipate Citric acid esters, e.g. acetyl tributyl citrate Cyclohexanedicarboxylate esters Alkylsulfonic acid esters Dipropylene glycol dibenzoate (DGD) Trimethyl pentanediol diisobutyrate (TXIB) Sebacates Azelates Chlorinated paraffins
Stabilizers	Stabilization against the influence of light and temperature	Cadmium stabilizers (forbidden in the EU) Lead stabilizers Orgotin stabilizers Calcium / zinc stabilizers
Pigments	Coloring of plastic products	Inorganic pigments (e.g. titanium dioxide, iron oxide, chromium oxide and iron blue, ultramarine and soot pigments), lead chromate

Table 2.3 (Continued)

Additive	Function	Substance classes used
Fillers	Improving workability and wear performance (comprise up to 50% of the PVC material)	Calcium carbonate (chalk) Magnesium silicate hydroxide (talc) Barytes
Flame retardants	Increasing fire resistance	Aluminum trihydrate (ATH) Phosphoric acid esters Antimony trioxide (ATO) Chlorinated paraffins
Lubricants	Improving flow during the thermoplastic processing (comprise up to 3% of the PVC material)	Waxes, etc.
Antistatic agents	Reducing electrostatic charging	Perchlorates, etc.
Surface active agents	Reducing surface tension	Esters of long chain alcohols, etc.
Reinforcement	Reinforcement for expanded PVC floorings	Glass fibers, etc.

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In addition to these intentional additives used at the processing stage, there is the possibility of having unintentional additives (e.g., the chemical impurities in the intentional additives used) and ‘interaction additives’ (new chemicals produced from chemical reactions between the additives in the system). As a result, any of these chemicals (from intentional, unintentional or interaction additives) can be easily released (leached or emitted) from the product into the environment, and since most of them are toxic, this possibility should also be considered in determining the overall toxicity of PVC (Akovali, 2007).

VCM, the monomer

Residual VCM, the monomer of PVC, can be left in the polymer matrix unreacted as an ‘impurity’ after the polymerization reaction, usually with a

concentration of less than 1 ppm. This residual VCM can leach from any PVC material, e.g. PVC pipe, to water. In fact, migration of VCM into drinking water from PVC bottles (Fayad *et al.*, 1997) and from PVC water pipes (Al-Malack, 2004; Bellen *et al.*, 1987) has been reported; and different factors that can affect the accumulation of VCM in PVC piping used in drinking water distribution systems are discussed (Walter *et al.*, 2011).

VCM is a strong toxic chemical that can cause a rare liver cancer, angiosarcoma (also known as hemangiosarcoma), and blood tumors. VCM is toxic both by inhalation (affecting the human reproductive system, with serious changes in spermatogenesis) and by contact with skin (it is a severe irritant to skin, eyes, and mucous membranes, causing skin burns) or if swallowed (moderately toxic by ingestion). VCM's carcinogenic effect on humans was first understood and realized during the 1970s, through the workers in PVC factories, who were exposed (routinely and for long times) to very high levels of VCM because of the 'open-loop' polymerization system they were using. Obviously, such toxic effects were not expected at all from VCM in the near past, because until its toxic effect was clearly understood, VCM was being used in aerosol spray propellants (e.g. in beauty parlors by hairdressers) and as an inhalational anesthetic at large for years, until the US FDA banned VCM use in 1974. Strict workplace exposure limits were established by the Occupational Safety and Health Administration (OSHA) by then. The occupational limits for VCM currently are set at 1 ppm (averaged over an 8-hour period) and 5 ppm (averaged over any period not exceeding 15 minutes), with annual maximum exposure limit of 3 ppm. The 1997 European Pharmacopoeia requires a maximum of 1 ppm of VCM residual in virgin PVC. By the end of 1995, 175 cases of angiosarcoma (due to VCM) had been diagnosed worldwide (Mulder and Knot, 2001).

Plasticizers

Various plasticizers are used in PVC formulations to create a softer and more flexible plastic, hence permitting its use in hoses, clothing (artificial leather), flexible toys and roofing membranes. More than 300 different types of plasticizers are known so far, and 50 of them are in commercial use. The most commonly used plasticizers are esters, such as adipates, mellitates and phthalates, the latter being the most widely used.

Phthalates are esters of phthalic acid and are used as plasticizers to increase the flexibility, softness and durability of PVC building materials. Phthalates have a clear syrupy consistency and in PVC they create a distinctive 'new car' odor. When added to PVC, they do not chemically combine or bond with the vinyl chloride, but are mechanically inserted between the long polyvinyl molecules, hence allowing them to slide one against another,

‘flexibilizing’ the system. Depending on the formulation of the PVC product, phthalates are generally used to make up 40–60% by weight of the final product. By 2010, it was estimated that more than 200 million kg of phthalate plasticizers were being used annually in PVC building materials.

There are three phthalate plasticizers that are most commonly used for PVC:

- Di-2-ethylhexyl phthalate (DEHP)
- Di-isodecyl phthalate (DIDP)
- Di-isononyl phthalate (DINP).

Of these, DEHP is the most common, primarily because of its low cost and efficiency; but it is the most toxic, and is the best-studied plasticizer. It is suspected that mono (2-ethylhexyl) phthalate (MEHP) is the major breakdown product of DEHP that both affects the respiratory system and causes asthma. DEHP is commonly used as a proxy for the toxicity and exposure assessments of other phthalates. In addition, benzylbutylphthalate (BBP) is used as a plasticizer specifically in foam flooring materials.

2-Ethylhexanol-ethyl-1-hexanol (2E1H), usually detected in indoor air at relatively high concentrations, is considered as a product of DEHP plasticizer in PVC flooring material, and from other existing compounds with the 2-ethyl-1-hexyl group (e.g., in the adhesive). 2E1H is considered to be one of the causes of bad odor in indoor air and sick building syndrome (Satoko *et al.*, 2009).

Toys made from pPVC with 10–40% phthalate plasticizers have been subject to an ‘emergency ban’ in the EU since the end of 1999.

Phthalates have high affinity for suspended particles and a study showed that when they vaporize into air, they are absorbed by suspended particles in air and in sediment dust samples from homes (Oie *et al.*, 1997). Hence they can migrate easily to sedimented house dust. Washing has also been shown to release phthalates into the water (Moller *et al.*, 1996).

Years ago, Swedish researchers observed that male workers in PVC plants have a high risk of developing ‘seminoma’ (a form of testicular cancer) in Sweden, with a probability six times higher, which was linked to the DEHP, which is a suspected ECD agent.

Another study showed that when DEHP is present at seven times the normal level which was the case for some Puerto Rican girls aged between 6 months and 2 years, there are cases of premature breast development (Lomenick *et al.*, 2010; Swan *et al.*, 2005).

A 1999 study made in Oslo, Norway concluded that young children may absorb phthalates from vinyl floor coverings, and that these children have almost double the chance of developing bronchial obstruction and symptoms of asthma. Research shows that DEHP can leach and emit easily, e.g. from PVC flooring, and it is found mostly in dust particles in the home and

in wash water from PVC floors whenever this happens. Hence any hazardous chemical in PVC flooring that leaches out leads automatically to human exposure in the indoor environment.

A good understanding of the toxicology of phthalates has been developed from studies using cell cultures, animals and human exposures. Human studies are primarily case control and ecological designs. So far, no controlled trials on humans have been performed for obvious ethical reasons, as the commonly used phthalates are commonly accepted as toxic.

There has been controversy for many years concerning the health hazards of phthalates, in particular DEHP. Strong criticism against any use of phthalates are expressed by certain non-governmental organizations such as Greenpeace and Friends of the Earth (Higgs, 2005).

In both wildlife and laboratory animals, phthalates have been linked to a range of possible biochemical effects (mainly reproductive health effects and autism) with the claims that most of them can function as ECDs. There have also been other claims such as that they are cancer-causing agents, specifically in liver and kidneys. In any case, negative health effects of phthalates in general have been suspected due to the existence of short ester chains (< C9) in them.

In 2000, the International Association for Research on Cancer (IARC), attached to the World Health Organization (WHO), reduced the carcinogenic rating of DEHP from 2B to 3, meaning a change of its standing from 'possibly carcinogenic to humans' to 'cannot be classified as to its carcinogenicity to humans' (Anon., 2000).

Since September 2004, the EU has not allowed the use of some phthalates (DEHP, DINP, DIDP) specifically in toys and personal care products made for children (where children can put the product in their mouths). The EU put forward the year 2002 as the key milestone to complete phthalate risk assessment. Two phthalates (DINP and DIDP) are shown to cause accelerated dehydrochlorination of PVC at high temperatures (Patrick, 2005).

Estimates of human health effects of DEHP have been used in risk assessment studies of PVC building materials. A recent US Green Building Council assessment of PVC building materials uses a combined lifecycle and risk assessment technique and uses data from a study by the Air Resources Board of California of indoor air samples of inspired phthalate concentrations from 125 homes in southern California (USGBC, 2007).

Stabilizers

Stabilizers are 'intentional additives' used to prevent environmental effects (of heat, UV light, etc.) on the polymer. They are added to plastics to afford protection against heat (thermal), UV and mechanical degradation of the polymer during both processing and use. They can function as antioxidants,

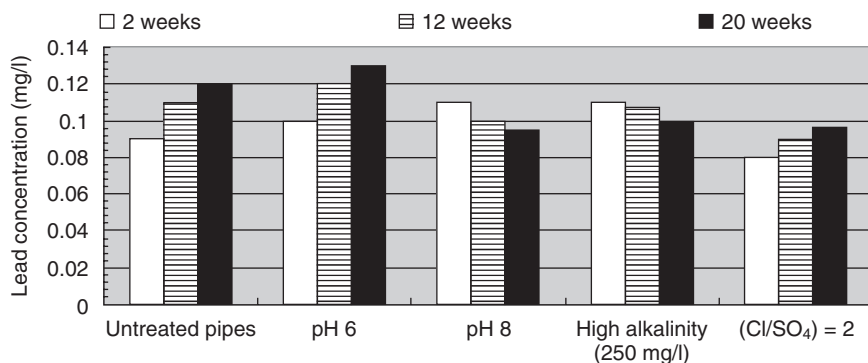
heat (thermal) and photo/light (UV) stabilizers, flame/fire retardants and oxygen scavengers. For PVC, the thermal decomposition temperature is close to the process temperature, hence use of proper heat stabilizers is essential both during its processing and afterwards.

Some of the stabilizers can contain certain heavy metals or their ions (e.g., stabilizers for PVC window profiles and pipes are mostly lead based or barium, cadmium, or zinc compounds, and in addition organonickel compounds are used for UV stabilization specifically), which can pose health hazards.

The main heat stabilizers available and used for PVC are:

- Compounds of lead (mainly basic lead sulfate and lead stearate). All forms of lead are extremely toxic to humans because of their cumulative effects. It has been shown that lead causes brain damage, learning disabilities, high blood pressure and even miscarriages. Exposure to lead-contaminated water is specially a persistent universal problem with a significant health risk. When ingested through the gastrointestinal tract, lead accumulates in organs and bones, and finally causes a number of diseases ranging from anemia to nervous system degeneration (Godwin, 2001). WHO recommended 10 µg/l for lead in drinking water (WHO, 2006).
- Organotin compounds, mainly mono-butyltin (MBT), dibutyltin (DBT) and tributyltin (TBT). In addition, dimethyltin (DMT) is another organotin detected in domestic water supplies arising from stabilizers used for PVC and chlorinated PVC (CPVC) products (Ehman *et al.*, 2007). There are suspicions that organotin compounds can be persistent and toxic to the central nervous and immune systems and to the liver (Korgiesen and Rice, 1998). Organotin compounds represent about 9.3% of European consumption of stabilizers (CEC, 2000).
- Cadmium (Cd) and its complex salt systems. Cd is an accumulative poison in the list of the top 10 hazardous pollutants of UN Environmental Programs; it can cause kidney damage and anemia, and once absorbed, can remain for 30 years in the human body. Inhalation of cadmium oxide fumes is the greatest hazard with a number of fatal consequences.
- Antimony (Sb) is used in PVC to enhance the flame-retardant effect of chlorine.
- Organochlorines are usually needed to enhance the flame retardancy characteristics as well as the impact strength characteristics of PVC.

There are various reports of the leaching of some of these toxic ingredients to the surroundings, such as tin compounds from PVC pipes (Sadiki, 1996; Sadiki and Williams, 1996, 1999; Nikolaou *et al.*, 2007; WHO, 2004), and other compounds (NIEH, 1997). For PVC products that are meant to be rigid, like vinyl siding or rigid water pipes, usually plasticizers are not of



2.2 Mean concentrations of lead release from PVC pipes (72 h stagnation) (from the paper by Lasheen *et al.*, 2008. Kind permission of Elsevier Ltd, UK, is gratefully acknowledged).

prime concern, but stabilizers are, e.g. lead compounds in stabilizers. In one study, it is shown that appreciable amounts of lead compounds are leached from PVC rigid water pipes (Al-Malack *et al.*, 2001; Lasheen *et al.*, 2008). Mean concentrations of release of lead after 72 h of stagnation, from this study, are presented in Fig. 2.2.

Since stabilizers used for PVC are usually in suspended form in the matrix, toxic ingredients can reach the exterior of the surface of the PVC in time, under either static-normal standing or dynamic operational conditions accelerated by temperature, by simple diffusion. After that, they can be transferred either by evaporation/sublimation or by simple leaching, or both.

It is expected that toxic effects of these additives individually, and those from the matrix material (PVC) itself, can probably have a 'combined effect' in the end: PVC flooring is expected to have both the 'plasticizer' and 'organotin' problems. Considering the fact that flooring usually has a substantial surface area within the home, these effects can be critical. In addition, if combustion of a vinyl floor is considered (as in a house fire or in cases of incineration), in addition to the 'plasticizer' and 'organotin', there will be the additional problem arising from the combustion of the matrix PVC itself.

Nevertheless, since the early 1990s the EU has restricted the use of Cd as a colorant and as an additive in plastics; and its use in PVC was stopped already by 2001 by most of the industry. There is an EU limitation for the use of cadmium from December 2010, with a concentration limit of 100 ppm for pipes, flooring and cabling but not for windows and other profiles, and roofing, introduced under the REACH legislation, which enables restrictions to be imposed on specific hazardous substances (*Chemistry World*,

2011). However, it does not apply to cadmium in electrical and electronic products which are controlled by the Regulation on Hazardous Substances (RoHS) directive.

Lead will be phased out by 2015. In other cases, research is continuing to ascertain for certain which plasticizers used in PVC are carcinogenic or have ECD properties.

PVC is inherently flame retardant, but in some cases it is needed to improve this property and flame-retardant additives are used. Chlorinated polyethylene, CPE, is usually the most suitable, but in this way, the chlorine content in the system increases and problems related to human health become a more serious issue. World demand for flame-retardant additives, in general, is expected to reach 2.2 Mt by 2014 (Anon., 2011a).

2.4.3 Health and safety concerns related to the disposal and recycling of PVC

There are three ways to recycle or dispose of PVC:

- Recycling by the direct recovery of scrap or waste plastics and reprocessing the material into useful products (mechanical recycling)
- Conversion of scrap or waste plastics into other useful chemicals or energy
- Disposal by simple landfill.

PVC can be processed into a wide variety of short-life or long-life products. With increasing consumption in recent years, the quantity of used PVC items entering the waste stream is gradually increasing; and there is considerable public concern about the problem of plastic wastes, specifically of PVC (Sadat-Shojai and Bakhshandeh, 2011).

Around 0.6% of the European domestic waste stream of 120 Mt per year is PVC waste. In 2001 PVC producers set a target of recycling 200,000 tonnes/year of PVC by 2010 (*Vinyl 2010*, 2001).

Recycling of PVC wastes by any of these methods has been difficult to achieve until very recently on the industrial scale, and the processes were also of interest environmentally and were criticized due to the expected possible health and safety concerns. Recycling of clean and homogeneous post-consumer PVC (or factory scrap) by direct reprocessing is possible and should be 'health and safety feasible', e.g., rigid PVC can be recycled and new pipes and profiles can be produced, although the process is not economic: recycled PVC is more expensive than the virgin resin.

Within the last decade, several viable methods have been developed for recycling of scrap PVC, such as the one developed in Europe called 'Texiloop', based on a technology already applied industrially in Europe and Japan called 'Vinyloop', consisting of recovery of PVC from composites

through dissolution and precipitation via a closed loop system (Texiloop, 2002). This type of recycling is expected to cause no health concerns, but it is certainly not economic.

Recycling by burning waste PVC has been heavily criticized, because of the high probability of emission of chlorinated by-products, e.g. dioxins. In fact, burning waste PVC seems to be the best option for energy recovery (Katami *et al.*, 2002; Wagner and Green, 1993). In this case, plastic, being the most important constituent of the waste, would provide the calorific energy necessary for burning. The effective heat of combustion of PVC is 17.95 MJ/kg. However, incinerators burning large amounts of waste PVC are shown to release large amounts of dioxin into the air at the same time (Beychok, 1987; NREL, 1993; Costner, 1995; Anon., 2007b).

In addition, it has been shown recently that TiO₂ encapsulated PVC (TEPVC) has a lower emission of toxic chemicals upon waste incineration as compared to PVC, most probably owing to the catalytic oxidation and decomposition of all toxic chemicals by the encapsulated TiO₂ nanoparticles. This certainly presents a potential application as an eco-friendly alternative to conventional PVC (Hyeongoo and Seung-Yeop, 2011).

An experiment to find out how much energy can be recovered from plastic material that has been reused and recycled has been carried out (Anon., 2011b).

Discarding waste PVC in landfill is not a real long-term solution, and the use of landfill for waste PVC should be the last option, because of the economy of the material involved. In addition, PVC is not inert in landfills, and there are concerns that various toxic additives can leach out and poison the soil, as well as water sources. According to some critics, PVC can increase the toxicity of any leachate. While PVC is not biodegradable, some of its additives are.

2.4.4 Bio-monitoring

The second industrial revolution spawned an immense chemical industry that provides materials now used in virtually every sector of commerce. Industrial processes into fuels, plastic, pesticides, cosmetics, food additives, and pharmaceuticals transform petroleum and other materials. In the United States, some 70,000 individual industrial chemicals are registered with the Environmental Protection Agency (EPA) for commercial use and are sold in the marketplace, some in billions of dollars per year. Only a very small fraction of these substances have been characterized for potential biological activity or human toxicity, and approximately 1500 new chemicals are introduced into the market each year. Thousands more novel compounds are generated as by-products of industrial processes or as degradation products and metabolites of other synthetic chemicals; even fewer

toxicological data are available for these substances. PVC is a very good case in point.

Residues of man-made substances can now be found in the air, soil, water, and food web in the most remote reaches of the planet. Pollutants that are distributed ubiquitously result in universal human exposure through inhalation, drinking water, and the food supply. Some of the substances to which the general human population is exposed resist metabolism and excretion and therefore accumulate in body tissues. The quantity of an exogenous substance or its metabolites that has accumulated in an individual or population is defined as a body burden.

Body-burden estimation

An individual's body burden of a pollutant is estimated by measuring the concentration of that substance in one or more tissues, usually by gas chromatography/mass spectrometry (GC/MS). Chemical body burdens are complex and dynamic in a number of ways, and these characteristics make a full characterization of the general public's body burden exceedingly difficult. First, the body burden of a pollutant is not stable over time. It reflects a dynamic balance between the amount taken in and the amount excreted or metabolized into another material. Many industrial chemicals, like formaldehyde, benzene, and some pesticides, are taken into the body but are broken down and rapidly excreted or metabolized, producing a negligible long-term body burden, although levels after an acute exposure may be high. Chemicals that are persistent are those that resist metabolic alteration and excretion and/or are tightly bound to the tissues in which they are stored.

Second, body burdens are not distributed homogeneously within an individual: the partitioning of a pollutant among various tissues and fluids reflects the substance's degradability and affinity for fats, minerals, and other endogenous materials. Metabolic models have been developed for a number of toxic chemicals. These models summarize available knowledge about the metabolism of a specific chemical and predict the distribution of the chemical in the body and the rate at which it will be eliminated.

Third, the body burden of an individual in today's environment consists of hundreds of synthetic substances. The ability of chemical analyses based on GC/MS to characterize the full range of contaminants is limited in a number of ways. Compounds can be identified only if they are present in concentrations above a detection limit (usually in parts per trillion or billion). Substances present in very low quantities will not be detected, but if there are hundreds or thousands of them, together they may make up the bulk of the total chemical burden. Moreover, routine analyses can identify only compounds that can be matched against a reference database

of chemical signatures, so substances that are not yet in the database go uncharacterized. Thus, novel or exotic compounds, such as many industrial by-products, environmental breakdown products, and metabolic products, will remain unidentified in even the most rigorous analysis. It has been estimated that the fatty tissues of the US general population contain at least 700 contaminants that have not yet been chemically characterized.

Bio-monitoring programs in the US

The human body burden of specific industrial substances has been well characterized in selected populations with high exposures, such as chemical accident victims, agricultural workers, workers in chemical and incineration industries, military personnel exposed to Agent Orange, and persons highly exposed to environmental chemicals through their diet or specific contaminated food. In addition, numerous studies have sought to identify specific compounds in samples drawn from individuals in the general population with no known special exposures.

Bio-monitoring surveys have studied broad samples of the US population. The National Health and Nutrition Examination Survey (NHANES II) studied lead and pesticide residues in blood during the period 1976 to 1980. In this national sample of nearly 6000 people aged 12 to 74 years, 36 pesticides and pesticide metabolites were quantified.

In 1991, a committee of the National Academy of Sciences called for a national program of monitoring body fluids from the general population for the presence of a list of target substances, based on a standardized protocol. Subsequently, the National Center for Environmental Health (NCEH), a division of the US Centers for Disease Control and Prevention (CDC), initiated the National Report on Human Exposure to Environmental Chemicals. Each year, the NCEH bio-monitoring laboratory will measure and report the exposure of a representative sample of the US population – a subsample of the ongoing National Health and Nutrition Examination Survey (NHANES) – to a number of priority toxic substances. In 2001, the CDC issued its first report from the National Report on human Exposure to Environmental Chemicals program.

A particular value of this national bio-monitoring program is its capacity to establish reference ranges for a large set of toxic chemicals. A reference range is defined as the concentration of a particular substance that is expected to be present in the general population with no unusual chemical exposure. The reference range is the standard against which a measuring laboratory can say that results for any group or individual are high, in a 'normal' range, or low. For materials like lead, cadmium, and some pesticides, good reference values exist because large numbers of persons have been studied using well-standardized and reproducible methods. For many

other substances, laboratory methods have varied over time, and few large nationally representative populations have been studied.

'Normal' body burdens

All humans are now exposed to organochlorines and other industrial chemicals in drinking water, air, and food. For bio-accumulative compounds, including dioxins, PCBs, and many pesticides, the food supply is the major source of exposure. Over 90% of the average American's dioxin exposures, for example, come through the diet. Animal foods – meat, dairy, fish, and eggs – contain the highest concentrations of dioxin, but smaller exposures also occur through grains, fruits, and vegetables and their oils. For the more volatile and less bio-accumulative chemicals, such as solvents, disinfection by-products, and pesticides in groundwater, exposures via air and water play more important roles. Direct exposures to organochlorines also occur via consumer products, home pesticides, dry-cleaned clothing and commonly used building materials.

As a result of these universal exposures, the general population now carries a body burden of numerous organochlorines. Over 190 synthetic organochlorines have been identified in samples of tissues and fluids drawn from the general populations of the United States and Canada. The studies on which this list is based are subject to the limitations discussed above, but they do indicate that a very large number of synthetic substances found in the environment and food supply have accumulated in the bodies of individuals who have had no special chemical exposures. As one might expect, the list includes the best-studied organochlorines: dioxins, PCBs, and restricted pesticides. Like the ambient environment, however, the bodies of the general human population contain a representative sample of the full range of organochlorines, from simple chlorinated refrigerants and solvents used for cleaning, coating, and degreasing, to little-known specialty chemicals, by-products, and second-generation pesticides. The concentrations are typically small, ranging from the low parts per trillion to the high parts per billion, but they indicate widespread exposure and a continuing internal dose of a variety of compounds, many of which are known to cause health damage.

It is now 'normal' for the general population to have body burdens of industrial chemicals and metals, in the sense that no reference or control population can be found without these exposures. But the existence of an appreciable body burden of industrial chemicals is a relatively recent phenomenon. Lead and other metals have been measured in human tissue since the 1920s. Dioxin is non-detectable or present at only a very small fraction of current concentrations in preserved human tissue samples from pre-industrial times.

2.5 Alternatives to polyvinyl chloride (PVC)

There are several alternatives available for most construction-related uses of PVC, some realistic and some hypothetical. To begin with, several databases, such as those offered by the Healthy Building Network (HBN, 2004) and Greenpeace (Greenpeace, 2004), can be mentioned that list some of these alternatives.

A large number of construction projects, including the Sydney 2000 Olympic Stadium and the new EPA headquarters in Washington, DC, have been constructed using little (or almost no) PVC. In each case and in principle, alternatives to PVC do exist, some being long-established and traditional while others are rather new. For example, among the former, for piping material there are chromed brass (for waste line pipes), chromed copper (for water supply), galvanized iron (for water supply and drainage), rigid and flexible copper or CPVC and PEX crosslinked PE (for water supply) and black iron (for gas).

In general, acrylonitrile butadiene styrene (ABS) and high density polyethylene (HDPE) can be used as general replacements, while polypropylene (PP) is suggested for extruded profile replacement applications. On the other hand, there is an ongoing continuous search for new replacements; for example, Ferro Corp, USA, has introduced two new non-lead heat stabilizers for wire and cable coating applications (Anon., 2004), and DuPont, USA, has recently introduced a chlorine-free floor tile to compete with vinyl and vinyl composite tiles.

Certain alternative plasticizers are used with the aim of making PVC compounds safer; however, these alternatives are more expensive and sometimes their technical performance is not as good as those obtained with the common phthalate plasticizers; in addition, it is not known for sure whether or not these alternatives can reduce health risks.

One such alternative is soybean oil. In the US, vegetable oil plasticizers already represented about 15% of the market in 1996. Soybean oils are more expensive than phthalates, but they provide the following advantages:

- They confer stability (they eliminate the need for additional heavy metal stabilizers).
- They do not leach out easily from the plastic, hence they also help to extend the life of the PVC product indirectly.

The complete isosorbide family and its esters are also another green alternative recommended as plasticizers: their toxicity data showed no acute toxicity, no sensitization, no mutagenic effects (Ames test), and no estrogenic effects (Kimpeks).

As far as the hepatotoxicity of PVC plasticizers is concerned, trioctyltrimellitate (TOTM) is suggested in place of DEHP. TOTM is less toxic to

certain animal species, and there is recently an increased market for diisononyl phthalate (DINP) for the same replacement. The US Consumer Product and Safety Commission accepted that there is no danger posed by some phthalate plasticizers like DINP. Meanwhile, while the debate in the US continues, in the EU producers have already begun replacing DEHP by its alternatives, with phthalates like C9 and C10 since 2000, and one of the main producers of DEHP, BASF in Ludwigshafen, Germany, shut down their factory during 2005, though they decided to continue offering similar production in Asia (Anon., 2005). However, at the moment, DEHP is the only phthalate that has European Pharmacopoeia approval for its use in flexible medical devices (Wang and Storm, 2005; Patrick, 2005).

Replacement of PVC or its additives with green alternatives is still a very active ongoing subject. A recent questionnaire asked PVC users to vote which alternative for soft PVC fits best with their requirements, and the alternatives suggested were olefinic elastomers, styrenic elastomers, other olefins, PLA and its blends, starch blends, and others (Omnexus, 2011).

As mentioned above, a very recent study related to TiO₂ encapsulated PVC (TEPVC) showed lower emission of toxic chemicals in waste incineration as compared to PVC alone most probably because of the catalytic oxidation and decomposition of all toxic chemicals by the encapsulated TiO₂ nanoparticles. This new nano technique certainly presents a potential new opportunity and a new eco-friendly alternative to conventional PVC, as converting and modifying PVC itself to a 'green' plastic (Hyonggoo and Seung-Yeop, 2011).

2.5.1 Analysis of alternatives

Risk assessments have been performed to quantify potential risks of developing adverse health effects following exposure to toxicants associated with building materials including phthalate and VCM.

Lifecycle assessment

As discussed above, the hazards from PVC must be approached from an integrated understanding of the full lifecycle of a material like PVC, including supply chain processes and materials, manufacture and installation through all the end-of-life fates including by-products, wastes and emissions at each stage. The obvious complexities of such assessments are obviously enormous. But science, design, and regulatory communities have a growing awareness of the need for such analysis.

A recent and rigorous lifecycle assessment of PVC as a building material was commissioned by the US Green Building Council and completed in

2007 by Norris and his colleagues. In 2000 the Council decided that it needed a technical basis for offering credit in its LEED (Leadership in Energy and Environmental Design) system for avoidance of PVC materials. The resulting study is titled 'Assessment of the Technical Basis for a PVC-related Materials Credit for LEED'. To compare the impacts of alternative material choices, two assessments were performed for each material in four applications: siding, piping, flooring and window frames.

A lifecycle assessment attempts to characterize and quantify all of the resource and pollution flows (inputs and outputs) associated with a particular material (PVC or an alternative) over its entire lifecycle: manufacture, use, reuse and disposal. The individual inputs and outputs are quantified in a lifecycle inventory and then characterized by their estimated contribution to environmental and health impacts. The study used an EPA system of categories and impacts including environment, ecosystem and human health impacts. A database of approximately 2500 publications was assembled and reviewed for the analysis. The database alone is a unique resource from this study. In addition to the LCA, three separate risk assessments were performed, including both cancer and non-cancer effects, on:

- Occupational health risks in PVC and alternatives manufacture
- Exposure to phthalates in residential indoor air and dust
- Residents exposed to VCM.

The findings are not easily summarized. The authors chose to frame the study's goal (or null hypothesis, if you will) as 'to determine whether, for the applications included, the available evidence indicates that PVC-based materials are consistently worse than alternative materials in terms of environmental and health impacts'. The results are very much qualified by 'it depends' statements. Across the four applications – windows, pipe, siding and flooring – PVC is not the worst alternative in the cradle-through-use portion of the lifecycle, but across the full lifecycle, including end-of-life incineration and dioxin production, PVC is in general the worst alternative.

Other analyses

LCA results can be dramatically altered or even reversed by the effects of assumptions in the design of the analysis and the uncertainty or unavailability of data. A case study of an LCA performed by the Vinyl Institute and several vinyl flooring manufacturers is presented in which the result appears to rate vinyl composition tile as having 3.98 times the (negative) environmental impact of linoleum, but only after the use of weighting schemes and the use of dioxin flow data that does not reflect total and so far unmeasured releases at such sources as landfill fires.

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2.6.1 Some related web-sites

ACE (Alliance for a Clean Environment): <http://www.acereport.org/orgs.html>

Healthy Building Network: www.healthybuilding.net

The Vinyl Institute: <http://www.vinylinfo.org/>

The Vinyl Siding Institute: <http://www.vinylsiding.org/about/>

WHO (World Health Organization) IARC (International Agency for Research on Cancer), Lyon, France: The USGBC document; An analysis by the Healthy Building network; <http://www.pvc.org/The-PVC-Industry/> (EVCN – The European Council of Vinyl Manufacturers – represents the 13 European PVC resin-producing companies that produce 100% of the PVC resin manufactured in Europe.)

Plastic materials: chlorinated polyethylene (CPE), chlorinated polyvinylchloride (CPVC), chlorosulfonated polyethylene (CSPE) and polychloroprene rubber (CR)

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Abstract: There are a number of plastic materials used in the construction industry that are known either to emit volatiles to indoor air or to leach organotins, both of which can affect comfort, health and productivity. Emissions or leaching can depend on the composition of the plastic material involved along with the various parameters associated with it. Within these plastics, there are chlorinated and chlorosulfonated polyethylene, chlorinated polyvinylchloride, and polychloroprene rubber, all which are the main subjects of interest for this chapter. Their properties, uses and health effects are briefly presented and some alternative materials for their use are presented.

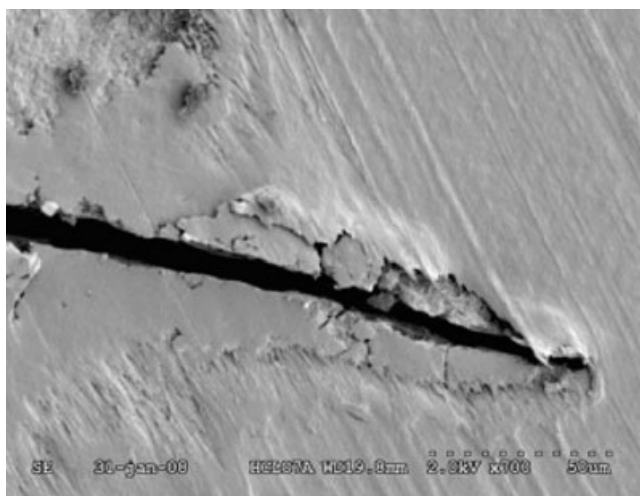
Key words: VOC, leaching, chlorinated plastics, neoprene.

3.1 Introduction

A range of various plastic materials are used in buildings for different purposes and for different applications, in a number of mechanical, electrical and plumbing (MEP) systems, due to their properties and the economy provided. However, there is also an ever growing concern about the potential health effects of these plastic products, composites and various chemicals that are being used in buildings. Some of these can emit volatile organic compounds (VOCs) into the indoor air, changing the indoor air quality (IAQ), that can affect human comfort, health and productivity. These VOCs depend on the type of plastic involved along with the various parameters associated with it (i.e., purity and the type of additives used during preparation, if not pure), as well as parameters like the temperature and relative humidity during their application, and even the circulation of the air above their surfaces. Effects of VOC can vary from irritation of mucous membranes to the introduction of a number of respiratory diseases and several adverse health effects, as well as to endocrine hormone disruption in humans (EDC). In a number of cases, it is shown that VOCs can even trigger cancer. In addition, various studies showed that there can be a number of harmful

organic contaminants in house dust, such as different polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), etc., some of which were commonly used until quite recently in electrical insulators.

A number of toxic heavy metals and compounds (e.g. lead, cadmium, chromium, mercury, bromine, tin, antimony, etc.) are used in additives (e.g., pigments, fillers, UV stabilizers, and flame retardants) for plastics. These compounds, although encapsulated in the polymer matrix in suspension form, are chemically unbound to polymer molecules and can be gradually released into the contacting environment over the service life of the plastic object, which can create serious health and environmental problems, as most of these elements are identified as toxic to humans. There are a number of examples that can be given for the leaching of these additives into the contacting medium from the plastic matrix. Most of these migrations can be direct, but they depend on time, temperature and characteristics of the environment at all times. Probably the most direct example is plastic water pipes prepared with organotin stabilizers as additives, from which toxic organotin compounds are shown to leach to the water, which can be most critical if drinking water is involved (Forsyth and Jay, 1997). These migrations are shown to be even accelerated by the existence of chlorine dioxide in the water, leading to the rather quick deterioration of pipe material in the end (Fig. 3.1) (Hassinen *et al.*, 2004; Yu *et al.*, 2011;



3.1 Scanning electron micrograph of a specimen obtained by sectioning through a region with a crack in a pipe exposed to water containing 4 ppm chlorine dioxide for 121 h (reprinted from the paper by Yu *et al.* in *Polymer Degradation and Stability*, 96(5), 790–797, 2011. Kind permission of Elsevier UK is acknowledged).

Whelton and Dietrich, 2009; Devilliers *et al.*, 2011; Ojeda *et al.*, 2011; Azhdar *et al.*, 2009; Skjevrak *et al.*, 2005; Hoang and Lowe, 2008).

Similarly, when disposing of these plastic wastes, either by incineration or by placing in landfill, toxic metal compounds can be released from plastics entering the atmosphere or leaching into the soil.

Within the various additives mentioned, there are also plasticizers which are in general organic esters of a low volatile nature, which can migrate directly as a result of leaching. Most of the plasticizers are carcinogenic. One common example is DEHP (di-ethylhexyl phthalate), a phthalate plasticizer largely used in PVC, for which replacement with its non-toxic alternatives is suggested.

In addition to the application of plastic materials in construction (and in all other applications of our everyday life) where plastics are in the processed form, and interest is mostly in health issues connected with their use, the possible health effects on the environment at the production stages have also drawn some criticism from time to time. In this connection, one should remember the Bhopal disaster in India, some 25 years ago, in which more than 40 tons of extremely toxic methyl isocyanate gas (used in pesticides and for production of polyurethane rubber) escaped from a plant in Bhopal and killed over 5000 people within days; according to local authorities, nearly 10,000 more people have subsequently died of complications from cyanide lesions (Bagla, 2010).

Concerning health effects on the environment, another well-known example is the effect of chlorofluorocarbons (CFCs) on the ozone layer. CFCs were used until recently by plastics processors as foaming agents for the production of polystyrene and polyurethane foams. Although they are non-toxic directly, they have indirect health effects because of their effect on ozone depletion, as well as global warming. CFCs and other halogenated ozone-depleting substances (ODS), like carbon tetrachloride and trichloroethane (in short, the haloalkanes), are mainly responsible for the increased UV radiation as the result of ozone depletion, which has a number of biological effects like skin cancer, cataracts, etc. (McFarland and Kaye, 1992). The Montreal protocol (2007), recognized by the UN, phases out the production and use of ODS, including CFCs, while encouraging the search for their ozone-friendly alternatives (UNEP, 2006).

Among the most commonly used plastics in buildings, there are polyethylene (PE) and polyvinylchloride (PVC) and several of their derivatives, such as chlorinated polyethylene (CPE), chlorosulfonated polyethylene (CSPE), chlorinated polyvinylchloride (CPVC), and polychloroprene rubber (or neoprene, CR), all of which, with their probable effects on human health, will be the main subject of our interest for this chapter.

In green building certifications, plastic materials like CPE, CSPE, PVC, CPVC and CR are in general considered among the most challenging group

of materials to take into account (in general, they are sometimes even termed 'red-listed materials').

3.2 Structure and properties of chlorinated polyethylene (CPE), chlorinated polyvinylchloride (CPVC), chlorosulfonated polyethylene (CSPE) and polychloroprene rubber (CR)

All of these materials are prepared by proper modification of the related base plastic material (PE and PVC, respectively), which involves a chlorination process for all, and additional sulfonation in the case of CSPE, yielding new systems with certain improved desired properties. CR is the product of a chlorine-containing monomer, chloroprene.

3.2.1 CPE and CSPE

CPE and CSPE are produced by chlorination (and additional sulfonation for the latter) of PE (polyethylene, also called polythene, or poly(1-chloroethylene) according to IUPAC), which is a low-cost general-purpose thermoplastic material. PE was initially introduced as a dielectric material specifically for high-frequency insulation, and later used also for piping (domestic and agricultural water piping, as well as gas piping) and extensively in cable and other wire-covering applications.

A number of different grades of PEs are involved, each giving rise to different CPE/CSPE products with different properties after chlorination; hence, it may be necessary first to give a brief summary of the different PEs available. Depending on the technique used in its production, it is possible to obtain many kinds of PE differing in density, percent crystallinity, molecular weight, molecular weight distribution and branches, such as (a) low-density LDPE, a highly branched, high-pressure grade of PE; (b) high-density HDPE, a linear, low-pressure grade; (c) linear low-density grade, LLDPE, etc.

Different grades of PEs were, and still are to some extent, used in the building industry with some inherent drawbacks. PEs in their pure state are free from odor and toxicity. However, they also have low softening temperatures, their low molecular weight grades are easily susceptible to environmental stress cracking (ESC) and easy oxidation, they can easily develop opacity in bulk, they have poor scratch resistance, and they lack rigidity with rather low tensile strengths and high gas permeabilities, all of which are their main limitations in use, that need improvement (Brydson, 1982). However, they are still used to some extent because they are economic and easily processable, they offer excellent electrical insulation and chemical

resistance/reactivity properties, and their toughness and flexibility can be retained even at low temperatures.

The reactions that occur during chemical modification of PEs are rather unique and different, firstly due to the chemical inertness of the molecule, and secondly due to the existence of crystalline and amorphous regions in the structure. The crystalline region is the part that is less readily attacked by any chemical (i.e., chlorine) as compared to amorphous parts, due to the difficulty of diffusion of any reactant into the crystalline areas. To overcome this difficulty, usually a pre-modification is performed in a good solvent with the aim of destroying any crystalline regions.

CPE (CAS number: 64754-90-1)

Chemical modification of PE can be accomplished in a number of different ways. Chlorination of PE is a simple halogen substitution reaction (Jones, 1964), which usually alters both the regularity of the chains and softening points significantly, with properties of products varying with degree of substitution as well as conditions of chlorination (Fettes, 1965). Chlorination can be done in bulk (fluidized bed), as emulsion or suspension in an inert medium or in solution (i.e., CCl_4), the first of which results in more crystalline products at comparable levels of chlorination. When carried out in solution, the chlorination is random, but when carried out with the polymer in the form of a slurry, the chlorination is uneven and is due to residual crystalline zones of CPE, the material remaining as a thermoplastic (Akovali and Vatansever, 1983, 1986; Chlorinated Polyethylene, 2011).

Chlorination in general increases interchain attraction; and, once there is sufficient bound chlorine to give rise to a completely amorphous product, chlorination can cause an increase in softening points. In fact, CPEs are usually rubbery in the 25–40% range, depending on the type of PE used (HDPE or LDPE, respectively); and at about 45%, the polymer becomes stiff at ambient temperatures. With a further increase in the percentage of chlorine, the polymer becomes brittle. Chlorination in all cases results in a considerable decrease in flammability, whereas solubility may be increased or decreased depending on the chlorine content.

CPE thermoplastic rubbers are commercially available and were first patented by ICI in 1938. They have several attractive physical, mechanical and chemical properties, such as very good chemical, oil, heat, flame, ozone and weathering resistances, good low-temperature performance, compression-set resistance, flame retardancy, high filler acceptance, tensile strength and resistance to abrasion, with competitive prices; and they are also available in powder form. In addition, they can range from crystalline (or rigid) thermoplastics to flexible elastomeric products, which makes them highly versatile. However, because of the difficulties involved in their processing

and particularly their vulcanization (crosslinking is done only by using peroxides), so far they have never been able to achieve much market value and commercial significance, and the market is already mostly taken up by CSPE.

Thermoplastic CPEs are seldom used on their own but primarily in blends with other polymers, mainly for white and brown profiles of PVC as impact modifiers. If chlorination is carried to a level at which the polymer is only semi-compatible with PVC, a blend with high impact strength may be obtained and the material is classified as an impact modifier (Feldman, 1989), and also as a modifier for PE, ABS, SAN and PP. CPE is used extensively, alone or in blends with acrylic impact modifiers, to achieve a desirable combination of ductile impact and processing performances. CPE is also used to improve the resistance to ignition and combustion of PVC systems. CPE finds uses in pipe applications, typically in specialty PVC pipe, CPVC pipe, electrical conduit, and any highly filled compounds in this category. Other important end-use applications of CPE include wire and cable jacketing, roofing membranes, geo-membranes, hose and tubing, coated fabrics, molded shapes, extruded profiles, damp-proofing under concrete floor slabs or to produce synthetic building wraps, and gaskets. CPE is the modifier of choice for cost/performance efficiency in vinyl siding substrate, providing toughness at low temperatures, ductility, and a high capability for filler acceptance. It provides excellent impact properties, filler acceptance, and ductility in vinyl fence substrates, and can also be utilized in capstock applications. All of these applications already exist in the construction industry.

China currently is the world leader in CPE production (83%), while China and the US were, and still are, the two largest consumers of CPE in 2008, (Ormonde and Klin, 2009). Specifically, in China, roughly 75–80% of CPE is used for impact modification of PVC for door/window profiles and pipe/drainage applications, and of certain styrenic copolymers, followed by 20–25% in flexible sheeting for various roofing applications, electrical wires and cables, and others (e.g., hoses and seals). In the US, 80–90% of CPE is consumed for impact modification and the rest is for other uses (wire and cable jacketing, roofing, hose/tubing and molded articles).

Some characteristic mechanical/physical properties of CPE are presented in Table 3.1.

The health effects of CPEs may be listed as follows.

- *Consumer exposure and environmental releases*
CPEs can be formulated to be hard or flexible without the need to use plasticizers, and special additives can be employed otherwise (as UV and heat stabilizers, antioxidants, etc.) to provide additional required properties. In such cases, these additives will be a serious concern for

Table 3.1 Some characteristic properties of CPE

Density	1.16 g/cm ³
Chlorine content	25–42% by weight (can be maximum 70%)
Hardness (Shore)	A 60
Tensile strength	12.5 MPa
Flexural modulus	0.02 GPa
Elongation at break	700%
Stable time at 165°C	8 minutes
Max. operating temperature	60°C
LOI (Limiting Oxygen Index)	22

any possible emission of VOCs at ambient and elevated temperatures and they should be selected carefully.

- *Workplace exposure*

This can occur in a CPE processing facility, where good housekeeping and dust control are necessary for safe handling. Dust particles of CPE may cause eye discomfort (hence chemical goggles are needed), and skin contact should be avoided.

- *Thermal degradation*

Thermal degradation (thermal decomposition and combustion, although CPE combusts with difficulty) of CPE can produce mainly HCl (hydrochloric acid) and CO (carbon monoxide), which are highly irritant and toxic, in addition to dioxin or dioxin-like products, which are highly toxic and carcinogenic. In fact, if only the base polymer (PE) is considered, its thermal degradation produces mainly CO (carbon monoxide), which is considered as a systemic toxin (Ammala *et al.*, 2011).

CSPE (CAS number: 9002-88-4)

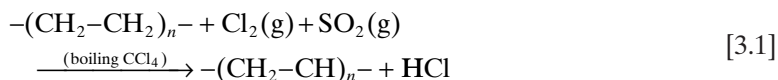
Chlorosulfonated polyethylene (CSPE or CSM rubber) is a synthetic rubber based on PE that is noted for its resistance to chemicals, to temperature extremes (i.e., suitable for continuous use up to about 130°C, and for intermittent use even up to some 30°C higher), and to aging and ultraviolet (UV) light. CSPE is patented by DuPont (DuPont Performance Elastomers, a subsidiary of DuPont), with the trade name of Hypalon (Tornqvist, 1986).

CSPE/CSM rubber is used in a variety of industrial and construction applications that require high performance. The driving force behind CSPE consumption in the world is the automotive sector. Nearly one-fourth of total world consumption of CSPE was in the automotive industries in 2008. The second-largest market for CSPE is in construction applications in roofing membranes and liners for ponds and reservoirs. They are widely and

specifically preferred and used in roofing. In fact, within the commercial roofing market, CSPE has the biggest share, followed by PVC and ethylene-propylene-diene monomer terpolymer (EPDM) (Griffin, 1982).

In addition to in (single-ply) roofing and geomembrane applications, CSPE/CSM rubbers are used in geosynthetic applications as liners, caps and floating covers as well as to make inflatable boats, gaskets, weather stripping, wire and cable insulation.

The first production of CSPE on a laboratory scale was achieved by McQueen (1939), who treated a suspension of LDPE (a newly discovered material at that time) in CCl_4 with SO_2 and chlorine, with the hope of producing a new water-soluble polymer containing sulfonic acid groups; this resulted in the introduction of both chlorine and sulfonyl chloride groups (SO_2Cl) by replacing some of the H atoms through elimination of HCl on the polymer backbone. The sulfochlorination of PE can be carried out either on the solid material or in solution. In sulfochlorination in solution, chlorine and sulfur dioxide are allowed to react, in the presence of UV or azo initiators, with PE dissolved in hot CCl_4 (equation 3.1):



Several years later, McAlevy and coworkers (McAlevy *et al.*, 1946; McAlevy, 1947) realized that sulfochlorinated PE of the right composition exhibited outstanding properties in a number of applications, mainly because of its good heat resistance and exceptional resistance towards aging, in general. For the PEs available at the time (1947), the optimum elastomeric properties were found to occur at chlorine contents between 27 and 30%. McAlevy and colleagues recognized that chlorine substituents were particularly important to the elastomeric properties (the chlorine atoms break up the regularity of the PE chain structure with decrease in crystallization, thus imparting an elastomeric character to the polymer), while the sulfonyl chloride groups made the polymers curable with metal oxides (MtO) and water (i.e., either MgO , ZnO or PbO and a hydrogenated wood resin as the source of water). Crosslinking through sulfonyl chloride to give OMtO crosslinks (with MtCl_2 elimination) is found to lead to an elastomer of commercial interest, i.e., a typical final amorphous CSPE product with 27 wt% chlorine and 1.2% sulfur can be made with a glass transition temperature (T_g) value of -55°C (Morton, 1959).

Based on these developments, DuPont started small-scale production of CSPE under the name Hypalon in 1954, followed by a full-scale commercial plant (Ziegler *et al.*, 1955). By that time, new types of PEs had become available through Ziegler/Muelheim catalysts (equation 3.2), such that Heuse (1958) tried to make 'higher density-more linear' PEs available successfully. He demonstrated that chlorine levels in the range of 38–48%

Table 3.2 Some characteristic properties of CSPE

Tensile strength at break	18 Pa
Elongation at break	200%
Hardness (Shore)	90
Continuous service temp.	–50°C (lower) to 200°C (upper)
Tear resistance	Good
Adhesion	Excellent
Weather/ozone resistance	Excellent (better than neoprene and butyl rubber)
Oil resistance	Good
Water swelling resistance	Excellent
Adhesion to metals	Excellent

could be advantageously used. When cured, these polymers exhibited additional outstanding resistance towards swelling (by oils and organic solvents). Fillers are not needed for optimum strength. Most grades of Hypalon today are based on the latter type of PE. In a typical commercial polymer, there is one 1-2-chlorosulfonyl group for each 200 backbone carbon atoms, namely, 25–42% CH_2CHCl and 1-2-($-\text{CH}_2\text{CH}(\text{SO}_2\text{Cl})-$) groups per ethylene group.

Some typical mechanical/physical properties of CSPE are presented in Table 3.2.

CSPE in general is poor in ‘snap’ and ‘rebound’ characteristics and some grades may have a small ‘permanent set’. Its abrasion resistance, flex life, low-temperature brittleness and resistance to crack growth are all good. CSPE is flame resistant. It is superior to polychloroprene (neoprene) in overall properties, and inferior to, but more cost-effective than, silicone or fluoro-elastomers. Compared with CPE, CSPE elastomers exhibit much better mechanical properties and abrasion resistance.

DuPont is still the dominant producer of CSPE, with some Japanese and Chinese competition.

CSPEs are considered as safe materials, in general. Possible (acute or chronic) potential health effects of processed CSPE materials arise mainly from the possible evolution of CCl_4 (Dupont MSDS, 2008). The route of entry of this chemical into the body is either through the skin or by breathing, which may cause skin, eye, nose, throat, and/or lung irritation; the ultimate target organ is the liver and central nervous system as well as the kidneys.

In addition, if any sort of additives are employed in CSPE formulations to provide additional required properties, then these additives may be of serious concern for any possible emission of VOCs at ambient and elevated temperatures, and they should be selected and followed carefully. Thermal degradation (thermal decomposition and combustion, although CSPE combusts with difficulty) can produce mainly HCl , SO_2 and CO , which are highly

irritant and toxic, in addition to possible dioxin or dioxin-like products, which are toxic and carcinogenic.

The carcinogenicity of CSPE is not known specifically. It is an IARC 2B (IARC stands for the International Agency for Research on Cancer) and ACGIH A2 (ACGIH stands for the American Conference of Governmental Industrial Hygienists) classified material, meaning it is a possible (suspected) carcinogenic substance for humans, where there is limited evidence of its carcinogenicity in humans and no (or inadequate) supporting evidence in experimental animals (Akovali, 2007).

3.2.2 CPVC (CAS number: 68648-82-8)

CPVC (chlorinated PVC, 'post-chlorinated PVC', or polychloroethene) is another modified polymer which is widely used in the construction industry. It is produced by subjecting PVC resin to a post-chlorination reaction (mainly to increase its T_g), which, with a free radical reaction, results in the addition of chlorine atoms on the base PVC molecule backbone to replace H, typically initiated thermally (or by UV) (equation 3.2):



CPVC can be made by any commercial chlorination process, such as by solution, fluidized bed, water slurry, thermal, or liquid chlorine (Noveon, 2003). Some of these methods have been associated with the use of swelling solvents. Depending on the variations on the methods employed, CPVC products with different chlorine contents can be obtained (ranging from 56.7% for the base for PVC to 74% by mass, but for most commercial resins 63–69%); at 70% mass of chlorine, CPVC becomes unstable.

CPVC is an amorphous thermoplastic material similar to PVC, with the following added advantages:

- Higher heat distortion temperature (operating temperature range is between 0–90°C as opposed to 0–60°C for PVC)
- Improved fire performance properties (with limiting oxygen index value of LOI = 60, CPVC does not support combustion).

In addition, CPVC keeps the same advantageous properties as for PVC, as follows:

- It has excellent environmental resistance to aggressive caustic and acidic fluids (but not to most solutions of acids, alkalis, solvents, aromatics, and some chlorinated hydrocarbons).
- It has good abrasion and long-term strength resistance with high stiffness values.
- CPVCs are cost-effective.

Table 3.3 Some characteristic properties of CPVC

Density	1.56 g/cm ³
Young's modulus (<i>E</i>)	2.9–3.4 GPa
Tensile strength	50–80 MPa
Elongation at break	20–40%
Notch test	2.5 kJ/m ²
Glass transition temperature (<i>T_g</i>)	106–115°C
Operating temperatures	0°C (lower) to 90°C (higher)
Resistance to acids, caustic substances, organic and inorganic solvents (except strong oxidizing acids)	Good

Some typical mechanical/physical properties of CPVC are given in Table 3.3.

CPVCs offer an economic solution for a wide diversity of both pressurized and non-pressurized corrosion-resistant hot and cold water plastic piping systems in use as plumbing materials, at both normal and elevated service temperatures, mainly due to their long-term strength characteristics, high stiffness and cost-effectiveness in domestic and industrial applications. In pressurized systems, they can be used with fluids up to 80°C. CPVC pipes are categorized by two criteria: basic short-term properties (including mechanical strength, heat resistance, flammability, and chemical resistance) and long-term hydrostatic strength. CPVC pipe, tube, and fittings have been successfully used worldwide in hot and cold water distribution systems in the construction sector since 1960. Usage of CPVC pipes and fittings in gas, sewage and water piping applications has tripled in the EU in recent years, and they are overwhelmingly used in construction as a main competitor to metallics. Bacteria build-up with CPVC is much lower than with alternate piping materials, including metallic materials (copper and steel) and other thermoplastics.

CPVC is a preferred material for the production of fire sprinklers, and CPVC applications as inner corrosion liners in (water) tanks and vessels are very common. Chlorinated paraffins, mainly CPVC, are also widely used in PVC for adhesive applications, in sealants (mostly polysulfide polymer-based ones) as plasticizers, and in PVC for wire and cable coats.

The main producer of CPVC is Noveon Corporation (successor to B.F. Goodrich, USA), followed by both Taiwan and China.

As regards the health concerns for the use of CPVC, no significant specific health hazard has been reported for its use at ambient temperatures, although there exist several possible expected effects of this material under different conditions, as follows.

Firstly, as in the case of PVC, mechanical properties of CPVC can be modified further at large by using conventional compounding techniques,

and CPVC pipe and fittings can have a number of different chemical constituents. The resin itself has certain strengths, i.e., combination of high temperature and high corrosive resistances, mechanical strength and excellent lifecycle economics, as well as weaknesses, such as low impact resistance, susceptibility to oxidation and thermal degradation at higher (extrusion) temperatures. Hence, first of all, suitable impact modifiers are needed, i.e. high rubber butadiene content, and high-efficiency methylmethacrylate–butadiene–styrene (MBS) and acrylonitrile–butadiene–styrene (ABS) impact modifiers are used at about 3 to 15 p.h.r., which are not expected to cause any health effects.

In addition, other additives are employed (Noveon, 2003). CPVC compounds are approximately 85% CPVC resin and 15% additives, such as antioxidants, lubricants, stabilizers, tinting colorants, pigments, T_g enhancing additives and processing aids. Each of these additives can pose a health hazard depending on their structure, concentration and conditions. As an example, if heat stabilizers are considered, suitable heat-stabilizing ingredients mostly include phosphate stabilizers (such as disodium phosphate), maleimides, sulfur compounds and alkyltin compounds. Until recently, the latter was preferred specifically for CPVC piping systems.

Various organotin compounds (mostly mono- and disubstituted alkyltins) are the most widely used heat stabilizers (organotin compounds are used at 2–4% in CPVC pipes) in the manufacture of PVC and CPVC plastics, including water pipes, which may leach into water easily when they come into contact with drinking water (Boettner *et al.*, 1982). Although still at low concentrations, a dibutyltin sulfide concentration of 100 µg/liter was reported after such a plastic pipe had been in contact with static water (Mazaev and Slepina, 1973); while studies by Health Canada found mono- and dibutyltin in potable water in PVC and CPVC pipes in the ng/liter range (Forsyth and Jay, 1997; WHO report, 2004). In similar studies (Sadiki, 1996; Sadiki and Williams, 1996, 1999) the majority of samples were found to contain levels below the limit of detection (of 0.5 ng/liter specifically); the same group later reported 28.5 ng/liter, (Sadiki and Williams, 1999). These values were found to increase with increasing time of contact, if conditions are stagnant.

Organotins are labeled as toxins that tend to be primarily distributed in the liver and kidney following oral administration to rodents (Evans *et al.*, 1979; Mushak *et al.*, 1982; Ehman *et al.*, 2007), and the thyroid glands (Penninks *et al.*, 1987). Dibutyltin dichloride (DMTCl) is reported as maternally toxic, but not teratogenic, at 20 mg/kg of body weight per day intake (Noda and Morita, 1994).

Although there are no direct adequate studies for the effects of dialkyltins on humans, human exposure to these compounds through drinking water is likely to be very low, apparently considerably less than 1 µg/day. The

German Federal Institute for Health Protection of Consumers and Veterinary Medicine published a tolerable daily intake of 0.25 µg/kg body weight per day for butyltin compounds (BGVV, 2000). This value was also reported in an English journal for the first time in 2003 (Rudel, 2003). There are several studies surveying the organotin compounds in reservoirs supplying drinking water (Nikolaou *et al.*, 2007).

Secondly, it is well known that PVC, the parent compound of CPVC, can leach vinyl chloride monomer (VCM) into the environment, including into drinking water if pipes are considered. VCM is listed as a carcinogen by OSHA (the Occupational Safety and Health Administration) and NIEH (the National Institute of Environmental Health) (NIEH report, 1997), causing VCM tumors of the liver, brain, lung, lymphatic and hematopoietic system. A study found that after 30 days of exposure, VCM concentrations leached from PVC pipe were generally greater than 2.5 µg/liter (Al-Malack *et al.*, 2000), which is higher than established (safe) values (0.5–2 µg/liter). Being derived from PVC, CPVC is expected to have the same monomer and dangers associated with it.

Thirdly, thermal decomposition, combustion or pyrolysis products of CPVC from fire (Fardell, 1993) include several hazardous gases, such as carbon monoxide, carbon dioxide, hydrogen chloride and small amounts of benzene, aromatic (and aliphatic) hydrocarbons, small amounts of chloroform and carbon tetrachloride, in addition to organotin and hydrocarbon compounds. Irritating peroxide fumes are formed when CPVC is heated up to and above its thermal decomposition point. It is well known that both PVC and CPVC have restricted thermal stabilities because of their tendency to dehydrochlorination. In fact, if thermal decomposition/degradation products of CPVC are considered to be similar to those of PVC, in addition to these chemicals there should be:

- VCM (considered as a carcinogenic and systemic toxin, as described above)
- HCl and phosgene (considered as mucous membrane and respiratory irritant)
- Dioxins, furans, PBTs (persistent bioaccumulative toxicants) and PCBs (polychlorinated biphenyls).

All are considered as potentially carcinogenic (Burke *et al.*, 2001; Ammala *et al.*, 2011).

Inhalation of decomposition (and/or combustion) products causes irritation of the respiratory tract, eyes and skin. Depending on the severity of exposure, physiological responses will be coughing, pain and inflammation. Chronic exposure to fumes and vapors from heated or thermally decomposed CPVC may cause an asthma-like syndrome due to the inhalation of process vapors or fumes. Due to the possible effects of CPVC on health,

which is a controversial issue, its use in PVC applications for cables as a flame retardant is decreasing.

Fourthly, CPVC piping and fittings are joined with CPVC cements, which can be a one-step or two-step process. The two-step process additionally requires the use of a primer. Most of the solvents that are used in pipe cements, primers and cleaners are considered as eye irritants. To be more specific, primers that contain solvents are acetone (0–1%), tetrahydrofuran (THF, 4–40%), methyl ethyl ketone (MEK, 30–85%), and cyclohexanone (5–15%). In addition, there may be disinfection by-products (DBP) including trihalomethanes (THM) such as chloroform, without mentioning that chloroform and vinyl chloride monomer may be found in the pipe itself. All of these chemicals are leachable into drinking water for long or short periods of time depending on the conditions. And among these solvents, THF raises more serious health concerns, as it is a known carcinogenic compound. Most of the solvents used in pipe cements, primers and cleaners are eye irritants.

Aiming to force the development of low-emitting/leaching CPVC piping materials, adhesives, sealants and primers are expected to comply with the ‘South Coast Air Quality Management District (SCAQMD) Rule No. 1168’ (effective as of 1 July 2005) in the USA, and for CPVC welding, a maximum VOC limit is put at 490 g/liter, less water.

3.2.3 CR (CAS number: 9010-98-4)

CR (chloroprene rubber, polychloroprene, poly[2-chloro-1,3 butadiene], also known by the generic names of first ‘DuPrene’ and later ‘neoprene’, is composed of mostly *trans*-1,4-polychloroprene with the formula $[\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2]_n$. It is an important diene-based elastomer produced from its monomer chloroprene, 2-chloro-1,3-butadiene, by free-radical emulsion polymerization (Campbell, 2000). Polymerization appears to take place almost entirely in the *trans*-1,4 form with some *cis*-structures, and CR is a crystallizable elastomer.

Vulcanization of CR is different from conventional methods, because electronegative chlorine interferes both with the double bond and with the α -methylenic group by deactivation, so that the common vulcanizing agent sulfur is ineffective and/or slow for the CR case. CR can be vulcanized by heating with zinc and magnesium oxides alone, by rearrangement and chlorine removal. This is exactly the same strategy employed for some of the other chlorinated polymers, i.e. CSPE.

CR is an extremely useful synthetic rubber, developed in 1931, and it was the first specialty elastomer with an annual consumption of above 3×10^5 tons worldwide. CR is mainly produced in the US, Germany, Japan, and China, and its largest consumption is in the US, China and the EU. CR was

particularly useful in the Second World War as an artificial rubber with good weathering properties and resistance to heat and oil.

For rubbers or elastomers, low values for T_g are essential. Most such materials have the general formula $-\text{[CH}_2\text{-CH = C(X)-CH}_2\text{]}_n-$; however, in the case of chloroprene rubber where $X = \text{Cl}$, the size of Cl is relatively large and polar, hence the T_g value of CR is not expected to be too low. In fact it is -20°C , compared with two common rubbers – BR (butadiene rubber) or poly(*cis*-1,4-butadiene), where $X = \text{H}$ and T_g is -108°C ; and NR (natural rubber) or poly(*cis*-1,4-isoprene), where $X = \text{CH}_3$ and T_g is -66°C .

CR has perfect mechanical properties and fatigue and tear resistances which are second only to those of NR, with excellent oil, chemical and heat resistances, low flammability, high ozone and weather resistance. CRs are widely used in general engineering applications, such as in the production of dipped articles (e.g. gloves), wraps and sheets, as improvers of bitumen, as the base material for (solvent- or water-based) adhesives, in various molded goods, in cable coatings, transmission/conveyor belts and profiles, and primarily as the material for gaskets, tubing, O-rings, seals, weather stripping and hose (for gasoline).

The damping capacity of CR is fairly high. Its low permeability to water makes it suitable for sealer-type finishes for masonry and concrete. Unlike many other elastomers, CR vulcanizates already have high tensile strengths in the absence of carbon black and no reinforcing effect is found with any filler.

Some specific physical and mechanical values of CR pure gum vulcanizates are given in Table 3.4.

Table 3.4 Some physical and mechanical values of CR pure gum vulcanizates

Density	1.23 g/cm ³
Glass transition temperature	-20°C
Melting point	40°C
Lower and upper use temperatures	-35°C and 180°C (continuous high temperature limit: 120°C)
Tensile strength at break	19 MPa
Elongation at break	800%
Modulus (at 300% elongation)	4.3 MPa
Hardness (Shore A)	50
Resistance to acids, alkalis, gasoline and oil	Good
Resistance to aromatic hydrocarbons	Fair
Resistance to ketones and chlorinated solvents	Poor
Resistance to oxidation and ozone	Excellent
Resistance to gamma irradiation	Poor
Resistance to flame	Good

Although specifically known and used for its oil resistance, CR is also a very good general-purpose rubber that can replace NR in most of its uses. Some 60% of CR produced is being used in the rubber industry for products such as molded goods, cables, transmission and conveyor belts. CR has been shown to make excellent tires (but cannot compete with other elastomers in price).

CR is also a very important source as a raw material for adhesives (both solvent-based and water-based as well as contact adhesives, *ca.* 33%). CR contact adhesives are used for bonding high-pressure laminates, automotive trim, roofing-membrane attachment, furniture, kitchen cabinets, custom display cabinets, interior and exterior panels, wall partitions, etc.

Different latex applications of CR are well known (*ca.* 6%). CR latexes are mainly aqueous colloidal dispersions of CR or of copolymers of it with other monomers (such as methacrylic acid or 2,3-dichloro-1,3-butadiene), which are used for various bonding and adhesive applications as well as for production of dipped goods that require toughness in the unreinforced film, e.g. gloves. CR latex uses include adhesives, binders, coatings, dipped goods, (elasticized) improved asphalt and concrete, and foams. Tough crystalline CR polymers are in general preferred for adhesives; whereas softer, more flexible polymers are preferred for mechanical goods applications which can be compounded and fabricated for manufacture of rubber goods by molding, extrusion, or calendaring operations. Other uses of CR include wire and cable coatings, industrial and gasoline hoses, coated fabrics, gaskets, tubing, O-rings and seals.

Civil engineering and construction studies in general require elastomers with exceptionally good resistance to weathering, long-term flexibility and good mechanical properties; and CR answers to all such needs. Extruded neoprene water stops, with dumb-bell center bulb cross-sections, are extensively used for contraction and expansion joints in concrete roofs, walls and foundations for sewage plants, bridges, overpasses, viaducts, tunnels, piers, dams, reservoirs and many other structures. Glazing neoprene gaskets are successfully used to accommodate thermal movements with retained elasticities. The lockstrip-type neoprene gaskets are particularly effective and also simple to install in construction applications. Preformed CR elastomeric joint seals are used for concrete pavements.

Various formulations based on neoprene are also used extensively in building adhesives, corrosion-resistant coatings, and a variety of mastics and waterproofing compounds, as well as several specific applications such as weather stripping for fire doors and noise isolation (i.e., for floating floors). One of the best known uses for CR fabric is for (scuba diving) wetsuits and orthopedic braces.

CR is considered as not classifiable as to its carcinogenicity to humans, if pure; and it is not considered as toxic. In fact, major CR types are on the

approved list of the FDA (Food and Drug Administration of the US Department of Health, Education and Welfare). However, various processed CR products, including solid rubber goods and adhesives, may have a number of ingredients that may stay or evolve (as a gas) that can be hazardous, or may cause skin sensitivities, as follows.

Firstly, volatile ingredients that may exist in CR include mainly chloroprene monomer (CM), toluene and butadiene (BD), in most cases, in addition to some lead-containing products (i.e., lead oxide) used as compounding agents, and thiourea and lead from the curing system (Ethylene Thiourea, Report on Carcinogens, 2002), and all of these may be left in the system even in small (trace) quantities.

Among these, CM is a volatile and highly reactive chemical, with an estimated residence time in the atmosphere of 4.8 hours, and a recognized carcinogen. It is also suspected to be a strong toxicant (specifically towards cardiovascular, blood, endocrine and neuro systems) that affects liver and kidney at high levels of acute exposure. CM is a federal hazardous air pollutant and was identified as a toxic air contaminant in April 1993 under AB 2728 in the US. CM vapors are irritating to the eyes and respiratory tract at very low concentrations. It is a central nervous system depressant at high levels.

BD is listed by the EPA as a toxic pollutant. It is used during production of CR and small quantities may remain in the bulk CR as impurities and be released as a gas during processing of CR (or later while standing). A study conducted at the EPA's Atmospheric Research and Exposure Assessment Laboratory showed emission levels of BD at 2–40% when processing CR (US EPA, 1985). Acute low-level exposure to BD causes irritation of eye, throat and other respiratory tract, and acute high-level exposure may cause nausea, lowering of the pulse and damage to the central nervous system. It is still debatable whether BD is a true carcinogen or not.

Both thiourea and lead compounds are known to be hazardous to health. Lead and its compounds (mainly lead oxide as mentioned above), irrespective of whether water soluble or not, are poisonous to humans, especially lead oxide. Exposure is mainly by inhalation, concentrated in soft tissues, mainly in liver and kidneys; it acts as a cumulative poison (Akovali, 2007).

Secondly, CR adhesives may contain rosin or colophony (*ca.* 4%), which is a skin contact sensitizer. The EU states that a colophony level of 0.1% or greater must be labeled as a potential skin contact sensitizer (EU Dangerous Preparations Directive 1999/45/EC, 2002).

Thirdly, the solution-bonding adhesives of CR, in the case of traditional solvent-based ones, usually contain a mixture of solvents (including a ketone or an ester, an aromatic and an aliphatic hydrocarbon such as naphtha, naphthalene, hexane, acetone, methyl ethyl ketone (MEK), benzene, and toluene); while pressure-sensitive and contact adhesives contain zinc oxide

and styryl phenol. Almost all of these chemicals are toxic to humans, and benzene is carcinogenic (Akovali, 2007). Rubber and gasket adhesives usually have solvents like hexane, naphtha, acetone and zinc oxide. Modified CR adhesives that contain water as the solvent do not pose such problems.

Fourthly, although CR has very low oral toxicity in general, it may cause mainly irritation and skin allergic reactions (for those with allergies or sensitive skin) upon direct contact or from wearing clothing, using gloves, boots or support braces made from PC fabric, i.e., dermatitis. This may be due to the thiourea left unused after vulcanization.

Fifthly, CR contains chlorine and there is a high possibility of dioxin release throughout its lifecycle, resulting from either manufacturing practices or from its intentional or unintentional combustion, i.e., fire. Dioxin is known to be a highly toxic chemical and a proven carcinogen to humans (IARC Group 1 carcinogen) (Akovali, 2007). Furthermore, if PC is burned in a fire, hydrogen chloride (HCl) gas is released, which is considered a severe eye and respiratory irritant.

3.3 Alternative materials

Although it is very difficult to replace completely the use of CPE, CSPE, CPVC and CR as construction materials in all aspects of performance and economy with safer plastics, several suggestions can be made:

- First of all, whenever possible, carefully selected and prepared completely pure versions of polymers which may cause VOC emissions as low as possible can be selected, preferred and used, although this may prove uneconomic.
- TPO (thermoplastic polyolefins) and EPDM (ethylene propylene diene monomer, 'M class', with a saturated chain of the polymethylene where ethylene content is 45–75%) both fulfill the criteria for single-ply membrane roof waterproofing applications, are readily available and are quite cost-competitive.
- Window treatments are available in TPO, fiberglass and polyesters.
- For plumbing, HDPE or PP can offer other alternatives.
- Materials such as PP (polypropylene), HDPE and EPDM are commonly available alternatives to CSPE and to CR in geomembrane applications.
- For soundproofing, for ultimate flooring and wall noise barrier systems for airborne sound control, either MLV (mass loaded vinyl barrier), green glue (a water-based viscoelastic damping compound) or cotton fiber can be considered in place of CR. Among these, probably the second and third (or their combination) can be more economically viable options.

- Solvent-based adhesives of PC can be avoided as much as possible, and can be replaced with those of all water-based ones; while as alternatives to CR contact adhesives, PU (polyurethane) and styrene block copolymers can be considered.

3.4 Sources of further information

Some suggestions for PBT (persistent bioaccumulative toxicant)-free building materials are as follows:

- GreenSpec Product Directory: <<http://www.buildinggreen.com>>
- Healthy Building Network, PVC free building materials chart: <<http://www.healthybuilding.net/pvc/alternatives.html>>
- Health Care Without Harm, Green Building: Alternatives to Polyvinyl Chloride (PVC) Building Materials for the Neonatal Intensive Care Unit (NICU) (includes information on PVC and HFR content): <<http://www.noharm.org/details.cfm?ID=1339&type=document>>

3.5 References and further reading

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Materials responsible for formaldehyde and volatile organic compound (VOC) emissions

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Abstract: Volatile organic compounds (VOCs) are an important class of indoor air pollutants; with indoor concentrations generally higher than outdoors. Formaldehyde is a priority VOC because of its frequent occurrence in indoor air and the serious health outcomes resulting from exposure. Taking formaldehyde as a representative VOC, this chapter reviews the knowledge necessary to develop solutions to indoor VOC pollution. The toxicology of formaldehyde is briefly reviewed. Then the current understanding of VOC emission behavior is discussed, including experimental techniques for measuring emissions, modeling approaches for predicting emissions, and the impacts of environmental factors on emissions. With a comprehensive understanding spanning emission characteristics and toxicology, it is possible to develop effective strategies to maintain indoor VOC concentrations below a safe threshold.

Key words: volatile organic compounds, formaldehyde, toxicology, emissions, testing, modeling, building materials.

4.1 Introduction

Since people typically spend over 80% of their time indoors (Klepeis *et al.*, 2001; Adgate *et al.*, 2004), indoor air quality (IAQ) has a substantial effect on occupants' comfort, health and productivity. Among all the causes of degradation of indoor air quality, volatile organic compounds (VOCs) have been recognized as one of the most important classes of indoor air pollutants (Weschler, 2009). VOCs are a large group of organic chemicals that have a low boiling point; according to the US EPA, VOC means 'any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions'. Common VOCs occurring in the indoor environment include formaldehyde, benzene, toluene, xylene, styrene, acetaldehyde, naphthalene, limonene, and hexanal (Weschler, 2009; Sarigiannis *et al.*, 2011). Exposure to VOCs may cause reduced worker productivity (Bako-Biro *et al.*, 2004; Fanger, 2006), acute health effects such as eye and respiratory irritations, headaches, fatigue, and asthmatic symptoms (Mølhave, 1989; Wolkoff and Nielsen, 2001; Billionnet *et al.*, 2011; Jie *et al.*, 2011), and chronic illnesses such as cancer (Rennix *et al.*, 2005; Sax *et al.*, 2006; Boeglin *et al.*, 2006). However, the health effect

of individual VOCs can vary greatly, ranging from being highly toxic to having little known health effects. For example, benzene is 'known to be a human carcinogen' (NTP, 2011) while toluene is much less toxic than benzene although it shares a similar molecular structure. There are many sources of VOCs in the indoor environment, including building materials, consumer products, and furniture (Bluyssen *et al.*, 1996; Missia *et al.*, 2010). Some major sources, such as paints, carpets, composite wood products, and floorings, are used extensively and permanently indoors, leading to ubiquitous and abundant presence of VOCs in the indoor air. It has been reported that indoor VOC concentrations generally far exceed outdoor levels (Ohura *et al.*, 2006; Jia *et al.*, 2008; Missia *et al.*, 2010).

Among all the VOCs in the indoor environment, formaldehyde is one of the most common and best-known compounds and a priority indoor air pollutant due to its wide distribution in indoor air and its highly toxic nature (Salthammer *et al.*, 2010). Different from most VOCs which are liquids or solids, formaldehyde is a colorless gas with a pungent odor at room temperature and pressure (Reuss *et al.*, 2003). It is soluble in water and is generally used in solution or in its polymerized form, paraformaldehyde (Lide, 2003). Formaldehyde is formed in large quantities via the oxidation of hydrocarbons naturally (WHO, 1989). It is also endogenously formed in most life forms and is present in tissues, cells, and bodily fluids (Heck and Casanova, 2004). The most important anthropogenic sources include direct emission from production and use of formaldehyde, and combustion, such as smoking and automotive exhaust from engines (WHO, 1989). Since the 1880s formaldehyde has been produced commercially, and in recent years global industrial production of formaldehyde is over 20 million tonnes (Bizzari, 2000), mainly used for the following (IARC, 2006):

- Production of synthetic resins including urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde. These resins are used as adhesives and impregnating resins in the manufacture of wood products and curable molding products, and in the textile, leather, rubber and cement industries.
- As an intermediate in the synthesis of other industrial chemicals.
- As a preservation and disinfection agent for human and veterinary drugs, biological specimens, pesticides and cosmetic products.

Under atmospheric conditions, formaldehyde is readily removed by photolysis and reaction with hydroxyl radicals in sunlight to carbon dioxide, resulting in a low background concentration from 0.1 to 2.7 $\mu\text{g}/\text{m}^3$ (WHO, 1989). Due to the presence of a large spectrum of formaldehyde emission sources indoors, such as the composite wood products made from urea-formaldehyde resin, and the slow removal rate in the indoor environment, the levels of formaldehyde in indoor air are mostly much higher than

outdoors, ranging from 10 to 4000 $\mu\text{g}/\text{m}^3$ (WHO, 1989; IARC, 2006). Therefore, although people can be exposed to formaldehyde through other sources such as food, indoor air is the most influential source for the general population while occupational exposures are important for specific populations such as employees in formaldehyde-related industry and sanitary services (Kauppinen *et al.*, 2000).

It has been well recognized that exposure to formaldehyde can cause irritation of the mucosa of the eye and upper respiratory system and may induce allergic contact dermatitis and contact urticaria (Paustenbach *et al.*, 1997; Koss and Tesseraux, 1999; Arts *et al.*, 2008). Chronic formaldehyde exposure can cause cancers, and therefore it has been classified as ‘carcinogenic to humans (Group 1)’ by the International Agency for Research on Cancer (IARC, 2006) and described as ‘known to be a human carcinogen’ by the US National Toxicology Program (NTP, 2011). However, the toxicological mechanisms of formaldehyde are complicated and require further study (Speit *et al.*, 2007; Bosetti *et al.*, 2008). Concerning the health risks associated with indoor formaldehyde exposure, various international guidelines and recommendations have been established for formaldehyde in indoor air (Salthammer *et al.*, 2010). Recently, new legislation on ‘Formaldehyde Standards for Composite Wood Products’ was passed by the US Congress and signed by the President.

The occurrences of formaldehyde and other VOCs in building materials and emissions during the use phase are closely related to the manufacturing procedures. For example, manufacturing of widely used medium-density fiberboard consists of several steps: firstly, wood chips are milled into wood fibers; the wood fibers are then blended with adhesive resins and the resulting mixture is dried by hot air; finally, the wood fibers after resin application are placed on a conveyer belt and hot-pressed into medium-density fiberboard (He *et al.*, 2012). With low cost and good performance, urea-formaldehyde and phenol-formaldehyde resins are the most commonly used adhesives in wood-based panels, both of which would release formaldehyde due to residuals and degradation. The application of adhesives and hot-pressing treatment therefore lead to high emissions of formaldehyde when the products are used indoors.

In this chapter, formaldehyde will be presented in detail as the representative of indoor VOCs. Its toxicology will be first discussed, including its toxicokinetics, major health effects, and the possible mechanisms of its primary toxicities. Then state-of-the-art knowledge for formaldehyde and other VOC emissions from building materials will be reviewed, including the experimental techniques for measuring emissions, modeling techniques for describing and predicting emissions, and impacts of environmental factors on emissions. These understandings could facilitate the screening-level assessment of exposure to indoor VOCs, product reformulation

strategies to reduce or prevent VOC emissions, and development of standards for both the VOC concentrations in indoor air and environmental performance of indoor materials.

4.2 Toxicology of formaldehyde

4.2.1 Toxicokinetics

Absorption

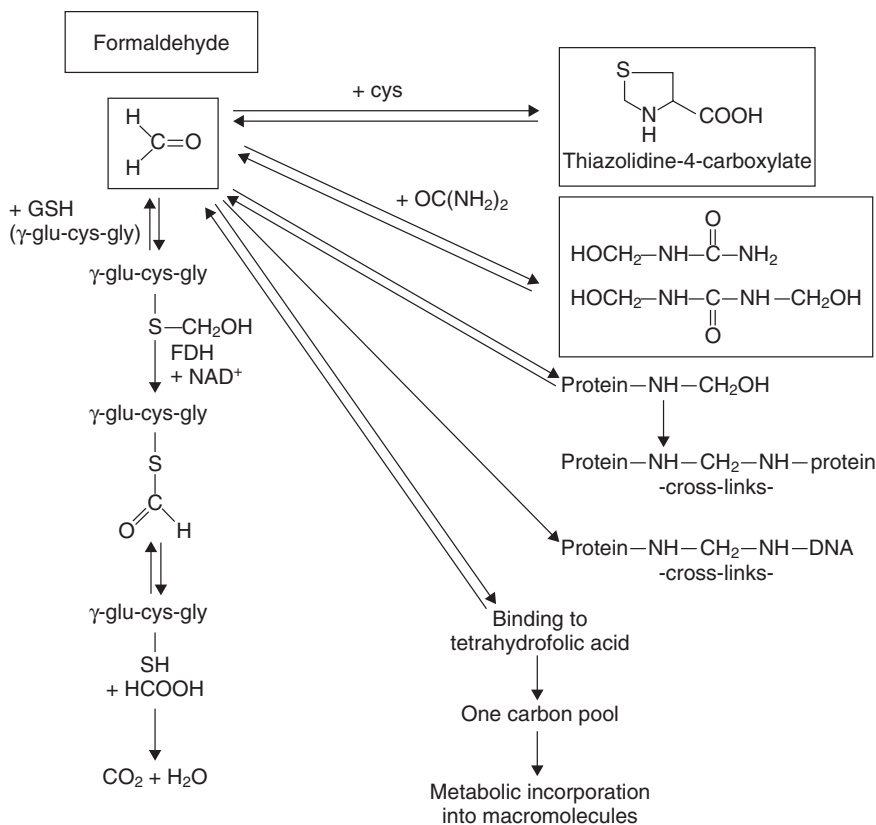
Due to its high water solubility, formaldehyde is rapidly absorbed in the respiratory tract once inhaled (WHO, 1989). Various airflow patterns due to anatomical differences in noses may cause different uptake of inhaled formaldehyde by different species of animals (Schreider, 1986; Morgan *et al.*, 1991; Georgieva *et al.*, 2003). A three-dimensional, anatomically realistic computational fluid dynamics (CFD) model of formaldehyde gas transport in the nasal passages predicted that over 90% of inhaled formaldehyde is absorbed in the upper respiratory tract for humans (Kimbell *et al.*, 2001). Formaldehyde can penetrate human skin but dermal absorption is expected to be slight when exposed to airborne formaldehyde (WHO, 1989).

Distribution

After absorption by animals and humans, formaldehyde can be metabolized and distributed rapidly to the entire body. For example, there was no exposure-related increase in the blood concentration of human volunteers after exposure to 2.3 mg/m³ formaldehyde for 40 minutes (Heck *et al.*, 1985). Following a six-hour inhalation exposure of rats to ¹⁴C-formaldehyde, radioactivity was extensively distributed in other tissues, indicating that absorbed ¹⁴C-formaldehyde and its metabolites are rapidly removed by the mucosal blood supply and distributed throughout the body (Johansson and Tjalve, 1978).

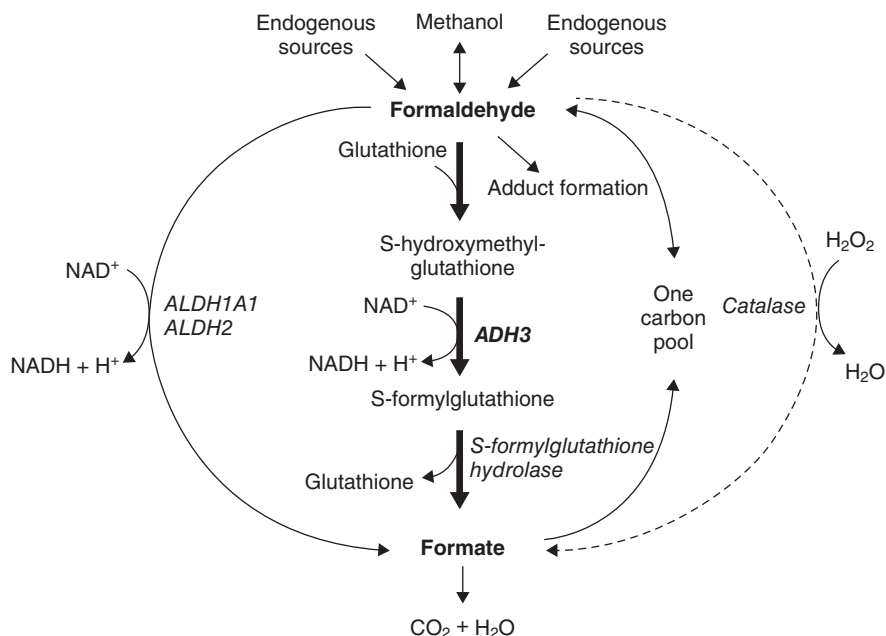
Metabolism

Formaldehyde undergoes rapid biotransformation immediately after absorption (WHO, 1989). Figure 4.1 shows the biological reactions and metabolism pathways of formaldehyde (Bolt, 1987). Formaldehyde can be oxidized into formate/formic acid and then carbon dioxide. It can also undergo nonenzymatic reactions with amino and other groups in DNA, RNA and protein molecules and can further cause crosslinks between two macromolecules. Formaldehyde and its metabolites can also be incorporated into the one-carbon pool for synthesis of certain nucleic acids and amino acids, and eventually, cellular macromolecules.



4.1 Biological reactions and metabolism pathways of formaldehyde (Bolt, 1987).

Figure 4.2 shows the detailed pathways for metabolic detoxification by oxidation and the enzyme systems involved (Hedberg *et al.*, 2002). The primary and generally most important system initially involves alcohol dehydrogenase 3 (ADH3), which oxidizes S-hydroxymethylglutathione, GSH-conjugated formaldehyde spontaneously formed by formaldehyde and reduced glutathione (GSH), to S-formylglutathione. This intermediate is then further metabolized by S-formylglutathione hydrolase to yield formate/formic acid and reduced GSH. Identical to any alcohol oxidation by ADH enzymes, the ADH3-dependent step requires catalysis by zinc and uses NAD^+/NADH (coenzymes found in all living cells) as the electron acceptor and donor (Höög *et al.*, 2001). The second enzyme system is the ALDHs – class 1 (cytosolic ALDH; ALDH1A1) and class 2 (mitochondrial ALDH; ALDH2) – which have an affinity for free formaldehyde. Catalase may also contribute to the oxidation of formaldehyde to formate/formic



4.2 Metabolism of formaldehyde (Hedberg *et al.*, 2002).

acid, but only when hydrogen peroxide is present (Jones *et al.*, 1978). Formaldehyde may also be reduced to methanol and then reconverted to formaldehyde (Pocker and Li, 1991).

Excretion

Elimination of formaldehyde from the blood takes very short time, with a half-time of about 1–1.5 minutes, via exhalation or renal excretion. Radioactive investigations on rats using ^{14}C -formaldehyde suggest over 80% of the radiolabel was recovered as carbon dioxide in exhalation (Du Vigneaud *et al.*, 1950; Neely, 1964). Small amounts are excreted in the urine as formate salts, methionine, serine, and other metabolites (WHO, 1989).

4.2.2 Health effects of human exposure

Predominant effects of short-term exposure to formaldehyde in humans include irritation of the eyes, nose and throat, and concentration-dependent discomfort, lachrymation, sneezing, coughing, nausea, dyspnoea and finally death (Table 4.1). Formaldehyde is also a sensitizer. There are several studies reporting asthma caused by sensitization effects of formaldehyde (Nordman *et al.*, 1985; Wantke *et al.*, 1996). Skin sensitization can be induced

Table 4.1 Effects of formaldehyde in humans after short-term exposure

Concentration range or average (mg/m ³)	Time range or average	Health effects in general population
0.03	Repeated exposure	Odor detection threshold (10th percentile)
0.18	Repeated exposure	Odor detection threshold (50th percentile)
0.6	Repeated exposure	Odor detection threshold (90th percentile)
0.1–3.1	Single and repeated exposure	Throat and nose irritation threshold
0.6–1.2	Single and repeated exposure	Eye irritation threshold
0.5–2	3–5 hours	Decreased nasal mucus flow rate
2.4	40 minutes on two successive days with 10 minutes of moderate exercise on the second day	Post-exposure (up to 24 hours) headache
2.5–3.7	Unspecified	Biting sensation in eyes and nose
5–6.2	30 minutes	Tolerable for 30 minutes with lachrymation
12–25	Unspecified	Strong lachrymation, lasting for 1 hour
37–60	Unspecified	Pulmonary edema, pneumonia, danger to life
60–125	Unspecified	Death

Sources: WHO (1989); IARC (1995).

by direct skin contact with formaldehyde solutions, causing allergic contact dermatitis and contact urticaria (WHO, 1989).

It has been confirmed that exposure to formaldehyde can cause nasopharyngeal cancer (IARC, 2006). Although a number of studies have found associations between exposure to formaldehyde and occurrences of other cancers, a causal role for formaldehyde in relation to them cannot be established until more evidence is available (IARC, 2006). The reasons for less opportunity to cause remote site cancers and systematic illnesses compared with the chance in the upper respiratory tract may include the fact that formaldehyde is absorbed almost completely in the upper respiratory tract when inhaled and then rapidly metabolized. There are also a variety of studies evaluating the neural and reproductive effects of exposures to formaldehyde in humans but the results are inconclusive overall (Hemminki

et al., 1982; Axelsson *et al.*, 1984; Taskinen *et al.*, 1994, 1999; Collins *et al.*, 2001; IARC, 2006).

4.2.3 Mechanisms of action

Reactions with macromolecules

Formaldehyde can form covalent bindings to specific sites on macromolecules by replacing active hydrogen atoms, and a two-step mechanism for the formation of methylene crosslinks between macromolecules has been proposed (Feldman, 1973). The first step is the fast, reversible formation of unstable methylol derivatives by formaldehyde and macromolecules. The irreversible formation of a stable methylene crosslink may then occur by way of nucleophilic attack on the methylene carbon. These crosslinks could occur between two proteins, between DNA and protein, or between DNA and DNA. By involving DNA, the latter two reactions can arrest DNA replication and lead to micronucleus (MN), sister chromatid exchanges (SCEs), chromosomal aberrations (CA), and DNA damage (Speit *et al.*, 2007; Costa *et al.*, 2008). Such damage to DNA, however, can be removed by spontaneous hydrolysis and active repair by cellular DNA repair systems and, therefore, cell division is required prior to DNA repair for mutagenesis to occur. Before formaldehyde reacts with amino groups in RNA, the hydrogen bonds forming the coiled RNA may break; formaldehyde hardly reacts with native double-stranded DNA since the hydrogen bonds holding DNA in its double helix are more stable (Feldman, 1973; Auerbach *et al.*, 1977). Therefore, unwinding of the double helix during cell replication may be required to expose critical sites on the DNA to covalent binding (Singer and Kusmierek, 1982). Convincing evidence supporting this theory is the apparent cell-cycle specificity of formaldehyde: mutagenesis in *Drosophila* is restricted to the period of chromosome replication preceding meiosis (Auerbach *et al.*, 1977). This theory also explains the experimental results that exponentially growing cultures of yeast have greater sensitivities to lethality and mutagenesis than stationary cultures (Chanet and von Borstel, 1979).

Cytotoxicity

As described in the previous subsection, formaldehyde can react with proteins and result in protein denaturation, precipitation and coagulation necrosis, inhibiting cellular physiologic functions or even killing the cells. Recent *in vitro* studies suggest oxidative stress increase caused by formaldehyde may be also an important mechanism for its molecular cytotoxicity (Teng *et al.*, 2001; Oyama *et al.*, 2002). High oxidative stress can cause toxic effects through the production of peroxides and free radicals that damage

all components of the cell. Inhibiting cell respiration and other cellular enzymatic antioxidant defense systems by formaldehyde, reactive oxygen species are further generated, thus contributing to oxidative stress. Furthermore, high levels of formaldehyde can significantly reduce GSH content, which actually can work to protect cells from oxidative stress (Meister and Anderson, 1983), and the decrease in cellular GSH content therefore increases cell vulnerability to oxidative stress (Kashiwagi *et al.*, 1994). Obviously, the various mechanisms of cytotoxicity of formaldehyde are correlated with each other, making the impacts complex. As a result of its cytotoxicity, formaldehyde can be used for disinfection and conservation in several circumstances.

The cytotoxicity of formaldehyde also plays an important role in its carcinogenicity. A prominent response to cell loss associated with cytotoxicity is compensatory cell replication, i.e. division of surviving cells to compensate for dead cells and maintain the functions of organisms. Several studies have shown that cell proliferation is stimulated after exposure to formaldehyde (Swenberg *et al.*, 1983; Tyihák *et al.*, 2001). During the increased cell division, the likelihood of interaction of formaldehyde with DNA would increase, as would fixation of adducts before DNA repair could occur. Therefore, carcinogenesis of formaldehyde is related directly to the increased cell division resulting from its cytotoxicity.

Irritation

It is well known that formaldehyde can cause irritation, which is defined as a chemically produced local inflammatory response characterized by edema, erythema or corrosion (Mathias and Maibach, 1982). Respiratory tract irritation and eye irritation can involve a chemosensory effect, i.e., formaldehyde molecules bind to specific receptors on sensory neurons at local nerve endings (nervus trigeminus) and therefore activate an opening ion channel via specific proteins, which is called trigeminal stimulation or sensory irritation. Over a broad range of concentrations, the trigeminal stimulation will not necessarily lead to cell or tissue damage but it may cause reflex responses such as sneezing, lachrymation, rhinorrhea, coughing, vasodilation and changes in the rate and depth of respiration, resulting in a decrease in the total amount of inhaled material, thus protecting the individual (Lang *et al.*, 2008). On the other hand, the irritation occurring at high concentrations is a localized pathophysiological response to formaldehyde involving local redness, swelling, pruritis or pain. These effects are comparable to those induced at the skin and can be termed pathological irritation (Arts, 2006). The pathological irritation of formaldehyde is believed to be similar to that caused by other irritant chemicals, such as toluene diisocyanate (TDI) and cotton dust, which cause histamine release from basophils.

Immunological basis of allergy

Some adverse effects caused by formaldehyde, such as allergic contact dermatitis and asthma, may result from its immunological effects as a sensitizer (Feinman, 1988). Most allergic reactions to formaldehyde can be divided into two basic types: delayed cell-mediated and immediate antibody-mediated, which follow different characteristic time courses and are explained by different mechanisms (WHO, 1989; Roberts and Adams, 2000). Allergic contact dermatitis (ACD), which can be induced by skin contact with formaldehyde, is an example of delayed cell-mediated hypersensitivity. T-cells, one specific group of lymphocytes, and Langerhans cells, one group of dendritic cells in the epidermis, are involved (Merad *et al.*, 2008). Formaldehyde can bind to skin proteins to produce complete antigen complexes (Basketter *et al.*, 2008). Langerhans cells can take up these complexes and present them to T-cells so that sensitization of T-cells occurs. Upon reexposure to formaldehyde, primed T-cells recognize the antigen and are triggered to produce effector cells, which initiate the immune reaction. There is a delay of 24–48 hours before this reaction is elicited. After elicitation, pharmacologically active mediators (such as enzymes and cytokines) are secreted, producing tissue inflammation.

Once established, ACD may persist for years (Feinman, 1988). In contrast, antibody-mediated immediate hypersensitivity reactions have a rapid onset and shorter duration. They are mediated by special antibodies produced in response to allergic stimulation in previously sensitized subjects. IgE is a specific antibody class important in the immediate allergic response to environmental antigens. IgE antibodies can bind to the mast cells, granulocytes, macrophages and platelets. These cells, after binding IgE and antigen, are triggered to release mediators, such as prostaglandins, histamine, leukotrienes, chemotactic factors, and platelet activating factors. These mediators directly or indirectly produce effects such as smooth muscle contraction, bronchoconstriction and capillary vasodilation that result in characteristic clinical syndromes like asthma and contact urticaria. The production of specific antibodies is under genetic control so that there are geographical and demographic differences in the incidence of antibody-mediated immediate hypersensitivity to a given allergen (Feinman, 1988).

4.3 Emission testing of formaldehyde and other volatile organic compounds (VOCs)

4.3.1 Analytical methods for measuring formaldehyde and other VOCs

To measure the concentration of formaldehyde and other VOCs in indoor air, two main analytical methods are generally deployed, i.e., the GC method and the DNPH method.

For the GC method, the VOCs are first collected from the indoor environment using air sampling pumps coupled with sorbent tubes containing appropriate sorbents, such as Tenax[®] TA sorbent, activated carbon and graphitized carbon blacks. Then the collected VOCs are released by thermal desorption and injected into a gas chromatography (GC) column, a common type of chromatography used in analytic chemistry for separating compounds. Different kinds of detectors can then be used for qualitative and quantitative determination of the compounds. The flame ionization detector (FID), photoionization detector (PID), and mass spectrometric detector (MS) have been successfully used for VOCs (Ulman and Chilmonczyk, 2007). Chung *et al.* (2003) used GC/FID to simultaneously measure the total non-methane organic carbon and speciated VOCs. Zhang *et al.* (2000) suggested that GC/PID is an easy, fast and reliable method for analyzing isoprene emissions. GC/MS procedure to determine VOC concentrations has been included in several standards such as ASTM D5466-01 (2001) and ISO 16000-6 (2004). The GC/MS analysis can also be used in conjunction with a solid-phase micro-extraction (SPME) technique. The SPME involves a very thin fiber coated with an extracting phase, which can extract different kinds of VOCs from samples. The extracted VOCs can then be analyzed by GC/MS. The combination of SPME and GC/MS techniques offers spectral analysis and high instrumental sensitivity, and allows simultaneous identification and quantification of several VOCs in a sample (Pecoraino *et al.*, 2008). Furthermore, SPME is generally convenient and fast, and can be performed without solvents, thus having great potential in laboratory and field applications (Pawliszyn, 2009).

The DNPH method is widely used for determining carbonyl compounds, such as formaldehyde, other aldehydes and ketones. It has been recommended by several standards (ISO 16000-3, 2001; ASTM D5197-03, 2003). This method is based on the specific reaction between carbonyl compounds and the 2,4-dinitrophenylhydrazine (DNPH) coated on a silica gel adsorbent, which forms stable hydrazone derivatives by nucleophilic addition of DNPH with the carbonyl group in the presence of a strong acid catalyst. During the sampling process, indoor air is pumped through cartridges containing silica gel coated with an acid solution of DNPH. Then the DNPH-carbonyl derivatives are extracted with acetonitrile and analyzed using high-performance liquid chromatography (HPLC). During the analysis process, the chromatographic separation of the hydrazones is achieved using a C18-column and water/acetonitrile solvent combinations, and an ultraviolet (UV) absorption detector is often used for detection (Vairavamurthy *et al.*, 1992; Salthammer *et al.*, 2010). However, the DNPH method still has some drawbacks. Foster *et al.* (1996) observed that air humidity would affect the formation rate of hydrazones due to the accumulation of water on the cartridge. The presence of ozone at high concen-

trations would interfere negatively by reacting with both DNPH and its carbonyl derivatives in the cartridge (ASTM D5197-03, 2003). Ho *et al.* (2011) suggested that the DNPH method is unsuitable for determining unsaturated carbonyls and alternative derivatizing agents or other analytical methods should be found.

4.3.2 Emission testing methods and chambers

The emission of formaldehyde and other VOCs is an important factor in evaluating the environmental performance and health impacts of building materials. Various emission testing methods have been developed and used, and some of them have been specified in standards. For the emission testing of formaldehyde from wood-based materials, the perforator method, desiccator method, and chamber method are commonly used.

The perforator method, established as European standard EN 120 (1993), determines formaldehyde content in wood-based materials by extraction in a perforator. The test material is first cut into pieces. Then the formaldehyde in the pieces is extracted by boiling toluene and transferred into water. Finally, the formaldehyde content in the aqueous solution is measured by a suitable analytical technique (Risholm-Sundman *et al.*, 2007). The entire procedure requires large and complicated equipment, and takes 2 h for extraction and a total of about 4 h. This method determines the total formaldehyde content in the test material.

For the desiccator method (JIS A1460, 2001), the sample with a given surface area is positioned over water in a desiccator at a controlled temperature. The formaldehyde released from the tested sample for 24 h is collected by the water and then determined by the acetylacetone method or the chromotropic acid method (Salthammer *et al.*, 2010). This method provides an accurate measurement for formaldehyde emission from the sample, but does not provide information about total formaldehyde content (Kim *et al.*, 2010).

The chamber method, which has been prescribed in many standards, is widely used for the emissions testing of formaldehyde and other VOCs. The sample is placed in a chamber with clean air passing through it and the chamber concentrations of target VOCs are measured over time, generally for several days to weeks. The emission testing chambers are often made of glass or stainless steel, and in a cylindrical or rectangular shape, with size varying from a few liters (small chamber) to several cubic meters (large chamber or full-scale chamber). Chamber testing conditions are commonly controlled or specified, such as temperature, relative humidity, air exchange rate, air velocity, and material volume or loading factor (ratio of the material surface to the volume of the chamber). For the chamber method specified in most standards, the result is reported as an area-specific

emission rate (emission factor) or as a chamber concentration at steady state (EN 717-1, 2004; ISO 16000-10, 2006; ASTM D 6670-01, 2001; ISO/CD 12460, 2007; Salthammer *et al.*, 2010). The main advantage of the chamber method is that it simulates the real scenario of emissions in the indoor environment.

Table 4.2 lists some typical emission testing chambers and their applications. In the table, the Field and Laboratory Emission Cell (FLEC) and the Chamber for Laboratory Investigations of Materials, Pollution and Air Quality (CLIMPAQ) are two specially designed chambers. The FLEC is circular and made of stainless steel with a volume of 0.035 L, which includes a cap and a lower chamber. When testing, the material is placed in the lower chamber, forming a cone-shaped cavity with the inner surface of the FLEC cap. Zhang and Niu (2003) analyzed the mass transfer process of VOC in the FLEC. The CLIMPAQ is made of panes of window glass with a volume of 50.9 L, and other main surface materials are stainless steel and eloxated aluminum. One internal fan circulates the air over the tested material with some metal grids in the flow direction. The air exchange rate and air velocity over the test material surface can therefore be adjusted independently.

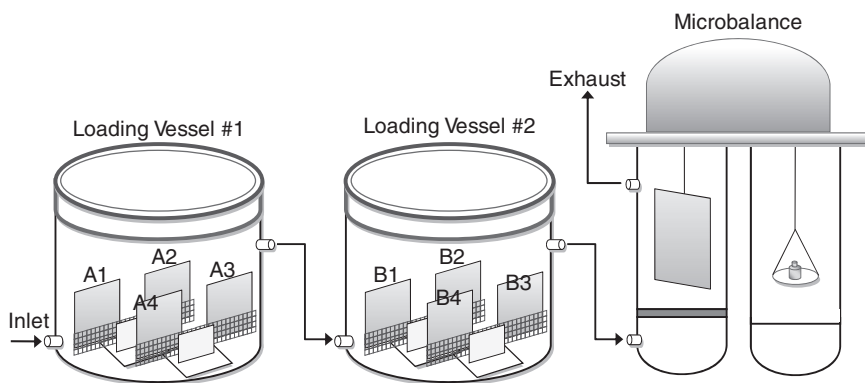
4.3.3 Reference materials for emissions testing

As introduced previously, the chamber method is widely used to determine emissions of formaldehyde and other VOCs from building materials. However, very different emission profiles are often obtained for the same material tested in different laboratories (Howard-Reed and Nabinger, 2006). There is thus a compelling need for a reference emission source that can be used to evaluate and calibrate the testing procedures. Till now, two different kinds of reference materials have been developed for VOC emissions testing (Cox *et al.*, 2010; Wei *et al.*, 2011).

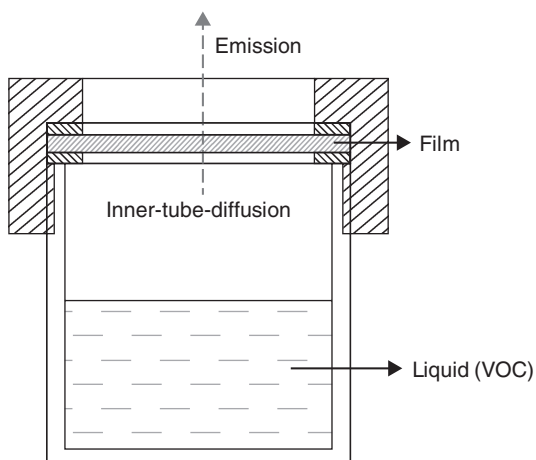
For the first reference material, polymethylpentene (PMP) film is selected as the substrate. Toluene, as a representative VOC, is infused into the film so that the loaded film has an emission profile similar to that of a typical building material that can be measured in emission testing chambers. As Fig. 4.3 shows, the toluene-laden dry air is passed through stainless steel vessels containing several PMP films. The effluent air from the last vessel is passed through a high-resolution dynamic microbalance which holds an extra film and monitors its mass throughout the loading process. During the loading process (about 2 weeks), toluene molecules diffuse from the air into the films until sorption equilibrium is reached between the material phase and the gas phase. The mass change data recorded by the microbalance is used to monitor the loading process and determine the material-phase concentration of toluene in the films when loading is complete. The loaded films are then sent to different laboratories for emission testing. Meanwhile,

Table 4.2 Some typical emission testing chambers and their applications

Testing chamber	Application	Standard/reference
20 L small chamber	Determination of formaldehyde release, formaldehyde emission by the chamber method	ISO/CD 12460, 2007
30 L small chamber	Determination of the emission characteristic parameters of formaldehyde and other VOCs from building materials	Xiong <i>et al.</i> , 2011
50 L small chamber	Measurement of VOC adsorption/desorption characteristics of typical building materials	An <i>et al.</i> , 1999
Dual 18.4 L small chamber	Measurement and simulation of VOC emission from materials	Yang <i>et al.</i> , 2001
	Study of some environmental factors on VOC adsorption	Huang <i>et al.</i> , 2006
	Measurement of the VOC diffusion and partition coefficients and study of the similarities between water vapor and VOC diffusion	Xu <i>et al.</i> , 2009
Dual 50 L small chamber	Measurement of the VOC diffusion and partition coefficients for building materials	Bodalal <i>et al.</i> , 2000
FLEC	Determination of the VOC emissions from building products and furnishing	ISO 16000-10, 2006
CLIMPAQ Dual CLIMPAQ	Determination of VOC emissions from indoor materials/products	ASTM D 7143-05, 2005
	Characterization of VOC emissions from building materials	Zhang and Niu, 2003
	Emission testing of materials and products in a controlled environment	Gunnarsen <i>et al.</i> , 1994
	Measurement of VOC diffusion and sorption parameters in building materials	Meininghaus <i>et al.</i> , 2000
1 m ³ chamber	Determination of formaldehyde release by the chamber method	ISO/CD 12460, 2007
Large chamber (≥20 m ³)	Determination of formaldehyde release by the chamber method	EN 717-1, 2004
20 m ³ large chamber	Determination of VOC emissions from indoor materials/products	ASTM D 6670-01, 2001
30 m ³ large chamber	Measurement of VOC emissions from new carpets	Little <i>et al.</i> , 1994
	Determination of the emission characteristic parameters of formaldehyde and other VOCs from furniture	Yao <i>et al.</i> , 2011



4.3 Loading process to produce reference materials.



4.4 A LIFE reference.

the emission characteristic parameters of the loaded film can be determined independently and a fundamental model can be used to predict its emissions accurately (Cox *et al.*, 2010; Liu *et al.*, 2011). Therefore, the model-predicted emission profile serves as a true reference value for validating the measured results by different laboratories, evaluating the test performance, and identifying the root cause of variability. This reference material has been successfully employed in some interlaboratory studies (Howard-Reed *et al.*, 2011a, 2011b).

The second reference material is called a LIFE (liquid, inner-tube-diffusion, film and emission) reference (Wei *et al.*, 2011), as shown in Fig. 4.4. The LIFE reference comprises a small Teflon cylinder containing a pure VOC in liquid phase, a thin film covering the opening of the cylinder, and some Teflon fastening pieces (washers and hole-cover). Therefore, VOC can

diffuse through the film and the emission rate can be adjusted by changing the film. Toluene is selected as the target VOC to develop the LIFE reference, and the preliminary results show that it has the following features (Wei *et al.*, 2011): (1) its emission rate is constant; (2) it has a long applied life of 1000 hours; and (3) it is easy to store, apply and maintain. Therefore the LIFE reference is very useful for calibrating emission testing procedures. In addition, the LIFE reference also has the equivalent emission characteristic parameters (initial emittable concentration, diffusion coefficient and partition coefficient), and can be treated as an equivalent building material. It can be thus used as a reference to determine whether a method for measuring emission characteristic parameters is reliable or not.

4.4 Emission models of formaldehyde and other volatile organic compounds (VOCs)

Although solid emission data can be obtained from emission chamber tests, they are only applicable for the specific testing conditions. Emission chamber tests are also often expensive and time-consuming. Therefore, much effort has been made to predict emissions using modeling techniques. Generally, existing models can be categorized into two groups (Zhang and Xu, 2003). The first one is empirical models constructed upon statistical analysis of emission test data (Guo, 2002a), such as the first-order decay model and the second-order decay model (Dunn, 1987; Clausen, 1993). Although simple to derive and use, empirical models lack a physical basis and provide little insight into the controlling mechanism, and therefore cannot be easily scaled from the test conditions to other conditions. In contrast, the second group of models, as will be introduced below, is based on mass-transfer mechanisms with model parameters having clear physical meanings, and therefore can predict emissions for various conditions.

Since VOCs emitted from building materials generally originate from inside the materials, the mass transfer within the materials is important in determining the emission rates and should be considered in modeling. Up to now, two kinds of diffusion models have been proposed, i.e., one-phase solid models (Little *et al.*, 1994; Huang and Haghighat, 2002; Xu and Zhang, 2003; Deng and Kim, 2004), and multi-phase solid models (Lee *et al.*, 2005, 2006; Haghighat *et al.*, 2005; Blondeau *et al.*, 2008; Marion *et al.*, 2011). Multi-phase solid models consider the porous structure of the material (pores and solid) and the mass transfer in both the pore-phase and the adsorbed-phase. Instead, one-phase solid models lump the microstructure of the building material into one uniform solid phase and are much simpler than multi-phase solid models. However, multi-phase solid models and one-phase solid models can be transformed from one to another and model parameters are also interrelated (Haghighat *et al.*, 2005; Blondeau *et al.*, 2008; Xu *et al.*,

2009). Therefore, typical physically based one-phase solid models for predicting VOC emissions will be presented in this section, and the mass-transfer mechanisms of VOC emissions will be discussed.

The first physically based diffusion model was developed by Little *et al.* (1994) for predicting VOC emissions from carpets, which also presents a widely accepted framework for later development of VOC emission models. With reference to Fig. 4.5, the transient diffusion within the material is described by Fick's second law,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad [4.1]$$

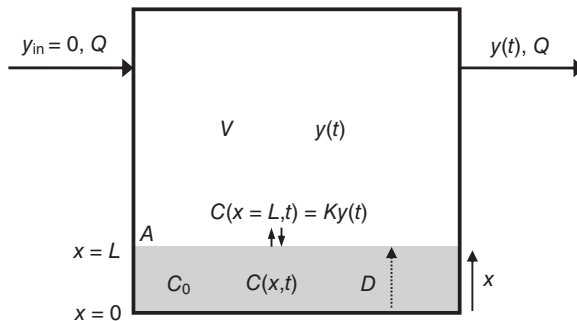
where $C(x,t)$ is the VOC concentration in the slab of material, D is the material-phase diffusion coefficient, t is time, and x is the distance from the bottom of the slab. The boundary condition at the bottom of the material assumes there is no flux, or

$$\left. \frac{\partial C}{\partial x} \right|_{x=0} = 0 \quad [4.2]$$

The boundary condition at the exposed surface is imposed by a mass balance on the VOC in the chamber air assuming the chamber air is well mixed,

$$V \frac{\partial y}{\partial t} = -D \cdot A \left. \frac{\partial C}{\partial x} \right|_{x=L} - Q \cdot y \quad [4.3]$$

where y is the concentration of VOC in the well-mixed chamber air, Q is the flow rate of air through the chamber, V is the chamber volume, and A is the emission surface area. A linear and instantaneously reversible equilibrium relationship is assumed at the material/air interface, or



4.5 Schematic representation of VOC emission from a solid material (Little *et al.*, 1994).

$$K = \frac{C|_{x=L}}{y} \quad [4.4]$$

where K is the partition coefficient between the material and air. Equation 4.4 implies that external convective mass transfer resistance near the interface is ignored. Assuming concentration-independent D and K and a uniform initial emittable concentration of the VOC, C_0 , an analytical solution to this equation set was obtained by Little *et al.* (1994) for calculating C and y at any time directly.

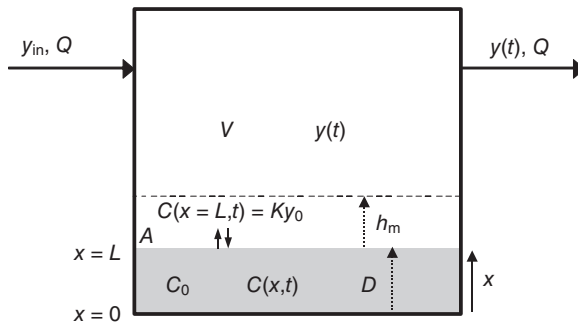
Without neglecting the external mass-transfer resistance, some improved models were then developed. Figure 4.6 shows the principle of VOC emission from a solid material adopted in several models (Huang and Haghghat, 2002; Xu and Zhang, 2003; Deng and Kim, 2004). The difference between Fig. 4.6 and Fig. 4.5 and thus the improvement is the introduction of the convective mass-transfer coefficient, h_m , to account for the external convective mass transfer. With the diffusion-governing equation 4.1 and the boundary condition at the bottom, equation 4.2, still valid, the boundary condition at the exposed surface, equations 4.3 and 4.4, should be replaced by

$$-D \cdot A \frac{\partial C}{\partial x} \Big|_{x=L} = h_m (y_0 - y) \quad [4.5]$$

$$V \frac{\partial y}{\partial t} = h(y_0 - y) - Q \cdot y = -D \cdot A \frac{\partial C}{\partial x} \Big|_{x=L} - Q \cdot y \quad [4.6]$$

$$K = \frac{C|_{x=L}}{y_0} \quad [4.7]$$

Equation 4.5 shows how external convective mass transfer is taken into account: the emission flux at the material surface is equal to the convective mass transfer through the boundary layer, where y_0 is the concentration of air at the material surface while y is the bulk air concentration. Equation



4.6 Schematic representation of VOC emission from a solid material.

4.6 is the transient mass balance in the chamber air, assuming influent concentration is zero. Similar to equation 4.4, equation 4.7 assumes instantaneous reversible partition equilibrium at the air/material interface. Deng and Kim (2004) obtained the fully analytical solution for this equation set, which can calculate the chamber concentration at any time directly. Generally, this improved model with a fully analytical solution is a desirable approach to predict the emissions from a single layer of homogeneous material. When influent concentration different from zero needs to be considered, the finite difference methods (Huang and Haghighat, 2002; Xu and Zhang, 2003) and the recently developed state-space method (Yan *et al.*, 2009) can be used.

These mass-transfer models discussed above provide not only tools for prediction but also comprehensive insight into the overall emission mechanisms. The mechanisms governing emissions of VOCs from a solid material include the internal diffusion of VOCs within the material (characterized by the diffusion coefficient, D), partition between the material and chamber air at the material/air interface (characterized by the partition coefficient, K), and external convective mass transfer from the air at the material surface to the chamber bulk air (characterized by the external convective mass-transfer coefficient, h_m). These three parameters together with the initial emittable concentration, C_0 , determine the emission strength and duration. Qualitatively, the relative magnitude of the internal mass-transfer resistance due to diffusion and the external convective mass-transfer resistance determines the emission-rate limiting factor. When internal mass-transfer resistance is small, external mass-transfer resistance has noticeable impacts on the emission rate. In contrast, the impact of external convective mass-transfer is negligible when internal mass-transfer resistance is very large, and emissions of VOCs under this condition are internal-diffusion controlled. Therefore, the model developed by Little *et al.* (1994) is a reasonable simplification for internal-diffusion controlled cases.

Based on this framework, several models have been further developed for various purposes. For example, sorption behaviors are found to be important for some building materials, and models concerning the sink effect of a single material have been developed (Little and Hodgson, 1996; Zhao *et al.*, 2002; Xu and Zhang, 2004; Kumar and Little, 2003a). Several models were also developed to account for more complicated conditions, such as the non-uniform initial emittable concentration and non-zero and time-dependent influent air concentration (Kumar and Little, 2003a). Furthermore, models for predicting emissions from a layered composite material (Kumar and Little, 2003b; Haghighat and Huang, 2003; Yuan *et al.*, 2007a; Hu *et al.*, 2007; Deng *et al.*, 2010) and several layered composite materials (Zhang and Niu, 2004; Li and Niu, 2007) have been developed for more realistic applications.

4.5 Determination of the characteristic emission parameters

The characteristic parameters for physically based models discussed in the previous section include the material-phase diffusion coefficient D , or effective diffusion coefficient for porous material cases, the material/air partition coefficient K , the initial emittable concentration C_0 , and the external convective mass-transfer coefficient h_m . The usefulness of a model is greatly determined by availability of the parameters (Guo, 2002b) and the accuracy of prediction is largely dependent on reliable model parameters (Huang and Haghighat, 2003). Therefore, reliable estimation of these model parameters is prerequisite to applying these models. Before feasible experimental approaches were available, a least-squares regression technique was often employed to estimate model parameters by fitting the emission models to emission chamber test data to obtain the ‘best-fitting’ model parameters. He and Yang (2005) concluded that the regression approach risks the problem of multi-solution when more than one unknown parameters need to be determined, and when this degree of freedom increases, the uncertainties of regression become larger. Therefore it is more rigorous to obtain the model parameters from independent approaches. In this section, primary approaches for determining D , K and C_0 are reviewed, while h_m is generally obtained based upon heat-mass transfer analogical empirical relations (Kays and Crawford, 1980).

4.5.1 Determination of the diffusion coefficient (D)

Chamber for laboratory investigation of materials, pollutions and air quality (CLIMPAQ) method

The CLIMPAQ method can test several VOCs simultaneously (Meininghaus *et al.*, 2000). The test material is placed between two CLIMPAQs (Gunnarsen *et al.*, 1994), called the primary and secondary chambers. Air flow with a desirable concentration of VOCs and a clean air stream is led into the primary and secondary chambers, respectively, and VOC concentrations in the supply and the exhaust air of each chamber are measured. At steady state, the mass flux through the testing material is equal to the mass leaving the secondary chamber, or

$$A \cdot D \frac{y_{\text{primary}}K - y_{\text{secondary}}K}{d} = Q_{\text{secondary}} \cdot y_{\text{secondary}} \quad [4.8]$$

where d is the material thickness, $Q_{\text{secondary}}$ is the flow rate of supply clean air in the secondary chamber, and y_{primary} and $y_{\text{secondary}}$ are the steady-state concentrations of the VOC in the primary and secondary chambers,

respectively. Besides, considering the mass balance from the beginning of the experiment until the steady state is reached, the absorbed mass of VOC into the testing material when the steady state is reached, m_{ab} , can be calculated by numerical integration based on discrete measurements of exhaust concentrations:

$$m_{ab} = \sum_{i=1}^n [Q_{primary} y_{supply} - (Q_{primary} y_{primary\_i} + Q_{secondary} y_{secondary\_i})] \cdot \Delta t_i \quad [4.9]$$

where $Q_{primary}$ is the flow rate of supply air in the primary chamber, y_{supply} is the supply air concentration in the primary chamber, $y_{primary\_i}$ and $y_{secondary\_i}$ are the i th measurements of the exhaust concentration of the primary and secondary chamber, respectively, and Δt_i stands for the time interval between single measurements. Assuming that the testing material is free of VOCs at the beginning and the concentration gradient in the material is linear when the steady state is reached, K can be calculated by

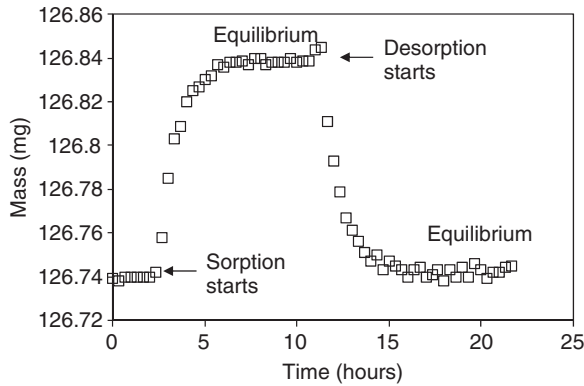
$$K = \frac{m_{ab} / (A \cdot d)}{\left(\frac{y_{primary} + y_{secondary}}{2} \right)} \quad [4.10]$$

which can be combined with equations 4.8 and 4.9 to determine D and K .

The CLIMPAQ method is in fact a specific representative of the steady-state twin chamber method, which can also be achieved using other types of chambers (Meininghaus and Uhde, 2002; Xu *et al.*, 2009; Farajollahi *et al.*, 2009). The main concern about this method comes from neglecting external convective mass-transfer resistance at the material surfaces when constructing equation 4.8, which may result in underestimation of D (Haghighat *et al.*, 2002).

Microbalance method

A method which could measure D and K separately was developed by Cox *et al.* (2001a) for vinyl flooring and later successfully applied for polyurethane foam (Zhao *et al.*, 2004), polystyrene foam and oriented strand board (Yuan *et al.*, 2007b). The testing material can be cut into a thin slab and a high-resolution dynamic microbalance is used to monitor the mass of the slab sample. Before testing, the sample is conditioned by sweeping clean air over it until its weight is stable, implying there is no VOC present in the sample. When the experiment begins, an air flow with a known concentration of VOC is passed over the sample for the sorption test, during which sorption of VOC increases its mass until partition equilibrium is reached between the sample and air. Then clean air is passed over the sample again for the desorption test, during which desorption of VOC from the sample



4.7 Transient mass gain/loss of a polymeric material during sorption/desorption of toluene.

decreases the mass of the sample until the sample is clean. Figure 4.7 shows the transient mass gain/loss of a polymeric material sample during the sorption/desorption test.

Based on microbalance test data, K can be determined directly by

$$K = C_{\text{equ}}/y_{\text{sorp}} \quad [4.11]$$

where C_{equ} is the equilibrium concentration in the sample, which can be calculated by dividing the mass increase at the end of the sorption test by the sample volume; and y_{sorp} is the corresponding concentration of the VOC in the air for the sorption test. D is determined by fitting a Fickian diffusion model for a thin slab to experimental sorption and desorption data, which is given by (Crank, 1975)

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4L^2}\right] \quad [4.12]$$

where M_t is the total mass of the VOC analyte that has entered or left the slab sample in time t , M_{∞} is the corresponding quantity when equilibrium is reached, and $2L$ is the thickness of the slab sample. The samples used for the microbalance method are quite small so that the D and K obtained may not be representative for non-uniform materials. Ignoring external convective mass-transfer resistance may also lead to the same problem as for the CLIMPAQ method.

C-history method

An innovative method which can determine D , K and C_0 simultaneously was recently developed by Xiong *et al.* (2011). The test material with

uniform distribution of target VOC has to be tested in an airtight chamber for emission profiles. The chamber concentration development, $y(t)$, and the equilibrium chamber concentration, y_{equ} , can be described by an emission model as shown by Fig. 4.6, with chamber flow rate set to be zero. Based on the model, it is found that the logarithm of the dimensionless excess concentration, which is defined as $(y_{\text{equ}} - y(t))/y_{\text{equ}}$, is linearly dependent on the emission time, or

$$\ln\left(\frac{y_{\text{equ}} - y(t)}{y_{\text{equ}}}\right) = \text{SL} \cdot t + \text{INT} \quad [4.13]$$

where SL and INT are the slope and intercept of the linear relationship, respectively. Furthermore, SL and INT are functions of both D and K as well as the geometries of the tested material slab and the airtight chamber, while y_{equ} is dependent on C_0 and K . Therefore, the measured chamber concentration over time can be treated as a form of the logarithm of the dimensionless excess concentration as in equation 4.13 to determine SL and INT by a linear regression over time. Then D and K can be calculated from SL and INT, and C_0 can be further determined from y_{equ} and the known value of K . This so-called C-history method has been well employed to determine the D , K and C_0 values of formaldehyde in several building materials (Xiong *et al.*, 2011). This promising method could determine three parameters simultaneously under realistic environmental conditions and is quite convenient and time-efficient to employ. The C-history method could be also extended to measure the equivalent emission characteristic parameters of formaldehyde and other VOCs from wood-based furniture (Yao *et al.*, 2011). Table 4.3 summarizes the results using the C-history method for several materials (MDF stands for medium-density fiberboard, and PB stands for particle board).

Porosity test method

Different from the methods above, the porosity test method calculates the diffusion coefficient based on the microstructure of porous materials. In the porous material, molecular, Knudsen and surface diffusion may exist simultaneously. The effect of molecular and Knudsen diffusion can be combined into an overall effective diffusion coefficient, D , which can be calculated as:

$$D = D^0 \frac{\varepsilon}{\tau} \quad [4.14]$$

where D^0 is the mean (reference) diffusion coefficient in the pores of the material, ε is the porosity of the material, and τ is the tortuosity factor of the material. The porosity and tortuosity factors of the building material can be obtained using the mercury intruding porosimetry (MIP) test and

Table 4.3 Some characteristic parameters determined by the C-history method

Material	VOCs	C_0 ($\mu\text{g}/\text{m}^3$)	D (m^2/s)	K
MDF1	Formaldehyde	$(1.91 \pm 0.10) \times 10^7$	$(5.58 \pm 0.25) \times 10^{-11}$	$(1.46 \pm 0.09) \times 10^3$
MDF2	Formaldehyde	$(4.01 \pm 0.34) \times 10^6$	$(2.72 \pm 0.21) \times 10^{-11}$	$(5.52 \pm 0.53) \times 10^3$
MDF3	Formaldehyde	$(1.53 \pm 0.12) \times 10^7$	$(9.25 \pm 0.71) \times 10^{-12}$	$(5.94 \pm 0.58) \times 10^3$
PB1	Formaldehyde	$(2.68 \pm 0.22) \times 10^7$	$(5.52 \pm 0.27) \times 10^{-10}$	$(1.64 \pm 0.15) \times 10^3$
PB2	Formaldehyde	$(2.80 \pm 0.21) \times 10^7$	$(4.16 \pm 0.17) \times 10^{-10}$	$(4.23 \pm 0.34) \times 10^3$
BB	Formaldehyde	$(4.19 \pm 0.27) \times 10^6$	$(3.38 \pm 0.22) \times 10^{-10}$	$(4.31 \pm 0.40) \times 10^2$
Furniture A	Formaldehyde	$(1.00 \pm 0.14) \times 10^6$	$(5.71 \pm 0.20) \times 10^{-11}$	$(4.32 \pm 0.36) \times 10^2$
Furniture B	Formaldehyde	$(5.10 \pm 0.49) \times 10^5$	$(3.13 \pm 0.22) \times 10^{-10}$	$(4.82 \pm 0.47) \times 10^2$
Furniture B	Toluene	$(2.89 \pm 0.20) \times 10^6$	$(2.52 \pm 0.21) \times 10^{-10}$	$(5.90 \pm 0.44) \times 10^2$
Furniture B	<i>o</i> -Xylene	$(2.31 \pm 0.29) \times 10^6$	$(5.72 \pm 0.25) \times 10^{-10}$	$(4.68 \pm 0.23) \times 10^2$
Furniture B	Acetic Acid	$(7.57 \pm 0.51) \times 10^6$	$(5.05 \pm 0.21) \times 10^{-10}$	$(6.27 \pm 0.64) \times 10^2$
Furniture B	<i>p</i> -Xylene	$(2.39 \pm 0.25) \times 10^6$	$(2.86 \pm 0.17) \times 10^{-10}$	$(6.86 \pm 0.59) \times 10^2$
Furniture B	Ethylbenzene	$(2.44 \pm 0.26) \times 10^6$	$(2.76 \pm 0.19) \times 10^{-10}$	$(5.14 \pm 0.56) \times 10^2$
Furniture B	Cyclohexanone	$(4.74 \pm 0.19) \times 10^6$	$(2.55 \pm 0.10) \times 10^{-10}$	$(5.67 \pm 0.24) \times 10^2$

the model developed by Carniglia (1986). Therefore, the key to using the porosity test method becomes how to determine D^0 . Blondeau *et al.* (2003) developed a parallel pore model, which calculates D^0 by a series of sums over every intruding volume difference in the experiment. This is equivalent to treating the pores as many parallel connections in the representative elementary volume (REV) and applies an arithmetic mean method for them. Seo *et al.* (2005) used a mean pore model to calculate D^0 by reducing all kinds of pores into an equivalent pore and using the formula depicting the transitional diffusion zone. In many cases, the parallel or mean assumption cannot reflect the essence of diffusion in porous building materials well, leading to large uncertainties in D^0 . Based on detailed microstructure analysis of the porous materials, Xiong *et al.* (2008) developed a macro–meso two-scale model to determine D^0 . This model categorizes all the pores into macro and meso pores according to the pore diameter, and considers the two kinds of pores to be connected in series. For the macro pores, the diffusion belongs to molecular diffusion, while for the meso pores, transition diffusion applies. Assuming the macro and meso pores have the same tortuosity factor τ , D^0 can be determined based on Fick's law (Xiong *et al.*, 2008). Knowing D^0 , equation 4.14 can be used to calculate D .

4.5.2 Determination of the partition coefficient (K)

The partition coefficient K describes the thermodynamic status of equilibrium between the material phase and the gas phase. As shown in the previous section, several methods can actually determine both D and K and therefore are not repeated here. The headspace method is simple and straightforward for determining K by measuring the material-phase concentration and the gas-phase concentration respectively in the equilibrium state (Zhang *et al.*, 2007). Analytical methods for measuring gas-phase concentrations of VOCs are very well developed, while methods for measuring the material-phase concentration will be presented in the following section. Furthermore, several delicate methods which employ the basic idea of the headspace method to measure K and C_0 simultaneously have been developed recently (Wang *et al.*, 2008; Wang and Zhang, 2009; Xiong *et al.*, 2009).

Multi-injection regression method

In the multi-injection regression method (Wang *et al.*, 2008; Wang and Zhang, 2009), the building material sample with initial emittable concentration C_0 is placed in a temperature-controlled airtight chamber. A certain amount of the target VOC is injected into the chamber several times, allowing the sample and chamber air to reach equilibrium after each injection.

For the i th equilibrium state, based on mass conservation and Henry's linear sorption law, it can be derived that

$$(C_{1,i} - C_{2,i}) \cdot V/V_m = K \cdot C_{2,i} - C_0 \quad [4.15]$$

$$C_{1,i} = C_{h,i} - C_{2,i-1} + C_{1,i-1} \quad [4.16]$$

where $C_{1,i}$ is the equilibrium gas-phase VOC concentration before injection; $C_{h,i}$ and $C_{2,i}$ are the peak and equilibrium gas-phase VOC concentrations after injection, respectively; and V_m is the building material volume. Equation 4.15 practically defines a linear relationship between the term on the left-hand side, which can be calculated from measured gas-phase concentrations, and the equilibrium gas-phase concentration, $C_{2,i}$. Therefore, after several discrete injections and corresponding equilibrium states, a linear regression can be carried out to determine K and C_0 from the slope and intercept. The accurate measurement of gas-phase concentrations is critical to obtaining reliable K and C_0 . However, the mass transfer between the chamber air and the material brings large uncertainty to the determination of $C_{h,i}$ and therefore may reduce the reliability of the regression results.

Multi-emission/flush regression method

To overcome the drawbacks of the multi-injection method, an improved method was developed (Xiong *et al.*, 2009; Xiong and Zhang, 2010). This method also involves multiple equilibrium cycles but entails flushing the chamber once the sample and chamber air have reached equilibrium in the airtight chamber. At each equilibrium state, the relationship between the equilibrium gas-phase concentration, $C_{a,i}$, and the equilibrium material-phase concentration, $C_{m,i}$, conforms to Henry's law, i.e., $C_{m,i} = KC_{a,i}$. For the i th cycle, it can be deduced that

$$\ln C_{a,i} = \ln \frac{K}{K + V/V_m} \cdot i + \ln \frac{C_0}{K} \quad [4.17]$$

Therefore, after several emission/flushing cycles, K and C_0 can be determined from the linear regression of measured equilibrium gas-phase concentration and i , according to equation 4.17.

4.5.3 Determination of the initial emittable concentration (C_0)

Traditional methods for measuring concentrations of VOCs in solid materials have used solvents or heat to extract target compounds. However, as discussed by Cox *et al.* (2001b), total VOC concentration can be apportioned to mobile and partially immobilized fractions. C_0 used in the

emission models should be the concentration of the readily emitted compound or the mobile fraction, which cannot be distinguished by solvent or heat extraction methods. Cox *et al.* also found that the emittable concentration of several VOCs in vinyl flooring measured by a new CM-FBD method is 30–70% lower than by a direct thermal desorption method. Experimental measurements of emittable formaldehyde concentrations in building materials using a multi-injection regression method (Wang and Zhang, 2009) are also much lower than the total concentrations measured by a thermal extraction method. Recently, it is reported that the emittable concentration of formaldehyde in building materials increases significantly with increasing temperature (Xiong and Zhang, 2010; see Section 4.6.1). Therefore, it is necessary to measure C_0 under environmental conditions resembling those of the actual indoor environment. In addition to the multi-purpose methods discussed above, two valuable methods measuring C_0 exclusively are discussed here, both of which actually aim to extract all the emittable analytes from the test materials under moderate environmental conditions and to measure the total amount.

Cryogenic milling – fluidized bed desorption (CM–FBD) method

As discussed previously, internal diffusion controls the emission rate quite often so that complete emission of VOCs from building materials may require a very long time. Therefore, Cox *et al.* (2001b) pulverized randomly selected small vinyl flooring samples into small particles in a ball mill under a liquid nitrogen bath at a temperature of -140°C . This cryogenic milling (CM) process reduces the diffusion path lengths and increases emission surface areas, reducing the VOC extraction time, while the low temperature significantly reduces VOC vapor pressure, minimizing VOC loss during the grinding process. Then the extraction of VOCs from the milled particles can be accomplished at room temperature by fluidized-bed desorption (FBD). The particles were placed in a fluidized-bed reactor ventilated continuously with clean air, which extracted VOCs out of the particles. The effluent concentration was measured at suitable time intervals until all the analytes were extracted and the total amount of emitted analytes can therefore be determined based on the air flow rate. The combination of CM and FBD accelerates the extraction greatly under room temperature; however, the experimental system is complicated and there is some concern that the properties of the materials may change when ground into particles.

Multi-flushing extraction method

For the multi-flushing extraction method, the building materials were first ground into powder and then placed in an airtight chamber, and the

subsequent procedures were similar to those of the multi-emission/flush regression method (Smith *et al.*, 2008). The test continues until the equilibrium chamber air concentration of the last cycle is less than 10% of that of the first cycle so that most of the VOCs are extracted from the materials. Therefore, a series of equilibrium chamber air concentrations can be obtained during the entire process, and the initial emittable mass, M_t , can be calculated by

$$M_t = \sum_{i=1}^n VC_{a,i} + \frac{VC_n}{C_{n-1}/C_n - 1} \quad [4.18]$$

The first term on the right-hand side is the amount of VOCs emitted during the entire experimental period, and the second term estimates the mass remaining in the material after the experiment, where V is the volume of the chamber, $C_{a,i}$ is the equilibrium VOC concentration in air for cycle i , and n is the last cycle of the experiment. Since this method requires many cycles to reach the required condition for the equilibrium concentration of the last cycle, a very long experimental period is needed.

4.6 Influence of environmental factors on emissions of formaldehyde and other volatile organic compounds (VOCs)

4.6.1 Temperature

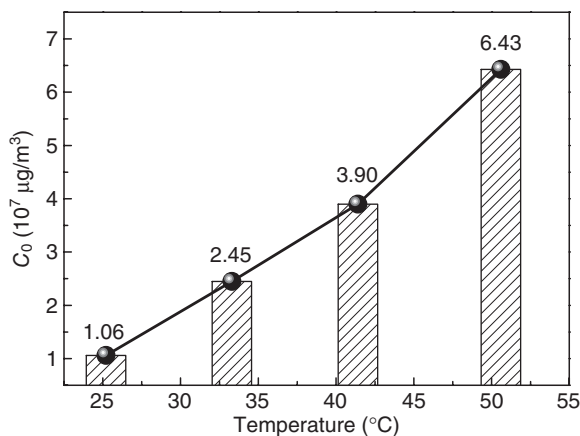
The temperature generally has significant impacts on the emissions of formaldehyde and other VOCs from building materials. The research on this topic can be classified into two categories: (1) direct study of the impact of temperature on the emission rate or chamber concentration; and (2) analysis of the impact of temperature on the emission characteristic parameters (initial emittable concentration, diffusion coefficient and partition coefficient).

The increase of emission rate or chamber concentration with increasing temperature has been frequently reported. Andersen *et al.* (1975) observed that the emission rate of formaldehyde from chipboard was doubled for every 7°C temperature rise within the temperature range 14–31°C, and a relationship was formulated between the chamber concentration and temperature and other environmental factors. Myers (1985) reported an exponential relationship between formaldehyde emission rate from wood-based products and temperature, with the emission rate from particle board increasing by a factor of 5.2 when the temperature increased from 23 to 40°C. The experimental results of Lin *et al.* (2009) suggested that when the temperature increased from 15 to 30°C, the VOC specific emission rates and chamber concentrations increased by 1.5–12.9 times. The same

phenomenon was also found by Crawford and Lungu (2011) when studying the styrene emission from a vinyl ester resin thermoset composite material. However, little or negligible effect of temperature on the emissions was found for some VOCs in several materials (Sollinger *et al.*, 1994; Wolkoff, 1998; Wiglusz *et al.*, 2002) and an adverse trend was also reported (Haghighat and Bellis, 1998). The reason for these phenomena is unclear. A possible explanation is different interaction patterns between different types of materials and VOCs (Wolkoff, 1998).

As far as the impact of temperature on the emission characteristic parameters is concerned, many interesting results are obtained. The first attempt at experimentally studying the impact of temperature on the initial emittable concentration (C_0) of formaldehyde in medium-density fiberboard was made by Xiong and Zhang (2010). It was observed that C_0 increased significantly with increasing temperature. When the temperature increased by 25.4°C, C_0 increased by about 507%, as shown in Fig. 4.8. However, the C_0 at room temperature is far less than the value measured by the perforator method recommended by European standard EN 120 (1993) or Chinese national standard GB/T 17657-1999 (1999) which measures the total concentration of formaldehyde in the material. A possible reason is that there is an interaction force between formaldehyde and the material matrix and only the formaldehyde molecules with sufficiently high kinetic energy can overcome the interaction force (binding force) and emit from the material. This part of formaldehyde forms the C_0 , which is obviously smaller than the total amount (Xiong and Zhang, 2010).

Based on the Langmuir equation (1918), a theoretical correlation between the partition coefficient (K) and temperature (T) is established as (Zhang *et al.*, 2007):



4.8 The increase of initial emittable concentration with increasing temperature.

$$K = P_1 T^{1/2} \exp\left(\frac{P_2}{T}\right) \quad [4.19]$$

where P_1 and P_2 are constants for a given material–VOC pair. This correlation improves the equation proposed by Goss and Eisenreich (1997) by means of analyzing the experimental data when studying the VOC sorption process. Good agreement between equation 4.19 and experimental data of formaldehyde emission from some building materials is obtained (Zhang *et al.*, 2007), which indicates a reduction of partition coefficient with increasing temperature. This is reasonable, because the desorption rate increases more rapidly than the adsorption rate when temperature increases, which leads to the decrease of the partition coefficient. However, some inconsistent results also emerged, while the reasons are unclear (Zhang *et al.*, 2002).

An Arrhenius-like behavior is sometimes used to describe the temperature dependence of the diffusion coefficient (D) (Yang *et al.*, 1998). However, the correlation lacks solid theoretical foundations. For VOC diffusion in porous building materials, when the molecular diffusion is dominant, a theoretical correlation can be applied to describe the temperature impact on D (Deng *et al.*, 2009):

$$D = B_1 T^{1.25} \exp\left(\frac{B_2}{T}\right) \quad [4.20]$$

where B_1 and B_2 are constants for a given material–VOC pair. This correlation agrees well with the experimental data (Deng *et al.*, 2009), which reveals a gradual increase in D when temperature increases. The parameters B_1 and B_2 can be obtained by fitting equation 4.20 to experimental data. Then the correlation can be used to predict the diffusion coefficient at other temperatures.

4.6.2 Relative humidity

The impacts of relative humidity on emissions of formaldehyde and other VOCs from building materials are more complicated. Relative humidity may affect the emission rate and the emission characteristic parameters. Table 4.4 summarizes some typical results from the literature. When relative humidity increases, the emission rate or chamber concentration would increase significantly for some material–VOC pairs. However, for some other cases, the change is negligible, and a decreasing trend is even found for a specific case (Wolkoff, 1998). The results indicate that the impact of relative humidity depends on the types of building materials and VOCs. Broadly speaking, possible causes of enhanced emission at a higher relative humidity may include smaller sorption capacity or increased generation of

Table 4.4 Some typical results of impact of relative humidity (RH) on the emission characteristics

Item	Material	VOCs	RH range	Trend	Reference
Emission rate	Chipboard	Formaldehyde	30%, 70%	Increase (double)	Andersen <i>et al.</i> , 1975
Concentration	Carpet	2-ethylhexanol, 4-PCH	0%, 50%	Increase first, then negligible	Wolkoff, 1998
	PVC flooring	2-ethylhexanol, phenol		Negligible after 1 day	
	Sealant	Hexane		Negligible	
	Sealant	Dimethyloctanol		Decrease first, then increase	
	Wall paint	1,2-propanediol		Increase	
Concentration	Floor varnish, wall paint	TVOC	30%, 50%, 70%	Increase	Fang <i>et al.</i> , 1999
	Carpet, PVC flooring, sealant	TVOC		Negligible	
Concentration, emission rate	Wooden flooring	Toluene, <i>n</i> -butyl acetate, ethylbenzene, <i>m,p</i> -xylene	50%, 80%	Increase (1–32 times)	Lin <i>et al.</i> , 2009
Partition coefficient	Ceiling tile	Cyclohexane, toluene, ethyl acetate, isopropyl alcohol	0%, 35%, 75%	Negligible	Huang <i>et al.</i> , 2006
Diffusion coefficient	Ceiling tile	Methanol		Decrease	
	Ceiling tile	Octane, isopropanol, cyclohexane, ethyl acetate, hexane	0%, 20%, 40%	Minor or negligible	Farajollahi <i>et al.</i> , 2009
Partition coefficient	Formaldehyde	Calcium silicate	25%, 50%, 80%	Negligible for 25–50%, increase for 50–80%	Xu and Zhang, 2011
Partition coefficient	Toluene	Calcium silicate		Decrease	
Diffusion coefficient	Formaldehyde, toluene	Calcium silicate		Negligible	

VOCs due to hydrolysis (Xu and Zhang, 2011). But the detailed mechanism of relative humidity effect is still not clear.

The relative humidity seems to have no significant impact on the diffusion coefficient, as shown in Table 4.4, while the partition coefficient is dependent on relative humidity. This may be due to the competition of adsorption sites between water vapor and VOCs. In addition, the capillary condensation phenomenon can also cause some differences in partition coefficient. In Table 4.4, the increase of partition coefficient of formaldehyde was probably because some formaldehyde molecules are absorbed by the adsorbed water under a high relative humidity level, while the decrease of partition coefficient of toluene was possibly due to the competition of water molecules for available adsorption sites with toluene molecules (Xu and Zhang, 2011).

4.6.3 Air velocity

The air velocity across the surface of building materials will affect the convective mass transfer coefficient (h_m) of formaldehyde and other VOCs. Higher air velocity can decrease the boundary layer thickness and increase h_m , and therefore facilitate the emissions. From the mass transfer point of view, the significance of this impact is dependent on the relative magnitude between the convection effect and the diffusion effect. If the latter is dominant, the impact of air velocity can be neglected. For most emission processes, the air velocity has some impacts on the initial-period emissions but insignificant impacts on the long-term emission. Neglecting convective mass transfer coefficient, i.e., taking h_m as infinite, tends to overestimate emission rate and chamber concentration at the initial stage (Xu and Zhang, 2003). Studies for VOC emissions from five commonly used materials have shown that the air velocity does not influence the emission rate after a few days to a week to any great extent (Wolkoff, 1999). For some chambers, the air velocity can be controlled by the mixing fan inside the chamber, while for other chambers that have no special design for controlling air velocity over the material surface, the air velocity in the test chamber is directly related to the chamber flow rate (Zhang *et al.*, 2002).

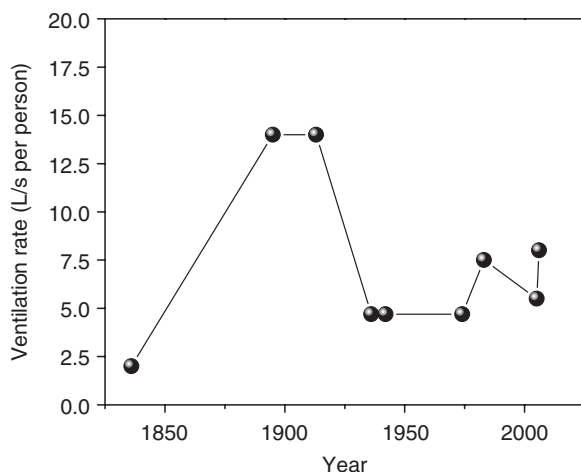
It should be pointed out that some other factors, such as the material use age, the physical and chemical properties of the materials and VOCs, the VOC concentration in the chamber, and the state of the material (dry or wet), can also influence the emission characteristics. Further experimental and theoretical work is necessary to clarify these questions.

4.7 Conclusion and future trends

Due to its wide distribution and high incidence of contamination, such as the serious formaldehyde contaminations in government-provided trailers

for victims of hurricane Katrina in the US, the toxicology of formaldehyde has been the subject of much concern. As reviewed in this chapter, the toxicokinetics and health effects caused by exposure to formaldehyde are quite well understood and some biochemical understanding of the toxicity mechanisms has been acquired. Some other common VOCs, such as benzene, have also been extensively studied for their toxicology. However, as reviewed by European project HealthyAir, the toxicological data are still very poor or lacking for most VOCs, and knowledge about the health effects due to inhalation exposure to them is very limited, especially those caused by simultaneous exposure to various VOCs (Bluyssen *et al.*, 2010). In addition, guidelines or recommendations for indoor VOC concentrations are unavailable for most VOCs. Further investigations into the toxicokinetics and health effects of individual VOCs at indoor-relevant concentration levels as well as those of combinations of common VOCs are therefore urgently required. As suggested by the US EPA ToxCast and ToxPi projects and the European Community Regulation on chemicals and their safe use (REACH), a feasible strategy for further studies of the health effects and risks of VOCs in indoor air should include prioritizing individual compounds or classes of compounds and combining knowledge about the nature of VOC, the degree of human exposure, and toxicology (Judson *et al.*, 2010; Reif *et al.*, 2010; Rudén and Hansson, 2010).

Appropriate ventilation has been considered the primary means of achieving good indoor air quality, and discussions on how much ventilation is sufficient to prevent noxious odors and the spread of disease started at the beginning of the nineteenth century and are still going on (Fig. 4.9). It should be pointed out that the minimum ventilation rates do not prevent occupants of a space developing health symptoms, and the threshold levels for all compounds seem unrealistic due to the numerous compounds and complex mixtures of compounds (Bluyssen, 2009). Generally speaking, a sufficient ventilation rate is effective in removing indoor air pollutants, including VOCs originating indoors. Given the prevailing trend of airtight buildings for less energy use, some energy-saving ventilation strategies have been developed (Laverge *et al.*, 2011). However, source control is regarded as a more straightforward and probably better approach: preventing rather than curing (Bluyssen, 2009). Experimental techniques for emission testing and understanding of emission mechanisms of VOCs presented in this chapter are therefore highly valuable for source control. It seems the overall mechanisms of emissions from individual homogeneous sources are quite well understood and the emission models reviewed above are capable of predicting emissions with good accuracy. The emission models can be used to characterize the source-to-effect continuum for VOCs by linking source types, emissions, transport in indoor air, exposure, and toxic effects. However, there are still many gaps in our understanding of indoor VOC emissions.



4.9 Changes in the recommended minimum ventilation rate over the years (Bluyssen, 2009).

For example, the emission characteristics of sources are much more complicated in the real indoor environment with several sources and sinks present at the same time; indoor and surface chemistry could generate secondary sources; and the impacts of various environmental factors on the emissions are not fully understood (Bluyssen, 2009). Therefore, further studies on the emission mechanisms and indoor chemistry for more realistic scenarios are urgently needed.

Finally, as shown by the HealthyAir project which aims to define, initiate and develop activities that will improve indoor air quality and reduce exposure of people to indoor air pollution, the awareness and education of manufacturers, architects, and end-users about the problems of indoor VOCs are generally poor (Bluyssen *et al.*, 2010). Therefore, in addition to further research on the toxicology of VOCs and emission characteristics of indoor sources, better education of stakeholders and appropriate policies and regulations (such as regulations of indoor VOC concentrations, product emission standards, and product labeling programs) are urgently needed to solve indoor VOC problems and improve indoor air quality.

4.8 Sources of further information

Suggested general standards or books on formaldehyde and other VOCs are as follows.

ASTM D 5197-03 (2003). *Standard test method for determination of formaldehyde and other carbonyl compounds in air (active sampler methodology)*. American Standard.

- ASTM D 5466-01 (2001). *Standard test method for determination of volatile organic chemicals in atmospheres (canister sampling methodology)*. American Standard.
- ASTM D 6007-02 (2002). *Standard practice for full-scale chamber determination of volatile organic emissions from indoor materials/products*. American Standard.
- ASTM D 7143-05 (2005). *Standard practice for emission cells for determination of volatile organic emissions from indoor materials/products*. American Standard.
- GB/T 17657-1999 (1999). *Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels*. Chinese National Standard.
- EN 120 (1993). *Wood-based panels – determination of formaldehyde content – extraction method called perforator method*. European Standard.
- EN 717-1 (2004). *Wood-based panels – determination of formaldehyde release – Part 1: Formaldehyde emission by the chamber method*. European Standard.
- ISO 16000-6 (2004). *Indoor air – Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS/FID*. International Organization for Standardization.
- ISO 16000-10 (2006). *Indoor air – Part 10: Determination of the emission of volatile organic compounds from building products and furnishing – Emission test cell method*. International Organization for Standardization.
- ISO/CD 12460 (2007). *Wood-based panels. Determination of formaldehyde release – formaldehyde emission by the chamber method*. International Organization for Standardization.
- JIS A 1460 (2001). *Building boards. Determination of formaldehyde emission-desiccator method*. Japanese Industrial Standard.

4.9 References

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Semivolatile organic compounds (SVOCs): phthalates and flame retardants

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Abstract: Among the many chemicals found indoors, semivolatile organic compounds (SVOCs) constitute an important class. While certain SVOCs are associated with adverse health effects, exposure is strongly influenced by the types of materials and products in which these SVOCs occur. This chapter begins with a brief summary of phthalates and flame retardants, two important types of SVOCs. Chamber experiments used to characterize the emissions process are then reviewed. A simple emission model that can be used to predict the steady-state indoor gas-phase SVOC concentration is described. Knowing the long-term concentration in the indoor air, the potential exposure via inhalation of air and airborne particles, ingestion of dust, and dermal absorption can be calculated using general relationships.

Key words: additive, emission, exposure, indoor, model, PBDE, polymer, phthalate, SVOC.

5.1 Semivolatile organic compounds (SVOCs) in the indoor environment

Potential risks to human health arise from the manufacture and use of thousands of chemicals (Collins *et al.*, 2008; Rudén and Hansson, 2010). Although indoor chemicals are not regulated (Sarigiannis *et al.*, 2011), building materials and furnishings contain a vast array of compounds that may be released indoors (Weschler, 2009) where people spend most of their time (Klepeis *et al.*, 2001; Schweizer *et al.*, 2007). Among the many chemicals found indoors, semivolatile organic compounds (SVOCs) constitute an important class (Weschler and Nazaroff, 2008; Weschler, 2009; Wang *et al.*, 2010; Król *et al.*, 2011) with examples including chlorpyrifos (a pesticide), triclosan (a biocide), bisphenol-A (BPA, a residual monomer in polycarbonate plastics), 2,2',4,4'-tetrabromodiphenyl ether (BDE-47, a flame retardant), and di(2-ethylhexyl) phthalate (DEHP, a plasticizer). In this chapter, we will focus on phthalates and flame retardants, both of which may be found as additives that are present in polymeric materials and products.

As reported by Rudel and Perovich (2009), phthalates are common plasticizers used in polyvinyl chloride (PVC). By weight, they may contribute

10–60% of plastic products. They are added because of their ability to increase flexibility and transparency. In 2004 worldwide production of phthalates was estimated to be 6,000,000 tons per year. Phthalates are found in a wide variety of products including vinyl upholstery, shower curtains, food containers and wrappers, toys, floor tiles, lubricants, sealers, and adhesives. Phthalates are also used as solvents in cosmetics such as perfume, eye shadow, moisturizer, nail polish, hair spray, and liquid soap. Because there is no covalent bond between phthalates and the plastics into which they are mixed, they may be slowly released into the environment. Phthalates are subject to various degradation processes and generally do not persist in the outdoor environment. Phthalates are ubiquitous in the indoor environment, with indoor air concentrations generally higher than outdoor concentrations. More volatile phthalates such as diethyl phthalate (DEP), dimethyl phthalate (DMP) and dibutyl phthalate (DBP) are present at higher concentrations in air, while heavier, less volatile phthalates such as di(2-ethylhexyl) phthalate (DEHP) and benzyl butyl phthalate (BBP) are more prevalent on interior surfaces and dust.

Rudel and Perovich (2009) also summarized the situation for polybrominated diphenyl ethers (PBDEs), which are used as flame retardants and are found in a variety of consumer products such as plastics, upholstery, construction materials, and electrical appliances. PBDEs are lipophilic and hydrophobic compounds that tend to persist in the environment. There are 209 PBDE congeners, named according to the total number of bromines off the phenyl rings. Generally the lower-brominated congeners (mono through penta) are thought to be more harmful to humans. While PBDEs tend to distribute between the aerosol and the gas phase in air, as the congeners get heavier (more bromine atoms) they are increasingly found in the particulate phase. PBDEs are sold as three commercial mixtures: penta-bromodiphenyl ether (penta-BDE), octa-bromodiphenyl ether (octa-BDE), and deca-bromodiphenyl ether (deca-BDE). About 67,000 tons of PBDEs were produced worldwide in 2001. Deca-BDE is the most widely used, with an estimated 56,100 tons produced worldwide in 2001, compared to 7500 tons of penta-BDE produced in the same year. While penta-BDE and octa-BDE are being phased out of production, many sources of exposure remain as these PBDEs are prevalent in a number of common products. Traditionally, penta-BDE was dominated by the BDE 47 and BDE 99 congeners and used in polyurethane foam, foam products, bedding, vehicle interiors, and furniture. Octa-BDE contained a mixture of hepta, octa and nona congeners while deca-BDE consists primarily of BDE 209. Both octa- and deca-BDE can be found in electronics such as computers and televisions and deca-BDE is also often in textiles. Because PBDEs are additives mixed into polymers, and are not chemically bound to the polymer matrix, they also tend to leach out of products and into the indoor air.

SVOCs are of concern because they are ubiquitous, abundant and often persistent contaminants, found in indoor air, in airborne particles, in settled dust, on indoor surfaces, and even in clothing, on human hair and on human skin. Biomonitoring has shown that people have high and increasing body burdens of some SVOCs (Rudel *et al.*, 2003, 2010; Weschler and Nazaroff, 2008; Rudel and Perovich, 2009; Weschler, 2009). Associations between adverse health effects and exposure to certain SVOCs have been identified, with several SVOCs categorized as endocrine-disrupting compounds (Weschler and Nazaroff, 2008; Rudel and Perovich, 2009). Although the specific sources and exposure pathways are not yet clear, an understanding of the indoor occurrence, transport and exposure to SVOCs is beginning to emerge (Bennett and Furtaw, 2004; Schettler, 2006; Xu and Little, 2006; Weschler and Nazaroff, 2008, 2010; Weschler *et al.*, 2008; Rudel and Perovich, 2009; Webster *et al.*, 2009; Zhang *et al.*, 2009).

Exposures are strongly influenced by the types of materials and products in which chemicals occur, and the ways in which the materials and products are used. For example, certain phthalates are used as plasticizers in soft polyvinyl chloride (PVC) products, while other phthalates are used as solvents in personal care products such as perfume, eye shadow, moisturizer, and nail polish (Rudel and Perovich, 2009). Exposure to phthalates in PVC products occurs following emission from the source into air and subsequent migration to different media such as dust and other indoor surfaces, including human skin, hair and clothing (Xu *et al.*, 2009, 2010), while exposure to phthalates present in personal care products is more likely a consequence of dermal absorption and/or accidental ingestion (Wormuth *et al.*, 2006; Wittassek *et al.*, 2011) and therefore largely controlled by human behavior. Phthalates are also found in food as a result of contact with materials used in processing and packaging (Wormuth *et al.*, 2006), with exposure to certain phthalates strongly controlled by diet (Dickson-Spillmann *et al.*, 2009).

5.2 Emission of semivolatile organic compounds (SVOCs) from building materials and consumer products

Only a few studies have been carried out to experimentally characterize emissions of SVOCs from building materials and consumer products, mainly due to the difficulties associated with sampling and analysis of the very low volatility chemicals. In this section, we briefly review some of the studies carried out in test chambers and then describe a simple model that has been developed to predict gas-phase emissions of SVOCs present in materials and products as additives.

5.2.1 Characterizing emissions of SVOCs in small chambers

Uhde *et al.* (2001) measured phthalate concentrations emitted from 14 PVC-coated wall coverings in regular emission chambers for 14 days and suggested that the chamber concentration of phthalates with lower boiling point tends to be higher than those with higher boiling point. Afshari *et al.* (2004) tested dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) emissions from several materials such as wallpaper, PVC flooring and electric wire in the Chamber for Laboratory Investigations of Materials, Pollution and Air Quality (CLIMPAQ) as well as the Field and Laboratory Emission Cell (FLEC), and found that the chamber concentration of DEHP reached steady state after about 150 days and that sorption by chamber surfaces had a strong effect on gas-phase chamber concentrations. Fujii *et al.* (2003) developed a passive-type sampler to measure the emission rate of phthalates from synthetic leather, wallpaper and vinyl flooring and found that emission rates of several phthalates increased significantly at higher temperature. Schripp *et al.* (2010) tested wall paints and pure phthalate liquid in two different chambers and measured concentrations of DEHP and DBP in the chamber air and in the dust placed in the chamber. Kawamura *et al.* (2011) estimated the emission rate of DEHP from building materials through micro-chamber studies with variable surface area.

5.2.2 Effect of sorption to chamber surfaces

Xu *et al.* (2011) designed a special stainless steel chamber that maximized the surface area of the vinyl flooring source and minimized the surface area of the internal sink (the interior stainless steel surface of the chamber) thereby reducing the time to reach steady state, compared to previous studies using conventional chambers such as CLIMPAQ and FLEC. In addition, three precision-ground stainless steel rods, matched to the interior stainless steel chamber surface, were inserted into the chamber and then periodically removed so that the adsorbed surface concentration could be measured. This allowed the instantaneous gas-phase concentration in the chamber to be related to the adsorbed surface concentration at that point in the chamber run. Because equilibrium was not fully established as the gas-phase concentration built up to higher levels, the partition coefficients obtained under these conditions were somewhat underestimated. In a second set of experiments, the rods were introduced into the chamber after the gas-phase concentration had reached steady state. It then took approximately 60 days for the rods to reach equilibrium with the chamber air, allowing the equilibrium between the stainless steel surface and the air in the chamber to be accurately quantified.

5.2.3 Effect of air flow rate

Clausen *et al.* (2010) measured emission of DEHP from vinyl flooring as a function of applied air flow rate in the FLEC. Initially, the air flow rate through all FLECs was 450 ml/min. After about 2 years the air flow rates were increased to 1000, 1600, 2300, and 3000 ml/min, respectively, in four of the FLECs, and maintained at 450 ml/min in the fifth FLEC. Air samples were collected from the effluent air at regular intervals. Because the flow within the FLEC cavity is laminar, diffusion determines how fast DEHP can be transferred from the vinyl flooring emission surface into the air. Higher air flow rates increase the air exchange rate and reduce the residence time of the air so that there is less time for vertical diffusion to take place, resulting in a lower gas-phase concentration within the FLEC cavity. Because the concentration of DEHP in the air adjacent to the emission surface is known to be constant, the vertical air concentration gradient is therefore larger at the higher flow rate, which in turn increases the concentration-gradient-driven diffusion and the emission rate. With low flow rates, the residence time is long enough to allow vertical diffusion to create a uniform gas-phase concentration in the FLEC chamber. Below a flow rate of 1000 ml/min in the FLEC the air exchange rate is the limiting step and the emission rate is linearly dependent on the flow rate. However, with increasing flow rate the vertical diffusion becomes the limiting step of the emission process and a concentration gradient builds up in the FLEC. When the flow rate is increased by about seven times (from 450 to 3000 ml/min) the emission rate is increased almost six times. Although increased flow rate introduces more dilution, the increased emission rate driven by the concentration gradient almost compensates for the decrease in gas-phase concentration so that the gas-phase concentration does not drop substantially. The system therefore maintains a relatively constant bulk gas-phase concentration despite the variation in the air exchange rates.

5.2.4 Effect of humidity

Clausen *et al.* (2007) measured the influence of relative humidity (RH) on the emission rate of DEHP from vinyl flooring in the well-characterized FLEC. The vinyl flooring with DEHP as plasticizer was tested in six FLECs at 22°C. The RH in the six FLECs was 10%, 30%, 50% (in triplicate) and 70%. The RH was changed after 250 days in two of the 50%-FLECs to 10% and 70%, and to 50% in the 10%- and 70%-FLECs. The data show that the emission rate of DEHP from vinyl flooring during a one-year period was independent of the RH. A physically based emission model for SVOCs (Xu and Little, 2006) helps to explain the RH results, because it appears

that RH does not significantly influence any of the identified controlling mechanisms.

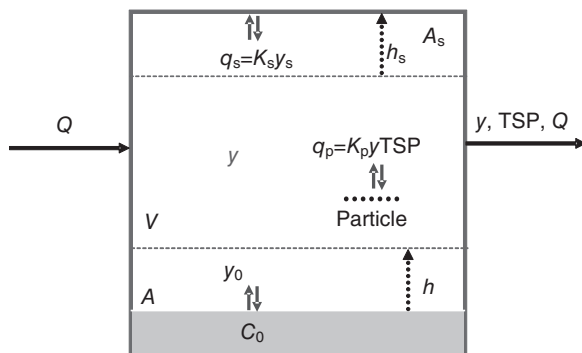
5.2.5 Effect of temperature

Clausen *et al.* (2011) measured emissions of DEHP from vinyl flooring in the FLEC. The gas-phase concentration of DEHP versus time was measured at an air flow rate of 450 ml/min at five different temperatures: 23°C, 35°C, 47°C, 55°C, and 61°C. The experiments were terminated two weeks to three months after steady state was reached, and the interior surface of all the FLECs was rinsed with methanol to determine the surface concentration of DEHP. The most important findings were as follows:

1. DEHP steady-state concentrations increased substantially with increasing temperature ($0.9 \pm 0.1 \mu\text{g}/\text{m}^3$, $10 \pm 1 \mu\text{g}/\text{m}^3$, $38 \pm 1 \mu\text{g}/\text{m}^3$, $91 \pm 4 \mu\text{g}/\text{m}^3$, and $198 \pm 5 \mu\text{g}/\text{m}^3$, respectively).
2. Adsorption to the chamber walls decreased substantially with increasing temperature (measured partition coefficient between FLEC air and walls: 640 ± 146 m, 97 ± 20 m, 21 ± 5 m, 11 ± 2 m, and 2 ± 1 m, respectively).
3. The gas-phase DEHP concentration in equilibrium with the vinyl flooring surface is close to the vapor pressure of pure DEHP liquid.
4. With an increase of temperature in a home from 23°C to 35°C, the amount of DEHP in the gas- and particle-phase combined is predicted to increase almost 10-fold. The amount in the gas-phase increases by a factor of 24 with a corresponding decrease in the amount on the airborne particles.

5.2.6 Effect of aerosol particles

Benning *et al.* (2011) measured the partitioning of gas-phase DEHP emitted from vinyl flooring onto to airborne particles. An experimental chamber was used to measure emissions of DEHP from vinyl flooring, and ammonium sulfate particles were introduced to examine their influence on emissions. When particles were introduced to the chamber at concentrations of between 100 and 245 $\mu\text{g}/\text{m}^3$ the total (gas + particle) DEHP concentrations increased by a factor of three to eight due to the enhanced emission rate. The measured DEHP partition coefficient was $0.032 \pm 0.003 \text{ m}^3/\mu\text{g}$. The DEHP-particle sorption equilibration time was shown to be less than 1 min, which agrees well with predictions from the literature. This study provided the first known measurements of the particle–gas partition coefficient for DEHP with results showing that emissions of SVOCs from materials will be enhanced in the presence of airborne particles.



5.1 Schematic showing mechanisms governing emissions of SVOCs, present as additives in materials and products, into a room or compartment (see text for symbols). For simplicity, we assume that no SVOC enters in the influent air.

5.2.7 Models to predict emissions and transport of SVOCs in the indoor environment

The mechanisms governing emissions of SVOCs from a solid material in which it is present as an additive (for example, DEHP in vinyl flooring or BDE-47 in polyurethane foam) are illustrated in Fig. 5.1 (Xu and Little, 2006). The variables are defined as follows: V is the room or compartment volume, A is the surface area of the source, Q is the ventilation rate, and y is the bulk gas-phase concentration of the SVOC. The SVOC in the source, at a material-phase concentration of C_0 , is assumed to be in equilibrium with the SVOC in the air in contact with the source, which has a gas-phase concentration of y_0 . SVOCs partition strongly to interior surfaces, and the sorbed SVOC concentration, q_s , on the interior surface, A_s , can be assumed to be in equilibrium with y_s , the gas-phase SVOC concentration in the air in contact with the surface. A boundary layer exists between the source and the bulk air in the room, with a mass transfer coefficient h , and between the bulk air and the interior surface, with a mass transfer coefficient h_s . The concentration of suspended particles in the room is TSP, and a partition coefficient, K_p , describes the equilibrium between the air in the room and the suspended particles.

For SVOCs present as additives, the depletion of the source occurs so slowly that C_0 and hence y_0 are usually effectively constant, which simplifies conditions so that the emission rate is given by

$$E = h \times (y_0 - y) \quad [5.1]$$

where the product of h , the convective mass transfer coefficient, and $(y_0 - y)$, the concentration driving force, determines the rate at which the SVOC

moves through the boundary layer of air into the bulk air in the room. SVOCs have low volatility (by definition), and consequently they partition strongly to surfaces in contact with the air. The resulting mass transfer between the bulk air and all interior surfaces (for example, walls, ceilings, windows, carpets, curtains, airborne particles, dust, clothing, human hair and skin) strongly influences the rate of change of the gas-phase concentration, y , and this in turn affects the emission rate, as shown in equation 5.1. A simple linear and reversible equilibrium relationship is assumed to exist between the exposed interior surface area A_s and the gas-phase concentration of the SVOC in immediate contact with the surface, or

$$q_s = K_s \times y_s \quad [5.2]$$

where q_s is the sorbed SVOC concentration on the surface, K_s is the surface/air partition coefficient, and y_s is the gas-phase SVOC concentration in the air in immediate contact with the surface. As with emission from the source, there is a boundary layer through which the SVOC must transfer to get either to or from the surface, and E_s , the mass transfer rate, is given by

$$E_s = h_s \times (y - y_s) \quad [5.3]$$

where h_s is the convective mass transfer coefficient associated with the surface. A linear and instantaneously reversible equilibrium relationship is also assumed to exist between the airborne particles and SVOCs in the air, or

$$q_p = K_p \times y \times \text{TSP} \quad [5.4]$$

Here, q_p is the sorbed SVOC particle phase concentration, K_p is the particle/air partition coefficient, and TSP is the total suspended particle concentration. Because airborne particles are small, the rate of mass transport to particles can usually be neglected for common indoor-air residence time scales, which are of the order of an hour (Weschler and Nazaroff, 2008). For emissions of DEHP from vinyl flooring, major elements of the model have been validated (Xu and Little, 2006; Clausen *et al.*, 2010) or are in the process of being validated. The model is illustrated here for DEHP in vinyl flooring placed in an idealized room. The model parameters used for the simulation are provided in Table 5.1 with predictions shown in Fig. 5.2.

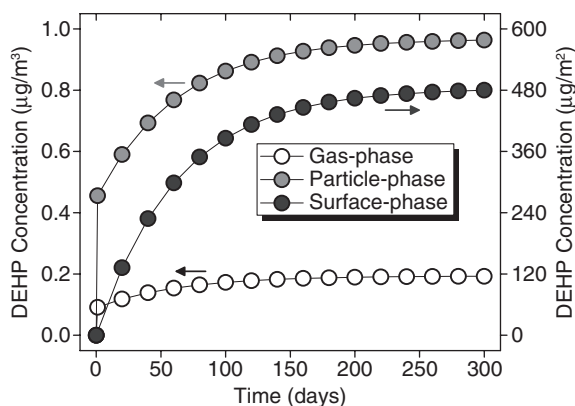
According to the simple model, during the first 100 days, approximately 150 mg of DEHP is emitted from the vinyl flooring. Of this, about 10% leaves the room in the air, 60% leaves the room sorbed to the particles suspended in the air, and the remaining 30% accumulates on the interior surfaces. Insight into SVOC persistence can be gleaned by comparing the amounts in the various compartments. On day 300, for example, there would

Table 5.1 Parameters used to estimate DEHP concentrations in indoor environments

Parameter	Value	Units	Source
Room volume (V)	50	m^3	–
Ventilation rate (Q)	50	m^3/h	–
Emission surface area (A)	20	m^2	–
Interior surface area (A_s)	120	m^2	–
Total suspended particle concentration (TSP)	20	$\mu\text{g}/\text{m}^3$	Weschler <i>et al.</i> , 2008
Gas-phase concentration in contact with emission surface (γ_0)	1	$\mu\text{g}/\text{m}^3$	Xu and Little, 2006; Clausen <i>et al.</i> , 2010
Convective mass-transfer coefficient over emission surface (h)	3.6	m/h	Huang <i>et al.</i> , 2004; Lin <i>et al.</i> , 2004
Convective mass-transfer coefficient over interior surface (h_s)	3.6	m/h	Huang <i>et al.</i> , 2004; Lin <i>et al.</i> , 2004
Interior surface/air partition coefficient (K_s)	2500	m	Xu <i>et al.</i> , 2009
Vapor pressure (VP)	1.9×10^{-5}	Pa	Xu <i>et al.</i> , 2009
Airborne particle/air partition coefficient (K_p)	0.24	$\text{m}^3/\mu\text{g}$	Xu <i>et al.</i> , 2009
Dust/air partition coefficient (K_{dust})	21000	m^3/g	Xu <i>et al.</i> , 2009
Octanol/water partition coefficient ($\log K_{\text{ow}}$) ^a	7.4		SPARC online calculator v4.5 (32°C)
Octanol/air partition coefficient ($\log K_{\text{oa}}$) ^a	12.89		SPARC online calculator v4.5 (25°C)
Water/air partition coefficient ($\log K_{\text{wa}}$) ^a	5.14		SPARC online calculator v4.5 (32°C)
Air permeability (p_{air})	5.9	m/h	Xu <i>et al.</i> , 2009
Skin/water permeability ($p_{\text{skin/water}}$)	0.0042	m/h	Equation in Table 5.2
Skin/air permeability ($p_{\text{skin/air}}$)	580	m/h	Equation in Table 5.2
Overall skin permeability (p)	5.8	m/h	Equation in Table 5.2

^a K_{oa} at 25°C is used to estimate K_p and K_{dust} in the room at 25°C; K_{ow} and K_{wa} at 32°C are used to estimate permeability through the skin at 32°C.

be ~10 μg of DEHP in the air, ~50 μg present on the airborne particles in the air, and ~58,000 μg present on the interior surfaces. Table 3 in Weschler (2003) provides similar information for a wide range of compounds. If, in an effort to clean the SVOC from the indoor environment, the windows in the room were opened, the air in the room would be rapidly replaced with



5.2 Predicted gas-, particle- and interior surface-phase concentrations of DEHP emitted from vinyl flooring.

fresh air and the 60 µg of airborne DEHP would be ventilated away. However, shortly after the windows were shut again, continued volatilization from the vinyl flooring (at ~1.2 µg/min) plus desorption from the interior surfaces (at ~1.4 g/min initially) would rapidly restore the airborne levels to the same value as before opening the windows. Because of the large reservoirs associated both with primary sources and with secondary sorbed SVOCs, the system tends towards homeostasis, restoring itself to the former conditions after transient perturbations.

Clearly, the processes taken into account in Fig. 5.1 constitute a highly idealized representation of reality. For example, all interior surface interactions are considered to be on 'hard' surfaces with no diffusion of the DEHP into the many soft or porous materials that are commonly found in indoor environments. In addition, a large variety of interior surfaces are lumped into a single surface represented by a 'typical' DEHP partition coefficient of 2500 m (Xu *et al.*, 2009). Although this idealization may seem extreme, it has been suggested that indoor environments age in a way that leads to thin organic films with fairly constant properties covering indoor surfaces (Weschler and Nazaroff, 2008). The relatively narrow range of partition coefficients estimated for different interior surfaces (Xu *et al.*, 2009) supports this view. The assumed interior surface area of 120 m² is only about twice the nominal surface area associated with walls and ceilings, and the actual interior surface in many indoor environments may be higher than this value. Finally, it is well known that DEHP sorbs strongly to dust (Weschler *et al.*, 2008; Weschler and Nazaroff, 2010). Such partitioning is not taken into account in this simple model, but will be accounted for in the exposure assessment.

5.3 Exposure to semivolatile organic compounds (SVOCs) emitted from building materials and consumer products

For SVOCs present as additives, the depletion of the source occurs so slowly that C_0 and hence y_0 are effectively constant. At steady state, the amount emitted from the source must equal the amount removed from the room, or

$$h \times (y_0 - y) \times A = Q \times y + Q \times (K_p \times \text{TSP} \times y) \quad [5.5]$$

and therefore

$$y = \frac{h \times y_0 \times A}{h \times A + Q^*} \quad [5.6]$$

where

$$Q^* = (1 + K_p \times \text{TSP}) \times Q \quad [5.7]$$

The parameter Q^* is an 'equivalent' air flow rate that includes the amount of SVOC present on suspended particles in the air. Thus, y is largely determined by y_0 , A , and other parameters that are relatively easy to estimate (h , Q , K_p , and TSP). The convective mass transfer coefficient, h , can be estimated using correlations based on the near surface flow velocity (Axley, 1991) with typical values of h indoors available in the literature (Huang *et al.*, 2004; Lin *et al.*, 2004).

In addition to inhaling SVOCs in indoor air, exposure via inhalation of airborne particles (Weschler and Nazaroff, 2008; Xu *et al.*, 2009, 2010), ingestion of dust (Weschler *et al.*, 2008; Xu *et al.*, 2009, 2010; Weschler and Nazaroff, 2010), and dermal absorption (Kissel, 2011) may play significant roles, contributing to total human intake rates. For SVOCs present as additives, equation 5.6 can be used to roughly estimate the gas-phase concentration, and emissions are considered to persist for the entire time in which the source is present in the indoor environment. We illustrate the exposure analysis approach here using DEHP as an example. With an estimate of the gas-phase concentration from equation 5.6, the particle-phase concentrations and dust-phase concentrations are estimated based on K_p and K_{dust} (i.e., the partition coefficients between particles and air and between dust and air, respectively). The amount sorbed through the skin is estimated in relation to overall permeability, p , based on mass transfer from air. Values for K_p , K_{dust} and p were obtained using the relationships listed in Table 5.2, with the required chemical properties for DEHP reported in Table 5.1. This information was then used to calculate exposure via inhalation, oral ingestion of dust, and dermal absorption for a three-year old child, as summarized in Tables 5.3 and 5.4.

Table 5.2 Relationships used to estimate exposure

Parameter	Units	Equation (source) ^a
Particle/air partition coefficient (K_p)	m ³ /μg	$K_p = f_{om\_part} \times K_{oa}/\rho_{part}$ (Weschler and Nazaroff, 2010)
Dust/air partition coefficient (K_{dust})	m ³ /g	$K_{dust} = f_{om\_dust} \times K_{oa}/\rho_{dust}$ (Weschler and Nazaroff, 2010)
Skin/water permeability ($p_{skin/water}$)	cm/s	$\log(p_{skin/water}) = 0.71\log(K_{ow}) - 0.0722MW^{2/3} - 5.25$ (Mitragotri, 2002)
Skin/air permeability ($p_{skin/air}$)	m/h	$\log(p_{skin/air}) = \log(p_{skin/water}) + \log(K_{wa})$
Overall permeability (p)	m/h	$p = [(1/p_{air}) + (1/p_{skin/air})]^{-1}$

^aMW is the molecular weight in units of g/mol; f_{om_part} and f_{om_dust} are the volume fractions of organic matter associated with airborne particles and settled dust (estimated to be 0.4 and 0.2), respectively; ρ_{part} and ρ_{dust} are density of airborne particles (1×10^6 g/m³) and settled dust (2×10^6 g/m³), respectively.

Table 5.3 Parameters used to estimate exposure for a three-year old child

Parameter	Child	Units
Inhalation rate (InhR)	0.64	(m ³ /kg)/d
Dust ingestion rate (IngR)	4.3	(mg/kg)/d
Skin surface area (SA)	0.61	m ²
Fraction skin exposed (f_{SA})	1	(–)
Exposure duration (ED)	21.9	h/d
Body weight (BW)	13.8	kg

Source: EPA (2009).

Table 5.4 Estimated exposure to DEHP for a three-year old child

Exposure pathway	(μg/kg)/d	Equation
Inhalation (air)	0.12	$y \times InhR \times ED$
Inhalation (particles)	0.57	$y \times K_p \times TSP \times InhR \times ED$
Ingestion (dust)	18	$y \times K_{dust} \times IngR$
Dermal absorption (from air)	1.1	$(y \times P \times SA \times f_{SA} \times ED)/BW$
Total	19.79	

Although it has been demonstrated that a compound’s octanol–air partition coefficient (K_{oa}) is a strong predictor of its abundance in settled dust based on the gas-phase concentration (Weschler and Nazaroff, 2010), for SVOCs with high K_{oa} values the concentration in dust may not have sufficient time to equilibrate with the gas phase. The same is true for SVOCs

with high K_{oa} values partitioning to human skin. Hence, exposure via ingestion of dust or direct air-to-skin transfer may be overestimated in these examples for the lower volatility SVOCs. We note here that the relationships that are used to estimate exposure are based on K_{oa} and K_{ow} (the octanol–water partition coefficient), which are generalized parameters that are readily available for many SVOCs (Weschler and Nazaroff, 2008, 2010).

Once exposure to SVOCs present in building materials and consumer products has been estimated, a toxicokinetic model (also referred to as a physiologically based, pharmacokinetic or PBPK model) is needed to account for the transport and metabolism of the compounds in the human body. For example, a toxicokinetic model for di(*n*-butyl) phthalate (DnBP) and its active metabolite, mono(*n*-butyl) phthalate (MnBP), as well as the glucuronide of MnBP, has been developed for the rat. The rodent-based model was evaluated by comparison with the only human kinetic study of DnBP reported in the literature, with good results (Clewell *et al.*, 2008). This suggests that human toxicokinetic models can be developed using allometric scaling of animal models, although *in vitro* metabolism data will be necessary to ensure the predictive ability of the human model to estimate target tissue dose (Clewell *et al.*, 2008).

Although a mechanistic understanding of the ultimate toxic mode of action remains elusive for many SVOCs in commerce, rapid methods are being developed and applied to evaluate hundreds of these compounds for potential hazard. The ToxCast™ program uses high-throughput screening, computational chemistry, and toxicogenomic techniques to profile bioactivity and prioritize toxicity testing for large numbers of chemicals (Dix *et al.*, 2007; Judson *et al.*, 2010). *In vitro* assays quantitatively characterize the pharmacodynamics of a chemical in concentration-response mode and new high-throughput methods are applied to estimate the corresponding pharmacokinetics of a potential toxicant (Rotroff *et al.*, 2010). In addition to this toxicological information, there is a strong need for screening-level procedures to estimate human exposure to SVOCs, such as those being developed in the ExpoCast™ program (Cohen Hubal *et al.*, 2010). Combined with rapid estimates of toxicity, the development of efficient exposure tools would enable a more complete risk-based prioritization of chemicals.

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Abstract: This chapter presents the main wood preservatives with respect to their potential hazard due to biocide release from treated wood products. The chapter first discusses the toxicological properties of the active substances and the chemistry of the treated wood products in the exposure conditions. Then, after presenting the main physico-chemical mechanisms at the origin of biocide release, a section is dedicated to methodologies applicable to toxicity assessment in service life scenarios. The main ecotoxic effects and examples of studies at laboratory or field scale are given, followed by several trends and alternative solutions.

Key words: wood preservatives, biocides, leaching, release mechanisms, treated wood toxicity.

6.1 Introduction

Due to its abundance in nature and its versatility, wood is one of the most important construction materials mankind has ever come across. The taxonomy of woody plants is very complex. Nevertheless, it is common to classify wood in two main categories: the wood from conifers (e.g. pine, spruces, cedars, etc.) is called softwood, and the wood from dicotyledons (usually broad-leaved trees, e.g. oak, maple, birch, etc.) is called hardwood. Each one of these categories contains thousands of species. It should be mentioned that these categories are a bit misleading, as hardwoods are not necessarily hard (e.g. balsa wood is actually softer than any commercial softwood) and softwoods are not necessarily soft (e.g. yew wood is harder than many hardwoods).

Because of its organic nature, wood is sensitive to biological attack. If a wood-based product is not naturally resistant to service conditions, in order to attain the performance level required by the user, an appropriate preservative treatment is carried out. The active substances used for the treatment are called biocides. Biocidal products are defined as (*OJEU*, 1998):

‘active substances and preparations containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means’.

Thus, by definition, a biocide could be a threat to health or environment. Therefore, the retention of the biocide in the product is very important for the effectiveness of the treatment but also for the health and environmental impacts due to its release into air, water and soil.

At the European level two main regulations concern biocides and construction materials with respect to the environmental and human health issues.

The Biocidal Products Directive (*OJEU*, 1998), which will be replaced by the Biocidal Products Regulation (*OJEU*, 2011a), aims to harmonise the European market for biocidal products and their active substances, including wood preservatives which are classified as product-type 8 (PT8). At the same time it aims to provide a high level of protection for humans, animals and the environment. In order to meet this requirement, the Organisation for Economic Cooperation and Development (OECD) was charged with harmonising methods for the assessment of biocides. This work led to the leaching protocols presented in prCEN/TS 15119 (CEN, 2007, 2010).

The Construction Products Regulation (305/2011/EU – CPR) (*OJEU*, 2011b), replacing the Construction Products Directive (89/106/EEC – CPD) (*OJEU*, 1989), lays down harmonised conditions for the marketing of construction products. The CPR provides more clarification of the concepts and use of CE marking. According to the CPR, construction works must satisfy seven Basic Requirements (BR). Among them, BR no. 3, Hygiene, Health and the Environment, states that

‘the construction works must be designed and built in such a way that they will, throughout their life cycle, not be a threat to the hygiene or health and safety of workers, occupants or neighbours, nor have an exceedingly high impact, over their entire life cycle, on the environmental quality or on the climate during their construction, use and demolition, in particular as a result of any of the following: ... the emissions of dangerous substances, ... into indoor or outdoor air; the release of dangerous substances into ground water, marine waters, surface waters or soil...’

In order to comply with this requirement, the European Commission mandated CEN (TC 351 – Construction products – Assessment of emissions of regulated dangerous substances from construction products) to prepare horizontal (i.e. product independent) test methods with which construction products can be tested with respect to the potential release of dangerous substances to water, soil and indoor air (CEN, 2011).

This chapter presents the issues linked to the environmental impacts of biocides released from treated wood. The potential hazard to the environment may arise at different stages of the product life cycle, i.e. manufacturing, distribution, construction, service life and end-of-life. During the service life and end-of-life (disposal or recycling) stages, both of which are usually spread over many decades, the release of substances due to contact with

water is the main potential hazard source, as a consequence of the leaching phenomenon.

Hereafter, the main preservatives used for wood treatment are presented together with their toxicological properties. Then, the wood chemistry is described in relation to the main biocide species interaction, resulting in biocide fixation/mobilisation. The exposure conditions of wood construction materials to environmental factors and especially the water contact scenarios are determining parameters for biocide release. After presenting the main physico-chemical mechanisms at the origin of biocide release, a section is dedicated to methodologies applicable to toxicity assessment in service life scenarios, together with the main experimental tools (leaching and toxicity tests) and current regulation. The main ecotoxic effects and examples of studies at field or laboratory scale are given, followed by several trends and alternative solutions.

6.2 Types of preservatives and their potential hazards

The hazardousness of treated wood is highly dependent on the nature and intrinsic toxicity of biocides (see Section 6.2.1) and also on the release potential of these molecules. The potential for biocide release depends on:

- The wood chemistry with respect to interactions with the biocides (see Section 6.2.2)
- The exposure conditions of treated wood products (see Section 6.2.3).

6.2.1 Biocide types and their toxicological properties

Different classes of biocides were used in wood treatment according to the legislative constraints of the time, which imposed increasingly strict conditions. Thus, in the 1960s, products such as aldrin, pentachlorophenol and creosotes were usually employed. Because of their known content of carcinogenic chemicals, they were restricted or prohibited (*JORF*, 1992; *OJEU*, 2001). Then alternative products known under the name of CCA (chromated copper arsenate) were extensively used. Nowadays, CCA treatment is prohibited for residential construction (with certain exceptions) (*AWPA*, 2001; *JORF*, 2004). The alternatives to these biocides are the so-called ‘new generation biocides’ (chromium and arsenic free), such as copper boron azoles (CBA), ammoniacal copper quaternary (ACQ), copper HDO (CuHDO), etc. Recently, preservatives containing micro- or nano-sized copper particles have been introduced to the market, usually with ‘micro-nized’ or ‘micro’ designations such as MCQ or MCA.

The number of commercial preservative products is very high but the number of active substances is relatively small. The main active substances are (FCBA, 2011):

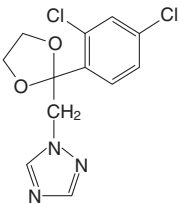
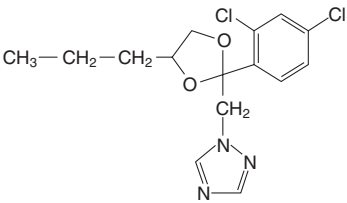
- Inorganic:
 - Copper as copper carbonate, copper hydroxide, copper oxychloride, copper sulphate, cuprous oxide, copper hydroxycarbonate or copper organic compounds
 - Boron as borax, boric acid or disodium octoborate tetrahydrate (DOT)
 - Chromium as chromium trioxide or sodium dichromate
 - Arsenic as arsenate in CCA.
- Organic (by chemical class):
 - Azole: azaconazole, propiconazole, tebuconazole, cyproconazole, thiabendazole
 - Ammonium quaternary compounds: dimethyl alkyl benzylammonium, chloride dimethyl coco benzyl ammonium chloride, dimethyl didecyl ammonium chloride, trimethyl coco ammonium chloride
 - Benzoylurea: noviflumuron, diflubenzuron, flufenoxuron, hexaflumuron
 - Benzimidazole: carbendazim
 - Carbamates: copper dimethyldithiocarbamate (CDDC), IPBC (3-iodo-2-propynyl-*n*-butyl carbamate), fenoxycarb
 - Diazenium compounds: bis-(*N*-cyclohexyldiazeniumdioxy)-copper (CuHDO)
 - Isothiazolone: DCOIT (4,5-dichloro-2-*n*-octyl-3(2H)-isothiazolone)
 - Morpholine: fenpropimorph
 - Neonicotinoids: thiamethoxam
 - Organophosphorus: chlorpyrifos
 - Pyrazole: chlorfenapyr, fipronil
 - Pyrethroid: cypermethrin, permethrin, bifenthrin, cyfluthrin, deltamethrin.

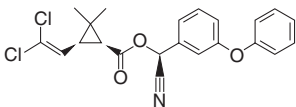
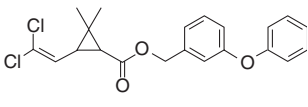
The class of toxicity of some biocides used for wood preservation treatment is given in Table 6.1. The classes of toxicity comply with the classification made by the World Health Organization (WHO, 2006).

Wood preservatives can be classified into four main categories:

- Water-borne preservatives
- Oil-borne preservatives
- Light organic solvent preservatives (LOSPs)
- Micro- and nano-sized-particle preservatives.

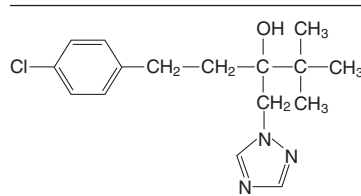
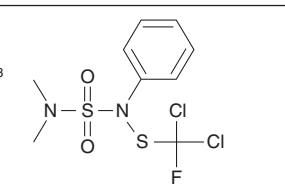
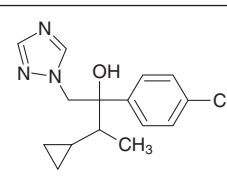
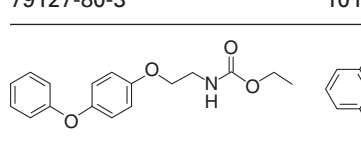
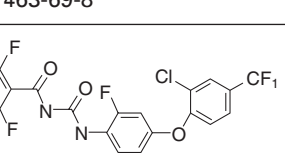
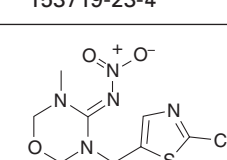
Table 6.1 Toxicity class of some biocides used as wood preservatives

Substance CAS no.	Azaconazole 60207-31-0	Propiconazole 60207-90-1
Chemical structure		
Toxicity class	II. Moderately hazardous	II. Moderately hazardous
Lethal dose (LD ₅₀), mg/kg	308	1520

Substance CAS no.	Cypermethrin* 52315-07-8	Permethrin* 52645-53-1
Chemical structure		
Toxicity class	IB. Highly hazardous or II. Moderately hazardous	II. Moderately hazardous
Lethal dose (LD ₅₀), mg/kg	79 to 250	500

*The toxicity data for pyrethroids is highly variable according to isomer ratios, the vehicle used for oral administration, and the husbandry of the test animals.

Substance CAS no.	Copper hydroxide 20427-59-2	Copper oxychloride 1332-40-7	Copper sulphate 7758-98-7, 7758-99-8
Molecular formula	Cu(OH) ₂	3Cu(OH) ₂ CuCl ₂	CuSO ₄ CuSO ₄ ·5H ₂ O
Toxicity class	III. Slightly hazardous	III. Slightly hazardous	II. Moderately hazardous
Lethal dose (LD ₅₀), mg/kg	1000	1440	300

Tebuconazole 107534-96-3	Dichlofluanid 1085-98-9	Cyproconazole 94361-06-5
		
III. Slightly hazardous 1700	U. Unlikely to present acute hazard in normal use >5000	III. Slightly hazardous 1020
Fenoxycarb 79127-80-3	Flufenoxuron 101463-69-8	Thiamethoxam 153719-23-4
		
U. Unlikely to present acute hazard in normal use >10000	U. Unlikely to present acute hazard in normal use >3000	III. Slightly hazardous 1563
Cuprous oxide 1317-39-1	Borax 1303-96-4	Chromium trioxide 1333-82-0
CuO II. Moderately hazardous 470	Na ₂ B ₄ O ₇ ·10H ₂ O U. Unlikely to present acute hazard in normal use 4500	CrO ₃ IB. Highly hazardous 80

The main water-borne preservatives are copper chromium arsenic (CCA), copper azoles, ammoniacal copper quaternary (ACQ), copper HDO (CuHDO) and borate-based formulations.

In CCA treatment, the copper acts primarily to protect the wood against decay fungi and bacteria, while the arsenic is the main insecticidal component of CCA. The chromium acts as a chemical fixing agent, which also provides ultraviolet (UV) light resistance and has little or no preserving properties. Its role is to help the other chemicals to fix in the wood, binding them through chemical complexes to the wood's cellulose and lignin. It should be mentioned that even though CCA treatment is presently prohibited for residential uses, some CCA-treated woods are still in service. Moreover, CCA products are still permitted for use in various industrial and public works, such as bridges, highway safety fencing, electric power transmission and telecommunications poles (FCBA, 2011). Thus, this kind of preservative continues to be of concern to the environment.

Copper azole is a fungicide and an insecticide. There are two types of copper azole: type A (CBA-A) and type B (CA-B). Copper boron azole type A contains the following ingredients: copper (49%), boron as boric acid (49%), and azole as tebuconazole (2%). Copper azole type B is composed of copper (96.1%) and azole as tebuconazole (3.9%) (EPA, 2011). Some commercial CBA also contains glycol (US DOI, 2011). Despite research efforts, no effective means has yet been found to keep borate preservatives from leaching out of wet wood (US DOI, 2011).

Ammoniacal copper quaternary (ACQ) contains copper as fungicide and a quaternary ammonium compound as insecticide. There are currently four AWWPA standardised ACQ formulations (types A to D). All ACQ types contain two active ingredients which may vary within the following limits: copper oxide (62–71%) and a quaternary ammonium compound (29–38%). ACQ is considered as an alternative to CCA treatment. Nevertheless, because of its higher level of copper, ACQ-treated wood is more corrosive to common steel and the use of double-galvanised or stainless steel fasteners is necessary for this kind of treated wood processing (US DOI, 2011).

Cu-HDO is composed of copper and *N*-cyclohexyl-diazeniumdioxide (HDO). Cu-HDO affects sulphhydryl groups of essential amino acids of fungi and causes protein denaturation (EPA, 2011). It is classified as moderately hazardous (toxicity class II, with a LD₅₀ of 380 mg/kg) (WHO, 2006).

Borate preservatives such as boric acid, oxides and salts (borates) are supplied under numerous brand names throughout the world. Borate-treated wood is considered of low toxicity (toxicity class U – see Table 6.1). However, borate compounds do not become fixed in the wood and can be readily leached out. They are efficient rather for use class 1 and 2 (see

Section 6.2.3), such as framing, sheathing, sill plates, furring strips, trusses and joists (EPA, 2011).

Oil-borne preservatives include creosote and some vegetal oils containing permethrin. Creosote is one of the oldest wood preservatives. Because of its known content of carcinogenic chemicals, it was restricted or prohibited (*JORF*, 1992; *OJEU*, 2001). However, it is still used for railroad ties and utility poles. In recent years linseed oil has been incorporated in preservative formulations as a solvent and water repellent together with preservatives of low water solubility, such as permethrin. Permethrin is a broad-spectrum non-systemic synthetic pyrethroid insecticide (Imgrund, 2003).

Light organic solvent preservatives (LOSP) are based on the use of white spirit, or light oils such as kerosene, as solvent carrier for biocides. Synthetic pyrethroids are typically used as an insecticide, such as permethrin, bifenthrin or deltamethrin. Other active compounds are propiconazole and tebuconazole as fungicides. These kinds of preservatives contain no heavy-metal compounds but they are still of concern for health and environmental impacts, due to the release of volatile organic compounds (VOC) and organic biocides.

For a few years now, preservatives containing micro- or nano-sized copper particles have been used for wood treatment. There are currently two particulate copper systems on the market. One system uses a quaternary biocide system (known as MCQ) and is based on ACQ. The other uses an azole biocide (known as MCA or μ CA-C) and is based on copper azole. This kind of preservative raises concerns regarding exposure to micro- and nano-sized particles, in the context of the general debate about the hazards of nanotechnology to humans and the environment (Evans *et al.*, 2008; Matsunaga *et al.*, 2008, 2010; ICTA, 2010).

6.2.2 Wood chemistry and its interactions with biocides

Wood is composed of mainly three biopolymers present in different proportions, namely cellulose (about 45% in weight), hemicellulose (about 30%) and lignin (20%) and a small fraction (about 5%) of low weight compounds extractible in water or other solvents, named extractives (Govin, 2004).

Cellulose is composed of linear chains of D-glucose linked by β -1,4-glycosidic bonds with a degree of polymerisation of about 10,000. Cellulose possesses hydroxyl groups and has the specific reactivity of primary and secondary alcohols (donor reactivity of hydroxyl groups).

Hemicelluloses are heteropolysaccharides (containing glucose, galactose, xylose, arabinose, mannose and uronic acids) with a lower degree of polymerisation (50–300) and amorphous structure. The chemical structure of hemicellulose varies from soft to hard wood. It contains mainly hydroxyl

groups but also carboxylic groups. Lignin is a complex network of polymers (molar mass exceeding 10,000) composed of phenolpropane units and containing characteristic methoxyl groups, phenolic hydroxyl groups and some terminal aldehyde groups. Lignin is associated with hemicellulose forming complexes that are resistant to hydrolysis. There is no evidence that lignin is associated with cellulose. Other minor polysaccharides present in wood are pectins, starch and proteins.

The low weight compounds are organics belonging to many chemical classes: fats, fatty acids, fatty alcohols, phenols, terpenes, polyphenols, tannins, lignans (combinations of two phenylpropane units), steroids, resin acids, rosin, waxes, etc. Wood contains also inorganic species represented by silica, and several major elements – Ca, Mg and K (up to 80% of the ash). These metals are probably bound to carboxyl groups in pectic materials, oxalates, carbonates and sulphates. Many other metals are present in lower quantity.

Wood is a slightly acid material, having pH values in contact with water in the range of 3 to 6, depending on wood species (e.g. pH 3 for western red cedar and pH 6 for ash). The acid/base properties and general reactivity of wood materials are determined by the functional groups linked to the polymeric structure. So, carboxyl groups are attached mainly to hemicelluloses and pectins and have acidity constant pK_a values between 3 and 5. Lignin contains phenolic groups ($pK_a = 7.5\text{--}10.5$) and small quantities of carboxyl as a result of oxidation processes. The acid/base properties of wood extractives in water are due mainly to carboxyl groups (pK_a of 5.0–6.5) and their solubility rises with the temperature and alkali content (Balaban and Uçar, 2001; Ravat *et al.*, 2000a; Duong *et al.*, 2004).

Complexation and ion exchange are the two main interaction mechanisms of metal ions with wood components. The ion exchange mechanism is possible at the level of carboxyl functional groups present in hemicellulose, pectins or lignin. It mainly concerns alkaline and alkaline-earth cations and is a non-specific electrostatic interaction. Heavy metals such as Cu, Cd, Ni, Zn and Pb are mainly involved through reactions of surface complexation with the functional groups phenol and carboxyl. The phenolic sites lying on lignin have significantly higher affinity for transition metals than the carboxylic sites. The conclusion of many studies is that cellulose has a lower sorption capacity for heavy metals compared to lignin. The extent of metal sorption depends on pH and aqueous ionic strength. Complexation constants for several heavy metals including Cu and Zn are reported in the literature (Ravat *et al.*, 2000a, 2000b; Merdy *et al.*, 2002; Guo *et al.*, 2008).

In the wood/water system, at low pH, metals exist predominantly as free cations in solution. When the pH increases, the deprotonated carboxylic sites contribute significantly to their fixation by forming complexes. At

higher pH, phenolic sites become deprotonated and participate in metal binding. These complexes are mostly monodentate, $S1-O-M^+$, and to a lesser extent bidentate, $S1-O-M-O-S2$ (here S1 and S2 are organic functional groups, and M is a bivalent metal). The proportion of the aqueous metal species and fixed complexes on biopolymers depends on pH and ionic strength, and can also be influenced by the presence of extractives.

The maximum metal quantity a wood material can fix by specific interactions is given by the number of binding sites. The site density depends on the wood species and biopolymer type. For example, a lignin isolated from black liquor (a residue of the paper industry) (Guo *et al.*, 2008) contains about 0.08 mmol carboxyl and 0.28 mmol phenolic groups per gram of dried wood. A hemicellulose extracted from cottonwood (DeGroot, 1985) contains about 0.08 mmol/g carboxyl groups.

The extractives are organic compounds able to undergo complexation reactions with free metals present in aqueous solution (by intermediation of carboxylic, phenolic groups, or other electron donor groups). Copper is particularly renowned for its capacity to complexate with dissolved organic matter, resulting in an increase of its global leachability.

In the aqueous phase chromium behaves as Cr(III) and Cr(VI). In contact with biomaterials like wood, Cr(VI) transforms into Cr(III) by an adsorption-coupled reduction mechanism involving adsorption steps of both species and reduction of Cr(VI) such that Cr(III) becomes dominant in the system (Dupont and Guillon, 2003; Park *et al.*, 2007).

According to Bernardo *et al.* (2009), Cr(III) adsorption on biomaterials follows a reaction path involving phenolic or carboxylic groups leading to mono- and polydentate complexes with free and hydroxylated Cr^{3+} ions. Despite the abundance of literature on the subject (Miretzky and Cirelli, 2010), no intrinsic complexation constants have been determined.

Boron leachability in treated wood is recognised to be high but its chemistry in wood is far from well understood. Most authors consider that boron does not react with wood materials and is completely available for leaching. Other authors consider that B (as boric acid) can form organic complexes via O bridges with hydroxyl groups on polysaccharides (Obanda *et al.*, 2008; Ramos *et al.*, 2006). No complexation constants are available in the literature.

Generally, wood preservatives are used as mixtures of several chemical substances with complementary biocidal effects. The chemical behaviour of these substances is dependent also on the additives used. Research on products containing ammonia and Cu has shown that ammoniacal copper is readily adsorbed to phenolic hydroxyls, such as are found in lignin or extractives, although, in the absence of ammonia, precipitation may occur as copper carbonates, copper oxides or copper arsenate complexes. Also, coarse deposits of almost pure copper were observed by spectroscopic

investigations localised within the cell wall and on the microfibrils (Lebow, 1996).

However, there is no unanimity concerning the formation of salt precipitates, since they are reasonably soluble. Many investigations on CCA-treated wood by XAFS (X-ray absorption fine structure spectroscopy) indicated that Cu is not chemically associated with any heavy element (Bull, 2001). The results of leaching tests performed with different extractants (acetic acid, EDTA, oxalic acid, etc.) show that Cu is not dependent on Cr and As and exhibits a different release behaviour. The most plausible fixation mechanism for Cu remains the complexation on carboxyl and phenolic sites. Similar mechanisms possibly occur in the case of Zn, although the binding forces are weaker.

Little information has been published on the fixation mechanism of organic biocides on wood materials (Woo *et al.*, 2010). It was observed that these molecules are rather leach resistant, suggesting possible interactions with the wood structure. It may be expected that the organic biocides interact with the different wood components at least by weak physical bonds (van der Waals, dipolar and charge transfer interactions), thus adsorbing on the biopolymers. Their partition between the aqueous solution and the biopolymers of the wood depends on the biocide's hydrophobicity and aqueous solubility. So, it is expected that hydrophobic molecules have more affinity for lignin than for cellulose. Stronger interactions can occur when biocides possess functional groups able to react with specific sites on wood, such as hydroxyls (hydrogen bonds).

Investigations (Kjellow *et al.*, 2010) on tebuconazole, propiconazole and IPBC behaviour during wood impregnation have allowed researchers to observe their partition between the carrier solvent and wood samples and have led to the conclusion that some (adsorption) interactions occur. The adsorption level decreases in the order tebuconazole > propiconazole > IPBC. It was suggested that tebuconazole forms stronger bonds with the hydrophilic biopolymers (hemicellulose, for instance) due to the presence of a hydroxyl group.

6.2.3 Exposure conditions of treated wood products

The service life and end life are the longest steps during the life cycle of treated wood products. Thus, during these two steps the environmental risk could be of more concern.

As a function of exposure conditions, European Standard EN 335 (CEN, 2006) defines five use classes which represent different service situations to which wood-based products can be exposed. The classes described in the European Standard are based on an existing classification agreed on by

the European Homologation Committee (EHC), after taking into account the possibility of harmonisation with three moisture categories of Eurocode 5 and with other classes used outside Europe. It has, however, been judged that the following five classes are the most appropriate solution for European conditions:

- Use class 1: situation in which the wood-based product is under cover, not exposed to the weather and wetting (exposure to wetting: maximum 20%), e.g. indoor window frames/sills, doors, floors, etc.
- Use class 2: situation in which the wood-based product is under cover and not exposed to the weather but where high environmental humidity can lead to occasional, but not persistent wetting (exposure to wetting: occasionally >20%), e.g. some indoor window frames/sills, doors, flooring, etc.
- Use class 3: situation in which the wood-based product is not under cover and not in contact with the ground. It is either continually exposed to the weather or is protected from the weather but subject to wetting (exposure to wetting: occasionally or frequently >20%), e.g. roofing, weatherboarding, façade cladding, outdoor window frames/sills and doors
- Use class 4: situation in which the wood-based product is in contact with the ground or fresh water and thus is permanently exposed to wetting (exposure to wetting: predominantly or permanently >20%), e.g. terraces, decks, playground equipment, garden furniture
- Use class 5: situation in which the wood-based product is permanently exposed to salt water (exposure to wetting: permanently >20%), e.g. decks, marine constructions, ship-decking, etc.

Use classes 1 and 2 are of concern mainly for the health impact via the indoor air emissions of eventual VOC contained in the treated wood, whereas use classes 3 to 5 are of concern for the environmental impact, especially via leaching phenomena.

During the service life, the biocide amount in wood products lessens following air emission, leaching and biodegradation processes. Nevertheless, the end-of-life management (incineration, recycling, landfill) must take into account the presence of specific toxic substances.

Landfill disposal is allowed for wood wastes whose composition complies with the admission standards in different landfill categories. The biocide release in these systems will affect the landfill leachate composition and thus its management.

Biotransformation of organic compounds by using adapted leaving species (fungi, bacteria) could be envisaged before the entrance of wood residues back in the carbon cycle (Woo *et al.*, 2010) by incineration.

Recent research (Tame *et al.*, 2007) found that the presence of Cu-based biocides favours dioxin formation during the combustion of treated wood. The explanation resides mainly in the catalytic activity of Cu for dioxin formation, the smouldering of wood char by the metals providing a favourable temperature environment, and the presence of chlorinated organic biocides as precursors for dioxin formation.

6.3 Potential toxic effects and ways they can be assessed

As water exposure of treated wood represents the main route for toxic biocide emission in the environment, this section is dedicated to the mechanisms and methodologies for assessing the toxic effect via leaching processes. The extent of biocide release from treated wood in contact with water is a crucial parameter determining the hazardous effect on human health and on that of other living organisms.

6.3.1 Release mechanisms and parameters of influence

Release of biocides from treated wood products is the result of coupled chemical reactions, transport processes and biological activity.

In contact with water, wood material undergoes chemical and structural changes, with the release of soluble compounds such as natural mineral salts and extractives. Fixed biocides are partially desorbed following thermodynamic equilibrium. All these chemical reactions are influenced by the pH. The natural pH of wood is often acidic, so contact with neutral water could cause chemical and structural modifications of the wood material (hydrolysis, deprotonation of acidic functions, dissolution/precipitation of extractives, etc.). The pH strongly influences the mineral biocides (Cu, Cr, As, B) binding by complexation reactions on carboxyl and phenol groups, but also the interaction between hydrophilic organic compounds. The presence of oxygen is a factor in wood ageing by oxidation of, for example, phenol groups and depolymerisation of lignin.

Besides chemical processes, the organic natural compounds and biocides can be transformed by biological activity of bacteria or fungi. The decay period of organic biocides is variable as well as the secondary compounds formed, following the surrounding conditions.

Wood is a porous, hygroscopic material; all the processes mentioned above take place in the porous structure. There are gradients of composition between the core and the product surface following the conditions of water contact experienced by the product. The dynamics of the biocide release from a given piece of wood are then determined by the diffusion processes

in the porous structure. Wood is an anisotropic material; the diffusion rate varies following the orientation, being maximal along the fibres, minimal in the tangential direction and intermediary in the radial direction.

Once the biocides reach the external surface of the wood, their dispersion in the environment is ensured by the water circulation in soils, surface and ground waters, potentially affecting the quality of environmental compartments (including water resources for human consumption) and the integrity of living targets. In some cases attenuation could occur through soil infiltration by chemical (retention, decay) and biological (degradation) mechanisms. Dispersion of the released pollutants into surrounding water and soils plays a diluting role for the initial leachate.

Numerous leaching studies have been realised at laboratory and field scales for determining the biocide release from wood products (Cooper, 1991; Lebow, 1996; Brooks, 1997; Hingston *et al.*, 2001; Solo-Gabriele, 2003; etc.) and have highlighted the role of different parameters of influence, described below.

1. *The nature of the preservation product and the treatment process used.* The chemical nature of biocide compounds and accompanying additives is determinant, as discussed in section 6.2. The method used for incorporating biocides in wood could modify the porous structure (effect of pressure or chemical reactions) and the speciation of metals at the beginning of the service life. Precipitation after wood drying can occur followed by subsequent redistribution of metals between the wood polymers, pore solution and mineral salts. A long period between treatment and immersion in water allows more effective biocide fixation and lessens the extent of release.
2. *The geometry of wood products and the type of water contact.* A large specific external surface (small pieces) enhances the mass transfer process and then the leaching rates. Water contact is an important factor: intermittent or continuous, stagnant or flowing – the total extracted amount depends on the accumulated liquid/solid ratio and the water residence time. The aqueous leachant can have various compositions following the exposure scenario: fresh, rain, seawater or soil water, containing salts, natural organic matter, dissolved gases, in different proportions and affecting the chemistry of the wood and the biocides to different extents (for example, Cu leaching is favoured by the presence of dissolved organic matter). The exposure time affects the quantity released; the leaching is more intensive at the beginning of the exposure scenario and slows with the product ageing.
3. *The exposure climate conditions.* Rain events determine the water contact type and parameters (discussed above). A temperature increase can accelerate chemical reactions and biological activity. UV radiation

and oxygen contribute to degradation by breaking and oxidation of wood polymers and thus enhance the release (Schiopu, 2007).

6.3.2 Methodologies of toxic effect assessment

Biocides are intrinsically toxic substances and their harmful effect will strongly depend on their release behaviour.

The extrapolation of partial field observations or laboratory assays to conditions encountered in real scenarios of service life is not obvious. The assessment of toxic effects needs comprehensive methodologies and adapted experimental and modelling tools, which is why the European authorities endeavour to develop standard assessment methods.

The potential harmful effects of biocides released in a given scenario of wood product utilisation can be assessed following classical methodologies of risk assessment on ecosystems and human health. These methodologies consist of the evaluation of three components of the cause–effect chain: the source of pollution (the wood product, for instance), the pollutant transport through environmental compartments (soils, waters) and the effects on living targets. A sound evaluation of the physico-chemical and biological processes at the level of these three terms is necessary and possible by using appropriate experiments, models and databases. A more detailed description is given in Chapter 14 of this book.

The hazardous effect of biocides as toxic molecules present in different environmental compartments is evaluated by bioassays (toxicity tests) on selected species, then the risk is evaluated by comparing the test results with toxicological parameters (lethal or effect doses and concentration).

The key point in the assessment process is the evaluation of the exposure of living targets to a biocide, i.e. knowledge of the biocide concentration and the evolution with time of the released flux from the wood product. So, knowledge of the wood product behaviour in its utilisation scenario (the source term of pollution) is fundamental for the evaluation of the exposure conditions. The most common experimental tools for studying the leaching phenomenon are the leaching tests. Some of these tests (i.e. static leaching tests) give information about different intrinsic properties of the material (e.g. acid/base neutralisation capacity, pH influence on pollutant release) and others (i.e. dynamic leaching tests) provide knowledge about the release dynamics – see also Chapter 14.

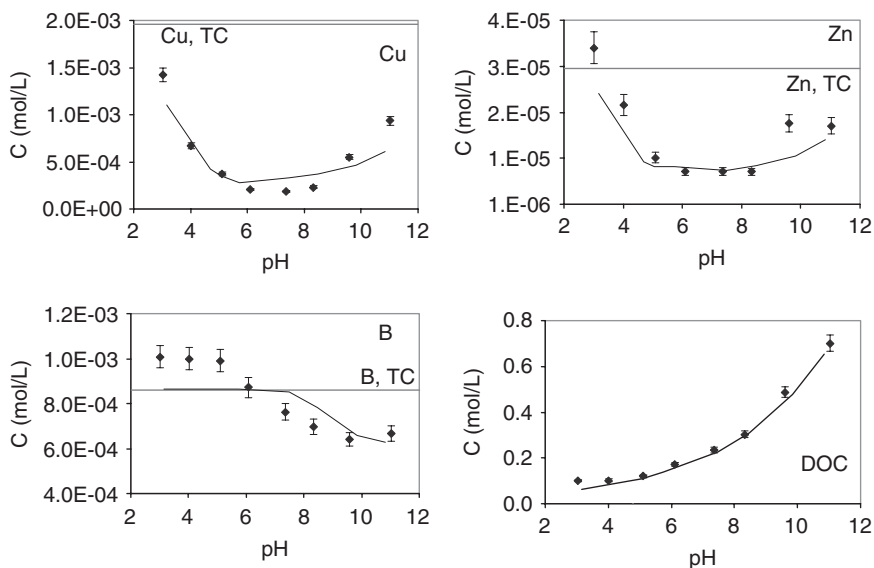
As mentioned above, the leaching of biocides from construction materials is a research subject receiving attention from the European regulation authorities. The main standards concerning the leaching behaviour that are presently under development are CEN/TC 351/WG 1 N 178 – Generic horizontal dynamic surface leaching test (DSLTL) for determination of surface dependent release of substances from monolithic or plate-like or

sheet-like construction products; CEN/TC 351/WG 1 N 177 – Guidance standard for CEN, Product TCs for selection of leaching tests appropriate for their product(s) – General principles; and CEN/TC 351/WG 1 N 162 – Generic horizontal up-flow percolation test for determination of the release of substances from granular construction products (CEN, 2011). Until these protocols, at the European level two standards referred to the leaching of wood preservatives: XP ENV 1250-2 (CEN, 1994) and EN 84 (CEN, 1997). XP ENV 1250-2 specified that *'the results cannot be connected to the conditions of exposure in the service life of wood based products, as part of the building'*. EN 84 was aimed at the accelerated ageing of treated wood prior to biological testing. These two standards are rather tests that aim to evaluate the effectiveness of the wood preservation treatment and not the environmental impact due to the leaching of biocides.

Much work aimed at characterising the leaching process has been carried out, at different scales and following different experimental protocols. As mentioned above, we distinguish between two types of leaching assays: (1) equilibrium tests – the wood material (generally of very small size, crushed) is put in contact with a leachant for a given duration, allowing chemical equilibria to occur (e.g. batch assays); and (2) dynamic tests – processes such as diffusion or leachant flow determine the time evolution of the released quantities (e.g. block diffusion, runoff). The results are weakly comparable and generalisation is not possible, especially when transport phenomena play a major role in the release process. For these reasons only few examples are given here; the interested reader may consult the many other journal articles.

Biocide solubilisation under different pH conditions has been investigated (Esser *et al.*, 2001; Schiopu, 2007; Schiopu *et al.*, 2011), showing similar leaching patterns for the inorganic biocides (Cu, Cr, As, B, Zn). In the case of wood samples treated with CCA and Cu-quat (copper oxide, didecyl-dimethylammonium chloride or DDAC) preservatives (Esser *et al.*, 2001), it was shown that Cu, Cr and As have a maximum fixation at pH 7–8 and solubilisation is augmented by many orders of magnitude at acid or alkaline pH. So, for natural pH values of most wood species (i.e. acid), the element fixation is not optimal (see Fig. 6.1 (Tiruta-Barna and Schiopu, 2011)). The most important variation was observed for Cu, while As behaviour is slightly different following the type of preservative. When the behaviour of extractives was observed, their global concentration (determined as dissolved organic carbon) was found to be augmented with solution alkalinity.

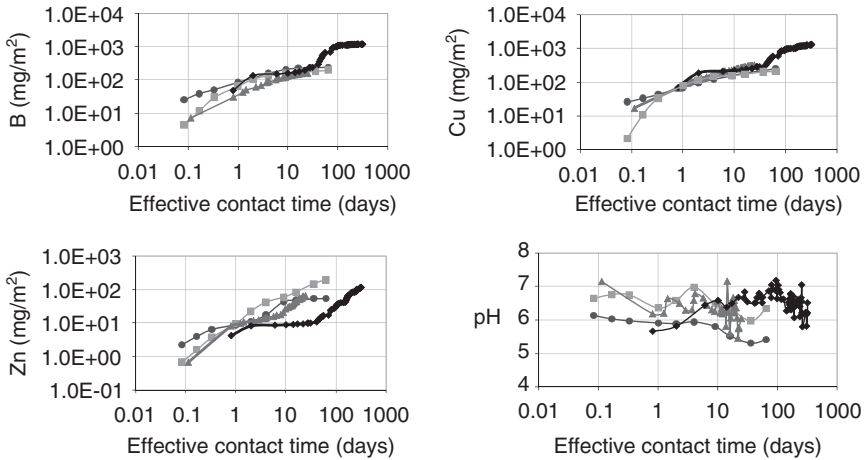
Dynamic tests were performed at laboratory and field scales (Esser *et al.*, 2001; Schiopu, 2007; Hingston *et al.*, 2002; Hasan *et al.*, 2010) and were made the subject of interlaboratory studies for the development of leaching assessment methods and leaching tests (Schoknecht *et al.*, 2005).



6.1 Influence of pH on release behaviour from a CBA-treated wood. Experimental data are shown by points, modelling data by lines. Experimental conditions: liquid/solid = 10 L/kg; crushed wood <1 mm, total content (TC): Cu = 1.25 g/kg of wood, B = 0.093 g/kg, Zn = 0.020 g/kg. DOC = dissolved organic matter (Tiruta-Barna and Schiopu, 2011).

A comparison was made (see Fig. 6.2) between the dynamic release in laboratory leaching tests (MBT sequential renewal of leachate, CMLT continuous renewal) and field assays on a commercial wood product treated with copper–boron–azole based preservatives (Schiopu, 2007; Schiopu *et al.*, 2007). The field pilot simulated two scenarios of intermittent rainwater contact: immersion in rainwater (stagnation) and runoff rainwater, during one year (leachate concentrations and rainfall events were monitored). It was observed that the accumulated release increases by many orders of magnitude with the effective leaching time (the duration of dry periods was not accounted for). More or less significant differences have been observed between the tests, following the target element (Cu: similar releases; Zn: different shapes). During one year of rain exposure, the stagnation scenario accounted for more effective contact time (about 300 days) than the runoff scenario (30 days). The increase of release in the stagnation scenario after 30 days could be explained by a weathering process of the wood samples. Therefore, the release level in this scenario tends to those of an aged wood sample after about 100 days.

Despite the abundance of literature on studies dedicated to biocide leaching and wood retention mechanisms, there are few studies that



6.2 Release dynamics in laboratory (MBT: circles; CMLT: squares) and field tests (runoff: triangles; stagnation: rhombus), showing pH and accumulated release as functions of the effective contact time for B, Cu and Zn.

structure the information and knowledge on mechanistic models. The interest in modelling of physico-chemical processes resides in the possibility of confirming hypotheses based on experimental observations, identifying and calculating related parameters, and foreseeing the system behaviour for different exposure conditions. Modelling could make interpretation bridges between different observed systems and different scales and resolve unexplained experimental results.

Diffusion transport in the wood pores was one of the earlier modelling trials (other than empirical regression equations). Recently, leaching from wood was modelled (Waldron and Cooper, 2010) by soluble species (no chemical reactions) and their three-dimensional diffusion following the wood anisotropy (along fibres, radial and tangential directions). Diffusion coefficients of 10^{-10} – 10^{-9} m²/s have been calculated for the longitudinal direction.

The transport mechanisms are not sufficient for representing the leaching behaviour. The chemistry of the wood/biocide system, although very complex, must be formalised and integrated on coupled chemical-transport models. Chemical models are very few in the literature. A realistic chemical model was established (Tiruta-Barna and Schiopu, 2011) for explaining the leaching behaviour of a wood product made from copper–boron–azole (CBA) treated *Pinus sylvestris*. The model considers the main fixation mechanisms for Cu, B and other trace species present in wood (Cr, Zn, Ca, SO₄²⁻). The influence of dissolved organic matter on Cu release was

modelled by pH-dependent complexation reactions. The model can explain the leaching behaviour in a closed system (at equilibrium) for a pH range from 3 to 11 (*cf.* prCEN/TS 14429 (CEN, 2002)) (Fig. 6.1). This kind of model represents a step forward but more efforts are needed to integrate transport and reliable chemical models into useful predictive tools for the assessment of leaching behaviour.

6.3.3 Toxicity studies – case examples

Despite the fact that the issue of biocide release gains more and more interest, there are few available studies in the literature evaluating the harmful effect or risk for real service-life scenarios of commercial products by using standard methodologies and tools. Ecotoxicological studies have been carried out mainly on conventional preservatives using different methods, experimental assays and conditions, and expressing the results in different ways that are often not comparable.

The compilation of field observations of biocide release from wood products in their service life (Lebow, 1996; Hingston *et al.*, 2001) highlighted the fact that the methods and experiments used for many dozens of years have varied from one study to another and a coherent analysis of the leaching process and the mechanisms involved is very difficult, due to the lack of complete information. The most monitored preservatives so far are Cu-based with different compositions: CCA (the most studied), ACA, ACZA, ACQ, DDAC, CC and CuAz. For all studies the behaviour of Cu, As and Cr was observed in terms of wood residual composition and soil or water concentration.

One of the most studied scenarios is of the ‘underground contact’ type (poles, posts, plywood, stakes), considered to be the worst example of biocide emission. The biocide emission and pollution are demonstrated by a higher soil concentration of the biocide than in the natural background. In these various studies, higher concentrations of up to 1000 times background were measured on the soil volume around the wood product within a radius of about 1 m. The biocide loss by the wood products was about 10–30% in several years, with various levels for Cu, Cr and As.

In marine environments, the immersed wood products release significant quantities of inorganic biocides, as was observed in the majority of reported studies. Biocide concentration depletion of the surface layer of wood samples of 40–85% was observed after several years of service life. It was noted that most biocide loss occurs in the first weeks of seawater contact. The contamination of living marine species was demonstrated by measuring the levels of Cu, Cr and As in green algae, oysters and crabs collected from the wood sites (including sediments); these were found to be higher than the natural concentrations.

Immersion in fresh water has been less studied. Slightly higher concentrations in CCA components were found downstream and depleted biocide concentration was measured in the wood surface layer.

'Above-ground' contact is considered less harmful because contact with water is rather intermittent, depending strongly on the surface area exposed to rain.

All the above-mentioned studies (based on field measurements of pollutant concentrations) concluded that there were non-impact or insignificant effects given the low concentration and the limited dispersion of the target biocides in soils and waters (effects of dilution and natural attenuation), although the toxic effect was not properly assessed.

Conversely, studies performed in controlled conditions, using leachates from treated wood with or without dilution and using various toxicity tests on living organisms, have concluded that there is a possible or effective harmful impact on aquatic compartments and, to a lesser extent, on topsoil organisms. Several case studies and their main findings are presented here.

The toxicity of commercial preservatives (propiconazole, tebuconazole, IPBC, cypermethrin) for aquatic organisms was studied (Adam *et al.*, 2009) using bioassays (freshwater amphipods *Gammarus pulex* (L.)) and the results obtained for individual biocides showed that the toxicity increases from propiconazole to cypermethrin, and that there are synergistic effects enhancing the harmful effect of the commercial mixture.

The topsoil ecotoxicity from a contaminated site with wood preservatives Cu sulphate and CCA was studied (Mench and Bes, 2009) using target organisms (radish, lettuce, slug *Arion rufus* L., and earthworm *Dendrobaena octaedra*). The levels of contamination (variables on the site) were 65–2600 mg Cu kg⁻¹, 0–52 mg As kg⁻¹ and 0–87 mg Cr kg⁻¹. The results showed a high Cu content in plants and a negative effect on plant growth for the most contaminated site.

Dubey *et al.* (2007) studied the aquatic toxicity of leachates obtained from blocks of wood treated with Cu-based preservatives (CCA, ACQ, CBA). A specific heavy metal toxicity assay was used, based on inhibition of β -galactosidase activity in an *E. coli* strain. Natural water compartments were considered (rivers, lakes, wetlands, and seawater) along with synthetic moderate hard water and deionised water. In their study, Cu was released from ACQ- and CBA-treated wood about 10–20 times more than from CCA-treated wood. The toxicity of aquatic compartments was found to correlate with the labile (non-complexated) Cu concentration in waters. The bioavailability (and hence the toxic effect) is reduced in the presence of organic and mineral complexes in natural waters.

The new generation of preservatives has replaced CCA for residential constructions; however, not enough hazard assessment has yet been performed. Furfurylated wood as an alternative to CCA-treated wood was

tested for its aquatic toxicity (Pilgård *et al.*, 2010). Aquatic organisms were used in Microtox and Daphtox, applied to leachates obtained from different treated woods, in two leaching tests. The most relevant results concern the influence of the treatment procedure on the potential toxicity: those processes which favour curing/polymerisation led to products with less impact. Hemlock stakes treated with different preservatives (e.g. CCA, creosote, ACQ, zinc naphthenate, copper naphthenate) were tested (Lalonde *et al.*, 2011) for aqueous toxicity, acute lethality tests being performed with *Daphnia magna*, *Vibrio fischeri*, rainbow trout and three-spine stickleback. For the samples tested, the toxicity varied in the order ACQ > creosote > zinc naphthenate > copper naphthenate > CCA.

6.4 Remedial action

Different remedial actions have been envisaged to replace the use of biocides for wood preservation. The most evident is to use naturally durable wood species such as red pine (*Pinus resinosa*), teak (*Tectona grandis*), merbau (*Intsia bijuga*) and ironbark (*Eucalyptus* spp.), instead of treated wood. Natural durability consists of the ability of wood to develop self-resistance by the presence of fungitoxic components (mainly polyphenols) formed by chemical reactions during the transition from living sapwood to dead heartwood. However, there is no evidence of such performance for all the service conditions required by the construction field. Moreover, economic issues (many of these species are prohibitively expensive for general construction applications) and global environmental impacts may restrain the use of such alternatives to using treated wood (sometimes they are logged in an unsustainable manner and many of these species grow only in specific areas, therefore the environmental impact due to worldwide transportation is high).

The use of composite materials made of wood fibres and recycled plastics has also been proposed as an alternative to treated wood. Their main advantages are considered to be that they do not warp, split, chip or rot, they require little maintenance, being resistant to moisture, and they present a variety of colours to choose from. Nevertheless, they have some disadvantages: they are not rated for structural use, they are susceptible to mildew, mould and stains, and they are also more expensive than treated wood (EPA, 2011).

Other alternatives are based on the well-known concept that the physical properties of any material are determined by its chemical structure. The degradation of wood is considered to be initiated by enzyme attack at the free hydroxyl sites contained in the wood (Rowell *et al.*, 2008). Therefore, in order to make the wood resistant to biological attack, the main alternative techniques are based on the sealing or transformation methods of these free hydroxyls.

One of these techniques is autoclave impregnation with linseed, sunflower or rapeseed oil (without synthetic preservative). Tung oil has also been used for hundreds of years in some countries (without any pressure treatment). The function of these oils as preservatives is related to their action as water repellents and drying agents rather than to direct biocidal activity. Nevertheless, their effectiveness is restricted to some specific applications.

Another method is based on glass encapsulation of the wood fibres. So-called 'glass fortified wood' or 'glass wood' is obtained through a process that intermixes a sodium silicate-based formula throughout the wood fibres (Flynn, 2006). Glass wood can be used in ground contact applications and in water applications.

Modification of the chemical structure of wood has been proposed by acetylation or heat treatments. The acetylation methods are based on wood's reaction with some anhydrides, such as acetic anhydride. The acetylation process changes the free hydroxyls within wood into acetyl groups. The acetylation of wood was first done in 1928 but the large-scale production of acetylated wood began only in 2007 (Rowell *et al.*, 2008).

Heat treatments have recently been developed. These processes (e.g. Retification[®], Thermowood[®], Plato[®], etc.) autoclave the wood, subjecting it to pressure and heat (180–230°C), along with nitrogen or water vapour for 24 to 48 hours (Xie *et al.*, 2002). These processes increase the durability, dimensional stability and hardness of the treated wood. However, there are changes in aesthetic and certain mechanical characteristics. Wood treated with this process is often used for cladding or siding, flooring, furniture and windows.

Other 'compromise' techniques are based on a combined treatment by biocidal products and natural compounds playing the role of water repellents. In addition, these compounds can have a biocidal effect. This method seems to be promising for reducing the leachability of boron-based preservatives, as reported by different studies. Temiz *et al.* (2008) propose the impregnation of boron-treated wood by tall oils in order to avoid water penetration in the wood's porous structure. Tall oils are extractives obtained as by-products of pulp processing of softwood (sulphate method). Their water repellency property is due to their chemical composition (variable following the wood species): 40–55% resin acids, 40–60% fatty acids, and 5–10% neutral compounds. Tall oil can protect the boron compounds against leaching, allowing the resistance of the wood to be preserved for longer periods and at the same time avoiding the release of toxic leachates. A similar effect was reported by Baysal *et al.* (2006). In this study, a treatment with polyethylene glycol-400 helped to decrease the water adsorption in wood, and an additional water repellent (styrene, methyl methacrylate and isocyanate) treatment diminished the boron leaching. Leaching tests

realised in continuous and discontinuous modes on treated wood impregnated with montan wax emulsion clearly showed reduction of boron leaching by 20–50% (Lesar *et al.*, 2009). In another study (Sen *et al.*, 2009) extractives from different plants were tested for their efficiency for wood preservation (by their high tannin content) and for avoiding the preservatives (salts containing B and Cu) leaching from different species of treated wood. The highest effects were seen in wood treated with sumac leaf extract and oak valonia extract, in the presence of 1–3% of salts.

6.5 Conclusion and future trends

The treatment of wood has been practised for almost as long as the use of wood itself. Different types of preservatives were used, according to consumer requirements and legislative constraints imposing increasingly strict conditions concerning both the effectiveness and the innocuousness of the wood treatment.

Concerning the potential hazard of treated wood, the service life and end life are the longest steps during the life cycle of treated wood products. Thus, during these two steps the environmental risk should be of more concern, because of the leaching of biocides used for the treatment. One could conclude that different experimental protocols co-exist to assess the leaching behaviour of biocides from treated wood. The objectives of these protocols are different. Moreover, the application of an experimental method alone is not sufficient for a pertinent and scientifically sound assessment. A mechanistic modelling approach is necessary. Indeed, the release of wood preservatives and risk assessment for ecosystems are closely linked to the physico-chemical mechanisms induced by wood/water contact. Despite the abundance of literature on studies dedicated to biocide leaching and wood retention mechanisms, there are few studies that structure the information and knowledge on mechanistic models. The interest in modelling physico-chemical processes resides in the possibility of confirming hypotheses based on experimental observations, identifying and calculating related parameters, and foreseeing the system behaviour for different exposure conditions. Modelling could make interpretation bridges between different observed systems and different scales and resolve unexplained experimental results. Also, different remedial actions have been envisaged to replace the use of biocides for wood preservation, such as the use of naturally durable wood species or the use of composite materials made of wood fibres and recycled plastics. In order to make wood resistant to biological attack, other alternatives to treated wood are based on the sealing of active sites (free hydroxyls) or the transformation of the wood's chemical structure.

The main issue for the future is to develop more knowledge on the chemistry and different treatment mechanisms of wood, in order to help decision

makers reach a balance between the treatment effectiveness, the global environmental and health impacts and the economic costs of the process, on the basis of the global thinking concept.

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Mineral fibre-based building materials and their health hazards

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Abstract: Asbestos minerals have always been considered somehow magic as they exhibit unique outstanding technological properties. Unfortunately, the fibrous crystal habit of asbestos minerals is thought to be the cause of their potential toxicity. There are two contesting fronts in the world today: those countries which consider all asbestos minerals as potentially carcinogenic substances and have banned them, and those which did not ban chrysotile asbestos and recommend its safe use. In the countries where all asbestos minerals are banned, the reclamation of asbestos containing material (ACM) requires specific outdoor and indoor techniques. The production of ACMs waste calls for another issue: should ACMs be destined to landfill burial or recycling?

Key words: asbestos, asbestos-containing materials (ACMs), cyto- and geno-toxicity, landfill, recycling.

7.1 Introduction

Asbestos minerals have been known and used for millennia (Skinner *et al.*, 1988). There is evidence that white asbestos (serpentine asbestos or chrysotile) was discovered and utilized for the first time in Cyprus, perhaps as long as 5000 years ago, for manufacture of cremation cloths, lamp wicks, hats, and shoes (Dilek and Newcomb, 2003). It was clear from the beginning that asbestos was a unique natural product, considered somehow magic, with outstanding physical, chemical and technological properties (especially incombustibility), usable for an endless number of applications in everyday life. The history of asbestos from classical times to the industrial age can be appreciated in Skinner *et al.* (1988) and Dilek and Newcomb (2003).

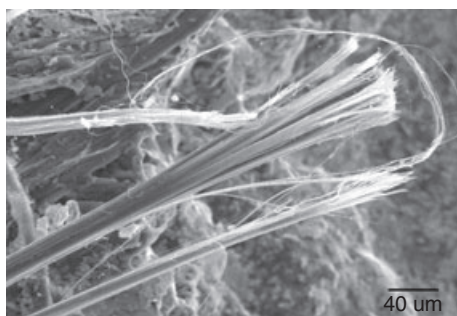
The modern asbestos industrial age began in the 1870s with the opening of large asbestos industries in Scotland, Germany and England for the production of asbestos boards. Active mining in Quebec (Canada) began in 1878 and by 1885 seven white asbestos mines close to the town of Thetford were active. In 1896 the first asbestos brake linings were made by Ferodo Ltd in England. In 1907 brown (amphibole amosite, an acronym of 'Asbestos Mines of South Africa') asbestos was discovered in Transvaal (South Africa) and mined. Mining and production of blue (amphibole crocidolite) asbestos began near the town of Koegas (South Africa) in 1926. Mining of anthophyllite (amphibole) asbestos started in 1918 in Paakkila,

eastern Finland. Chrysotile and tremolite (amphibole) asbestos from the Italian Alps were first exploited in Roman times but it was not until the early 1800s, when manufacture of asbestos threads, paper and fabrics was perfected, that the alpine deposits (especially the Balangero mine in the Lanzo valley near Torino) became economically important (Dilek and Newcomb, 2003). It is not a surprise that the first asbestos pipes were developed in Italy in 1913.

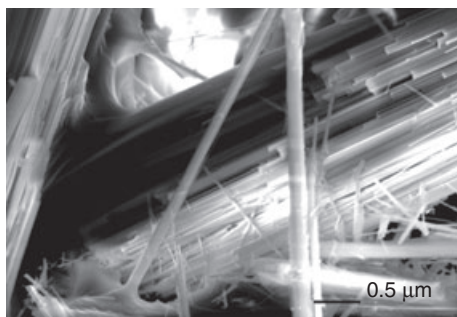
For the reasons described in section 7.3, asbestos minerals are considered carcinogenic substances and their use is consequently restricted or banned by national laws in 55 out of the 195 countries (28%) of the world (see www.ibasecretariat.org). In the other countries worldwide, asbestos is exploited and used. The 2009 asbestos trade data (from the United States Geological Service) reported that the top five asbestos producers (t/year) in decreasing order are Russia (1,000,000), China (380,000), Brazil (288,000), Kazakhstan (230,000), and Canada (150,000). The top five asbestos users (t/year) in decreasing order are China (565,313), India (340,544), Russia (276,820), Brazil (140,272), and Thailand (102,738). In the countries where asbestos is banned, it has been progressively removed from the environment and eventually substituted by synthetic fibres. The most common substitute materials are inorganic fibres which are divided in two classes: *man-made mineral fibres* (MMMF) and *man-made vitreous fibres* (MMVF).

7.2 Classification of asbestos and mineral fibres, their structure, microstructure and properties

The term ‘asbestos’, from the Greek ἄσβεστος or *asbestinon* which means ‘unquenchable’ or ‘inextinguishable’, was used in the beginning to describe any of the several fibrous minerals and usually those found as concentrated aggregates or in veins amenable to mining (Skinner *et al.*, 1988). The nomenclature we now apply was coined in Germany in the eighteenth century and refers to minerals that occur as bundles of flexible fibres that can be separated into thin, durable threads. Frayed ends observed on a fibrous particle (Fig. 7.1(a)) indicate that it is composed of smaller fibrillar components, usually referred to as *fibrils* (Skinner *et al.*, 1988). This peculiar crystal habit is called fibrous-asbestiform. The length of a single fibril usually ranges from a few microns up to decimetres. The outer diameter is in the range 10–50 nm whereas the inner diameter is in the range 1–10 nm. The length of a fibre usually ranges from a few microns to decimetres, whereas the diameter is usually less 0.5 μm . Stoichiometric chrysotile tubular nanocrystals (length in the range 200–500 nm and outer diameter in the range 20–50 nm) have also been synthesized as possible starting materials for applications towards nanotechnology (Falini *et al.*, 2004).



(a)



(b)

7.1 (a) A chrysotile asbestos fibre showing the typical fibrils at one end observed by SEM; (b) the crystal habit of an amphibole asbestos fibre by SEM.

Asbestos minerals are divided into two major groups: serpentine asbestos and amphibole asbestos. The fibrous-asbestiform variety of serpentine is called chrysotile. Chrysotile is the most commonly used form of asbestos. The amphibole asbestos family includes five minerals: actinolite, tremolite, anthophyllite, crocidolite (a fibrous variety of riebeckite), and amosite (a fibrous variety of grunerite). With respect to chrysotile, amphibole asbestos fibres are more brittle and usually exhibit a straighter, more needle-like crystal habit (Fig. 7.1(b)). The chemical composition of the six asbestos minerals together with their crystal symmetry are reported in Table 7.1.

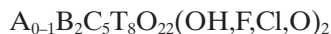
Chrysotile and amphibole asbestos are both silicates sharing the same fibrous-asbestiform crystal habit but very different structural units at a molecular scale. The way nature assembles the different molecular units to realize similar output at macroscopic scale is very elegant. Chrysotile is a layer silicate composed of Si-centred tetrahedral (T) sheets in a pseudo-hexagonal network joined to Mg-centred octahedral (O) sheets in units with a 1:1 (TO) ratio (Fig. 7.2(a)). Since the TO unit is polar and a misfit exists between the smaller parameters of the T sheet and the larger ones

Table 7.1 The chemical composition and crystal symmetry of the six asbestos minerals

Mineral	Chemical composition	Crystal system
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	Monoclinic
Actinolite	$\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	Monoclinic
Grunerite var. amosite	$(\text{Fe}^{2+},\text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Monoclinic
Anthophyllite	$(\text{Mg, Fe}^{2+})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Orthorhombic
Riebeckite var. crocidolite	$\text{Na}_2(\text{Fe}^{2+},\text{Mg})_3\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$	Monoclinic
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	Monoclinic

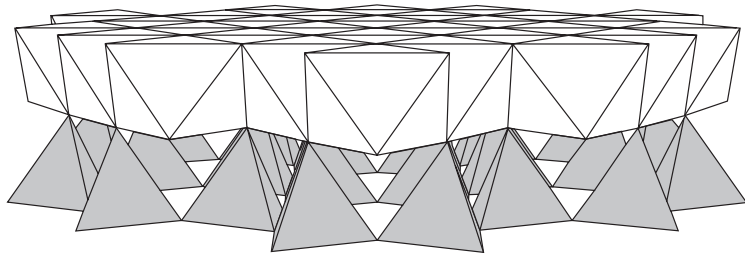
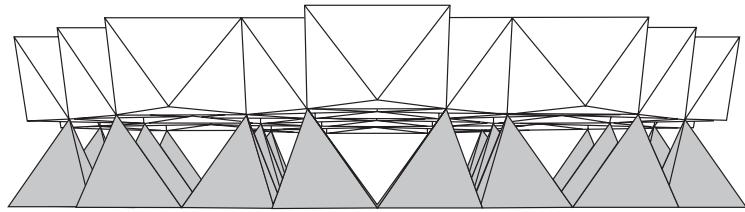
of the O sheet (Bailey, 1988), a differential strain occurs between the two sides of the layer. The strain is released by rolling the TO layer around the fibril axis, which is usually the crystallographic *a* axis (clinochrysotile and orthochrysotile) and more rarely the crystallographic *b* axis (parachrysotile). The fibrils are thus composed of concentrically or spirally curved layers, forming a tubular structure (Yada, 1971). By this mechanism, a layer silicate assumes a fibrous crystal habit (see Fig. 7.2(b)). Because the layers cannot energetically withstand too tight a curvature, the rolls possess hollow cores with a diameter of about 5–8 nm (Cressey *et al.*, 1994). The earlier X-ray diffraction studies on chrysotile showed a remarkable distortion (curvature) of the unit cell with respect to the conventional crystal structures, so that a new theory specially formulated for cylindrical lattices was developed (Whittaker, 1956; Jagodzinski and Bagchi, 1953; Devouard and Baronnet, 1995).

Amphiboles are double-chain silicates with a Si(Al):O ratio of 4:11 (Fig. 7.2(c)) and the oxygen atoms of the chains coordinated not only to Si(Al) but to a variety of other cation sites, yielding the following simplified general formula (Veblen, 1981):

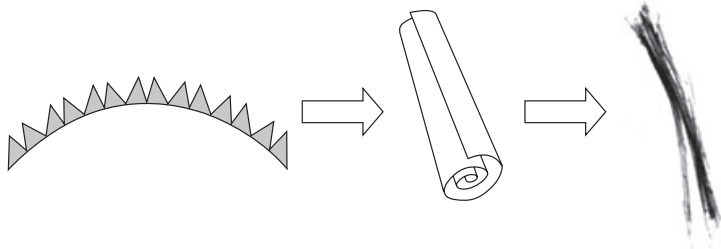


where T = tetrahedral sites within the silicate chain; C = fairly regular octahedral cation sites; B = less regular octahedral or eight-fold coordinated cation sites; and A = irregular cation sites having coordination in the range 6 to 12. Generally, in the rock forming amphiboles A = Na^+ , K^+ ; B = Na^+ , Li^+ , Ca^{2+} , Mn^{2+} , Fe^{2+} , Mg^{2+} ; C = Mg^{2+} , Fe^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Ti^{3+} , Ti^{4+} ; and T = Si^{4+} , Al^{3+} . Because of the presence of strong bonds, amphiboles normally crystallize along the crystallographic *c* axis (Ferraris, 2002). Hence, the fibrous crystal habit is due to the monodimensional character of their structural units (chains).

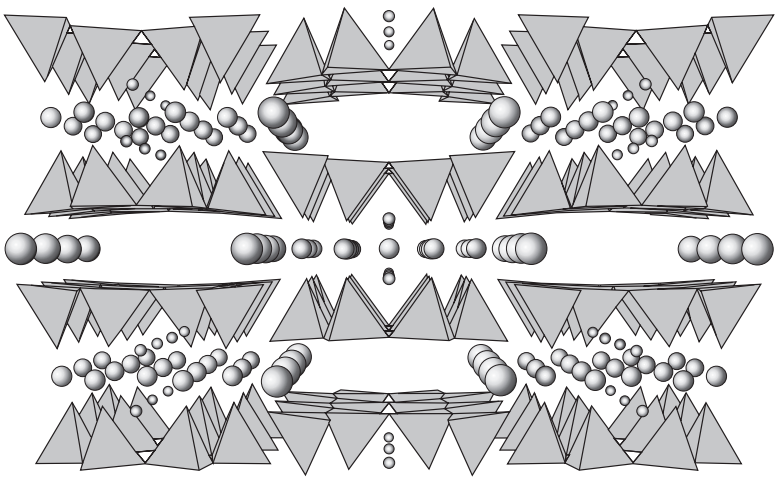
Both serpentine and amphibole asbestos minerals display outstanding properties which have been exploited for the development of building



(a)



(b)



(c)

7.2 (a) A sketch of the structure unit of chrysotile asbestos with an Si-centred tetrahedral sheet joined to an Mg-centred octahedral sheet (b–c crystallographic plane); (b) bending of the layers in chrysotile at a molecular scale results in a rolled carpet-like microstructure which is a fibril at the microscale (see text for details); (c) a sketch of the structure unit of amphibole asbestos composed of one-dimensional double-chains (a–b crystallographic plane).

materials. The main chemical-physical and technological properties of the commercial chrysotile, amosite and crocidolite asbestos minerals are illustrated in Table 7.2.

In those countries where asbestos is banned, asbestos substitute materials are eventually used in building materials, the most common being synthetic inorganic fibres belonging to two distinct classes: *man-made mineral fibres* (MMMF) and *man-made vitreous fibres* (MMVF).

Some methods of classification of non-asbestos fibres have emphasized the origin (e.g., *natural* vs. *man made*) while others are based on their chemistry (e.g. *inorganic* vs. *organic*), structure, physical/technological properties or field(s) of application. Table 7.3 shows a general classification scheme of natural and man-made fibres (modified from Gualtieri *et al.*, 2009a). The term *man-made* is designated to distinguish natural fibres (erionite or morденite, wollastonite, and others) from synthetic ones. The MMMF group includes polycrystalline fibres whereas fibres belonging to the MMVF group are amorphous. MMVF are often referred to as silicate-based glass fibres, as the largest volume of MMVFs produced worldwide is of this type. However, in addition to fibreglass and fused silica, there are other amorphous fibres used in commerce. Some examples are alumina and silica combinations, rock and slag wool, as well as fibres with non-silicate compositions such as carbon. The dimensions (i.e. length, diameter, and length to

Table 7.2 Major physical–chemical and technological properties of the three commercial asbestos minerals

Property	Chrysotile (white asbestos)	Amosite (brown asbestos)	Crocidolite (blue asbestos)
Acid resistance	Not resistant	Resistant	Resistant
Alkali resistance	Resistant	Resistant	Resistant
Decomposition point (°C)	450–700°C	950–1050°C	950–1050°C
Density (g/cm ³)	2.52–2.56	3.4–3.5	3.3–3.4
Flexibility ^a	Good	Fair	Good
Melting point (°C)	1500	1400	1200
Mohs hardness	2.5–3	3.5–4.5	3.5–4.5
Sound transmission coefficient (STC) ^b	70–90	60–70	60–70
Surface area (m ² /g)	10–20	5–15	5–15
Tensile strength (kg/cm ²) ^a	0.031	0.025	0.035
Thermal conductivity (W/m ² K)	0.1–0.2	0.2–0.4	0.2–0.4

^aFrom Skinner *et al.* (1988).

^bSTC is an integer number which rates how well a material attenuates airborne sound according to the ASTM International Classification E413 and E90 in the USA and the Sound Reduction Index (SRI) ISO standard outside the USA.

Table 7.3 General classification scheme of natural and man-made fibres

Natural fibres		
Inorganic		Organic
Minerals (asbestos fibres, sepiolite, attapulgite, erionite, wollastonite)		Vegetables (cotton, wool, flax, jute, hemp, sisal)
		Wood
		Animal (silky, tendinous)
Man-made fibres		
Inorganic		Organic
MMVF	MMMF	
Glass wool	Polycrystalline fibres	Carbon
Rock wool		Cellulose
Slag wool		Polyalkalene
Ceramic fibres		Polyester
Glass Microfibres		Polyvinyl
Others		Others

Source: modified from Gualtieri *et al.* (2009a).

diameter ratio) of the fibres are used to distinguish between continuous fibres, discontinuous fibres, and wools. Fibres with diameters $>3\ \mu\text{m}$ are generally regarded as non-breathable and, therefore, cannot present an inhalation hazard (Vu, 1994).

Most of the non-asbestos fibres that are widely used in commerce today belong to the man-made 'vitreous silicate' category. However, the lack of a conclusive mode of classification of fibres in this group has permitted the use of the commercial terms fibreglass (glass wool), rock wool, slag wool and ceramic fibre (CF). The rock and slag wool products typically contain high amounts of calcium and magnesium oxides and are sometimes referred to as alkaline earth silicate glasses. CFs which contain higher concentrations of alumina are also called alumino-silicate glasses. The European Community recently introduced new definitions to describe MMVFs in order to amend Annex I of European Council Directive 67/548/EEC for the classification, packaging and labelling of dangerous substances. The directive subdivided 'vitreous silicate fibres' into 'mineral wools', which are understood to include glass, stone, rock and slag wools, and 'refractory ceramic (RCF) and special purpose fibres'. The differentiation of these two categories, according to the European Community Directive, is based on the concentration of certain alkali and alkaline earth oxides (i.e. Na_2O , K_2O , CaO , MgO , and

BaO). Fibres containing >18 wt% and ≤ 18 wt% of these oxides belong to the first and second category, respectively. The sum of the alkali and alkaline earth oxides (as defined above), denoted here by the symbol Z , is presumably related to the potential hazard posed by exposure to these fibres. Fibres with Z values greater than 18 (i.e. mineral wools) are believed to be less hazardous than those for which the value of Z is less than 18 (i.e. RCF and special-purpose fibres). For all these fibres, the EC scheme provides another test that relies on the *in vivo* measurement of biopersistence (see, for example, Mast *et al.*, 2000; Maxim *et al.*, 1999) and Commission Directive 97/69/EC of 5 December 1997 defines the circumstances under which certain fibres must be labelled as carcinogens based on biopersistence.

7.3 Health effects of asbestos minerals

Worldwide, the number of workers passing away each year in asbestos-related cancer is estimated to be 100,000–140,000 (asbestos pandemia). In Western Europe, North America, Japan and Australia, 20,000 cases of diagnosed lung cancer and 10,000 cases of mesothelioma result every year from exposures to asbestos (Tossavainen, 2000).

The first evidence of the potential health hazard of asbestos minerals was reported at a time when these minerals were massively used in society. The history of the epidemiological reports of asbestos-related diseases is well described in Skinner *et al.* (1988) and will not be reported here.

Although many epidemiological studies since the early 1980s have provided convincing evidence that amphibole asbestos crocidolite and tremolite are clearly more dangerous than chrysotile asbestos (Hodgson and Darnton, 2000), all six asbestos minerals (chrysotile, actinolite, amosite, anthophyllite, crocidolite, and tremolite) have been assumed to be equally harmful to human health. This assumption was made for regulatory purposes.

Research into the toxicity of asbestos, initially performed to understand why the inhalation of asbestos had such devastating effects on health (Mossman *et al.*, 1990), became relevant to the investigation of possible hazards from other fibres and led to the so-called *fibre paradigm* (Miller *et al.*, 1999). The fibrogenicity and carcinogenicity of asbestos are now known to be related primarily to four factors: (1) a length greater than 5–15 μm , as below this size the fibre can be easily cleared by lung macrophages; (2) a diameter less than about 3 μm , allowing the fibre to be inhaled to the gas-exchanging part of the lung (asbestos fibres with length >5 μm and diameter <3 μm are termed ‘regulated’); (3) insolubility in the lung milieu; and (4) a sufficient dose to the target organ. The mechanism that leads to lung cancer appears to be frustrated phagocytosis, whereby the macrophage is injured in an attempt to engulf long fibres and releases

cytokines, mitogens and oxidants that initiate the process of fibrosis and carcinogenesis (Seaton *et al.*, 2010).

The results of the epidemiological, *in vitro* and *in vivo* cohort studies indicate that exposure, via inhalation of asbestos minerals, causes lung diseases, in particular the following (Skinner *et al.*, 1988; Dilek and Newcomb, 2003):

1. *Asbestosis*: a non-malignant diffuse interstitial fibrosis of the lung tissue. High asbestos exposure leads to scarring of the lung, causing it to become stiff, resulting in a restriction in pulmonary function and a reduction in the lung's ability to exchange CO₂ for oxygen. It is a typical lung disease developed after continuous exposure in the working environment (Filkenstein, 1983) with a latency period of about 10–20 years.
2. *Lung cancer* or *carcinoma*: includes squamous carcinoma, small- or oat-cell carcinoma, and adeno-carcinoma. As for asbestosis, the development of lung cancer is also a typical lung disease provoked by a contaminated working environment with a latency period of about 15–20 years.
3. *Mesothelioma*: a cancer of the pleura, pericardium and peritoneal membranes which surround the lung, heart and abdominal cavities, respectively. Mesothelioma may develop as a consequence of exposure in both working and living environments with a latency period of about 20–40 years.
4. *Pleural plaques*: localized scars consisting of collagen deposits, sometimes calcified, normally found in the parietal pleura but occasionally also near the ribcage. Although benign, they may indicate future development of asbestos diseases.

Asbestos was declared a proven human carcinogen by the US Environmental Protection Agency, the International Agency for Research on cancer (IARC) of the World Health Organization, and the National Toxicology Program more than 20 years ago (Nicholson, 1986; IARC, 1977, 1988; Collegium Ramazzini, 2010). The global scientific community agrees that there is no evidence of a threshold level of exposure to asbestos fibres below which there is no risk of mesothelioma (Collegium Ramazzini, 2010). From the late 1980s, many countries worldwide began to ban or restrict the use of ACMs in response to the pressure of a large part of the scientific community, asbestos victims' associations, environmental protection groups and many political parties.

In 1989, the United States Environmental Protection Agency (EPA) issued the Asbestos Ban and Phase Out Rule which was subsequently overturned in the case of *Corrosion Proof Fittings v. EPA*, 947 F.2d 1201 (5th Cir. 1991). This ruling leaves out many consumer products that can still legally contain trace amounts of asbestos. A complete ban on

asbestos-containing material in Australia was introduced in 1991, although some building materials in storage were still being used in the years that followed. In the United Kingdom, blue and brown asbestos were banned in 1985. The ban included also white asbestos in 1999. According to the regulation, importation, supply and use of all forms of asbestos is prohibited. This also comprises second-hand use of asbestos products such as asbestos cement sheets and asbestos boards and tiles including panels which have been covered with paint or textured plaster containing asbestos.

Asbestos has been banned in Italy since 1992 (Law no. 257 issued on 27 March 1992). Since 1997, asbestos has been banned in France by Decree no. 96-1133 issued on 24 December 1996. On 26 July 1999 a document updated Annex 1 of Directive 76/769/EEC on dangerous substances and preparations and proclaimed the end to the use of asbestos throughout all member states of the European Union (EU). Recently, chrysotile asbestos has been included in the list of chemicals in Annex III of the Rotterdam Convention.

If asbestos minerals are considered carcinogenic substances, why is their use restricted or banned in only 55 of 195 countries (28%) in the world and still exploited and used in the remaining countries? The answer is still a matter of controversy and raises a global issue still far from being worked out. The pro-asbestos side claims that only amphibole asbestos minerals are carcinogens whereas chrysotile asbestos is not. This is the so-called *amphibole hypothesis* which is based on the assumption that chrysotile asbestos has little potential for provoking mesothelioma (see, for example, Liddell *et al.*, 1997; McDonald *et al.*, 1997; Camus, 2001) and that lung diseases are actually due to amphibole minerals (especially tremolite) which are likely to contaminate chrysotile asbestos.

The amphibole hypothesis is supported by knowledge of chrysotile and amphibole behaviour in the lungs. Chrysotile dissolves quickly (low biodeurability) in the lung fluids (especially in the macrophage environment at pH = 4) whereas amphiboles are much more durable (high biodeurability) and remain in the lungs for a very long time (Hume and Rimstidt, 1992; Bernstein *et al.*, 2008; Oze and Solt, 2010). Although the position is not shared by the overall scientific community (see, for example, Stayner *et al.*, 1996; Hodgson and Darnton, 2000; Berman and Crump, 2008), there are few studies in which dose–response relationships have been estimated separately for cancer risk and exposure to different fibre types in the same exposed population and this somehow leaves the issue open to debate. Wagner (1997) claims that no mesotheliomas have been reported to have occurred in chrysotile-exposed workers, unless the exposure has been intense and for more than 20 years. This author claims that there must be tremolite contamination of the chrysotile and that a prolonged exposure to large quantities of fibres is a situation that rarely exists today.

For these reasons, today 72% of the countries worldwide ban only amphibole asbestos species whereas the use of chrysotile asbestos is permitted with its exposure controlled by technology or by regulations of work practices.

A further source of argument comes from the asbestos substitute materials. Chrysotile substitutes include *p*-aramid, polyvinyl alcohol (PVA), cellulose, polyacrylonitrile, glass fibres, graphite, polytetrafluoroethylene, ceramic fibres and SiC whiskers. There are reasons to doubt the safety of these substitutes (Camus, 2001). Actually glass and ceramic fibres, SiC whiskers, and rock and slag wools have been classified as possible or probable carcinogens by IARC (Camus, 2001). PVA and *p*-aramid fibres are less respirable but more biopersistent than chrysotile. *P*-aramid fibres have induced fibrosis and mesothelioma in inoculation studies (Friedmann *et al.*, 1990). Cellulose displays cytotoxic effects (Huuskonen *et al.*, 1998).

In this scenario of global uncertainty, one side of world's countries calls for a global ban on all asbestos minerals whereas the other side calls for the dismissal of the ban on asbestos and the controlled use of chrysotile in high-density products, provided that permissible maximum exposure limits of 1.0 fibres/cm³ are respected (recommendations of WHO Group of Experts).

7.4 Use of asbestos in building materials

ACMs are generally divided into two classes: friable asbestos and compact or non-friable asbestos. Friable asbestos refers to any ACM that when dry, can be easily crumbled or pulverized to powder. In practice, free asbestos fibres can easily be scratched off the surface of friable ACM by hand. Virtually any friable asbestos material (with more than 1 wt% asbestos) is considered to be Regulated Asbestos-Containing Material (RACM). Usually, friable asbestos is composed of 70–95 wt% chrysotile and/or amphibole asbestos fibres. A few examples of products of friable asbestos are acoustic ceilings, tiles, plasters and wallboard. Compact asbestos is by definition a composite material in which chrysotile and/or amphibole asbestos fibres are compacted or cemented in a cement or polymeric matrix. The most noteworthy example of compact asbestos material is asbestos-cement in which 4–15 wt% chrysotile and generally 0–5 wt% amphibole asbestos fibres reinforce an ordinary cement matrix. Compact asbestos does not tend to release fibres, unless it is sawn or scratched by mechanical tools (e.g. a chisel).

As discussed in the previous section, the use of asbestos in new construction projects has been banned in many developed countries. In the United States building materials containing asbestos such as asbestos-cement pipes continue to be used in construction. Prior to the ban, asbestos was widely

used in building materials. Consequently, many old buildings all over the world still contain asbestos.

Chrysotile has been used more than any other asbestos species and is still by far the most used one (94% of the world's production). The largest user of chrysotile fibres is the asbestos-cement industry, accounting for about 85% of the total use. For the reasons discussed in section 7.3, chrysotile is probably the only asbestos species that will be used in the future. It is estimated that more than 95% of the commercially developed asbestos ore deposits are chrysotile asbestos (Ross *et al.*, 2008). Due to its availability, some countries have used amphibole species in place of chrysotile in many applications. Friable asbestos is made of nearly pure asbestos fibres, whereas asbestos fibres are diluted in compact composite products (Becklake *et al.*, 2007; D'Orsi, 2007; Virta, 2006; Health and Safety Executive, 2011).

In building materials, friable asbestos has been used in the following applications:

- Artificial ashes and embers for gas-fired fireplaces, household products
- Cavities, partitions of floors and ceilings, beneath windows, panels to lift shafts
- Cork board, covering and filled mastics
- Corrugated paper
- Expansion and compound joints
- Fire-door gaskets in furnaces, wood stoves, and coal stoves
- Fireproofing spray and fire door interiors
- Gaskets in pipes and vessel joints
- Gunning mix
- Insulating boards/panels: duplex filler and covering, flat-boards and flex-boards, acoustic panels and finishes, fireboards, paper used as insulation around furnaces and wood-burning stoves, millboards, panels on access hatches to service risers and lining service risers and floors, bath panels
- Insulation of oil and coal furnaces
- Insulation and covering of ventilation and air conditioning (HVAC) systems, refrigerators/freezers, clothes dryers
- Insulation of electrical wires and panels
- Lagging: steam pipes, boilers, pipework, calorifiers, furnace ducts insulated with an asbestos blanket or asbestos paper tape, anti-vibration gaiters
- Machine room ceilings, floors, ducts and walls
- Patching and joint compounds for walls and ceilings, and textured paints/coatings
- Range hoods
- Roof flashing

- Rope seals on boiler access hatches and between cast-iron boiler sections
- Soundproofing or decorative spray coatings or roofing felt for ceilings, walls, horizontal or vertical beams and columns
- Roadboards.

In building materials, compact asbestos has been used in

- Bonding and finishing cement, masonry filler, mortars, mastics, caulk, (window) putties and trowelled coatings
- Ceiling tiles as filler material to improve mechanical strength and lightness
- Asbestos-cement products with 4–15 wt% chrysotile asbestos and/or 0–6 wt% amphibole asbestos: planar or corrugated roofing (Fig. 7.3(a),(b)), shingles, siding, pipes, insulating blocks, wall cladding
- Chimney flues and tops (Fig. 7.3(c))
- Decorative, insulating, fireproof, acoustic, and woodfibre plasters
- Fire brick
- Flexible duct connectors and duct tapes
- Floor tiles, textiles and composites (resilient floor tiles, linoleum, vinyl asbestos, flooring backing vinyl finishing, asphalt, and rubber, vinyl sheet flooring and adhesives used for installing floor tiles, insulating seals)
- Fuse boxes
- Glassbestos
- Guttering and drainpipes
- Refractory furnace cements
- Transit wallboards, manufactured mixing Portland cement with chrysotile asbestos (generally 12 to 50 wt%)
- Wallboards
- Water tanks.

ACMs in house building materials are illustrated in Fig. 7.4.

Leading developing countries such as China and Russia have continued the widespread use of asbestos. The most common ACM is corrugated asbestos-cement sheets for roofing and side walls. As discussed in section 7.2, the countries where asbestos is banned use *man-made mineral fibres* (MMMF) or *man-made vitreous fibres* (MMVF) as substitutes in building materials. The most common commercial asbestos substitute MMMFs are produced from a liquid melt of the starting raw materials by mechanical drawing, blowing with hot gases, and centrifuging as fiberizing methods (Klingholtz, 1977). The most common products are rock/slag wool, which is a furnace product of molten rock, generally a basalt, formed at a temperature of about 1500–1600°C (De Vuyst *et al.*, 1995; Öhberg, 1987). The



(a)

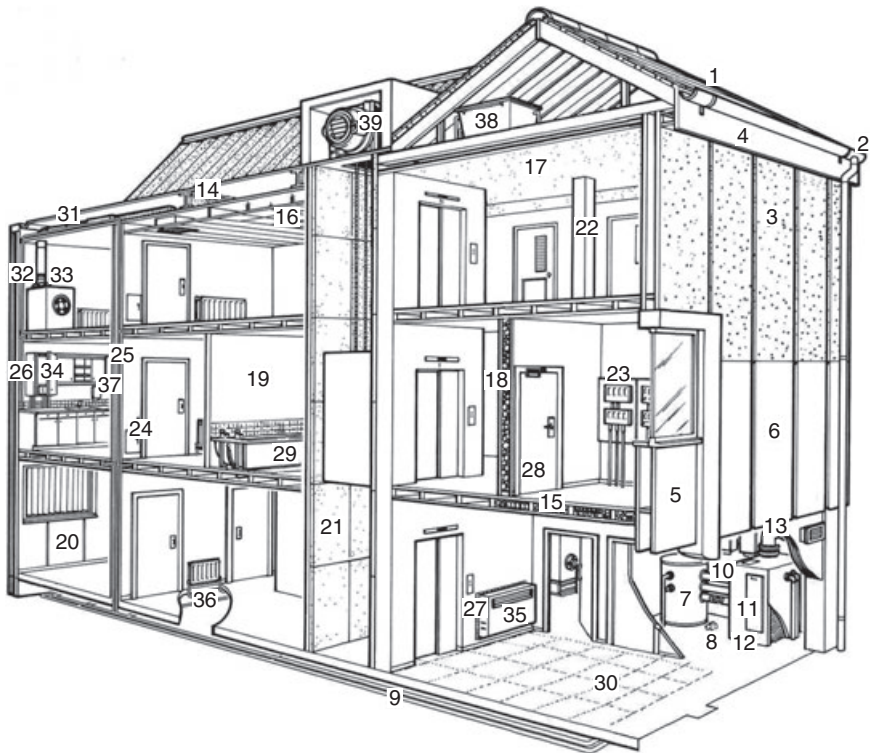


(b)



(c)

7.3 (a) A planar asbestos-cement roofing; (b) a corrugated asbestos-cement roofing; (c) an asbestos chimney top.



- 1 = roof sheets and tiles; 2 = guttering and drain pipes; 3 = wall cladding;
 4 = soffit/fascia boards; 5 = panels beneath windows; 6 = roofing felt;
 7 = lagging on boiler and pipework; 8 = damaged lagging;
 9 = paper lining under non-asbestos pipe lagging; 10 = gasket in pipe and vessel joints;
 11 = rope seal on boiler access hatch; 12 = paper lining inside steel boiler casing;
 13 = boiler flue; 14 = spray coating to ceilings and walls;
 15 = loose asbestos in ceiling/floor cavities;
 16 = tiles, slats, canopies and firebreaks above ceilings;
 17 = textured coatings and paints; 18 = loose asbestos inside partition walls;
 19 = partition walls; 20 = panel beneath window; 21 = panel lining to lift shaft;
 22 = panelling to vertical and horizontal beams; 23 = panel behind electrical equipment;
 24 = panel on access hatch to service riser; 25 = panel lining service riser to floor;
 26 = heater cupboards; 27 = panel behind/under heater; 28 = panel on or inside fire door;
 29 = bath panel; 30 = floor tiles; 31 = lagging; 32 = gaskets; 33 = anti-vibration gaiter;
 34 = gaskets, rope seals and panels in domestic boilers;
 35 = insulating blocks, panels, paper in domestic heater;
 36 = string seals on radiators; 37 = fire blanket; 38 = water tank; 39 = brake/clutch lining.

7.4 ACMs in house building materials (modified from City Environmental Service, 2011).

maximum working temperature of rock wool is around 750°C. Glass wool is a furnace product of sand and glass slag rich in alkalis and boron and molten at 1000–1200°C. The maximum working temperature of glass wool is around 230°C.

Refractory (ceramic) fibres are synthetic blends of refractory oxides such as alumina and silica molten at 1600–2000°C with maximum working temperature in the range 1250–1600°C. They are resistant to chemicals and thermal shock, are light in weight, are sound absorbers, and provide a low thermal conductivity. The major difference between synthetic fibres and asbestos is the fibre morphology. Synthetic fibres invariably display an inflexible habit with a relatively large diameter (1–15 µm) and do not split longitudinally into fibrils but may break transversely into shorter segments. Rock and glass wool replace asbestos as friable insulating material. They can also be used together with an active binder to manufacture sheets and panels to insulate flat surfaces such as cavity walls, wall and ceiling panels, air conditioning ducts and panels, pipes and acoustic frames. They replace asbestos in fireproofing spray and fire door interiors, duplex filler and covering, flat-boards/tiles, acoustic panels and finishes, fireboards, panels on access hatches to service risers and lining service risers and floors, insulation of oil and coal furnaces, insulation and covering of ventilation and air conditioning systems, refrigerators/freezers, clothes dryers, insulation of electrical wires and panels, lagging (steam pipes, boilers, pipework, calorifiers), machine room ceilings, floors, ducts and walls, soundproofing or decorative spray coatings or roofing felt for ceilings, walls, horizontal or vertical beams and columns.

Highly refractory ceramic fibres are especially used for the manufacture of refractory furnace elements such as bricks. They are well used as loose fibres for thermal and/or acoustic insulation and fireproofing in felts, vacuum forming boards/panels/tiles, special papers, textiles, high-temperature adhesives, insulation of oil and coal furnaces, insulation and covering of ventilation and air conditioning systems, refrigerators/freezers, and lagging (International Program on Chemical Safety, 1988).

Asbestos-cement has been substituted by ecological fibre-cement (Bentur and Akers, 1989; Van Zijl and Wittmann, 2010) which contains organic polymers like cellulose $[(C_6H_{10}O_5)_n]$ or polyvinyl alcohol $[(C_2H_4O)_x]$ or recycled materials (Savastano *et al.*, 2005) in place of asbestos fibres.

7.5 The reclamation of asbestos

There are three major steps in the site analysis for the elimination of asbestos in buildings. The first step is the assessment of the presence and nature of asbestos in the building material. The second step is the evaluation of the degree of integrity of the ACM. The third step is the choice of the

best reclamation method suitable for that specific case. There are different reclamation techniques which will be discussed in this section.

In general, if the presence of asbestos fibres is suspected, the best way to make a decision about removal is to request a consultancy to a licensed asbestos inspector. The inspector usually identifies the ACMs in the home and determines their friability. Samples of these materials are collected to verify the presence of asbestos fibres. In addition, air samples are collected in order to reveal any environmental exposure to airborne asbestos fibres.

Based on the results of these analyses, the risk of fibre release from the materials is assessed (www.asbestos.com).

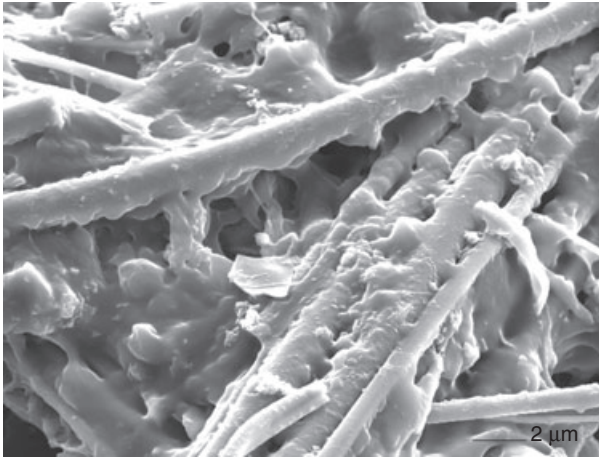
Different countries apply different quantitative indicators for the assessment of the exposure limits to asbestos fibres in *indoor* environments and set different threshold limits of fibre concentration that impose the reclamation of the ACM. There are two different approaches: a direct measurement for the *indoor* environment and an indirect evaluation for the *outdoor* environment. For the indoor environment, the threshold limits consider the concentration of fibres in air (generally ff/l = fibres per litre). For the outdoor environment, the assessment considers the degree of integrity of the ACM, namely, whether the ACM is prone to release asbestos fibres in the environment. In 1987, the World Health Organization (WHO) fixed limiting values of 1 ff/l and 0.5 ff/l if scanning electron microscopy (SEM) and optical microscopy, respectively, are used for the determination of fibre concentration (Cecchetti *et al.*, 2005). The Italian law (Italian D.M. 06/09/1994) compels the reclamation of the ACM in the indoor environment whenever the fibre concentration is >20 ff/l if measured with phase contrast optical microscopy (PCOM) or >2 ff/l if measured with SEM. In outdoor environments, reclamation of the ACM is mandatory if more than 10% of the total exposed area of the ACM has deteriorated (Italian D.M. 06/09/1994). There are attempts to establish a direct evaluation even for outdoor environments but the issue remains open (Gualtieri *et al.*, 2009b). One indication is provided by the State of California that established, in Proposition nr. 65, a concentration level of 100 ff/day (hypothetically 0.005 ff/l) as the risk threshold (Minoia *et al.*, 1997). The US Environmental Protection Agency has established that the probability of developing cancer (mesothelioma) is $1:10^6$ if the individual was to continuously breathe air with an average asbestos concentration of 0.004 ff/l for their entire life. This probability increases if the concentration increases (0.04 ff/l $\rightarrow$ $1:10^5$, 0.4 ff/l $\rightarrow$ $1:10^4$, etc.). In Italy, the threshold for ambient asbestos concentration in an environment where removal work is under way (work environment) is 50 ff/l for a day's exposure. A suggested concentration limit for outdoor living environments may be 0.1 ff/l determined by SEM or transmission electron microscopy (TEM) (Gualtieri *et al.*, 2009b).

Current opinion considers that ACMs in good conditions do not represent a priority risk and that the reclamation event causes much more fibre dispersion in the environment than the long-term fibre release during the entire life of the ACM itself. On the other hand, although ACMs in good conditions may not represent an immediate priority risk, as potential source of asbestos fibre dispersion they certainly persist as quiescent hazard. As a matter of fact, fibre dispersion may arise due to natural events (floods, earthquakes, thunderstorms) or human-induced catastrophic events (e.g. vandalism). A well-known example is the crime against humankind committed on 11 September 2001. More than 1000 t of asbestos are thought to have been released into the air during the destruction of the Twin Towers (Nolan *et al.*, 2005). Many thousands of people are now thought to be at risk of developing cancer due to this exposure. For these reasons, in many countries ACMs are being progressively removed from the environment regardless of their conditions.

ACMs (namely asbestos-cement roofing) reclamation techniques in outdoor environments can be classified as follows (Gualtieri, 2000):

1. *Ex situ*:
 - (a) Abatement, widely used even for large industrial sites (Cecchetti *et al.*, 2005).
2. *In situ*:
 - (a) Encapsulation, by applying specific products which enable the fixing and sealing of the asbestos fibres contained in the ACM (Fig. 7.5). The ACMs should not be extremely deteriorated. There are two sub-methods. The first is encapsulation *sensu lato*, which is realized by spray-coating with an acrylic-based substance, resulting in a thin layer covering the asbestos-cement material. The penetration depth of the polymer is usually a few microns. The second sub-method is encapsulation *sensu stricto* obtained by spray-coating with a two-component epoxy resin that penetrates hundreds of microns within the cement matrix and fixes the fibres. The two-component epoxy resin consists of an epoxy polymer component and a hardener. The solvent is composed of water and 1-methoxy-2-propanol (Gualtieri, 2000).
 - (b) Isolation by chemically inert low-weight rigid panels (generally aluminium layers) that cover and seal the exposed areas. This remediation method is indicated even for extremely deteriorated ACMs (D'Orsi, 2007).

Abatement is the most common reclamation technique as it has the advantage that the asbestos fibres are totally removed from the reclamation site after the operation (Fig. 7.6). It has some disadvantages such as the production of toxic refuse, risks of exposure for removal workers, and risk



7.5 The SEM micrograph shows asbestos fibres cemented within the epoxy matrix after the encapsulation of an asbestos-cement material using a permeating resin.



7.6 Workers removing asbestos-cement roofing.

of environmental pollution during and after the operation. These disadvantages are partly circumvented when *in situ* techniques are applied. However, asbestos is still present *in situ* and the status of the reclaimed site should be periodically monitored following an inspection and maintenance programme.

The methods for ACM reclamation in indoor environments are analogous to those applied in outdoor environments. They can be classified as follows (Gualtieri, 2000):

1. *Ex situ*:
 - (a) Abatement.
2. *In situ*:
 - (a) Encapsulation. This method is very common but not viable if the thickness of the sprayed friable asbestos composing the suspended ceiling is >2 cm because the encapsulating agent generally cannot penetrate so deep within the asbestos matrix and, under its own weight, may favour the detachment of the suspended ceiling off the ceiling substrate.
 - (b) Isolation by chemically inert low-weight rigid panels (generally aluminium layers or gypsum boards). It is possible to use plastic wrapping securely taped over pipe coverings, a new floor over the old one, new insulating materials to flatten and contain the old siding, and many other solutions.
 - (c) Making chemically inert by spraying a foam on the exposed area that selectively decomposes the asbestos fibres (Raloff, 1998).

Although the reclamation methods for outdoor and indoor environments are basically identical, there are major differences in the application of the methods. In both cases, during the recovery operations, workers are obliged to wear head-to-toe protection such as overalls and a high-efficiency particulate air (HEPA P3) respirator (see Fig. 7.7). In direct contrast to outdoor intervention, indoor building reclamation sites must be efficiently sealed. The static confinement is obtained by dividing the area into smaller lots separated by temporary rigid gypsum boards or panels. All the doors and windows should be sealed and protected using polyethylene wraps. All the openings and sockets, air-conditioning systems and others should be sealed.



7.7 Worker removing indoor friable asbestos.

Fissures and holes in the walls should be sealed off with silicone paste or expanding foams. Dynamic containment is also applied by negative air pressure units to keep the building recovery site in negative pressure with respect to the external areas so as to prevent the release of fibres outside the containment area (D'Orsi, 2007). The pressure difference between the containment area and the external areas should be around 0.3–0.9 psi. According to D'Orsi (2007), air extracted by the pumping system should be filtered using high-efficiency HEPA filters (99.97 DOP). Access to the abatement area is possible exclusively through the so-called decontamination units or *decon units*. These units must always be constructed and operational prior to the preparation of the building reclamation site. They shall be fully framed. Once the framework is in place, the inside of the unit is required to be wrapped with polyethylene sheeting.

A common worker decon unit consists of three successive rooms: a clean room, a shower room and an equipment room. Each room is separated by curtain doorways and airlocks on each side of the shower room. No asbestos contaminated items shall be found in the clean room. Workers use this area to remove clothes and personal belongings and to wear protective clothing and respirators. Workers move to the shower room on their way into the work area. On the way out of the contaminated work area, workers leave the equipment room and all contaminated clothes behind and enter the shower area with the respirator still on. The equipment room is a contaminated area where all of the equipment is stored after the reclamation operations. Here, the worker removes the disposable suit and places it in a properly labelled polyethylene disposal bag or lined container (Cecchetti *et al.*, 2005). A special decontamination unit is used to allow passage of the removed ACM to be disposed from the work area during the abatement activities.

The ACM decontamination unit consists of three rooms: a washing room where the sealed polyethylene bags with the removed ACM are washed; a packing room where the washed polyethylene bags with the removed ACM are packed into another polyethylene bag and finally sealed off with suitable adhesive paper; and a storage room where all the double-sacked bags are stored waiting to be moved out to the external disposal area (D'Orsi, 2007). Before it is pumped off to the drainage system, the water used for washing the bags in the first room is filtered through MgO-rich filters.

When ACMs are removed from the environment, hazardous wastes are produced. Their destiny is an important environmental issue. There are nowadays two possible ways to dispose of ACMs:

- In special landfills for toxic refuse
- Making inert via chemical–physical (i.e. thermal) transformation followed by industrial recycling of the transformation product as a secondary raw material.

The next section discusses the advantages and disadvantages of both these methods.

7.6 The disposal of asbestos-containing materials (ACMs) and recycling

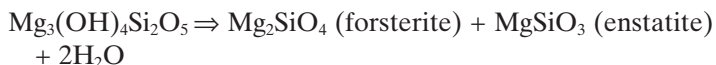
In the countries where asbestos is banned and reclamation policies are adopted, removed ACM is usually disposed of as hazardous waste in specially committed landfills. The use of inactive mines such as open pit mines and underground mines as disposal sites for ACM wastes is common all over the world, and especially in Europe (Austria, France, Germany, Italy, Slovenia, Sweden, Switzerland, United Kingdom, and others). In Germany, underground mines such as salt and iron mines have been used for the deposition of waste including ACM (Gidarakos *et al.*, 2008). Landfill cannot be regarded as the ultimate solution for the disposal of ACM, as a zero risk of fibre dispersion in air and water cannot be guaranteed. Fibre dispersion during disposal operations may occur because, although the sealed packages of ACM should be handled with great care, avoiding any possible breakage of the packages or contact with water, the opposite is frequently observed in the real case (see Fig. 7.8). Fibre dispersion in the leachate occurs in the



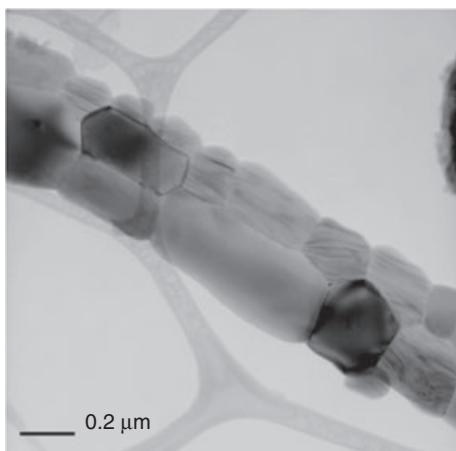
7.8 Cement-asbestos slates in a controlled landfill. During the disposal operations ACMs are often piled up in a messy way without care for package breakage or water contact necessary to prevent release of fibres in the air or water.

medium to long term. The polyethylene packages decompose with time and water solutions percolating through the asbestos-cement slates slowly dissolve the cement matrix and prompt the release of the fibres which concentrate in the leachate itself (Paglietti *et al.*, 2002). Hence, in the long term, the landfill should no longer be considered a closed system and hypothetically leachate should be collected and disposed of as hazardous waste forever.

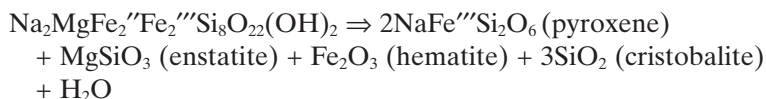
Preference for material recycling instead of landfill dumping has been included in the recent Directive 2008/98/EC of 19 November 2008 on waste and repealing certain Directives. An alternative solution to landfill disposal of ACM is the thermal transformation into supposedly non-hazardous products, and safe recycling of the transformation product as secondary raw material. This process relies upon the well-documented scientific evidence that the asbestos minerals are transformed into stable silicates at high temperature (Martin, 1977; MacKenzie and Meinhold, 1994; Cattaneo *et al.*, 2003; Gualtieri and Tartaglia, 2000; Gualtieri *et al.*, 2008a, 2008b). Chrysotile asbestos between 700 and 800°C undergoes dehydroxylation and subsequent recrystallization which leads to the later formation of forsterite and enstatite: at equilibrium



The result of the solid-state recrystallization of a chrysotile fibre is shown in the TEM image displayed in Fig. 7.9. Crocidolite asbestos at 1100°C shows a more complex reaction path which involves iron oxidation (Gualtieri *et al.*, 2004):



7.9 The result of the thermal transformation of a chrysotile fibre into newly formed forsterite and enstatite crystals observed by transmission electron microscopy (TEM).



The importance of transforming and recycling ACM is witnessed by the existence of a huge number of research (laboratory and pilot) projects and patents – see, for example, the CORDIAM project for the production of cordierite refractories by Abruzzese *et al.* (1998), the Asbestex process (Johannes, 2003), the A.R.I. process (Downey and Timmons, 2005), the KRY•AS process (Gualtieri *et al.*, 2008a), the GeoMelt process (Finucane *et al.*, 2008), and many others which employ for example mechanochemical treatments (Plescia *et al.*, 2003), microwaves (Leonelli *et al.*, 2006), or Joule heating vitrification (Dellisanti *et al.*, 2009). Among these, at the moment only the INERTAM process (Borderes, 2000) has been successfully converted into a fixed large-scale industrial plant that has been operating for more than 10 years in Morcenx (France).

The challenge concerning the transformed ACMs is to find suitable and attractive recycling solutions. Recently, it was demonstrated that the product of transformation of asbestos-cement can be successfully recycled in the production of traditional ceramics (Gualtieri *et al.*, 2008a), clay bricks, glasses, glass-ceramics, ceramic frits, ceramic pigments and plastic materials (Gualtieri *et al.*, 2010). The recycling of up to 20 wt% of thermally treated asbestos-cement for the production of concrete has also been successfully attained (Gualtieri and Boccaletti, 2011). Because it is mainly composed of calcium and silica, the use of this secondary raw material as a CO₂-free source of Ca in place of calcium carbonates, for example in the production of clinker or concrete, is welcomed in view of a reduction of the CO₂ emissions during the industrial manufacturing processes.

7.7 Conclusion and future trends

The next years of this millennium will hopefully witness the solution of the global issue of asbestos. Undisputed results from toxicological tests on pure and well-characterized natural fibres and epidemiological studies should finally assess whether or not the ban on chrysotile asbestos is supported by scientific evidence and whether it is recommended to continue or ban the use of ACMs in building materials. The extensive use of chrysotile asbestos prompted the discovery of new outstanding applications for catalysis, production of silica fibres and non-linear optics (Silva and Jesus, 2003; Wang *et al.*, 2006; Bardosova *et al.*, 2007). However, in the countries where asbestos is banned, new solutions and new materials to be used as asbestos substitute materials are proposed. An outstanding result is the

so-called nano-chrysotile synthesized by an Italian group (Falini *et al.*, 2004). The determination of the potential toxicity of fibres other than asbestos widely used as building materials is another challenging field of research. It is legitimate to ask whether asbestos-like minerals such as sepiolite (Bellmann *et al.*, 1997) are safe.

In a world that shares the policy of recycling, it seems unwise to simply dump ACMs in landfills. Innovative technological solutions now exist to convert and recycle ACMs as secondary raw materials and turn the problem into a new source for building materials such as concrete (Gualtieri and Boccaletti, 2011). It is an economic and social opportunity not to be missed. Recycling of ACMs in building materials has the potential to save primary raw materials and decrease the overall emissions of CO₂. New technologies for the transformation and recycling of ACMs have been recently elaborated, and the development of large-scale plants is expected in a few years.

7.8 Sources of further information and advice

Suggested general books on asbestos:

- H. Schreier (1989) *Asbestos in the Natural Environment*. Elsevier, New York, pp. 158.
- M.A. Benarde (1990) *Asbestos: the Hazardous Fiber*. CRC Press, Boca Raton, FL, pp. 490.
- G.D. Guthrie, Jr. and B.T. Mossman, eds (1993) Health effects of mineral dusts. *Reviews in Mineralogy and Geochemistry*, Vol. 28, Mineralogical Society of America, pp. 58.
- M.E. Beard and H.L. Rook, eds (1999) *Advances in Environmental Measurement Methods for Asbestos*. ASTM STP 1342, Philadelphia, PA, pp. 413.
- J. McCulloch and G. Tweedale (2008) *Defending the Indefensible: The global asbestos industry and its fight for survival*. Oxford University Press, Oxford, UK, pp. 325.

Interesting readings on biological activity of asbestos minerals:

- B.W.S. Robinson and A.P. Chahinian (2002) *Mesothelioma*. Martin Dunitz, London, pp. 380.
- V.L. Roggli, T.D. Oury and T.A. Sporn eds (2004) *Asbestos-associated Diseases*. 2nd edition, Springer-Verlag, New York, pp. 431.
- R.F. Dodson and S.P. Hammar (2005) *Asbestos: Risk Assessment, Epidemiology, and Health Effects*. Taylor & Francis, Boca Raton, FL, pp. 425.
- J.E. Craighead (2008) *Asbestos and Its Diseases*. Oxford University Press, Oxford, UK, pp. 403.

Asbestos in building materials:

US Department of Agriculture (2000) *Selecting and Renovating an Old House. A Complete Guide*. Dover Publications, New York, pp. 231.

T. Godish (1995) *Sick Buildings: Definition, Diagnosis, and Mitigation*. Lewis Publishers, Boca Raton, FL, pp. 398.

A number of selected websites are reported below. The information contained in the sites should be carefully considered and cross-checked with peer-reviewed existing scientific literature evidence and opinions because it is occasionally biased by personal views, unreliable sources and manipulations.

<http://www.allaboutasbestos.co.uk>

<http://www.asbestos.net>

<http://www.chrysotile.com>

<http://www.epa.gov>

<http://www.ibansecretariat.org>

7.9 References

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Abstract: The chapter deals with radioactivity of building materials. The main terminology used in radiology protection is introduced. Naturally occurring radioactive materials (NORM), such as radium ^{226}Ra , thorium ^{232}Th , potassium ^{40}K and radon ^{222}Rn , are discussed. Special attention is given to radon, which is considered as the main source of natural radiation to which the building occupants are exposed. The difference between radon exhalation and emanation is explained. The role of radon diffusion length influencing the radon flux from the surface of building products and air exchange rate in living spaces is emphasized. Main experimental methods of measurement of radionuclide composition and radon exhalation rate are reviewed. Building materials with both enhanced concentrations of natural radionuclides and enhanced radon exhalation, including the mechanisms resulting in elevated exposures of building occupants to gamma radiation and inhalation of radon, are discussed in detail. Finally, the existing national and international regulations concerning radioactivity of building materials in dwellings are reviewed. The chapter ends with a short discussion of the future challenges in the regulations.

Key words: building materials, radioactivity, natural radionuclides, radon, exhalation, emanation, diffusion, measurements, gamma-spectrometry, regulations.

8.1 Introduction

The present chapter deals with radioactive substances in building materials. Increased interest in measuring radionuclides in building products and their components is due to their health hazards and environmental pollution. Let us introduce first the terminology and definitions that may be helpful to readers who may not be familiar enough with radioactivity issues.

8.1.1 Radiation basics

Radioactivity is a process by which certain naturally occurring or artificial nuclides undergo spontaneous decay releasing a new energy. This decay process is accompanied by the emission of one or more types of radiation, ionizing or non-ionizing, and/or particles. This decay, or loss of energy, results in an atom of one type, called the parent nuclide, transforming to an atom of a different type, named the daughter nuclide. The SI derived unit

of radioactivity is the *becquerel* (symbol Bq), which is defined as the activity of a quantity of radioactive material in which one nucleus decays per second; in other words, Bq is equivalent to s^{-1} .

Ionizing radiation is electromagnetic (in the form of waves with a wavelength of 100 nm or less, i.e. a frequency of 3×10^{15} Hz or more) or corpuscular radiation that has sufficient energy to ionize certain atoms of the matter in its path by stripping electrons from them. This process can be direct (as with alpha particles) or indirect (gamma rays and neutrons).

Gamma radiation composed of high-energy photons, which are weakly ionizing but have high penetrating power (more than the X-ray photons used in radiodiagnosis), can travel through hundreds of meters of air. Thick concrete shielding or lead helps to protect personnel. Gamma radiation is primarily responsible for *external exposure*. As far as *internal radiation* exposure hazard is concerned, the high penetrating power means that the energy released by gamma rays and taken up by a small volume of tissue is comparatively small. Hence the harm to the organ is also smaller. Therefore, the internal radiation exposure hazard caused by gamma rays is not as severe as that induced by other types of radiation (alpha and beta).

Alpha radiation consists of ^4He nuclei and has low penetrating power. Its path in biological tissues is no longer than a few tens of micrometers. This radiation is strongly ionizing, i.e. it easily strips electrons from the atoms in the matter it travels through, because the particles shed all their energy over a short distance. Alpha emitters are primarily responsible for *internal exposure*, which includes inhalation, ingestion and skin contact.

Beta radiation is made up of electrons and has moderate penetrating power. Hence, exposure to beta particles presents greater external irradiation hazard and less internal radiation hazard than exposure to alpha particles. However, as the external irradiation brought by beta particles is mostly confined to the epidermis and outer skin tissue, such external irradiation hazard is not too severe.

Exposures are not limited to the intake of large amounts at one time (*acute exposure*). *Chronic exposure* may arise from an accumulation of small amounts of radioactive materials over a long period of time.

8.1.2 Radiation dosimetry

Radiation dosimetry deals with the calculation of the absorbed dose in matter and tissue resulting from the exposure to indirectly and directly ionizing radiation. The *absorbed dose* is the mean energy imparted by ionizing radiation to the matter per unit mass. To remind readers, dose is reported in grays (Gy) for the matter or sieverts (Sv) for biological tissue, where 1 Gy or 1 Sv is equal to 1 joule per kilogram. The distinction between absorbed dose (Gy) and dose equivalent (Sv) is based upon the biological

Table 8.1 Organ dose weighting factors W_T

Red bone marrow, lung, colon, stomach	Remainder tissues*	Gonads	Bladder, oesophagus, liver, thyroid	Bone surface, brain, salivary glands, skin	Whole body
0.12	0.12	0.08	0.04	0.01	1.0

*Remainder tissues include adrenals, extrathoracic region, gall bladder, heart, kidneys, lymphatic nodes, muscle, oral mucosa, pancreas, prostate (male), small intestine, spleen, thymus, uterus/cervix (female).

Source: IAEA (2011).

effects of the weighting factor (denoted w_r); tissue/organ weighting factors (W_T) have been established, which compare the relative biological effects of various types of radiation and the susceptibility of different organs.

X-rays and gamma rays have a weighting factor of unity, such that 1 Gy = 1 Sv (for whole-body irradiation). Values of w_r are as high as 20 for alpha particles and neutrons, i.e. for the same absorbed dose in Gy, alpha particles are 20 times as biologically potent as X- or gamma rays.

The weighting factor for the whole body is 1, such that 1 Gy of radiation delivered to the whole body (i.e. an evenly distributed 1 joule of energy deposited per kilogram of body) is equal to one sievert (for photons with a radiation weighting factor of 1). Therefore, the weighting factors for each organ must sum to 1 as the unit gray is defined per kilogram and is therefore a local effect. Organ dose weighting factors W_T recommended in IAEA (2011) are given in Table 8.1. For example, for the lungs a tissue-weighting factor of 0.12 is recommended.

The interaction of ionizing radiation with biological material results in ionizations and excitations of molecules and atoms, which may cause molecular changes in the DNA in the cell nucleus. Building inhabitants are exposed mainly to alpha and gamma radiation, which may result in chromosomal abnormalities and gene mutations, if the doses are high.

The induction of a radiation-induced cancer is assumed to be probabilistic in nature and proportional to the radiation dose, with no threshold. Such a model is known as the linear, non-threshold theory (LNT). According to LNT, doubling the exposure will double the number of cells struck, and so doubles the chances of developing a cancer, yielding a linear dose-response relationship. However, several studies reported a hormetic dip in the low dose range suggesting a beneficial, protecting effect at low exposures. On the basis of the current literature ICRP (2007) judged that the knowledge of these phenomena is insufficient to be incorporated in a meaningful way into the modeling of epidemiological data. Therefore, the LNT model is considered as the most appropriate in radiological protection at

present. The legislation in the field of radiological protection is based on a fundamental concept called ALARA (as low as reasonably achievable), which is a direct derivative of the LNT model.

To convert the absorbed dose rate in air due to exposure to gamma radiation into an effective dose, various coefficients are available, which depend on radiation geometry and gamma-ray energy. A conversion coefficient of 0.7 Sv Gy^{-1} can be adopted from ICRP publication 74 (ICRP, 1996). Cosmic radiation contributes to the absorbed dose rate indoors. At the same time, the building materials of the dwelling partly shield this component. Shielding factors range from 1 for wooden houses down to 0.3 for lower floors of concrete buildings (Miller and Beck, 1984). Julius and Van Dongen (1985) have determined an average value of 0.6 for the Netherlands.

8.1.3 Radiation sources

Radiation sources can be *natural* or *artificial* (man-made). People are now exposed to both types of radiation, and have been exposed to radiation from the natural environment throughout history. The predominant part of the natural radiation in the environment and in humans is caused by cosmic radiation and telluric radiation. In addition to the natural exposure, human activities involving the use of radiation and radioactive substances cause radiation exposure. Man-made activities include the fallout from atmospheric testing of nuclear weapons and radiological events like the Chernobyl accident. Deposition studies of these activities indicate that radioactive particles travel around the world on streams of air.

This chapter deals mainly with natural radioactivity from building materials, although a few cases related to the presence of artificial radionuclides in building materials have been described in the literature. Natural radiation, which accounts for 85% of total radioactivity (natural plus artificial), is made up of 14% cosmic radiation and 71% telluric radiation.

Cosmic radiation is caused by radionuclides, which are formed by the interaction of cosmic rays arriving from stars, and especially the Sun, with the nuclei of elements present in the atmosphere (oxygen and nitrogen). Cosmogenic radionuclides include carbon ^{14}C , tritium ^3H and beryllium ^7Be . Cosmic radiation increases with altitude above sea level, and is higher in high floors of buildings.

Telluric radiation is caused by so-called *primordial radionuclides* – naturally occurring radioactive materials, or briefly NORM. The primordial radionuclides are present in bedrock, soil, building materials, water, air, and the human body. Primordial radionuclides are left over from the creation of the earth. They typically have half-lives of hundreds of millions of years. The telluric radiation of primordial radionuclides is a key source of external gamma radiation, both inside and outside buildings.

Examples of primordial radionuclides are uranium (^{235}U and ^{238}U), thorium ^{232}Th , and potassium ^{40}K . The contents of the natural radioactive substances vary widely between different rocks and soil types, due to the different ways in which they were formed. The presence of these isotopes in building materials can cause the levels of radiation indoors to be even greater than those found outside. Whereas buildings made from wood do not have this problem, the downside is that wood acts as a poor shield from the gamma radiation coming from the soil.

8.2 Naturally occurring radioactive materials (NORM)

Most building materials of terrestrial origin contain small amounts of NORM. These radionuclides cause two types of radiation and radiation exposure: external and internal. The external radiation is caused by the gamma-emitting radionuclides, which in the uranium series mainly belong to the decay chain segment starting with radium ^{226}Ra . The internal radiation in the human body is caused by natural radionuclides in food, water and air. The internal (inhalation) radiation exposure is due to radon ^{222}Rn (which belongs to the ^{238}U decay chain), and marginally to its isotope thoron ^{220}Rn (which belongs to the ^{235}U decay chain), and their short-lived decay products, exhaled from building materials into the room air. Radon ^{222}Rn , a gaseous radioactive descendant of ^{238}U and ^{232}Th , emanates from the soil and building materials, and along with its short-lived alpha-emitting descendants constitutes a source of internal exposure through inhalation. Radon is the most abundant source of natural radiation (about 40% of total radioactivity).

As was mentioned before, most building materials contain naturally occurring radioactive elements, the most important of which are ^{40}K , and members of two natural radioactive series, which can be represented by the isotopes of uranium ^{238}U (or radium ^{226}Ra) and thorium ^{232}Th . These two main decay chains occurring in nature, commonly called the ^{238}U (or ^{226}Ra) and ^{232}Th series, terminate in two different, stable isotopes of lead (^{206}Pb and ^{208}Pb , respectively). The long-lived starting isotopes ^{238}U and ^{232}Th of these two decay series have existed since the creation of the earth.

8.2.1 Potassium-40

Potassium-40 (^{40}K) is a naturally occurring radioactive isotope of the common element potassium (potassium represents about 2.4% by weight of the earth's crust). Two stable (non-radioactive) isotopes of potassium exist, ^{39}K and ^{41}K . Potassium-39 comprises most (about 93%) of naturally occurring potassium, and potassium-41 accounts for basically all the rest. The half-life of ^{40}K is 1.27×10^9 years. Radioactive ^{40}K comprises a very

small fraction (about 0.012%) of naturally occurring potassium. Because potassium-40 represents 0.012% of naturally occurring potassium, its concentration in the Earth's crust is about 1.8 mg/kg, or 480 Bq/kg. The report of United Nations Scientific Committee on the Effects of Atomic Radiation gives the mean ^{40}K concentration of 400 Bq/kg in soil (UNSCEAR, 2000).

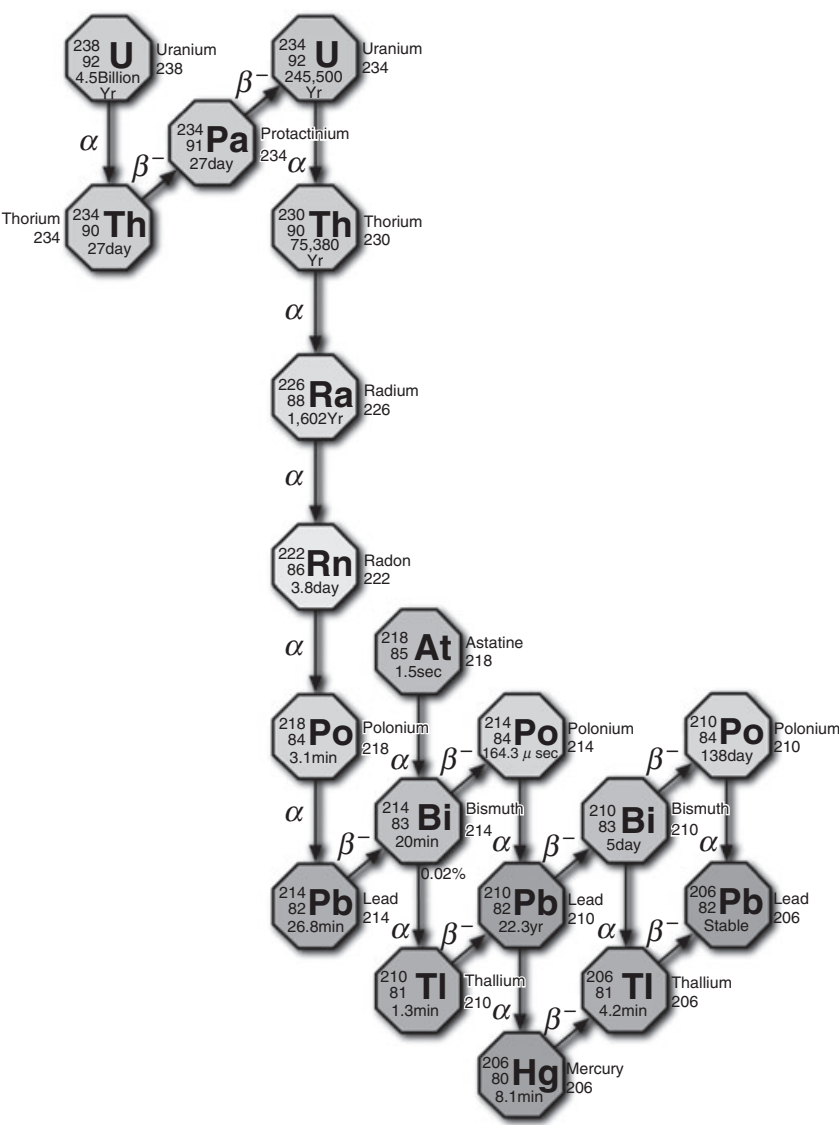
Potassium-40 is an important radionuclide in terms of the dose associated with naturally occurring radionuclides. The health hazard of ^{40}K is associated with cell damage caused by the ionizing radiation that results from radioactive decay, with the general potential for subsequent cancer induction.

8.2.2 Decay chain of radium-226 (uranium-238)

Uranium was isolated by Martin Heinrich Klaproth in 1789 from the mineral pitchblende. At that time uranium was not considered as particularly dangerous and was used for coloring pottery and glass. In 1896 Henri Becquerel observed that uranium was emitting invisible rays that fogged a photographic plate as if it was exposed to daylight (Emsley, 2003). In honor of his discovery of radioactivity, the unit for radioactivity is given the name becquerel (Bq), corresponding to one disintegration per second. Natural uranium mainly contains ^{238}U , which is the parent of a decay series schematically presented in Fig. 8.1. The ^{238}U series is often called the ^{226}Ra series. As shown in this figure, each member of this series is unstable and decays by either alpha or beta emission until stable ^{206}Pb has been formed. Besides ^{238}U natural uranium contains 0.73% ^{235}U . This isotope is also the parent of a decay series ending at ^{207}Pb . Uranium-238 is the most common isotope of uranium found in nature. Around 99.284% of natural uranium is uranium-238, which has a half-life of 4.468×10^9 years. Uranium is not as rare as it was once thought. It is now considered to be more plentiful than mercury, antimony, silver, or cadmium, and is about as abundant as molybdenum or arsenic (Hammond, 2000). It occurs in numerous minerals such as pitchblende, uraninite, carnotite, autunite, uranophane, davidite, and tobernite. It is also found in phosphate rock, lignite and monazite sands, and can be recovered commercially from these sources. Traces of uranium (as well as thorium ^{232}Th , which is described later) can be found in practically all the mineral raw materials used for production of concrete and other construction cementitious products.

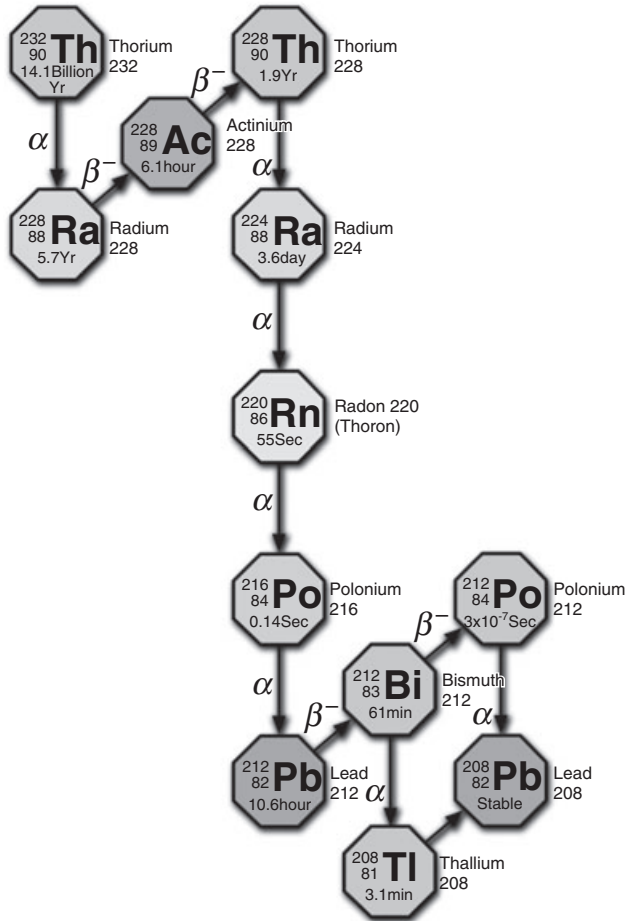
8.2.3 Decay chain of thorium-232

Thorium, ^{232}Th , occurs naturally and has a half-life of 14.1×10^9 years. Thorium occurs in thorite and thorianite (Hammond, 2000). Its trace amounts are also found in the majority of building materials of mineral



8.1 Uranium-238 (radium-226) series decay chain.

origin, including concrete. The decay chain of ^{232}Th is presented in Fig. 8.2. One of the isotopes of this chain is radon ^{220}Rn , called thoron. However, of the two main radon isotopes, ^{220}Rn and ^{222}Ra , which will be discussed in the next section, thoron has a shorter lifetime and accounts for a minority of radiation exposure.



8.2 Thorium-232 series decay chain.

8.2.4 Radon-222

Radon (^{222}Rn) is the most stable radon isotope, with a half-life of 3.8 days. It is created as part of the normal radioactive decay chain of uranium ^{238}U (radium ^{226}Ra) (see Fig. 8.1). Uranium, radium, and thus radon, will continue to occur for millions of years at about the same concentrations as they do now. Chemically, radon is a radioactive, colorless, odorless, tasteless noble gas, occurring naturally as the decay product of radium ^{226}Ra . It is one of the densest substances that remains a gas under normal conditions and is considered to be a health hazard due to its radioactivity.

Radon ^{222}Rn , like ^{220}Rn , decays to isotopes of solid elements, the atoms of which attach themselves to the dust particles present in air. When the radon equilibrium factor (the ratio between the activity of all short-period radon progenies, which are responsible for most of radon's biological effects, and the activity that would be at equilibrium with the radon parent) is 1, it means that the decay products have stayed close to the radon parent long enough for the equilibrium to be reached. These conditions are usually not met in most buildings. Because of their electrostatic charge, radon progenies adhere to surfaces or dust particles, whereas gaseous radon does not. Attachment removes them from the air, usually causing the equilibrium factor in the atmosphere to be less than 1. The typical value of the equilibrium fraction in dwellings is 0.4 (UNSCEAR, 2000). The equilibrium factor is also lowered by air circulation or air filtration devices, and is increased by airborne dust particles, including cigarette smoke. In high concentrations, airborne radon isotopes contribute significantly to human health risk.

Radon ^{222}Rn is responsible for the majority of the mean public exposure to ionizing radiation. It is often the single largest contributor to an individual's background radiation dose and is the most variable from place to place. Radon gas from natural sources can collect in buildings, especially in limited areas such as attics and foundations. It can also be found in some spring waters and hot springs. Epidemiological proof shows a connection between breathing high concentrations of radon and incidence of lung cancer. Therefore, radon is considered a significant contaminant that affects indoor air quality worldwide. Radon is the second most frequent cause of lung cancer after cigarette smoking, causing 21,000 lung cancer deaths per year in the United States (Agency for Toxic Substances and Disease Registry, 1990).

Radon emanates naturally from the ground and from mineral building materials, wherever traces of uranium or thorium can be found, and particularly in regions with soils containing granite or shale, which have a higher concentration of uranium. In fact, every square mile of surface soil, to a depth of 6 inches (every 2.6 km² to a depth of 15 cm), contains approximately 1 gram of ^{226}Ra , which releases radon in small amounts to the atmosphere (Agency for Toxic Substances and Disease Registry, 1990). Due to its very short half-life (3.8 days for ^{222}Rn), its concentration decreases very quickly when the distance from the production area increases. Its atmospheric concentration varies greatly depending on the season and conditions. For instance, it has been shown to accumulate in the air if there is a meteorological inversion and little wind (Steck *et al.*, 1999).

As a frame of reference, typical domestic exposures are about 10–20 Bq m⁻³ outdoors (Office of Radiation and Indoor Air, 2003) and about 100 Bq m⁻³ indoors (Agency for Toxic Substances and Disease Registry, 1990). Depending on how houses are built and ventilated, radon may accumulate

in foundations and dwellings. Radon concentrations in the same location may differ by a factor of 2 over a period of 1 hour. Also, the concentration in one room of a building may be significantly different from the concentration in an adjoining room.

Typical excess indoor radon concentrations due to building materials are low: about $10\text{--}20\text{ Bq m}^{-3}$, which is only 5–10% of the design value of 200 Bq m^{-3} introduced by the European Commission (RP-112, 1999; European Commission, 2010). However, in some cases the building materials may be an important source also, and occasionally the concentration may rise to 1000 Bq m^{-3} or more (European Commission, 2010). For example, in Sweden, the radon emanating from building materials is a major problem in some areas, where many dwellings with walls made of lightweight concrete based on alum shale – so-called ‘blue concrete’ – have been built (The Radiation Protection Authorities in Denmark, Finland, Iceland, Norway and Sweden, 2000). The problem of enhanced radon exhalation from building materials will be discussed in more detail in further sections.

Radon ^{222}Rn has been classified as being carcinogenic to humans (UNSCEAR, 2000). The primary route of exposure to radon and its progeny is inhalation. Radiation exposure from radon is indirect. The health hazard from radon does not come primarily from radon itself, but rather from the radioactive products formed in the decay of radon. The general effects of radon on the human body are caused by its radioactivity and consequent risk of radiation-induced cancer. Lung cancer is the only observed consequence of high-concentration radon exposures; both human and animal studies indicate that the lung and respiratory system are the primary targets of radon daughter-induced toxicity (Agency for Toxic Substances and Disease Registry, 1990).

The range of dose conversion factors for radon, derived from epidemiological studies and physical dosimetry, varies from 6 to $15\text{ nSv (Bq h m}^{-3})^{-1}$ (UNSCEAR, 2000; Chen, 2005). Assuming 7000 hours per year indoors (an occupancy factor of 80%), and an equilibrium factor of 0.4, and using the UNSCEAR (2000) recommendation for a radon conversion factor of $9\text{ nSv per (Bq h m}^{-3})$, exposure to radon at 100 Bq m^{-3} will be equivalent to an annual effective dose of $100\text{ Bq m}^{-3} \times 0.4 \times 7000\text{ h} \times 9\text{ nSv (Bq h m}^{-3})^{-1} = 2.5\text{ mSv}$.

Recently the ICRP (2009) published a statement that it indeed intends to publish dose coefficients that result in an increase of the effective dose per unit exposure.

8.3 Radon exhalation, emanation and diffusion length

Because radon is an inert gas, it can move rather freely through porous media such as building materials, although usually only a fraction of that

produced in the material reaches the surface and enters the indoor air. The radon emanation coefficient, ε , is defined as the fraction of the total amount of radon produced by radium decay that escapes from the solid phase and gets into the pores of the material. It is also called the emanating power, emanating fraction, release ratio, and escape-to-production ratio. The radon emanation coefficient is a dimensionless parameter and is represented as either a fraction or a percentage. The emanation coefficient ranges from 0 (no radon escapes) to 1 (all radon escapes). The rest of the produced radon (fraction $1 - \varepsilon$) remains trapped in the material.

It has to be mentioned that not only radon in the air phase decays but also the radon adsorbed to pore walls and dissolved in the water phase. Radon that is generated in water and adsorbed to pore walls is included in the definition of the emanation coefficient.

Sometimes there is confusion between the terms radon emanation and radon exhalation. Usually the radon emanation coefficient is determined from the measured radon exhalation rate of some sample with a certain mass and geometry. If we assume all emanated radon is exhaled during the radon-release measurement, i.e. radon decay in the sample due to adsorption and low diffusion rates is negligible, the emanation coefficient ε can be calculated either from the ^{226}Ra activity concentration of the material and the measured mass radon exhalation rate, E_m :

$$\varepsilon = \frac{E_m}{\lambda A_{\text{Ra}}} \quad [8.1]$$

or from the measured surface exhalation rate, E_s (assuming that radon exhales freely from the infinite wall with a constant thickness symmetrically towards both outdoors and indoors):

$$\varepsilon = \frac{2E_s}{\delta \rho \lambda A_{\text{Ra}}} \quad [8.2]$$

where: ε = radon emanation coefficient; E_m = free mass radon exhalation rate ($\text{Bq kg}^{-1} \text{ s}^{-1}$); E_s = free surface radon exhalation rate ($\text{Bq m}^{-2} \text{ s}^{-1}$); $A_{\text{Ra}} = ^{226}\text{Ra}$ activity concentration (Bq kg^{-1}); λ = radon decay constant (s^{-1}); δ = wall thickness (m); and ρ = material density (kg m^{-3}).

While the true radon emanation coefficient should be determined from the production rate of radon per unit of interstitial space, the radon emanation coefficient (factor), which is often determined in practice by the measurement of the exhalation rate, would be more accurately called the radon release factor (de Jong, 2010). To explain the difference between radon emanation and radon release factors, we introduce an additional term: radon diffusion length.

The diffusion process of radon through porous building materials, like concrete, mortar, plaster, gypsum, coatings, etc., is described by the diffusion

coefficient D . The radon diffusion length L can be calculated from the diffusion coefficient D as $L = (D/\lambda)^{1/2}$. The diffusion length is defined as the characteristic distance traveled by the radon atoms during one half-life. Another popular definition of radon diffusion length is the distance through which the radon concentration decreases to 37% (because $e^{-1} = 0.37$) of its initial value.

In contrast to the diffusion coefficient D , which is independent of the thickness of the element, the flux through a sample decreases with the thickness. To get a thickness-independent parameter which describes the permeability (or impermeability, i.e. tightness) of building products to radon gas, Keller *et al.* (1999) suggested using the quotient of the sample thickness and the diffusion length. According to this approach, if the thickness of the sample is three times the diffusion length, less than 5% (because $e^{-3} = 0.05$) of the initial radon only passes the material, which in this case can be called radon-tight. Table 8.2 shows the experimental mean values of the diffusion coefficient and the diffusion length in popular building materials obtained by Keller *et al.* (1999).

Concrete, especially with polymer admixture, can hinder the diffusion. Radon mitigation recommendations often require casting concrete slab of 150 mm combined with polyethylene, bituminous or other membranes as a passive protection preventing entry of radon from the soil into the building basement. The polymers usually fill most of the pores in the material and close the diffusion path.

As reported by Kovler *et al.* (2004a), the radon diffusion length varies from about 0.06 m for dense concretes to 0.30 m for lightweight building materials. The relation between F_{Rn}/ε and radon diffusion length is derived by de Jong *et al.* (2011) and shown in Fig. 8.3. Thus, for the majority of building materials the radon release factor F_{Rn} underestimates the true radon emanation coefficient ε by ~10% at most. As a result, the radon release factor is often used in engineering estimations, instead of the true radon emanation coefficient.

Let us discuss now indoor radon concentrations, which are formed in indoor air of dwellings as a result of exhalation from building materials as a function of air exchange rate in the living space. If the building materials are the only sources of radon in indoor air, their airborne activity concentrations can be solved from the following equation (RP-96, 1997):

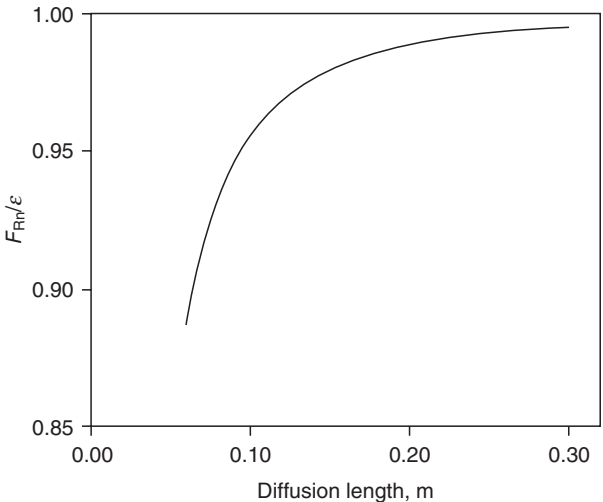
$$\frac{dC}{dt} = E \frac{S}{V} + C_0 \lambda_v - C(\lambda + \lambda_v) \quad [8.3]$$

where C_0 is the outdoor radon concentration (Bq m^{-3}), t is time, E is the radon exhalation rate from building materials ($\text{Bq m}^{-2} \text{ h}^{-1}$), v is the ventilation (air exchange) rate, when the incoming air is from outdoors (h^{-1}), λ_v is the decay constant of radon (0.00755 h^{-1}), and S/V is the ratio of the area

Table 8.2 Experimental mean values of radon diffusion coefficient and radon diffusion length in popular building products and sealants

Material	Thickness (mm)	Diffusion length (mm)	Remarks
Gypsum	100	1100	Permeable
Pumice	150	850	Permeable
Limestone	150	400	Permeable
Brick	150	400	Permeable
Sandstone	100	1000	Permeable
Aerated concrete	100	800	Permeable
Heavy concrete	100	60	Permeable
Polymer concrete	40	7	Tight
Granite	30	160	Permeable
Glass foam plate	70	<0.7	Tight
Asphalt-asbestos	3	<0.7	Tight
Bitumen	3	<0.7	Tight
High-density polyethylene	1	<0.7	Tight
Silicone rubber	3	<0.7	Tight
Lead foil	0.1	<0.7	Tight
Butyl rubber	1.5	2	Permeable
Polyurethane coating	5	<0.7	Tight
Plastic foil	3	<0.7	Tight
Epoxy resin	3	<0.7	Tight

Source: Keller *et al.* (1999).



8.3 Radon release factor to radon emanation factor ratio vs radon diffusion length.

exhaling radon to the dwelling volume. Assuming that the ventilation rate in normal dwellings is usually more than 0.1 h^{-1} , the indoor radon concentration can be expressed as:

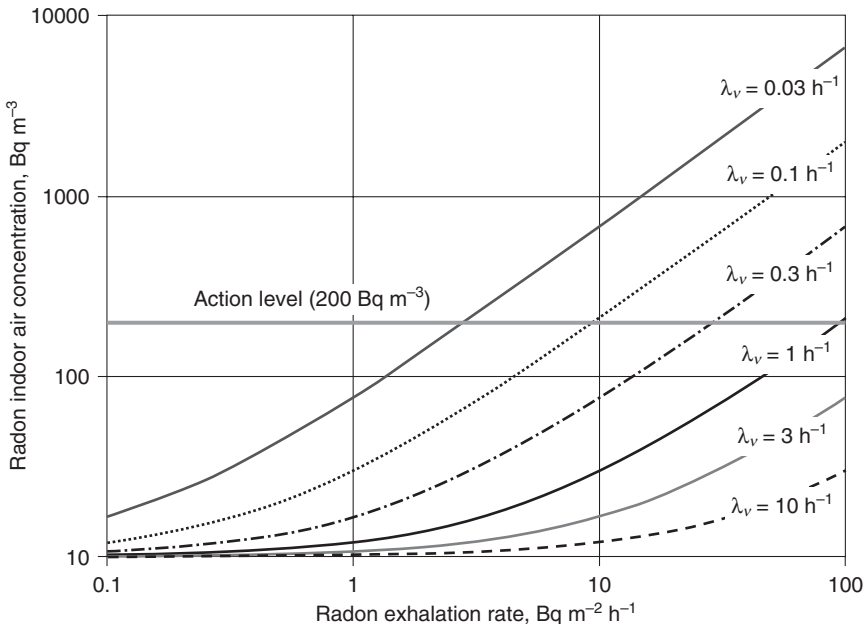
$$C(t) = \left(\frac{E}{\lambda_v} \frac{S}{V} + C_0 \right) (1 - e^{-\lambda_v t}) \quad [8.4]$$

or, in the steady state as:

$$C(t) = \frac{E}{\lambda_v} \frac{S}{V} + C_0 \quad [8.5]$$

Figure 8.4 shows the dependence of radon concentration on radon exhalation rate for different ventilation rates, assuming that the dwelling has surface radon-exhaling area to volume ratio of 2 m^{-1} and the outdoor radon concentration is 10 Bq m^{-3} . As will be shown later, the radon exhalation rate usually does not exceed $10 \text{ Bq m}^{-2} \text{ h}^{-1}$ for the majority of building materials.

The European Commission (2010) proposes that Member States shall establish national reference levels not exceeding (as an annual average):



8.4 Steady-state radon indoor air concentrations vs radon exhalation rate of building material in dwelling with surface radon-exhaling area to volume ratio of 2 m^{-1} and outdoor radon concentration of 10 Bq m^{-3} , for different ventilation rates, from 0.03 to 10 h^{-1} .

- 200 Bq m⁻³ for new buildings
- 400 Bq m⁻³ for existing dwellings and buildings with a high occupancy of the public (such as nursing homes, schools and prisons)
- 1000 Bq m⁻³ for existing workplaces and other public buildings.

Taking into account that the ventilation rate in dwellings is usually no worse than 0.1 h⁻¹, we can see that building materials are hardly the reason for high radon concentrations in dwellings to exceed the minimum action level of 200 Bq m⁻³ accepted in most European (and other) countries.

8.4 Measurements of radionuclide composition

8.4.1 Gamma-ray spectrometry

Spectrometric measurements indicate that the three components of the external radiation field, particularly from the gamma-emitting radionuclides in the ²³⁸U and ²³²Th series and ⁴⁰K, make approximately equal contributions to the outwardly occurring gamma radiation dose to individuals in typical conditions both outdoors and indoors. Each material may have a unique radiation spectrum, which can serve as its 'fingerprint' in quality control operations.

Gamma-ray spectrometers are typical instruments used in a wide variety of scientific and industrial applications. In order to measure the radioactivity concentration and estimate the radiation hazards from building materials, gamma-spectroscopy is usually applied using different detectors. Two main types of gamma-spectrometers are presently in use, high-pure germanium (HPGe) crystal spectrometers and scintillation NaI(Tl) spectrometers. Their pros and cons will be discussed below.

The main advantages of gamma-ray spectrometry are:

- Sensitivity of the method
- Non-destructive mode of operation
- Short test duration
- Simplicity.

These advantages, allow using gamma-spectrometry not only for controlling the radioactivity of building products available on the local market, but also for controlling the radionuclide and phase composition of various building materials, such as hardened concrete.

At the same time, the method has the following limitations and difficulties:

- The need to measure raw materials, which is not always possible
- The need to use special spectrometric systems based on HPGe detectors, which are costly and require cooling to liquid nitrogen temperatures.

If the first limitation is an intrinsic property of the method, in our opinion the second problem can be technically solved.

A literature review shows that gamma-spectrometry could be effectively applied for controlling concrete composition; however, a number of limitations exist. In the publications of Kovler and Manasherov (1999), Rowbottom *et al.* (1997) and Pakou and Assimakopolous (1994) the application of gamma-spectrometry for determination of concrete mix composition in hardened specimens is described; however, there was no precedent to test fresh concrete mixes. One of the problems in measuring specimens immediately after placing them in the container is a possible disequilibrium in the decay chains of ^{226}Ra . Hence, testing fresh concrete mixes is usually impossible; the limitation to the test is related to the need to seal the probe and wait until equilibrium occurs between radium, radon and radon progeny. Usually the standards require sealing the probe and waiting three weeks before the measurement, which is about five times longer than the half-life of ^{222}Rn . It should be noted that both of the long decay chains described previously (of radium and thorium) pass through a step involving isotopes of radon, which is a noble gas. If radon escapes from a sample to any appreciable extent, radioactive equilibrium is disturbed. This alters the ratio of the number of gamma rays emitted from radionuclides located before and after radon ^{222}Rn . The extent of radon escape and its effect on the gamma-ray spectrum can be gaged by comparison with a sealed source, in which radioactive equilibrium is maintained.

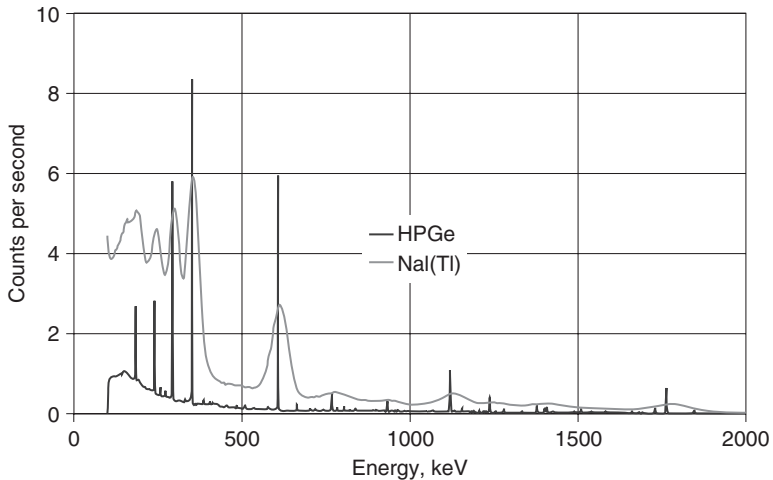
Another source of uncertainty in gamma-ray spectrometry is a possible diffusion of radon gas through the walls of the container, made of plastic material. It is known that plastics are generally permeable to gases, including radon.

8.4.2 High-pure germanium (HPGe) vs scintillation NaI(Tl) spectrometers

The activity concentrations of natural radionuclides ^{226}Ra , ^{232}Th and ^{40}K can be determined by γ -ray spectrometry. Practice shows that NaI(Tl)-based detectors could be successfully used for quantitative determination of activity concentrations of compounds of few and known radionuclide composition, such as those containing natural radionuclides.

Most common detectors include sodium iodide doped with thallium, or NaI(Tl), scintillation counters and high-purity germanium (HPGe) detectors. HPGe detectors show the best energy resolution, while NaI(Tl) detectors have the highest efficiency and the lowest minimum detectable activity (Perez-Andujar and Pibida, 2004).

NaI(Tl) detectors yield good efficiency but have poor resolution. For this reason they are often considered as not suitable for the identification of



8.5 Comparison of spectra from the same calibrated source of ^{226}Ra obtained by means of HPGe and NaI(Tl) detectors.

complicated mixtures of γ -ray-producing materials and quantitative determination of their radionuclide composition. Figure 8.5 shows spectra from the same calibrated source of ^{226}Ra obtained by means of HPGe and NaI(Tl) detectors. It can be seen that the HPGe spectrum demonstrates clear and sharp peaks characteristic of ^{226}Ra (located at energies of 295, 392 and 609 keV), while the peaks obtained by the NaI(Tl) detector are wide. This makes the identification of radionuclides and the quantitative determination of activity concentration of radionuclides by means of scintillation detectors rather difficult, especially in cases when the peaks are close and overlap. Finally, when radionuclide composition of the tested material is complex and unknown, scintillation spectrometers become practically useless for quantitative determination of activity concentrations.

The energy resolution of a scintillation spectrometer is significantly worse than that predicted by photon-statistics alone. The additional degrading effects are a consequence of several factors. A first effect is the variance in the scintillation efficiency of the crystal itself, which is energy dependent and cannot be corrected for in a simple way. A second effect is the non-uniformity of the response of the photo-cathode. A third effect is the variance in the light-collection efficiency of the crystal and photo-multiplier assembly for events that occur in different locations within the detector crystal.

One of the methods to compensate for the lower spectral resolution of NaI(Tl) detectors is to apply spectral deconvolution to the raw energy-loss data collected by the spectrometer. Deconvolution is a technique used in

spectroscopy and other diverse fields, in which a raw data spectrum obtained with a detection system is deconvolved with a response function representing the response of the detection system to known input signals (Meng and Ramsden, 2000).

HPGe detectors provide significantly improved energy resolution in comparison to NaI(Tl) detectors; however, cryogenic temperatures are vital to their operation, which makes the maintenance of the spectrometric system more complicated and more costly. One of the disadvantages of the HPGe detector is that it can only function as a spectrometer if cooled to liquid-nitrogen temperatures, otherwise electrons can be thermally excited into the conduction band and so generate a high level of noise. This means that an HPGe detector is neither compact nor rugged. The second disadvantage is that in order to provide a stopping power equivalent to a commonly available size of scintillation spectrometer, the germanium crystal becomes very expensive to fabricate (Perez-Andujar and Pibida, 2004).

At the same time, the practice shows that NaI(Tl)-based detectors can be successfully used for quantitative determination of activity concentrations of mixtures of few and known radionuclide composition, such as those containing natural radionuclides (NORM) only. In many applications, such as the mass control of radioactive contaminants in building materials, it is not practical to use a high-purity germanium spectrometer cooled to liquid-nitrogen temperatures. The improved efficiency, for the same size detector, and the lower cost of a NaI(Tl) detector must be traded off against the better resolution of an HPGe detector. However, for performing a quantitative analysis, the NaI(Tl)-based system should have special software capable of distinguishing between different radionuclides in the mixture and accurately determining their activity concentrations (Kovler *et al.*, 2010).

8.5 Measurement of radon exhalation

The radon exhalation rate of building materials can be measured by one of the following groups of methods (the description of experimental methods in this section is based on the classification suggested by Petropoulos *et al.*, 2001):

- Closed-chamber methods (CCM), which, in their turn, can be divided into two categories:
 - Enclosed sample method (ESM)
 - Accumulator method (AM)
- Open-chamber methods (OCM).

According to Stranden (1988), closed-chamber methods (CCM) are the most common way to assess the exhalation rate of a building material: the

sample is enclosed in an airtight container and the radon concentration growth in the air volume is followed. CCM are based on the assumption that the radon exhalation rate does not depend on time.

It should be taken into account that the concentration is not a characteristic of the material, because it increases with time until achieving a constant value C_∞ corresponding to the saturation condition. Maximum radon concentration in a hermetically closed space under saturation at infinite time, C_∞ (Bq m^{-3}), is related to radon concentration $C(t)$ at a given time t (s) as follows:

$$C(t) = C_0 e^{-\lambda t} + C_\infty (1 - e^{-\lambda t}) \quad [8.6]$$

where C_0 is the initial radon concentration (Bq m^{-3}) in the container at time $t = 0$, i.e. the background. After measuring the radon concentration at a given time $C(t)$ and calculating C_∞ , the radon exhalation rate E (if the background is small) can be determined by the formula:

$$E_M = C_\infty \lambda V/M \text{ or } E_S = C_\infty \lambda V/S \quad [8.7]$$

where

M and S = mass (kg) and surface area (m^2) of the source (building material), respectively;

V = volume occupied by air (volume of the chamber minus volume of the specimen, m^3);

λ = radon decay constant ($2.1 \times 10^{-6} \text{ s}^{-1}$);

E_M and E_S = radon exhalation rates of the building material, per unit mass ($\text{Bq kg}^{-1} \text{ s}^{-1}$) or per unit surface area ($\text{Bq m}^{-2} \text{ s}^{-1}$), respectively.

It is well understood that Eq. 8.6 is valid if:

- (a) there is no leakage of radon out of the container; and
- (b) the activity concentration in the container air is low compared to the activity concentration in the pore air of the sample.

Leakage and back diffusion effects may be taken into account if the effective decay constant λ_{eff} is further introduced, replacing the theoretical value of radon decay constant λ in Eq. 8.6.

The accumulator method (AM) is another common technique for measuring the radon exhalation rate from slab/wall/floor/ceiling specimens. AM is based on sealing a container called an accumulator to a part of the exhaling area and measuring the radon concentration growth inside the container. A disadvantage is that it is not always easy to make airtight the joining of the accumulator to building material. The same growth equations apply but in this method back-diffusion and leakage effects are even more pronounced.

The common disadvantage of the AM in particular, and the CCM in general, is that, as the ^{222}Rn concentration in the accumulator (can) increases, the exhalation rate decreases due to a lower concentration gradient between pore and ambient air. In practice, the ambient air will be practically free from ^{222}Rn , resulting in a 'free exhalation rate'. According to Jonassen (1983), the difference between the free exhalation rate and the rate determined using AM could be as large as about 15%.

Measurements by open-chamber methods (OCM) are performed in continuously well-ventilated containers or accumulators under near-zero concentration conditions (de Jong, 2010). The container or accumulator gas is continuously removed using a constant flow pump, providing a known gas-exchange rate. The steady-state radon concentration in the container gas is given by the following equation:

$$C(t) = C_0 + \frac{E}{V\lambda_v} \quad [8.8]$$

where λ_v is the air-exchange rate and C_0 is the radon concentration of the gas being used to flush the container, i.e. the background (Bq m^{-3}).

The advantages of this method are that it determines the free exhalation rate, and that the influence of external factors, such as vapor pressure, on the exhalation rate can be easily studied. At the same time, measurements in well-ventilated containers require high sensitivity of radon detectors, especially when radon exhalation rates are low.

8.6 Building materials as gamma emitters

All building materials contain various amounts of natural radionuclides, and some of them may also contain artificial nuclides, although seldom insignificant amounts. Knowledge of the concentration of natural radionuclides in building materials is important in the assessment of population exposures, as most individuals spend 80% of their time indoors and natural radioactivity in building materials is a source of indoor radiation exposure (Krisyuk, 1989; Zikovsky and Kennedy, 1992; Othman and Mahrouka, 1994). Indoor elevated external dose rates may arise from high activities of radionuclides in building materials.

The most important natural radionuclides are ^{40}K and members of two natural radioactive series, which can be represented by the isotopes ^{226}Ra and ^{232}Th . The presence of these radioisotopes in the building materials causes external exposure to the people that live in the house. ^{226}Ra and ^{232}Th can also enhance the concentration of radon isotopes ^{222}Rn and ^{220}Rn and of their daughters in the house. ^{40}K and part of the radionuclides mentioned before cause external exposure, while the inhalation of ^{222}Rn and ^{220}Rn and

their short-lived progeny leads to internal exposure of the respiratory tract to alpha particles (Keller *et al.*, 1987; Savidou *et al.*, 1996).

Artificial radionuclides, of which the most important is ^{137}Cs , originate from past nuclear explosions in the atmosphere and accidental releases at nuclear power plants, such as those of 1986 (Chernobyl in the former USSR) and 2011 (Fukushima, Japan).

Chronic exposure of human beings to low doses of ionizing radiation can cause health damage which may appear 5–30 years after the exposure (ICRP, 1991). The most critical damage which can result from such exposure is an increase in the probability of contracting malignant diseases by the person who was exposed and by his offspring. The risk increases with the dose, and the probability of the appearance of the damage is greater when the exposure starts at a younger age.

Radionuclide composition of building materials influences directly the indoor exposure of building occupants to gamma radiation. Usually indoor exposure to gamma radiation is greater than outdoor exposure, if building materials of mineral origin have been used. Buildings constructed of timber add little to indoor exposures.

Indoor exposures (absorbed dose rate in air from terrestrial gamma radiation) are, in general, 40% greater than outdoor exposures. The lowest values are typical for New Zealand, Iceland and the United States, all below 40 nGy h^{-1} , which reflects the preponderance of wood-framed houses. The highest values ($95\text{--}115 \text{ nGy h}^{-1}$) are in Hungary, Malaysia, China, Albania, Portugal, Australia, Italy, Spain, Sweden, and Iran, which reflects wide use of stony building materials. At the same time, in Thailand, the United States and Iceland, where wood-frame construction is common, indoor is similar to that outdoors. High values of the ratio, more than 2, result from high levels indoors (in Sweden and Hong Kong) relative to outdoors or from low values outdoors (in the Netherlands) relative to indoors (UNSCEAR, 2000).

The specific radioactivity of building materials depends on their mineral source and composition. The radioactivity of building stones depends on the rock used as a raw material for their manufacture. Natural stone finds its way into homes as part of the bricks, cement, sheet rock, floor and wall tiles, as well as counter tops. The rock can be of three types – igneous, sedimentary and metamorphic. The highest activities of natural radionuclides are characteristic of igneous rocks (such as tuff, pumice, pegmatite, and carbonatite) or metamorphic rocks (such as granite and acidic gneiss). The lowest activity concentrations are observed usually for sedimentary rocks, such as limestone, dolomite, sandstone, quartz, natural gypsum, anhydrite, unconsolidated layers of clay, silt and sand, and shale (but not black shales such as alum shale, a uranium-rich Cambrian black shale which occurs in Sweden, Norway and the Danish island of Bornholm) (The Radiation

Table 8.3 Typical activity concentrations in common rocks in Nordic countries, by G. Åkerblom

Type of rock	Typical activity concentrations (Bq kg ⁻¹)		
	²²⁶ Ra	²³² Th	⁴⁰ K
Granite, normal	20–130	20–80	620–2400
Granite, uranium- and thorium-rich	100–500	40–350	1200–1900
Carbonatites	10–650	40–10,000	100–1000
Diorite, gabbro and basic volcanic rocks	1–30	2–40	50–1000
Sandstone and quartz	5–60	5–40	60–1500
Limestone and dolomite	2–30	0.5–10	<30–150
Shale	10–150	10–60	600–1900
Alum shale	100–4300	10–40	1100–1900

Source: The Radiation Protection Authorities in Denmark, Finland, Iceland, Norway and Sweden (2000).

Protection Authorities in Denmark, Finland, Iceland, Norway and Sweden, 2000).

In Sweden, the gamma radiation (mainly due to high content of ²²⁶Ra) from lightweight concrete based on alum shale is a major problem. There are about 300,000 dwellings with walls made of this kind of material.

Table 8.3 illustrates typical activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K in rocks used for producing concrete aggregates in the Nordic countries, reported by G. Åkerblom (The Radiation Protection Authorities in Denmark, Finland, Iceland, Norway and Sweden, 2000).

Building materials made of timber or metals have very low concentrations of both natural and artificial radioactive substances. For example, Finnish timber contains on average 0.4, 0.7 and 10 Bq kg⁻¹ of ²²⁶Ra, ²³²Th and ⁴⁰K, respectively (Mustonen, 1984). In composite mineral materials, like concrete, the concentrations depend on the specific radioactivity of the constituents and their contents.

The worldwide average concentrations of radium, thorium and potassium in the earth's crust are about 40 Bq kg⁻¹, 40 Bq kg⁻¹ and 400 Bq kg⁻¹, respectively (RP-112, 1999), with radium equivalent activity of about 130 Bq kg⁻¹. The median values of the activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K in the earth's crust are 35, 30 and 400 Bq kg⁻¹, respectively (UNSCEAR, 2000).

As can be seen from Table 8.4, which is based on the information reported in the EC documents RP-96 (1997) and RP-112 (1999), radioactivity concentrations in most of the common building materials are similar to or higher than the worldwide average concentrations (except sand-lime bricks and natural gypsum). This table presents also typical radium equivalent

Table 8.4 Typical, minimum and maximum activity concentrations (Bq kg⁻¹) in common building materials and industrial by-products used for building materials in Europe

Building material	Typical activity concentration		Radium equivalent activity	Minimum activity concentration			Maximum activity concentration		
	²²⁶ Ra	²³² Th	⁴⁰ K	²²⁶ Ra	²³² Th	⁴⁰ K	²²⁶ Ra	²³² Th	⁴⁰ K
<i>Most common building materials (may include by-products)</i>									
Concrete	40	30	400	1	1	1600	240	190	1600
Aerated and lightweight concrete	60	40	430	9	6	230	2600	190	1600
Clay (red) bricks	50	50	670	10	12	100	200	200	2000
Sand-lime bricks	10	10	330	6	4	160	25	30	700
Natural building stones	60	60	640	0.6	<1	<4	500	310	4000
Natural gypsum	10	10	80	2	1	7	70	100	200
<i>Most common industrial by-products used in building materials</i>									
Phosphogypsum	390	20	60	3	0.4	<4	1100	160	300
Blast furnace slag	270	70	240	8	1	20	2100	340	1000
Coal fly ash	180	100	650	26	14	170	1100	300	1500

Sources: RP-96 (1997); RP-112 (1999).

activity, which is a convenient common index for comparing specific radioactivity of materials containing different radionuclides in different concentrations (Hamilton, 1971):

$$A_{\text{Ra,eq}} = A_{\text{Ra}} + 1.43A_{\text{Th}} + 0.077A_{\text{K}} \quad [8.9]$$

where A_{Ra} , A_{Th} and A_{K} are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K , respectively (in Bq/kg).

Special attention should be given to industrial by-products with enhanced activity concentrations, which can be used for construction purposes. In general, materials used in construction that may be of radiological significance include marl, blast furnace slag, fly ash, alum concrete, phosphogypsum, Portland cement clinker, by-product anhydrite, clay, and radium- and thorium-rich granites (used as aggregates in concrete or in dimension stone products). Typical examples of such building materials are discussed below.

8.7 Building materials with enhanced concentrations of natural radionuclides

This section deals with types of building materials which can contain enhanced concentrations of natural radionuclides.

Types of building materials considered for control measures with regard to their emitted gamma radiation (European Commission, 2010) include:

1. Natural materials:
 - Alum-shale
 - Building materials or additives from natural igneous origin, such as:
 - Granite
 - Gneiss
 - Porphyries
 - Syenite
 - Basalt
 - Tuff
 - Pozzolana
 - Lava.
2. Materials incorporating residues from industries processing naturally occurring radioactive materials, such as:
 - Phosphogypsum
 - Fly ash
 - Phosphorus slag
 - Tin slag
 - Copper slag
 - Red mud (residue from aluminum production)
 - Residues from steel production.

8.7.1 Granite

Granite is a common, coarse-grained, hard igneous rock consisting chiefly of quartz, orthoclase or microcline, and mica. Granite has been used as a building material since ancient times. It is one of the oldest and most durable building products available, and will far outlast the building in which it is installed. It has become the material of choice for today’s luxury homes and offices because of its enduring beauty, and because no synthetic material can yet compare to its elegance and performance. Granite is a popular choice for kitchen and bathroom counter tops. Granite tiles of 20 to 50 mm thickness are widely used as covering and building materials for counters, cashier desks, shelves, benches and tables. These surfaces are often referred to as granite, but in fact they can consist of different stone types that include granite and marble.

The concern of using granite products available in the market is the external radiation dose from them. Activity concentrations of the natural radionuclides (Bq kg⁻¹) of a large number of granite samples from different countries measured by Chen and Lin (1996) and by Pavlidou *et al.* (2006) are shown in Table 8.5.

8.7.2 Phosphogypsum

Phosphogypsum is a waste by-product from the processing of phosphate rock in plants producing phosphoric acid and phosphate fertilizers, such as superphosphate. The wet chemical phosphoric acid treatment process, or ‘wet process’, in which phosphate ore is digested with sulfuric acid, is widely used to produce phosphoric acid and calcium sulfate, mainly in dihydrate form (CaSO₄·2H₂O):

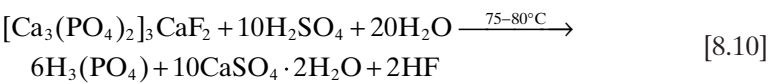


Table 8.5 Activity concentrations of the natural radionuclides (Bq kg⁻¹) of granite

Reference	Nuclide	²²⁶ Ra	²³² Th	⁴⁰ K
Chen and Lin, 1996	Mean	42	73	1055
	Standard deviation	35	51	357
	Range	0.2–160	<MDA–253*	<MDA–2355
Pavlidou <i>et al.</i> , 2006	Mean	64	81	1104
	Standard deviation	53	79	407
	Range	2–170	<MDA–354	49–1592

* Minimum detectable activity.

Annual world production of phosphogypsum is estimated to be ~300 Mt (Yang *et al.*, 2009). This by-product is contaminated by various impurities, both chemical and radioactive, and is usually stockpiled within special areas. The problem of contaminated phosphogypsum has already become an international ecological problem. For example, a huge amount of phosphogypsum has accumulated in Florida (more than 1 billion (!) tons), in Europe (where the contaminated phosphogypsum is discharged into the River Rhine close to the North Sea), in Canada, Morocco, Togo, India, China, Korea, Israel, Jordan, Syria, Russia, and other parts of the world.

The building materials industry seems to be the largest among all the industries which is able to reprocess the greatest amount of this industrial by-product and benefit man. However, because of the contamination, only 15% of world phosphogypsum production is recycled as building products and asset retarder in the manufacture of Portland cement (a small amount is recycled as agricultural fertilizer or for soil stabilization amendment), while the remaining 85% is disposed of without any treatment (Tayibi *et al.*, 2009). Disposed phosphogypsum is usually dumped in large stockpiles, occupying considerable land areas and causing serious environmental damage due to both chemical and radioactive contamination.

Typical concentrations of radium (^{226}Ra) in phosphogypsum are 200–3000 Bq kg⁻¹ (US Environmental Protection Agency, 1990). They are similar to those in phosphate ores. Digestion with sulfuric acid causes the selective separation and concentration of naturally occurring radium (^{226}Ra), uranium (^{238}U) and thorium (^{232}Th): about 80% of ^{226}Ra is concentrated in phosphogypsum, while nearly 86% of ^{238}U and 70% of ^{232}Th end up in phosphoric acid (Tayibi *et al.*, 2009). In other words, most of the ^{226}Ra follows phosphogypsum, which is responsible for its enhanced radioactivity, and most of the ^{238}U and ^{232}Th remain in the phosphoric acid product.

In addition to radionuclides, phosphogypsum contains some trace contaminants which may pose health and environmental hazards, such as arsenic, lead, cadmium, chromium, fluorine, zinc, antimony, and copper (US Environmental Protection Agency, 1990). These trace elements may be leached from phosphogypsum, as radionuclides, migrate to the nearby surface and ground water, and cause fluorescence on the surface of building elements.

The key problem restraining the utilization of phosphogypsum in construction is its radiological effect on the human population, and it is not solved yet. Unfortunately, no effective technologies are known for processing phosphogypsum and for its utilization in the construction industry. The main problem is the slightly elevated radioactivity of phosphogypsum, which is due to the high activity concentration of ^{226}Ra , while the remaining impurities can be extracted relatively easily, for example by using phase transformations between different kinds of calcium sulfate hydrate and

filtering the obtained solution. Traditional technologies of purification of phosphogypsum from radium are not effective, because of the similarity of chemical properties of radium sulfate and calcium sulfate salts, when the radioactive salt is isomorphously included in the gypsum crystal lattice (Kovler, 2004).

There have been several attempts to manufacture building materials from phosphogypsum in different countries. For example, phosphogypsum was used some time ago by a New Jersey company for the manufacture of wallboard, partition blocks, and plaster for distribution in the northeastern United States (Fitzgerald and Sensintappar, 1978). Due to the absence of low-cost natural gypsum and the lack of long-term storage place, phosphogypsum has been used extensively for wallboard and other building materials and also as a cement retarder in Japan and South Korea.

Among European countries phosphogypsum is used in limited amounts (or was formerly used) in Austria, Belgium, Germany, the Netherlands, the United Kingdom, Finland, Greece and some other countries that are not members of the EU (RP-96, 1997). However, the modern environmental norms, which are getting stricter year by year in different countries, leave almost no chance for commercial application of phosphogypsum in construction without previously solving the awkward problem of its elevated radioactivity. No wallboard containing phosphogypsum is commercially manufactured now in the USA, and the situation is not going to change in the near future.

8.7.3 Building products containing coal fly ash

The building industry uses large amounts of by-products from other industries. In recent years there is a growing tendency to use new recycled materials with technologically enhanced levels of radioactivity. Coal fly ash is one of the best known examples.

Large quantities of coal fly ash are expelled from coal-fired thermal power plants and these may contain enhanced levels of radionuclides along with other toxic elements. More than 280 Mt of coal ash (fly ash and bottom ash combined) are produced annually. About 40 Mt of these are used in the production of bricks and cement (IAEA, 2003). Since most of the process residues further processed into building materials do not meet the required technical specifications, they are typically mixed with pristine raw materials. The net effect is a dilution of the NORM (naturally occurring radioactive material) content relative to the process residues.

Recycling and utilization of coal fly ash (FA) in concrete construction has clear environmental, technological and economic advantages. Fly ash, a by-product of coal combustion, is widely used as a cementitious and pozzolanic ingredient in Portland-cement concrete. It may be introduced

either as a separately batched material, or as a component of blended cement. The use of coal fly ash in concrete construction is increasing because it often results in lower-cost concrete and improves some properties of concrete. Among the positive technological effects are workability improvement, bleeding reduction, lowering heat of hydration, refinement of pore structure and decrease of permeability. The continued pozzolanic activity of fly ash contributes to increased strength gain at later ages if the concrete is kept moist.

The use of coal fly ash in concrete is a well-recognized source of gamma exposure that is due to the presence of activity concentrations of ^{226}Ra , ^{232}Th and, to a lesser extent, ^{40}K , while the effect of coal fly ash via radon exhalation is controversial, in particular due to the low emanation coefficient from the ash (Kovler *et al.*, 2004b). This effect will be discussed in a following section. Most of the coal fly ash is reused by cement or concrete producers. Concrete is the most popular building material in the world: annual production of concrete is about 1 m^3 per capita. The radionuclide composition of concrete depends on its constituents: cement, aggregates and mineral additives, and their dosages.

As can be seen from Table 8.4, radioactivity concentrations found in ordinary concrete are rather close to the worldwide average concentrations of radium, thorium and potassium in the earth's crust, which are about 40 Bq kg^{-1} , 40 Bq kg^{-1} and 400 Bq kg^{-1} , respectively, and lower than the values found in the most common building materials and industrial by-products used for construction.

Concrete aggregate consisting of crushed stone often has the greatest significance for the total radioactivity of the material, because its total mass content is usually the highest among concrete constituents. If radium-rich and thorium-rich granites are included as aggregates in concrete, the indoor gamma radiation from the walls and floors may be appreciably higher than the average outdoors. In buildings with walls and floors made of concrete containing aggregate of granite or basic gneiss origin with high contents of ^{238}U , the indoor gamma radiation level can reach $0.3 \mu\text{Sv h}^{-1}$. Such radiation levels also occur in Swedish buildings with walls of certain types of bricks made of glacial clays with enhanced ^{238}U and ^{232}Th concentrations (The Radiation Protection Authorities in Denmark, Finland, Iceland, Norway and Sweden, 2000).

The highest radium contents, from 42 to 62 Bq kg^{-1} , have been measured in Finnish concrete (Mustonen, 1984). The measured mean rates of radon exhalation rate (E) were 20 to $32 \text{ Bq m}^{-2} \text{ h}^{-1}$. The corresponding airborne radon concentration was 46.2 Bq m^{-3} with a mean air exchange rate of 0.64 h^{-1} when calculated for radon exhalation rate of $20 \text{ Bq m}^{-2} \text{ h}^{-1}$. The enhanced radium concentrations can be explained by the fact that granite aggregates are popular in Finland.

Commonly used aggregates manufactured from natural stone of sedimentary origin (such as limestone or dolomite) do not normally enhance the radionuclide content of concrete mix. However, some mineral additives, such as blast furnace slag or ash (either coal fly ash, or peat ash, which is often used in Finland, or oil shale ash), although not introduced in high dosages, can cause enhanced activity concentrations of concrete. Phosphogypsum, when used as a set retarder in cement in small amounts not exceeding 4–5% by cement mass, usually has almost no influence on the ^{226}Ra activity concentration of concrete, because the mass fraction of phosphogypsum in concrete does not exceed even 1%.

As an example, let us consider typical concrete compositions, with and without coal fly ash, which can be introduced into the mix as a partial replacement for cement and fine aggregates (sand). Activity concentrations of coal fly ash, which has been subject to a kind of enrichment as a result of the coal combustion process in the thermal power plant, are usually higher than of those of cement and aggregates, which can be seen from Table 8.6.

The simple calculation of the activity concentrations expected in these concrete mixes, taking into account the mass contents of the raw materials they contain, shows that NORM activity concentrations in the concrete with fly ash are higher than in the reference concrete (Table 8.7). For example,

Table 8.6 Example of mix design for concrete with and without fly ash (kg m^{-3}), typical activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K and radium equivalent activity ($A_{\text{Ra-eq}}$) in raw materials (Bq kg^{-1})

Raw materials	Reference concrete	Concrete with FA	A_{Ra}	A_{Th}	A_{K}	$A_{\text{Ra-eq}}$
Cement	300	270	80	40	140	150
Aggregates	1900	1800	20	10	70	40
Coal fly ash	–	120	200	200	200	500
Water	150	150				

Source: Kovler (2011).

Table 8.7 Calculated activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K (A_{Ra} , A_{Th} and A_{K}) and radium equivalent activity $A_{\text{Ra-eq}}$ in concrete mixes, with and without fly ash (Bq kg^{-1})

Concrete mix	A_{Ra}	A_{Th}	A_{K}	$A_{\text{Ra-eq}}$
Reference concrete (no coal fly ash)	26	13	74	51
Concrete with coal fly ash	35	23	80	73

radium equivalent activity calculated by equation 8.9 is higher by 44% in the mix containing fly ash.

Similarly to coal fly ash, some other materials, like blast furnace slag and peat ash (the latter has been widely used in Finland instead of coal fly ash), can be used as an aggregate material replacing virgin natural stone aggregate, or as an additive in cement manufacturing. These industrial by-products may cause also enhanced concentrations of natural radionuclides.

In general, the tendency to reuse industrial by-products and wastes as raw materials in construction is growing, for both economic and environmental reasons.

8.8 Building products with enhanced radon exhalation rate

Radium activity concentration (A_{Ra}), radon emanation coefficient (ϵ) and effective radium activity as their product ($A_{Ra}\epsilon$), as mean values and variation range for the main building materials, according to Krisyuk (1989), are assembled in Table 8.8.

The radon production rate ($Bq\ m^{-3}\ h^{-1}$) of building materials depends on its ^{226}Ra content A_{Ra} , the porosity of the material, the decay constant of radon, the density of the material and the emanation coefficient of the material, which varies from 0.002 for coal fly ash to 0.40 for concrete (Stranden, 1988). This is also illustrated by Eq. 8.2. Table 8.9 reports minimum and maximum values of radium activity concentrations A_{Ra} and radon exhalation rates E for the main building materials. The results are given in descending order according to the maximum radon exhalation rate.

It can be seen that the enhanced radon exhalation rates are characteristic of granite products, which can be used for decoration, internal and external walls, floors, kitchen counter tops, etc. The second place is taken by gypsum wallboards made of phosphogypsum, a by-product of phosphoric acid plants. The third place is taken by concrete. These three types of building materials with enhanced radon release rate are discussed in the next sections.

8.8.1 Granite

Measurements of radon exhalation for a total of 205 selected samples of building materials used in Saudi Arabia (Al-Jarallah and Fazal-ur-Rehman, 2005) showed that granite samples were the main source of radon exhalation. The radon exhalation rates per unit area from these granite samples varied from below MDA (minimum detectable activity, or minimum detection limit) up to $13.1\ Bq\ m^{-2}\ h^{-1}$. The ^{226}Ra contents were measured in 27 granite samples and varied from below MDL up to $297\ Bq\ kg^{-1}$. A linear

Table 8.8 Mean values and variation range of radium activity concentration A_{Ra} , radon emanation coefficient ε and effective radium activity as their product, for popular building materials

Material	No. of samples	A_{Ra} (Bq kg ⁻¹)	ε (%)	$A_{Ra}\varepsilon$ (Bq kg ⁻¹)
Clay	23	48 (10–255)	21 (13–39)	7.0 (1.4–25)
Soil	7	21 (15–28)	21 (5.7–44)	4.1 (1.6–6.7)
Coarse crushed aggregate	11	35 (14–81)	9.1 (3.0–17)	3.5 (4.4–14)
Sand–gravel mix	10	18 (8.1–41)	19 (7.4–35)	3.4 (1.1–6.7)
Mortar	4	15 (11–20)	24 (16–42)	3.3 (2.3–4.4)
Normal-weight concrete	15	27 (11–48)	11 (3.4–26)	3.1 (1.0–4.1)
Sand	14	9.6 (3.7–20)	20 (4.3–46)	1.9 (0.41–5.2)
Gravel	5	16 (5.6–23)	11 (7.1–14)	1.7 (0.67–7.0)
Lightweight concrete	5	23 (13–44)	9.5 (1.2–23)	1.5 (0.56–3.5)
Silicate brick	6	14 (6.3–30)	10 (6.9–14)	1.3 (0.81–2.1)
Plaster	3	9.6 (6.7–14)	12 (9.1–16)	1.0 (0.59–1.4)
Slag	17	104 (21–192)	0.9 (0.1–1.5)	0.92 (0.15–4.4)
Lime, chalk	6	26 (8.1–70)	3.5 (2.7–4.0)	0.92 (0.04–2.4)
Tuff	5	48 (37–67)	1.4 (0.5–2.4)	0.59 (0.22–1.1)
Red brick	16	36 (13–56)	1.5 (0.4–3.8)	0.55 (0.18–1.7)
Fly ash	8	107 (52–155)	0.8 (0.1–2.4)	0.55 (0.07–1.6)
Cement	13	41 (23–59)	1.3 (0.5–2.3)	0.48 (0.11–1.0)
LECA (Lightweight Expanded Clay Aggregate)	7	28 (23–74)	1.0 (0.3–1.7)	0.41 (0.15–0.5)
Gypsum plaster	4	8.9 (7.0–10)	4.4 (1.9–7.3)	0.37 (0.15–0.5)
Limestone	4	3.7 (3.7–4.1)	4.6 (1.4–13)	0.18 (0.04–0.5)

Source: Krisyuk (1989).

correlation coefficient between exhaled radon and radium content was found.

Emanation of radon (^{222}Rn) from granite used for counter tops and mantels was measured on 24 granite samples. Measured radon flux ranged from 0.6 to 86 Bq m⁻² h⁻¹, with most granites emitting <5.6 Bq m⁻² h⁻¹ (Kitto *et al.*, 2009). Granite counter tops, in particular, have received recent media attention regarding their potential to emit radon. Allen *et al.* (2010) measured radon flux on 39 full slabs of granite from 27 different series. Flux was measured at up to six pre-selected locations on each slab and also at areas identified as potentially enriched after a full-slab scan using a Geiger–Müller detector. Whole-slab average emissions ranged from less than MDA to 79.4 Bq m⁻² h⁻¹, similar to the range reported in the literature for convenience samples of small granite pieces. Modeled indoor radon concentrations were less than the average outdoor radon concentration (15 Bq m⁻³)

Table 8.9 Minimum and maximum values of radium activity concentrations A_{Ra} and radon exhalation rates E for popular building materials

Building material	A_{Ra} (Bq/kg)		E (Bq m ⁻² h ⁻¹)		References
	Min.	Max.	Min.	Max.	
Granite	<MDA*	297	<MDA	86	Carrera <i>et al.</i> , 1997; Al-Jarallah & Fazal-ur-Rehman, 2005; Kitto <i>et al.</i> , 2009; Allen <i>et al.</i> , 2010; Chen <i>et al.</i> , 2010
Wallboard (phosphogypsum)	470	700	1.5	42	Poffijn <i>et al.</i> , 1984; Mustonen, 1984; Ackers <i>et al.</i> , 1985;
Normal-weight concrete	11	75	1.1	32	van Dijk & de Jong, 1991
Aerated concrete	6	22	0.4	32	Mustonen, 1984; Ackers <i>et al.</i> , 1985; Krisyuk, 1989; Keller, 1991; van Dijk & de Jong, 1991; Louizi <i>et al.</i> , 1995; Orlando <i>et al.</i> , 1995; de Jong, 2010
Wallboard (natural gypsum)	< MDA	14	< MDA	21	Folkerts <i>et al.</i> , 1984; Keller, 1991; van Dijk & de Jong, 1991; de Jong, 2010
Limestone	4	20	0.1	11	Poffijn <i>et al.</i> , 1984; Folkerts <i>et al.</i> , 1984; Krisyuk, 1989
Tuff	40	70	< MDA	10	Krisyuk, 1989; Orlando <i>et al.</i> , 1995
Clay brick	7	73	0.01	8	Poffijn <i>et al.</i> , 1984; Siotis & Wrixon, 1984; Krisyuk, 1989; van Dijk & de Jong, 1991; Orlando <i>et al.</i> , 1995; Louizi <i>et al.</i> , 1995; Ngachin <i>et al.</i> , 2008; de Jong, 2010
Pumice blocks	40	60	0.6	6	Folkerts <i>et al.</i> , 1984
Silicate brick	7	73	1.9	5	Krisyuk, 1989; de Jong, 2010
Lightweight concrete	7	44	<MDA	3	Siotis & Wrixon, 1984; Green, 1986; Krisyuk, 1989; Carrera <i>et al.</i> , 1997
Plaster	7	14	<MDA	0.2	Krisyuk, 1989

* MDA = minimum detectable activity (the smallest value that can be measured by a specific instrument).

and average indoor radon concentrations (50 Bq m^{-3}) found in the United States. Finally, significant within-slab variability was observed for stones on the higher end of whole slab radon emissions, underscoring the limitations of drawing conclusions from discrete samples.

Chen *et al.* (2010) determined radon exhalation rates for 53 different samples of drywall, tile and granite available on the Canadian market for interior home decoration. The radon exhalation rates ranged from non-detectable to $13 \text{ Bq m}^{-2} \text{ h}^{-1}$. It was found that slate tiles and granite slabs had relatively higher radon exhalation rates than other decorative materials, such as ceramic or porcelain tiles. The average radon exhalation rates were $1.2 \text{ Bq m}^{-2} \text{ h}^{-1}$ for slate tiles and $1.8 \text{ Bq m}^{-2} \text{ h}^{-1}$ for granite slabs of various types and origins. Analysis showed that even if an entire floor was covered with a material having a radon exhalation rate of $12.5 \text{ Bq m}^{-2} \text{ h}^{-1}$, it would contribute only 18 Bq m^{-3} to a relatively tightly sealed house with a ventilation rate of 0.3 h^{-1} . It was concluded that the local building materials for interior home decoration studied in the research project make no significant contribution to indoor radon for a house with adequate air exchange.

8.8.2 Phosphogypsum

Ulbak *et al.* (1984) found that samples of ordinary Danish concrete, where phosphogypsum has been used as an additive in cement, showed a significant increase of radon flux.

The porous microstructure of gypsum in building elements, such as wallboards, explains the relatively high values of the radon emanation factor, which can reach 30–50% (Bossey, 2003; Stoulos *et al.*, 2004; Kovler *et al.*, 2004b). Taking this into account, together with the elevated concentrations of ^{226}Ra in phosphogypsum, the radon concentration in the living areas of buildings should be high as well. This was proved recently by Máduara *et al.* (2011), who measured radon concentrations of $\sim 100 \text{ Bq m}^{-3}$ during long-term radon tests (three months) conducted in a special model room built of wallboards with 10–15 mm thickness produced from phosphogypsum having ^{226}Ra activity concentration of $\sim 400 \text{ Bq kg}^{-1}$. Because of elevated levels of ^{226}Ra and high values of the radon exhalation rate, building materials containing phosphogypsum could result in elevated radiation exposures (from both gamma radiation and inhalation of radon) to building occupants.

8.8.3 Concrete

The results obtained in Finland, Greece, Germany and the Netherlands (RP-96, 1997) show that concrete has the highest normalized radon exhalation rate (exhalation rate per unit area and per unit content of ^{226}Ra), about

0.2 to 0.5 Bq m⁻² h⁻¹/Bq kg⁻¹. Therefore, concrete in buildings can contribute to indoor radon levels more than other building materials with the same ²²⁶Ra content. This fact can be explained by the relatively thick building elements (walls, floors and ceilings) made of concrete, and the high specific surface area of cement hydrates, which facilitates the release of radon atoms into the porous microstructure and their transport to the surface. In addition, concrete usually contains some moisture in its capillary pores. Radon can be easily trapped and transported to the surface of concrete elements with water and water vapor flow. As a result, moisture of concrete significantly influences its radon exhalation rate.

It is known that the recoil distance of the radon atoms in air is about 900 times higher than in water. Thus, water traps the recoiled radon atoms more easily than air. A thin water film, which continuously engulfs cement particles and hydration products, would be sufficient to stop the recoiled atoms in the water. Radon is being produced in soil and building materials as a result of the presence of trace amounts of ²³⁸U. Depending on the properties of the materials such as porosity, tortuosity, permeability and the presence of cracks, and the conditions such as moisture content, rate of saturation and pressure gradients, surface coating, radon diffusion length in the material and thickness of the building element, radon can be transported through the soil and building materials and enter the dwelling. The amount of radon from the soil and building materials entering the indoor air can range over several orders of magnitude due to changes in these properties.

It was shown by Strandén *et al.* (1984) and Yu *et al.* (1996) that the radon-trapping ability of pore water and the probability of radon emanation from the pores decreased when concrete dried. It has been reported that high moisture content increases the radon emanation power of materials but reduces the radon diffusion coefficient. Tanner (1964) gave the following explanation of the effect of high moisture content: if the pores are filled with water, radon must diffuse through the water, but the radon diffusion coefficient for water is very low, only 10⁻⁵ cm² s⁻¹, compared to the diffusion coefficient of about 10⁻² cm² s⁻¹ for air. Strandén *et al.* (1984) found that the increase in radon emanation due to moistening will more than compensate the reduction in radon diffusion coefficient up to a certain level of moisture content, at which the pores have some liquid water but are not completely filled with water. When the pores are completely filled with water, the reduced diffusion will reduce the radon exhalation dramatically. They discovered that the effects of moisture are rather dramatic and a factor of about 20 between the highest and lowest exhalation rate could be found in several cases.

An attempt has been made recently to study the relationship between the moisture content and the radon exhalation rate of hardening cementitious systems (Kovler, 2008). The radon flux from the hardening cement

paste observed in these experiments reached unusually high values of 0.6–1.0 mBq kg⁻¹ s⁻¹ when the cement set. Such values significantly exceed those known before about normal building materials (including those made of Portland cement). The most reasonable explanation for the sharp increase of radon exhalation rate while the cement sets seems to be a synergy of the following main mechanisms:

- Quick microstructural formation when cement sets, which produces an extremely high specific surface area and exposes radon to free emanation, while the porosity of the material is still high
- Intensive flow of water, which traps radon from the newly formed solid surfaces of cement hydrates to the sample surface and enhances the radon emanation power
- High evaporation rate from the surface, as a result of hydration heat and intensive flows of water and water vapor to the surface.

It has to be underscored that the elevated radon concentrations which develop in a few hours after mixing cement with water are very short-lived. So, comparing these findings with an action level that is meant to be applied to average long-term radon concentrations is fraught with danger. In addition, most construction sites are drafty and have much activity going that will increase air exchange, so the true radon exposure is likely to be on the lower side. Let us not forget that workers often move from one construction site to another, so it is unlikely that they are always exposed to the low ventilation. Finally, the minimum air exchange rate usually accepted in design practice (0.5 h⁻¹) guarantees that the concentrations in most cases will not exceed the action level and that they are not of any radiological concern for construction workers.

As was mentioned before, the use of coal fly ash in concrete and other building materials is a well-recognized source of gamma exposure that is due to the presence of activity concentrations of the three primordial radionuclides, ²²⁶Ra, ²³²Th and, to a lesser extent, ⁴⁰K, while the effect of coal fly ash via radon exhalation is controversial, in particular due to the low emanation coefficient of the ash particles. The radon exhalation rate of concrete does not change significantly with its introduction into building materials. Although the radon exhalation rate of concrete containing coal fly ash sometimes can be slightly higher than that of concrete without fly ash, the radon emanation coefficient of such concrete is usually lower (Kovler, 2011). This phenomenon can be explained by the low radon emanation power of fly ash (Kovler *et al.*, 2004b). Van Dijk and de Jong (1991) studied the radon emanation of concrete with ordinary Portland and Portland-fly ash cements and found that the radon emanation coefficient of concrete made with Portland-fly ash cement was lower by ~20%. Roelofs and

Scholten (1994) concluded that under certain conditions, the addition of coal fly ash to the concrete mix could even reduce the radon exhalation rate.

Alum shale was formerly used in both ordinary and lightweight (aerated) concrete mainly in Sweden, but also to a very limited extent in Denmark. About 300,000 dwellings with walls made of lightweight concrete based on alum shale were built in Sweden, where elevated radon exhalation rates became a major problem (The Radiation Protection Authorities in Denmark, Finland, Iceland, Norway and Sweden, 2000). This can be explained by the extremely high ^{226}Ra content (up to 4500 Bq kg^{-1} , see Table 8.3) and porous structure of lightweight concrete, which has a long radon diffusion length and high emanation power. As a result, all the concrete production based on alum shale was shut down in 1975 because of concerns about radioactivity (Mjönes, 1986).

8.9 Control of radioactivity of building materials in regulations

8.9.1 Existing regulations

The convenient parameter used in the norms to limit the overall content of radionuclides in concrete and other building materials of mineral origin is the so-called activity concentration index. The activity index in the EC document (RP-112, 1999) and in many other national standards regulating radioactivity of building materials is calculated on the basis of the activity concentrations of radium (^{226}Ra) in the uranium (^{238}U) decay series, thorium (^{232}Th) in the thorium (^{232}Th) decay series, and potassium (^{40}K). Other nuclides are sometimes taken into consideration as well: for example, the activity concentration of cesium (^{137}Cs) from fallout is regulated in the Finnish guidelines (ST12.2, 2005).

If the activity index exceeds 1, the responsible party is required to show specifically that the relevant action level is not exceeded. If the activity index does not exceed 1, the material can be used, so far as the radioactivity is concerned, without restriction. The criterion of meeting the standard is the non-dimensional value of the so-called activity concentration index taking into account the total effect of the three main natural radionuclides, which can be present in building materials:

$$I = \frac{A_{\text{Ra}}}{300} + \frac{A_{\text{Th}}}{200} + \frac{A_{\text{K}}}{3000} \leq 1 \quad [8.11]$$

where A_{Ra} , A_{Th} and A_{K} are the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K , respectively, in Bq kg^{-1} (RP-112, 1999). According to RP-112 (1999),

Table 8.10 Dose criteria recommended by the EC

Dose criterion	0.3 mSv yr ⁻¹	1.0 mSv yr ⁻¹
Materials used in bulk amounts, e.g. concrete	$I \leq 0.5$	$I \leq 1$
Superficial and other materials with restricted use: tiles, boards, etc.	$I \leq 2$	$I \leq 6$

Source: RP-112 (1999).

the activity concentration index I shall not exceed the values listed in Table 8.10, depending on the dose criterion and the way and the amount in which the material is used in a building.

The EC guidelines allow for controls to be based on a lower dose criterion, if it is judged that this is desirable and will not lead to impractical controls. It is recommended to exempt building materials from all restrictions concerning their radioactivity if the excess gamma radiation originating from them increases the annual effective dose of a member of the public by 0.3 mSv at the most.

Similarly to the guidelines of the European Commission (RP-112, 1999), the draft of the new European Basic Safety Standard Directive (European Commission, 2010) refers to two types of building products: those used in bulk amounts and those used as superficial and other materials with restricted use. In addition, two categories of building products are defined:

- A. Building products causing an equivalent dose below the reference level (1 mSv yr⁻¹)
- B. Building products causing an equivalent dose above the reference level.

According to this directive, type A building products and raw materials will be exempted at national level (except activity concentration surveillance), while type B building products and raw materials should be controlled by the national authorities.

The Member States will also be required to insert in their legislation a list of the different types of building materials which need to be controlled with regard to their emitted gamma radiation. Materials incorporating by-products or residues from NORM industries, such as fly ash, are in this list.

In spite of the fact that the overall radiation hazard due to ionizing radiation from building materials includes both the gamma radiation component, which depends on their radionuclide content, and the component caused by their radon exhalation, most of the standards in the world that regulate the radioactivity of building materials, including concrete, address the gamma radiation only (Kovler, 2011). Indeed, the evaluation of the excess dose caused by building materials for the radon pathway is rather complicated (Markkanen, 2001). One of the reasons is that the actual correlation

between the radon exhalation rate measured in the laboratory and the excess indoor radon concentration on site might be rather poor. Numerous factors, such as temperature (both indoors and outdoors), air pressure and humidity fluctuations, total porosity, pore distribution and pore type (open or closed), surface treatment at the building site and type of coating material applied, influence significantly radon exhalation in dwellings. Finally, it is extremely difficult to take into account the effect of the behavior of the occupier, particularly concerning ventilation. That is why most of the standards regulating radioactivity of building materials address the radon exhalation in a very simplified form, through the limitation of ^{226}Ra , the precursor of ^{222}Rn in the ^{238}U radioactivity chain.

For example, the amount of radium in building materials is recommended to be restricted to a level where it is unlikely to be a major cause for exceeding the design level for indoor radon. In most of Europe the design level for indoor radon is 200 Bq m^{-3} (RP-112, 1999). Taking into account that the most important source of indoor radon is the underlying soil, the majority of indoor radon on the upper floors of a building is expected to originate from building materials. Typical excess indoor radon concentration due to building materials is usually very low: about $10\text{--}20 \text{ Bq m}^{-3}$, which is only 5–10% of the design value introduced in the European Commission Recommendation (RP-112, 1999). In a practical sense, taking into account that within the European Union, gamma doses due to building materials exceeding 1 mSv yr^{-1} are very exceptional and can almost be disregarded from the radiation protection point of view, the limitation on ^{226}Ra concentrations is reduced to the assumption that when gamma doses are limited to levels below 1 mSv yr^{-1} , the ^{226}Ra concentrations in the materials are below the design level (200 Bq m^{-3}). This recommendation is, of course, too general.

Some countries apply separate restrictions for ^{226}Ra content in building materials. For example, Nordic countries recommend 100 and 200 Bq kg^{-1} , respectively, as an exemption level and an upper allowable level for the activity concentration of ^{226}Ra in building materials for new constructions as a source of indoor radon (The Radiation Protection Authorities in Denmark, Finland, Iceland, Norway and Sweden, 2000). The maximum allowable concentration of ^{226}Ra in building materials used for dwellings is limited at 200 Bq kg^{-1} in Poland (Regulation of the Council of Ministers, Republic of Poland, 2007, January 2) and China (GB-6566, 2001).

The norms in the Czech Republic are slightly more complicated (Hůlka, 2008). Radon emanation from building materials is taken into account by limiting the ^{226}Ra content in premises, depending on their character (inhabited or uninhabited) and on the type of building products (products used in bulk amounts, or products with restricted use, such as superficial products) (Table 8.11). Raw materials, such as aggregates of coal fly ash, are

Table 8.11 Limitation of ^{226}Ra concentration in the Czech Republic

Type of building products	Limit value for ^{226}Ra (Bq kg^{-1})	
	Inhabited buildings	Uninhabited buildings
Building products used in bulk amounts, such as concrete	150	500
Building products with restricted uses (such as tiles), and raw materials (such as aggregates and ash)	300	1000

included in the same category as products with ‘restricted use’. In addition to ^{226}Ra concentrations, Czech regulations take into account radon emanation coefficient, radon diffusion length in building materials and air exchange rate (Hůlka *et al.*, 2008).

Two recently published national standards, Austrian Standard ÖNORM S 5200 ‘Radioactivity in Construction Materials’ (2009) and Israeli Standard SI 5098 ‘Content of Natural Radionuclides in Building Products’ (2009), address radon emanation from building materials as a part of their controls criteria. Both standards include the dose from radon inhalation in the total dose excess for the inhabitants.

ÖNORM S 5200 sets the following controls criterion for natural radionuclides:

$$I = \frac{A_{\text{Ra}}}{880}(1 + 0.07\epsilon\rho d) + \frac{A_{\text{Th}}}{530} + \frac{A_{\text{K}}}{8800} \leq 1 \quad [8.12]$$

where ϵ is the emanation coefficient, ρ is the density and d is the wall thickness.

According to ÖNORM S 5200 (2009), if the emanation factor is not known, the activity concentration index I can be calculated using the precondition value $\epsilon = 10\%$. The real emanation factor can be also determined in the direct experiment, but its value should not be higher than the precondition value. The coefficients A_{Ra} , A_{Th} and A_{K} consider external radiation exposure, and the part including the radon emanation coefficient is responsible for radon inhalation in the final dose criterion. The precondition values for the wall thickness and density are $d = 0.3$ and $\rho = 2000 \text{ kg m}^{-3}$, respectively. It can be seen that the part of this combined dose criterion responsible for gamma exposure does not depend on the density and geometry of the building element, but the part responsible for radon inhalation does. SI 5098 (2009) uses a similar approach and allows using the following values of emanation coefficient, if the measurement data are not available: 6% for

masonry blocks made with lightweight aggregate (such as pumice), 7% for masonry blocks made of normal-weight aggregates, and 12% for other building products, including concrete. This standard sets the following expression for the activity concentration index I :

$$I = \frac{A_{\text{Ra}}}{A_1}(1 - \varepsilon) + \frac{A_{\text{Ra}}}{A_2}\varepsilon + \frac{A_{\text{Th}}}{A_3} + \frac{A_{\text{K}}}{A_4} \leq 1 \quad [8.13]$$

where the first, third and fourth components are responsible for the direct gamma-radiation exposure of inhabitants, and the second for the radon inhalation dose.

It can be seen that the first component of this criterion takes into account the reduction of gamma radiation dose caused by ^{226}Ra , because of its disintegration and emanation of ^{222}Rn . The coefficients A_1 , A_2 , A_3 and A_4 depend on the specific surface mass, i.e. mass per unit surface area of the building product (ρd). For example, for building products made of normal-weight concrete with $\rho d = 450 \text{ kg m}^{-2}$ the coefficients A_1 , A_2 , A_3 and A_4 are equal to 421, 11.6, 298 and 4150 Bq kg^{-1} , respectively.

8.9.2 Challenges in regulation of radioactivity of building materials

The legislation in the field of radiological protection is based on a fundamental concept called ALARA (as low as reasonably achievable). At the same time the question remains how to define the term ‘reasonably achievable’. The second important related principle of radiological protection provides that no level of radiation exposure is acceptable without justification. Restricting the use of certain building materials might have significant economic, environmental or social consequences, which should be assessed and considered when establishing binding regulations. Coal fly ash is an example of an industrial by-product for which recycling and utilization in construction is technologically and economically beneficial. In view of the tendency observed in recent years to make environmental norms stricter, the only alternative left would be making a cost–benefit analysis. Indeed, the stricter are the restrictions, the more expensive would be their implementation. The environmental protection, including the radiological protection of populations exposed to ionizing radiation, is under the financial and juridical responsibility of governmental authorities. The expenses are usually shared between governments, the private sector and the public. However, the budget resources are usually limited, and implementation of strict regulations is often impossible and remains as a declaration only. Two different approaches available for such cost–benefit analysis, based on estimating the cost of a person-mSv, have been described by Kovler (2009), but more approaches are available.

Such cost–benefit analysis should serve as an instrument for deciding how strict the regulations should be. The cost–benefit analysis should also address the aspects of recycling of industrial by-products and wastes in manufacture of building materials. When considering the justification for recycling, the radiation exposure of the public and workers is the negative aspect, and saving the natural resources and protection of the environment are the positive aspects. In addition, different social–economic and political aspects have to be taken into account. For example, when deciding to exclude a certain class of building products or industrial by-products from being manufactured or imported, alternative sources of mineral resources or building products for the construction market should be provided, otherwise the additional expenses are laid on the public. In cases where the import of raw materials, building items or industrial by-products and wastes is restricted, there is also a need to ensure that the international laws related to free trade, import and export are not violated.

8.10 References and further reading

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Materials that release toxic fumes during fire

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Abstract: This chapter discusses important matters related to the toxicity of fumes released from building materials in fire events. The chapter briefly reviews the combustion and the products and discusses the materials used in buildings and the toxic fumes produced in the combustion. The effects of conditions on the combustion reactions and products are discussed. Toxicity of combustion products and assessment of combustion toxicity, specifications and standards, fire safety regulations and smoke toxicity test methods are reviewed. Improvements in the safety of building materials in fire, progress in the development of safer materials, and enhanced methods of reducing the toxic combustion products are discussed. Resources for fire properties of materials are also presented.

Key words: building materials, fire, toxicity, health, toxic fumes.

9.1 Introduction

Fire has always been a major hazard to cities, buildings and transport facilities through accidents, arson or war. There have been numerous fires throughout history that resulted in many casualties and great damage. Notable among these were the great fires of Rome (64), Amsterdam (1452), London (1666), New York (1776), Toronto (1849, 1904 and 1940), San Francisco (1906), Tokyo (1923) and many other major cities on several occasions, with thousands dead and numerous buildings and infrastructures destroyed (Arnold, 2005).

The primary causes of home fires are cooking (40%), heating systems (18%) and intentional (8%) (Diekman *et al.*, 2011). In 2008, approximately 54,500 people suffered fatal unintentional injuries in homes in the USA, in which fire events were the third leading cause of these deaths. During the period 2003–2007, more than 1000 home fires were reported each day. These home fires resulted in a civilian injury every 40 minutes and a civilian death about every three hours (Ahrens, 2010).

Fire protection and behaviour of materials used in construction have long been a serious concern. People spend most of their time inside buildings; therefore, buildings play a crucial role in their safety and lifestyle. In spite of significant progress in the science and technology of materials, we still

observe that in the event of fire, buildings or vehicles often burn to the end with huge damage.

An estimated 1800 fatal residential building fires are reported to US fire departments each year, causing an estimated 4000 deaths, 25,000 injuries, and \$196 million in property loss (Karter, 2003). According to the figures published by World Fire Statistics (Woodrow, 2010), the direct cost of fire, about 1% of GDP in most developed countries, has received much less attention than the cost of crime and road accidents. The fire deaths figures (deaths only in buildings, excluding firefighters and deaths in hospital) in the past decade show a decreasing trend. The figures for deaths in fire range from 1.2 people per million population in Singapore to 19.3 in Finland. Fume toxicity has been found to be the most critical factor for fatal casualties in building fires (Gann *et al.*, 1994). The heat and flames from fires are obvious risks; however, the effect of toxic smoke may actually be the greatest danger in fire (Richardson, 2007). Approximately half of the fatalities and a third of all injuries in buildings fires are caused by exposure to toxic products and fumes (Purser, 2002). With improved building design, materials quality and better regulations, the fire death rate in the USA fell by 46.3%, from 36.3 fire deaths per million population in 1979 to 19.5 fire deaths per million population in 1992 (FEMA, 1997).

Fire is a chemical reaction in which a material reacts with an oxidant and releases heat. Fuel, an oxidizer, and an ignition source are three essential elements for combustion. Fire is rapid oxidation of ignited materials, which always occurs in the vapour phase. The high temperature of fire thermally decomposes the materials and converts them to vapours before burning. The presence of all three elements is necessary in order for burning to happen. Fire is an exothermic (heat-producing) and irreversible process involving flame, heat and oxygen depletion, and releasing fumes, toxic gases and light energy. Despite the fatal incidents in fire, a larger number of people experience non-fatal fire injuries, including various degrees of burns and internal (lung) damage. According to some studies (Zhang, 2004), about 20% of those who die in airplane crashes are killed by fire, most often because several polymers that are used in seat fabrics, overhead bins, wall and windows will burn, leaving passengers limited time to escape.

Smoke is a mixture of various combustion products of gases, vapours and aerosols. Smoke properties are the particle yield and size, and the type and amount of toxic gases adsorbed on the particulate. Factors affecting smoke transport allow one to estimate the smoke exposure of a person at a target location in a building and to give information about the distribution of the smoke in different places in the building (Butler & Mulholland, 2004).

The chain reactions between combustible substances and the oxidizing agent during combustion complete the conditions of a sustainable fire. Oxygen is the most common oxidizing agent present in fire events, constitut-

ing approximately 21% of the air and being available everywhere. Oxygen plays a major role in the spread of fire. In general, when the concentration of oxygen in the air reduces to less than 10%, combustion with flame will fade away (Mahoney *et al.*, 2007). Smouldering, the combustion process without flame, might take place at oxygen concentrations of less than 10%. Fire can be ignited by various sources of thermal energy: mechanical, chemical, electrical, biological and nuclear (Martin & Pepler, 2000). Ordinary individuals may be exposed to fire by chance, but fire fighters and emergency personnel are always in contact with fire products.

Many different materials are used in the construction of buildings. In general, they can be classified as inorganic and organic based materials. Inorganic materials, such as concrete, glass, and metals, are usually non-flammable and do not burn but require special design considerations (Levesque, 2006; Phan & Carino, 2000). However, organic materials, like polymers and wood products, are mostly flammable and burn readily in air. The flammability of organic materials and polymers is a serious concern and rigorously limits their applications. Recent fire safety concerns put more stringent requirements for the materials used in enclosed and escape-proof areas, such as electronic enclosures, high-rise buildings, submarines, ships, and aircraft cabins.

The toxicity of fumes generated in fire has been studied for more than six decades (Zapp, 1951). Toxicity is a property that affects organisms. Toxic hazard is the chance of damage to organisms based on exposure resulting from usage and transport of substances. Although the toxicity of substances cannot be changed, the toxic hazard of a substance can be reduced by application of appropriate methods (Crowl & Louvar, 2002).

After the toxic substance enters the body, it moves into the bloodstream. It may be eliminated from the body or transported to the target organ, where the damage is done. The toxic substance may enter the body in various ways. When exposed to toxic fire fumes, entry to the body can be controlled by application of methods and equipment, like using masks. Ventilation, proper masks and other means of personal protection can be used to control entry of fumes by inhalation through the mouth and nose. The respiratory system plays an important role in the entry of toxic substances through inhalation in fire events. The main function of the respiratory system is to exchange oxygen and CO₂ between blood and the inhaled air. A normal person at rest uses about 250 millilitres of oxygen and expels approximately 200 millilitres of CO₂ in one minute. The need for oxygen significantly increases with physical activity (Davies & Moores, 2010).

Toxic substances are classified and compared for relative toxicity based on their LD₅₀ values (Lethality Dose 50), which is the dose that results in 50% lethality (Derelanko & Hollinger, 2002). Other values, like LD₁₀ or LD₉₀, are also reported for substances. Another value representing toxicity,

commonly used for gases, is LC (Lethal Concentration). Threshold limit values (TLV) of toxicants evaluate the lowest value below which the body can detoxify and eliminate the toxic agent without any detectable adverse effects. There are three types of TLVs. Time-weighted average TLV (TLV-TWA) represents what people can be exposed to for a normal working day without adverse effects (Derelanko & Hollinger, 2002).

Concrete provides the best fire resistance of building materials and does not burn. It does not emit any toxic fumes, smoke or drip molten particles when exposed to fire. This excellent fire performance is mainly because of its constituent materials that, when chemically combined, form a material that is essentially inert and has good thermal insulation. The slow rate of heat transfer enables concrete to act as an effective fire shield not only between adjacent spaces but also to protect itself from fire damage (Milner, 2007).

The chance of incapacitation and lethality from the inhalation of toxic gases was studied and a mathematical model for estimating the lethality was presented (Stuhmiller & Stuhmiller, 2005). The model finds an internal dose that is used to extrapolate results across species. The internal dose is correlated with each result that allows estimating the tolerances of any population incidence. The model compares favourably to the combined gas and large animal data.

The present knowledge about the relationships between materials and fire is insufficient and research should be focused on fundamental studies. New and more reliable experimental techniques to characterize the thermal decomposition and flammability of materials need to be developed and relationships between materials structure, composition and their macroscopic flammability should be established. Moreover, we need to have better understanding about the effects of various flame-retardant additives on material flammability and the toxicity of fumes. A deep knowledge about the mechanisms of the thermal decomposition and fire resistance of materials is necessary for improving the safety of buildings. Knowledge about the health effects of fire is insufficient and more research on the effects of fire fumes on the organs and on the toxicity level of building materials is necessary.

9.2 Fire behaviour of building materials

In this section, building materials, their combustibility and behaviour in fire and the chemical composition of toxic fumes and particles they release are reviewed. A correlation between polymer structure, material composition and flammability is established and experimental techniques to characterize the thermal decomposition and flammability of polymers are discussed.

A large number of researches have been conducted on the flammability of polymers. All flammable materials have minimum ignition energy (MIE)

values, which is the lowest amount of energy required to initiate combustion. The value of MIE depends on factors including the chemical structure of the material, pressure and temperature. An increase in pressure decreases the MIE value. Methane has an MIE value of 0.28 mJ; therefore, a static discharge of 22 mJ energy generated by walking on a rug can ignite a fire in an atmosphere containing methane (Glassman & Yetter, 2008). Many fire incidents are initiated because of the heat produced from slow oxidation of materials (autoxidation). Materials such as oils and cottons are susceptible to oxidation when stored in warm and humid storage rooms.

Fire behaviour of materials is a critical factor in their selection. The materials selected for use in the building must obey certain standards of fire performance appropriate for the application. The fire performance of materials is determined through flammability tests. When exposed to heat, materials are thermally degraded, mainly in three ways: oxidative pyrolysis, anaerobic pyrolysis and combustion with flame. Most fire events occur in aerobic conditions. Many materials, particularly polymers, thermally degrade below 400°C and release flammable gases, and likely toxic compounds.

The ratio of the heat release and the time response parameters (HRP/TRP) provides an estimation of how fast fire would spread on a material. A combination of the HRP, TRP and heat flux values is related to the flame spread behaviour of materials and is expressed as the fire propagation index (FPI). These properties and parameters are taken from the flammability diagrams.

Light and high-performance organic materials offer many advantages in buildings over conventional metal and ceramic materials, but they greatly increase the fire risk because of their flammability and potential release of toxic fumes. Polymers, because of their versatility, ease of forming and good performance to cost ratio, have grown into many applications, including building materials. However, their high flammability greatly increases fire risk, particularly in buildings.

Chemical structures of polymers mainly consist of carbon and hydrogen atoms that make them combustible. Many polymers, when subjected to some ignition sources, will undergo self-sustained combustion in air. Chemical reactions may take place in three interdependent regions: within the condensed phase, at the interface between the condensed phase and the gas phase, and in the gas phase.

Polymers can be classified in a variety of ways: as natural or synthetic materials, based on their physical and mechanical properties (elastomers, plastics and fibres), and in terms of their chemical structures. Polymers are often further subdivided into thermoplastics (whose softening at elevated temperature is reversible) and thermosets (which undergo irreversible changes when heated). Polymers behave differently in production of smoke and fume when they burn. All these types of classifications of polymers

are useful and, depending on the situation, a particular type may be selected. For instance, classification of polymers based on chemical structure is more useful when dealing with their reactivity and role in chemical reactions. When the response of the polymer to heat is under consideration, the classification of polymers as thermoplastics and thermosets may be selected.

Polymer combustion occurs in a few steps: heating, pyrolysis (decomposition), ignition and combustion. The material is first heated to pyrolysis temperature, producing bubbles and releasing usually combustible gaseous products. On most occasions, the pyrolysis process is necessary for the combustion. Pyrolysis is a chemical reaction that usually occurs in three main mechanisms, producing many products that diffuse into the flame. Some polymers undergo crosslinking reactions during pyrolysis, producing a solid char that does not spread fire. The presence of contaminations, such as oils and water, may direct the pyrolysis to the production of some other substances. For instance, pyrolysis of polyesters in the presence of water directs the process to the hydrolysis reaction and production of oligomers (shorter-chain polymers) (Moldoveanu, 2005).

The fire point (or flame point) of a substance is the lowest temperature at which it produces sufficient amounts of vapours to form an ignitable mixture that will sustain combustion. When a liquid reaches its fire point and is ignited, combustion will be sustained until the material is totally consumed or other extinguishing action is taken (Davletshina, 1998; Davletshina & Cheremisinoff, 1998). If there is an ignition source, the pyrolysis products will undergo combustion in the gas phase and produce more heat. Under steady-state burning conditions, some of the heat is transferred back to the material surface, producing more volatile polymer fragments to sustain the combustion cycle.

Flames are self-propagating combustion reactions in which both the fuel and the oxidant are present in the gas phase. Because the majority of polymers are hydrocarbon based, the flame above burning polymers is usually a hydrocarbon flame. Smoke formation in flames is highly dependent on the structure of the gaseous fuel and on the fuel-to-air ratio. In general, polymers containing purely aliphatic structural units produce relatively little smoke, while polymers with aromatic groups in the main chain produce larger amounts of black smoke (Gallo, 2009).

A variety of physical changes result from pyrolysis, including char development, intumescences, melting and vaporization. Char is a black and porous residue of burning of some organic materials. Thermoplastic polymers tend to soften when exposed to heat and melt without forming char. For example, poly(methyl methacrylate) (PMMA) burns with very little melt and leaves no residue. However, rigid poly(vinyl chloride) (PVC) and polyurethane (PU) foams char when burned. The char layer may act as an

insulating barrier between the external heat source and the rest of the material. This will slow the pyrolysis rate unless the external heat flux increases to compensate for the insulating char layer.

Intumescence is defined as the process of swelling up or bubbling up. There are many coatings on the market for fire protection purposes. The intumescent coatings, when heated, expand, similar to the development of a char layer. When the intumescent char layer is formed, a blowing agent is released, creating a low-density, relatively thick carbonaceous layer. As the material expands, the water is released, maintaining the surface temperature. The char can expand to 50 to 100 times the original thickness of the intumescent coating (Troitzsch, 2004).

A large number of toxic compounds are present in fire smoke with a highly variable composition that depends on the composition of the materials and the temperature of the fire. Respiratory irritant compounds (including ammonia, acrolein, SO_2 and formaldehyde), by causing chemical tracheobronchitis, pulmonary oedema, upper airway obstruction, or pneumonia, produce shortage of oxygen supply and hypoxia. The asphyxiant compounds (such as CO_2 , methane and CO), by displacing oxygen from the surroundings, cause hypoxia too.

The behaviours of a large number of polymers in flame have been studied (Panagiotou, 2004). When exposed to an external heat flux, the polymer surface begins to produce small bubbles that start to break and release fuel vapour. The burning process continues along the same lines with an increased rate of bubbling. The bubbling covers the entire surface of the sample and resembles a boiling liquid. No residue is left over after burnout. Some polymers (like styrene polymers) produce a lot of soot on burning (see Fig. 9.1).

Furniture is part of the building that makes it more vulnerable to fire and plays a major role in fatal fires. The fire safety aspect of furniture has been studied by several researchers (Sundstrom, 1995, 1996; Fowell, 1994; Krasny *et al.*, 2001). Recently, Shousuo (2006) carried out an in-depth study of fire safety of furniture. Ignitability, flammability of the volatiles, total heat and its release rate, flame spread, smoke obscuration and fume toxicity are the main hazardous factors of fire. Furniture is usually made of polymers, textiles and wood. The fire behaviour of some major materials used in buildings is reviewed below.

9.2.1 Polyurethane

Polyurethane (PU) can be found in a wide range of applications in buildings, including expanded rigid boards, sprayed insulation, flexible foams, coatings and paints, adhesives, sealants and elastomers (such as wood sealers and caulks), window treatments, resin flooring, gaskets and also in

thermoplastics rubbers and elastic fabrics. PU is produced from isocyanates and releases isocyanates and some other highly toxic substances when heated or burned (Paabo & Levin, 1987; Blomqvist *et al.*, 2003). PU used in furniture mainly in mattresses burns with a steady flame in both ventilated and vitiated (less available air) conditions. The combustion of PU, in addition to CO₂ and CO, produces HCN, NO and NH₃. HCN has been found in both ventilated and vitiated conditions, whereas NO was found only in ventilated and NH₃ only in vitiated conditions. The higher production of HCN, together with NH₃ production instead of NO, is typical for vitiated combustion of N-containing materials (Blomqvist, 2005). The average CO yield in ventilated conditions has been 40 mg/g. A yield of 0.9 mg/g has been found for HCN in examinations with flexible PU.

Rigid PU insulation burns with an unsteady flame in ventilated and vitiated conditions and HCN has been detected in both conditions. The average HCN yield has been measured at 8 mg/g in ventilated conditions and 17 mg/g in vitiated conditions on a mass-loss basis. Data given by Tewarson (2002) for HCN yields from ventilated conditions for various rigid PU products are 10–12 mg/g. NO and NH₃ were found in both the ventilated and the vitiated tests, which indicate a similarity in the smoke gas composition between the two combustion conditions for the flame-retarded PU insulation. A rigid PU yielded 2.7 mg/g HCN (Blomqvist *et al.*, 2003). Of the 22 different substances analysed in PU fume, the principal species found were CO₂, CO, H₂O, NO and hydrocarbons (Valencia *et al.*, 2009).

9.2.2 Fibre-reinforced polymer composites

Fibre-reinforced polymer composites (FRP) have found a wide range of applications in aerospace, marine and automotive industries because of their good mechanical properties compared with the conventional materials. Applications of FRPs in buildings are increasing dramatically (Hollaway, 2010). They are being used more often in buildings and in making furniture and some other items, like bathroom cabins. Despite many advantages, FRPs are easily combustible to varying degrees (Grenier, 1996; Kim *et al.*, 2008). Glass, carbon and aramid (and more recently cellulose fibres) are the most common reinforcing fibres used in FRPs. When exposed to fire, the polymeric matrix of composites burns and the fine fibres with diameters in the range of micrometres are released to the atmosphere, posing similar threats to health as asbestos. The potential health risk of carbon fibre FRP in producing dangerous inhalable fibres has been investigated (Hertzberg, 2005). It was found that the health risk is related to the surface temperature, the oxygen level and the airflow field close to the material surface.

9.2.3 PVC

PVC products are widely used in buildings, such as in piping, window frames, low-voltage cables, insulating sheathing and carpets. Chapter 2 presents detailed information about PVC and its applications in buildings. PVC is rigid and thermally unstable; therefore, significant amounts of various additives are added, such as plasticizers, stabilizers, fillers, lubricants and colorants. The behaviour and yields of different compounds from PVC sheathing in fire are similar to the combustion of PVC floor coverings and carpets.

When in fire, PVC and other chlorinated polymers initially flash intermittently, but after some time PVC burns steadily in both ventilated and vitiated conditions (Blomqvist *et al.*, 2007). A large number of substances have been found in the combustion products of PVC (Huggett & Levin, 1987). For PVC, the differences between CO₂ and CO yields in ventilated and vitiated conditions are not significant. The reason is most likely the disturbance of the combustion by chlorine, resulting in poor combustion, even in ventilated conditions. The average HCl yield based on mass loss was 240 mg/g in ventilated conditions and 180 mg/g in vitiated conditions. The lower yield during vitiated conditions could be due to a lower conversion rate of chlorine to HCl and thus a higher proportion of chlorine in the form of organochlorine compounds. It has also been shown that properly stabilized PVC materials do not emit large amounts of HCl at working temperatures, even after a very long period of use (Hirschler, 2005).

9.2.4 Wood and wood products

Wood has been a major load-bearing building material for a long time. It has also been a source of heat as an efficient solid fuel. Wood consists primarily of two natural polymers: cellulose (50–70%) and lignin (approximately 30%). The effective material parameters of wood in fire were found to be thickness, density and the fire retardant treatment (Lazaros, 2003). The rate of heat release of wood was found to be the most important fire parameter. The time to ignite is an increasing linear function of incident heat flux. Thin materials have a short burning time and show two maximum values. The maximum and average rate of heat release are an increasing function of incident heat flux. Fire retardant-treated wood products can achieve improved fire rating of wood.

Wood fume contains numerous chemicals, many having adverse health effects, including such common pollutants as fine particles, CO, and nitrogen oxides (NO_x) as well as ciliotoxic respiratory irritants, such as phenols, cresols, acrolein and acetaldehyde; carcinogenic organic compounds, such as benzene, formaldehyde and butadiene; and carcinogenic cyclic

compounds, such as PAHs (Bhargava *et al.*, 2002). Wood fume contains at least five substances classified as potential human carcinogens by the International Agency for Research on Cancer. CO and NO_x are two principal gases emitted by wood combustion (Dubick *et al.*, 2002; Sällsten *et al.*, 2006). Exposure to CO present in wood fume leads to formation of carboxyhaemoglobin (COHb), which can be measured directly in venous blood (Burgess *et al.*, 2001) or indirectly as CO in exhaled breath (Cone *et al.*, 2005). Health impacts of exposure to these substances and some of the other wood smoke constituents (e.g., benzene) are well characterized in many publications (Naeher *et al.*, 2007; Simpson & Naeher, 2010).

Wood products such as particle boards and fibreboards consist of significant amounts of other materials such as binders like phenol formaldehyde, melamine formaldehyde and urea formaldehyde resins. Combustion of these binders adds several other kinds of harmful compounds to the produced fumes. Results from measurements of CO₂ and CO in tests with wood showed that the yields of CO from ventilated combustion in the tube furnace were about 7–9 mg/g (Blomqvist *et al.*, 2007). CO yields have been reported of 4–5 mg/g of wood for ventilated combustion (Tewarson, 2002) and approximately 140 mg/g for vitiated combustion, which is similar to the value of 0.2 g/g reported by Tewarson (2002).

9.2.5 Fluoropolymers

Wires and cables are widely used in buildings for power transmission and communications. Various polymers are used as insulator coatings of wires. Blomqvist *et al.* (2007) investigated the fire behaviour of fluoropolymer (FP) coated cables. The cable material FP is highly flame resistant. The poor burning and flashing behaviour of FP is due to the low and unsteady yields of CO₂ and CO. Average yields were 390 mg/g for CO₂ and 170 mg/g for CO in ventilated conditions. Similar results were obtained in vitiated conditions. Average yields of 130 mg/g of HCl and 20 mg/g of HF were found in ventilated conditions. Sometimes, a multilayer of FP and PE covers cables. The yields of CO in ventilated and vitiated combustion of FP were found to be approximately 60 mg/g and 110 mg/g, respectively.

9.2.6 Polyesters

Polyesters are made by esterification of polyacids (or esters) and polyols, resulting in various structures (saturated and unsaturated) for various applications. They are very common in applications such as fabrics (clothing, curtains, carpets) and bottles and as composites in furniture and appliances. Polyesters are flammable and, depending on the conditions and atmosphere, in addition to CO, H₂O and CO₂, combustion of polyesters

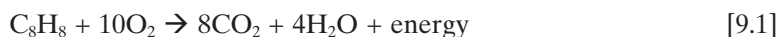
produces various kinds of toxic substances, such as benzene, acetaldehyde, formaldehyde and different kinds of hydrocarbons (both saturated and unsaturated) (Hraun & Levin, 1986).

9.2.7 Textiles

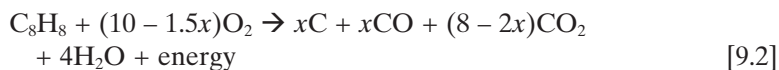
In addition to building materials, flammable interior furnishings and decorative materials (particularly textiles) are major sources of fire hazards in buildings. Polyamides are widely used in fabrics and consumer and industrial applications. Aliphatic polyamides (nylons) are extensively used in textiles and are important engineering plastics. Aromatic polyamide (aramid) is used mostly in advanced composites and is thermally more stable than nylon. Combustion of polyamides in air produces heavy hydrocarbons and various, mainly toxic, substances such as CO, CO₂, NH₃, HCN and NO_x (Braun & Levin, 1987).

9.2.8 Styrene polymers

Polystyrene (PS), and other polymers containing styrene, are widely used in buildings. PS is an organic material consisting of carbon and hydrogen with a formula of (C₈H₈)_n and, like many other organic materials, is combustible. The thermal decomposition and the toxic fume products of PS have been studied (Gurman *et al.*, 1987). The complete combustion of polymers composed of carbon and hydrogen in an atmosphere with plenty of oxygen supply gives off CO₂ and water:



Based on this stoichiometric equation, complete combustion of one gram of PS requires approximately 2150 cm³ of oxygen. Considering the composition of air, which is a mixture of 21% oxygen and 78% nitrogen, for complete combustion of one gram of PS, 10,750 cm³ of air is needed. This large quantity of oxygen is usually not available for combustion. When the available oxygen is limited, the reaction produces other products, mainly CO and soot particles (C). The combustion of PS in an atmosphere with limited available oxygen was proposed as below (Doroudiani & Omidian, 2010):



These scenarios are ideal mechanisms of the combustion of PS in ventilated and vitiated conditions. In reality, in addition to soot, CO, CO₂ and H₂O and some aromatic compounds are produced, including styrene and styrene oxide. Fire behaviours of various types of expanded polystyrene (EPS) and the effects of density and thickness on fire performance of PS foam have

been studied (Bakhtiyari *et al.*, 2010). The authors found two contradictory roles for the thickness of the specimens on fire behaviour of EPS.

9.2.9 Other polymers

Polycyanurates are thermoset polymers that are used to produce void-free castings and composites with good surface finish. They are used mainly in aerospace structures, but also for printed circuit boards in electronic devices and appliances. The flammability and fire behaviour (Walters *et al.*, 1998) of cyanate esters and the relationship between their flammability and chemical structures have been studied (Lyon *et al.*, 2006a).

The effects of thickness of thermoplastics on their combustion behaviour have been investigated (Xie *et al.*, 2009). The thicknesses of PP and PS sheets were found to play an important role in increasing the heat release rate and the peak values.

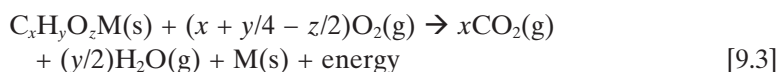
The thermal stability of polymers depends mainly on the structure of the monomer and, in particular, on the weakest chemical bonds in the structure. The flammability tests and methods have been comprehensively studied (Panagiotou, 2004). A flammability diagram is a single plot showing the energy release rate, time to ignite and flame spread rates for a material as a function of the incident heat flux. The ultimate uncertainty of material fire properties has been analysed and studied based on NIST and ISO guides (Lie, 2005). Based on the study, uncertainties were heat release rate, volume flow rate, extinction coefficient, smoke production rate and heat of combustion.

There are a number of factors that influence polymer flammability, such as chemical structure, molecular weight, free radicals in the polymer, and composition of copolymers and blends. Introducing aromatic or heteroaromatic rings and heteroatoms into the polymer main chain can increase thermal stability and reduce polymer flammability. The bulky side groups, for instance in PMMA, can be easily cleaved off and released as fuels. However, they can also expand the decomposition temperature range by multiple decomposition stages. Consequently, the mass loss rates are reduced. The CN substituent group is a very efficient flame-retardant unit to be incorporated into a polymer structure to increase char formation and reduce heat release. The silicon-based or halogen-based comonomers that have low heats of combustion can be used as reactive flame-retardant additives to adjust polymer flammability. The silicon-based inorganic network structure can greatly promote the char formation. The effects of molecular weight on polymer flammability depend on the thermal decomposition mechanisms of polymers.

Aromatic polymers usually produce relatively high char yields. The char can reduce the amount and release rate of volatile fuels, and act as a barrier

for heat and mass transfer. Therefore, aromatic polymers generally have lower flammability. The introduction of halogen atoms into polymer structures can efficiently reduce the flammability of the polymers because the halogenated decomposition volatiles have relatively low flammability and can make some flame-retardant effect in the gas phase. The polymers containing both halogens and aromatic structures have extremely low flammability.

The composition and quantities of gases produced in combustion depend on several factors, including flammability and chemical composition of the materials and the specific fire conditions. Organic materials, like polymers and wood products, usually consist of carbon, hydrogen, oxygen and sometimes a metal element. For such a molecule, we can write the following combustion equation (Doroudiani & Omidian, 2010):



The equation reveals the combustion in the presence of abundant oxygen. In reality and in the event of fire, complete combustion is rare because of the limited access to air. The proportions of different components depend on the quantity of available oxygen. Less oxygen available for combustion leads to a greater proportion of soot particles and carbon monoxide (Brohez1 *et al.*, 2008).

9.3 The effects of conditions on the initiation and propagation of fire

The materials and conditions essentially determine the initiation and spread of fire, and the composition of the combustion products. Temperature, pressure, water, oxygen content, and ventilation are major factors affecting fire. As stated, inhalation of toxic fumes is a major cause of death or permanent injury in fire events. The products of the combustion of the materials are highly dependent on the fire conditions; therefore, it is necessary to evaluate the combustion products of the material under various conditions to understand the effects of conditions on the toxicity of the fumes. As the fire develops, the conditions change; the temperature increases, oxygen concentration decreases and the concentrations of combustion products increase.

The toxicity of fire fume depends on both the material and the fire environment and conditions. There are a number of methods to determine the toxicity of fire effluents. These methods yield apparently contradictory information and confusing results (Hull & Paul, 2007). The need for international harmonization of toxicity testing has been emphasized. The fire fume toxicity is essentially determined by CO levels, and to a lesser extent by other toxicants (Purser, 2002), particularly HCN. A chemical kinetics

model for calculation of the formation of HCN showed that recycling of the combustion products to the fire increases the formation of HCN and CO, and less ventilated conditions increase the formation of these toxic substances, which is in good agreement with the experimental measurements (Tuovinen *et al.*, 2004).

Fires may occur in various stages and conditions, from smouldering to completely ventilated flaming. In all fires, the combustible gases produced from the thermal decomposition of the materials react with oxygen. Solid fuels are converted to gas, through the pyrolysis process, prior to the combustion reaction. In the smouldering process (similar to glow on charcoal), combustion occurs on the surface of the solid fuel, which needs less oxygen than flame combustion. The fume products comprise complex mixtures of fully oxidized products, such as CO₂, partially oxidized products (for instance CO or aldehydes), fuel or fuel degradation products (such as aliphatic or aromatic hydrocarbons), and other stable gas molecules (like nitrogen and hydrogen halides). Stec *et al.* (2008) studied the relationships between the ventilation conditions and product yields at different temperatures using online Fourier transform infrared spectroscopy (FTIR) for identification and quantification of the products.

The British Standards Institution has divided fires into a number of stages, from smouldering combustion and partly ventilated flaming through to completely developed under-ventilated flaming (BS, 2003). The flaming stages are strongly dependent on the fuel-to-oxygen ratios, which are controlled by the air supply (Hull *et al.*, 2000). In stoichiometric conditions, the amount of available oxygen equals the required oxygen as fuel for complete combustion. In the event that less oxygen than the stoichiometric amount is available, it is vitiated, and if the available air requirement is exceeded, then the conditions are ventilated. The yields of at least two major toxicants, CO and HCN, are critically dependent on the degree of ventilation. The CO/CO₂ (v/v) ratio in the ventilated conditions has been approximately 0.01, whereas in vitiated conditions the ratio was approximately 0.24 (Blomqvist *et al.*, 2007).

The values of yields obtained from combustion of various polymers have been shown to be highly dependent on the fuel to oxygen ratio and on the nature of the material. It is therefore vital that in any standard method for determination of toxic product yields, the relationships of products yields with the variables affecting the decomposition conditions are established. The PE, PS and nylon 66 results clearly showed similarities in behaviour for yields of CO, HCN and hydrocarbons at various temperatures studied, which were independent of the temperature over the range of 650–850°C. The combustion behaviour of PVC was different from that of the other polymers, and the toxic product yields for PVC were almost independent of the fire conditions (Stec *et al.*, 2008).

9.4 Health effects and analysis of combustion products

In most countries, pathology information and data from fires are usually not published. There are a large number of substances known to be products of materials combustion, but what substances produced in fire events may be considered toxic? According to Swiss physician and father of toxicology, Paracelsus: 'All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy' (Paracelsus, 1493–1541), in other words, dose makes the poison. Dose is the amount of the substance entering the body.

Smoke inhalation injury is a major effect of fire on human beings, in addition to direct burn, which increases the mortality of patients with thermal injury (Cancio, 2005). Care of patients with smoke inhalation injury, and of patients with similar injuries secondary to the inhalation of toxic industrial chemicals, should be conducted in burn centres with a multidisciplinary, research-oriented focus. In a recent fire event in a residential building under construction (1 May 2011), the fumes produced from burning of the EPS blocks used in the ceilings incapacitated the workers, causing the death of at least six workers (ISNA, May 2011). The images in Fig. 9.1 show thick fume produced from burning of EPS. According to the regulations, only flame-retarded EPS with specific mechanical performance is permissible in buildings. The core EPS must be completely covered and protected by a non-flammable skin, such as cement-based sheets, and the use of open fires in construction sites is strictly prohibited. In the said fire event, regular EPS was used and there had been an open fire in the construction site (BHRC, 2010). Recently, the US Department of Health and Human Services (June 2011) reported a new list of carcinogenic substances, including styrene. Animal studies indicated that styrene caused lung tumours in several strains of mice.

Chemicals are potentially harmful to biological tissues and human health. In the event of fire, significant amounts of substances are produced from materials combustion. The effects of these substances depend mainly on the quantity of the compounds, the time of exposure and the closeness of the exposed organs to the fire. Smoke is considered as an opaque cloud of small, individually invisible particles. Fumes are less opaque forms of smoke. Combustion gases and smoke are different because they can have different effects, and different methods are used for their measurement (Price *et al.*, 2001).

Gases and fumes can easily diffuse into rooms from adjacent exterior space. In the interior space of the building, high airflow and ventilation with an open inside door significantly decreases the dangerous conditions. While high airflow dilutes the concentration of CO gas in the interior space, in the



(a)



(b)

9.1 Under-construction building on fire (courtesy of ISNA).

event of fire more airflow extends the flame by making more oxygen available for combustion. Therefore, ventilation plays two contradictory roles in reducing fire casualties.

Trauma, respiratory disease, cardiovascular illness, reproductive hazards, toxic substances, and carcinogenic hazards are some of the important health concerns for people in fire areas, especially firefighters. In fire events, only a minority of deaths and injuries are due to the heat and flames, while many victims die from the effects of poisonous fire effluents (Stefanidou *et al.*, 2008). It has been estimated that more than 50% of fire-related deaths occurring each year in the USA can be attributed to inhalation-related injuries (Locatelli *et al.*, 1994).

The most common source of CN poisoning occurs from exposure to fires (Walsh & Eckstein, 2004). In fire events, CN is produced when the temperature reaches approximately 315°C and is released from the toxic fumes in gaseous form that may then be inhaled by the victim. HCN is developed from incomplete combustion of any N-containing material, such as polyamides, wool or silk (Gracia & Shepherd, 2004). Cyanide can also be a product of burning of materials without nitrogen. For instance, burning cotton develops 130 µg HCN/g and burning paper makes 1100 µg HCN/g, while burning wool produces 6300 µg HCN/g (Lawson-Smith & Hyldegaard, 2011).

Nitric oxide (NO), as one of the toxic gases in fire events, has a very different toxic effect from that produced by NO₂. Formation of NO and NO₂ in fire fume, their potential toxic effects and the need to reconsider the methods of calculating toxic potency values have been investigated (Paul *et al.*, 2008). The authors recommended that the complex chemical reactions and the toxicity of NO should be studied to improve the accuracy and reliability of the methods used to calculate the toxicity of the fire fumes.

Information about the production of toxic gases is important in order to estimate the time for evacuation in fire events. Quantitative information on toxic gases for an evacuation scenario has been determined in real-scale fire experiments (Blomqvist, 2005). The study showed that the gases produced are the greatest danger and that HCN, in particular, had a major impact on the fire casualties.

Blomqvist (2005) studied some important components that typically are found in fire fumes, including CO, HCN, HCl, polycyclic aromatic hydrocarbons (PAH), furans, isocyanates and particulate matter. PAH and dioxins have important sublethal effects on humans and emissions of these types of compounds are of potential environmental concern. Isocyanates are potent irritants and are known to cause hypersensitivity from exposure, which is of particular concern to firefighters and others who are exposed to fire fumes. The small particles and soot in fire fumes are of concern as they have a tendency to penetrate deep into the lungs.

The total time of exposure to fumes is a key factor on health that must be considered in fire events. Many people are trapped at an early stage of fire by relatively thin smoke, and loss of visibility is often an indirect cause of death.

Exposure to wood smoke is associated with a variety of adverse health effects in humans. However, there is much to learn about the relationship between wood smoke exposure and disease. Most available animal studies indicate that exposure to wood combustion fume results in significant impacts on the respiratory immune system and at high doses can produce long-term or permanent lesions in lung tissues. Wood smoke is also mutagenic and possibly carcinogenic, but less so than coal smoke.

Insufficient information about the toxicological effects of various types of biomass smoke (e.g., smoke from combustion of wood versus agricultural wastes) is available. More work in this area is needed for better understanding the mechanisms by which adverse effects observed in exposed individuals might occur. Because wood smoke is made up of such a large mixture of various substances, it is hard to attempt to accurately assess its health impacts by simply summing the potential effects of individual constituents. Particularly, in high exposure situations with fresh wood smoke, as with occupational exposures or vegetation fire episodes, there may be a need to derive indices of exposure that take into account a range of toxic endpoints because of the wood smoke, for instance including acute acting and chronic toxicants, so that appropriate protective actions can be taken (Naeher *et al.*, 2007).

Fire in buildings usually consists of generation of heat, reduction of available air and production of various substances, including CO. Combustion of materials yields heat, smoke and different amounts and types of toxic agents, such as HCl, HCN, CO_x, SO_x and NO_x. This mainly depends on the flammability of the material and the conditions, such as temperature, ventilation level, and available fuel. Fire-retardant additives may affect the amount and type of fumes released in the fire. Combustion of the materials under poorly ventilated conditions results in less heat and more CO and other toxic products of incomplete combustion.

The toxicity test of the inhaled fumes and compounds consists of measuring the biological response of the subject, which usually falls into three categories: mortality, incapacitation and sensory irritation. CO often acts synergistically with CN and other compounds released through combustion of various materials. Life-threatening complications, such as pulmonary oedema, may suddenly develop up to several days after exposure to the smoke.

Estrellan and Iino (2010) reviewed the toxic emissions from fire and concluded that combustion involving traditional and recreational practices, such as incense burning, firework displays and grilling over charcoal are

sources of hazardous emissions. Considerable levels of soot, gaseous PAH, inorganic gases and aldehydes were detected in ambient air in temples burning incense. Fireworks contribute significantly to ambient air metal concentrations during detonation episodes, while charcoal was found to emit mercury and benzene during grilling.

Various analytical techniques are used to evaluate the flammability and to analyse thermal decomposition products of materials. Gas chromatography (GC) and mass spectrometry (MS) are two main techniques that are comprehensively used to analyse the composition of smoke and other fire products (de Hoffmann & Stroobant, 2007; McMaster, 2008). Pyrolysis gas chromatography/mass spectrometry (PGC/MS), simultaneous thermal analysis (STA) and pyrolysis–combustion flow calorimetry (PCFC) are three common methods that need only a very small amount of sample. These methods are efficient screening tools for newly synthesized fire-safe materials. They consist of submitting a sample to GC to separate the components of the mixture based on different properties, such as boiling point and polarity.

Infrared polarization spectroscopy (IRPS) has been used to detect HCl *in situ* in the combustion test. The method allows one to obtain valuable information that could not be extracted from sampling methods, for instance from GC/MS or FTIR. The method is in the development stage and is predicted to be able to detect toxic gases in the fire fume other than HCl, like HCN, NO₂, and HF (Sun *et al.*, 2011). Moreover, the FTIR technique was used to determine the toxic components of combustion gases in fire events (Hakkarainen *et al.*, 2000; Bulien, 1996; Pottel, 1996).

The fire behaviour of materials has been investigated at bench scale under laboratory conditions, which are somewhat different from the conditions in real fire events. Hull *et al.* (2008) compared the toxic product yields of burning electric cables in bench and large-scale experiments and found only minor differences in toxic product yield between the methods and conditions of the test.

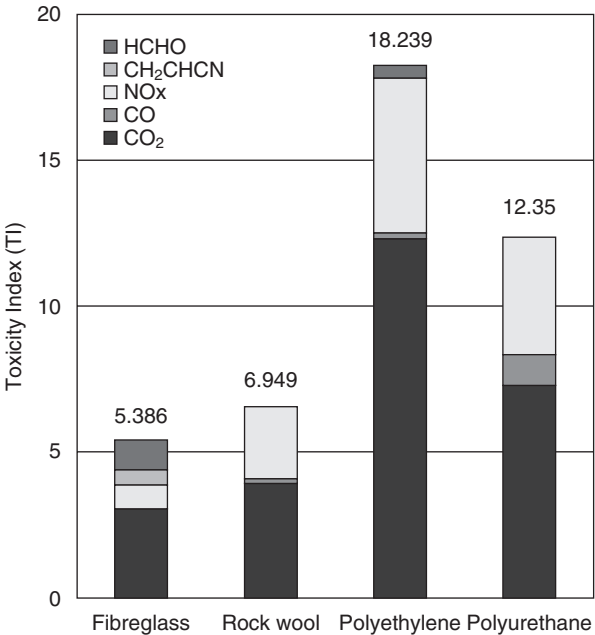
Toxicity of CO and other toxic gases increases in the presence of CO₂. For inhalation experiments, the concentration of the chemicals in air that kills 50% of the test animals in a given time (usually four hours) is the LC₅₀ value. For instance, the LC₅₀ value of CO as a single gas was measured as 7560 mg/m³, while in the presence of 5% CO₂ the lethal concentration decreased to 4470 mg/m³. For NO₂ gas in the absence and presence of 5% CO₂, the values of LC₅₀ were 376 mg/m³ and 169 mg/m³, respectively (Levin & Kuligowski, 2005).

Flammable furnishing and decorative materials (particularly textiles) are among the main fire hazards in buildings. Textiles, as the first ignited material, cause about 20% of fires of houses in the UK (Horrocks & Price, 2001). These textiles are responsible for about 50% of deaths in these fire events.

Toxicity index values (W_{LC50}) have been introduced as the minimum mass of fabric, in a proportionate volume of air, that produces limiting toxic concentrations of individual gases evolved at various combustions. Analyses of W_{LC50} showed that the largest toxic hazard for the majority of the fabrics investigated occurred at 550°C (emissions of CO and HCN) and at 750°C (emissions of CO₂ and NO_x). In fabrics containing flame retardants, the toxic hazard created by CO was reduced at 450°C and 550°C and increased at 750°C (Wesolek & Kozlowski, 2002). Products are ranked as very toxic, relatively toxic and moderately toxic when $W_{LC50} \leq 15$, $15 < W_{LC50} \leq 40$, and $W_{LC50} > 40$, respectively.

Liang and Ho (2007) used a toxicity index (TI) to compare the toxic products resulting from four different thermal insulation materials. TI values were then used to evaluate the combustion characteristic of the toxic gas of fibreglass, rock wool, PE foam and PU foam. Figure 9.2 reveals the TI of these building materials.

Most of the knowledge related to the behaviour of materials in fire comes from standards and product examinations. There are only a few compulsory standards that address the toxicity of fumes. While these standards classify the materials and products based on their fire properties, they usually do not include any requirement on combustion products toxicity. Most of the



9.2 Average values of toxicity index of fibreglass, rock wool, PE foam and PUR foam in Taiwan (Liang & Ho, 2007).

existing studies of fume toxicity have solely relied on data from small-scale physical fire models. It is, however, generally not straightforward to interpret such data in terms of fume composition in real-scale fires. There is generally a lack of quantitative chemical data concerning fire effluents from real-scale fires.

Carbon monoxide (CO), a major source of poisoning deaths in fire events, is colourless, tasteless, odourless and non-irritating; thus, it is hard to detect by an exposed person. When inhaled, CO is readily absorbed from the lungs into the bloodstream, where it forms COHb, a tight but slowly reversible complex with haemoglobin. The presence of COHb in the blood decreases the oxygen-carrying capacity, reducing the availability of oxygen to body tissues and resulting in tissue hypoxia. A reduction in oxygen delivery, because of the elevated COHb level, will potentially impair the cellular oxidative metabolism (Doroudiani & Omidian, 2010; Raub *et al.*, 2000).

Sulphur oxides (SO_x) are produced during the burning of wool and other sulphur-containing materials, such as S-vulcanized rubbers. SO₂ is a moderate to strong acidic irritant. Most of the inhaled SO₂ only penetrates as far as the nose and throat, with minimal amounts reaching the lungs unless the person is breathing heavily or breathing only through the mouth or the concentration of SO₂ is high. The liver metabolizes SO₂ via a molybdenum-dependent SO_x pathway. The subsequent metabolites, sulphate esters and sulphate, are eliminated through the urine (Miller, 2004).

Clinical examinations of individuals rescued from fire events have provided valuable information. Firefighters are usually exposed to various kinds of toxic fumes; therefore, useful information can be found through their clinical examination and biochemical measurements. In clinical examinations, the delay between the initial exposure to the fire fumes and the clinical examination significantly affects the results. The concentrations of most toxicants in blood decrease rapidly at the beginning and gradually level up (Zikiria *et al.*, 1976).

The degree of toxicity depends on the phase of burning of the fire, including oxidative pre-ignition, flaming combustion or fully developed combustion, and the level of the ventilation. Smoke toxicity plays an important role during fire events in buildings, where the majority of people die from smoke inhalation. Lestari *et al.* (2006) have studied an alternative method for *in vitro* fume toxicity assessment of materials using human lung cells, which can be used to screen the toxicity of materials and select the appropriate materials.

A range of building materials, including PE, PP, PC, PMMA, PVC, FRP, and melamine–plywood laminates (MPL) were examined. The results revealed that fume from PVC combustion was the most toxic, followed in toxicity by the combustion fumes from PE, PP, FRP, PC, PMMA, and MFP. Some materials exhibited more toxicity under flaming combustion (PP, PC,

and FRP), while others (PVC, PMMA, PE, and MPL) appeared to be more toxic under non-flaming combustion (Lestari *et al.*, 2011).

Research results have revealed that both styrene and styrene oxide, products of PS thermal degradation, are toxic substances (Vainio *et al.*, 1977). The effects of styrene on the variation of apoptotic proteins and gene expression in the cord blood cells were studied to understand the toxicological mechanism (Diodovich *et al.*, 2004). The findings supported the classification of styrene as a group 2B carcinogen to humans (possibly carcinogenic) by the International Agency for Research on Cancer (IARC).

Fire hazard and risk analyses establish the basis for providing useful information, including about the people who are more sensitive to fire smoke than others. In an interesting piece of research, Gann (2004) developed a method to estimate the safety conditions, to translate the database on lethal and incapacitating exposures for rats to the incapacitation of human beings. In another study, a mathematical model to estimate the chance of incapacitation and lethality from the inhalation of toxic gases was presented, comparing favourably to the combined gas and large animal data (Stuhmiller *et al.*, 2006).

Most toxic smoke fatalities are found in areas remote from the fire epicentre (Gann *et al.*, 1994). The results of the combustion examination of materials and the toxicity of the fumes are usually considered at locations immediately adjacent to the fire source. It is useful and necessary to estimate the concentrations of the gaseous fire products in areas far from the fire source. Various toxicity models to predict toxic gas concentrations within fire enclosures have been developed (Lattimer *et al.*, 2005; Hyde, 2000; Wang *et al.*, 2011a).

CO and HCN are found in the fumes of burning materials containing nitrogen, like wool, PU and polyamides. Correlations between the yields of CO and HCN resulting from the combustion of N-containing materials have been formulated, and are in good agreement with the corresponding measured data (Wang *et al.*, 2011b). The relationship is useful in fire engineering assessments of toxicity in which only one of the two species, CO or HCN, is measured in the fire experiments.

The amount of atmospheric HCl produced from the combustion of some materials tends to decay because of mixing with the fresh air and absorption by surrounding solids. A model has been developed to describe and predict the HCl decay trend (Wang *et al.*, 2007b). HCl is released from burning PVC as a dense white smoke, followed by dense soot with a very high CO content (Caldwell & Alarie, 1991). It is a much more potent and a faster incapacitating chemical than CO but less potent than HCN (Alarie, 2002).

Polymeric foams and non-woven fabrics are widely used as insulators in buildings and appliances. The toxicity of various kinds of insulation materials has been investigated (Liang & Ho, 2007). The toxicity indices of the

examined materials were found to be in the range 5.386–18.239, and ranked as PE (18.239) > PU (12.35) > rock wool (6.949) > fibreglass (5.386). It appeared that the toxicity of these materials was greater than those of the untreated wood and the organic foams, like PE and PU foams, which did not meet the requirements of the low fire hazard material. The relationships between exposure concentration, death, LT_{50} , and COHb or blood cyanide concentrations are summarized in Table 9.1 (Alarie, 2002).

The respiratory system plays a major role in injuries during fire. The system consists of upper and lower parts. The functions of the upper part, consisting of the nose, sinuses, mouth, pharynx, larynx (voice box) and trachea (windpipe), are filtering, heating, and humidifying the inhaled air (NIH, 2011; Rogers, 2010). Toxic substances are treated differently in the upper and lower parts of the respiratory system. Water-soluble toxic substances in the fume usually affect the upper respiratory tract by reacting or dissolving to form acids or bases. Some toxic substances affect the lower respiratory system by blocking the transfer of fumes or reacting to produce other corrosive and toxic agents. The lower part of the respiratory tract is mainly affected by organic agents (such as halides, monomers, phosgene and methyl cyanide), dusts (silica, asbestos) and soot produced in fire.

Table 9.1 Relationships between exposure concentration, death percentage, time at 50% death (LT_{50}), and COHb or blood cyanide concentrations

Toxicant	Exposure concentration (ppm or %)	% of animals dead within 30 min	LT_{50}	% COHb or HCN (mg/l)
CO	3000 ppm	50	26 min	65%
CO	6060 ppm	100	13 min	67%
CO	10,000 ppm	100	7 min	78%
HCN	177 ppm ^a	50	29 min	0.95 mg/l
HCN	873 ppm	100	<40 s	1.0 mg/l
O ₂	7.7% ^a	50	6 min	
CO ₂	33.8% ^a	50	19 min	
CO + O ₂	3000 ppm + 20%	50	25 min	66%
CO + O ₂	3000 ppm + 8%	100	6 min	52%
HCN + O ₂	177 ppm + 20%	50	24 min	0.95 mg/l
HCN + O ₂	177 ppm + 8%	100	2.5 min	0.10 mg/l
HCN + CO	106 ppm + 1815 ppm	50	32 min	45% + 0.56 mg/l
CO + HCN + O ₂	6060 ppm + 181 ppm + 12.2%	100	3 min	30% + 0.25 mg/l

^a LC_{50} values for these gases for a planned 30-min exposure.
Source: Alarie (2002).

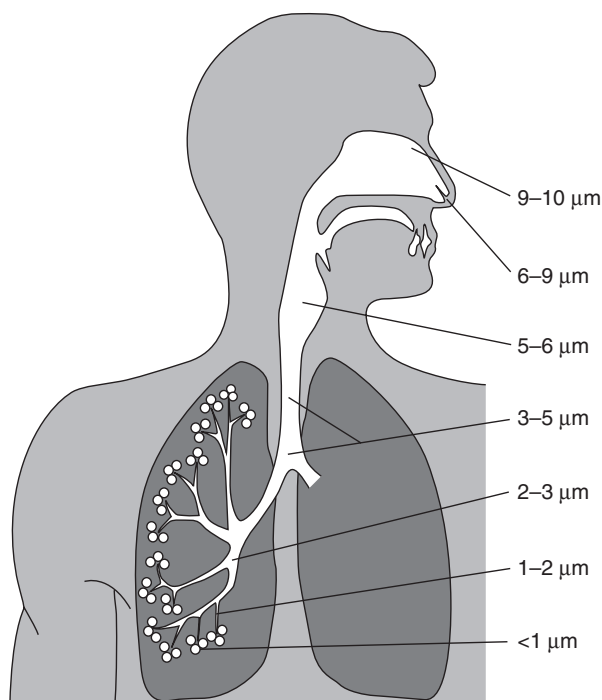
Dusts, depending on their particle size, can penetrate to different parts of the respiratory system; the smaller particles can penetrate further and deeper into the system. In general, particles larger than 5 micrometres are filtered in the upper respiratory system and smaller ones can reach bronchial and alveolar areas. The alveoli are small air sacs, consisting of small capillaries, where gas is exchanged with blood (NIH, 2011).

Van Belle *et al.* (2010) investigated the health risk of fumes emitted from burning polyamide chairs when fire broke out on a grandstand in a stadium. The authors identified HCN, CO, NO_x, NH₃, and volatile organic substances among the emitted compounds. Simulation of the fire under controlled laboratory conditions confirmed the emission of a wide variety of substances in the fume. In the simulation, the concentrations of CO and NO_x were found to be high, while emissions of HCN and NH₃ were less than expected.

The effects of toxicants on body organisms may be reversible or irreversible (Derelanko & Hollinger, 2002). They may also be local or systemic and could be immediate or delayed. Some effects, like dermatotoxicity, could be reversible and recoverable (Crowl & Louvar, 2002). Toxic substances that cause cancer, chromosome damage and birth defects are irreversible. In this regard, the chemical composition of fume is very important; therefore, when exposed to fumes, the physical state and composition of the fume should be identified.

Carson (1988) developed a method for measuring the effects of inhaling the fumes from burning plastics on the lungs. The products of burning materials in fire also include solid particles, in addition to gaseous products, which, depending on their amount and size, may carry a health risk. The maximum quantities of particles were found to come from materials that did not burn well (for example FRP, PS, PVC and flame-retarded materials), while well-burning materials, like wood, tend to fully oxidize and thus minimize the amount of particles in the fire fume (Hertzberg & Blomqvist, 2003). Very small fibrous particles resembling asbestos could be produced from underventilated combustion of composite materials. It is possible to inhale particles having a diameter of less than 10 µm; the smaller the particle, the less probable it is that the defence system of the body (nose and throat) can prevent the material from reaching deep into the lungs (Fig. 9.3).

In addition to the toxicity of the combustion products, the emotional conditions (stress) and other factors of human behaviour play a crucial role in the health effects of fire events. Studies from the World Trade Center incidents in New York in 1993 and, particularly, the 11 September 2001 disaster revealed the importance of human factors in fire events (Kobes *et al.*, 2010). Stress has a significant effect on the lethality of toxic substances of combustion fume (Larsen *et al.*, 2000).



9.3 Particle deposition in the respiratory system (Hertzberg & Blomqvist, 2003).

9.5 Remedial actions

In this section, improvements in fire safety of materials and remedial actions in terms of combustion toxicity are discussed. Minimizing use of materials with significant health risk in fire and replacing them with alternative materials, fire-resistant materials and flame-retardant additives are reviewed. Understanding the effects of various flame-retardant additives on polymer flammability and on combustion products are crucial issues that will be addressed.

Therapeutic measures of intoxication by CO and other toxic fume gases include general supportive care as well as the treatment of burns and related toxicity. Arterial blood gases, COHb and CN levels should be monitored. Patients exposed to significant concentrations of CO require hyperbaric oxygen therapy. Suspected cyanide poisoning must be treated without waiting for laboratory confirmation. Untimely or incorrect intervention may compromise the chances of survival and seriously affect the future health status of fire victims (Locatelli *et al.*, 1994).

The most efficient way to prevent polymer combustion is to design inherently fire-resistant polymers that offer high thermal stability, resistance to the spread of flame and low burning rate. The heat-resistance property of polymers can be improved by increasing the interactions between polymer chains (increasing the crystallinity and the hydrogen bonding) or by chain stiffening through inclusion of aromatic or heterocyclic structures in the polymer backbone. Polymers consisting of aromatic groups have a strong tendency to condense into chars on heating. Therefore, they produce less flammable gaseous products in a fire event. In general, polymers with high thermal stability that generate less flammable volatiles on decomposition are the most desired fire-resistant polymers (Frazer, 1968). For instance, polymers based on bisphenol-C (BPC) and dichlorodiphenylethene offer an exceptional combination of good properties, processability and extreme fire resistance (Lyon *et al.*, 2006b). Polymers with better fire resistance include the engineering thermoplastics polycarbonate, polyarylate, polysulfone and thermoset resins. Semi-inorganic fire-resistance polymers have also been produced based on polysilphenylene-siloxane and polyphosphazene elastomers, with comparable fire safety to heat-resistant engineering plastics (Lyon *et al.*, 2003).

Another strategy to slow down the combustion of polymers is to use flame-retardant additives, especially for the commodity polymers. Demands for better fire safety of buildings have led to greater interest in fire-retardant materials (Horrocks & Price, 2001). Horrocks *et al.* (2007) investigated the feasibility of creating fire-retardant PP nanocomposite fibres comprising dispersed nanoclay. In nanoclay composites of EVA, the production of CO in fire increased because of the presence of nanoclay filler. The increased yield of CO under stoichiometric conditions is attributed to the reduction in access to oxygen caused by the presence of a protective layer of nanoclay particles (Hull *et al.*, 2003). The assessments of fire hazard and fire risk of polymers containing fire retardants have been studied in detail (Hall & Bukowski, 2000). Use of fire-resistant materials in buildings delays the extension of flame and significantly decreases casualties and damage.

Polybrominated diphenyl ethers (PBDE) are used as flame retardants in polymeric materials, such as furnishing foams, rigid plastics and textiles, to make these materials less flammable. There are, however, environmental pollution concerns about PBDEs because they have the potential for environmental consequences and to remain in the environment for years (Yogui & Sericano, 2009).

Various methods are used to reduce the hazards and casualties in fire events. Positive pressure ventilation is an approach in which a fan is used to force flammable gaseous products of combustion out and to spread the fume (Beal *et al.*, 2009; Lin *et al.*, 2008). To use this method, the driving forces behind the movement of smoke in buildings, like fire-induced buoy-

ancy and expansion, wind effect and mechanical ventilation should be considered (Mowrer, 2009).

In addition to houses, fire events in large atria of airport terminals, shopping malls and railway stations occur, usually endangering large numbers of occupants. In fire events, the smoke can affect human health seriously and people may be unable to reach a safe place. On the other hand, the conventional facilities and methods used in smaller buildings, like sprinklers, usually do not work in large buildings. Computer modelling, simulation and analytical methods provide invaluable information about the smoke distribution pattern and evacuation strategy (Capote *et al.*, 2009). The spread of fire and smoke in atria has also been investigated in practice, leading to the installation of a smoke management system to keep the smoke layer at higher levels (Huo *et al.*, 2005; Chow & Chow, 2005).

In designing safer furniture, electronics and appliances in fire, both thermal resistance and fume toxicity and opacity should be considered (Shousuo, 2006; Blomqvist *et al.*, 2004). To have useful information about the behaviour of furniture in fire, it is necessary to perform full-scale burning tests on material components of the furniture (foams, wood, plastics, and wood panels). Based on the results, a fire safety ranking system can be established that would be useful for measuring the degree of fire safety of furniture.

The safety of materials used in furniture is classified based on the behaviour of various materials in different burning conditions. Shousuo (2006) recommended establishing a fire risk diagram combining key factors influencing the fire safety of furniture as a unique criterion of ranking furniture materials. The factors might be based on the thermal properties of the materials (such as ignition temperature, time to ignite, heat of combustion, heat release rate and mass loss rate) and amount and toxicity of the fumes.

Reduction of the fire risks in buildings is a very crucial issue. Fundamental understanding of the thermal decomposition and fire-resistant mechanisms of materials must be thoroughly investigated. There are still many issues that need to be addressed. Mineral fillers have been used for a long time to enhance the fire retardancy of polymers (Le Bras *et al.*, 2005). Flame-retardant chemicals significantly improve the thermal resistance of materials, increase their ignition temperature, reduce the combustion rate and decrease the amount of heat released. While most flame-retardant materials are quite non-reactive and have low toxicity, their presence in the environment could threaten their future use. The amounts of substances entering the air, water and land should be evaluated and the amount used should be reduced. While flame-retardant materials are commonly added to polymers, there are some restrictions, such as poor compatibility with the polymer, high volatility, adverse effects on the properties of the polymers, and increase of the production of CO and smoke in fire events.

Flame-retardant systems can perform either physically (by cooling, forming a protective layer or through fuel dilution) or chemically by reacting in the condensed or gas phase (Horrocks & Price, 2001). All flame retardants act either in the vapour phase or in the condensed phase through a chemical or physical mechanism to interfere with the combustion process during heating, pyrolysis, ignition, or flame spread.

Alkali earth carbonates (BeCO_3 , MgCO_3 , CaCO_3 , and BaCO_3) are widely used as polymer fillers. All of the carbonates release CO_2 at elevated temperatures to form an oxide, which can perform as a flame retardant to prevent fire extension. Carbonates decrease flammability by replacing fuel (polymer) with a non-combustible inorganic mass. Calcium carbonate is commonly used in this way as a filler in commodity plastics, such as PVC and PE (Bellayer *et al.*, 2010). Metal hydrates (like aluminium and magnesium hydroxides) are efficient and effective flame retardants in a wide range of polyolefins, EVE, and EEA applications. The relative yields of CO from the fire-retardant EVA composite samples showed very similar yields of CO under ventilated conditions to the pure EVA, but they generally yield more CO than the base polymer under the most toxic fuel-rich conditions (Hull *et al.*, 2002). Some magnesium carbonate-based substances provide effective flame retardancy in EVA and EEA (Morgan *et al.*, 2007). On exposure to fire, PVC-sheathed electrical cables containing flame-retardant intumescent smoke suppressant, did not show any surface spread of flame and production of smoke was very small (Sharma & Saxena, 2004).

PE and EVA are widely used in various applications, for example in cable sheathing. Both polymers have poor fire resistance. The use of halogen compounds as fire-retardant additives releases toxic fumes in fire events (Delfosse *et al.*, 1989). Halogen-free fire-retardant compounds containing aluminium oxide trihydrate (ATH) or magnesium hydroxide alone (McGarry *et al.*, 2000) or combined with clay nanofillers (Beyer, 2001) have been investigated as a more viable and safer alternative strategy, which protects the polymer by the formation of a layer at temperatures up to 450°C. There have been attempts to develop new fire retardants based on the esterification of melamine phosphate and pentaerythritol (Wang *et al.*, 2007a).

PP has a wide range of applications, including as a building material, because of its versatility and a good performance to cost ratio. In such applications, the occurrence of fire is very likely; therefore, it is required to be flame retarded. PP is generally used for wire sheathing and consumer electronics products. Usually, a bromide-based compound is added to PP as a flame retardant, but toxic fumes are released in the event of a fire. Some flame retardants, like metal hydroxides, degrade the properties of PP. The effects of lanthanum oxide as a synergistic agent on the flame retardancy

of intumescent flame-retardant PP composites have been investigated (Li & Xu, 2006; Li *et al.*, 2008). Effects of organo-bentonite, as a non-halogenated flame retardant, on the flame retardancy and properties of intumescent flame retardant (IFR) PP were investigated. The presence of organo-clay enhanced the flame retardancy and strength of PP/IFR composites, but larger organo-clay amounts degraded the mechanical properties (Du *et al.*, 2009).

Yu *et al.* (2010) have compared the combustibility performance of five main thermoplastics (PC, PP, HIPS, ABS and PVC) and analysed the results. They found that fire hazards of HIPS-phosphate fire retardant (PFR), PVC-non-flame retardant, ABS-brominated flame retardant (BFR) and PC/ABS-PFR were larger than hazards of PC-BFR and PP-non-halogenated flame retardant.

PC, ABS and their blends are generally used in appliances, electronics, compact discs (Chow & Han, 2004) and furniture and can be found all around buildings. PC, ABS and PC/ABS blends, like other thermoplastics, are combustible; therefore, to reduce the flammability in a fire event, flame-retarding additives are added. Commercially available flame retardants for PC are usually halogen-based and phosphorus-containing compounds, while commercially available flame retardants for ABS are mostly halogen-containing and silicon-containing substances (Lu & Hamerton, 2002). The thermal stability and flame retardancy of PC/ABS alloy have been improved by incorporation of a flame retardant containing silicon, phosphorus and nitrogen (Zhong *et al.*, 2007).

As stated in the previous section, wood is one of the most common structural materials used in buildings. Wood is combustible and there have been numerous efforts to make it inflammable. The treatment of spruce wood boards with $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Na}_2\text{S}_2\text{O}_5$ resulted in a decrease of heat release rate. The total amounts of CO and CO_2 production were reduced by this treatment and the specific extinction area and mass loss rate decreased too (Simkovic *et al.*, 2007). Wood panels, made of urea-formaldehyde as binder, are widely used in buildings and are highly combustible. It was found that the addition of fly ash to these composites, as a replacement for mineral and organic flame retarders, effectively enhances the fire resistance of particle boards (Guru *et al.*, 2009).

Coating flammable fabrics with flame-resistant materials is a viable strategy to enhance the fire safety of fabrics. PU resins are usually used as coatings for textiles in order to improve some properties, for instance water repellency. Similar to fabric, these resins are flammable, releasing highly toxic fumes in fire events. Montmorillonite clay and polyhedral oligomeric silsesquioxanes (POSS) additives have been added to the coating resin to provide flame retardancy to the coated textile structure (Devaux *et al.*, 2002).

Thermoplastic polyesters are used as insulating parts in electrical devices, where they compete with polyamides. Poly(butylene terephthalate) (PBT) is growing more rapidly than PET, mainly because of its processing advantages. Phosphorus–nitrogen containing intumescent was developed as a flame retardant of PBT to obtain halogen-free flame-retarded polyester (Gao *et al.*, 2006). Recycled PET has been flame retarded using red phosphorus combined with metallic oxides Fe_2O_3 and MgO . The use of mineral oxides in combination with red phosphorus leads to synergistic effects on fire performance (Laoutid *et al.*, 2006).

The increasing need to develop more environmentally friendly additives and to abandon halogenated additives has led to the introduction of new flame-retardant additives to minimize smoke density and toxicity of fumes in fire events. Organically modified clays have provided satisfactory fire behaviour to polyester matrices with the possibility of avoiding the addition of conventional flame-retardant additives with detrimental effects in producing toxic fumes in fire (Gianelli *et al.*, 2006).

PMMA has been flame retarded by adding phosphorus-containing compounds (Price *et al.*, 2002). The method was found to be unfavourable because of the high loadings required to achieve a sufficient level of flame retardancy. There were negative effects on the polymer's physical and mechanical properties and leaching of the flame-retardant additive. The authors recommended copolymerization of MMA with phosphorus-containing monomers as an alternative method to reduce significantly the flammability of PMMA without the potential problems related to the flame-retardant additive.

Epoxy resins offer good performance in many industrial applications, but their flammability restricts their usage in cases requiring fire resistance. Addition of flame-retardant additives may adversely affect the performance of products made of epoxy resin. It was found that mixtures of epoxy and phenolic resins provide improved fire retardancy compared with the epoxy resin alone because of the thermal stability of phenolic resin (Laza *et al.*, 2008).

Combustion of polyester resin generates dense smoke, which greatly reduces visibility. Halogenated flame-retardant additives used for polyester composites reduce flammability but increase the corrosiveness, toxicity and smoke content of the resultant combustion products. Inorganic tin compounds performed as smoke suppressants and as an effective synergist for flame retardants (Nazare *et al.*, 2008). Recently, a model was developed to predict thermal and mechanical responses of polymer composites subjected to fire (Bai *et al.*, 2010).

There is a wide variety of materials and procedures, combustible and non-combustible, for thermal insulation of buildings (Stec & Hull, 2011). Polymeric foams are used in sandwich panels as core filler and as thermal

insulator. The skins are made of composites, cement-based sheets, or metallic sheets. As was explained earlier, despite the inflammable skins, the panels are major sources of fuel to extend fire and generate huge quantities of fume and soot. Polymers commonly used as the core of sandwich composites are PVC, PS, and PU. Nanocomposites offer a potential solution to improve both the fire retardancy and mechanical performance of foams in sandwich panels (Wang & Chow, 2005).

Despite some advantages of using flame-retardant additives and methods, various risks are linked to their use. Exposure and contact of people during manufacture and use, emission of toxic gases (CO , CO_2 , NO_x , HCl , HBr , HCN and SO_2) during use or in the event of fire, in addition to the costs, are some of the concerns related to application of fire retardants (Chivas *et al.*, 2009). Therefore, in using fire retardants, all of the important factors should be thoroughly investigated. Nanocomposites could avoid the disadvantages associated with conventional fire-retardant systems, of course at a higher cost (Fu *et al.*, 2010; Beyer, 2002; Kashiwagia *et al.*, 2005).

Training in fire safety and regular emergency exercises can lead to significant reductions in casualties in the event of fire (Huseyin & Satyen, 2006), which is related to the human factor. The toxic hazards accumulate mainly in a layer just below the ceiling, including hot smoke, organic and inorganic irritants, CO , HCN , HCl and other toxicants. The occupants can minimize their effects by dropping to the floor, also minimizing hyperthermia from radiant heat from the flames, and crawling out of the room (Alarie, 2002).

9.6 Future trends for reducing toxic substances in fire and related resources

Standards and building codes play crucial roles in the regulation of building materials and enhance safety and protection conditions against fire. Researchers at Forintek Canada have compared fire losses in selected wooden buildings with losses in similar buildings made of non-combustible materials to evaluate the adequacy of building code requirements (Richardson, 2007). Based on these investigations, approximately three of every five fires in hotels, motels and care homes for the elderly could be prevented by improving housekeeping and maintenance practices and security. It was found that the type of construction has no significant effect on the safety of the occupants in hotels and motels, though the use of non-combustible materials reduced property losses in unsprinklered structures.

Adequate fire safety in the design of electrical appliances is extremely important. Some fires start from the malfunction of an electrical appliance

and extend flame to the appliance body. Therefore, in designing appliances, manufacturers must not only ensure the safety of the electrical system, but also consider the fire behaviour of the materials used in the body of the appliance (Babrauskas & Simonson, 2007).

There are a fair number of references providing information about performance of materials in fire. In addition to national standards of various countries, there are handbooks that cover the subject thoroughly and are frequently updated based on the recent findings and changes in standards and regulations. The subject of fire and combustion of materials in general has received extensive attention. Combustion is an important chemical reaction producing different chemicals and release of energy. Combustion may occur under close control in a boiler and heat-generating equipment or in uncontrolled conditions in the event of fire. Research on the debris of fire is common practice in forensic investigations. Forensic fire experts and scientists have produced a significant part of the information and knowledge about fire and combustion. There is an extensive literature on the analysis and investigation of fire debris and products from the forensic view (e.g., Stauffer *et al.*, 2007; De Haan, 2006; Quintiere, 1997).

Several research and technical service institutions around the world are involved in fire studies; only a few are named here. The Center for Fire Research at the National Institute of Standards and Technology (NIST) in the USA is involved in the measurements, standards and technology needs of buildings and fire safety, sustainable materials, innovative fire protection and disaster-resilient structures. In Canada, the fire research programme of the NRC Institute for Research in Construction develops methods and technologies for improving the fire safety design of buildings and transportation systems, enhancing fire detection and suppression systems, and reducing the risks and costs of fire. The Building and Housing Research Centre in Iran is involved in research, standards and regulations related to fire in buildings and the behaviour of materials in fire, and issues licences for fire safety of building materials. The Fire Technology Department of the SP Technical Research Institute in Sweden offers a wide range of services for evaluation and investigation of the fire performance and behaviour of materials and products, testing fire-fighting equipment and carrying out theoretical studies on the growth of fires and the spread of smoke. The Building Research Establishment's Fire Research Department (UK) is the largest set of fire research facilities in Europe, offering research, testing and technical services on all fire issues concerning buildings, infrastructure and transport.

In some universities, there are centres with activities focused on fire, such as the Center for Fire Research and Outreach of the University of California at Berkeley. The Department of Fire Protection Engineering at Worcester Polytechnic Institute (DFPE-WPI) is one of the institutions that offers a

comprehensive fire protection engineering programme, leading to Master and Doctorate degrees and other advanced certificates. Victoria University, in Melbourne, Australia is also offering comprehensive programmes in fire engineering. The Department of Fire Protection Engineering in the University of Maryland (DFPE-UM) provides advanced research, undergraduate and graduate degree programmes in fire engineering. There are useful lists of more educational, research and industrial institutions and consulting firms with their URL links at the websites of DFPE-WPI and DFPE-UM. There is useful information and literature on the websites of these institutions. Moreover, there are several journals focusing on fire in buildings or publishing articles related to the subject, which have been cited widely in this chapter.

9.7 Conclusion

Fire is a potential hazard for human life, especially in an enclosed and escape-proof area, such as in buildings. Fire in buildings consists of many different aspects of which materials comprise only one. Lightweight, high-performance polymers offer many advantages in buildings, but their inherent flammability greatly increases the fire risk. The intrinsic relationships between the structure, composition and fire behaviour of materials, and understanding the thermal decomposition and fire-resistant mechanisms of polymers, are essential issues that help to identify and design new fire-safe materials.

The current knowledge about the relationships between materials and fire is insufficient and research should be focused on fundamental studies. The present environmental regulations require the development of new environmentally friendly flame retardants to replace the halogenated ones, which are the most efficient and are used in the largest volume but release toxic and corrosive gases in fire. Some new phosphorus- or silicon-based additives have been developed as substitutes, but they are not as efficient as the halogenated flame retardants. Therefore, searching for both environmentally friendly and efficient flame retardants is still a very demanding research direction. To achieve the maximum efficiency and reduce the amount of addition, a combination of different additives needs consideration. Because various additives act in different mechanisms and have diverse effects on various polymer systems, some fundamental understanding of the flame retardancy mechanisms of these additives needs to be applied. Additionally, the mechanism of polymer crosslinking and char formation by special chemical reactions is another possible way to reduce polymer flammability.

The twin buildings of the World Trade Center could sustain and survive the impact of the airplanes on 11 September 2001, but they

collapsed because of the fire, and the majority of the victims died from incapacitation and toxication by fire fume. Review of the fire events reveals that the available information and knowledge about fire are not sufficient and generally we are not prepared to act properly and efficiently with fires.

The standards and methods of measurement and analysis of fire products and fire safety regulations are mostly at the national level of countries and currently there are no international and harmonized protocols related to fire. Better and more accurate and dynamic computer simulations of fire are needed to enable us to have a clear view about the concentrations and composition of fire fumes in various situations. These simulation programmes should provide invaluable tools to designers of buildings concerning safety in fire in order to give better protection.

Fire usually leads to a large number of casualties and damage in high-rise buildings. It is necessary to develop better technologies of fire-fighting and to perform more studies on the behaviour of occupants. It is also crucial to train occupants to behave properly in fire events and to enhance evacuation techniques and practices.

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Abstract: Lead pipes were widely used up to the mid-1980s to connect houses to the public water supply and most remain in service. A preliminary estimate is that up to 25% of houses in Europe have a lead connection pipe. Lead pipes were also used within buildings and many of these also remain in service. The lead that can dissolve from the lead pipes into the drinking water is of major health concern, particularly as lead ingestion has been demonstrated to reduce the IQ of young children. Total lead pipe replacement is the obvious solution but is hampered by high cost (as much as €200m in Europe), split ownership and a reluctance for home-owners to take action. Centralised corrosion control treatment, by pH elevation and dosing orthophosphate, offers a low-cost solution in the short to medium term. However, corrective action has been limited in many European countries because problems with lead in drinking water have been greatly underestimated due to sampling deficiencies.

Key words: lead, drinking water, health, pipe replacement, treatment, sampling.

10.1 Introduction

Lead metal has been used since Roman times as a building material, particularly for conveying water. It has also been used widely as a roofing material. Lead metal is malleable and corrodes very slowly, making it an ideal material for these applications. Unfortunately, lead is toxic, the full extent of which has been increasingly realised in the modern era since the 1970s, as outlined in Section 10.3 below. Earlier accounts of the impact of lead on human health speculate the fall of the Roman Empire being influenced by lead poisoning (Dutrizac *et al.*, 1982; Hodge, 1981; Nriagu, 1983) whereas Troesken (2006) gives an historical account of lead poisoning from lead pipes that spans the nineteenth and early twentieth centuries.

Health problems from lead roofing and guttering will be limited to occupational exposure through skin absorption and are unlikely to be much of a problem today if simple precautions are observed, particularly the use of gloves. Routine health and safety risk assessments should identify any workers at risk and lead exposure can easily be checked in blood samples.

The major issue relates to the historic use of lead pipes to supply drinking water. Lead pipes were commonly used to connect dwellings to the water main in the street, the latter being constructed of cast iron and more

recently of asbestos-cement and various plastics. Lead pipe connections (also known as service lines) had the advantage of being able to withstand localised ground movements better, such as the expansion and shrinkage of clay soils, resulting in fewer bursts and less leakage.

This chapter describes the extent of lead piping in Europe, the associated potential extent of health problems and options for control.

10.2 Use of lead in buildings and drinking water contamination

It is common for a lead connection pipe to come under joint ownership. The first part, owned by the water company or local municipality, runs from the water main to the boundary of the property. The second part (in continuity) runs from the boundary of the property to the dwelling (house or apartment building) and is normally owned by the property holder. This split ownership has legal and financial implications when lead connection pipe removal is contemplated. As lead connection pipes are buried in the ground, their presence or absence is difficult to determine. Lead piping was also used in household plumbing and will often be more conspicuous except when buried in walls.

The use of lead connection pipes and lead pipes within dwellings began with the industrial revolution of the early 1800s when industrialisation prompted urbanisation and mass housing. Despite concerns about the health hazards of lead pipes being expressed since the nineteenth century (Troesken, 2006), the installation of lead pipes continued until the mid-1980s in both Europe and North America.

The greater the length and diameter of the lead piping, the greater the risk, which depends on the surface area of the lead piping in contact with the water. Lead pipe lengths commonly vary from just a few metres to several hundred metres, depending on the connection distance and size of dwelling. The most common lead pipe internal diameter is half-inch or 12 mm and is typical for connections to individual dwellings that house a single family. For larger buildings such as apartment blocks, internal diameters are often 18 or 25 mm and sometimes 37 mm.

It is estimated (Hayes and Skubala, 2009) that up to 25% of houses could be supplied with drinking water through a lead pipe in Europe, on the basis of the early estimates shown in Table 10.1. The percentage of homes with lead pipes is known to be as high as 75% in some older cities and towns in Europe. In the US and Canada, the percentage of homes with lead service lines is estimated at between 2 and 3% (IWA, 2010a).

The amount of lead that builds up in the drinking water depends on its corrosivity and how long the water is in contact with the lead pipe; concentrations can vary from <1 to several hundred µg/l. The basic mechanism is

Table 10.1 Occurrence of lead pipes in Europe

Country	% Pb communication pipes	% Pb supply pipes or internal Pb plumbing
Belgium	19	15 to 30
Denmark	0	0
France	39	38
Germany	3	9
Greece	<1	0
Ireland	50	51
Italy	2 (?)	5 to 10
Luxembourg	7	0
Netherlands	6	8
Portugal	?	32
Spain	>3 (?)	?
UK	40	41

Source: Van den Hoven *et al.* (1999).

one of dissolution of the lead corrosion film inside the lead pipe. The corrosion film is typically dominated by lead carbonate unless phosphate-based corrosion inhibitors are in use. Particulate lead can also form if loose iron corrosion products (rust from old cast iron water mains) come into contact with the lead pipe corrosion film. A further mechanism for lead dissolution is organic chelation by natural organic matter present in the drinking water, particularly humic and fulvic acids (organic colour from peat bogs).

Particularly with corrosive waters, elevated lead in drinking water can occur, even with newer plumbing systems when no lead pipes are present, arising from brass or leaded solder. Brass alloys contain lead to improve machining characteristics and brasses with up to 8% lead have been permitted in the US since 1986, although recent legislation in the US will in the future limit the lead content of brass to 0.25%. Leaching of lead from brass to drinking water has been demonstrated (Kimbrough, 2007) and Triantafyllidou and Edwards (2011) point out that 77% of the homes in the USA (built pre-1986) could have brass plumbing components in which the lead content exceeds 8%, putting 81 million homes at risk in the USA from 'legacy leaded brass'.

Solders containing high percentages of lead were in common use for jointing copper pipes but were banned in the mid-1980s throughout Europe and North America. Galvanic corrosion of the lead in the solder can result in very high concentrations (>100 µg/l) in drinking water (Gregory, 1990), although the extent to which such effects diminish over time is largely unquantified. Water quality changes that would affect galvanic corrosion

reactions, such as changes in disinfection or oxidants, lowering of pH and significant increases in the chloride content of the drinking water relative to sulphate, have been observed (Edwards and Triantafyllidou, 2007) to aggravate lead release from 'legacy leaded solder'.

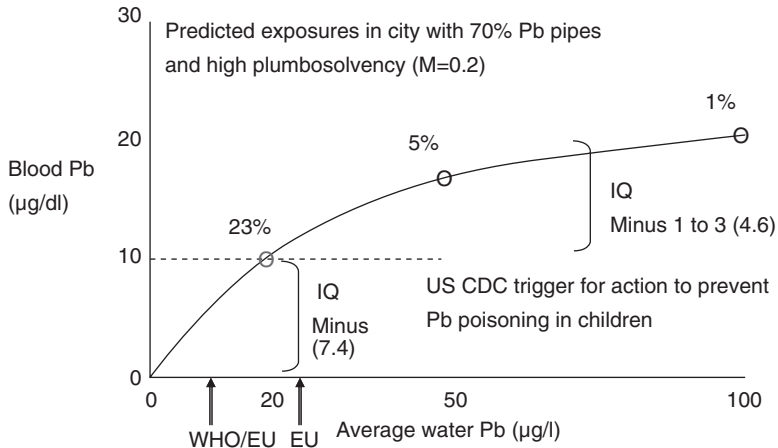
10.3 Toxicity of lead to humans

Lead is toxic to humans and lead poisoning is exhibited by a wide range of clinical conditions (Canfield *et al.*, 2003; Gump *et al.*, 2008; Jusko *et al.*, 2008; Labat *et al.*, 2006; Lanphear *et al.*, 2000, 2002; Menke *et al.*, 2006; Khalil *et al.*, 2009; Pocock *et al.*, 1994; Rabin, 2008; Tararbit *et al.*, 2009; Wilhelm and Dieter, 2003). Adverse health effects include interference with haemoglobin biosynthesis, interference with calcium and vitamin D metabolism, gastrointestinal irritation, dullness, restlessness, irritability, poor attention span, headaches, muscle tremor, abdominal cramps, kidney damage, hallucination, loss of memory, encephalopathy, hearing impairment, gonad dysfunction, and violent behaviour. Lead can accumulate in bone and fatty tissue, with subsequent release, particularly during the later stages of pregnancy. In the US for several years, the trigger for corrective action has been lead in blood above 10 µg/dl (CDC, 1991). Most attention has been directed towards the retardation of child development, especially reductions in IQ. The World Health Organization in its booklet on Childhood Lead Poisoning (WHO, 2010) has drawn attention to the following:

- Recent research indicates that lead is associated with neurobehavioural damage at blood levels of 5 µg/dl and even lower.
- There appears to be no threshold level below which lead causes no injury to the developing human brain.
- An increase in blood lead level from <1 to 10 µg/dl has been associated with an IQ loss of 6 points.
- Further IQ losses of between 2.5 and 5 points have been associated with an increase in blood level over the range 10 to 20 µg/dl.

The Joint FAO/WHO Expert Committee on Food Additives re-evaluated lead in June 2010 and withdrew the provisional tolerable weekly intake guideline value for lead on the grounds that it was inadequate to protect against IQ loss. This guideline value had been used as a basis for determining WHO's guideline value for lead in drinking water of 10 µg/l. The new WHO guidelines (WHO, 2011) retain the guideline value for lead in drinking water of 10 µg/l, but as a provisional value due to current achievability.

Environmental exposure to lead includes paint, dust, petrol in those few countries that have yet to stop using lead additives, air pollution from burning waste containing lead and lead battery recycling, in addition to lead



10.1 Pb and IQ – a risk assessment.

from drinking water (WHO, 2010). Circumstances will vary very much on a local basis; however, lead from drinking water will pose risks if lead pipes are still in service (Hayes and Hoekstra, 2010) and from lead leaching from brass and solder in some cases.

Lead in drinking water has been correlated with lead in blood in numerous studies (IWA, 2010a) in general terms. The relationship between lead in drinking water and lead in blood will vary for individuals as a function of the amounts ingested, age and body weight. On the basis of the epidemiological studies reported by Quinn and Sherlock (1990), a general curvilinear relationship applies where an average water lead concentration of around $20 \mu\text{g/l}$ equates to a blood lead level of 10 to $15 \mu\text{g/dl}$ (as illustrated in Fig. 10.1).

10.4 Assessing the risk associated with lead in drinking water

The extent of problems with lead in drinking water has been underestimated or even overlooked completely as a consequence of poor sampling or not even taking samples at all (IWA, 2010a), undermining regulatory efforts to control lead in drinking water in both Europe and North America. On the basis that lead contamination arises predominantly from domestic pipework systems (pipes and fittings), samples taken upstream from a distribution network are meaningless. The most appropriate sampling point must be where water is drawn for drinking or cooking purposes. However, samples taken from the consumer's point of use (i.e. at the tap outlet,

normally in the kitchen) after flushing the domestic pipework system are equally meaningless.

The most appropriate sampling methods for use at the consumer's tap are as follows:

1. Taking the first litre drawn from the tap without prior flushing at a random time during the day, that is random daytime (RDT) sampling, preferably from dwellings selected at random from a water supply system; this method is suitable for system-wide assessment if sufficient samples are taken to minimise reproducibility problems (Hayes, 2009; Hoekstra *et al.*, 2009; Hayes and Croft, 2011) but is not suitable for investigating lead emissions at an individual dwelling.
2. Taking the first litre drawn from the tap after flushing and a period of stagnation (normally 30 minutes); this method can be useful for tracking water treatment changes if an individual dwelling is sampled repeatedly but it is not suitable for system-wide assessment because of the variable dilution effects from water stood in non-lead pipework. Sequential sampling can help to overcome these dilution effects.
3. Taking the first litre drawn from the tap after overnight stagnation; this method is used in North America for regulatory purposes but is susceptible to variable dilution effects from water stood in non-lead pipework and to changes in the pool of dwellings used for sampling.

An advantage of methods 1 and 2 is that they are amenable logistically to the use of trained sampling personnel, as opposed to having to rely on consumers (method 3).

In Europe the current standard for lead in drinking water is 25 µg/l, dropping to 10 µg/l in December 2013, the same as the current WHO guideline value. In all cases, these standards relate to the weekly average concentration ingested. At the zonal level, RDT sampling provides an adequate basis for assessing compliance (IWA, 2010a). In the US, the lead standard is 15 µg/l based on the 90th percentile of survey samples (first draw after at least 6 hours' standing) taken from dwellings where lead service lines are present and/or leaded solder was used after 1983. Recent developments in risk assessment at the zonal level (Hayes, 2010) indicate that many water supply systems in Europe can be expected to have significant levels of non-compliance with the WHO guideline value of 10 µg/l (and EU standard from December 2013), with up to 50% dwellings affected. This extent of non-compliance is borne out by numerous case studies (IWA, 2010a) and confirms the need for widespread corrective action. Computational modelling (Van der Leer *et al.*, 2002; Hayes, 2010) can predict the extent of non-compliance with the WHO guideline value, based on the plumbosolvency of the water supply and the system's pipework characteristics, and can

predict a zonal failure profile of the extent and severity of non-compliance. This is illustrated in Fig. 10.1 for a city in which 70% of houses have a lead pipe and for high plumbosolvency water supplies. The figure shows an assumed general relationship between water lead and blood lead (from Quinn and Sherlock, 1990), and the percentage of houses where blood lead concentrations are predicted to be 10, 17 and 20 µg/dl. In this example, 23% of houses are associated with a risk condition equating to an IQ loss of 6 points and 1% of houses are associated with a risk condition equating to an IQ loss of between 8.5 and 11 points (with 5% of houses having an intermediate risk level).

The borderline nature of the current EU standard of 25 µg/l, in terms of risk reduction, is apparent and even the future EU standard of 10 µg/l (and current WHO guideline value) can be seen not to afford total risk reduction as defined by IQ loss. For the time being, the WHO guideline value of 10 µg/l should be taken as the basis for determining risk, even though it is now a provisional guideline value (WHO, 2011). In recognition of the severity of health effects in children, there is a clear need to establish the extent of compliance with the WHO guideline value, in every water supply system operated by a water company or municipality, consistent with recommendations made to the European Commission (Hoekstra *et al.*, 2008) concerning revisions to EC Directive 98/83/EC. Risks from lead in drinking water also need to be assessed in the very numerous small and very small water supplies that are often privately owned (IWA, 2010b).

Assessment tools that can help to establish the extent of risk in a water supply system are as follows (IWA, 2010a):

- Laboratory plumbosolvency testing – this can quickly determine a water's corrosivity and its response to corrosion inhibitors
- Computational modelling – this can predict the extent of non-compliance and the likely benefit of corrective options; such modelling has been validated by numerous case studies (Hayes *et al.*, 2006, 2008)
- Pipework inspections to determine the extent of occurrence of lead pipes
- Water quality surveys – RDT sampling from randomly selected dwellings should be undertaken over a sufficient period of time that includes seasonal changes
- Holistic diagnosis of water quality data with a knowledge of system operation.

Health concerns relating to lead in drinking water at individual properties can be assessed by sequential stagnation sampling (to get an indication of how much lead is present), pipework inspection and blood lead surveillance (particularly in children).

10.5 Lead pipe replacement and fittings containing lead

There are two common myths which need to be dispelled:

1. That all the lead pipes have been removed a long time ago – in truth, very few lead pipes have been removed, compared to the number likely to still be in service.
2. That the water company has removed all the lead pipes in the city – in cities like Brussels, The Hague and Vienna, the water companies have removed most or all of the lead pipes for which they had responsibility (from the water main to the boundary of the property) but they have removed very few lead pipes that are the responsibility of the home owner (IWA, 2010a).

Partial lead pipe removal by water companies does not solve the problem when, as is commonly the case, the home owners' lead service pipes and/or internal lead piping remain (DWI, 2010). Indeed, it can exacerbate the situation, at least in the short term (Renner, 2010). Where concerted efforts have been made to remove all lead pipes, home owners have mostly failed to cooperate (as in The Hague) because of the costs and inconvenience involved. Total lead pipe removal is of course the ambition, but because this is both expensive and disruptive, it will remain unrealistic until such time as legislation requires owners to make their homes lead pipe-free. One way would be to require a home to be certified lead pipe-free at the time of sale or letting. The estimated cost for total lead pipe removal at a home (IWA, 2010a) is between €1000 and €4000, equating to many tens of billions of euros at the European scale.

Because of the practical and financial constraints associated with total lead pipe removal, the most robust solution in the short to medium term for larger systems will be centralised corrective water treatment. Flushing pipework prior to drinking water use has been advocated, but recent research (Hayes and Croft, 2011) suggests that flushing would be required prior to every flow event, resulting in unacceptable increases in water consumption. The application of point-of-use filters that can remove lead from water might also be considered, particularly for very small supply systems or as an interim measure at individual dwellings.

Brass fittings containing >8% lead were used until the mid-1980s. Thereafter, lead-free brass with up to 8% lead has been permitted. As brass fittings have been in common use for many years, it follows that a very large number of homes that have a domestic pipework system will have brass fittings in service that have an appreciable lead content. It is difficult to envisage the removal of these brass fittings except under specific circumstances where lead leaching problems are considered significant. The use of

leaded solder was also permitted up to the mid-1980s to joint copper pipes. Again, a very large number of homes will still have pipework in service that was jointed by leaded solder and it is clearly impracticable to replace these pipework systems, except under specific circumstances. The implication is that all water supply systems need a corrosion control strategy to minimise these potential legacy effects. Concurrently, all countries need to move towards the use of brass with <0.25% lead (as in the US) and prohibit the use of leaded solders, using effective regulatory controls.

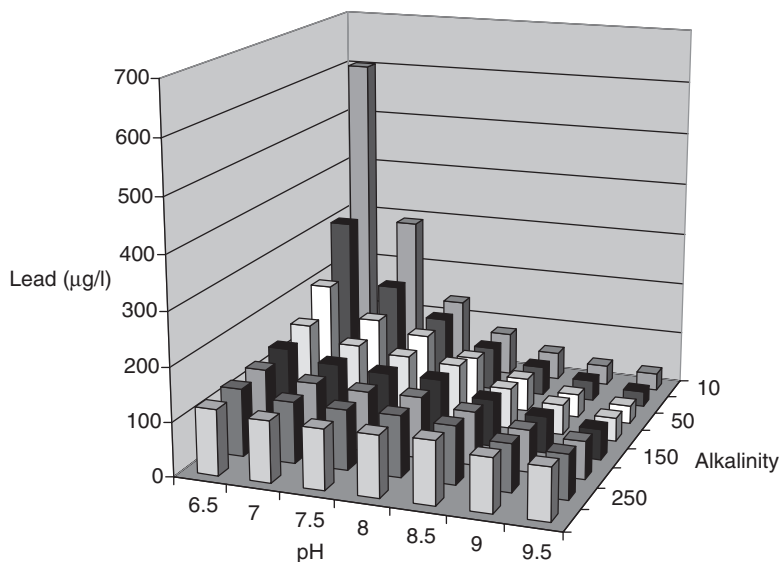
10.6 Corrective water treatment

Laboratory testing (Hayes, 2008) has indicated that *all* types of drinking water are sufficiently plumbosolvent to be capable of dissolving lead to concentrations that exceed the WHO Guideline Value of 10 µg/l when in contact with a lead pipe for 30 minutes, unless specifically treated to reduce plumbosolvency. To reduce the plumbosolvency of drinking water it is necessary to either increase pH (often to above 9.0) or add a corrosion inhibitor (orthophosphate works best) or both. Plumbosolvency reduction by treatment is widely practised in the UK, the Netherlands and the USA (and increasingly in Canada) but not elsewhere to the same extent. This means that most drinking water outside the UK, the Netherlands and North America continues to be sufficiently plumbosolvent to cause problems (as defined by the WHO Guideline Value).

Again, there are several common myths which need to be dispelled:

1. That hard water is not corrosive to lead – untrue; even groundwater can be highly plumbosolvent in relation to modern-day lead standards.
2. That with hard waters a protective calcite layer forms inside the lead pipes – at the pH conditions and cold water temperatures involved in water supply, significant calcite deposition is rarely encountered; the lead carbonate that forms inside a lead pipe is normally wafer-thin and is sufficiently soluble for lead standards to be exceeded.

The relationship between lead solubility, pH and alkalinity (Fig. 10.2) can of course be exploited and pH elevation can be successful in overcoming problems with lead in drinking water in some areas. However, particularly in areas with a high number of lead pipes, pH elevation alone may not be successful, a good example being The Hague (IWA, 2010a) where after corrective water treatment (softening and pH elevation) and the removal of most of the water company's lead pipes, 23% of random samples continued to exceed the WHO Guideline Value. In such cases, and in cases where natural organic matter is present in the drinking water, a corrosion inhibitor must be used if high levels of compliance with the WHO Guideline Value are to be achieved.



10.2 Equilibrium concentration of lead in drinking water as a function of pH and alkalinity (mg/l as CaCO₃) (from Croll, 2000).

The most successful corrosion inhibitor is orthophosphate (IWA, 2010a; Cardew, 2009). In the UK, 95% of the public water supplies are dosed with orthophosphate and after optimisation 99% of random samples in England and Wales complied in 2010 with the WHO's Guideline Value. In Scotland and Northern Ireland the level of compliance was slightly lower but improving. The UK experience clearly demonstrates that effective plumbosolvency control can be achieved by dosing orthophosphate and that childhood lead poisoning from drinking water can be considerably abated during the time it will take to remove all the lead pipes. There is no evidence that orthophosphate dosing has any health or adverse environmental consequences. It is apparent that orthophosphate dosing also reduces cuprosolvency (Comber *et al.*, 2011) and the leaching of nickel from chrome-nickel plated components (Hayes, 2011).

The unit cost of orthophosphate is about 0.2 p/m³ and NPV analysis confirms that this is a considerably lower cost option than lead pipe replacement (IWA, 2010a).

10.7 Recommendations

10.7.1 New buildings

1. Do not use lead piping under any circumstances.
2. Do not connect any new pipework to an old lead connection pipe.

3. Do not use solders containing lead for jointing copper pipes.
4. If brass fittings are used, ensure that they are lead-free with a content of lead less than 0.25%.
5. Issue a certificate that the building's pipework system is 'lead-free'.

10.7.2 Old buildings: refurbishment and management

6. If lead piping, old leaded brass fittings or old leaded solder are thought to be present (from an inspection), obtain a minimum of three sequential water samples (each of one litre) after flushing the pipework for at least 2 minutes and allowing the water to stand for at least 30 minutes. Action will be required if lead concentrations in any sample exceed 10 µg/l.
7. If a lead connection pipe is removed, take out all known lead piping up to the point of use (kitchen tap) – legal and financial responsibilities will first need to be established. Partial removal of lead connection pipes is not recommended as it is ineffectual and potentially can increase lead concentrations in the drinking water.
8. Any lead pipes or fittings with appreciable amounts of lead that are removed must be disposed of in a proper manner as hazardous waste.
9. After corrective action, a building may be certified as 'lead-free' if samples, taken as in recommendation 6, are all below 1 µg/l.

10.8 Sources of further information and advice

The Best Practice Guides published by the International Water Association (IWA, 2010a, 2010b) will provide the reader with much more detail than that given in this chapter. These are available via www.iwap.co.uk.

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Other heavy metals: antimony, cadmium, chromium and mercury

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Abstract: Building materials can be significant pollutant emission sources and can therefore be of public health importance. Transition elements, which form coloured ions, are utilized in making pigments which are used in various sections of the economy; electric lamps emit mercury, and various other household wares have been shown to consist of heavy metals other than lead. This chapter considers the heavy metals antimony, cadmium, chromium and mercury employed as building materials with respect to their history, structure, properties and uses. The biomonitoring, toxicological mechanisms and health effects of these metals as regards indoor pollution and remedial measures are discussed.

Key words: building materials, heavy metals, pollution, toxicology, public health.

11.1 Introduction

Interior building materials can be significant pollutant emission sources and can therefore affect indoor air quality (IAQ) decisively (US EPA, 1994). The emission rates and number of compounds emitted can vary by several orders of magnitude among different common interior materials, and this occurs even within the same category of materials. The recognition of this fact has resulted in a number of significant campaigns in the building design industry. The argument is that if in a building design stage, a material is known to be a significant pollutant source that requires an increased ventilation rate, it would be more economical to specify an alternative material that has a lower pollutant emission rate (CIBSE, 1996). Indeed, a high ventilation rate means increased cost of the ventilation system, and more significant energy uses in running the fans and in cooling, dehumidifying, and/or heating the ventilation air. Therefore, source control by means of interior building material selection becomes a more sensible engineering solution.

Transition elements, which form coloured ions, are utilized in making paints (pigments), which are used in various sections of the economy (Liptrot, 1984). Non-adherence to manufacturing standards, inefficient storage, handling and transportation may lead to significant introduction of metals into the environment. Determination of heavy metal levels in flaked

paints in Nigeria where there is a paucity of data and a weak or non-existent regulatory and legal framework revealed the presence of cadmium and chromium (Table 11.1) (Nduka *et al.*, 2007).

As a class of agents, toxic metals are a concern of highest priority for human exposure. The metals have a vast array of remarkably adverse effects, including those of carcinogenicity, neurotoxicity and immunotoxicity. Metals are also non-biodegradable and persist in the environment. Anthropogenic use has led to global dispersion of metals in the environment. Because of their wide distribution and extensive use in modern society, some human exposure to these metals is inevitable. Defining the mechanisms of metallic toxicity has been problematic because of the intricate nature of the interactions of metals with living systems.

There is a growing need for accurate, representative data on daily exposures of urban populations to metal concentrations in airborne particulate matter. Metals present in particulate matter have been implicated in a variety of cardio-respiratory illnesses associated with exposure to urban air pollution in recent epidemiology studies (Burnett *et al.*, 2000; Claiborn *et al.*, 2002) animal models (Vincent *et al.*, 2001) and studies involving human volunteers (Sorensen *et al.*, 2005). Some transition metals receive

Table 11.1 Cadmium and chromium levels in flaked paints in four Nigerian cities

City	Age range of building (years)	Use of building	Cd (mg/kg)	Cr (mg/kg)
Enugu	0–5	Residential	9.032 ± 0.000	1.208 ± 0.000
	6–10	Residential	8.543 ± 0.002	12.793 ± 0.002
	11 and above	Residential	10.575 ± 0.000	0.940 ± 0.000
Onitsha	0–5	Residential	8.030 ± 0.000	1.613 ± 0.002
	6–10	Residential	10.028 ± 0.002	7.988 ± 0.002
	11 and above	Church	6.845 ± 0.000	15.140 ± 0.000
Aba	0–5	Commercial	7.464 ± 0.002	15.206 ± 0.000
	6–10	Residential	9.343 ± 0.002	39.215 ± 0.000
	11 and above	Residential	7.493 ± 0.002	21.635 ± 0.000
Port Harcourt	0–5	Residential	7.293 ± 0.002	33.118 ± 0.002
	6–10	Residential	7.793 ± 0.002	55.418 ± 0.002
	11 and above	Residential	9.395 ± 0.000	40.815 ± 0.273

Source: adapted from Nduka *et al.* (2007).

particular emphasis due to linkages between oxidative stress and impaired lung function (Osonio-Vargas *et al.*, 2003).

In contrast to many organic pollutants, which are anthropogenic and often degraded in the soil, metals occur naturally and are conserved (Wade *et al.*, 1993). Due to their immutable nature, heavy metals are a group of pollutants of much concern. The danger of heavy metals is aggravated by their almost indefinite persistence in the environment. Although some metals are essential for life (i.e., they provide essential cofactors for metalloproteins and enzymes), at high concentrations they can act in a deleterious manner by blocking essential functional groups, displacing other metal ions, or modifying the active conformation of biological molecules (Collins and Stotzky, 1989). In addition, they are toxic for both higher organisms and microorganisms. In fact, many metals affect directly various physiological and biochemical processes causing reduction in growth, inhibition of photosynthesis and respiration, and degeneration of main cell organelles (Vangronsveld and Clijsters, 1994). Heavy metals cannot be destroyed biologically (no 'degradation', change in the nuclear structure of the element, occurs) but are only transformed from one oxidation state or organic complex to another. As a consequence of the alteration of its oxidation state, the metal may become either (1) more water soluble and able to be removed by leaching, (2) inherently less toxic, (3) less water soluble so that it precipitates and then becomes less bioavailable or removed from the contaminated site, or (4) volatilized and removed from the polluted area (Garbisu and Alkorta, 1997).

This chapter considers the heavy metals antimony, cadmium, chromium and mercury employed as building materials with respect to their structure, properties, uses and human toxicological implications. Remedial measures to mitigate the potential toxic effects of these metals and suggestions for alternative measures and future trends are also highlighted.

Human biomonitoring is an important tool in environmental medicine to assess and evaluate the level of internal exposure of the general population, population groups and individuals to environmental pollutants. Biomonitoring has been used to evaluate exposure and risks for various environmental pollutants by means of biomarkers of exposure (internal dose) and biomarkers of effects. The project of biological monitoring includes the monitoring of toxic substances (traces elements or heavy metals). Cadmium, mercury and some other heavy metals occur naturally, but most human exposure occurs as a consequence of human activities. Mounting awareness and concern about environmental pollutants and their adverse health effects have led to an increase in measures to protect the public from avoidable exposures. The level of toxic metals in human tissues may represent an important indicator of the health status.

11.2 Antimony

11.2.1 History and uses of antimony

Antimony is a fascinating element that has been used by human cultures since the Early Bronze Age. Excavations at Tello in Ancient Chaldea found fragments of an antimony base that dates back to 4000 BC. Antimony is an element present in relatively small concentrations in the earth's crust. It is rarely found in pure form in nature, a fact recognized since antiquity. This may be the source of the name, which comes from the Greek words 'anti' (not) and 'monos' (alone). Antimony compounds are found in several types of ore and in petroleum. Although not used in large quantities, antimony is used extensively for many purposes, including being alloyed with a number of metals to improve their properties. Antimony (Sb) and its compounds are mainly used for the production of alloys, flame retardants, and in the glass industry. Antimony has been a constituent not only of printing-metal but also of lead acid batteries, pigments, an opacifier under glazes and enamels (the white oxide), and in the present day it has been used widely as a flame retardant in fabrics and in brake linings of motor cars. The most significant use of antimony is the production of antimony trioxide for flame retardation (ATSDR, 1992; Buttermann and Carlin, 2004).

Antimony trioxide (+3 antimony), a white powder, is the single most important economic form, used primarily as a fire retardant. It is a stable substance that is not volatile and dissolves in water slightly. According to Buttermann and Carlin (2004), 'More than one-half of the primary antimony consumed goes into flame retardants. The remainder is used principally in glass for television picture tubes and computer monitors, and in ammunition, cable covering, friction bearings, lead-acid (LA) batteries, and solders. It is used in the same applications worldwide, but its distribution among applications differs from country to country.' Antimony trioxide is also used in the manufacturing of ceramics and in glassware to remove bubbles and stabilize colour (ATSDR, 1992). The oxychloride ($\text{Sb}_6\text{O}_6\text{Cl}_{14}$) has wide applications as a flame retardant in which the reaction with Hd and OHd radicals reduces the rate of flame propagation so that the treated material will smoulder rather than burst into flames. Other uses are in semiconductors, pewter, Babbitt metal, and as pigments in paints and lacquers, glass and pottery. Modern use of antimony chloride as a flame retardant means that antimony may be present in domestic and other fabrics in the home, and in conveyor belting in workplaces. Antimony compounds are used as fire-retardants, in an attempt to meet the requirements of legislation designed to reduce the fire risk of furniture and furnishings. Antimony compounds added to fabrics have the property of

Table 11.2 History, uses and properties of antimony**History of antimony**

Dates back to antiquity and used by many ancient peoples. First reported scientifically by Tholden in 1450

Associated use of antimony as building material

Flame-proofing compounds

Paint

Ceramic products

Properties of antimony

Name of element: Antimony

Symbol of element: Sb

Atomic number of antimony: 51

Atomic mass: 121.76 amu

Melting point: 630.0°C (903.15 K)

Boiling point: 1750.0°C (2023.15 K)

Number of protons/electrons in antimony: 51

Number of neutrons in antimony: 71

Crystal structure: rhombohedral

Density at 293 K: 6.684 g/cm³

Colour of antimony: silver-white, bluish

restraining the spread of fire so that they smoulder and do not burst into flames.

Table 11.2 summarizes the history, uses and properties of antimony.

11.2.2 Structure and properties of antimony

Antimony is a metalloid residing in the fourth row of group 15A in the periodic table between arsenic and bismuth. It has four oxidation states: Sb(−3), (0), (+3), (+5) and two stable isotopes of atomic weights 121 (57%) and 123 (43%). Antimony in its elemental form is a silvery white, brittle, fusible, crystalline solid that exhibits poor electrical and heat conductivity properties and can sublime upon heating. A metalloid, antimony resembles a metal in its appearance and in many of its physical properties, but does not chemically react as a metal. It is also attacked by oxidizing acids and halogens (CRC, 1989). Metallic antimony is insoluble and inert at room temperature, but can burn when heated, forming white fumes of Sb₂O₃. Antimony compounds are soluble in very strong acid and basic solutions; under neutral conditions the predominant species is Sb(OH)₆ for pentavalent forms and Sb(OH)₃ for trivalent forms. Antimony is not readily convertible between its two cationic forms under neutral conditions (ATSDR, 1992).

Antimony is geochemically found in the common ore stibnite, which is primarily Sb₂S₃. The substance has been used since antiquity as a cosmetic

to darken eyebrows. In ancient Egypt it was called 'mšdmṯ' (variant mes-demēt) which is derived from the Coptic CTDM [stem].

11.2.3 Toxicology of antimony

Antimony is a common contaminant of the atmosphere particularly in industrialized societies, largely because of its widespread presence in the surface of the earth, and to this is added contamination with the element from domestic use or from the neighbourhood of factories. Antimony is potentially toxic at very low concentrations and has no known biological functions (Smichowski, 2008). Elemental Sb is more toxic than its salts and inorganic species of Sb are more toxic than the organic ones. Sb(III) compounds are about 10 times more toxic than Sb(V) species. The International Agency for Research on Cancer (IARC) has reported that there is sufficient evidence for the carcinogenicity of antimony trioxide in experimental animals (IARC, <http://www.inchem.org/documents/iarc/vol47/47-11.html>). On the other hand, the US Environmental Protection Agency and the German Research Community have listed Sb as a priority pollutant but it has not been classified for carcinogenicity (US EPA, 1999; DFG, 1994). There is evidence that Sb is not detoxified via methylation in mammals, but the mechanism responsible for antimony's genotoxicity is not clearly known. Daily intake of inhaled Sb from ambient air is approximately 0.6 µg assuming a volume of 20 m³ of air to be inhaled daily on average (Patriarca *et al.*, 2000). Absorption from the lungs is on average ~15% depending on the size of the particles and the solubility of the specific Sb compounds. Children below five years of age have a higher air intake per unit and may absorb a higher percentage of inhaled metals (Patriarca *et al.*, 2000).

Prior to the mid-1990s there was little evidence for microbial methylation of antimony (Craig, 1986). However, this possibility became of interest when a possible cause for sudden infant death syndrome (SIDS) (also known as cot death) was suggested (Richardson, 1994). The hypothesis was that flame retardants in mattresses and covers might undergo methylation to toxic gases by the action of *S. brevicaulis* or other microorganisms. Since one flame retardant was antimony, trimethylstibine might have been produced. It was claimed that *S. brevicaulis* had actually been isolated from damp crib mattresses. The hypothesis was vociferously supported by some groups, and there were accusations of a cover-up of important facts by 'authorities' (Sprott, 1996). Later work indicated that the predominant organism isolated from crib mattresses was not *S. brevicaulis* but a mix of common environmental *Bacillus* spp. (Warnock *et al.*, 1995). A very detailed re-examination of old evidence and consideration of new information, carried out by an independent advisory committee for the British Department of Health, found no justification for the toxic-gas hypothesis

(Lady Limerick, final report to British Government Department of Health, 1998, www.doh.gov.uk/limerch.htm).

The non-microbial leaching of antimony (as Sb_2O_3) from polyvinylchloride crib mattresses could account for the high variability associated with antimony levels in livers for both SIDS victims and other infants and for the elevated Sb levels in the hair of some healthy infants (Jenkins *et al.*, 1998). The polyurethane inner foam of crib mattresses might be a site for toxic gas formation of group 15 elements, but determination of the level of Sb in crib mattress foam showed no correlation with the occurrence of SIDS. No volatile forms were detected in the headspace of mixed or mono-septic cultures of anaerobes containing polyurethane foams. There was no evidence for a causal relationship between levels of trimethylantimony or total trimethylantimony forms and SIDS (Jenkins *et al.*, 2000).

Antimony produces an irritating skin rash affecting the trunk and limbs which is worse in warm weather and has been a major nuisance in process workers but quickly resolves on ceasing exposure for a few days. These so-called 'antimony spots' have been known for many years and have been likened to smallpox in appearance. They are symptomatic of excessive exposure to dirty working conditions and the remedy lies in controlling the dustiness of the process (Stevenson, 1965). Antimony workers have been considered prone to cardiac disease (Brieger *et al.*, 1954). While it appears that when antimony compounds are given therapeutically, in schistosomiasis or leishmaniasis, there is a risk of toxic action on the heart, the evidence for heart disease from human exposure to antimony is not sustainable, and the findings of this study have not been confirmed.

Pneumoconiosis has been described in antimony miners (Karajovic, 1958; Klucik *et al.*, 1962) although the observation was compounded by simultaneous silicosis. Antimony has been found in the lungs of process workers at very high levels with a long retention period. Lung cancer has also been associated with antimony exposure, especially due to occupational exposure. Animal experiments seem to confirm the carcinogenicity of antimony, but the quality of the investigations and the findings of animal exposures have been questioned. In studies of antimony as a trace element in the lung by neutron activation, small amounts of antimony were found in neoplastic tissue but did not increase with time, and there were no statistically significant differences in quantity between those with and without lung cancer (Kennedy *et al.*, 1962).

11.2.4 Biomonitoring of antimony

In a study carried out by Komaromy-Hiller and coworkers 96% of random and 82% of 24-h urinary data of antimony were below the detection limits of their study (Komaromy-Hiller *et al.*, 2000) (Table 11.3). The highest

Table 11.3 Representative samples of urinary antimony, cadmium, chromium and mercury

Analyte	n	Central 95% after exclusion of top 10%	Mean	SD	Median	X ± 2 × SD	
Sb	µg/l	1527	0–0	0	0	0	0–0
	µg/day	67	n/a	0	0	0	0–0
	µg/g CRT	1527	0–0	0	0	0	0–0
Cd	µg/l	6008	0–1.0	0.37	0.34	0.3	0–0.
	µg/day	2005	0–2.1	0.66	0.62	0.6	0–1.9
	µg/g CRT	4224	0–1.4	0.41	0.42	0.3	0–1.2
Cr	µg/l	1045	0–3.5	1.2	1.4	1.0	0–4.1
	µg/day	439	0.5–6.7	3.1	2.2	2.6	0–7.5
	µg/g CRT	632	0.3–4.5	1.9	1.3	1.5	0–4.5
Hg	µg/l	2197	0–7.0	1.4	1.8	1.0	0–5.0
	µg/day	1529	0–13.6	2.1	3.1	1.0	0–8.3
	µg/g CRT	2196	0–8.1	1.5	2.1	0.8	0–5.8

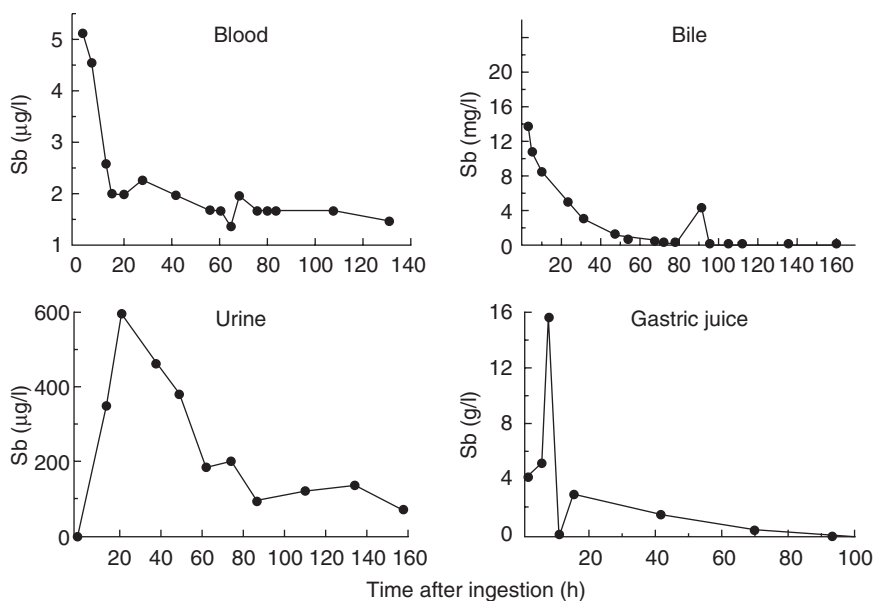
Source: adapted from Komaromy-Hiller *et al.* (2000).

measured result was 48 µg/l corresponding to 64.9 µg/gCRT. Reference values for urinary antimony from the literature are in general less than 2 µg/l (0.19–1.1 µg/l (Minoia *et al.*, 1990), 1 µg/l (Dezateux *et al.*, 1997), or 1.23 µg/l median (Gebel *et al.*, 1998)). However, a much higher toxic cutoff limit was recommended in another publication, 10 µg/l (Tietz, 1995).

The major metabolic pathway of Sb is oxidation in humans and methylation to a minor extent. Sb(III) is known to have 10 times higher toxicity than Sb(V) (Ogra, 2009).

Regardless of the route of administration, 45–55% of antimony will be excreted within the first four days (most being eliminated on the first day). After intravenous administration of Sb about the same percentage of the administered dose was excreted in the urine and faeces, whereas after intraperitoneal administration, about four times more Sb was excreted in the faeces than in the urine (Bailly *et al.*, 1991). It is mainly excreted in bile and in urine. In bile the metal is combined with glutathione, the hepatic concentration of which may modulate the relative importance of these excretion routes. The Sb excreted in bile is partly reabsorbed in the intestine. Hematuria, dermatitis, nausea, vomiting, diarrhea, pharyngitis, and nephrotoxicity have been reported to be the clinical features of Sb toxicosis (McCallum, 2005).

The concentration of Sb in whole blood, urine, bile, and gastric fluid from an adult woman who had attempted to commit suicide by ingestion of an



11.1 Evolution of antimony concentration in various biological fluids (adapted from Bailly *et al.*, 1991).

unknown amount of Sb_2S_3 was followed up for 160 hours. Figure 11.1 illustrates the evolution of the concentration of Sb in the various biological fluids. In bile and in gastric fluid, Sb is not detectable 100 hours after the ingestion, whereas in blood and in urine, the concentration is above the normal value (blood $> 0.1 \text{ pg}/100 \text{ ml}$; urine $> 1 \text{ pg/g creatinine}$) one week after the ingestion.

Unanticipated increases in urinary antimony during infernos on buildings are associated with exposure (Edelman *et al.*, 2003). Antimony in plastics is an integral part of fire retardant formulations (Einhorn, 1975; Landrock, 1983; Liepins and Pearce, 1976) as a charring agent, and acts with halogenated hydrocarbons to suppress fire. Plastics may have 7–30% antimony by weight. Combustion of plastics or particulate dusts containing antimony from the building collapse probably explains the increase in exposed fire-fighters. Although antimony concentrations were significantly higher in fire-fighters present during the collapse of the World Trade Center, and in Special Operations Command firefighters, they were well below recommendations for maximum exposure guidelines for workplace antimony exposures (35 $\mu\text{g/g creatinine}$) or the general population (3 $\mu\text{g/g creatinine}$) (Lauwerys and Hoet, 2001) and were less than reported industrial exposures (Kentner *et al.*, 1995; Ludersdorf *et al.*, 1987).

11.3 Cadmium

11.3.1 History and uses of cadmium

The use of cadmium has a short history. It was discovered in the nineteenth century, but the amounts used before the Second World War were limited. The major uses of cadmium have been rechargeable nickel–cadmium (Ni–Cd) batteries, pigments, stabilizers in polyvinylchloride plastics and protective plating for metals. The metal industry, the mining of zinc and lead ores and the manufacturing of phosphorus fertilizers have been the dominant sources of industrial cadmium emissions to the environment. In summary cadmium has five principal uses: (1) in pigments, (2) in stabilizers, (3) in Ni–Cd batteries, (4) as protective plating on steel, and (5) in various alloys (Bergbäck *et al.*, 1994).

Cadmium is a rare element. Estimates of its abundance in the earth's crust range from 0.1 to 0.2 ppm, making it the 67th element in order of abundance (Bewers *et al.*, 1987). Because there are no separate ores of cadmium, at least none of commercial importance, cadmium is produced exclusively as a by-product, mainly in the recovery of primary zinc from its ores, from zinc-bearing lead ores, or in the processing of secondary materials, e.g. scrap metal.

Table 11.4 summarizes the history, uses and properties of cadmium.

Table 11.4 History, uses and properties of cadmium

History of cadmium

Discovered in Germany by Fredrich Stromeyer in 1817

Associated use of cadmium as building material

Pigments

Chemical stabilizers

Nickel-cadmium batteries

Coatings and platings

Properties of cadmium

Name of element: Cadmium

Symbol of element: Cd

Atomic number of cadmium: 48

Atomic mass: 112.411 amu

Melting point: 320.9°C (594.05 K)

Boiling point: 765.0°C (1038.15 K)

Number of protons/electrons in cadmium: 48

Number of neutrons in cadmium: 64

Crystal structure: hexagonal

Density at 293 K: 8.65 g/cm³

Colour of cadmium: bluish-white

Common oxidative states: +2

11.3.2 Structure and properties of cadmium

Cadmium is the 48th element and a member of group 12 in the periodic table of elements. The most common oxidation number of cadmium is +2. About 13,000 tons of cadmium is produced yearly worldwide, mainly for nickel–cadmium batteries, pigments, chemical stabilizers, metal coatings and alloys.

Cadmium is a silver-white metal which is ductile and easily worked; it can be rolled into sheets and drawn into wire and it is easily soldered. Cadmium appears naturally as Cd^{2+} , often in complexes with inorganic (e.g. Cl^- , F^-) or organic ligands. In soil, the solubility of CdCO_3 and possibly $\text{Cd}_3(\text{PO}_4)_2$ controls cadmium mobility (Kabata-Pendias and Pendias, 1984). However, the solubility of cadmium is highly dependent on the pH and in acidic soils cadmium is one of the most mobile of heavy metals.

11.3.3 Toxicology of cadmium

The main route of exposure is through the lungs. Soluble cadmium salts accumulate and result in multi-organ toxicity, namely in the kidney, liver, lungs, brain, testes, heart, and central nervous system. Cadmium is listed by the US Environmental Protection Agency as one of 126 priority pollutants. The most dangerous characteristic of cadmium is that it accumulates throughout a lifetime. Cadmium accumulates mostly in the liver and kidney and has a long biological half-life of 17 to 30 years in humans (Hideaki *et al.*, 2008). Cadmium can cause osteoporosis, anaemia, non-hypertrophic emphysema, irreversible renal tubular injury, eosinophilia, anosmia and chronic rhinitis. Cadmium is a potent human carcinogen and has been associated with cancers of the lung, prostate, pancreas, and kidney. Because of its carcinogenic properties, cadmium has been classified as a #1 category human carcinogen by the International Agency for Research on Cancer (IARC, 1993).

Unlike other heavy metals, cadmium does not generate free radicals by itself; however, reports have indicated superoxide radical, hydroxyl radical and nitric oxide radicals could be generated indirectly (Galan *et al.*, 2001). Watanabe *et al.* (2003) demonstrated generation of non-radical hydrogen peroxide which by itself became a significant source of free radicals via Fenton chemistry. Cadmium could replace iron and copper from a number of cytoplasmic and membrane proteins like ferritin, which in turn would release and increase the concentration of unbound iron or copper ions. These free ions participate in causing oxidative stress via the Fenton reactions (Casalino *et al.*, 1997; Waisberg *et al.*, 2003). Watjen and Beyersmann showed evidence in support of the proposed mechanism. They showed that copper and iron ions displaced by cadmium were able to catalyse the

breakdown of hydrogen peroxide via the Fenton reaction (Watjen and Beyersmann, 2004).

Casalino *et al.* (2002) suggested that cadmium binds to the imidazole group of the His-74 in superoxide dismutase SOD which is vital for the breakdown of hydrogen peroxide, thus causing its toxic effects. Cadmium inhibition of liver mitochondrial MnSOD activity was completely removed by Mn(II) ions, suggesting that the reduced effectiveness of this enzyme is probably due to the substitution of cadmium for manganese. These workers also observed antioxidant capacity of Mn(II) ions, since they normalize the increased TBARS levels occurring when liver mitochondria were exposed to cadmium.

Numerous reports in animal models have depicted that cadmium intoxication significantly increased the malondialdehyde (MDA) and glutathione peroxidase (GSH-Px) (Yang *et al.*, 2003; Cosic *et al.*, 2007). Free radicals generated by cadmium were scavenged by GSH directly or via the GSH peroxidase/GSH system. Acute intoxication of animals with cadmium has shown increased activity of antioxidant defence enzymes like copper–zinc containing superoxide dismutase, catalase, glutathione peroxidase, glutathione reductase and glutathione-S-transferase (Ognjanovic *et al.*, 2003).

Beside oxidative stress-mediated toxicity, cadmium is also known to cause its deleterious effect by deactivating DNA repair activity (McMurray and Tainer, 2003). Although a number of mechanisms exist to prevent DNA mismatch such as direct damage reversal, base excision repair, nucleotide excision repair, double strand break repair and mismatch repair (MMR), cadmium inhibits only the MMR mode of repair. Jin *et al.* have shown that cadmium-induced inhibition of MMR in human extracts leaves about 20–50% of DNA mismatch unrepaired (Jin *et al.*, 2003). Inhibition of MMR leads to the propagation of cellular errors, thus the toxic effects of cadmium can be amplified in cells by creating mutations in genes that induce further faulty functions. Studies have also shown that the number of cells with DNA single strand breaks and the levels of cellular DNA damage were significantly higher in cadmium-exposed animals.

Reports have shown that antioxidants like vitamin C and Vitamin E have shown protection against cadmium-induced toxicity in different animal models (Ognjanovic *et al.*, 2003; Beytut *et al.*, 2003).

11.3.4 Biomonitoring of cadmium

According to the IARC, cadmium and cadmium compounds are classified as class 1 human carcinogens. Besides that, Cd may affect renal function (Kjellstrom *et al.*, 1977). For biological monitoring, blood, and urine cadmium levels are used. Blood cadmium generally reflects current exposure and the levels are usually between 0.2 and 0.8 pg/l (0.0018–0.007 pmol/l).

Considerably higher concentrations (1.4–4.5 µg/l, i.e. 0.012–0.04 pmol/l) are observed in smokers (Elinder *et al.*, 1994). According to McKelvey *et al.* (2007), crude weighted geometric blood cadmium concentrations range from 0.73–0.79 µg/l in males and 0.76–0.82 µg/l in females with means of 0.76 and 0.79 µg/l (95% CI) respectively. This data, which was obtained in a US population, showed that Asian non-Hispanic subjects had the highest mean blood cadmium level of 0.99 µg/l (95% CI).

In the study by Komaromy-Hiller and coworkers (Table 11.3), the pattern of urinary cadmium was shown to follow a lognormal distribution. A second group of individuals forming a second peak at higher concentration correspond to those with significant cadmium exposure. Their representative values for urinary cadmium agreed well with the results from two European study groups (0.38–1.34 µg/l (Minoia *et al.*, 1990); 0.05–1.24 µg/l and 0.05–1.23 µg/g CRT (White and Sabbioni, 1998)) but were between some previously published results (0.5–4.7 µg/l (Iyengar and Woittiez, 1988); 0.59–0.77 µg/l (Kowal *et al.*, 1979)). The 24-h urinary excretion of cadmium is a biomarker of lifetime exposure, while the concentrations of cadmium in blood reflect more recent exposure (Staessen *et al.*, 1996).

11.4 Chromium

11.4.1 History and uses of chromium

Chromium is a critical metal used in dozens of products that we rely on every day, but it is seldom used alone. The most common application is in metallurgical end uses in alloys, consuming 90% of virgin chromium. The addition of chromium adds corrosion and oxidation resistance to metals, making steel ‘stainless’. While other alloying elements, such as nickel and molybdenum, may also be added, chromium is an essential ingredient and no suitable substitute is known. Corrosion resistance extends the life of products, allows industrial activities to occur in harsh environments and with harsh chemicals, and reduces replacement costs.

On a worldwide basis, about 80% of the chromium mined goes into metallurgical applications. Much of this goes into the manufacture of stainless steel. About 15% is used in chromium chemicals manufacture and the remainder is used in refractory applications. In nearly all of these uses, the chemical properties of chromium are integral to its effectiveness. In metallurgical applications, the physical properties that chromium imparts to alloys are a major factor in its selection. However, in addition, the corrosion-resistant properties that are provided by chromium are usually essential. Indeed, chromium is what makes stainless steel ‘stainless’. In refractory applications, the inert nature of trivalent chromium oxide, either by itself or in combination with other refractory oxides such as those of iron,

Table 11.5 History, uses and properties of chromium

History of chromium

Discovered by Louis Vauquelin in 1797. A lead chromate named Siberian Red
Lead was found by Johann Gottlob Lehmann in 1761

Associated use of chromium as building material

Dyes and paints
Stainless steel
Metallurgy
Chrome plating
Green rouge metal polish

Properties of chromium

Name of element: Chromium
Symbol of element: Cr
Atomic number of chromium: 24
Atomic mass: 51.9961 amu
Melting point: 1857.0°C (2130.15 K)
Boiling point: 2672.0°C (2945.15 K)
Number of protons/electrons in chromium: 24
Number of neutrons in chromium: 28
Crystal structure: cubic
Density at 293 K: 7.19 g/cm³
Colour of chromium: steel-grey
Common oxidative states: +6, +3, 0

aluminium and magnesium, is the reason it is used in the most severe applications.

In addition to metallurgical uses, chromium is also used in refractoriness and foundry sands for its heat resistance, and in chemicals for leather tanning, pigmentation and wood preservation (Johnson *et al.*, 2006). Copper chrome arsenic (CCA) wood preservatives contain arsenic pentoxide, hexavalent chromium (chromium trioxide or sodium dichromate) and copper(II) oxide or copper(II) sulphate. They are supplied as pastes or water-based concentrates that are diluted to between 1 and 10% w/w total salts and used in the industrial vacuum-pressure impregnation of timber. These products are used as a wood preservative to prevent fungal decay and infestations by wood-boring insects (Cocker *et al.*, 2006).

Table 11.5 summarizes the history, uses and properties of chromium.

11.4.2 Structure and properties of chromium

Chromium and its compounds have a long history of industrial uses in the manufacture of a large number of high-volume products, such as stainless steel and pressure-treated wood. Occupational exposure to chromium is found among about half a million industrial workers in the US and several

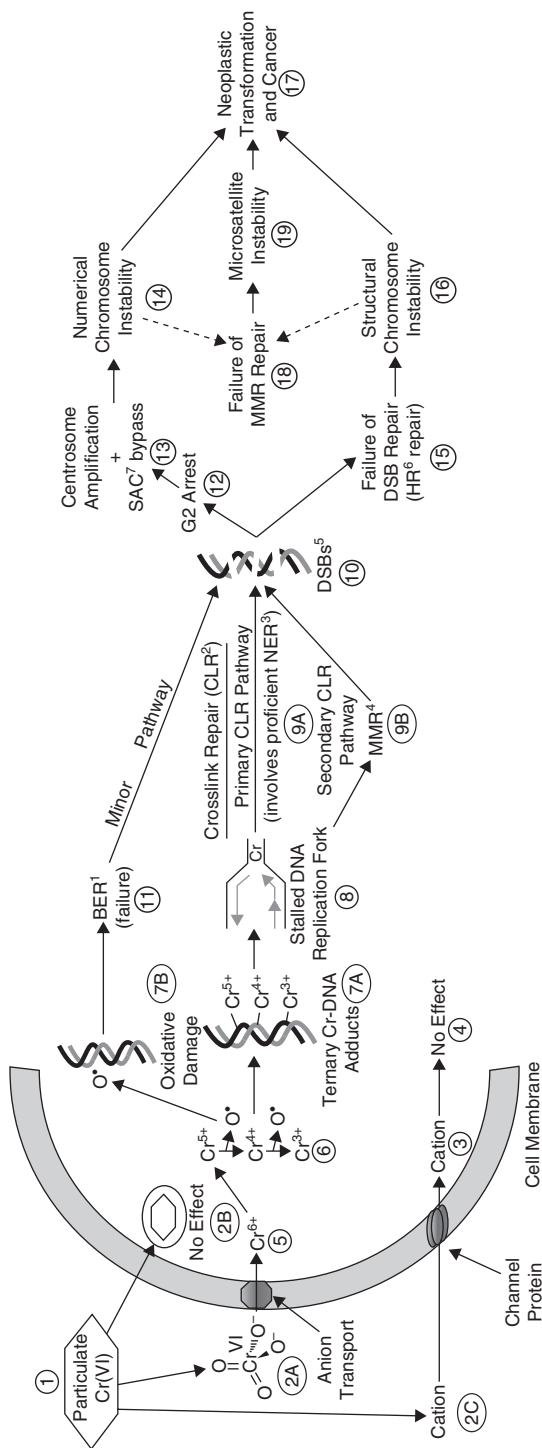
million worldwide (Zhitkovich, 2002; OSHA, 2006). Environmental exposure likely impacts dozens of millions of people drinking Cr-containing water, residing in the vicinity of numerous toxic sites and chemical manufactures and other industrial users. Although chromium can exist in several valence states, the most commonly encountered products contain this metal in the +6, +3 and 0 oxidative forms (Zhitkovich, 2005). Cr(0) is usually present in its metallic form, which typically occurs in alloys with other metals, particularly Fe and Co. Welding and other strongly oxidizing conditions convert chromium(0) to chromium(III) and chromium(VI). Chromium(III) is thermodynamically stable and is the final oxidative form found in all biological systems. Depending on the nature of the counterion, the solubility of Cr(VI) compounds varies from very high (salts with alkali metals) to moderate (salts of Ca, Mg, Sr, Zn) to very low (barium and lead salts).

Exposure to hexavalent chromium, Cr(VI), is associated with a wide range of toxic effects (Whiting *et al.*, 1979; Costa *et al.*, 1996). The greatest human exposures are from industrial uses, including chromate pigments, zinc chromate primer paints and other corrosion inhibitors, stainless steel machining and welding, chrome plating, leather tanning, and others.

11.4.3 Toxicology of chromium

Significant attention has been paid to the adverse health effects of chromium, which are highly dependent on oxidation state. There is sufficient evidence to demonstrate carcinogenicity in humans of hexavalent chromium in the chromate, chromate pigment, and chromium plating industries; limited evidence for carcinogenicity of chromic acid and sodium dichromate; and inadequate evidence for metallic and trivalent compounds (IARC, 1990a). Effects of hexavalent chromium exposure include respiratory cancer, kidney damage, and skin irritation (Fig. 11.2). The highest exposure to Cr(VI) occurs in chromate manufacturing, chrome plating, ferrochrome production and stainless steel welding. Welders employed in construction and small car repair shops are at particular risk of heavy exposure because of the absence or practical difficulties in the installation of exhaust systems removing Cr(VI)-containing fumes from the breathing area.

Exposure to Cr(VI) compounds, but not other oxidative forms of Cr, is a well-documented cause of respiratory cancers (IARC, 1990; Langard, 1990; Gibb *et al.*, 2000). Cr(VI)-associated neoplasms are typically located in the lung, but risk of nasal cancers is also significantly increased (Davies *et al.*, 1991; Satoh *et al.*, 1994; Sunderman, 2001). Contrary to some very optimistic views that Cr(VI) carcinogenesis is caused only by massive exposures and therefore is no longer a concern (De Flora, 2000), recent epidemiological and risk assessment studies have actually found as much as 25%



11.2 Proposed mechanism of Cr (VI)-induced carcinogenesis (adapted from Holmes *et al.*, 2008).

Particulate Cr(VI) (1) partially dissolves outside the cell producing a chromate anion (2A) and a cation (2C). The cation enters into the cell through a channel protein (3, 4) and intact particles are phagocytosed into the cell (2B). Both appear to have no adverse effect on the cell. The chromate anion enters the cell through an anion transporter (5) and is rapidly reduced to Cr(III) generating Cr(V), Cr(IV) and reactive oxygen species in the process (6). Cr(III) and possibly Cr(V) and Cr(IV) form ternary Cr-DNA adducts (7A) leading to a stalled DNA replication fork (8). These ternary adducts can be repaired by crosslink repair involving nucleotide excision repair (9A) or mismatch repair (9B) or possibly both. Both pathways cause a DNA double strand break during the repair process (10). The failure of base excision repair to repair oxidative damage could also contribute to DNA double strand break formation, but this is likely to be a minor component as it requires failure of repair (7B, 11). These DNA double strand breaks induce a prolonged G2 arrest (12) leading to both centrosome amplification and spindle assembly checkpoint bypass (13). These both lead to numerical chromosome instability (14) and ultimately neoplastic transformation and cancer (17). The failure to properly repair the DNA double strand breaks (15) results in structural chromosome instability (16) which also contributes to neoplastic transformation and cancer (17). Lastly, we propose that failure of mismatch repair (18) is the result of chromosome instability and mismatch repair failure leads to microsatellite instability (19) which may also contribute to neoplastic transformation and cancer (17). (1BER = base excision repair; 2CLR = crosslink repair; 3NER = nucleotide excision repair; 4MMR = mismatch repair; 5DSBs = double strand breaks; 6HR = homologous recombination; 7SAC = spindle assembly checkpoint).

lifetime risk of dying of lung cancer under $52 \mu\text{g}/\text{m}^3$ permissible exposure limit (Gibb *et al.*, 2000; Park *et al.*, 2004). This standard originally adapted by OSHA in 1971 was lowered 10-fold to $5 \mu\text{g}/\text{m}^3$ in 2006 (OSHA, 2006), but even the new standard is expected to result in an additional 10–45 deaths per 1000 exposed workers (Salnikow and Zhitkovich, 2008).

Several Cr(VI) compounds are soluble (e.g. sodium or potassium chromates) and readily enter cells via an anion carrier (Buttner and Beyersmann, 1985). Once inside cells, Cr(VI) is reduced by a variety of chemical and enzymatic reductants (Myers *et al.*, 2000; Borthiry *et al.*, 2007), eventually to the next stable oxidation state, Cr(III). During this reduction, reactive Cr species (Cr(V) and/or Cr(IV)) are formed. These can directly cause oxidative-like damage (Sugden, 1999; Sugden *et al.*, 2001) or they can generate ROS via redox cycling (Tsapakos *et al.*, 1983; Borthiry *et al.*, 2007). Inhalation of Cr-containing fumes, dusts, and particles is a prominent form of exposure, so respiratory effects of Cr (pulmonary fibrosis, chronic bronchitis, and lung cancer) are of special concern (Franchini *et al.*, 1983; Deschamps *et al.*, 1995). In the lung, bronchial epithelial cells line the airways and are therefore directly exposed to inhaled chromium.

The redox balance of cellular thiols is critical for normal function and viability. A major role of the thioredoxins is to maintain intracellular proteins in their reduced state (Arner and Holmgren, 2000), and the redox status of the thioredoxin (Trx) system in some cells may be more critical to cell survival than is glutathione. The thioredoxins are presumed to be essential for cell survival as knockout mice lacking either Trx1 or Trx2 do not survive (Powis and Montfort, 2001; Nonn *et al.*, 2003). Genetic suppression or inhibition of Trx results in increased ROS and apoptosis (Hansen *et al.*, 2006) and increased sensitivity of cells to oxidants (Chen *et al.*, 2006), whereas overexpression of Trx2 enhances protection from oxidant-induced apoptosis (Chen *et al.*, 2006; Hansen *et al.*, 2006). Factors which enhance Trx oxidation would therefore be expected to interfere with Trx activity and could decrease cell survival. Some heavy metals can cause Trx oxidation (Myers *et al.*, 2008) but the mechanisms involved are not clear.

11.4.4 Biomonitoring of chromium

The scientific literature is replete with reports of biological monitoring of urine chromium in exposed populations (Minoia and Cavalieri, 1988; McAughey *et al.*, 1988; Randall and Gibson, 1987). However, little use has been made of biological monitoring to investigate the exposure of residential populations potentially exposed to environmental chromium. This is largely due to the difficulty in the interpretation due to extremely high levels of urine chromium in both exposed and control populations.

Operator exposure occurs during the handling of copper chrome arsenic (CCA) treated timber and associated equipment contaminated with CCA (Garrod *et al.*, 1999). Dermal exposure and ingestion were thought to be the main routes of absorption, and exposure by inhalation was considered to be low. Workers exposed to copper chrome arsenic (CCA) wood preservatives have concentrations of chromium in urine that are significantly higher than those from non-occupationally exposed people but below the biological monitoring guidance value (BMGV) that would indicate inhalation exposure at UK occupational exposure limits for hexavalent chromium and arsenic.

A significant problem with the biomonitoring of residential chromium exposure is that, except in cases of gross exposure, it may be difficult to detect relatively small statistical increases above the background variation inherent in the normal population. This is particularly the case when there is a significant degree of misclassification in the potentially exposed population. Using dust sampling techniques, Stern *et al.* (1992) identified an elevated exposure to chromium in household dust in a population in Hudson County, New Jersey, residing on or adjacent to chromate production waste sites. They showed a statistically significant elevation in creatinine-adjusted urine chromium levels in a subgroup of this population with the highest levels of chromium in household dust. This association between elevated exposure to chromium in household dust and elevated chromium concentration in urine is consistent with environmental exposure to the chromate production waste.

Distribution of urinary chromium has been shown to follow a lognormal pattern (Komaromy-Hiller *et al.*, 2000) (Table 11.3). The upper limit of their representative range was significantly higher than published reference values (0.04–1.5 µg/l (Minoia *et al.*, 1990), 0.05–0.48 µg/l and 0.02–1.2 µg/g CRT (White and Sabbioni, 1998), 0.10–0.52 µg/l and 0.09–0.46 µg/g CRT (Brune *et al.*, 1993), 0.68 µg/l (Kristiansen *et al.*, 1997), and 0.57 µg/l (Kiilunen *et al.*, 1987)).

11.5 Mercury

11.5.1 History and uses of mercury

Mercury is one of two elements that are liquid at ambient temperature. It is 13 times heavier than water, and its unique properties have led to a wide variety of uses in industry and elsewhere. It is also found in a number of technological applications such as thermometers, barometers, thermostats, switches, gas meters, and especially fluorescent lights that may be found in residential buildings. In the past, organic mercury compounds were widely used as preservatives in household paints, and mercury antiseptics are still

Table 11.6 History, uses and properties of mercury

History of mercury

Known to the ancient Egyptians

Associated use of mercury as building material

Fluorescent lamps

Properties of mercury

Name of element: Mercury

Symbol of element: Hg

Atomic number of mercury: 80

Atomic mass: 200.59 amu

Melting point: -38.87°C (234.28 K)Boiling point: 356.58°C (629.73 K)

Number of protons/electrons in mercury: 80

Number of neutrons in mercury: 121

Crystal structure: rhombohedral

Density at 293 K: 0.53 g/cm^3

Colour of mercury: silvery-white

Common oxidative states: +1 (mercurous), 2+ (mercuric)

in use. Both the technologic applications and cultural uses of mercury provide the opportunity for it to be an indoor air pollutant in residential settings. Elemental mercury evaporates at a rate of $7\text{ }\mu\text{g/cm}^2/\text{h}$ at 20°C (Andren and Nriagu, 1979).

Mercury (Hg) is a globally spread pollutant due to characteristics such as low melting and boiling points, conversions between chemical forms and participation in biological cycles. As a result of anthropogenic emissions, the global atmospheric Hg deposition rate is approximately three times higher than in pre-industrial times and has increased by a factor of 2–10 in and around the most industrialized regions (e.g. Lamborg *et al.*, 2002).

Mercury compounds are widely used as anti-fouling and mildew-proofing additives in paints, and smaller quantities are often added as preservatives against bacterial attack during storage. Mercury-containing paints are sold for both industrial and domestic purposes. The mercury content of a commercial paint is about 0.05% and the compounds are more or less volatile and may cause air pollution (Taylor, 1965).

Table 11.6 summarizes the history, uses and properties of mercury.

11.5.2 Structure and properties of mercury

Mercury is the 80th element of the periodic table of elements. Mercury is unique in that it is found in nature in several chemical and physical forms. At room temperature, elemental (or metallic) mercury exists as a liquid with a high vapour pressure and consequently is released into the

environment as mercury vapour. Mercury also exists as a cation with an oxidation state of +1 (mercurous) or +2 (mercuric). Of the organic forms of mercury, methyl mercury is the most frequently encountered compound in the environment. It is formed mainly as the result of methylation of inorganic (mercuric) forms of mercury by microorganisms in soil and water. In the environment, humans and animals are exposed to numerous chemical forms of mercury, including elemental mercury vapour (Hg), inorganic mercurous (Hg(I)), mercuric (Hg(II)) and organic mercuric compounds (Fitzgerald and Clarkson, 1991). Mercuric fulminate is explosive in its dry state.

11.5.3 Toxicology of mercury

Mercury has been known as a toxic agent since the time of the earliest medical authors, and as an occupational hazard, in certain industries, it has received much attention. On the other hand, the general contamination of the biosphere has only recently been recognized by ecologists. The consumption of mercury and its compounds has, since World War II, shown a strong upward trend, especially in such uses that empirically lead to considerable losses of mercury to the environment. A large percentage of these losses include highly toxic and persistent mercury compounds.

Divalent mercury is covalently linked to a carbon atom to form organic mercury compounds. Methyl mercury (CH_3Hg^+), thus formed, is extremely toxic and readily absorbed from the gastrointestinal tract of humans and animals. Environmental mercury is ubiquitous and consequently it is practically impossible for humans to avoid exposure to some form of mercury. All forms have toxic effects in a number of organs, especially in the kidneys (Zalups, 2000). Elemental, inorganic, and organic forms of mercury exhibit toxicologic characteristics including neurotoxicity, nephrotoxicity, and gastrointestinal toxicity with ulceration and haemorrhage. However, organic mercury has a lesser insult on the kidneys. Pars recta of the proximal tubules of the nephrons are the most susceptible region for the toxic effects of mercury (Zalups, 2000). Mercurous and mercuric ions impart their toxicological effects mainly through molecular interactions, for instance mercuric ions have a greater affinity to bind to reduced sulphur, especially in the thiol-containing molecules like GSH, cysteine, and metallothionein (MT) (Hultberg *et al.*, 2001). However, the binding affinity of mercury to oxygen and nitrogen atoms is relatively very low when compared to sulphur (Valko *et al.*, 2005). Therefore, toxic effects in the kidneys are mainly controlled by the biological interactions between MT, GSH and albumin (McGoldrick *et al.*, 2003). Once inorganic mercuric ions gain entry into proximal tubular cells, it appears that they distribute throughout all intracellular pools (Houser and Berndt, 1988; Baggett and Berndt, 1985). The cytosolic fraction was found to contain the greatest content of mercury. Interestingly, the rela-

tive specific content of mercury was shown to increase to the greatest extent in the lysosomal fraction when rats were made proteinuric with an aminoglycoside or when rats were treated chronically with mercuric chloride (Madsen and Hansen, 1980). Although the current model of mercury-induced nephrotoxicity revolves around the conjugation of mercury ions with GSH and cysteine, other thiols, especially homocysteine and NAC, also play a vital role in handling mercury in the kidneys (Zalups and Barfuss, 1998; Zalups, 1998).

One of the major molecules that help in scavenging and reducing the toxic effects of mercury is metallothionein, a small, low molecular weight (6–7 kDa) protein, rich in sulphhydryl groups (Yoshida *et al.*, 2006). Not only mercury chloride but even mercury vapours have been shown to elevate the levels of MT (Cherian and Clarkson, 1976).

There are several *in vivo* and *in vitro* reports suggesting that when experimental animals were exposed to mercury (organic or inorganic) there was an induction of oxidative stress mainly because of the depletion of the naturally occurring thiols, especially GSH. Lund *et al.* (1993) demonstrated that administration of mercury resulted in GSH depletion and lipid peroxidation and also increased the formation of H_2O_2 in the kidneys of rats. They further demonstrated that it was the mitochondria of the rat kidney which were responsible for oxidative stress (Lund *et al.*, 1991). In the *in vitro* experiment they showed that when mitochondria were supplemented with the respiratory chain substrate (succinate or malate) and blocker of complex I (rotenone) or complex III (antimycin A), there was a four-fold increase in the H_2O_2 formation with inhibition of complex III and a two-fold increase with complex I inhibition (Lund *et al.*, 1991).

Mahboob *et al.* (2001) showed that when CD-1 mice were exposed to mercuric chloride, there were alterations in the lipid peroxidation (LPO), glutathione reductase (GR), glutathione peroxidase (GPx), superoxide dismutase (SOD) and GSH levels in different organs apart from kidneys (Yee and Choi, 1996).

Toxic insult of mercury also induces a number of stress proteins (Papaconstantinou *et al.*, 2003; Goering *et al.*, 2000). These large groups of proteins include heat shock proteins (HSPs) and glucose regulated proteins (GRPs). Papaconstantinou *et al.* (2003) showed an enhanced *de novo* synthesis of several stress proteins when chick embryos were exposed to mercury. Goering *et al.* (2000) also evaluated the differential expression of four HSPs in the renal cortex and medulla of rats exposed to mercuric chloride. It has also been demonstrated that there is a time- and dose-dependent accumulation of HSP72 and GRP94 stress proteins on mercury(II) exposure (Mahboob *et al.*, 2001). While the accumulation of HSP72 was localized in the cortex, the GRP94 was accumulated in the medulla. In whole kidney, Hg(II) induced a time- and dose-related

accumulation of HSP72 and GRP94. Accumulation of HSP72 was predominantly localized in the cortex and not the medulla, while GRP94 accumulated primarily in the medulla but not the cortex. The high, constitutive expression of HSP73 did not change as a result of Hg(II) exposure, and it was equally localized in both the cortex and medulla. HSP90 was not detected in kidneys of control or Hg-treated rats (Valko *et al.*, 2005).

Delayed detoxification of mercury severely impairs methylation reactions (such as DNA, RNA, cobalamin, protein, phospholipids, histone, and neurotransmitter methylation), which further adversely affects growth factor-derived development of the brain and attention performance. Studies on monkeys have shown that ethyl mercury, like mercury vapour, crosses the cell membrane and is then converted intracellularly to inorganic mercury (Hg^{2+}), which accumulates preferentially in the brain and the kidneys (Magos *et al.*, 1985). Intracellular accumulation of mercury was shown to be higher for ethyl than for methyl mercury but the clearance rate was higher for ethyl mercury (Magos *et al.*, 1985).

Toxic effects of mercury have also been observed in oligodendrocytes, astrocytes, cerebral cortical and cerebellar granular neurons obtained from embryonic and neonatal rat brains (Yee and Choi, 1996). The foetal brain is more susceptible than the adult brain to mercury-induced damage. Methyl mercury inhibits the division and migration of neuronal cells and disrupts the cyto-architecture of the developing brain.

11.5.4 Biomonitoring of mercury

Although dermal exposure and ingestion of metallic mercury are unlikely to cause acute toxicity, mercury vapour is efficiently absorbed into the bloodstream when inhaled (WHO, 1991) and distributed to other tissues. Up to 80% of inhaled mercury is absorbed and readily crosses the blood–brain barrier (Clarkson, 2002). Significant mercury excretion occurs within one week following exposure and can be found in urine and faeces at low levels after many months (Goldfrank *et al.*, 1994). Blood mercury levels higher than 35 $\mu\text{g}/\text{dl}$ and 150 $\mu\text{g}/\text{dl}$ in urine are considered toxic in man (NPIS, 1996). Safety standards require that Hg vapour should not exceed 0.1 mg m^{-3} in air. Harada *et al.* (1997) reported that 200 mg l^{-1} of Hg in blood and 50 mg g^{-1} in hair are the provisionally established standards and anyone with higher concentrations is considered to be at risk of poisoning.

Blood and urine are common biological samples for the assessment of occupational mercury exposure, whereas hair is considered the best indicator for environmental exposure to methylmercury (Satoh, 2000). For those chronically exposed to mercury vapour, a good correlation has been observed between intensity of exposure and blood mercury concentration at the end of a work shift (Roels *et al.*, 1987). Mercury in the blood peaks

rapidly, however, and decreases with an initial half-life of approximately two to four days (Cherian *et al.*, 1978). Thus, evaluation of blood mercury is of limited value if a substantial amount of time has elapsed since exposure. Without selective determination for organic and inorganic mercury (and this is usually the case), dietary methylmercury also contributes substantially to the amount of mercury measured in blood at low levels of elemental mercury exposure, limiting the sensitivity of this biomarker.

In general, the atmospheric concentration of mercury vapour equals the urinary concentration. The mean urinary concentration in the US general population is 0.72 µg/l (95% confidence interval, 0.6 to 0.8), and the mean blood concentration is 0.34 µg/l (95% confidence interval, 0.3 to 0.4) (CDC, 2003). In Europe (Brune *et al.*, 1993) and other parts of the world (WHO, 1990), blood concentrations appear to be somewhat higher.

For most occupational exposure events, urinary mercury has been used to estimate exposure. The toxicokinetics of mercury in urine are much slower than in blood: urinary mercury peaks approximately 2–3 weeks after exposure and decreases at a half-life of 40–60 days for short-term exposures and 90 days for long-term exposures (Roels *et al.*, 1991; Barregard *et al.*, 1992). Therefore, urine is a more appropriate indicator for longer exposures than blood. Moreover, little dietary methylmercury is excreted in the urine, rendering the contribution of ingested methylmercury less significant. Although good correlation has been observed between urinary mercury levels and air levels of mercury vapour, such correlation was obtained after adjusting data for creatinine or specific gravity and after standardizing the amount of time elapsed after exposure (Roels *et al.*, 1987) as considerable intra- and inter-individual variability has been observed in the urinary excretion rate (Barber and Wallis, 1986; Piotrowski *et al.*, 1975). Exhaled air has been suggested as a possible biomarker of exposure to elemental mercury vapour because a portion of absorbed mercury vapour is excreted via the lungs.

Blood and scalp hair are the primary indicators used to assess methylmercury exposure. Methylmercury freely distributes throughout the body, and thus blood is a good indicator medium for estimating methylmercury exposure. Blood levels may not necessarily reflect mercury intake over time, however, as levels fluctuate with dietary intake (Sherlock and Quinn, 1988; Sherlock *et al.*, 1982). Blood haematocrit and mercury concentration may be measured in both whole blood and plasma/serum, allowing the red blood cell to plasma mercury ratio to be determined, and interference from exposure to elemental or inorganic mercury to be estimated.

Scalp hair is also a good indicator for estimating methylmercury exposure (Phelps *et al.*, 1980). Methylmercury is incorporated into scalp hair at the hair follicle in proportion to its content in blood. The hair-to-blood ratio in humans has been estimated as approximately 250–300:1 expressed as µg

Hg/g hair to mg Hg/l blood. However, some difficulties in measurement do arise, such as inter-individual variation in body burden, differences in hair growth rates, and variations in fresh and saltwater fish intake, leading to varying estimates (Skerfving, 1974; Birke *et al.*, 1972). Methylmercury is stable once incorporated into hair, and therefore the mercury concentration in hair gives a longitudinal history of blood methylmercury levels (Phelps *et al.*, 1980; WHO, 1990).

Urine mercury concentrations show a bimodal distribution with the majority of the results at lower concentration values showing a lognormal distribution (Komaromy-Hiller *et al.*, 2000) and calculated representative ranges agreed with an Italian study (0.1–6.9 µg/l, Minoia *et al.*, 1990). However, the values presented by Komaromy-Hiller *et al.* (2000) were less than those from previous studies (10 µg/l (White and Sabbioni, 1998), 20 µg/l (Iyengar and Woittiez, 1988), and 20.1 µg/l and 17.7 µg/g CRT (Lie *et al.*, 1982)).

Because mercury has a short half-life in blood (3 days), blood analysis is typically performed only shortly after an acute exposure (Agocs and Clarkson, 1995). All three forms of mercury (elemental, organic, and inorganic) can be detected in blood after an acute exposure, although the absorption and distribution to body tissues varies with the form. In contrast, urine is the best biological specimen when chronic inorganic mercury exposure is suspected (Agocs and Clarkson, 1995). Organic mercury is not detected appreciably in urine because it is excreted through the biliary system and faeces (Koos and Longo, 1976). The optimal sample for detecting inorganic mercury is a 24-hour urine collection, but improper collection and storage of the specimen may skew the results. The spot urine specimen can provide a close approximation of a 24-hour collection, particularly if it is adjusted for the concentration of the urine using specific gravity or the amount of creatinine present (Agocs and Clarkson, 1995). In addition, the spot urine has the practical advantage of easy collection, which may prevent collection and storage problems encountered with the 24-hour specimen.

11.6 Remedial actions

In order to reduce environmental input and human exposure, efforts have been directed at reducing metal emissions from industries, waste incinerators and coal-fired power plants. Mercury emissions from cement kilns, roasting of sulphide ores for production of sulphuric acid and smelters processing sulphide ores (i.e. in the production of metals such as gold, copper, iron, lead and zinc) have been well documented, but local emissions from primary mercury production are generally missing in mercury emission inventories (Pacyna and Pacyna, 2002).

In schools, older fluorescent bulbs contained mercury, but many new, energy efficient bulbs, which also produce higher quality light, do not. Some states in the USA like Vermont have banned mercury from light bulbs and required labelling. In addition, mercury may be present in secondary schools in chemistry laboratories, and in general in health clinics (thermometers) and thermostat and computer hardware. If potential sources are identified as present, they should be carefully contained and their use managed until replaced with alternatives and properly disposed of as hazardous waste. Also, new sources should not be introduced. To date, in many countries, there are no clean-up standards for spills inside schools.

Attempts by power companies to replace pressure-control devices for the domestic gas supply have led to spills of liquid mercury, affecting some 200,000 homes in one incident (Gibson and Taylor, 2000). Spills of liquid mercury in the home carry a risk of vapour inhalation. Infants and young children, whose breathing zones are closest to the floor, are at highest risk, since mercury vapour is heavy and tends to form layers close to the floor.

It is also universally accepted that trees improve the quality of urban life. Trees capture particles through a number of simple physical processes. As such, their effectiveness in particle uptake results mainly from the properties and area of their surfaces. Trees and other vegetation are effective at trapping and absorbing many pollutant particles.

11.7 Future trends

Cadmium emissions, from production and consumption, will eventually end up in soil or sediment sinks. To a varying degree, cadmium adsorbs to clay minerals and/or organic matter, for example, and an accumulation takes place.

Man's present exposure to cadmium is close to levels that are detrimental to health (Friberg *et al.*, 1986). Thus, in areas with a low soil buffer capacity, cadmium may become a major future pollution problem. In addition, the change in land use as a result of abandoning arable land and discontinuing liming will constitute a major cause of soil acidification. Agricultural soils have often been the recipient of cumulative doses of heavy metals over long periods, and a sudden decline in pH could trigger the release of cadmium. Finally, even if the future societal weathering rate is less than the natural rate, cadmium will continue to be a health problem until the accumulated amounts of soil cadmium have eventually been immobilized in sediments.

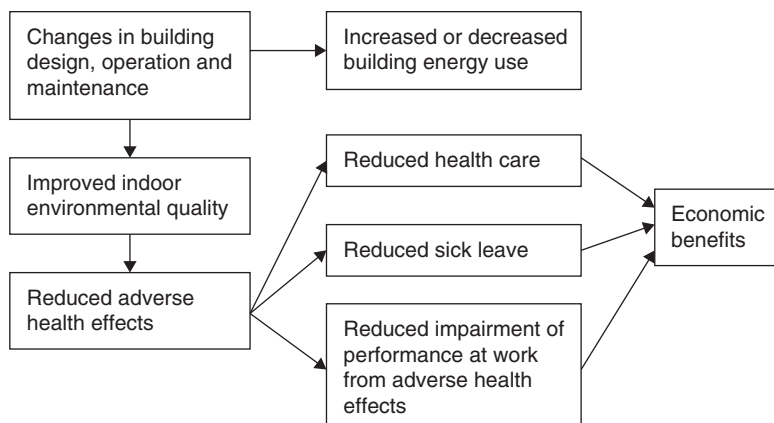
Recently White *et al.* (1998) emphasized the need to improve residential exposure assessments by disaggregating dirt ingestion into separate categories for indoor house dust and exterior dirt. Currently however, there is a scarcity of data that distinguish indoor dust from exterior soil (White *et al.*,

1998). Such data are needed to more accurately determine exposures of pre-school children, especially older infants and toddlers, who spend most of their time indoors and ingest dust through normal repetitive hand-to-mouth activities (Duggan and Inskip, 1985; White *et al.*, 1998; Mushak, 1998). Urban survey data indicate wide variations in metal concentrations of dust and soil in different activity areas within a residence, amongst different residences within a community, and amongst different communities (Elhelu *et al.*, 1995; Gulson *et al.*, 1995; de Miguel *et al.*, 1997; Meyer *et al.*, 1999), underscoring the need for more representative, site-specific data to improve residential exposure assessments.

In a study carried out in the city of Ottawa, house dust samples contained significantly higher concentrations of certain key elements, such as lead, cadmium, mercury and antimony, than either garden soil or street dust (Rasmussen *et al.*, 2001). Although the results of that study did not permit the authors to draw any firm conclusions on the indoor sources of contamination, they do indicate that dust generated within the house itself can be an important source of exposure for certain elements. It is important to note that indoor/outdoor concentration ratios vary widely from one element to another, and from one residence to another within the community. These variations, combined with the distinct multi-element signature of house dust compared to exterior soil and dusts in Ottawa, make it difficult to accurately predict the contribution that soil makes to element concentrations in house dust. It might be plausible therefore to imagine that the likely source is the building materials.

The arguments therefore underscore (1) the importance of obtaining separate measurements for indoor dust and exterior dirt to improve residential exposure assessments; and (2) the validity of developing a separate set of guidelines for elemental concentrations in indoor dust. Calculations by Rasmussen *et al.* (2001) indicate that indoor sources could account for at least 30% of total daily exposure if geometric means are used (69% if 95th percentiles are used). Therefore, for cities with few industrial sources, a significant reduction in childhood exposure to lead and other elements of concern, such as mercury, cadmium and antimony, will not be accomplished through continued lowering of exterior soil clean-up criteria and guidelines, but through increased attention to indoor sources of exposure, and improved parental attention to personal hygiene and housekeeping practices.

Analyses by Fisk and Rosenfeld (1997) provided the first broad review of the potential to improve both health and productivity through improvements in indoor environments. Subsequent papers (Fisk, 2000a, 2000b) have upgraded and updated the analyses (Fig. 11.3). As shown in the figure there are three pathways to health-related economic benefits. In all cases, the starting point is a change in building design, operation, and maintenance that improves indoor environmental quality (IEQ) and enhances the health



11.3 Pathway to health and economic gains (adapted from Fisk, 2000c).

of the building's occupants. Improvements in the indoor environment depend on changes to building design, operation, maintenance, use, or occupancy.

11.8 Conclusions

Cadmium, and mercury toxicity all involve similar pathways of cellular damage; i.e., mitochondrial damage, inhibition of mitochondrial enzymes, suppression of protein synthesis, and production of free radicals (Lyn Patrick, 2002). The two metals have a strong affinity for sulphhydryl-containing ligands (glutathione, alpha-lipoic acid, etc.), and each result in depressed levels of reduced glutathione (Muller and Menzel, 1990). Metal toxicity is a significant clinical entity, as they may be ubiquitous in the environment and pose serious risk to human health.

11.9 References

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Abstract: In recent years the presence of moulds inside buildings has considerably increased, despite the fact that better quality is required for living spaces. The main cause of this is the need to limit energy consumption, which has led to a deterioration in the indoor environment and the working conditions of the external finishes, favouring, more than in the past, the growth of these organisms. Numerous epidemiological studies have demonstrated that long-term exposure in unhealthy environments, subject to the proliferation of moulds and fungi, is one of the main causes of allergies and irritative reactions. This phenomenon is mainly due to the facility with which spores and their metabolic waste can be inhaled. Some remedial action could be conducted by means of RH and temperature control and choosing materials that are not able to retain moisture while at the same time being fairly 'nutritive'.

Key words: mould fungi, algae, construction materials, toxicity, building.

12.1 Introduction

It is impossible to contemplate life on Earth without the presence of fungi, algae, bacteria and other microorganisms. Some of these are in fact responsible for the rapid decomposition of dead organic matter and for its subdivision into components which are then involved in starting a new life cycle (Heseltine and Rosen, 2009). However, despite their utility for the ecosystem, the presence of these organisms on the inside or outside surfaces of building components is not welcome, both because of the well-known implications for human health when they infest the indoor environment and because of their contribution to the defacement of paint and finishes. Moreover, in recent years the presence of moulds and algae inside buildings has considerably increased, despite the fact that better quality is required for living spaces. The main cause of this is the need to limit energy consumption, which has led to a deterioration in the indoor environment and the working conditions of the external finishes, favouring, more than in the past, the growth of these organisms.

12.2 Mould fungi in construction materials

The problem of mould growth inside buildings has been observed in different geographical areas and various types of building (Rousseau, 1983;

Hud, 2004). The main characteristic of mould fungi is that they do not have chloroplasts and therefore they are not able to carry out photosynthesis. Their life cycle is divided into four phases: sporulation, germination, hyphal growth (vegetative growth) and reproduction (Moon, 2005).

During the germination phase, the spores settle on the surfaces and remain inactive until they can absorb moisture and nutrients from the substrate. If the substrate does not provide adequate nourishment and moisture, the spores do not germinate. The growth of hyphae (pluricellular filaments) occurs immediately after germination and as these thicken they form a mass called mycelium. From this time onwards the fungi metabolize the substrate material by extracting the necessary nutrients and retaining the moisture needed for growth. In the final phase the fungi constitute a reproductive organism producing spores.

The development and proliferation of organisms of biological origin (moulds, bacteria, fungi) inside a building require high levels of humidity, associated with adequate nutrients in the substrate (Heseltine and Rosen, 2009). Mould fungi specifically need oxygen, a temperature of between 22°C and 35°C, indoor relative humidity ranging between 71% and 95% (Baughman and Arens, 1996; Ayerst, 1969), and an adequate substrate to provide the nutrients (Hens, 1999). Other secondary factors are the pH value and the roughness of the substrate on which the moulds grow, light, biotic interactions between different cultures, exposure time, and indoor air velocity (Górny, 2004; Krus *et al.*, 2001; Adan, 1994).

Grant *et al.* (1989) showed that, with adequate nourishment, fungal growth on substrates already occurs at values of $a_w = 0.65$ and the colonizing strains may be subdivided into three groups according to the minimum value of a_w at which growth begins (Table 12.1). Clarke *et al.* (1999) carried out experiments on six different categories of fungi which can be found in buildings on the basis of temperature and indoor relative humidity.

Most fungi are saprophytes, which means that they can feed on carbohydrates, proteins and lipids. Sources are varied and abundant: plants, pets, dust and building materials (such as wallpaper and fabrics), condensation/deposit of cooking fat, paint and glue, timber, packed products (such as food), books and other items made of paper. Therefore, in indoor environments, fungi have numerous sources of nutrients. Some building materials which are particularly rich in carbon, like cellulose or carbonates (wallpaper, wood-based building materials), are more propitious to the development of moulds compared with others that have a lower carbon content (for example, plaster and glass wool) (Górny, 2004; Vacher *et al.*, 2010). The relationship between construction materials and mould growth has been studied by several authors. However, the results available are not easily summarized because of the great variety of materials and other factors which intervene to condition the development of moulds. Sedlbauer (2001)

Table 12.1 Levels of moisture needed for the growth of selected microorganisms in buildings, on finishes and furnishing materials

Moisture level*	Category of microorganism	Examples
High ($a_w > 0.9$; ERH > 90%)	Tertiary colonizers (hydrophilic) Actinobacteria (or Actinomycetes)	<i>Alternaria alternata</i> ; <i>Aspergillus fumigatus</i> ; <i>Epicoccum</i> spp; <i>Exophiala</i> spp; <i>Fusarium moniliforme</i> ; <i>Mucor plumbeus</i> ; <i>Phoma erbarum</i> ; <i>Phialophora</i> spp; <i>Rhizopus</i> spp; <i>Stachybotrys chartarum</i> (<i>S. atra</i>); <i>Trichoderma</i> spp; <i>Ulocladium consortiale</i> ; <i>Sporobolomyces</i> spp
Intermediate (a_w 0.8–0.9; ERH 80–90%)	Secondary colonizers	<i>Aspergillus flavus</i> ; <i>Aspergillus versicolor</i> ; <i>Cladosporium cladosporioides</i> ; <i>Cladosporium sphaerospermum</i> ; <i>Mucor circinelloides</i> ; <i>Rhizopus oryzae</i>
Low ($a_w < 0.8$; ERH < 80%)	Primary colonizers (xerophilic)	<i>Alternaria citri</i> ; <i>Aspergillus (Eurotium) amstelodami</i> ; <i>Aspergillus candidus</i> ; <i>Aspergillus (Eurotium) glaucus</i> ; <i>Aspergillus niger</i> ; <i>Aspergillus penicilloides</i> ; <i>Aspergillus (Eurotium) repens</i> ; <i>Aspergillus restrictus</i> ; <i>Aspergillus versicolor</i> ; <i>Penicillium variatii</i> ; <i>Penicillium aurantiogriseum</i> ; <i>Penicillium brevicompactum</i> ; <i>Penicillium chrysogenum</i> ; <i>Penicillium commune</i> ; <i>Penicillium expansum</i> ; <i>Penicillium greseofulvum</i> ; <i>Wallemia sebi</i>

* a_w = water activity; ERH = equilibrium relative humidity.

Sources: Grant *et al.* (1989), Gravesen *et al.* (1994), ISIAQ (1996).

provided a classification based on the relationship between temperature, RH% and type of substrate (Table 12.2). On the basis of these categories the same author also developed isopleth systems which correlate the temperature with the relative humidity (Sedlbauer, 2001) (Table 12.3). Isacson *et al.* (2010) have recently proposed a model on the basis of the ‘dose–response’ ratio.

Ritschkoff *et al.* (2000) conducted experiments on wood-based composite materials (chipboard planks, wood wool and plywood boards), plaster, concrete, and insulating materials (glass wool and rock wool) in different temperature and relative humidity conditions. The results show that all the materials in a building may contribute to the growth of moulds if their relative humidity reaches 90%. Other authors (Rowan *et al.*, 2003; Viitanen and Ritschkoff, 1991) have indicated that mould fungi do not grow with

Table 12.2 Categories in which building materials can be divided on the basis of their mould growth potential

Category of the substrate	
0	Optimal culture medium
I	Biologically recyclable building materials such as wallpaper, plasterboard, building materials made with biodegradable materials, joint materials
II	Biologically adverse recyclable materials, such as mineral-based building materials with a porous structure like mortar for coating, some types of wood and insulating materials not covered with materials belonging to substrate type I
III	Building materials that are neither biodegradable nor contain nutrients.

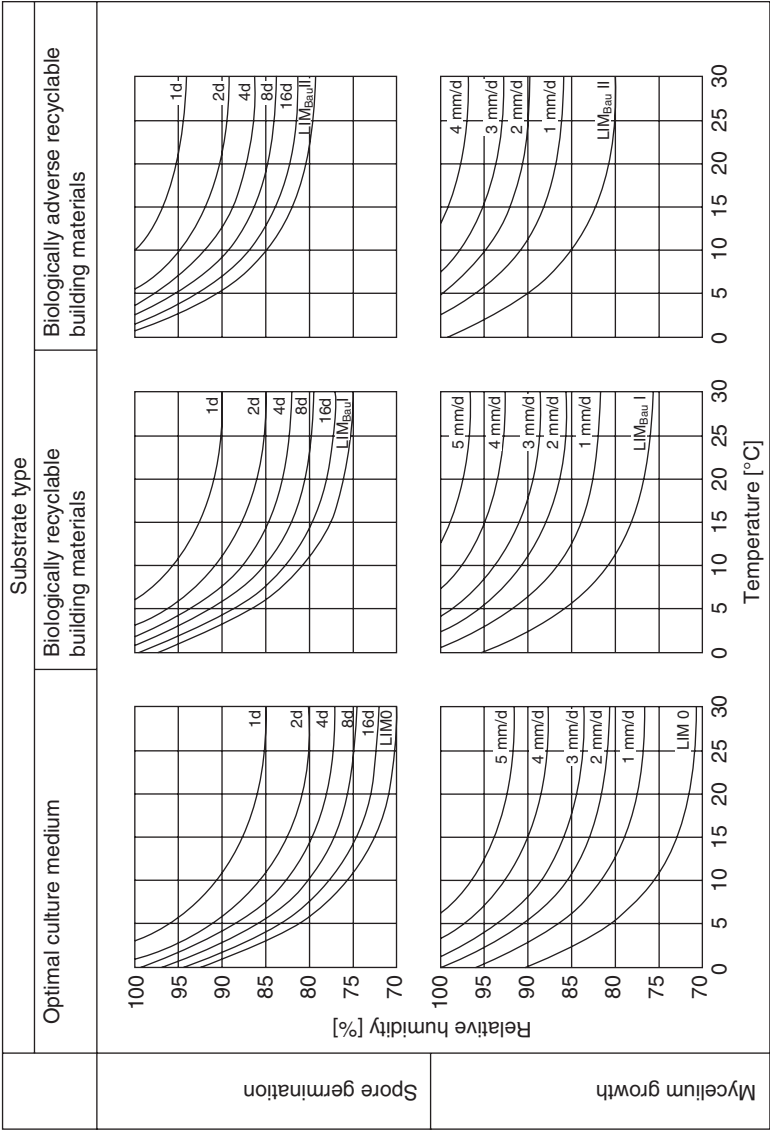
Source: Sedlbauer (2001).

RH < 80% (Adan, 1994) or with RH < 75% when the temperature is between 5 and 40°C. Johansson *et al.* (2005), after analysing the literature, summarized the critical values of RH for different materials which, if exceeded, encourage microbial growth (Table 12.4).

Some inorganic materials, such as metals and plastic, are not in themselves nutrients which are suitable for mould fungi, although the dust which deposits on top of them may represent a source of nourishment. For this reason some studies show that in existing buildings the rate of deterioration due to the action of fungi is similar for both organic and inorganic materials (Kowalski and Bahnfleth, 1999). D'Orazio *et al.* (2008) showed that there is a direct correlation between the growth rate of some fungal species (*S. chartarum*, *P. chrisogenum*, *A. versicolor*) and the content in organic matter which various coatings and indoor finishes are able to provide as nutrients for the spores (Fig. 12.1). Moreover, D'Orazio *et al.* (2008) showed that although various types of plaster and finish (experimentally analysed) belong to the same class of substrate (II) according to the classification of Sedlbauer (2001), in reality there are sometimes quite remarkable differences in the results for the various substrates. Experimental results showed that the species *S. chartarum* (the most highly toxic for human health) had the greatest development on the various types of support surface used.

The exposure time needed for the formation of moulds varies considerably according to the environmental conditions in which the building material is located (Pasanen *et al.*, 2000; Sedlbauer *et al.*, 2003). Inorganic building materials have higher minimum humidity requirements and a longer exposure time compared with the optimal medium for fungi germination. In favourable environmental conditions (surface temperature and relative humidity) a shorter exposure time is required in order for germination to occur. However, it is necessary to consider that surface conditions may vary considerably inside the same building as a result of thermal bridges and

Table 12.3 Speed of mycelial growth and spore germination according to the different types of substrate

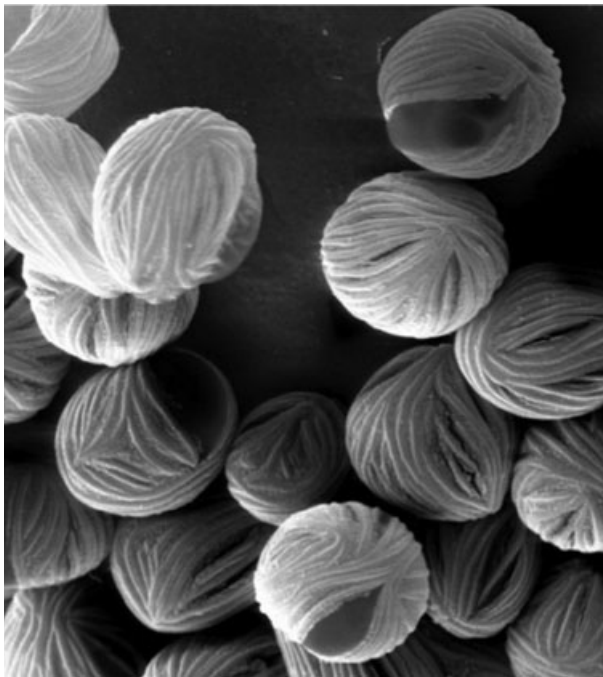


Source: Sedlbauer (2001).

Table 12.4 Critical relative humidity for different materials

Materials	Relative humidity (%)
Wood and wood products	75–80
Wallpaper and plastic coating	80–85
Mineral insulators (e.g. calcium silicate)	90–95
Thermal insulators (EPS, XPS)	90–95
Cement	90–95
Brick	90–95
Plaster	90–95

Source: Johansson *et al.* (2005).



12.1 Spore germination.

cracks in the walls. Some authors point out that the rate of microbial growth increases in proportion to the amount of nutrient available in the substrate (D’Orazio *et al.*, 2008; Vacher *et al.*, 2010).

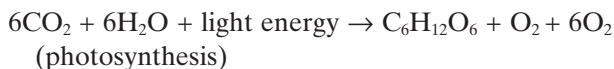
12.3 Algae in construction materials

Unlike moulds, algae are ‘pioneer organisms’ of outdoor environments and are widespread on the external surfaces of buildings (Escadeillas *et al.*, 2007;



12.2 The availability of moisture is essential for the growth and development of algal species.

Künzel *et al.*, 2006a) since they are able to survive through frequent freeze-thaw and dehydration cycles. Algae are classified in two main groups: green algae and blue algae (cyanobacteria), according to their bacterial structure. Green algae develop with RH = 70–80% (Zillig *et al.*, 2003), while blue algae develop with RH = 100% (Zillig *et al.*, 2003) and a temperature of between 15 and 50°C (Karsten *et al.*, 2005), even if the range 20–25°C is the ideal temperature (Zillig *et al.*, 2003). Algae exploit photosynthesis, moisture, carbon and other elements which may be present as a result of either run-off rainwater or pollution. Green algae and cyanobacteria (Fig. 12.2) (mistakenly called blue algae, blue-green algae or cyanophyta) are a phylum of photosynthetic bacteria (Nay and Raschle, 2003); they are unicellular or pluricellular organisms which may be eukaryotic (green algae) or prokaryotic (cyanobacteria). One important characteristic which distinguishes algae from (heterotrophic) mould fungi is their autotrophy, which is the ability of an organism to synthesize its own organic molecules starting from inorganic substances, using energy which is not derived from assimilated organic substances. Therefore the algae, by means of chlorophyllian photosynthesis, transform light energy into chemical energy (Johansson, 2005) managing to synthesize inorganic compounds such as carbon dioxide, water and some elements, and thereby obtain organic substances which guarantee their long-term survival (Hofbauer *et al.*, 2003):



These phototrophic organisms which develop outdoors are particularly resistant to the wind and rainfall, although they are not well protected against evaporation. For this reason they require more moisture than

moulds (present in the surrounding environments), but manage to survive very easily even with few nutrients. The characteristic feature which distinguishes algae from moulds is their resistance to drying (also called anhydrobiosis), which allows them to survive even if greatly dehydrated. In fact, in these circumstances, the algae manage to survive by accumulating saccharose and trehalose, thereby permitting the cell to maintain its integrity during dehydration (Johansson, 2005). The algal cells reactivate their biological processes when moisture in both vapour and liquid state (Johansson *et al.*, 2010) again becomes available.

The growth of algal species is favoured by an optimal combination of biotic and abiotic factors, in particular nutrients coming from the substrate, type of organisms present, moisture (Sedlbauer, 2001) and other environmental factors (Nay and Raschle, 2003; Gaylarde and Gaylarde, 2000) (Fig. 12.2).

If any one of these three macro-conditions is missing, vegetative growth becomes unlikely. Algae do not have roots and they absorb moisture through their cell walls by osmosis (Lengsfeld and Krus, 2004). Hofbauer *et al.* (2003) studied and classified the types of organisms that contribute to the deterioration of the external façades of buildings and reported the presence of four groups of autotrophic plants: algae, lichens, moss and ferns, and (non-autotrophic) fungi.

Various authors have highlighted the fundamental role of moisture, and the way in which it runs off the surface layer of the external vertical walls, in the formation of organisms. It has been demonstrated that porosity, roughness and the composition of the external finishes all participate in retaining rain (Barberousse *et al.*, 2007), while even the shape of the building may create preferential routes where the rainwater stagnates, creating the ideal conditions for the growth of microorganisms (Nay and Raschle, 2003). Once the algae have grown, the run-off rainwater contributes to replacing the old cells with new cells and favours the spread of spots of biofilm to other non-contaminated building components (Künzel, 2007). Even the tendency to heavily insulate buildings encourages the presence of algae (Kastien, 2003) on the external surfaces of buildings. High insulation determines a lowering in the surface temperatures of the construction components during the night-time compared with the temperature of the air ('undercooling') and consequently favours condensation on these surfaces (Künzel, 2007; Adan, 1994; Blaich *et al.*, 2000). The effects of moisture may be amplified by exposure, the season and ventilation. Deterioration due to algal species is found mainly on north and north-west facing surfaces (Nay and Raschle, 2003), since these are hardly ever irradiated by the sun throughout the daytime, and remain damp for a longer time. Walls which have good exposure to the sun receive more light and more heat and therefore dry out in a short time; consequently they are not suitable for microbial growth. Direct sunlight may also damage the photosynthetic pigments of

the algae: the optimal light intensity for algae is about 1000 lux, usually corresponding to north-facing walls (Karsten *et al.*, 2005; Nay and Raschle, 2003).

Even the season is important for the formation of algae on the façade. In fact, during the hot season the external surfaces tend to dry out more quickly, hindering the development of these organisms. However, if algae develop when conditions are more favourable, the season is decisive for their survival: in the summer the external surface temperature of buildings may reach temperatures close to 60°C, causing the death of the algal cells (Karsten *et al.*, 2005), while in the winter temperatures lower than 15°C inhibit their development (Künzel *et al.*, 2001, 2006b).

Studies conducted on the relationship between building material components and the development of algal species show the importance of the physical (porosity, absorption, etc.) and morphological (roughness, etc.) rather than the compositional characteristics of the materials.

Barberousse *et al.* (2007) evaluated susceptibility to the growth of green algae and cyanobacteria (blue algae) on various types of external façades. The final results indicate that porosity and roughness are the parameters which most influence the growth of algae on building materials. The most porous materials tend to shorten the periods of algal dehydration: for this reason the evolutionary capacity of the algae grows in proportion to the increase in the porosity of the underlying material. On the contrary, roughness facilitates the conservation and adhesion of the algae to the material. Venzmer *et al.* (2008) showed how the propensity for algal growth depends mainly on the hydration and desiccation of the microorganisms present on the infected surfaces. Algae appear earlier on hydrophobic than on hydrophilic substrates, since the moisture is completely available for the organism. The more frequent appearance of algae nowadays is also related to greater thermal insulation (Aelenei and Henriques, 2008), above all in buildings with low thermal inertia (Kehrer and Schmidt, 2008; Johansson, 2005; Johansson *et al.*, 2010).

Various studies have been carried out regarding the use of antifungal chemicals to reduce the growth of algae and lichens. The results show that biocide treatment has an impact for about 3–4 years, that no significant differences have been recognized as regards the level of biodiversity (Shirakawa *et al.*, 2002; Tretiach *et al.*, 2007) and that the formation of biofilm is conditioned more by the environmental conditions (irradiance, humidity and temperature) than by the use of the biocide. Moreover most antifungal chemicals are non-specific to the organism affected and can have detrimental effects on the environment, including toxicity for plants and animals. Photocatalysis has recently been discussed as a solution to this problem. The antifungal activity of titanium dioxide (anatase) has been examined intensively on several fungal species (Markowska-Szczupak *et al.*,

2011; Pacheco-Torgal and Jalali, 2011), and in comparison with other biocides (Fonseca *et al.*, 2010). When TiO₂-based coatings are applied to exterior surfaces, such coatings also allow the microorganisms to be washed away by rainfall.

12.4 Potential toxic effects and ways they can be monitored

The organisms described so far are harmful for humans when they develop inside buildings, since people spend 90% of their time indoors. Numerous epidemiological studies have demonstrated that long-term exposure in unhealthy environments, subject to the proliferation of moulds and fungi, is one of the main causes of allergies and irritative reactions. This phenomenon is mainly due to the facility with which spores and their metabolic waste can be inhaled.

Moulds may cause allergy-based illnesses (rhinitis and conjunctivitis, bronchial asthma, extrinsic allergic alveolitis) and infectious diseases (Legionnaire's disease, Pontiac fever) (Hoffman *et al.*, 1993; Górný, 2004; Baughman and Arens, 1996). High concentrations which develop in very damp environments may be responsible for bronchial asthma and the onset of extrinsic allergic alveolitis. The same organisms present in surrounding environments may cause infectious diseases which are easily transmitted in closed and overcrowded spaces. Epidemics of 'Legionnaire's disease' are particularly serious; this often fatal pneumonia is caused by the development and spread of *Legionella pneumophila* through air-conditioning systems (Fraser *et al.*, 1977).

Studies conducted by Johanning *et al.* (1996), Górný (2004) and the World Health Organization (Heseltine and Rosen, 2009) show that the toxins produced by some types of mycetes (mycotoxins) may cause serious illnesses. In particular an association was found between the exposure to mycotoxins (satratoxins) produced by the metabolism of *Stachybotrys chartarum* and irritative symptoms (skin, eyes and mucous), asthenia and immunological alterations (Johanning *et al.*, 1996). Subsequent experiments (Beyer *et al.*, 1997) showed that damp environments favour not only the growth of spores but also the formation of harmful bacteria (mycotoxins). Among these, actinomycetes, which provoke granulomatous tissue infections, are very common. Mould fungi are found in the environment as mycelial filaments and spores, which are easily airborne (being between 0.5 and 50 µm in size) and are highly resistant to environmental stress (Górný, 2004). The micro-fungi most frequently encountered in closed environments belong to the genera *Aspergillus*, *Alternaria*, *Cladosporium* and *Penicillium* (Górný, 2004). In general it is possible to divide the illnesses provoked by moulds into three categories: mycoses, mycotoxicoses and allergies. Mycosis refers to fungal

growth on human organs. In medicine the names of the various forms of this illness derive from the type of fungus it is caused by, followed by the suffix -osis (from mycosis). The most widespread diseases are aspergillosis and penicilliosis. Mycosis does not usually represent a threat for human health, although in the presence of immunodeficiency it can become a serious danger. The organs which are most subject to this illness are the skin, the respiratory organs, the eyes, heart, liver and kidneys and above all the digestive tract. The most important fungal species which can cause mycosis are (Senkpiel *et al.*, 2000) *Absidia* sp., *Aspergillus* sp., *Basidiobolus ranarum*, *Cephalosporium* sp., *Cladosporium* sp., *Fusarium* sp., *Mortierella* sp., *Mucor* sp., *Penicillium* sp., *Rhizopus* sp., *Scopulariopsis* sp. and *Verticillium* sp.

Mycotoxigenesis is an intoxication of the human organism caused by toxic substances produced by the fungi metabolism. Fungi are assumed to release these toxins to defend themselves against rival species. Reiß (1998) and Senkpiel *et al.* (2000) have indicated the main toxins produced by moulds: aflatoxin and ochratoxin A, patulin, citrinin, citreoviridin, sterigmatocystin and mycophenol acid. Aflatoxins, for example, may be created in the blood after the inhalation of dust or spores. Generally these toxins are not harmful for individuals, but if the intoxication becomes chronic the human body is no longer able to break down and expel these compounds. The most widespread disease of this type is cancer of the liver (hepatocellular carcinoma) (Reiß, 1998). Toxic responses by the organism, as a result of the inhalation of spores, generally occur with high concentrations, $>108 \text{ CFU/m}^3$, which occur only in workplaces with high dust loads. Particular attention must be paid to the species *Stachybotrys chartarum* which has a high toxin content and may have toxic effects on the immune system even at concentrations as low as 10 CFU/m^3 (Senkpiel *et al.*, 2000). Moulds which produce these types of toxins are *Aspergillus* sp., *Penicillium* sp., *Fusarium* sp., *Cladosporium* sp. and *Stachybotrys* sp.

Allergies involve an exaggerated response of the immune system. The various types of allergy can be divided into four groups, according to the reaction which they provoke in the individual (Reiß, 1998; Kahle, 2000). Allergies in the first group are caused by the inhalation of allergens produced by fungi and lead to rhinitis and asthma; allergies in the second group are due to the reaction of antibodies towards the allergens that have been introduced into the organism. Unlike the first group, in this case the allergens are not inhaled but enter the body via the mouth. The allergies in the third group are caused by a complex combination of antigens and antibodies. This occurs approximately 4–6 hours after exposure and is therefore a delayed reaction. The allergies in group four come about when some kinds of lymphocytes develop sensitivity to an allergen.

The moulds which develop on the indoor surfaces of houses may cause allergies due to the inhalation of spores. In many types of fungi the spores

are only 2 μm in size and can therefore easily penetrate the bronchial tubes, causing asthma. Spores which have a diameter of greater than 10 μm cannot arrive at the bronchial cavities but are retained in the mucous membranes of the pharynx and may give rise to allergic rhinitis. Moulds may also be responsible for the pathologies grouped together under the acronyms SBS (Sick Building Syndrome) and SHS (Sick House Syndrome). Redlich *et al.* (1997) and Mizoue *et al.* (2004) have conducted studies on a vast sample of subjects and have highlighted and classified the characteristic symptoms of SBS/SHS. Koskinen *et al.* (1999) showed that an increased risk of the onset of SHS is closely related to the level of damp and to the growth of moulds inside buildings. Engvall *et al.* (2002) showed that SHS is most frequent in places with a high level of humidity together with pungent odours and moulds. Kishi *et al.* (2009) have studied the possible causal relationship between SHS and indoor air quality and describe how the pathology is found more often in environments characterized by the presence of moulds. A survey of sampling methods for analysing the concentration of spores in the air, which is useful for assessing the risks connected with the presence of these organisms in indoor environments, is reported in Cabral (2010).

12.5 Remedial action and future trends

Moulds develop on surfaces as a result of both a critical level of RH and indoor temperature and the specific property of the building material to retain water (a_w) together with its capacity to be a nutritive substrate. To hinder the development of moulds different courses of action are required: control of the indoor climate conditions, avoiding fluctuations in temperature and RH% (Cabral, 2010) which favour an increase in the surface moisture content, choice of low-carbon, basic finishes and coatings with a limited adsorption capacity. It is also possible to resort to antifungal chemicals, although it should be borne in mind that they are effective for only about 3–4 years. Moreover most antifungal chemicals are non-specific to the organism affected and can have detrimental effects on the environment, including toxicity for plants and animals (Markowska-Szczupak *et al.*, 2011). On the contrary, algae develop according to the temperature of the substrate, the availability of moisture on the surface, and the capacity of the substrate material to make the moisture immediately available. Even in this case, to avoid these problems, the most common course of action is to use biocides in paints. Photocatalysis has recently been discussed as a valid alternative to traditional antifungal chemicals (Markowska-Szczupak *et al.*, 2011; Fonseca *et al.*, 2010; Makowski and Wardas, 2001). Studies highlight that since the availability of moisture is the fundamental element for the development of algae, it is necessary to reduce the surface absorption capacity and to avoid materials which are characterized by surface roughness

since they are able to increase moisture retention. When TiO_2 -based coatings are applied to exterior surfaces, such coatings also allow the microorganisms to be washed away by rainfall (Pacheco-Torgal and Jalali, 2011).

Moreover, an adequate thickness of the exterior façade must be guaranteed so as to avoid the effects of surface undercooling, which is, in turn, a source of condensation on external surfaces. Considering the current tendency to insulate buildings, studies should therefore be concentrated on identifying external building façades which are able to minimize these potential negative effects.

12.6 Sources of further information and advice

This information is in two main parts. The first part gives some suggestions for further reading. The second part lists a number of institutions and agencies which can offer information.

12.6.1 Further reading

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- Hofbauer W.K., Breuer K., Sedlbauer K. *et al.* (2003) Algen, Flechten, Moose und Farne auf Fassaden. *Bauphysik*, 25(6), 383–396.
- Johansson P, *et al.* (2005) Microbiological growth on building materials – critical moisture levels. State of the art. Swedish National Testing and Research Institute, Borås, Sweden.

12.6.2 Institutions and agencies

- American Academy of Allergy, Asthma and Immunology (AAAAI): www.aaaai.org
- American Society of Heating, Refrigerating and Air-Conditioning Engineers: www.ashrae.org
- Asthma and Allergy Foundation of American (AAFA): www.aafa.org
- Elsevier search engine: www.sciencedirect.com
- National Center for Environmental Health (NCEH): www.cdc.gov
- National Institute of Allergy and Infectious Diseases (NIAID): www.niaid.nih.gov
- Springer search engine: www.springerlink.com
- Technical Research Institute of Sweden: www.sp.se
- US Environmental Protection Agency (EPA): www.epa.gov
- WHO, World Health Organization: www.who.int
- Wiley-Blackwell search engine: www3.interscience.wiley.com

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Abstract: To limit exposure to indoor biological contamination a risk-management approach which employs various antimicrobial treatments can effectively control contaminants and reduce exposure. Antimicrobial treatment of biological contaminants, especially mold in buildings, is often necessary to control the sources of indoor air pollution, and eliminate potential irritant, allergen, toxin, carcinogen and pathogen exposure to occupants. Antimicrobial agents, called fungicides, sporicides or biocides, have long been used to control, prevent, and remediate microbial growth. The antimicrobial efficacy of EPA-FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act) registered chemicals and encapsulants, over-the-counter cleaners, and mechanical devices (such as UV irradiation) to reduce concentrations of mold and bacteria have only recently been investigated. Standard methods to test these control measures have recently been established, and now pertain to a wide set of applications. ASTM 6329-98 (2003) is a standard method to measure efficacy, established and utilized in a wide set of applications. Specific problem applications, such as controlling biological growth on gypsum wallboard, are addressed in this chapter from multiple applications, such as antimicrobial cleaners, paints, and new product developments. Both antimicrobial product efficacy results and testing methodology are summarized.

Key words: antimicrobial, efficacy, treatment, indoor air.

13.1 Introduction

The past 30 years have brought the recognition that an important factor in the health of people in the indoor environment is the dampness of the buildings in which they live and work, and the potential for mold colonization (Dearborn *et al.*, 1999; Vesper *et al.*, 2000; Vesper and Vesper, 2002). Furthermore, it is now recognized that the principal biological organisms responsible for the health problems in these environments are fungi rather than bacteria and viruses (Scheel, 2001). It has been estimated that upwards of 40% of all homes in North America contain fungal growth, while numbers in Northern Europe are in the range of 20–40% fungal contamination (Brunekreef *et al.*, 1989; Nielsen, 2003). Exposure to mold for most humans is a constant, often resulting in adverse health effects such as asthma, rhinitis or bronchitis. These adverse health conditions have often been associated with moisture-induced biological contaminants in the indoor environment, often referred to as Sick Building Syndrome (SBS) or building-related



13.1 Bedroom mixture of *Cladosporium*, *Aspergillus*, and *Penicillium* on painted drywall surface.

illness as seen in Figs 13.1 and 13.2 (Crook and Burton, 2010; Dearborn *et al.*, 1999; Vesper *et al.*, 2000; Vesper and Vesper 2002). Although traditionally, fungi have been viewed as a source of allergens (and in unusual circumstances, pathogens), data have accumulated to show that the adverse health effects resulting from inhalation of fungal spores are due to a variety of factors (Murtoniemi *et al.*, 2001). One characteristic associated with certain fungi is the low molecular weight toxins (mycotoxins) they produce. Mycotoxin-producing fungi are important in human and animal health because of their production of toxins associated with food and animal feed. However, in the indoor environment, mycotoxins tend to concentrate in fungal spores and thus present a potential hazard to those exposed who inhale them (Murtoniemi *et al.*, 2001; Scheel, 2001).

Although only a small percentage of fungal species have been associated with adverse health effects, increased awareness and continuing research will likely result in the identification of many more pathogenic and toxigenic fungi. Organisms such as *Stachybotrys chartarum*, *Penicillium purpurogenum*, *Aspergillus versicolor*, and *Cladosporium cladosporioides* are frequently found in buildings which are heavily contaminated with mold and are potentially associated with adverse health effects in humans (Meklin *et al.*, 2004; Vesper *et al.*, 2004). These health effects may include itchy eyes, stuffy nose, headache, fatigue, and in severe cases idiopathic pulmonary hemosiderosis (IPH) in infants (Andersen *et al.*, 2002; Etzel, 2003; Gent



13.2 Bathroom mixture of *Cladosporium*, *Aspergillus*, and *Penicillium* on painted drywall surface.

et al., 2002; Kuhn and Ghannoum, 2003; Mahmoudi and Gershwin, 2000). In numerous cases the mold *S. chartarum* has been found to be associated with idiopathic pulmonary hemorrhage in infants (Dearborn *et al.*, 1999; Vesper and Vesper, 2002). It is also studied for toxin production and its occurrence in water-damaged buildings. Growth of *S. chartarum* on building materials such as gypsum wallboard (GWB) has been frequently documented. Indoor exposure to mold has also been linked to pulmonary disease, including allergies and asthma. Given this significant risk of exposure and frequency of occurrence, environmental factors regarding the growth of mold have been studied (Andersen *et al.*, 2002; Brunekreef *et al.*, 1989; Dearborn *et al.*, 1999; Etzel, 2003; Gent *et al.*, 2002; Kuhn and Ghannoum, 2003; Mahmoudi and Gershwin, 2000; Meklin *et al.*, 2004; Murtoniemi *et al.*, 2001; Nielsen, 2003; Scheel, 2001; Vesper and Vesper, 2002; Vesper *et al.*, 2004).

Biological contamination in the indoor environment is also recognized as a major health concern (Dearborn *et al.*, 1999). Exposure to airborne biocontaminants or their metabolites can induce irritation, allergic and infectious responses, including acute reactions such as vomiting, diarrhea, hemorrhage, convulsions, and, in some cases, death (Dearborn *et al.*, 1999; Novotny and Dixit, 2000; Sudakin, 2000; Vesper *et al.*, 2000, 2004; Vesper and Vesper, 2002) Reducing occupant exposure to these indoor

biological contaminants is a major goal of indoor air quality (IAQ) research. Extensive research has been conducted to evaluate options to control biological contamination in the indoor environment. This research has been conducted with the goal of developing engineering guidelines to prevent, mitigate, and control biocontaminants. The application of effective engineering controls within the building is essential to prevent biological pollution in the indoor environment. For many indoor biocontaminants (e.g., microorganisms), the main growth locations are the structural and finishing materials and furnishings of the building (Andersen and Nissen, 2000; Gravesen *et al.*, 1999).

It is well recognized that fungi can colonize and amplify on a variety of building materials if sufficient nutrients and moisture are present. Mold contamination has been associated with a variety of building and furnishing materials including carpet, ceiling tile, gypsum wallboard, flooring, insulation, and heating and air-conditioning components (Andersen and Nissen, 2000; Gravesen *et al.*, 1999). Mold contamination can also cause significant damage to materials in buildings that leads to expensive repairs (Andersen and Nissen, 2000; Gravesen *et al.*, 1999).

The goal of risk-management research has been to provide industry, academia, and regulators with information tools or methods to test product efficacy. These methods can be used to test products which ultimately provide engineering guidelines for the prevention, mitigation, and control of biological contaminants in the indoor environment.

The objectives of this chapter are to provide information on (1) the scientific basis for studying building material colonization by microorganisms, (2) management of biological contaminants using indoor climate control, and (3) engineering solutions and control techniques that reduce exposure to indoor biological contaminants.

13.2 Research programs

This chapter provides information on three areas of applied research and development on antimicrobial treatment techniques and efficacy measurement. The specific research projects presented here were funded and managed by the US Environmental Protection Agency, through its Office of Research and Development. The projects were part of the Biocontaminant Program within the Air Pollution Protection and Control Division. In addition to research on antimicrobial treatment and efficacy, the Biocontaminant Program engaged in research into other areas of biological research, such as molecular and gaseous identification of microorganisms and ambient monitoring.

Reducing building occupant exposure to indoor mold was the goal of this research, through the development of techniques to test the efficacy of

antimicrobial treatments. The efficacy of antimicrobials to remove and control the growth of microorganisms can be tested on both porous and non-porous surfaces. Finding effective control techniques and accurate methods to measure efficacy is the objective. However, the testing of antimicrobial efficacy on porous surfaces, such as those found in the indoor environment like gypsum board, can be more complicated and prone to incorrect conclusions regarding residual organisms. A variety of microorganisms, building materials, and antimicrobial treatment techniques have been addressed. *S. chartarum* is an example of a species of mold studied in this chapter which has also been studied by researchers for its occurrence in water-damaged buildings and its significant health effects (Dearborn *et al.*, 1999; Vesper *et al.*, 2000; Vesper and Vesper, 2002). The results of the EPA-directed research as well as a synthesis of relevant literature are discussed in the following sections of this chapter:

- 13.5 Effects of moisture, relative humidity (RH) and dust
- 13.6 Duct cleaning effectiveness on microbial growth
- 13.7 Evaluation of antimicrobial treatments as control technologies
 - 13.7.1 Encapsulants
 - 13.7.2 Cleaners
 - 13.7.3 Paints
 - 13.7.4 UVC irradiation
 - 13.7.5 Ozone

Each of the research areas listed above benefited from and was the product of the static and dynamic microbial growth chambers which are described below. These chambers provide unique research tools which facilitate many of these biological investigations.

13.3 Static microbial test chamber

The static microbial test chamber (SMTC), depicted in Fig. 13.3, is constructed from acrylic sheeting (measuring 32 × 39 × 51 cm) with shelves for samples and a saturated salt solution on the chamber bottom to control the equilibrium relative humidity (ERH) (Foarde *et al.*, 1996a; ASTM 6329-98, 2003). The SMTC was tested using ASTM 6329-98, *Standard Guide for Developing Methodology for Evaluating the Ability of Indoor Materials to Support Microbial Growth Using Static Environmental Chambers* (2003) (Foarde *et al.*, 1996a). The SMTC was developed to assess potential microbial growth on a variety of common building materials. Multiple SMTCs have been used to evaluate fungal growth on 2.5 to 3.8 cm square sections of fiberglass duct-liner (FGDL) at various environmental conditions. Temperature and relative humidity (RH) are controlled to simulate the desired environmental conditions. Prior to chamber testing, materials can



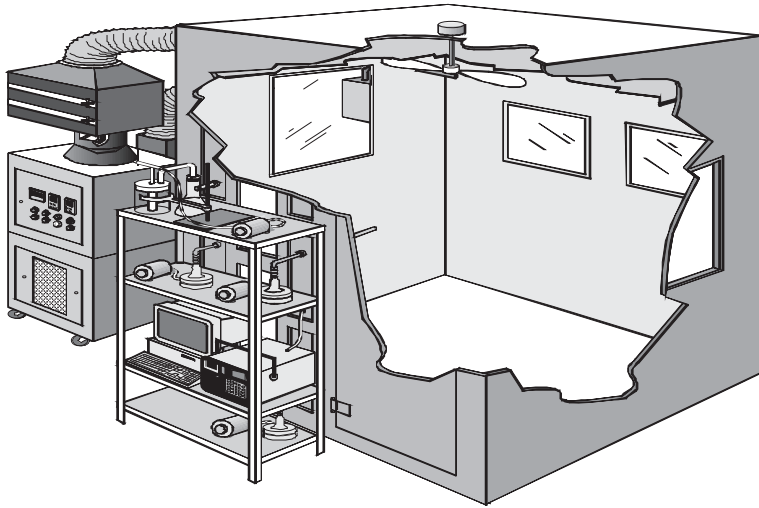
13.3 Static microbial test chamber.

be treated by soaking to simulate a wetting event or treated with an anti-microbial to simulate mitigation practices (ASTM, 2003; Chang *et al.*, 1995a, 1995b, 1995c; Foarde *et al.*, 1995, 1996a, 1996b, 1996c).

13.4 Dynamic microbial test chamber

To allow for experiments which involve air movement over contaminated surfaces and the release of biocontaminant particles into the air, research was conducted in the dynamic microbial test chamber (DMTC) depicted in Fig. 13.4. The stainless steel and glass chamber is a room-sized $2.44 \times 2.44 \times 3.05$ m cube (18.16 m^3), designed and constructed under a cooperative agreement between EPA and the Research Triangle Institute (RTI) (Chang *et al.*, 1995a, 1995b, 1995c; Foarde *et al.*, 1995, 1996a, 1996b, 1996c, 1999). Chamber air was conditioned by an air-handler unit (AHU) which kept the chamber at a temperature of $18\text{--}32^\circ\text{C}$, a controlled relative humidity (RH) ranging from 55 to 95%, and an air circulation rate of 1.4 to $4.8 \text{ m}^3/\text{min}$. Air temperature and RH can be either raised or lowered depending on the requirement of the experiment (Chang *et al.*, 1995a, 1995b, 1995c; Foarde *et al.*, 1995, 1996a, 1996b, 1996c, 1999).

The DMTC has been constructed to study the growth, emissions, and transport of biological contaminants (see Fig. 13.4). The chamber can test HVAC ducts (mini-ducts) scaled to simulate horizontal duct velocities and duct materials in the mini-duct apparatus (VanOsdell *et al.*, 1996), or vertical



13.4 Dynamic microbial test chamber.

low-velocity air flow against gypsum wallboard with room wall simulators (Foarde *et al.*, 1997a, 1997b, 1997c; Menetrez and Foarde, 2002; Menetrez *et al.*, 2004, 2007, 2008a; Shechmeister, 1991; VanOsdell *et al.*, 1996). The DMTC allows for a variety of microbiological research to be performed involving biological growth on building materials, evaluation of emission and deposition of bioaerosols, the impact of HVAC mechanical system components on biological contaminants, and in-duct tests of air cleaners. The chamber permits a contained and highly controlled approach to the study of bioaerosol characterization (VanOsdell *et al.*, 1996).

13.5 Effects of moisture, relative humidity (RH) and dust

This research area focused on evaluating physical and environmental factors favorable to the growth of biological contamination in indoor spaces (ASTM 6329-98, 2003; Foarde *et al.*, 1996a). A static chamber test method (SCTM) based on ASTM 6329-98, *Standard Guide for Developing Methodology for Evaluating the Ability of Indoor Materials to Support Microbial Growth Using Static Environmental Chambers* (2003) and using multiple SMTCs (see Fig. 13.3) described above, and laboratory equipment, materials, and reagents to provide closed controlled environments, was applied to perform these scientific investigations (ASTM 6329-98, 2003; Foarde *et al.*, 1996a).

With the use of multiple SMTCs and the development of the SCTM, three varieties of fiberglass duct liner (FGDL) and ceiling tile materials

were evaluated for their ability to support the growth of the fungus *Penicillium chrysogenum* (Foarde *et al.*, 1996b). Fungal growth was evaluated on 2.5 to 3.8 cm square sections of FGDL. Wetting clean samples of FGDL materials was found to not increase amplification of the *P. chrysogenum* over levels seen without wetting (Foarde *et al.*, 1996c). Soiling FGDL samples with dust accumulated and previously harvested from HVAC systems exhibited a significant association with the growth of *P. chrysogenum* (Foarde *et al.*, 1996c). At moderate soiling levels (0.4–0.7 mg cm⁻²), growth occurred on FGDL ductboard and flexible ductboard, but not galvanized steel (Chang *et al.*, 1995a). At heavy soiling levels (9–18 mg cm⁻²) growth was seen on all three types of ductliner (Chang *et al.*, 1995a). This suggests that dust accumulation should be properly controlled in any HVAC duct to prevent the growth of *P. chrysogenum* (Chang *et al.*, 1995a; Foarde *et al.*, 1996b).

Most of the existing standard test protocols for evaluating antimicrobial efficacy focus on applying the active chemical compound (antimicrobial or biocide) to the surface of a building material (Chang *et al.*, 1995c; Foarde *et al.*, 1995, 1996c). VanOsdell *et al.* (1996) provides a practical hands-on evaluation protocol that is important to SCTM testing of materials under realistic environmental conditions (i.e., temperature, and humidity) in which soiling with sterilized dust was applied. The dust was obtained from the National Air Duct Cleaners Association (NADCA) and was gathered from actual HVAC systems which were cleaned by member companies. This method was developed for evaluating fungal growth on indoor materials and has been used successfully to evaluate the ability of different types of materials (i.e., ductliner) inoculated with *Penicillium glabrum*, *Aspergillus niger*, *A. versicolor*, and *P. chrysogenum* (Foarde *et al.*, 1996a). The use of this method enables the quantitative start and endpoint to be known for growth to be evaluated in a well-controlled environment with improved repeatability and comparability between tests and materials.

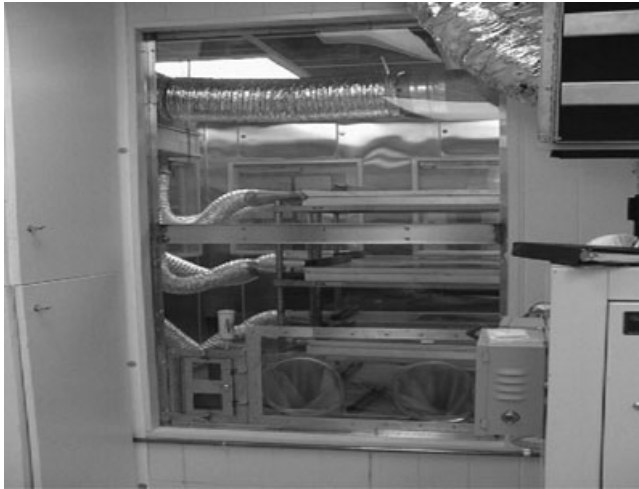
The same SMTC environmental chambers (see Fig. 13.3) were used to study the impact of different levels of moisture and RH on the ability of ceiling tiles to support the growth of *Penicillium glabrum*. Amplification occurred at RH levels above 85%. Lowering RH was demonstrated as effective in controlling fungal contamination on ceiling tiles (Chang *et al.*, 1995c).

Water incursion or standing water is not required for growth on materials (Chang *et al.*, 1995a, 1995c; Foarde *et al.*, 1995, 1996c). For some species of mold, humidity alone can provide sufficient moisture to permit growth on building materials (material and organism dependent), relative to the hygroscopicity of the material (Chang *et al.*, 1995a; Foarde *et al.*, 1995, 1996c). Using this method of artificially soiling materials allows antimicrobial efficacy testing methods to simulate realistic environmental conditions

and laboratory experiments that more closely resemble real-world applications (Foarde *et al.*, 1996b). Under equilibrium conditions, RH and moisture content correlate well with mold growth, depending on the moisture requirements of the test organisms (Chang *et al.*, 1995a, 1995c). However, under non-equilibrium conditions (such as flooding, and breaks in the building envelope, or plumbing), mold growth correlates better with increasing moisture content (in duct liner, ceiling tile and gypsum wallboard) than with relative humidity (Chang *et al.*, 1995a, 1995c; Foarde *et al.*, 1995, 1996c, 1999).

HVAC duct liner can accumulate both moisture and dust, and resultant biological contaminants which then are circulated throughout the building (Foarde *et al.*, 1995, 1996c, 1999; VanOsdell *et al.*, 1996). Resistance to fungal growth was demonstrated to vary for three types of newly purchased fiberglass duct liner (FGDL) (FGDL, FGDL with biocide, and FGDL ductboard) inoculated with *Penicillium chrysogenum*. Of these three types of FGDL tested, the FGDL ductboard demonstrated growth after inoculation and six weeks of static chamber isolation at 97% RH in analogous testing. Wetting the three types of FGDL produced growth on FGDL ductboard and FGDL, and soiling FGDL with dust collected from residential heating and air-conditioning systems caused growth on all three types of FGDL, including one which contained a manufacturers-applied fungal biocide (Chang *et al.*, 1995b; Foarde *et al.*, 1995). When considering these findings and the expected soiling which is produced by normal HVAC operation, the importance of maintaining low indoor RH is demonstrated to be imperative.

The impact of RH, air velocity, and surface growth on the emission rates of fungal spores has been measured by using a dynamic approach (Foarde *et al.*, 1999; VanOsdell *et al.*, 1996). The DMTC (see Figs 13.4 and 13.5) utilized a separate air handling unit (AHU) which forced conditioned air through a High Efficiency Particulate Air (HEPA) filter and eight miniducts. Each miniduct (28.0 × 84.0 cm) contained a single large sheet of FGDL material to be tested. Eight miniducts were tested simultaneously to simulate HVAC duct use with single pass air velocity rates of 250 cm/s. The DMTC was operated at 23.5°C and 95% RH, testing three encapsulant coatings applied to one set of three soiled (with duct dust obtained from NADCA) FGDL samples, one set of three unsoiled FGDL samples, and two control FGDL samples, for a total of eight miniduct samples. Conditioned, HEPA-filtered air passed over the surface of the FGDL samples, traveling horizontally within the miniduct apparatus, exited the duct and returned to the external air-handler for filtration and conditioning. The research indicates that emission rates are inversely proportional to RH but directly related to air flow and surface loading (Foarde *et al.*, 1999).



13.5 Dynamic microbial test chamber.

Experiments using both SMTC and DMTC test results were generated under conditions of constant temperature, varying degrees of RH and conditions of wetting. Microorganisms (*Penicillium glabrum*, *Aspergillus niger*, *A. versicolor*, and *P. chrysogenum*) were used to evaluate the extent of biological growth upon building materials of differing moisture content. Used and new FGDL (both wet and dry samples) and ceiling tile materials were evaluated. Emphasis was on correlating the moisture content of building materials with microbial growth. Growth was determined to be a function of organism, RH, and the degree of soiling. The extent of soiling or dust deposited on FGDL and ceiling tile materials was also shown to be a significant determinant of growth (Chang *et al.*, 1995a, 1995c; Foarde *et al.*, 1995, 1996b, 1996c, 1997a, 1999; VanOsdell *et al.*, 1996). The research showed that emission rates for these materials for *A. versicolor* and *P. chrysogenum* are inversely proportional to RH but directly related to air flow rate and surface loading (Foarde *et al.*, 1995, 1996b, 1996c, 1997a, 1997b, 1997c, 1999).

The growth of *Stachybotrys chartarum* on building materials was investigated given the significant risk of exposure and frequency of reported occurrence. The environmental factors leading to the growth of *S. chartarum* have been studied. Commonly used building materials were sterilized, inoculated with *S. chartarum* and exposed to controlled levels of relative humidity and wetting. A quantitative analysis of viable *S. chartarum* was performed on the building materials during a seven-month period. The research indicates that, for environments with a relative humidity below total saturation, wetting was necessary for visible growth to occur. Conversely, high levels

of relative humidity without wetting did not initiate growth. Porous materials, after becoming sufficiently wet and measuring saturation on a moisture meter, exhibited mold growth in every experiment conducted (Menetrez *et al.*, 2004).

Variations in the characteristics of similar building materials can impact the fungal resistance of that material (Chang *et al.*, 1995a, 1995c; Foarde *et al.*, 1995, 1996c, 1999; Menetrez and Foarde, 2002). Both new and used materials are capable of supporting mold growth, but generally used materials (soiled) were more susceptible (Chang *et al.*, 1995a, 1995c; Foarde *et al.*, 1995).

An effective means of source management control of mold is by reducing the moisture content of wet materials (within two days) before fungal growth becomes established (Chang *et al.*, 1995a; Foarde *et al.*, 1999). However, if mold contamination has already become established, remediation practices that lower RH levels or the moisture content of contaminated materials will initially increase fungal spore emissions and lead to increased airborne contamination (Chang *et al.*, 1995c; Foarde *et al.*, 1996b, 1997c). This strategy points out the need for containment of contaminated areas to prevent the spread of mold (Foarde *et al.*, 1997c). Established microbial growth may continue even after the moisture content of a particular material is lowered below that required to initiate growth (Foarde *et al.*, 1999). The results indicate that growth of *S. chartarum* was not detected in environments with a RH below total saturation and no wetting occurred. Wetting was necessary for visible growth to occur. Porous materials, after becoming sufficiently wet and measuring saturation on a moisture meter, exhibited mold growth at all relative humidity levels tested (Menetrez *et al.*, 2004). However, the control of moisture, RH and dust in the indoor environment is an effective method of preventing most common biological contaminants.

13.6 Duct cleaning effectiveness on microbial growth

HVAC systems have been shown to act as a collection source for dust. The accumulated dust can consist of such contaminants as mold, fungi, and bacteria. The potential health risks associated with exposure to these contaminants make removal of the dust a consideration, especially if improving indoor air quality is required. Because of their potential to rapidly spread contamination throughout a building, ventilation system materials are of particular significance as potential microbial contamination sources. Portions of ventilation systems near cooling coils and drain pans are known to be exposed to high moisture levels for extended periods, and fibrous duct insulation materials are known to have become sources of microbial contamination in some buildings (Gravesen *et al.*, 1999; Foarde *et al.*, 1996a).

The evaluation of duct cleaning as a means of control or prevention of microbial growth on insulated and galvanized duct surfaces has been conducted (Foarde *et al.*, 1996c). Although duct cleaning is effective in removing accumulated dust and contaminants from the inner duct surface, the effects on air quality have not been substantiated. In addition, the abrasive action of rotary brushing used in duct cleaning could weaken the integrity of interior duct insulation. Possible erosion of duct insulation can, however, be avoided if a surface encapsulant is applied. Field evaluation of duct cleaning was performed as part of a larger project which focused on the use of antimicrobial encapsulants (Foarde *et al.*, 1996a, 1996b; Gravesen *et al.*, 1999). Most commercial applications of duct cleaning (rotary brushing or vacuuming) include the use of an antimicrobial encapsulant on FGDL. This improves the integrity or structure of the surface and helps to reunite any loose fibers which may have become partly dislodged by the actions of the cleaning process. It also deposits a surface which should be hostile to potential microbial growth. Three different commercially available antimicrobial encapsulants/sealants were monitored after being applied to FGDL surface that was contaminated with mold and cleaned. This field evaluation was conducted using the EPA test house located in Cary, NC (Foarde *et al.*, 1996c).

As covered in the previous section, concurrent laboratory testing was performed which revealed that if dust is allowed to build on FGDL within the air distribution duct network, mold growth can become established at elevated RH levels even when an antimicrobial encapsulant is applied to duct surfaces (Foarde *et al.*, 1996b, 1996c).

Understanding the cause of microbial contamination, the means of controlling or preventing microbial growth, and the consequential effects of the uncontrolled spread of microbial growth in typical operating conditions has been addressed (Chang *et al.*, 1995a, 1995c; Foarde *et al.*, 1995, 1996b, 1996c, 1997a, 1999; VanOsdell *et al.*, 1996). To facilitate biological research on duct materials, the design and construction of the static and dynamic chambers and the development of methods of testing microbial growth under constant temperature and RH and conditions of static or dynamic air movement were demonstrated (Foarde *et al.*, 1996a, 1996b; VanOsdell *et al.*, 1996). The evaluation of fungal growth on FGDL and ceiling tiles has been discussed.

Findings confirm that fungal growth on FGDL is intrusive throughout the materials and that guidelines which recommend discarding microbial contaminated porous duct material should be followed (Foarde *et al.*, 1997a, 1997b, 1997c). Mechanical cleaning by high-efficiency particulate arresting (HEPA) air-vacuuming was able, at best, to reduce imbedded fiber soiling and temporarily decrease fungal levels. These fungal populations were able to reestablish growth within six weeks (Foarde *et al.*, 1997b, 1997c). The

control of dust, especially in areas of high humidity such as in air handlers and ducting downstream to cooling coils in HVAC systems, is a potential concern to prevent the growth of mold (Foarde *et al.*, 1996c; Menetrez and Foarde, 2002; Menetrez *et al.*, 2004). The National Air Duct Cleaners Association (NADCA) in *ACR 2006 Assessment, Cleaning, and Restoration of HVAC Systems An Industry Standard Developed*, recommend annual HVAC inspections for dust and biological contamination. The American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. (ASHRAE) in ANSI/ASHRAE/ACCA 180, *Standard Practice for Inspection and Maintenance of Commercial Building HVAC System* recommend semi-annual HVAC inspections for commercial buildings. HVAC system inspections should be part of all standard building operation and maintenance.

13.7 Evaluation of antimicrobial treatments as control technologies

The efficacy of antimicrobial treatments to eliminate or control biological growth in the indoor environment can easily be tested on nonporous surfaces. However, the testing of antimicrobial efficacy on porous surfaces, such as those found in the indoor environment, i.e., GWB, HVAC duct-liner insulation (see Fig. 13.6), and wood products, can be more complicated and prone to incorrect conclusions (Foarde *et al.*, 1997a, 1997b, 1997c; Menetrez and Foarde, 2002; Menetrez *et al.*, 2004).



13.6 Encapsulant application.

13.7.1 Encapsulants

Research to control biological growth using three separate antimicrobial encapsulants which were spray-painted on FGDL contaminated with *Aspergillus versicolor* (see Figs 13.6 and 13.7) has been performed in both field and laboratory testing ASTM 6329-98 (ASTM 6329-98, 2003; VanOsdell *et al.*, 1996; Menetrez and Foarde, 2002) using visual inspection to estimate growth on coupons. The estimation of growth was made by optical inspection of the coupon surfaces. The numerical ranking of mold growth was:

0 = no growth

1 = minimal growth

2 = growth covering 33.3% of the coupon

3 = growth covering 50% of the coupon

4 = growth covering 75% of the coupon

5 = growth covering the majority of the coupon with few bare spots remaining.

Triplicate sample coupons were processed for surface growth on encapsulant-coated FGDL. The results indicate differences in antimicrobial efficacy for the period of testing (ASTM 6329-98, 2003; Menetrez *et al.*, 2007, 2008a; Menetrez and Foarde, 2002; VanOsdell *et al.*, 1996). An encapsulant or coating is a covering that is applied (spray paint as in Fig. 13.6) to a surface. The aim of applying coatings is to improve surface properties of a bulk material, usually referred to as a substrate (as in Fig. 13.7).

Three common HVAC (or HAC) antimicrobial encapsulants were evaluated for their use on FGDL in both laboratory and field application experiments. The antimicrobial encapsulants tested are manufactured for use in



13.7 HVAC duct encapsulant lining.

HVAC system components and on duct surfaces. Coating I was a polyacrylate copolymer containing 9% barium metaborate and 0.16% iodo-2-propynyl butylcarbamate. Coating II was an acrylic coating containing decabromodiphenyl oxide and antimony trioxide. Coating III was an acrylic primer containing phosphoric acid compounds with a phosphated quaternary amine complex (diethanolamine *n*-coco alkyl derivatives; 2,2'-(coco ankylimino) bis-ethanol).

The results of the chamber experiments are shown in Tables 13.1 and 13.2, for sections of FGDL that were removed from the test house. Surface samples indicated that the population of *A. versicolor* on untreated FGDL increased by 3 logs (1000-fold) by the end of the first month (see Table 13.1), and remained approximately level through the 3.5-month study.

Table 13.1 shows a slight variation (an increase followed by a decrease) in the *A. versicolor* population for Coatings I and III on FGDL, for the period of 3.5 months. This was in contrast to the increased populations observed in samples with Coating II. The increase in fungi population for Coating II was comparable to that observed in the untreated samples, as compared with successful limiting of growth accomplished by Coatings I and III.

Table 13.1 Growth of *A. versicolor* on the surface of FGDL maintained at 94% RH dynamic chamber

FGDL sample	Biological growth (log CFUs/10 cm ²)			
	Start	Month 1	Month 2	Month 3.5
Untreated	0	3.8	4.40	4.2
Coating I	0	0.9	0.7	0.1
Coating II	0	2.9	3.1	3.3
Coating III	0	1.0	1.1	0

Table 13.2 Growth of *A. versicolor* on the surface of soiled FGDL maintained at 94% RH dynamic chamber

FGDL sample	Biological growth (log CFUs/10 cm ²)			
	Start	Month 1	Month 2	Month 3.5
Untreated	0	2.9	4.1	3.8
Coating I	0	1.5	1.6	1.0
Coating II	0	3.3	3.8	4.3
Coating III	0	1.5	0.8	0

Soiled FGDL experiments resulted in similar populations of *A. versicolor* for untreated and Coating II samples, as shown in Table 13.2. The results were again similar for Coatings I and III, in which variations in fungi populations were observed to increase in month 1, and then decrease. The results indicate that antimicrobials can remain effective with moderate dust loading.

A comparison of the results obtained with dynamic and static chamber testing is shown in Table 13.3. The additional static chamber testing was performed at 70, 85, 90, and 94% RH, for comparison with the 94% RH dynamic chamber testing. Table 13.3 indicates that static chamber results at 94% RH are in good agreement with dynamic chamber results at 94% RH. Studies also demonstrated that static chamber fungi growth decreases with decreasing RH. Both methods indicate greater effectiveness in controlling growth with Coatings I and III.

Laboratory SMTc experiments conducted at 21.7°C (71°F) and from 65% to saturated relative humidity showed differences in degrees of efficacy for three antimicrobial coatings. Two antimicrobial coatings limited fungal contamination for the duration of testing. The most effective coatings were Coatings I and III while Coating II was ineffective. Although all three antimicrobials are registered with the EPA, they were not equally effective, nor should they be expected to perform equally in field use (Menetrez *et al.*, 2004, 2007, 2008a; Menetrez and Foarde, 2002).

Although the importance of efficacy testing cannot be overstated, it has not received priority until the last 10 years. Additional methods of testing antimicrobial efficacy need to be standardized to evaluate differences in products having or seeking EPA registration. The standard methods should

Table 13.3 Change in log CFUs/10 cm² of *A. versicolor*

Treatment	Static chamber				Dynamic chamber
	70% RH	85% RH	90% RH	94% RH	94% RH
<i>Not soiled</i>					
Untreated	BDL*	1.4	4.4	4.4	4.2
Coating I	BDL	BDL	BDL	<1.0	<1.0
Coating II	<1.0	1.9	3.4	4.3	3.3
Coating III	<1.0	BDL	BDL	BDL	<1.0
<i>Artificially soiled</i>					
Untreated	BDL	<1.0	4.4	5.0	3.8
Coating I	<1.0	<1.0	BDL	<1.0	1.0
Coating II	BDL	3.6	4.7	4.7	4.3
Coating III	<1.0	BDL	BDL	BDL	<1.0

*BDL = Below Detection Limit.

cover treatment techniques pertaining to liquids, fumigants and irradiation. The following text addresses these research subjects and is the first step in the development of standard methods. Additionally, the series of experiments described in Menetrez and Foarde (2002), are adequate tests for viable mold (ASTM 6329-98, 2003; Menetrez *et al.*, 2004, 2007, 2008a; Menetrez and Foarde, 2002; VanOsdell *et al.*, 1996). However, in addition to viable mold antimicrobial efficacy, additional testing may be needed for viable bacteria (bacteria cells and spores), nonviable mold (mycotoxins) and bacteria (endotoxins), as well as viruses and some forms of allergens (e.g., dust mites), to determine whether the manufacturers' claims apply (Foarde *et al.*, 1997a, 1997b, 1997c; Menetrez and Foarde, 2002; Menetrez *et al.*, 2007, 2008a). The results demonstrated a significant variation in the antimicrobial efficacy of encapsulants. This variation indicates a need for product efficacy testing (Menetrez *et al.*, 2007; Menetrez and Foarde, 2002).

13.7.2 Cleaners

Mold-contaminated materials are often not entirely removed from problem buildings. These colonized porous materials frequently have surface cleaners applied in an attempt to alleviate the problem. The efficacy of antimicrobial cleaners to remove, eliminate or control mold growth on surfaces can easily be tested on nonporous surfaces. However, the testing of antimicrobial cleaner efficacy on porous surfaces, such as those found in the indoor environment (e.g., gypsum board), can be more complicated and prone to incorrect conclusions regarding residual organisms and microbial toxins (Foarde *et al.*, 1997a, 1997b, 1997c; Menetrez and Foarde, 2002; Menetrez *et al.*, 2004). The mold *Stachybotrys chartarum* has been found to be associated with idiopathic pulmonary hemorrhage in infants and has been studied for toxin production and its occurrence in water-damaged buildings. Growth of *S. chartarum* on building materials such as gypsum wallboard has been frequently documented. Research to control *S. chartarum* growth using 13 separate antimicrobial cleaners on contaminated gypsum wallboard has been performed in laboratory testing. Laboratory SMTC experiments conducted at 21.1°C (70.0°F) and 100% relative humidity showed differences in degrees of efficacy. Common brands of cleaning products were tested by following directions printed on the product packaging and are listed in Table 13.4. A variety of gypsum wallboard surfaces were used to test these cleaning products at high relative humidity using a modification of ASTM 6329-98 (Foarde *et al.*, 1997a, 1997b, 1997c; Menetrez and Foarde, 2002; Menetrez *et al.*, 2004).

Visual inspection for *S. chartarum* regrowth of the coupons within static chambers extended up to six months. Only those samples that exhibited heavy amounts of regrowth were stopped prior to six months. The

Table 13.4 Cleaning products tested for removing *Stachybotrys chartarum* growth

Cleaning product	Directions for use	Concentration
Lysol (concentrated)	To disinfect/deodorize hard, non-porous surfaces, remove heavy soil first, then add 1.3 oz to one gallon of water then apply with a sponge or mop wetting all surfaces thoroughly. Let stand 10 minutes, then wipe away excess.	189 mL H ₂ O 1.89 mL Lysol
Lysol All Purpose Cleaner-Orange Breeze scent	For a cleaner, fresher household, dilute 2 oz. with a gallon of warm water. Good for everyday cleaning throughout the house. For your toughest household messes; use full strength and rinse thoroughly.	Full strength
Lysol All Purpose Cleaner-Orange Breeze scent	For a cleaner, fresher household, dilute 2 oz. with a gallon of warm water. Good for everyday cleaning throughout the house. For your toughest household messes; use full strength and rinse thoroughly.	250 mL H ₂ O 3.75 mL Lysol Orange Breeze
Lysol IC – Brand Quaternary Disinfectant Cleaner	Remove heavy soil deposits from surfaces, then thoroughly wet them with a solution of 1/2 oz of the concentrate per gallon of water. The solution can be applied with a cloth, mop, sponge or coarse spray or soaking. Let solution remain on surface for a minimum of 10 minutes. Allow to air dry.	378.5 mL H ₂ O 1.48 mL Lysol I.C.
Spray Nine Multi-Purpose Cleaner and Disinfectant	1. Spray on soiled surface. 2. Wipe immediately with a clean, damp sponge or cloth. 3. Repeat application making sure to wet all surfaces thoroughly. 4. Allow to stand for 3 minutes when treating for fungus. 5. Wipe off with a clean, damp sponge or cloth then rinse thoroughly.	Full strength
Johnson Wax Professional Mildew Stain Remover with Bleach	Spray using full strokes, 6–8" from surface. Wait until stains disappear. Wipe with sponge. Rinse promptly.	Full strength

Commercial Solutions Ultra Clorox Germicidal Bleach	Prewash surface, then mop or wipe with bleach solution. Allow solution to contact surface for at least 2 minutes. Rinse well and air dry. Dilute 2/3 cup bleach to 1 gallon water.	189 mL H ₂ O 7.89 mL bleach
SporKlenz	Remove any obvious debris or organic material from the surface to be sterilized. Dilute SporKlenz concentrate 100x (1 part SporKlenz to 99 parts purified water). Spray onto surfaces using a plastic spray bottle. Allow to remain on surface for 10 minutes. Let air dry or rinse with purified water.	175 mL H ₂ O 1.75 mL SporKlenz
Borax	Sprinkle borax into water and wipe with damp sponge.	473 mL warm water 1 tablespoon borax
Pine Sol	For general disinfecting: Apply Original Pine Sol Brand cleaner with a sponge or cloth full strength. Wet surfaces, let stand 5 minutes, then remove excess. For highly soiled areas, clean excess dirt first.	Full strength
Tilex	Spray surface until thoroughly wet, let stand 5 minutes and rinse. Do not use on wood or painted surfaces. Avoid contact with aluminum, clothes, fabric, carpet or paper surfaces as they will discolor.	Full strength
Fantastik Orange Action	Spray 6–8 inches from surface. After spraying, wipe with a dry paper towel or cloth.	Full strength
Orange Glo Multipurpose Degreaser	Spray on soiled area and wipe clean. Rinse if necessary. For baked-on grease or thick soap film, wait several minutes before wiping.	Full strength
Formula 409 Multipurpose Cleaner	Spray 6–8 inches from surface. General cleaning: Spray product straight onto soils and wipe clean with a dry paper towel or lint free cloth. Repeat for heavily soiled areas. Not recommended for use on soft vinyl, varnishes or aluminum.	Full strength

estimation of regrowth was made by optical inspection of the coupon surfaces. The numerical ranking of mold growth followed was:

- 0 = no growth
- 1 = minimal growth
- 2 = growth covering 33.3% of the coupon
- 3 = growth covering 50% of the coupon
- 4 = growth covering 75% of the coupon
- 5 = growth covering the majority of the coupon with few bare spots remaining.

Triplicate sample coupons were processed for each of the 14 cleaning products and six GWB surface types. Visual inspection for *S. chartarum* regrowth of the coupons within the static chambers occurred for six months or until it was judged to have extensive growth (a numerical ranking of 5). The results were numerically ranked from best (0 represented no growth) to worst (5 represented extensive growth) and are listed in Table 13.5. Six varieties of surfaces were used to evaluate *S. chartarum* growth. The surfaces were constructed over standard GWB and were as follows:

1. Plain GWB, no paint
2. Vinyl (100% vinyl)-covered GWB
3. GWB with vinyl-coated wallpaper removed before cleaning and replaced
4. GWB with vinyl-coated wallpaper not removed before cleaning
5. GWB with oil-based paint
6. GWB with acrylic (latex) paint.

The object of this research was to test the antimicrobial efficacy of these cleaning and disinfectant products for removing and preventing *S. chartarum*, or restricting its growth, on the six varieties of GWB surfaces listed above, and with variations in RH.

The mean results (of triplicate samples) for 14 cleaning products for the six types of GWB surfaces varied extensively (see Tables 13.5 and 13.6). However, three cleaning products exhibited significantly better results than others. Lysol All-Purpose Cleaner-Orange Breeze (full strength) demonstrated results which ranked among the best in five of the six surfaces tested. Both Borax and Orange Glo Multipurpose Degreaser demonstrated results which ranked among the best in four of the six surfaces tested (Menetrez *et al.*, 2007).

Other cleaning products ranked among the best in at least one surface test: Formula 409, Lysol IC, Pine Sol, Bleach, Spray Nine, Mildew Stain Remover with bleach, SporKlenz, Tilex, Fantastik Orange Action, and Lysol All-Purpose Cleaner-Orange Breeze (diluted). Every product tested demonstrated to be among the best in at least one surface test (Menetrez *et al.*, 2007).

Table 13.5 Comparison of *Stachybotrys chartarum* growth for cleaners on six GWB surface types

Mean growth ranked 0 to 5 for each surface type	Surface type*					
	1	2	3	4	5	6
Lysol All-Purpose Cleaner-Orange Breeze (full strength)	0.0	3.7	0.0	0.0	0.0	0.0
Borax	0.0	0.0	1.0	2.0	0.0	0.0
Orange Glo Multipurpose Degreaser	0.0	0.0	0.0	0.0	1.0	4.0
Fantastik Orange Action	0.0	3.3	2.3	0.7	0.3	2.3
Lysol IC – Brand Quaternary Disinfectant Cleaner	0.7	0.0	1.0	1.0	3.0	5.0
Formula 409 Multipurpose Cleaner	1.3	0.0	2.0	1.0	1.0	4.0
Lysol (concentrated)	3.0	0.0	1.0	3.0	0.0	1.7
Tilex	2.0	0.0	1.7	2.7	0.7	2.0
Spray Nine Multi-Purpose Cleaner and Disinfectant	2.7	0.0	1.0	3.0	1.0	1.7
SporKlenz	2.3	0.7	0.7	2.0	2.0	0.0
Pine Sol	2.0	0.0	0.3	2.0	0.7	0.7
Commercial Solutions Ultra Clorox Germicidal Bleach	5.0	0.0	1.0	3.3	1.7	0.7
Johnson Wax Professional Mildew Stain Remover with Bleach	3.7	0.0	1.0	2.3	1.7	1.3
Lysol All Purpose Cleaner-Orange Breeze scent (diluted)	4.0	4.3	5.0	0.0	3.0	3.3

* Surface type:

1 Plain GWB, no paint

2 Vinyl (100% vinyl) covered GWB

3 GWB with vinyl-coated wallpaper removed before cleaning and replacement

4 GWB with vinyl-coated wallpaper not removed before cleaning

5 GWB with oil-based paint

6 GWB with acrylic (latex) paint.

The results of *S. chartarum* regrowth listed in Table 13.5 were sorted in a comparative ranking of antimicrobial efficacy performance. Those products listed in Table 13.5 which best limited regrowth were given a ranking of 1, and those that demonstrated the most regrowth were given a ranking of 5. The 14 products tested are listed from 1 (best performance) to 14 (worst performance) in Table 13.6. Numerous products received the same equivalent ranking in Table 13.6 when their test results listed in Table 13.5 were equal. Table 13.6 compares antimicrobial cleaning product performance (Menetrez *et al.*, 2007).

The results indicate differences in antimicrobial efficacy for the six-month period of testing by not allowing mold regrowth (Menetrez *et al.*, 2007). The preferred antimicrobial cleaner to choose is often dependent on the type

Table 13.6 Comparison ranking of cleaner performance for six GWB surface types

Cleaners ranked for each surface type	Surface type*					
	1	2	3	4	5	6
Lysol All-Purpose Cleaner-Orange Breeze (full strength)	1	13	1	1	1	1
Borax	1	1	5	7	1	1
Orange Glo Multipurpose Degreaser	1	1	1	1	7	12
Fantastik Orange Action	1	12	13	4	4	10
Lysol IC – Brand Quaternary Disinfectant Cleaner	5	1	5	5	13	14
Formula 409 Multipurpose Cleaner	6	1	12	5	7	12
Lysol (concentrated)	11	1	5	12	1	7
Tilex	7	1	11	11	5	9
Spray Nine Multi-Purpose Cleaner and Disinfectant	10	1	5	12	7	7
Sporklenz	9	11	4	7	12	1
Pine Sol	7	1	3	7	5	4
Commercial Solutions Ultra Clorox Germicidal Bleach	14	1	5	14	10	4
Johnson Wax Professional Mildew Stain Remover with Bleach	12	1	5	10	10	6
Lysol All Purpose Cleaner-Orange Breeze scent (diluted)	13	14	14	1	13	11

* Surface type:

1 Plain GWB, no paint

2 Vinyl (100% vinyl) covered GWB

3 GWB with vinyl-coated wallpaper removed before cleaning and replacement

4 GWB with vinyl-coated wallpaper not removed before cleaning

5 GWB with oil-based paint

6 GWB with acrylic (latex) paint.

of surface to be cleaned of *S. chartarum* contamination. For Plain GWB, no paint, the best cleaners were Borax, Lysol All-Purpose Cleaner-Orange Breeze (full strength), Orange Glo Multipurpose Degreaser, and Fantastik Orange Action (Menetrez *et al.*, 2007). For vinyl (100% vinyl, removed, cleaned and replaced) covered GWB, the best cleaners were Formula 409, Lysol IC, Pine Sol, Borax, Lysol, Bleach, Spray Nine, Mildew Stain Remover with bleach, Tilex, and Orange Glo Multipurpose Degreaser (Menetrez *et al.*, 2007). For GWB with vinyl-coated wallpaper removed before cleaning and replaced, the best cleaners were Lysol All-Purpose Cleaner-Orange Breeze (full strength) and Orange Glo Multipurpose Degreaser (Menetrez *et al.*, 2007). For GWB with vinyl coated wallpaper not removed before cleaning, the best cleaners were Lysol All-Purpose Cleaner-Orange Breeze (full strength), and Orange Glo Multipurpose Degreaser and Lysol All-Purpose Cleaner-Orange Breeze (diluted) (Menetrez *et al.*, 2007). For GWB

with oil-based paint, the best cleaners were Lysol All-Purpose Cleaner-Orange Breeze (full strength), Lysol and Borax (Menetrez *et al.*, 2007). For GWB with acrylic (latex) paint, the best cleaners were Borax, Lysol All-Purpose Cleaner-Orange Breeze (full strength) and SporKlenz (Menetrez *et al.*, 2007).

Lysol All-Purpose Cleaner-Orange Breeze (full strength) demonstrated results which ranked among the best in five of the six surfaces tested. Both Borax and Orange Glo Multipurpose Degreaser demonstrated results which ranked among the best in four of the six surfaces tested. Every product tested was demonstrated to be among the best in at least one surface test (Menetrez *et al.*, 2007).

13.7.3 Paints

Employing antimicrobial paints can in some cases prevent mold regrowth. The accepted recommendation in handling *S. chartarum*-contaminated gypsum wallboard is removal and replacement. This practice is, however, not always followed completely. Often mold contaminated building materials are not properly removed, some surface cleaning is performed, and paint is applied in an attempt to alleviate the problem. The efficacy of antimicrobial paints to eliminate or control mold regrowth on surfaces can easily be tested on nonporous surfaces. However, the testing of antimicrobial efficacy on porous surfaces found in the indoor environment such as gypsum wallboard can be more complicated and prone to incorrect conclusions regarding residual organisms. Growth of *S. chartarum* on building materials such as gypsum drywall has been frequently documented (Vesper and Vesper, 2002; Dearborn *et al.*, 1999; Vesper *et al.*, 2000, 2004; Scheel, 2001; Brunekreef *et al.*, 1989; Mahmoudi and Gershwin, 2000). Research to control *S. chartarum* growth using seven separate antimicrobial paints and two commonly used paints on contaminated gypsum wallboard has been performed in laboratory testing. The nine paint products and manufacturers tested are listed in Tables 13.7 and 13.8 along with the product active ingredients (Menetrez *et al.*, 2008a).

Laboratory SMTC experiments conducted at 21.1°C (70.0°F) and 100% relative humidity showed differences in degrees of efficacy. Manufacturers' directions were followed and common gypsum wallboard was used as the base to test these products at high relative humidity. The results indicate differences in antimicrobial efficacy for the six-month period of testing by not allowing mold regrowth. When the cost of replacing walls may prevent remediation, antimicrobial paint can lend a possible low-cost alternative (Menetrez *et al.*, 2008a). Each coupon is visually assigned a numerical ranking of mold growth from 0 to 5 for the entire averaged coupon surface. Each paint result was the average of three coupons' surfaces. Inspection for

Table 13.7 Antimicrobial encapsulant paint products

Manufacturer	Antimicrobial paint products	Active ingredients
Alistagen Corp. New York, NY 10016	Caliwel 1 Caliwel 2 with BNA (Bi-Neutralizing Agent)	18.7% hydrated lime (calcium hydroxide)
PPG Industries Pittsburgh, PA 15272	Portersept	10.0–20.0 wt% titanium dioxide 1.0–10.0% propylene glycol 1.0–10.0% kaolin <1% crystalline silica-quartz
Homax Products Inc. Bellingham, WA 98226	Mil-Kil Additive	40.0 wt% diiodomethyl <i>p</i> -tolyl sulfone added to acrylic/latex paint
Jomaps, Inc. Alpharetta, GA 63052	M-1 Additive	51.8% chlorothalonil 2,4,5,6-tetrachloroisophthalonitrile added to acrylic/latex paint
Masterchem Industries, Inc. Imperial, MO 63052	Kilz (interior/ exterior water based)	Acrylic resin emulsion Titanium dioxide Calcium carbonate Ethylene glycol
Zinsser Company, Inc. Somerset, NJ 08873	Permawhite (satin, water based)	Limestone Titanium dioxide Ethylene glycol Mica Zinc oxide Magnesium aluminum silicate

Table 13.8 Paint products

Manufacturer	Paint products	Paint type
The Valspar Corporation, Wheeling, IL 60090	American Tradition, Interior 100% Acrylic	Acrylic/latex
The Valspar Corporation, Wheeling, IL 60090	Interior one coat Oil Semi-Gloss Enamel	Oil-based

S. chartarum regrowth of the coupons within the static chambers extended up to six months. The estimation of regrowth was made by visual inspection of the coupon surfaces. Triplicate sample coupons were processed for each of the nine paint products and two cleaning techniques. The numerical ranking of mold growth followed was:

0 = no growth

1 = minimal growth (growth covering less than 33.3% of the sample)

2 = growth covering 33.3% of the sample

3 = growth covering 50% of the sample

4 = growth covering 75% of the sample

5 = growth covering the majority (greater than 75%) of the sample with few bare spots remaining.

Two techniques of preparing the GWB surfaces were used (cleaned with water only and cleaned with a bleach and water solution) to test these paint products at high relative humidity using a modification of ASTM 6329-98. The observed regrowth results were averaged for each of the seven antimicrobial paint products and the two standard paint products listed in Tables 13.9 and 13.10. Results of regrowth of *S. chartarum* on GWB are listed in Table 13.9. The test results of Table 13.9 list paint used on water-cleaned

Table 13.9 Growth ranking for cleaned and painted GWB

Paint products used on cleaned GWB	Mean <i>S. chartarum</i> growth ranking for water-cleaned GWB	Mean <i>S. chartarum</i> growth ranking for bleach and water-cleaned GWB
Permawhite	0	0
Portersept	0	0
Mil-Kil	0	0
M-1 Additive	0	0.3
Caliwell 1	4.0	1.7
Caliwell 2	4.0	0.7
Acrylic/latex	4.0	4.0
Oil-based	4.0	4.0
Kilz	5.0	5.0

Table 13.10 Comparison ranking of cleaned and painted GWB

Paint products used on cleaned GWB	Mean <i>S. chartarum</i> growth ranking for water-cleaned GWB	Mean <i>S. chartarum</i> growth ranking for bleach and water-cleaned GWB
Permawhite	1	1
Portersept	1	1
Mil-Kil	1	1
M-1 Additive	1	4
Caliwell 1	5	6
Caliwell 2	5	5
Acrylic/latex	5	7
Oil-based	5	7
Kilz	9	9

GWB, and paint used on bleach and water-cleaned GWB (the method recommended by most manufacturers) (Menetrez *et al.*, 2008a).

Results for the nine types of paint products on GWB surfaces varied. However, three antimicrobial encapsulant paint products exhibited no mold regrowth. Permawhite, M-1 Additive, and Portersept demonstrated results which ranked among the best in tests (see Table 13.9). Mil-Kil ranked among the best for water-cleaned GWB (Table 13.9), and near the best for bleach and water-cleaned GWB (Table 13.10). The remaining three antimicrobial encapsulant paints and two common paints did not perform as well. The Kilz performance was not even as good as the acrylic/latex or oil-based paint (Menetrez *et al.*, 2008a).

The results of *S. chartarum* regrowth listed in Table 13.9 were sorted in a comparative ranking of antimicrobial efficacy performance. The nine products tested are listed from 1 (best performance) to 9 (worst performance) in Table 13.10. Numerous products received the same equivalent ranking in Table 13.10 when their test results listed in Table 13.9 were equal. Table 13.10 compares antimicrobial paint product performance (Menetrez *et al.*, 2008a).

Based on the study results, the best antimicrobial encapsulant paints for dealing with *S. chartarum* contamination on GWB were Permawhite, M-1 Additive, and Portersept. The results for Mil-Kil were close in comparison. Although two of these four products contain titanium dioxide, they all contain unique formulations that make it difficult to draw conclusions regarding antimicrobial performance (Menetrez *et al.*, 2008a).

These results are not meant to endorse the incomplete removal of mold-contaminated building materials. However, it is recognized that complete removal may not always be economically possible. Solutions to control mold regrowth can contribute to reduced occupant exposure. In some instances when mold damage is not substantial, cleaning surfaces and then painting with Permawhite, M-1 Additive, Portersept, or Mil-Kil can offer a practical alternative. In most cases, current recommendations of removal and replacement of porous building materials should be followed (Menetrez *et al.*, 2008a).

13.7.4 UVC irradiation

Ultraviolet (UV) irradiation has been used for the disinfection of air streams for many years (Cole and Foarde, 1999; Shechmeister, 1991). The range of UV wavelengths found to be most effective was 220 to 300 nanometers (nm), and the peak effectiveness was determined to be 265 nm (VanOsdell and Foarde, 2002). The production of UV light employs an electrical discharge through low-pressure mercury vapor enclosed in a quartz glass tube (VanOsdell and Foarde, 2002). This technique produces a

tube-type bulb with a primary wavelength of 253.7 nm, and is within the 'C' band of UV (UVC) (VanOsdell and Foarde, 2002). The UVC or UV germicidal (UVGI) form of irradiation has been demonstrated to deactivate bacteria, fungi, viruses, and mycoplasmas (Morey, 1988; Lidwell, 1994; Calvo *et al.*, 1999; Slieman and Nicholson 2000; Peccia *et al.*, 2001).

Ultraviolet irradiation has commonly been used in the indoor environment to eliminate or control infectious diseases in medical care facilities. HVAC system components such as duct-liners, cooling coils, drip-pans, interior insulation and areas subjected to high levels of moisture can create an environment which is prone to the establishment of biological microorganisms (Foarde *et al.*, 1997a, 1997b, 1997c; Menetrez *et al.*, 2004). The movement of indoor air is dominated by HVAC system operation. Biological contaminants that have become established in HVAC components, or that have been brought into the HVAC intake air (unintentionally or intentionally), can become distributed throughout the building interior. Air supplied to the building interior can carry these biological contaminants which expose numerous occupants to potential toxigenic, allergenic, and pathogenic bioaerosols.

A single UVC light was placed inside a galvanized steel square HVAC duct mock-up. The exposure chamber was maintained at room temperature, which was 22°C (71.6°F). A method to determine the antimicrobial efficacy of UVC irradiation was developed and tested on the surface of agar plates with four species of vegetative bacteria (*Deinococcus radiodurans*, *Pseudomonas fluorescens*, *Serratia marcescens*, and *Staphylococcus epidermidis*), three species of yeast (*Candida albicans*, *Geotrichum candidum*, and *Rhodotorula mucilaginosa*), four species of mold (*Aspergillus versicolor*, *A. fumigatus*, *Penicillium chrysogenum*, and *Cladosporium cladosporioides*) and eight varieties of *Bacillus* bacteria spores (*B. subtilis* var. *orange*, *B. subtilis* var. *cream*, *B. stearothermophilus*, *B. pumilus*, *B. megaterium*, *B. cereus*, *B. thuringiensis*, and *B. anthracis* *stern*.) exposed to UVGI irradiation (Menetrez *et al.*, 2006, 2008b). Most of these microorganisms have been identified as being present in HVAC air-handling units (Levetin *et al.*, 2001) and responsible for the transmission of airborne disease (Brickner *et al.*, 2003). *B. anthracis* surrogates were used for their expected similar inactivation responses to UVC irradiation. The exposure time (from 5 to 900 seconds depending on the microorganism) was initiated when an internal guillotine was very quickly lifted, allowing the UV light to travel down the duct to impact the plates. At the end of the exposure time, the guillotine was quickly lowered back into the duct mock-up. In all experiments, the plates were kept the same distance from the light (144.0 cm, or 56 in). With distance and irradiance constant, time of exposure is the controlling variable. The percent kill and *k* value for each organism were calculated for various periods of exposure (Menetrez *et al.*, 2006, 2008b).

For constant and uniform irradiance, the disinfection effect of UVC on a population of microorganisms can be expressed by the following set of equations (Philips Lighting Division, 1992):

$$N_t/N_0 = \exp(-k \times \text{dose}) \quad [13.1]$$

where:

N_t = the number of microorganisms at any time t

N_0 = the number of microorganisms at start, before exposure begins

N_t/N_0 = the fraction of microorganisms surviving

k = a microorganism-dependent rate constant, $\text{cm}^2/\mu\text{W C s}$

dose = the product of $E_{\text{eff}} C_{\text{I}} t$, in $\mu\text{W C s/cm}^2$ (measured irradiance C seconds of exposure)

W = watts

E_{eff} = the effective irradiance received, in $\mu\text{W C s/cm}^2$ (measured)

$^a t$ = exposure duration in seconds, s, between the start and time t .

The concentration–time product calculated in Equation 13.1 depicts the exponential decay of a population of viable organisms with constant exposure to UVC. Equation 13.1 can also indicate the ability of populations of microorganisms to withstand low to high doses of UVC irradiation (Brickner *et al.*, 2003; Levetin *et al.*, 2001; Menetrez *et al.*, 2006, 2008b; Philips Lighting Division, 1992).

The plates were incubated until moderate growth was visible, then the colony forming units (CFUs) were counted. The percentage killed was obtained by the following equation:

$$\% \text{ kill} = 100 \times \{1 - (C_E / C_{NE})\} \quad [13.2]$$

where C_E is the number of colonies on the side of the plate exposed to UV (N_t) and C_{NE} is the number of colonies on the side of the plate not exposed to UV (N_0). Significant kill was achieved with increasing periods of exposure (up to a high kill rate of 81% for a 120-second exposure). HVAC surfaces such as cooling coil fins within an air-handler which is exposed to a constant dose of UV irradiation would be expected to be relatively free of biological growth. This research demonstrated that UVC lamp irradiation inactivated biological growth to a reproducible degree with conditions of controlled doses. The k value and kill rate were calculated with the above equations (Brickner *et al.*, 2003; Levetin *et al.*, 2001; Menetrez *et al.*, 2006, 2008b; Philips Lighting Division, 1992).

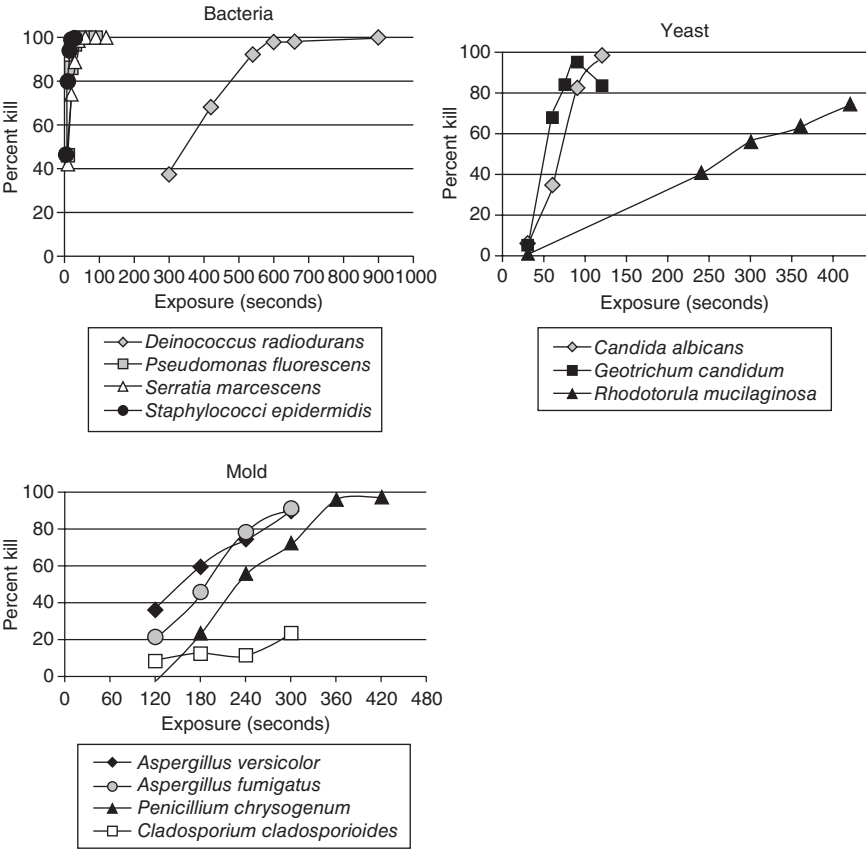
In one experiment, eight varieties of *Bacillus* spores were tested and exhibited similar effects to UVGI irradiance. Each species had large variations in surviving populations, and no significant difference in resistance between species. The k values ranged from a high of $7.46 \times 10^{-5} \text{ cm}^2\text{W-s}$ (for *B.*

s. orange) to a low of $3.23\text{e}^{-5} \text{ cm}^2\text{W-s}$ (for *B. megaterium*) (Menetrez *et al.*, 2006).

In another experiment, the k value results showed variability for three normally susceptible vegetative bacteria from $1.05\text{e}^{-3} \text{ cm}^2\mu\text{W-s}$ to $3.60\text{e}^{-5} \text{ cm}^2\mu\text{W-s}$ (with a range of relative standard deviation from 74% to 105%); yeast varied from $1.83\text{e}^{-4} \text{ cm}^2\mu\text{W-s}$ to $1.73\text{e}^{-5} \text{ cm}^2\mu\text{W-s}$ (with a range of relative standard deviations from 68% to 166%); and mold varied from $2.78\text{e}^{-5} \text{ cm}^2\mu\text{W-s}$ to $7.39\text{e}^{-6} \text{ cm}^2\mu\text{W-s}$ (with a range of relative standard deviation from 56% to 139%). Although highly variable, the k values are both reproducible and similar for all varieties tested. *D. radiodurans* (bacteria), *R. mucilaginosa* (yeast), and *C. cladosporioides* (mold) were the most difficult organisms to destroy in their groups. As anticipated, the four species of mold required a period of exposure in excess of 300 seconds to exhibit significant die-off, about twice that required for vegetative bacteria. It is difficult to infer further UVC exposure effects between microorganisms as comparatively diverse as fungi and bacteria (Menetrez *et al.*, 2008b). The ability to eliminate microorganism contaminants within commercial HVAC and residential HAC systems should contribute toward reducing occupant exposure and the opportunity for the spread of these organisms based on infectious diseases.

An example of the results of this work is listed in Fig. 13.8 which depicts the percent kill as a function of the period (in seconds) of UV exposure. *D. radiodurans* (bacteria), *R. mucilaginosa* (yeast), and *C. cladosporioides* (mold) were the most difficult organisms to destroy. *G. candidum* and *C. albicans* of the yeast, and *S. epidermidis*, *S. marcescens* and *P. fluorescens* of the bacteria, were the organisms which were most rapidly destroyed. Other than these specific microorganisms the four species of mold microorganisms, required a longer period of exposure to exhibit significant die-off. It is difficult to infer further UV exposure effects between microorganisms as comparatively diverse as fungi and bacteria.

Heating, ventilating, and air-conditioning (HVAC) systems become colonized by microorganisms after a period of use, and distribute those organisms as well as those in the return air. Depending on the amount and type of microorganisms (bacteria, viruses and mold), the amount of dust and stationary film, cooling coil fouling may occur. It has been suggested that this fouling biofilm is responsible for a diminished coil capacity and increased energy consumption. UVC used to maintain HVAC equipment can potentially result in lower energy costs while providing cleaner air. This could also greatly reduce occupant exposure and the opportunity for the spread of disease and allergic reactions (Brickner *et al.*, 2003; Levetin *et al.*, 2001; Menetrez *et al.*, 2006, 2008b; Philips Lighting Division, 1992).



13.8 Comparison of percent kill by UV period of exposure.

13.7.5 Ozone

This work evaluated the effects of exposing a variety of microorganisms (two bacteria and two fungi) to elevated gaseous ozone concentrations ranging from 100 to 1000 ppm. In order to evaluate ozone under realistic ‘real world’ conditions, the test organisms were inoculated onto the surfaces of building materials (Menetrez *et al.*, 2009). Inoculated organisms were allowed to dry on selected coupon surfaces. The concentration of organisms in colony forming units (CFU) was based on levels of contamination ranging from 10^3 to 10^7 CFU/cm² which have been isolated from surfaces of contaminated buildings. Inoculated materials were exposed to a range of RH levels, specifically low RH (20–45%) and high RH (80–95%). Temperature and RH were measured by a factory-calibrated EdgeTech Model 2000 Series DewPrime dew point hygrometer (Menetrez *et al.*, 2009).

The microorganism exposure experiments were carried out in a commercially available desiccator cabinet constructed of polished stainless steel and glass. The interior dimensions of the chamber were approximately $30 \times 25 \times 30$ cm (L $\times$ W $\times$ H). The total chamber volume was approximately 22 liters. The chamber was set up for use by opening the test gas entry, exit, and sampling ports, placing the support shelves within the chamber, and placing the test surfaces (glass microscope slides and glass Petri dishes holding squares of gypsum wallboard). A steady-state ozone concentration was established at the desired concentration, with measurement in the chamber center and at various locations to ensure that the test gas was well mixed. The air flow rates and ozone production were then adjusted to achieve the desired ozone concentration and RH for each experiment (Menetrez *et al.*, 2009).

The objective of this study was to evaluate the effects of exposing a variety of microorganisms to elevated gaseous ozone concentrations. Both porous and nonporous building materials were used to represent actual indoor surfaces, and controlled chamber exposures were conducted to maintain consistent exposure concentrations (Menetrez *et al.*, 2009).

Both gypsum wallboard (porous) and glass slide (nonporous) building materials were employed as the test surfaces in a series of experiments. Four separate microorganisms and two levels of relative humidity (RH) were tested. The four organisms selected for testing in this study were *Rhodotorula mucilaginosa*, *Penicillium brevicompactum*, *Bacillus atrophaeus*, and *Staphylococcus epidermidis*. Two fungal organisms (*R. mucilaginosa* (vegetative yeast cells) and *P. brevicompactum* (mold spores)) and two bacterial organisms (*B. atrophaeus* (Gram-positive bacterial spores) and *S. epidermidis* (vegetative bacterium)) were used (Menetrez *et al.*, 2009).

The ozone efficacy results varied for the organisms inoculated on the surface of glass slides and gypsum wallboard coupons. Exposures on the glass slides at low RH had no observed effect on the concentration of *B. atrophaeus* and *R. mucilaginosa*, while the *S. epidermidis* and *P. brevicompactum* both decreased at least 4 logs at the maximum exposure. The high RH exposures on both glass slides and gypsum wallboard affected all of the organisms. However, the *R. mucilaginosa* were inactivated by 4 logs. On the gypsum wallboard at low RH, none of the organisms exposed was inactivated by as much as 2 logs. The organisms exposed to high concentrations of gaseous ozone were more readily killed on glass slides than on gypsum wallboard. Additionally, increasing RH was found to increase the biocidal capability of high levels of ozone (Menetrez *et al.*, 2009).

The overall results of this study indicate that, even at concentrations of ozone approaching 1000 ppm, it is difficult to get significant inactivation of

organisms on surfaces. In agreement with earlier experiments conducted at low ozone concentrations, the organisms exposed to high concentrations of gaseous ozone were more readily killed on glass slides than on gypsum wallboard. Increasing RH increases the biocidal capability of high levels of ozone (Menetrez *et al.*, 2009). However, unlike the application of previously discussed antimicrobial treatments such as cleaners, paints or UV irradiation, the efficacy result for gaseous ozone indicates that it is not a realistic alternative for remediating biological contamination (Menetrez *et al.*, 2009).

Although the specific results vary according to each of the four test organisms and the test surfaces, the overall results of this study indicate that, even at relatively high concentrations of ozone, it is difficult to get significant inactivation of organisms on surfaces. Maintaining consistently high concentrations of 1000 ppm of ozone gas could be difficult throughout the volume of air contained in a building remediation application due to unwanted reactions with building materials. Achieving a significant reduction of biocontamination concentrations on surfaces, as well as inside porous materials, wall cavities and voids, within a building would be very difficult and impractical (Menetrez *et al.*, 2009). In addition to the difficulty in achieving these elevated concentrations, and the inadequate ability of gas-phase ozone to reduce concentrations of microorganisms, the high risk to human health of exposure makes this treatment technique both ineffective and hazardous (Menetrez *et al.*, 2009).

13.8 Antimicrobial product acknowledgment

The results of antimicrobial product testing are not meant to endorse the incomplete removal of mold-contaminated building materials. However, it is recognized that complete removal may not always be possible and solutions to control mold regrowth may contribute to reduced occupant exposure. Current recommendations for removal and replacement of porous building materials should be followed. It was not the intention of this discussion to endorse any product. Reporting on the performance of these products under the stated conditions was and remains the only purpose.

The US Environmental Protection Agency, through its Office of Research and Development, funded and managed the research described herein. It has been subject to an administrative review but does not necessarily reflect the views of the Agency. No official endorsement should be inferred. EPA does not endorse the purchase or sale of any commercial products or services. The findings listed above cover a broad expanse of research related to detecting and controlling mold contamination. Additional work is needed to further reduce human exposure to biological contaminants.

13.9 Conclusions

The areas of research covered in this chapter are as follows: 13.5 Effects of moisture, relative humidity (RH) and dust; 13.6 Duct cleaning effectiveness on microbial growth; and 13.7 Evaluation of antimicrobial treatments as control technologies: 13.7.1 Encapsulants, 13.7.2 Cleaners, 13.7.3 Paints, 13.7.4 UVC irradiation, and 13.7.5 Ozone. Advances in research and development of prevention and control as well as mitigation practices for a variety of molds have been achieved. Understanding the growth requirements of mold, developing the test methodology ASTM Standard 6329-98 (2003) and the static and dynamic microbial test chambers for determining antimicrobial efficacy, and determining the most effective techniques to identify, handle and mitigate contaminated materials will ultimately improve the ability to control biological contaminants and reduce human exposure.

13.10 Future trends

Future areas of microbiological research are being planned. Progress into these areas of research will be subject to change and reevaluation over time. However, these six research areas are a logical next step from past and present accomplishments.

13.10.1 Microbial-resistant building materials product evaluation – gypsum wallboard

When building materials become exposed to moisture by weather events, leaks in the building envelope, or inadequate control of relative humidity, absorption and transport of moisture through those materials often render it susceptible to the growth of biological contaminants. Microbial colonization, and the rapid growth and dispersion of mold, can expose building occupants and produce severe illnesses including pulmonary, immunologic, neurological and oncogenic disorders. Removal of substrates from building materials, or the incorporation of antimicrobial agents in the manufacturing of building products, may prevent mold growth and the spread of contaminants. The manufacture of microbial-resistant building materials (such as wallboard, ceiling tiles and flooring) can inhibit or prevent mold growth. Limiting or preventing mold growth by the manufacture of microbial-resistant building materials creates a product which can sustain temporary adverse conditions and is less likely to become a source of biological contamination, or to need replacement.

The manufacture of wallboard that has a greater ability to withstand moisture and prevent mold growth will be less problematic and in need of

replacement. Possible methods of gypsum wallboard improvement are being studied, including treatment with antimicrobials, ozone and heat during the manufacturing process. The ability to produce wallboard that may impair or prevent mold growth could greatly impact indoor air quality and reduce the need to remove and dispose of wallboard in landfills.

The manufacture of microbial-resistant gypsum wallboard has been initiated by a number of companies producing building materials. Each company has established its own manufacturing strategy for producing this material. The resultant wallboard materials could potentially have a longer product life and be both environmentally friendly and less likely to need replacing.

13.10.2 Microbial-resistant building materials product evaluation – ceiling tiles and flooring

Analogous to wallboard, the generation of ceiling tiles and flooring that has a greater ability to withstand moisture and prevent mold growth will be less problematic and in need of replacement. Possible methods of ceiling and flooring improvement should be studied. The prevention of mold growth could prevent contamination, human exposure and having to remove and landfill these products. This would ultimately create product sustainability which is the focus supported by the EPA.

Analogous to wallboard, the evaluation of ceiling tiles and carpet flooring would test the following: (1) microbial growth, (2) moisture absorption, and (3) VOC emission. The same established methods developed for wallboard would be used to form the basis of evaluation.

Acoustic ceiling tiles and carpeting used as building materials should be evaluated by this grading process. The impact on the building product industry and the consumer public can be significant, with both gaining advantages through the sales of better products.

13.10.3 HVAC biological film (biofilm) research

The presence of moisture on HVAC system cooling coils and drip-pans from condensate flow establishes conditions favorable for microbial growth. The established microbial growth can then be responsible for releasing gases (microbial volatile organic compounds or MVOCs, 'Dirty Socks Syndrome') or particles (BioPM) into the conditioned airstream. The presence of a microbial film on the cooling coils is also responsible for loss of heat transfer efficiency, overall component operation and the possible cause of condensate 'blow-by' into the supply air-duct. The characterization

of fungal organisms and their byproducts (MVOCs and BioPM) which are responsible for this condition and the most effective form of treatment (UV) would give building owners, building occupants, and building remediators accurate information in identifying and dealing with this problem.

The use of UV to destroy any biofilm which has been established on HVAC surfaces and not to allow regrowth is the most efficacious manner of long-term treatment. The use of UV to deactivate airborne biological contaminants transported within existing HVAC systems adds additional benefit to this treatment alternative. Also, the prevention of biofilm build-up on cooling-coil surfaces increases thermal transfer efficiency and decreases HVAC system energy use while preventing organisms from establishing a foothold in the indoor environment, increasing the sustainability of current building systems.

MVOC characterization of gases and polymerase chain reaction (PCR) identification of particles will be used to find the best way to identify biofilms. UV treatment of an HVAC system which has an established biological film will be performed. Measurements of biological contaminants and heat transfer efficiency from before and after treatment will be conducted. Laboratory and field demonstrations will be performed concurrently.

13.10.4 Reduced infectious disease

The spread of infectious disease in humans can be attributed to communication by touch, and inhalation of the infectious agents (virus and bacteria). Air conveyance through the HVAC can transport the infectious agents along with other particles throughout a building. One infectious person can spread viable organisms to many other through the conveyance of conditioned air.

Research should focus on developing optimal air treatment techniques of fine and ultrafine biological particles (viral, bacterial) which are responsible for the spread of infectious disease. Biological surrogates of viral and bacterial organisms will be inoculated into the airstream traveling through an HVAC system. Improving methods of treatment can result in less transmission of infectious disease as well as better biological indoor air quality.

Research will involve ultraviolet (UV) irradiation to destroy viral and bacterial microorganisms on a surface and in a moving stream of air. The use of UV to destroy *Bacillus* spores and mold has been demonstrated. However, the antiviral or anti-pneumonia efficacy of UV on surfaces and in a moving airstream is largely unknown. The use of UV to clean air within an existing HVAC system can have other beneficial effects such as preventing fungal growth and decreasing energy use.

13.11 Sources of further information

13.11.1 Books and publications

1. Wu, R., *Statistical and Computational Pharmacogenomics* (available at Las Vegas, call # QV 38W959 2009): Contains joint functional mapping of drug efficacy and toxicity, and modeling of drug responses.
2. Kempter, J., *Antimicrobial Products Used to Inactivate Bacillus anthracis Spores* (available at NTIS, call # ADA453105): EPA document of an efficacy study involving *Bacillus anthracis*.
3. Schneider, B., *Pesticide Assessment Guidelines: Subdivision G, Product Performance* (available at NTIS, call # PB83-1539240, as a guideline for the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), Subdivision G): Provides guidance to the registrant on developing product performance data that the Agency may require to demonstrate the effectiveness of their pesticide product in controlling the pests specified in the claims on their product label. This subdivision is organized into section series which describe efficacy data for specific types of pesticides used on distinct classes of pests. Guidance on test methodology and protocols to support label claims are also presented. Discussions concerning when the submission of efficacy data is required are also presented as a foundation for the regulatory pesticide data requirements (40 CFR Part 158).
4. Haynes, H., *Analysis of Specialized Pesticide Problems Invertebrate Control Agents – Efficacy Test Methods, Volume VII. Human and Pet Treatments* (available at NTIS, call # PB-266 209): Testing procedures stated and referenced in this document are accepted methods for determining the effectiveness of pesticides against pests of humans and pets. The procedures mentioned are not intended to exclude other procedures. This document may serve as a guideline for the development of information relating to pesticide efficacy. Species named in this document are not necessarily the only ones which might be used. Other species may also be considered when of economic importance or when they provide practical data. When numbers of test animals are referred to in this document, the minima are given. However, the researcher may want to increase numbers of test subjects, animals or other organisms when practical or economically feasible.

13.11.2 Online resources

1. <http://www.epa.gov/oppad001/antimicrobial-testing-program.html>: Overview of the EPA's antimicrobial testing program, results, and methods.

2. <http://apps.americanbar.org/environ/committees/pesticides/newsletter/oct03/pdf/pesticides1003.pdf>, 'EPA's Role in the Regulation of Antimicrobial Pesticides': A feature in the newsletter of the Pesticides, Chemical Regulation, and Right to Know Committee Newsletter. Contains a detailed overview of the testing program, the different types of antimicrobials, and laws governing regulation of antimicrobials.
3. <http://www.epa.gov/oppad001/sciencepolicy.htm>, EPA's antimicrobial science policies.

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Potential hazards from waste based/recycled building materials

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Abstract: This chapter presents the main waste categories used in construction materials with a focus on aggregates and cement-based materials. The chemical composition and properties of the selected wastes are presented in relation to their intrinsic toxic or ecotoxic hazard potential. The factors influencing the leaching of hazardous substances and the toxicity of construction materials in relation to their utilisation scenario are discussed. Methods and tools (including leaching and ecotoxicity tests and models) for assessing the toxic/ecotoxic properties of construction materials are presented and their relevance and application are discussed through practical case examples available in the literature.

Key words: waste recycling, toxicity, risk assessment, leaching tests, ecotoxicity tests.

14.1 Introduction

The accelerated development of all activities in the context of globalisation increases dramatically the environmental pressure exerted by humanity. It is more and more clear that the different material resources are limited or under depletion, so that the economic system is evolving towards a closed-loop operation. The appropriate reuse of residues in different activity fields can make an important beneficial contribution to reducing the environmental impact, e.g. by limiting the extraction of mineral resources and the associated energy consumption (extraction, transport, manufacturing, etc.), reduction of greenhouse gas emissions, waste, etc. This change represents a challenge for all economic activities. About 50% of the materials taken from the earth's crust are used in building materials (EC, 2006); during their life-cycle building materials are responsible for high energy consumption and greenhouse gas emission. Building materials generate about 25% of all waste in Europe during the construction and demolition stages. If interest in reusing appropriately all these materials is obvious, the process has to be strictly controlled to eliminate all risks, particularly to human health.

At the European level, a Regulation has been published (repealing the older European Construction Product Directive CPD 89/106/EC) creating

new conditions for the functioning of the unified market for the manufacturing of construction materials ('laying down harmonised conditions for the marketing of construction products' (EU, 2011)). Among the basic requirements of the construction works and implicitly of building materials, listed in Annex I of the Regulation, importance is given to health, hygiene and environmental impacts and to the sustainable use of natural resources, including the 'use of environmentally compatible raw and secondary materials in the construction works'. The Technical Committee CEN/TC 351 'Construction products: Assessment of release of dangerous substances' of the European Standardization Committee works on the elaboration of harmonised standards in the field of the assessment of building materials for their reuse. Different working groups have been created to answer questions concerning radiation/air emissions, release of pollutants from construction materials into water, soil, etc. The proposition of a global methodology is in progress; its further application will lead to changes and adjustments in manufacturing processes for building materials and linked practices.

This chapter first presents the main waste categories used in or as substitutes for construction materials. Among the most important construction materials, aggregates and cement in association with different aggregates take the prominent place. Therefore, we give special attention to cement-based construction materials by presenting some of the additional components, and to the wastes used as structural aggregates. Then, the chemical composition and properties of the selected wastes are presented in relation to their intrinsic toxic or ecotoxic hazard potential. The identification of the waste's potential hazard is not sufficient for estimating the toxic properties of a construction material containing the respective waste for at least two reasons: (1) chemical transformations (composition and structure) take place when processing a waste-containing material; and (2) the conditions of use of the construction material are factors influencing the chemical behaviour (the leaching behaviour for instance) and consequently the toxicity potential. These aspects are discussed in Section 14.4. Section 14.5 presents the methods and tools (including leaching and ecotoxicity tests and models) for assessing the toxic/ecotoxic properties of construction materials. The relevance of methods and tools is discussed through practical case examples available in the literature. Finally the conclusion points out the state of the current practice in the field of toxicity/ecotoxicity assessment for construction materials and future trends.

14.2 Main types of building materials containing wastes

For decades the building sector has offered an important outlet and market for the reuse and recycling of a wide range of wastes. The term *reuse* here

designates the utilisation of a waste material (also called a residue or a secondary material) in a transformation process in order to obtain a different material/product, while *recycling* signifies the processing of a used material for supplying a fresh material of the same kind.

The possibilities for a waste to be reused or recycled in building materials are commonly determined by its chemical binding properties (pozzolanic or hydraulic binder, or with other binding properties), structural properties (aggregates, fibres, etc.) or energetic content (combustibility). In this section we discuss the waste used in two main construction material categories: cement-based materials and structural/aggregate materials.

14.2.1 Clinker, cement and concrete containing wastes

The use of potentially pollutant recycled materials can be observed at different stages in the processing of cement and cement-based materials.

Portland clinker is obtained at high temperature (1450°C) from limestone, clay and a combustible mixture defined to obtain a fixed composition of Ca, Si, Al and Fe oxides. The high energy demand of the process is partially satisfied by the replacement of fossil combustibles by waste materials, a substitution that is also called co-processing or co-incineration. Recycled materials with convenient characteristics for the combustion process and for the clinker quality are used: high calorific power, composition, size distribution, humidity, etc. The fossil combustible substitution rate is between 14% and 90% of the total energy demand (ADEME, 2009), impacting the different factories economically and environmentally. Traditionally the substitution combustibles (called alternative fuels and raw materials, AFR) are composed of high caloric residues (waste oils, tyres, plastics, etc.), dried sewage sludge, and solid residual fuels (SRF) containing plastics, wood, paper, cartons, etc. The control of AFR composition is highly important and specific operations are necessary to prepare it (GTZ-Holcim, 2006). They are typically fed to the kiln system via the raw material supply in the high-temperature zone. The clinker reactions allow the incorporation of ashes and binding of metals to the clinker. Statistically, the effect of AFR on the heavy metal composition of clinker is marginal, except for Zn content in the case of bulk use of tyres (GTZ-Holcim, 2006). The use of substitution combustibles in the cement rotary kilns does satisfy precise compositional constraints for high-quality clinker, e.g. sulphur, chlorine (SRF), heavy metals (waste oils, SRF, etc.) or phosphorus content (meat and bone meal, sewage sludge, etc.).

Commercial cements are mixes of fine crushed clinker with different mineral admixtures designed to improve their specific properties, e.g. to improve the pozzolanic properties or the setting and/or to reduce price. To clinker are added gypsum (up to 5 wt%) for setting regulation and different

other secondary materials with pozzolanic action: granulated blast furnace slag from iron metallurgy, coal combustion fly ashes, burned shale, calcareous limestone, silica fumes. The composition of the common European commercial cements is detailed in the EN 197-1 standard, e.g., CEM I (Portland cement) is composed of 95% clinker and up to 5% secondary constituents, while CEM VA contains clinker (40–64 wt%), furnace slag (18–30 wt%), pozzolanes and siliceous fly ashes and up to 5 wt% secondary constituents. Compositions of special cements are also standardised, e.g. cements to be used in marine environments or in sulphate-rich waters. The characteristics of these admixtures are consequences of precisely defined limits for the cement properties, e.g. the insoluble residue, the S and Cl content, the pozzolanicity, etc. In the composition of these admixtures, specific parameters, like their heavy metal content, are subject to investigation because of their potential environmental impact.

The granulometry of the aggregates used in cement-based materials divided them traditionally into mortars (granulometry less than 4 mm) and concrete. The concrete formula is correlated with the utilisation scenario: mechanical and environmental requirements, planned lifetime, conditions and constraints of implementation. This defines the composition to be ensured: content and type of cement, additives, size classes and composition of aggregates, water content, and fabrication protocol. The economic and environmental benefits of replacing more or less totally the natural aggregates by aggregates with similar properties from the reuse of materials like inert waste, demolition concrete, residues from different thermic processes like municipal waste incineration, slags and sands from metallurgical processes, are obvious. The feasibility of the substitution requires not only good physical parameters (such as particle size, density, colour, etc.), chemical and mineralogical composition of the aggregates but also easy implementation, risk and traceability control.

Concrete admixtures are obtained from secondary materials like lignin or issue from specific chemical synthesis. Strictly speaking, they are not all recycled materials, but their long-term life cycle in concrete can lead to their degradation to potentially hazardous products. Plasticisers, superplasticisers, air-entraining admixtures, waterproofing compounds, retarders, setting and hardening accelerators, grouting aids and stabilisers, defoaming agents, etc. are used because of their beneficial effects during concrete processing; workability and setting behaviour can be better controlled. The properties of the hardened concrete (strength, impermeability, etc.) can also be improved by adding additives. Therefore, important technological, economic and energetic (and thus environmental) benefits are achieved by using these additives. It is estimated that more than 90% of commercial concretes are produced with admixtures, the majority of them being plasticisers/superplasticisers, basically composed of modified lignosulfonates,

melamine–formaldehyde sulfonate polymers, naphthalene–formaldehyde polymers, naphthalenesulfonate, etc. Generally 80–90% of the initial additive mass is sorbed by the hydrated cement phases. The unsorbed part of the admixtures remains in the pore solution and can be subject to coupled transport and reaction (degradation) processes and subsequent hazardous effects on the environment and human health.

14.2.2 Structural materials and aggregates

Reuse/recycling of wastes to substitute and/or complement natural aggregates is mostly encountered in road construction and other earthworks (embankments, backfilling of mines, quarries, excavations, etc.).

A common road structure is composed of several layers of different natural aggregates with or without binders. The embankment comprises at least two layers realised with coarse aggregates at the bottom, and fine aggregates used alone and with a hydraulic binder (lime) at the top. The sub-base and the base layers confer mechanical resistance and require aggregates consolidated by hydraulic binders or bitumen. Finally, the pavement layers are generally composed of aggregates and asphalt. The wastes suitable for use in road construction are those providing a good mechanical resistance, compacting property and binding capacity. The wastes most often employed are the municipal solid waste incineration bottom ashes (MSWI-BA), fly ashes from coal combustion, slags from metallurgy, waste concrete, mining wastes, and foundry sands.

For waste use in backfillings the same general characteristics are requested as for embankments. In addition, lightness and ease of pumping are useful properties for such operations, and could be ensured by coal fly ashes.

14.2.3 Main waste streams used in construction materials

The European statistics on waste production and management are of poor quality. Some data on production and reuse/recycling in the construction sectors of the main waste streams in Europe in recent years are presented in Table 14.1.

MSWI-BA residues represent about 80% of the incineration residues of municipal solid wastes and are considered to be non-hazardous. Their chemical composition depends on the municipal waste composition and incineration process. The main components are silica, lime, alumina, limestone, traces of heavy metals and unburned organic matter. The material could be reactive in contact with water, releasing soluble salts and evolving through more stable solid phases. A pre-treatment of the fresh waste allows improving the chemical stability by separation of different fractions and by ageing (hydration–carbonation) for immobilisation of certain pollutants.

Table 14.1 Production and main methods of reuse/recycling of mineral wastes in Europe

Waste	Production (Mt/year)	Road construction, embankments	Concrete addition	Cement fabrication, additives	Cement replacement	Other construction materials	Sources
MSWI bottom ash	10.6	NA*	NA			NA	Abbott <i>et al.</i> , 2003
Coal combustion products (CCP)							ECOA, 2011
CCP – Fly ash	37.5	3.5	6.7	6.3	2.4	1 (asphalt filler, bricks, ceramics, grouting)	ECOA, 2011
CCP – Boiler slag	1.4	1				0.07 (grouting)	ECOA, 2011
CCP – Bottom ash	4.9	1	0.1 1	0.4	0.12	0.03 (bricks, ceramics, grouting)	ECOA, 2011
CCP – FGD gypsum	11.2		0.64			8 (gypsum based)	ECOA, 2011
Blast furnace slag	25	32.6%	64%			NA	EUROSLAG, 2006

Steel slag	15	45%	1%	NA	EUROSLAG, 2006
Demolition and construction waste	850 540	NA	NA	NA	EIONET EC/DG ENV, 2011
Waste concrete	380	Forecast up to 75%	Forecast up to 40–50%		EC/DG ENV, 2011
Bricks, tiles, ceramics	NA	NA	NA		EC/DG ENV, 2011
Asphalt	47	NA		Asphalt mixes, NA	EC/DG ENV, 2011
Wood	10–20			Timber	EC/DG ENV, 2011
Gypsum	>4		Possible, NA	Plasterboards	EC/DG ENV, 2011
				Forecast up to 30%	
Mining, quarrying and ore-processing wastes	> 350–400	x	x	x	BRGM, 2001

*NA = not available.

The material is suitable as a secondary aggregate, mainly used for road embankments, foundations and backfilling, but also for minor applications like sound-insulating walls, breeze blocks, or non-structural safety-related purposes such as concrete and bituminous concrete aggregate (Abbott *et al.*, 2003; data for eight EU countries, estimations for the period 1990–2000).

Coal combustion for heat and electricity production generates several coal combustion products (CCP) depending on the combustion process and coal origin:

- The fly ashes are collected in the flue gas dry-treatment system and, following their chemical composition, are classified in two categories. Class F fly ashes contain mainly silica and alumina and less than 20% lime, therefore having pozzolanic properties. Class C contain more than 20% lime and possess pozzolanic and hydraulic properties; when in contact with water they harden and gain strength over time. In addition, fly ashes contain variable quantities of many other chemical species and elements such as magnesium and iron oxides, but also heavy metals, arsenic, unburned organics, and dioxins.
- Flue gas desulfurisation gypsum (FGD Gypsum) is a solid residue recovered from the gas treatment process for sulfur dioxide removal using lime or limestone. This product is close to mined natural gypsum.
- The bottom ashes are collected in a dry-bottom pulverised boiler. The boiler ash is obtained in wet-bottom boilers by quenching of the molten slag. These ashes contain the same elements as the fly ashes, in different proportions.

According to ECOBA (2011), production of CCP in 2008 was approximately 56 million tonnes in EU-15 and 100 million tonnes in EU-27, with the following composition: fly ashes (66.6%), FGD Gypsum (20%), bottom ash (8.6%) and boiler slag (2.4%). Applications for CCPs in construction materials are numerous: as additives in concrete, as a cement replacement material, as an aggregate or binder in road construction (good compacting, pumping and binding properties), and as a filler.

Slags are rock-like or glassy materials composed chiefly of lime and silica. Minor components are magnesia and alumina. The exact ratio of these constituents depends on the process at the origin of the slag.

- Blast furnace slag is a co-product of iron fabrication, obtained by rapid chilling with water and having a glassy structure. It is a porous material having hydraulic-binding properties which can be used rather for asphalt road bases or subbases, but not for surface layers.
- Other crystallised slags obtained by slow cooling are denser, mechanically resistant and chemically stable and are used as granulate only.

Post-furnace treatment is carried out to enhance and optimise the properties and qualities of slags to ensure that the requirements of the end user are completely matched. Data published by EUROSLAG (2006) for European countries concerning steel and blast furnace slag production by the EU steel industry in 2004 are presented in Table 14.1. These wastes are mainly reused as aggregates and binders for road construction, public works, concrete, mortars and grouts, in cement fabrication, and in other materials like bricks, pavements, breeze blocks, etc.

Construction and demolition wastes represent about 31% of total waste generated in Europe (ETC/SCP, 2009; statistical data from 2008 for EU countries and Norway). Many components in this waste category are easily recyclable and have the potential to replace up to 10% of raw materials. The composition is very variable and changes in time and from one country to another. Data on recycling and reuse in the construction sector are not reliable for many countries. However, a mean EU value for total recycling/reuse of 46% is reported (EC/DG ENV, 2011; data for the EU-27 countries).

Concrete, bricks and tiles represent together about 78% of construction and demolition wastes. Other components are ceramics, gypsum, glass, metals, asphalt, plastics, treated and untreated wood, dredging soil, track ballast, sand, gravel, stones, etc. In addition, if not separated at source, such waste can contain small amounts of hazardous wastes (insulating foams, paints, asbestos, etc.), the mixture of which can raise particular risks to the environment and can hamper recycling. The mineral fraction represents the great majority of construction and demolition wastes, up to 85%. This mineral part can replace natural aggregates in road construction, earthworks and structural concrete. Asphalt is 100% recyclable in hot or cold mixing, replacing virgin aggregates and binder. Waste treated wood can be reused for timber product fabrication if it complies with the chemical contamination limits (EC/DG ENV, 2011).

Construction and demolition waste has been identified as a priority waste stream by the European Union. In particular, there is a reuse market for aggregate wastes in roads, drainage and other construction projects. In addition, technology for the separation and recovery of construction and demolition waste is well established, readily accessible and in general inexpensive.

Mining, quarrying and ore-processing wastes represent about 27% of the total waste produced in Europe per year (EC-EDG, 2004). Most mining and quarrying wastes are waste rocks (resulting from the excavation of the mine sites) and tailings which are generated at all levels of the recovery process to upgrade the minerals, and are considered as ultimate waste impoverished in useful elements. These wastes are of great chemical variety depending on the natural resource exploited, the chemical species extracted

from them and the extraction process used (BRGM, 2001). The main categories related to the extraction process and chemical composition are waste from coal extraction, waste minerals from industrial mineral extraction usable as such after concentration or purification (talc, kaolin, bentonites, etc.), and wastes from metal or other element extraction by physico-chemical separation processes. Coarse mining waste and especially barren rock is sometimes considered as material for roads, building foundations or cement factories, depending on its geotechnical and geochemical characteristics.

Various other wastes can be used in construction materials, such as glass, foundry sands, rubber from tyres, plastics, sewage sludge, etc.

14.3 Waste properties and potential hazards

14.3.1 Waste used as alternative fuels and raw (AFR) materials in cement kilns

Depending on the properties of the waste feed, pre-processing could be necessary, such as sorting, neutralisation, drying, etc. The major part of AFR is solid with various shapes, dimensions and densities, so special operations are necessary to grind it optimally to convenient homogeneous dimensions and facilitate metal extraction (magnetic, hydraulic, etc., processes), for meeting the required conditions for kiln feeding. Some other wastes can be liquids (oils and solvents, from chemical, transport or agricultural industries) or slurries. The composition of the AFR and its variability in time can be important parameters influencing the cement quality and its potentially hazardous impact. Some classes of waste are prohibited, like radioactive waste, explosives, electronic waste, batteries and unsorted municipal waste because of their variable properties or high content of heavy metals.

The mineral part of AFR must bring a material value to the cement kiln. Limit values for the content of some elements of AFR are proposed by national regulation or different industrial permits (ADEME, 2009; GTZ-Holcim, 2006), taken individually or by group of elements with close properties (such as total halogens, alkalis, etc.), as a function of the origin of the waste or otherwise. Here are some examples showing quite large differences between the composition of admitted waste/AFR in the cement kiln: Cu (less than 100–700 mg/kg), Pb (less than 150–800 mg/kg), Zn (less than 400–500 mg/kg), Cr (less than 50–500 mg/kg), As (less than 13–20 mg/kg), Co (less than 12–100 mg/kg), Ni (less than 30–200 mg/kg), Cd (less than 2–30 mg/kg), Sb (less than 5–800 mg/kg), Be (less than 2–5 mg/kg), Hg (less than 0.5–10 mg/kg), V (less than 10–100 mg/kg), Sn (less than 10–100 mg/kg), S (less than 10–400 mg/kg), Cl (less than 0.2%–2%), F + Br + I (less than 0.2%–1%), etc.

The organic part of AFR represents a calorific value for the cement kiln. However, particular toxic organic components are monitored, like PCBs (less than 50 mg/kg to 1%), cyanides (less than 100 mg/kg), benzene, dioxins, etc. The admission of AFR in the high-temperature zone of the kiln should allow the complete degradation of the organic components (exothermic oxidation) and stable incorporation of metals in the clinker phases.

14.3.2 Additives used during the hydration process of cement for mortar and concrete fabrication

As shown before, the different organic additives added during cement processing into mortar or concrete can remain partially sorbed on the hydration phases and therefore in direct contact with the pore solution contained in the porous system. In fact, the pore solution is very concentrated in alkaline species ($\text{pH} > 13$) and can interact with the additive molecules, breaking them down into more soluble and mobile molecules (Spanka and Thielen, 1995). If the initial additives do not have hazardous properties, the molecules obtained by their degradation can be potentially hazardous. Due to their higher mobility they can be leached out from the material in more or less short term. The global mechanism can be diffusional, controlled by species release in the leachant. Literature data point out, for example, that lignosulfonates are broken down into by-products like vanillin and eluted, while melaminesulfonates are rapidly broken down into insoluble by-products, less eluted in relatively short-term experiments (Duchesne and Bérubé, 1994). Parts of the generated species are known to be hazardous, potentially carcinogenic pollutants: phenols, formaldehyde, naphthalene, etc. However, the environmental impact of leached organics from concrete (produced by the degradation of the additives) has traditionally been considered insignificant because of the low proportion of additives used in commercial concretes (about 1% of the cement weight) and the small amount of the added quantity that is affected by degradation and release.

14.3.3 Recycled aggregates

The potentially hazardous character of recycled aggregates resides in their chemical composition. Generally, these wastes are composed of a solid matrix that is relatively inert (silicates and oxides stable in contact with water), crystalline (often very porous) or vitreous, which also confers the mechanical properties of the aggregates. Various trace elements are also present depending on the origin of these recycled materials: ores, coals, residues from thermal processes, and municipal wastes (in the case of MSWI-BA). Some of these trace elements can have toxic properties

depending on their chemical speciation, solubility in contact with water, and means of exposure. Several examples are given below.

The slags issued from different metallurgical processes represent annually huge quantities potentially available for reuse: e.g. Waelz slag from the recycling of electric arc furnace dusts (weight composition: 7–23% CaO, 4–7% Al₂O₃, 0.1–0.5% Cr₂O₃, 4–40% FeO, 0.01–0.1% As, 0.3–0.5% Cu, 0.4–4.2% Pb, 0.2–4% Zn, 0.8–2% S, etc.) (Barna *et al.*, 2000a), Imperial Smelting Furnace slag (average weight composition: 18.1% CaO, 10.4% Al₂O₃, 33.7% FeO, 0.1% As, 0.7% Pb, 7% Zn, 1.6% S, 21.9% SiO₂, etc.) and Lead Blast Furnace slag (average weight composition: 20% CaO, 1.9% Al₂O₃, 33.4% FeO, 0.15% As, 3.5% Pb, 11.2% Zn, 0.7% S, 23% SiO₂, etc.) from the primary non-ferrous metallurgy (Barna *et al.*, 2004), etc.

MSWI-BA composition is variable depending on the municipal solid waste composition and type of incineration process, the major elements being Si, Ca, Al, Fe, Na, Mg, K and C. Elements like Cl, Ti, Zn, Cu, Ba, S and Mn could be found in concentrations of about 1–10 g/kg. Trace elements (less than 1 g/kg) include Pb, N, Sn, Cr, Zr, F, B, Ni, Sb, V, Co, Cd, Ga, Li, La, Mo, Ba, As, Be, Au, Sc, Hg, Se and cyanide (Jeong *et al.*, 2005). The organic part composed of unburned matter varies up to 30% of the MSWI-BA dry mass.

The chemical composition of fly ashes (CCP) depends on the coal origin and combustion process used. Besides the major constituents (Si, Al, Fe, Ca) a large variety of chemical elements are present in trace quantities, some of them being targeted for their potential hazard. These are Cr, Cu, Ni, Pb, V and Zn present in several hundreds of mg per kg of dry fly ash, As and Se as dozens of mg/kg, and Hg, Cd and Sn up to 1 mg/kg (Rakotoarisoa, 2003). Concerning the chemical speciation, the trace elements are mostly captured in stable alumino-silicates and oxides, reducing their solubility and availability in contact with water. Condensation of volatilised elements during combustion can also occur, especially at the surface of ash fine particles.

Significant European research programmes have been dedicated in recent decades to the characterisation of waste materials in parallel with the development of an environmental assessment methodology (Barna and Blanc, 2011). A huge bibliography is available concerning the leaching properties of MSWI-BA, fly ashes and slags (obtained by laboratory leaching tests, Section 14.4).

Generally, the amount of pollutants released can be linked to their total content. However, their mineralogical characterisation can explain apparently contradictory behaviours, e.g. the encapsulation of small metallic droplets in the glassy phase of slag (5–47 wt%) explains a reduced release of Pb and Zn between the different Waelz slags (Barna *et al.*, 2000a). Leaching conditions such as leachate composition or exposure conditions

(carbonation, cycles like wetting/drying, freezing/thawing, etc.) can contribute to particular behaviours. For example, organic compounds having complexation capacity can explain the high level of Cu release in materials containing MSWI-BA (Bröns-Laot *et al.*, 2004), and acidic conditions increase the release from 'reactive' materials like phosphates (apatites) or cement-based materials containing pollutants.

14.3.4 Potential toxicity of wastes used in construction materials

In the European Waste Catalogue (EC, 2001), Annex III is dedicated to the hazardous wastes characterised by at least one of the 14 EWC-defined hazardous properties. Criterion H14 defines ecotoxic wastes as '*substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment*'. The ecotoxic properties of a hazardous waste can be assessed using chemical composition and/or biological methods, realised on solid waste and/or on the leachate (standardised as EN 14735, CEN, 2003). The biological method is based on ecotoxicity tests (bioassays) realised on a set of selected species and has the advantage of integrating all pollutants with their synergistic, antagonistic and additive effects as well as their bioavailability.

The classification of wastes as hazardous is determined by the presence of at least one toxic effect or by at least one concentration higher than a maximal accepted value (standard). The concentration limit values are not consensual in the EU; specific national regulations coexist (e.g. the composition of water destined to potabilisation or landfill acceptability).

The ecotoxic potential of several waste types used in construction has been determined following the prescriptions of EN 14735 and applying different ecotoxicity tests; several results are given here.

MSWI-BA is one of the most investigated wastes. Different studies performed over the last 10 years and in different laboratories confirmed that the incinerator ashes can be hazardous or not, depending on their origin and combustion process. In all cases the leachates have basic pH and high concentrations of Cl^- , SO_4^{2-} and dissolved organic carbon.

A set of seven MSWI-BA of different origins were investigated for ecotoxicity potential (Lapa *et al.*, 2002) using bioassays on leachates (with a bacterium, a freshwater alga, a crustacean, and a vegetable). This study showed that the identification and classification of the ecotoxic potential (and finally the decision concerning the waste's valorisation) depend on the control parameters chosen (chemical composition vs standard limit values, chemical composition vs bioassay, and different bioassays) and pointed out the necessity of a common regulation in this field. In this study, all wastes were found to be ecotoxic according to the chosen standard.

A test battery applied (Römbke *et al.*, 2009) on leachate (algae, *Daphnis*, and luminescent bacteria) and on solid waste (plants, earthworms and bacteria) showed that globally the aged MSWI-BA is slightly less toxic than the fresh samples. No correlation was found between toxicity and heavy metal concentrations in the leachate and solid waste samples; the toxicity seems to be due to the high salt concentration.

Concerning the ecotoxicity assessment, the method described here lacks clear choices for ecotoxicity tests and standard limit values; as of today, no consensus is established for a mandatory method (Wilke *et al.*, 2008).

14.4 Scenarios of pollutant emission from construction materials

The life cycle of construction materials containing wastes comprises the following stages: raw materials extraction – fabrication – service life – demolition – end of life. The end of life could be after the demolition operation, a new cycle of reuse/recycling (reincarnation) or an appropriate elimination by treatment and (ultimate) waste disposal. Concerning the duration of each stage, construction and demolition are usually the shortest (from days to several months) while service life and end of life disposal are the longest, spreading out over many decades.

When wastes are used in construction materials, it is legitimate to enquire about the hazardous potential in the different stages. The potential hazard depends on the chemical/mineralogical composition of the waste used (toxic elements or compounds) and on its physical form (blocks, aggregates, dust, volatile compounds, etc.) but also on the duration of the respective stage and degree of material/environmental contact.

When comparing the different stages with respect to their potential environmental and health impacts, two groups are distinguished: the construction and demolition stages on the one hand, and the service life and disposal on the other.

14.4.1 Health risks in the construction and demolition stages

A risk for human health could arise directly in the fabrication and demolition stages, when the workers are directly exposed, mainly through inhalation. Fugitive dust emissions occur from stockpiles, deposits and unfinished works. Operations like transport, handling, different processing steps (e.g. sorting, crushing, grinding, shredding, sieving, pulverising, chipping, abrasion, spreading, compacting) generate fine particles which are dispersed in the atmosphere. Whatever the chemical composition, dust causes harmful

stress for workers and over long exposure can induce industrial diseases. The harmful effect is amplified if the particles contain toxic compounds.

Another source of health problems is represented by materials based on organic compounds which can be released in the atmosphere by volatilisation at ambient or process temperatures. This could be the case with plasticisers, solvents, glues, etc. existing in waste materials (mainly construction/demolition wastes). Semi-volatile organic compounds (e.g. aromatic hydrocarbons, dioxins, furans, etc.) can be released during heating in specific processes such as hot processing of asphalt and gas-phase reactions after combustion of organic wastes in cement rotary kilns.

Dust and condensed compounds can be deposited in the neighbourhood of the work site and contaminate soil, vegetation and water resources, and then be transmitted by the food chain to animals and humans. The emission of dust can in certain cases be avoided by water spraying, or by covering or enclosing the machinery; dust inhalation can be avoided by using gas masks.

Another aspect to be considered here is the potential leaching of the particulate materials by rainwater during the fabrication and demolition steps. The leaching phenomenon generates soluble compounds and their dispersion in soils and natural waters, and also the runoff of fine and colloidal particles. The more the material is divided in finer particles, the more the leaching process is amplified and the release of toxic compounds increased. So, if a block-compacted material can be relatively inert, the same material dispersed in small particles can become a real threat.

Very poor information on the harmful effect on workers during the construction/demolition steps, or via the food chain, is available. General aspects such as those discussed above are mentioned by EC/DG ENV (2011) for construction demolition wastes, and by Abbott *et al.*, (2003) for MSWI-BA. These latter authors present a risk assessment study considering a mean scenario of road construction using MSWI-BA as aggregate in asphalt pavement. This study is based on a series of worst-condition hypotheses for the emission of dust (containing pollutants like As, B, Ba, Cd, Cr, Cu, Hg, Mo, Pb, Sb and Zn), for organic volatile compounds (dioxin-like molecules) and also for leaching by rainwater on the road construction site. The dynamic of pollutant concentration in air, water and soil was calculated, and pollutant transmission by the food chain was estimated. Intake by inhalation was considered for the workers and the ingestion route for the local foodstuff consumers. Finally, the exposure parameters for target humans (the hypothetically most exposed individuals) were estimated (means of exposure, concentration, duration and dose), then the predicted doses by pollutant were compared with toxicological effect parameters. For all scenarios considered, the predicted doses were small compared with relevant reference doses for metals and dioxins, and even

in the worst-scenario hypothesis the method did not foresee any impact on human health. The authors stress the fact that the study was carried out on a given waste sample and the results could not be extrapolated for all MSWI-BA streams due to the variability of their chemical composition.

14.4.2 The service life – emission scenarios

During the service life of construction materials studied in this chapter, the main hazard potential is represented by contact with water, a common component of the litho- and biosphere. Water is the major pollution vector in the environment; in contact with a material, the soluble/mobile constitution substances are dissolved and carried out through soils and water to the biosphere. The leaching phenomena are thus responsible for mobilising potentially hazardous substances, impacting the quality of soil, water and finally the biosphere and human health via contact and intake routes (water and food). Given the long-term spread and the multitude of situations, this stage will be presented in more detail. The leaching and emission scenarios are defined with respect to the way the construction material comes into contact with water.

A first criterion of classification may be the vector characteristics associated with the conditions of exposure to water (Schiopu *et al.*, 2007): (1) outdoor exposure to water – meteoric, surface and underground water; (2) indoor exposure to vapours and cleaning solutions; (3) exposure to particular water: sea, sulphate reach, etc.; (4) exposure to water intended for human consumption; (5) exposure to wastewater; and possible combinations between these classes. The last two classes concern particular devices for water consumption and treatment, and, with the second class, are marginal to the present topics. In the following, attention is paid to the first class because of the variety of situations and the quantity and type of construction materials involved.

Retaining the first class of outdoor exposure to natural waters, a second criterion could be the type of contact with water: how the water circulates at the material surface and in the material. Four typical scenarios generate different impacts for the same exposed material, as described below (Schiopu, 2007):

1. Sloping plane – corresponds to a slope higher than 15% and is characteristic of pitched roofs, roofing and covering materials generally, for which the main water contact type is runoff.
2. Horizontal plane – corresponds to the same construction products as in (1) but in a horizontal configuration: materials for terraces (concrete, pavement bricks and asphalt, wood, metal slabs, different granulates, etc.), materials used in public works such as roads (with different layers

exposed directly or indirectly by water infiltration), etc. Rainwater in contact with horizontal surfaces can (1) form stagnant layers or ponds, (2) runoff, or (3) infiltrate and percolate the material if it is porous.

3. Vertical – corresponds to façade-type products exposed to rainwater (bricks, concrete, wood, etc. and their surface treatments). Rainwater runs off and to a certain degree infiltrates if the material is porous.
4. Contact with the soil – corresponds to buried foundations for all categories of civil works and earthworks. All contact types are possible: water runoff, stagnation, infiltration, percolation.

A fifth category could be introduced corresponding to works completely immersed in water like dykes, piles and basins made generally of concrete-based materials, granulates, wood, etc.

14.4.3 Parameters of influence

The main mechanisms involved in pollutant emission from construction materials (source terms) are chemical and transport processes. In contact with water, the material undergoes chemical and structural changes. At the liquid/solid interface dissolution/precipitation, adsorption/desorption, and different complex surface biochemical reactions occur, depending on the chemical composition of the material and also on the presence of exogenous chemical species like gases (e.g. atmospheric CO₂ and O₂), and dissolved species existing in the natural water (rain, underground or surface, sea, etc.).

If the material is non-porous (e.g. glass, metallic slabs), only the contact surface is reactive and participates in pollutant emission. If the material is porous – as in the majority of cases – the reactions occur not only at the ‘apparent’ surface but also in the pores, anywhere a liquid phase is present.

The dispersion of the pollutants takes place by different transport mechanisms:

- Diffusion occurs when a concentration gradient exists in the liquid phase: it is the main transport mechanism for stagnant liquids in pores. Dissolved substances inside a porous block material are diffused to the surface of the block and then released in the environment.
- Convection is the movement of a liquid volume, the water flow transporting also the dissolved substances. Convection takes place at the surface of a material (runoff) but also in the pores (percolation) if their size and structure allow water movement (open pores, larger than capillaries). Percolation is a typical mechanism responsible for leaching through granular (compacted) materials.

The chemical reactions and transport of dissolved species out of the material are complicated dynamic processes producing structural changes,

e.g. modification of the porous structure, erosion, modification of the chemical composition of the solid matrix, etc., finally influencing the further release behaviour of the material. Generally, increase of the water/solid contact surface leads to intensification of the chemical interactions and pollutant release. A granular material will release greater quantities than a block of the same mass.

The life span of the material and the contact with water (duration, flow, etc.) are parameters influencing the quantity of pollutant released. The dynamics of pollutant release generally vary over time because the materials themselves evolve, the chemical composition and structure (and implicitly the pollutant speciation) changing. Water contact is generally not continuous (except in situations of immersion) but intermittent, depending on climate. A periodic sequencing of similar events can be observed, e.g. rain periods in a season. The influence of the water contact duration and sequencing on the pollutant release is difficult to foresee and still remains a research and standardisation objective.

The temperature influences the chemical processes (equilibrium constants and kinetics) and also the water's physical state. Humidification and drying cycles of porous materials play an important role in the evolution of mechanical and chemical structures. Material humidification favours dissolution and diffusion of substances, while drying determines the migration of water from deep pores towards the material surface and precipitation of dissolved species. Phenomena like swelling or cracking are encountered for certain materials. Finally, ageing, which is the modification of the chemical, physical and mechanical structure of the material under the effect of natural factors (time, UV, temperature variations, humidity, etc.) and functioning stresses, influences the pollutant behaviour through the mechanisms described above.

To conclude, all the parameters of influence can be classified as (1) material intrinsic parameters, i.e. chemical composition, porosity, size of the product, state of the surface in contact with water (profile, geometry, roughness) and homogeneity, and (2) scenario parameters, i.e. water composition, contact mode (intermittency, velocity), life span, mechanical conditions, climate conditions, air, water, temperature, humidity, UV, etc.

14.5 Potential hazard assessment for construction materials in their service life

During the service life of construction materials, a threat to human health and the environment could exist mostly by emissions through water contact and to air (in the case of volatile compounds). The most significant variety and quantity of construction materials containing waste are likely to release pollutants in water. Pollutants released by the construction

products in their utilisation scenarios are transported through environmental compartments such as soil, surface and groundwater, affecting their quality, causing ecotoxic damages to plants and animals, and finally toxic effects on humans.

14.5.1 Methodologies and tools

To evaluate the toxic effects of pollutants for humans and the environment, specific methods and tools must be used. All the methods are based on the general methodologies of human Health Risk Assessment (HRA, described in a series of documents available from national organisations for health surveys (EPA, 2011)) and Ecological Risk Assessment (ERA guide (EPA, 1998)). The main steps of HRA are (1) hazard identification: type of problem the pollutant can cause; (2) exposure assessment: how the target person is exposed to the pollutant in time, at which concentration or dose; (3) dose–response assessment: how the pollutant quantitatively affects the target; and (4) risk characterisation: calculation of the risk of occurrence of harmful effect for the exposed persons. The ERA methodology is based on (1) exposure assessment, (2) assessment of the pollutant effect on living organisms, and (3) risk characterisation.

If HRA steps 1 and 3 and ERA step 2 characterise a given substance with respect to a target organism, the ‘exposure assessment’ step in turn determines the way the pollutant is emitted by the source (in waste containing construction materials in service life scenarios) and transported to the living targets. This implies a good knowledge of the pollution source in terms of emitted pollutant flux and its dynamics over the period of concern and represents the key step for a reliable HRA or ERA.

Often it may be sufficient to determine the exposure model, i.e. the time-dependent pollutant concentration in a given environmental compartment (soil, sediments, groundwater, surface waters, etc.). Then the pollutant concentrations can be compared with acceptable limit values for a given harmful effect. This is the principle of many simplified methodologies proposed and applied in different countries for assessing the eco-compatibility of waste reuse as secondary materials in earthworks and road construction (Sweden, Hartlen *et al.*, 1999; Netherlands, Eikelboom *et al.*, 2001; Denmark, Hjelmar *et al.*, 2001; Norway, Petkovic *et al.*, 2004). The limit values are taken for each hazardous pollutant from toxicology/ecotoxicology databases or are already specified in specific regulations (like the water directive – water destined for human consumption). However, questions remain concerning, for instance, synergy effects between pollutants in complex dynamic release.

The European standardisation organisation has elaborated a methodological approach for the characterisation of the pollution source term in

scenario conditions, EN 12 920. The key point is the link between the leaching behaviour of the waste material and the exposure conditions. The methodology proposes an iterative experimental and modelling multistep approach intended to provide predictive up-scaled pollutant releases.

In the following, we focus on the material leaching behaviour as a key point for hazard assessment. The above-mentioned methodologies call for experimental tools in order to determine the intrinsic material properties like chemical and mineralogical composition, porosity and pore size distribution, etc., as well as the scenario parameters and the time evolution of these characteristics. Then the information obtained can be used in models with the aim of calculating missing parameters (not available from experiments), extrapolating, forecasting and simulating different situations.

14.5.2 Leaching and toxicity tests

The information on material/water contact conditions and their influence on potential release of pollutants may be obtained from appropriate leaching experiences at laboratory, pilot or field scales. Many conventional leaching tests have been designed to compare leachate composition to regulatory thresholds: the compliance tests. For example, EN 12457.1 to 4 concern four different but quite close leaching protocols on granular material each during 24 hours. Beyond them, tests dedicated to the 'characterisation of the leaching behaviour of waste' have been elaborated for understanding the release mechanisms and provide necessary data for their modelling. The main leaching tests elaborated at the European level are presented below; these tests are expected to be transposed for construction material assessment.

Because of the complexity of waste-containing materials, the use of solubility thermodynamic models for the different species is considered not reliable enough and it is necessary to complete data by experimental means. Two tests have been elaborated to satisfy this objective using similar principles, i.e. to reach a steady state in solid/liquid processes at controlled pH, for different pH values: CENTS 14429, 'Influence of pH on leaching with initial acid/base addition' and CEN TS 14997, 'Influence of pH on leaching with continuous pH-control'. In order to facilitate the achievement of a steady state, specific procedures are foreseen: fine crushing of the material, efficient stirring, negligible atmospheric CO₂ uptake, long contact time, etc. The data (elemental eluate concentrations) collected by these pH-dependent solubility studies are useful in the analysis of the leaching results and are implemented in the modelling process of leaching, including the steps of calculating the local dissolution/precipitation processes at the pore level.

CEN TS 14405, 'Up-flow percolation test (under specified conditions)', is specifically designed for the characterisation of pollutant release by

percolation of water in a column filled with granular material by means of leachate time-dependent composition analysis. The controlled constant up-flow has to be performed until a cumulative liquid/solid ratio of 10 L/kg dry matter is reached. However, characterisation of the residence time distribution of the leachant in the system is missing.

The leaching of 'monolithic' blocks (at the laboratory scale) allows study of the leaching behaviour in the context of the solid material, at a fixed leachate (water) volume/surface of the sample. The leachates are collected in time and analysed. Two variants exist (CEN TS 15863 and CEN TS 15864) differentiated by the protocol of the leachate renewal (periodic leachant renewal and continuous flow of leachant). These tests allow calculation of the fluxes of released pollutants and supply important input parameters for leaching process modelling.

Although standard experimental tools exist for the leaching assessment of waste and waste-containing materials issued from waste stabilisation/solidification processes, there are no standard experimental tools for construction materials evaluation so far. Experimental difficulties can be foreseen, like very low supposed pollutant concentrations, the long testing time, the coupling of biophysico-chemical processes, etc. Research studies have been performed in particular cases but it is too early to come to universal conclusions and methods.

Several regulation texts are being drafted concerning the experimental tools dedicated to assessing the release of dangerous substances from construction materials. The Technical Committee TC 351 of CEN (European Committee of Normalization) launched the concept of a horizontal testing procedure (CEN/TR 16098:2010) which might be a common methodology for testing any substances and construction products covered by the Construction Products Directive. At the European level, the CEN/TC 351/WG1 working group is mandated to study the 'release from construction products into soil, ground water and surface water' and to propose the appropriate experimental (horizontal) leaching tests. The emerging leaching tests (and corresponding EU standards) are a monolith leaching test and an up-flow percolation test, very close to those already used for waste characterisation.

The toxic or ecotoxic parameters are usually determined by bioassays – experimental tools for measuring the pollutant effects on living organisms. The bioassays can be applied at different steps in a risk assessment approach. In very upstream steps, the bioassays could be applied to materials in order to estimate an intrinsic toxic/ecotoxic potential. However, the results are relevant only for the laboratory conditions used in the tests. The real toxic/ecotoxic effect must be determined at the scenario level: in the utilisation conditions influencing the chemical and leaching behaviour of the exposed material and with the target living species. The experimental conditions of

the bioassays must therefore be as effective as possible in simulating the real scenario conditions.

As already shown in the presentation of the leaching tests, the construction materials are not covered by the waste regulations. In Section 14.3.4 on waste characterisation, the requirements of the toxic character evaluation are satisfied by an experimental procedure based on ecotoxicity tests, realised on solid waste and on a leachate (obtained by a given protocol). As of today, there is neither regulation nor guidance for how the bioassays must be performed on construction materials. Generally, the ecotoxicity assays can be performed on different media (solids, liquids) using appropriate living species for these media and sensitive to the studied pollutant. The experimental conditions (dilution, temperature, light, culture medium, etc.) are specific for the species used and for the monitored effect (mortality, growth, reproduction, luminescence, etc.). In the case of a chemically complex matrix (solid or liquid), complex effects like synergy, antagonism and bioavailability exist and render the test results difficult to interpret. In the case of construction materials like those discussed in this chapter, typical mixture effects such as many toxic elements (heavy metals, metalloids, extreme pH values, high salinity of leachates) contribute to the bioassay response. It is therefore difficult to correlate the chemical composition and structure of the material with the ecotoxicity test result. Specific bioassays are developed for evaluating chronic, acute and genetic toxicity, for different trophic levels: producers (plants, algae), consumers (fish, larvae) and decomposers (bacteria, earthworms). There are numerous standard ecotoxicity tests at both international and national levels elaborated initially for chemical substances, and then developed for different matrices such as industrial wastewaters and polluted soils.

A huge amount of documentation on toxicity and ecotoxicity tests is available on the websites of regulating organisations such as the OECD (Organisation for Economic Co-operation and Development, OECD, 2011), ISO (International Organization for Standardization, ISO, 2011), US EPA (United States Environmental Protection Agency, EPA, 1994), and others. The direct application of these tests on wastes and materials containing wastes, on solid or leachate, raises the issue of the significance of experimental conditions (especially the dilution and the leaching duration) and consequently of the relevance of the ecotoxic result and interpretation. Ideally, the bioassays should be realised on a great variety of species and effects relevant to the scenario conditions.

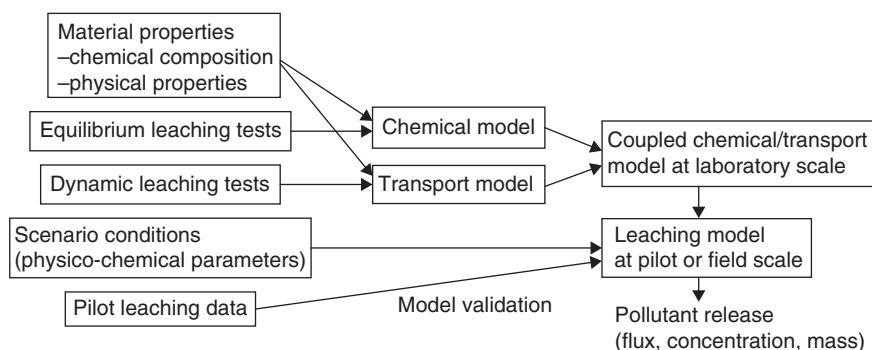
14.5.3 Modelling

The leaching of hazardous substances from construction materials in a specific real scenario (the exposure assessment) could be evaluated by

modelling the physico-chemical (and biological) processes, based on experimental data as mentioned above and on the scenario's physico-chemical parameters.

Leaching behaviour interpretation and modelling require taking into account different mass transport and chemical phenomena with different complexity levels. The modelling methods employed in practice are various, from empirical to completely mechanistic, with different prediction capabilities. Effective case-adapted models are proposed in the literature, some of them using 'home' developed models and software, most being reduced to the main processes and having limited extrapolation capabilities. As the chemistry is very complex because of the chemical nature of the studied materials, high-performance numerical tools coupled with huge thermodynamic databases are needed. Such modelling tools for aqueous chemistry are well known as geochemical software, some being used more and more in the field of waste and materials leaching, e.g. PHREEQC, ORCHESTRA, MINTEQA2, CHESS, EQ3/6, WATEQ4F and Geochemist's workbench. Appropriate software suites coupling chemistry and transport are fewer and contain different transport models (PHREEQC, HYTEC, PHAST) for particular applications.

Figure 14.1 schematises the conceptual structure of a coupled model for leaching behaviour assessment in a real scenario. The modelling procedure should be based on the three main steps: (1) specific hypotheses for chemical and transport processes – mathematical development and model resolution, (2) identification of the unknown model parameters by using laboratory experimental data and (3) model validation by using pilot measured data. This last step is not always realised because of cost and time constraints.



14.1 Principles of the elaboration of a leaching model for a real scenario.

14.5.4 Case studies

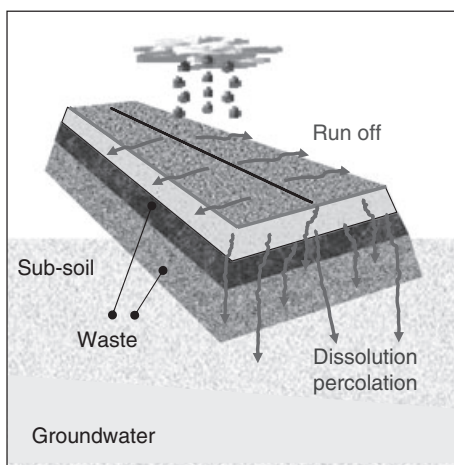
The materials used in earthworks and road construction have been the most studied until now, by methods and tools usually employed for the environmental assessment of wastes. There are very few leaching-scenario studies on materials used, for example, in house-type scenarios. There are no complete studies for human health risk assessment linked to the leaching of pollutants from construction materials in real utilisation scenarios. The existing studies concern mostly the leaching properties of materials and very few studies are extended to pollutant dispersion in soil and groundwater.

Globally, the research studies available in the literature concern different construction materials containing different wastes in various proportions and destined for particular utilisation scenarios. It is therefore not possible to generalise the results and conclusions, so several example studies are mentioned hereafter in their particular context.

Waste recycling as granulates

The most studied scenario of waste use is for road construction using MSWI-BA as sublayers (Fig. 14.2). The results and conclusions of these studies, concerning potentially adverse effects on the environment and human health, are different, proving the importance of the influence of specific parameters characterising materials and scenarios.

The 'Eco-compatibility' ERA method was applied for MSWI-BA use in an embankment for road construction (ADEME, 2002). The pollutant



14.2 Waste used as road sub-base.

release through leaching was studied at laboratory and pilot scales (leading to the calculation of cumulative emitted pollutant quantities for a time period of 30 years) and was found to affect groundwater, soil and river. This complete ERA method demonstrated through a specific case that an environmental impact is effective. The biological functions of the soil were investigated with respect to three populations of microorganisms, whereas the phytotoxicity was studied by monitoring the evolution of two species of plants; adverse effects were observed through a decrease of biomass. On the contrary, the evolution of two species of earthworms in contact with leachates (diluted or not) was monitored and no adverse effect was observed. Chlorides and sulphates were the most soluble species liable to affect groundwater salinity. Target aquatic species were put in contact with leachates filtered by the transfer soil and a weak toxicity was observed. The pilot study realised in artificial rivers showed that mortality increases with the proportion of leachate in the river.

The leaching of pollutant was also studied within the European project Alt-mat (Alternative materials in road construction) in a similar scenario: the use of untreated MSWI-BA as road sub-base. Three roads situated in France and Denmark were investigated after many years of service (Reid *et al.*, 2001). The concentration of sulphates and some metals, as well as the pH, were measured in the soil below the road at different depths and in the surrounding soil. For the two French sites, the concentrations were slightly augmented in the underneath soil, while for the Danish site, no significant effect on the soil composition was observed for the first five years of road life (the period of investigation). Despite the leaching process, the contaminant concentrations remained below the soil quality criteria values, i.e. the Dutch soil 'intervention values' based on health and ecological risk assessment.

In another study (Pagotto *et al.*, 2003), the same scenario was modelled by considering the meteorological conditions (oceanic and mediterranean), road soil types (sand, clay, silt), road quality (good or altered upper layer) and groundwater movement (parallel and perpendicular to the road direction). The soil and groundwater were considered as environmental targets. Experimental leaching tests and powerful modelling tools (geochemical coupled with transport models) allowed the estimation of the pollutant fluxes released and transported in the environmental compartments (soil and groundwater). Estimations were performed for 20 years of road life. The pollutant concentrations were compared to the French soil guideline values and limited concentrations for water destined to potabilisation. The worst results were obtained for oceanic conditions, permeable sand and an altered upper layer. But even in this conservative case, the pollutant release over 20 years was estimated to be low enough to cause no significant environmental burden.

Much research work has investigated only the pollution source term without considering the pollutant dissemination in the different environmental compartments (soils, waters). The results are expressed as pollutant concentration in the outflow leachates as a function of time, over different time spans. This option allows a good knowledge of the pollutant flux emitted by the construction scenario considering that ulterior calculations could be done for evaluating the impact on each compartment (e.g. by comparing the calculated concentrations with the standard limit values).

Laboratory and modelling approaches combined with monitoring of pollutant release on experimental roads containing MSWI-BA showed (de Windt *et al.*, 2011) that the pH decreases from alkaline levels (above 11) to 8 in the first years of the road, depending on the waste chemical composition (buffering capacity) and scenario parameters like the atmospheric CO₂ uptake and material carbonation. The concentration of most soluble elements (Ca, Na, Cl, organic matter, Cu) decreased in time, while the behaviour of other minor elements followed more complicated shapes obviously depending on the chemical context at a given time (such as, for example, sulphate and Pb concentrations initially decreased, then increased, with variations observed over several orders of magnitude).

A 23-year-old road containing MSWI-BA was studied (François and Pierson, 2009) for the leaching behaviour and impact on the underlying and surrounding soil and seepage. A very complete sampling system was implemented on site, allowing detailed analysis of soils and seepage in relation to the road structure and geometry. An overall rainwater infiltration ratio of 0.08 L kg⁻¹year⁻¹ was estimated. The analyses demonstrated modifications of soil and seepage composition with respect to the natural composition of the site. Compared to the natural soil, the soil under the road contains more K, Na and Cl⁻, As, Cd, Cu, Cr, Ni, Al and Fe. However, the concentrations did not exceed the pollution threshold standard used as quality reference in this study (the Dutch Soil Protection Act). Concerning the seepage, downstream effects are relevant only for soluble salts (Cl⁻, Na, K, and SO₄⁻² to a lesser extent) and this with respect to the river and groundwater quality reference standard (the French system of water quality assessment). Besides, the trace elements revealed no downstream effects.

Another study performed on a field pilot (Ore *et al.*, 2007) showed that Cl, Cu, K, Na, NH₄⁺ and organic matter, Al, Cr, and NO₂⁻ were the most common contaminants during the first year. Their concentration decreased strongly during the first three years except in the case of the last three species named above. Compared to a conventional road construction, the pilot road produced more concentrated leachates in all elements at the beginning, while after three years only a few elements exceeded (by two

orders of magnitude) the conventional leachate concentration: Al, Cu and NO_2^- . Several ecotoxicity tests were performed on the leachates collected in the outflow from the pilot road. The results showed that the toxicity is linked mostly to the salinity (the authors reported 13.8 g/L total salts) particularly in the initial leaching period, and that it is very difficult to assess specific toxicity linked to the presence of target elements. This kind of ecotoxicological investigation cannot give a definitive response to the question of the hazardous potential of the road scenario, because the outflow leachate will suffer chemical transformations in contact with the surrounding soil and waters.

A highway pavement material composed of crumb rubber asphalt concrete (cement content 5.4%) was studied for ecotoxic effects (Azizian *et al.*, 2003). The methodology was based on laboratory assays: the leachates were obtained on crushed and monolithic material following an EPA standard protocol. The eluates were submitted to two aquatic ecotoxicological tests (*Selenastrum capricornutum* algal chronic toxicity and *Daphnia magna* acute mortality). The most significant pollutants found in the leachates were Hg (which originated in the asphalt used), Al (which originated in the natural aggregates used) and benzothiazole and 2(3H)-benzothiazolone, released probably by the rubber – all highly toxic substances. Only the leachate obtained on crushed material exhibited significant toxicity. The leachates were also studied for removal/reduction/retardation by the surrounding/underlying soil; these processes determined the removal of the toxic effect. This study highlights the complexity and importance of the scenario parameters, i.e. water/material contact (monolith), pollutant transfer into the soil, and biophysico-chemical processes outside the construction materials, which could radically modify the hazardous effect.

Cement-based materials containing wastes

Cement-based materials are reactive porous materials containing soluble phases. The assessment of their environmental quality has to be proved by leaching tests, established in agreement with the exposure scenarios. An abundant literature is available on the leaching properties (application of laboratory leaching tests) of solidified/stabilised wastes. However, in most available studies, these cement-based materials are destined for waste disposal and very few studies actually concern construction materials. Moreover, there are actually no risk assessment (ERA or HRA) studies on cement-based construction materials containing wastes.

Nevertheless, important information on the leaching mechanisms can be extracted from the huge experience accumulated in the field of cement-stabilised wastes. The chemistry of wastes incorporated in cement or concrete materials is dominated by the very alkaline medium generated by

the hydraulic binder (portlandite and hydrated calcium silicates). The stabilisation of wastes by cement is a very well-known method to render certain pollutants less soluble. The mechanisms of pollutant fixation in cement matrix are mainly:

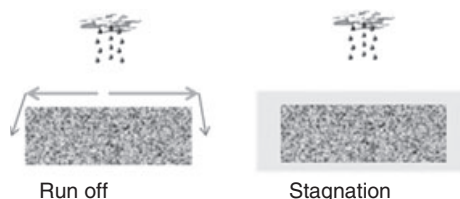
- Fixation of metals during hydration as hydroxides and oxides in the very alkaline medium (if the waste is added in the hydration process)
- Incorporation of metals in the structure of silicates and aluminosilicates by substitution of generic ions (if the waste is added as AFR).

For known toxic elements, one distinguishes several types of chemical behaviour:

- The amphoteric behaviour of some heavy metals (e.g. Pb, Zn, etc.) should increase the metal solubilisation because of the particularly high alkalinity of the pore water.
- The presence of organic matter (from additives, unburned OM, etc.) favours the mobilisation of some species by complexation, as in the case of Cu.
- Anionic forms of elements like Mo, Cr⁺⁶, As, B and V, as well as SO₄⁻², have a tendency to be leached in mild alkaline (pH 7–9) media and to be fixed at high pH values (e.g., at high pH sulphates are fixed by ettringite). The pH is not the sole factor explaining this behaviour; the concentration of accompanying cations (Ca, Ba, etc.) is also a determinant.

Studies performed by different authors on different cement materials containing wastes show similarities in pollutant chemistry. Four types of materials were compared through the results of the pH-dependent leaching test (van der Sloot, 2002). These materials are a mortar with regular Portland II B cement, a mortar with cement obtained with AFR and alternative raw materials, a mortar containing MSWI-fly ash in low proportion (<10%), and two stabilised MSWI-fly ashes (>80%). The observation of solubility vs pH and the use of geochemical modelling confirmed the above fixation mechanisms and allowed the conclusion that the same solid phases control the solubility of a given pollutant in the different materials, with very little exception in the case of high waste content.

The effect of partial replacement of clinker with blast furnace slag for cement production was studied in the case of paving concrete products (Marion *et al.*, 2005). By applying the dynamic leaching test and comparing the results it was proven that the replacement of CEM I with CEM III/A (36% to 65% of slag) has no effect on the leaching behaviour of the concrete. In the case of high pollutant content or high waste proportion in the material, the stabilisation capacity of cement should not be sufficient. A monolith leaching test was applied to cement products containing waste

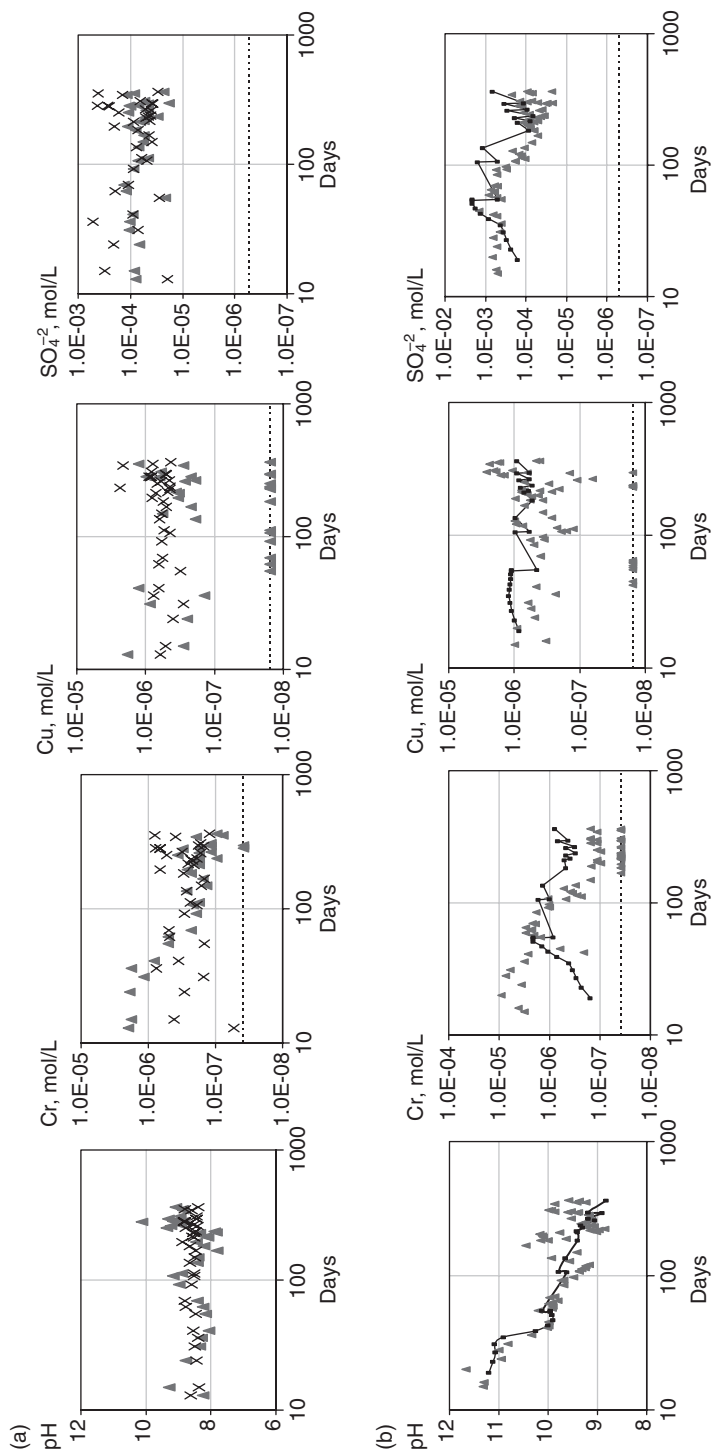


14.3 Leaching scenarios for cement-based materials.

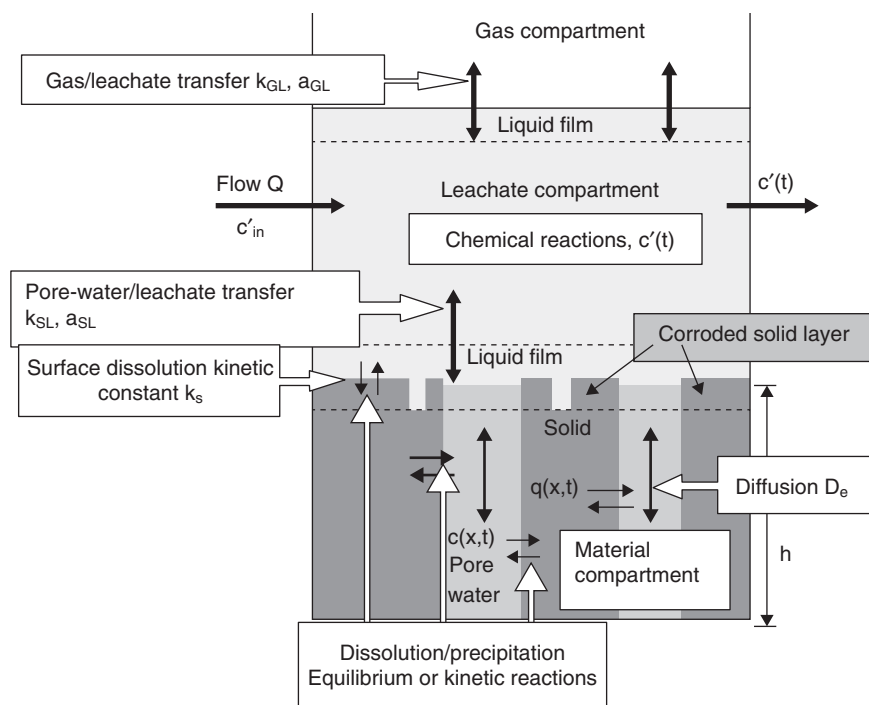
from pilot scale bioleaching of refractory gold, copper and copper/nickel sulphide flotation concentrates (Chan *et al.*, 2009). The results showed relatively high concentrations of As, Cr and Cu in the leachates for those wastes containing high quantities of these elements.

A step forward for the environmental assessment of concrete materials is the consideration of the real leaching scenario. With this aim, a true commercial construction product was studied for determining its leaching behaviour, in laboratory (leaching tests) and pilot conditions (Schiopu *et al.*, 2009). Concrete paving slabs manufactured with CEM I concrete were exposed for one year in two types of leaching scenarios under outdoor conditions, 'runoff' and 'stagnation' (Fig. 14.3), and the released elements were monitored. The leachate composition was then used for validating a leaching model composed of the material's geochemical model coupled with appropriate transport models for each scenario. Figure 14.4 shows the concentration of the leachate in contact with the concrete slab in real conditions: the pH is different following the water contact type, the highest concentration is given by the soluble species Na, K, Cl (not shown here) and SO_4^{2-} and the heavy metal concentration is rather low. The concentrations drop after 100 days and correspond, for example, to threshold values for good quality groundwater (following the French system for water quality assessment).

A cement material containing MSWI-APC (Air Pollution Control residues) was investigated at laboratory and pilot scale in order to determine its leaching behaviour in real scenario conditions (Barna *et al.*, 2000a, 2000b). At field scale, the material was used for a pool construction destined to be stocked with non-potable water (capacity 20 m³). The results of laboratory tests (influence of pH on the leaching and dynamic monolithic tests) were used for coupled geochemical and transport model development (Tiruta-Barna *et al.*, 2001), complete with specific factors of the scenario, i.e. immersion in water and carbonation. The whole physico-chemical processes are described in Fig. 14.5. The monitoring of the pool water composition allowed validation of the model, and showed that the leaching of pollutants, especially Pb, was very low, close to the quantification limit of the analytical



14.4 Pilot results for concrete slabs leaching in outdoor conditions: (a) run-off: experiments (triangles) and simulations (crosses); (b) stagnation: experiments (triangles) and simulations (lines).



14.5 Leaching mechanisms for a monolith material in an immersion scenario.

method. This low concentration was due to the carbonation process of the material and radical changes in the pH values at the water/material interface. This study showed that even in the case of a hazardous waste (MSWI-APC), the construction scenario could be safe.

14.6 Conclusion and future trends

The assessment of the potential hazard of construction materials containing wastes becomes an actual challenge in the context of the increasing reuse/recycling of wastes and the very stringent demand for a fully safe and sustainable construction sector. The safeness of the construction materials is a general problem, not only for materials containing wastes. Current policies dominated by the Construction Product Directive (in its new form; EU, 2011) endeavour to create general frameworks for ensuring health and environmental guarantees. However, there is still a lack of appropriate and dedicated methods and tools (experimental tests and models) for assessing the toxicity potential of construction materials in their utilisation scenarios,

especially via emissions in water and dispersion in the surrounding natural environment.

Therefore, hitherto there have been very few studies dedicated to these aspects. The main studied materials are those destined for road construction, due to the direct recycling of wastes and evidence of the potential pollutant emission in contact with rainwater. Even in this case, there have been no conclusive outcomes concerning the toxicity hazard. It must be underlined that a toxicity hazard could arise not only from the wastes used but also, or exclusively, from the other usual constituents of a construction material, since no toxicity evaluation has been carried out on the leaching from traditional materials towards natural compartments, e.g. concretes, pavements, etc.

Actually the pollutant emission through leaching processes and their dispersion towards environmental compartments represent a real threat for ecosystems, water resources destined for human consumption and food. In the field of waste management, standard methodologies (based on classical HRA and ERA methodologies) and experimental tools (leaching tests) exist for evaluating the pollution potential and toxicity in specific disposal, elimination or reuse scenarios. Attempts to extrapolate these methodologies and tools to construction materials are in progress, but the process of setting up standards and regulations is very long, since it requires time-consuming and expensive validation studies and expertise.

The various utilisation scenarios and exposure conditions, as well as the variability in the chemical composition of the wastes used, could make questionable the application of one single methodology for hazard assessment. Nevertheless, for sake of transparency but also of control and regulation, it is necessary to adopt a unique methodology for the assessment of all material/scenario cases, provided with a (limited) set of experimental tools (leaching tests coupled with ecotoxicity tests) applicable for all relevant situations. This is the principle of the 'horizontal' approach currently being studied for implementation at the European level. The experience accumulated in the field of wastes shows that the leaching tests have to be designed for investigation of the material behaviour in its scenario (including its evolution in time). Their coupling with ecotoxicity tests performed in relevant conditions for the scenario/environmental compartments will comply with the need for an integrated approach. Besides, an efficient traceability method of the wastes used and of the waste-containing construction materials on their life cycle (their origin, transformation, destination, use and end of life) could facilitate eventual identification of their hazard potential and management. Then an observation/interpretation/action loop on a local construction scale could augment the expertise and by feedback allow the damage to be limited.

The massive utilisation of wastes could also lead to radical changes in the construction sector (with impacts on the economic, social and environmental levels) including new materials and new fabrication processes for existing materials.

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Abstract: This chapter summarizes the most important applications of nanotechnology in the construction industry together with aspects of nanoparticles toxicity. Nanotechnology is currently applied in the construction industry predominantly in cement, coatings, paints and insulating materials. Nanoparticles incorporated into existing construction materials confer them novel and extraordinary properties, such as increased strength, self-sensing, self-cleaning, antimicrobial, or pollution remediation capabilities. On the other hand, nanoparticles from construction materials that are released into the environment can be extremely detrimental to health. Nanoparticles can enter the human body via inhalation, ingestion, or skin contact. The range of pathologies related to exposure to nanoparticles encompasses respiratory, cardiovascular, lymphatic, autoimmune, neurodegenerative diseases, and a variety of cancers that can manifest immediately following exposure or many years later.

Key words: nanomaterials, nanoparticles, construction industry, nanotoxicity, nanocoatings, photocatalytic properties, antimicrobial properties, self-cleaning properties, fireproof materials, scratch resistant properties, water repellent properties.

15.1 Introduction to nanoparticle and nanomaterial toxicity

15.1.1 Definition and general information

A nanoparticle is defined as a particle with length in two or three dimensions larger than 1 nm and smaller than about 1000 nm (Buzea *et al.*, 2007), although some authors prefer a narrower range, from 1 nm up to 100 nm (Borm *et al.*, 2006; Shvedova *et al.*, 2010; Dobrovolskaia and McNeil, 2007). Nanoparticles are a growing subclass of the larger classification of nanomaterials, which includes all materials with a structural component smaller than 1000 nm in at least one dimension. In addition to nanoparticles, the class of nanomaterials includes complex nanostructures attached to a substrate, such as computer chips or thin films with a porous structure. While nanomaterials that are fixed on a substrate are benign as long as they do

not detach and become airborne, many types of free nanoparticles can be associated with negative health effects.

From the physico-chemical point of view, there are two main subtypes of nanoparticles: soluble and insoluble. Soluble or biodegradable nanoparticles, depending on their composition and as a result of biological and/or photo-chemical decomposition, may convert into molecular by-products. These resulting molecular components may be easier to clear from the body, sometimes making them less harmful than their nanoparticle progenitor (Park *et al.*, 2009). The insoluble, or biopersistent, subtype comprises nanoparticles made of metals and/or their compounds, such as titanium dioxide (TiO₂) or quantum dots. They can also be non-metals such as carbon-based nanoparticles including fullerenes C₆₀, carbon nanotubes, carbon soot, and silicon-based nanoparticles, among others.

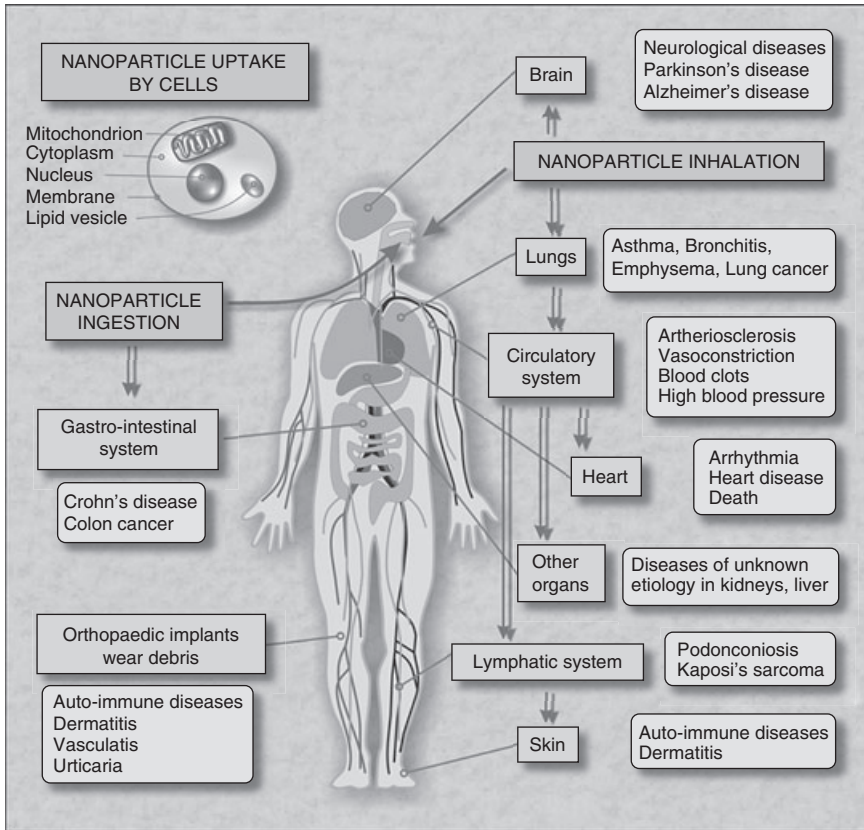
Natural and anthropogenic nanoparticles can be toxic to life forms due to their noxious interactions with intracellular organelles, proteins or genes. A schematic depicting the pathways of exposure with nanoparticles and their adverse effects in humans is shown in Fig. 15.1. Three types of research give insight on nanoparticle toxicity: epidemiological studies directed to determine whether there is an association between environmental or occupational exposure to nanoparticles and human disease; *in vitro* experiments, utilizing either human or animal cell lines, designed to elucidate the molecular determinants of potentially toxic nanoparticles; and *in vivo* studies performed on animals that are usually the correlate for initial *in vitro* observations.

15.1.2 Sources of nanoparticles on Earth and their toxicity

One might be inclined to associate the terms nanoparticle and nanomaterial with nanotechnology alone. However, the sources of nanoparticles on Earth are varied, encompassing natural as well as man-made. The nanoparticle pollution resulting from both anthropogenic and natural sources on Earth is considerable in very populated parts of the globe, and can be readily visualized from satellite images.

Natural nanoparticles

The main natural causes of nanoparticle generation are incomplete combustion during volcanic eruptions, physical and chemical weathering of rocks, incomplete combustion from forest fires, water evaporation, and extraterrestrial dust. Natural nanoparticles such as dust, smoke, and ash, are ubiquitous on Earth. Dust particles with interplanetary origin accrete on Earth at a rate of about 40 kilotons per year (Johnson, 2001). Nanoparticles



15.1 Schematic of the human body detailing pathways of exposure to nanoparticles, affected organs, and associated diseases based upon epidemiological, *in vivo* and *in vitro* studies.

from large volcanic eruptions can affect regions up to hundreds of kilometers from the volcano by means of volcanic aerosols. Nanoparticles from dust storms are not confined only to the desert regions on Earth, but have been shown to travel across and among continents, with global impacts (Husar *et al.*, 2001; McKendry *et al.*, 2001). Natural nanoparticles can create a wide range of undesired health effects, ranging from respiratory conditions related to incomplete combustion and dust nanoparticles, swelling of the limbs due to the blockage of lymphatic vessels by volcanic soil particles, and diseases involving calcifications associated with nanoparticle production by nanobacteria, such as renal stone formation (Ciftcioglu *et al.*, 2005; Wood and Shoskes, 2006).

Anthropogenic nanoparticles

These are substantial in the most populated regions of the world (Murr and Garza, 2009). Sources of anthropogenic nanoparticles include incomplete combustion due to vehicle and automobile exhaust, burning of wood, coal, combustion of petroleum and their derivatives for cooking, heating, and power generation, waste incineration, and smoking. Occupational activities, such as welding, mining, or building demolition (Buzea *et al.*, 2007; Lowers and Meeker, 2005), are also an important source of nanoparticle exposure for workers and their immediate environment. Furthermore, commercialized products containing engineered nanoparticles are rapidly becoming an important source of nanoparticle exposure. Among anthropogenic sources, arguably the most important source of nanoparticle pollution is incomplete combustion due to vehicle and automobile exhaust. Vehicle pollution comprises not only greenhouse gases, such as carbon dioxide, but a large array of nanoparticles that compose more than 90% of the number of diesel generated particles (Westerdahl *et al.*, 2005; Sioutas *et al.*, 2005). A high concentration of such nanoparticles has been found in the air hundreds of meters away from major roads and highways (Sioutas *et al.*, 2005). Studies have found an association between exposure to these particles and increased cardiopulmonary mortality (Vermeylen *et al.*, 2005). Multiple epidemiological studies link vehicle particulate pollution to a wide range of adverse health effects, ranging from respiratory to cardiovascular disease (Garshick *et al.*, 1988; Vermeylen *et al.*, 2005; Hoek *et al.*, 2002; Knox, 2005; Bigert *et al.*, 2003). Few studies have associated the exposure to engine exhaust with specific childhood cancers (Knox, 2005). Researchers have also reported higher incidences of heart attack and lung cancer in professional drivers (Bigert *et al.*, 2003; Garshick *et al.*, 1988). In conclusion, there is a growing body of epidemiological evidence that correlates high levels of outdoor microparticle/nanoparticle pollution to an increased incidence and mortality from lung and cardiovascular disease.

Engineered nanoparticles

Engineering nanoparticles are a class of nanomaterials that are likely to become a significant source of nanoparticle pollution if not properly handled and recycled. Some engineered nanoparticles are already commercialized in a variety of everyday use products such as cosmetics, sunscreens, toothpaste, food additives, stain-resistant clothing, sporting goods, tires and in construction materials (Buzea *et al.*, 2007). There are currently more than 300 products on the market containing nanomaterials (Maynard *et al.*, 2006). The health effects of the long-term use of these products are basically unknown. Despite the fact that many nanoparticles may be potentially

toxic, an increasing number of consumer products containing engineered nanoparticles are commercially available long before their safety is assessed (Kulthong *et al.*, 2010; Hagens *et al.*, 2007).

Recent concern has been raised on the widespread use of titanium dioxide nanoparticles in a variety of products as a colorant and UV-ray blocking agent. Due to its tinctorial effects (white pigment), it is currently used as a colorant for food, medications, toothpaste, paint, and plastic; as an active UV blocking agent it is used in sunscreens and cosmetic creams (European Commission, 2007). Titanium dioxide has proved to be safe when introduced to similar products in bulk form. However, studies to determine its safety at the nanoscale are lacking. The long term effects of incorporating titanium dioxide, if any, remain to be discovered.

In vitro studies indicate that silver nanoparticles are even more toxic to human and animal cells than asbestos (Soto *et al.*, 2005). Inhaled silver nanoparticles migrate via the circulatory system and may reach several target organs. Silver nanoparticles have been found in the blood of patients with blood dyscrasias (Gatti *et al.*, 2004), and in the intestine of patients with colon cancer (Gatti, 2004). Whether silver nanoparticles are directly involved in the pathogenesis of these diseases has not been properly addressed. Furthermore, there are reports indicating that silver nanoparticles have been discovered lodged in the liver, kidneys and heart of otherwise healthy patients (Takenaka *et al.*, 2001). Why and how silver nanoparticles have reached these organs was not explained or understood. Silver nanoparticles are now used due to their antiseptic properties in fabrics, socks, washing machines, vacuum cleaners, and food storage containers, and as burn wound dressings.

15.2 Morphology, classification, and properties of nanomaterials

'Nano' can be considered a different state of aggregation of matter in addition to the solid, liquid, gas, and plasma states. This is because nanoparticles of a specific material exhibit quite different physical (optical, electromagnetic), chemical (catalytic), and mechanical properties from the same material in bulk form. The two main factors that make nanoparticles behave differently from bulk form are surface effects and quantum effects. As a result, nanomaterials may have different chemical reactivity, mechanical, optical, electrical and magnetic properties compared to their bulk counterparts.

Surface effects manifest as smooth scaling of physical properties due to an increased fraction of the atoms at the particle surface compared to the interior. These effects include increased chemical reactivity and reduced melting point of nanoparticles compared to larger particles or bulk material

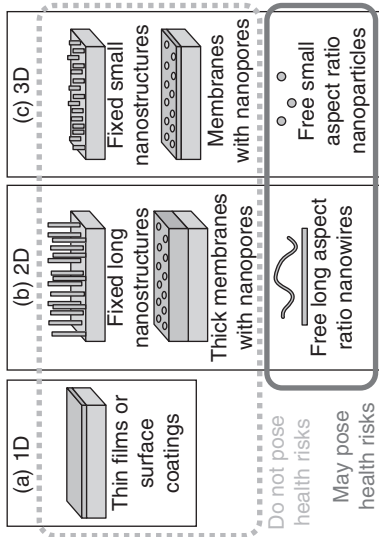
(Buzea *et al.*, 2007). Nanoparticles have a very large relative surface area (and a large particle number per unit mass) compared to microparticles or larger particles (Buzea *et al.*, 2007). Hence, nanoparticles have a much larger surface area available for chemical reactions compared to microparticles. For instance, if we consider the same mass of nanoparticles (with diameter of 60 nm) and compare them with their microparticle counterpart (with diameter of 60 microns), nanoparticles will exhibit 1000-fold enhanced reactivity. This is explained by the fact that the atoms at the surface of a nanoparticle have fewer neighbors than the atoms in bulk. Consequently, the binding energy per atom decreases with particle size (Roduner, 2006). This translates to a reduced melting point as a function of particle diameter, according to the Gibbs–Thomson equation where T_{bulk} is the melting point of the bulk material, d is the diameter of the nanoparticle, and c is the material constant (Roduner, 2006). For example, the melting temperature of 3 nm diameter gold nanoparticles is more than 300 K lower than the melting temperature of bulk gold, 1336 K.

We can classify nanoparticles based on their dimensionality, morphology, composition, uniformity, and agglomeration (Fig. 15.2). Among the nanostructures presented in Fig. 15.2, those that can easily be released into the environment are nanoparticles that may pose a serious health risk. One must emphasize that various coatings, due to wear and finite lifetime, could release nanoparticles that may become airborne and be inhaled or get into dermal contact. In contrast, if the nanoparticles are firmly attached to substrates or larger objects and will not be released into the atmosphere, they are considered not to pose a health risk. Figure 15.3 shows transmission electron microscope (TEM) and scanning electron microscope (SEM) images of nanoparticles with various morphologies and compositions.

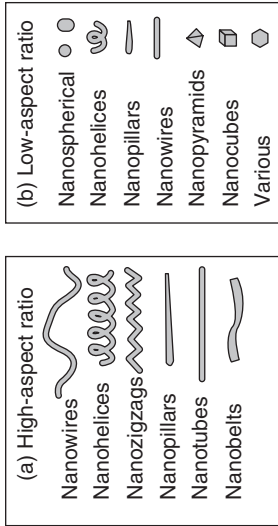
15.2.1 Carbon nanotubes

A very important class of newly engineered nanomaterials are carbon nanotubes (CNTs). Similarly to asbestos fibers, CNTs have a long aspect ratio. CNTs can be visualized as graphite sheets (hexagonal patterns of carbon atoms) rolled up in a tube structure (Makar and Beaudoin, 2003) that may have a single wall (single-walled CNT; SWCNTs) or multiple walls (multi-walled CNTs; MWCNTs). CNTs can be modeled to exhibit a variety of shapes and sizes. Their diameter can vary between 0.4 and 100 nm, while their length ranges between several nanometers up to centimeters (Dai, 2002). Some MWCNTs have exposed edge planes along the surface, constituting potential sites for chemical and physical interactions (Sanchez and Sobolev, 2010). CNTs can be synthesized with different types of chirality (the orientation of the hexagonal patterns with respect to the tube axis)

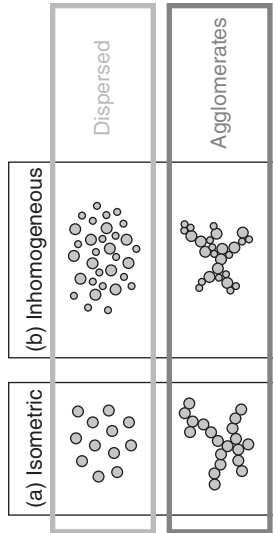
1) Dimensionality



2) Morphology



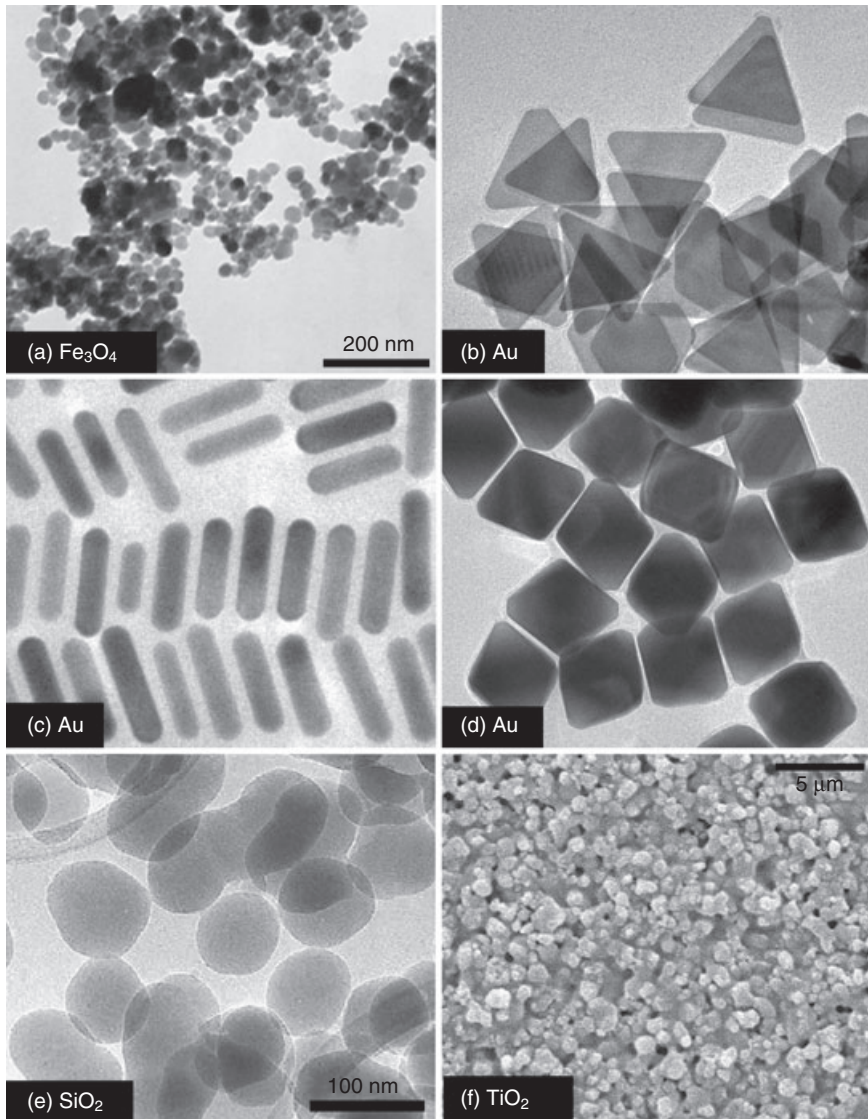
4) Uniformity & agglomeration state



3) Composition



15.2 Classification of nanostructured materials from the point of view of dimensionality, morphology, composition, uniformity and agglomeration state (Buzzea *et al.*, 2007).



15.3 TEM images of (a) Fe_3O_4 nanoparticles (reprinted from Zhu *et al.*, 2011, copyright 2011, with permission from Elsevier); (b), (c), (d) gold nanoparticles with various morphologies (image by Byeongdu Lee, courtesy of Argonne National Laboratory); (e) SiO_2 nanoparticles (reprinted from Sanchez and Sobolev, 2010, copyright 2010, with permission from Elsevier); (f) TiO_2 nanoparticles embedded in paint (reprinted from Caballero *et al.*, 2010, copyright 2010, with permission from Elsevier).

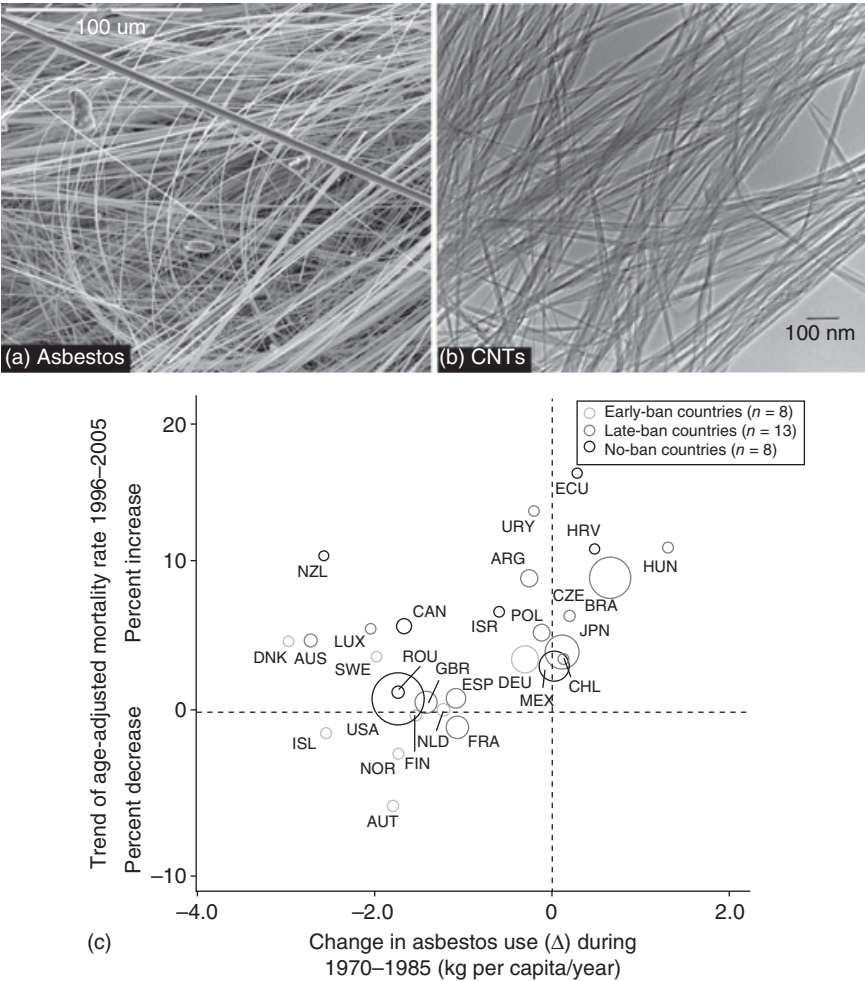
(Ma *et al.*, 2010). Interestingly, two tubes with the same diameter may have different structures and hence different properties.

CNTs present unique electronic, chemical, mechanical, and thermal properties (Ajayan, 1999; Salvetat *et al.*, 1999). They exhibit a low density, ranging between 1.3 and 2 g/cm³, high flexibility and high aspect ratio – 1000 (Sahoo *et al.*, 2010; Wernik and Meguid, 2010). Their electronic behavior ranges from metallic to semiconductor, depending on their chirality (Makar and Beaudoin, 2003) and oxygen doping (Collins *et al.*, 2000). CNTs seem to be the strongest materials, having Young's elasticity modulus of approximately 1 TPa (Salvetat *et al.*, 1999) and a tensile strength of 50–200 GPa (Ma *et al.*, 2010). Thus, not surprisingly, CNTs are very flexible, and can be bent to form circles or create knots (Lourie *et al.*, 1998). Moreover CNTs can be scrolled enabling yarn weaving, sewing or braiding. CNTs have been used as scaffolding to fabricate yarns of superconductors and TiO₂ used for photocatalysis (Lima *et al.*, 2011). CNTs suspended in liquids exhibit a remarkably high thermal conductivity (Choi *et al.*, 2001), approaching the theoretical limit for carbon materials (Berber *et al.*, 2000). The thermal conductivity of SCNTs and MWCNTs can attain 6000 W/(mK) and 2000 W/(mK), respectively. Thus, they possess a negligible coefficient of thermal expansion (Ma *et al.*, 2010). Due to their anisotropic structure, it is believed that their thermal conductivity is also anisotropic, being much higher along than across the tube (Makar and Beaudoin, 2003).

The superior mechanical properties of CNTs make them of great interest as structural materials; however, due to their similar morphology to asbestos (Fig. 15.4 (a), (b)) and the lack of rules and regulations regarding their handling, they might soon become a public health issue as well (Donaldson *et al.*, 2010). Despite the institution of strict regulations in many countries, asbestos continues to have severe consequences on the health of workers and consumers for many years to come. After decades of debate, it is now well accepted that mesothelioma, a cancer of the lining of the lungs, may develop after either environmental or occupational exposure to asbestos (Nishikawa *et al.*, 2008). Although some countries have opted to ban the use of asbestos, unfortunately a few others have not established any regulatory measures. These trends are illustrated in Fig. 15.4 (c), showing the mortality trends for mesothelioma in relation to change in asbestos use.

15.3 Types of building materials incorporating nanomaterials

To date, the majority of nanotechnology applications in construction on the market have focused on developing coatings, paints and composites that exploit the photocatalytic properties of TiO₂ nanoparticles. TiO₂'s photocatalytic properties may be regulated by either UV-light or light of the



15.4 SEM images of (a) asbestos fibers (courtesy of United States Geological Survey (USGS) at Denver, CO, <http://usgsprobe.cr.usgs.gov/picts2.html>) and (b) multi-wall carbon nanotubes (reprinted with permission from Ajayan, 1999, copyright 1999 American Chemical Society); (c) mortality trends for mesothelioma in males in relation to change in asbestos use (reprinted from Environmental Health Perspectives, Nishikawa *et al.*, 2008).

visible spectrum. Depending on the association, TiO_2 composites may acquire self-cleaning, microbicidal, anti-fog or hydrophilic properties; remarkably, they may also gain anti-pollutant effects. Multiple composite materials have already been generated by admixing various nanomaterials and conventional building materials such as concrete, glass, ceramics, poly-

mers or metals. It is envisioned that nanomaterials will not only improve the properties of the conventional materials, but they may also be designed as self-sensing devices to monitor structural integrity. Besides composites, nanoparticle coatings have been used to confer fireproof, scratch resistance, antireflective, or antimicrobial properties to already edified structures. A schematic of nanotechnology application in the construction industry is shown in Fig. 15.5.

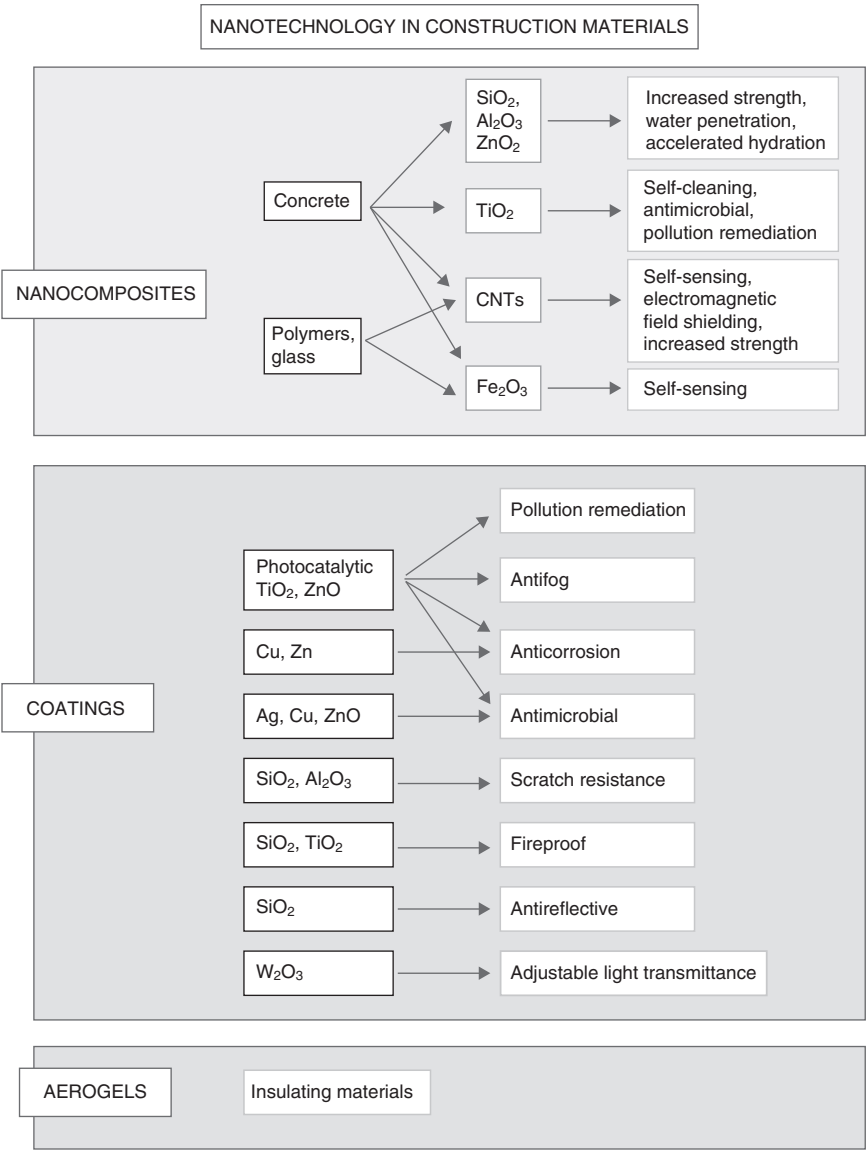
15.3.1 Concrete–nanoparticles composites

Nanocomposites incorporate nanoparticles into a matrix such as polymers, metals, or ceramics. The incorporation of nanoparticles can improve drastically the properties of the nanocomposite compared to that of the matrix alone, including mechanical strength, toughness and electrical or thermal conductivity. Although greater nanoparticle concentrations may be used, the usual range reported varies from 0.5% to 5.0% (v/v).

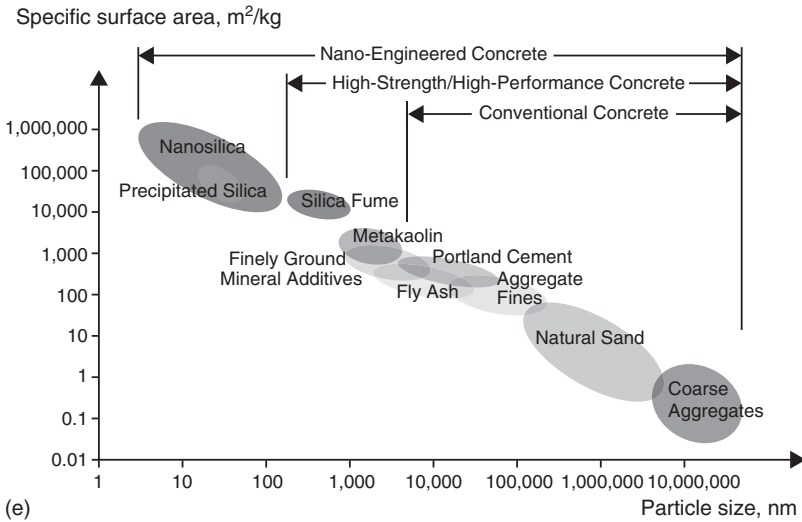
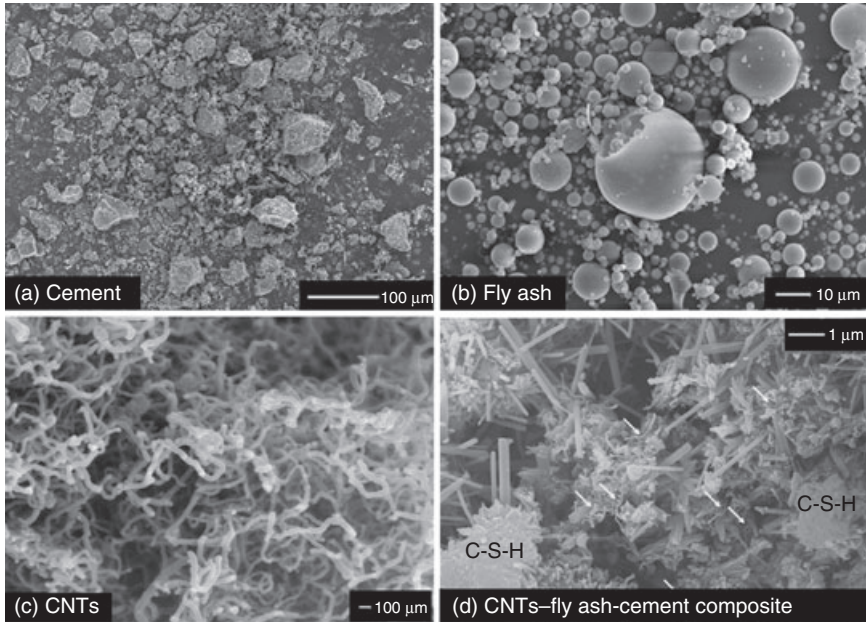
Concrete is probably the most important construction material nowadays, and ordinary Portland cement is the most common form of cement binder used in concrete. Portland cement is formed by grinding amorphous masses of various oxides, such as tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite, together with gypsum into powder (Makar and Beaudoin, 2003). After mixing it with water, the oxides suffer hydration reactions rendering them into solid cement binders. The cement grains have usual dimensions between 5 and 30 microns; however, grains with smaller dimensions are also present (Makar and Beaudoin, 2003). A typical microscale image of Portland cement is shown in Fig. 15.6(a). Cement nanocomposites are expected to have improved mechanical properties. It is thought that nanospheres would interrupt cracking, while nanofibers would act as reinforcing systems. In general, nanoparticles would have a high surface area to volume ratio, resulting in increased chemical reactivity (Fig. 15.6).

Various types of nanoparticles have been added to concrete and the resulting composites have shown improved properties compared to simple concrete, such as strength and reduced permeability to water. Most of the research in nanocomposite cement has been done by incorporating nanoparticles of SiO_2 (Bjornstrom *et al.*, 2004; Tao, 2005; Jo *et al.*, 2007; Hui *et al.*, 2004; Li *et al.*, 2006b, 2007; Ye *et al.*, 2007; Lin *et al.*, 2008; Potapov *et al.*, 2011; Li, 2004) and TiO_2 (Li *et al.*, 2006b, 2007) into concrete.

The addition of SiO_2 nanoparticles to concrete improves concrete workability and structural strength (Sobolev and Gutierrez, 2005a, 2005b; Li *et al.*, 2004), accelerates the hydration reaction (Bjornstrom *et al.*, 2004; Lin *et al.*, 2008), increases the compressive and flexural strength of mortar



15.5 Schematics of nanotechnology application in construction materials and their resulting properties.



15.6 SEM images of (a) Portland cement; (b) fly ash; (c) carbon nanotubes and (d) carbon nanotubes-fly ash cement composite (reprinted from Chaipanich *et al.*, 2010, copyright 2010, with permission from Elsevier); (e) particle size and specific surface area related to concrete materials (reprinted from Sanchez and Sobolev, 2010, copyright 2010, with permission from Elsevier).

(Li *et al.*, 2004; Sanchez and Sobolev, 2010) and increases resistance to water penetration (Tao, 2005).

The addition of TiO_2 nanoparticles to concrete provides the mix with outstanding self-cleaning and anti-pollutant capabilities. The concrete- TiO_2 composite will induce the photocatalytic degradation of NO_x , CO, VOC, chlorophenols and aldehydes, common pollutants present in vehicle and industrial emissions (Ruot *et al.*, 2009; Chen and Poon, 2009). More detailed description of the photocatalytic mechanism is provided in Section 15.3.4. Self-cleaning and de-polluting concrete is already commercially available and has been used in the construction of buildings and roads in Italy and Japan (see Fig. 15.9 on page 447). In addition to photocatalytic benefits, TiO_2 nanoparticles accelerate the early-stage hydration of cement, and enhance the compressive and flexural strength as well as the abrasion resistance (Sanchez and Sobolev, 2010; Li *et al.*, 2006b, 2007).

Similarly, the addition of Fe_2O_3 nanoparticles confers concrete self-sensing capabilities and enhanced compressive and flexural strength (Hui *et al.*, 2004; Li *et al.*, 2004), while incorporating Al_2O_3 leads to a remarkable increase of the modulus of elasticity (Li *et al.*, 2006c).

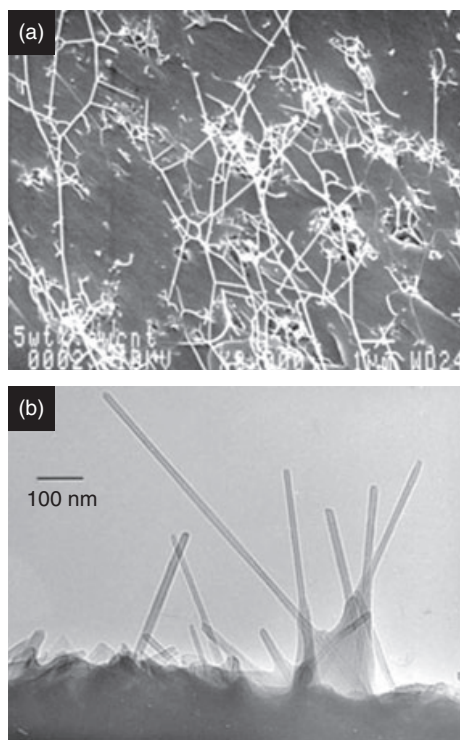
Due to their unique mechanical and electrical properties and a high aspect ratio, CNTs are probably the most promising nanomaterial to be used as cement composite. CNTs are likely to enhance cement's mechanical properties and make it more resistant to crack propagation. Remarkably, CNT-cement composites exhibit electromagnetic field shielding and self-sensing properties that may have numerous applications in the near future (Sanchez and Sobolev, 2010).

Successful incorporation of CNTs into cement requires proper dispersion of the CNT particles and suitable bonding to the cement (Makar and Beaudoin, 2003; Ma *et al.*, 2010). Van der Waals forces make CNTs adhere to one another, making even dispersion difficult. This impediment can be overcome by using specific surfactants, solvents (Forney and Poler, 2011), acid treatment of the nanotubes (Park *et al.*, 2011), sonication (Ma *et al.*, 2010), or surface functionalization (Ma *et al.*, 2010; Sahoo *et al.*, 2010), among other methods. CNT-cement matrix bonding is currently under investigation and is proving to be a great challenge.

Several authors have reported improved properties of CNT-cement composites, including increased compressive and flexural strength, enhanced fracture resistance properties, decreased porosity, increase in the hydration rate, and the development of strong bonds between CNTs and cement (Chaipanich *et al.*, 2010; Konsta-Gdoutos *et al.*, 2010; Li *et al.*, 2005; Makar and Chan, 2009; Luo *et al.*, 2011). In addition to giving increased strength, CNT networks embedded in a cement matrix act as *in situ* sensors for wireless detection of damage in concrete structures (Saafi, 2009).

15.3.2 Glass, ceramic, metallic and polymer nanocomposites

CNT composites also include polymers, metals and alloys, and glass. Glass CNT composites are promising materials due to their increased mechanical properties while retaining light transmittance. CNTs have been used for reinforcing polymers, such as epoxy, polyurethane, and phenol-formaldehyde resins, polyethylene, polypropylene, polystyrene, and nylon (Fig. 15.7) (Ma *et al.*, 2010; Sahoo *et al.*, 2010). As before, the mechanical properties of CNT composites depend on the dispersion state of the CNTs and their bonding to the matrix, in addition to the properties of the matrix material. It has been demonstrated that the technique employed for CNT dispersion can influence the mechanical properties of CNT–polymer nanocomposite (Ma *et al.*, 2010). In addition, the random orientation and alignment of CNTs can also alter significantly the composite properties (Ma *et al.*, 2010).



15.7 (a) SEM image of a fracture surface in a SWCNT–epoxy resin composite; (b) TEM image of a broken surface of a MWCNT–polymer composite (reprinted with permission from Ajayan, 1999, copyright 1999 American Chemical Society).

While polymer–CNT composites have achieved some improved mechanical properties, research is ongoing to advance their performance. For example, polystyrene nanocomposites reinforced with 1.0 wt% CNTs with a high aspect ratio exhibited more than 35% and 25% increases in elastic modulus and tensile strength, respectively (Qian *et al.*, 2000). CNTs can also confer self-sensing capabilities to the polymer matrix (Zhang *et al.*, 2006).

Attempts to fabricate CNT–Al metal composites (Kuzumaki *et al.*, 1998; Choi and Bae, 2011) and CNT–ceramic composites (Ma *et al.*, 1998) have also been made. They encountered similar problems as with the concrete–CNT and polymer–CNT composites and additional difficulties due to the higher temperatures required for the matrix materials.

Enhanced scratch resistance can be attained by the addition of silica nanoparticles to polycarbonate. The resulting nanocomposite had a remarkably enhanced scratch resistance and significantly improved hardness compared to simple polycarbonate (Luyt *et al.*, 2011).

The incorporation of copper nanoparticles at the steel-grain boundaries in steel offers the resulting composite materials a higher corrosion resistance and weldability (Agrawal and Agrawal, 2011).

15.3.3 Nanocoatings with scratch resistance, antireflection, anticorrosive, and fireproof properties

Coatings and paints with nanoparticles are probably the most successfully commercialized application to date. This is probably for several reasons: nanoparticles have a greater surface area interaction with the underlying substrate, penetrate deeper than common coatings, have an improved coverage and are transparent to visible light (van Broekhuizen and van Broekhuizen, 2009). Nanocoatings with different particles can confer the substrates various properties, such as water-repellence properties, scratch resistance, UV protection, antireflection, anticorrosive, fireproof, or self-cleaning abilities. These coatings can be applied to almost any kind of surfaces, from plastic and glass, to metals. Paints incorporating nanoparticles are mostly used for their photocatalytic, antibacterial, and self-cleaning properties.

Anticorrosive properties

Nanozinc coatings can have anticorrosive properties (Pereyra *et al.*, 2010).

Fireproof properties

Nanosilica-based coatings have fireproof properties, and magnesium hydroxide nanoparticles together with micro-trihydrated alumina act as

flame-retardant pigments (Pereyra *et al.*, 2010). Silica nanolayers sandwiched between two glass sheets confer fireproof properties (Mann, 2006). In addition to photocatalytic abilities, TiO_2 coatings can confer flame-retardant capabilities, hindering the ignition or growth of fire (Moafi *et al.*, 2011).

Scratch resistance properties

Scratch resistance properties can be conferred to coatings by the addition of SiO_2 or Al_2O_3 nanoparticles (van Broekhuizen and van Broekhuizen, 2009).

Antireflective and adjustable light transmittance properties

Nanocoatings for glass are also very interesting for indoor climate control by blocking the infrared and visible light. The coating of glass with nanosilica results in antireflective properties, contributing to energy conservation (Troitskii *et al.*, 2010). Nanocoatings can use thermochromic, photochromic, or electrochromic technologies to reversibly change their absorption of infrared light by reacting to temperature, light intensity, or applied voltage (van Broekhuizen and van Broekhuizen, 2009). For example, tungsten oxide and Prussian blue are materials that exhibit electrochromism—the property of reversibly changing color when placed in an electric field. They are used in smart windows with adjustable visible light transmittance between 75% and 8%, and solar transmittance between 56% and 6% (Kraft and Rottmann, 2009).

15.3.4 Photocatalytic coatings and composites

Photocatalytic nanomaterials like TiO_2 , ZnO , and other semiconductor materials are very promising for antiseptic properties and pollution remediation. TiO_2 is a semiconductor with a band gap of 3.2 eV and 3.02 eV in anatase and rutile forms, respectively (Markowska-Szczupak *et al.*, 2011). Upon excitation by UV light, an electron-hole pair is generated on its surface (Geng *et al.*, 2008). These highly unstable states are very reactive and lead to the conversion of water and oxygen molecules into reactive oxygen species, such as hydroxyl radicals, superoxide ion, and hydrogen peroxide, which chemically react with microbes and pollutant molecules, and degrade them (Linsebigler *et al.*, 1995). The photocatalytic reactions kill microorganisms and ultimately oxidize them to water and carbon dioxide (Hochmannova and Vytrasova, 2010). The hydroxyl radicals have a short lifetime and are produced only on the surface of TiO_2 molecules in contact with water, while superoxide ions are long lived (Markowska-

Szczupak *et al.*, 2011). Hydrogen peroxide is highly reactive and can penetrate cell membranes. Upon light irradiation and in the presence of water, photocatalytic coatings are able to kill a wide range of bacteria, fungi, algae, viruses, and prions (Markowska-Szczupak *et al.*, 2011; Caballero *et al.*, 2010). TiO₂ nanoparticles are very effective in killing a wide range of bacteria, both Gram-negative, such as *Escherichia coli* (Rincon and Pulgarin, 2004; Liou *et al.*, 2011), *Salmonella Typhimurium*, and *Vibrio cholerae* (Berney *et al.*, 2006), and Gram-positive bacteria, such as *Staphylococcus aureus* (Cheng *et al.*, 2009). TiO₂ is also very effective in suppression of antibiotic-resistant bacteria, such as methicillin-resistant *Staphylococcus aureus*, and bacteria highly resistant to UV light, such as *Enterobacter cloacae* (Dunnill *et al.*, 2011; Page *et al.*, 2009; Markowska-Szczupak *et al.*, 2011). Under UV irradiation, TiO₂ photocatalysts were shown to deactivate most viruses, including herpes simplex virus, hepatitis-B, poliovirus, rotavirus and influenza virus (Markowska-Szczupak *et al.*, 2011).

There are several mechanisms by which photocatalytic nanoparticles are assumed to kill bacteria. First, light-irradiated nanoparticles in contact with the bacterial membrane generate reactive oxygen species that damage the membrane in less than 20 minutes (Liou *et al.*, 2011). Second, nanoparticles smaller than 20 nm penetrate the bacteria and give rise to photocatalytic processes inside bacteria, damaging intracellular components and producing the oxidation or reduction of intracellular Coenzyme A that causes loss of bacterial respiratory activity and cell death (Maness *et al.*, 1999). Most of the studies show that the bactericidal action occurs within hours or earlier, depending on the TiO₂ concentration and the amount of light exposure.

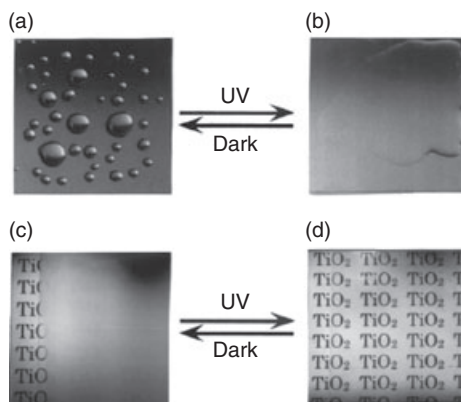
Most of the studies of photocatalytic activity of TiO₂ have focused on antibacterial activity under UV light; however, the use of this process would be limited only to environments with enough UV light. This impediment can be overcome by doping TiO₂ with metals such as Fe, Ag, Ni, Pt, Au, Ag, Cu, Rh and Pd, oxides such as: ZnO, WO₃, SiO₂ and CrO₃, or non-metals such as N, C and S, that can shift their photocatalytic properties in visible light (Markowska-Szczupak *et al.*, 2011; Zhang *et al.*, 2003, 2007; He *et al.*, 2008; Anpo, 2000; Fujishima *et al.*, 2008). For example, the addition of Fe to TiO₂ powders in latex paint leads to a redshift into visible light of the absorption threshold of TiO₂, making possible the use of photocatalytic paints indoors under visible light irradiation (He *et al.*, 2008). The photocatalytic sterilization of *Escherichia coli* with Fe-doped TiO₂ paints exceeded 99% in less than 4 h under visible light irradiation.

The photocatalytic reactions occur not only with organic species, such as bacteria and viruses, but with inorganic compounds, such as ammonia, NO_x, SO_x, NH₃, CO gases and VOC (Steyn, 2009; Geng *et al.*, 2008; Maggos *et al.*,

2007, 2008; Chen *et al.*, 2011; Auvinen and Wirtanen, 2008). International pilot projects have tested and demonstrated the benefits of using these photocatalytic composites and coatings in air pollution remediation: Photocatalytic Innovative Coverings Application for Depollution Assessment (PICADA) 2006, and CAMDEN 2007. Experimental data demonstrate that TiO_2 -treated mortar lowers significantly the levels of NO_x gases compared to untreated mortar, between 36% and 82% (Maggos *et al.*, 2008). The coating of several substrates (glass, gypsum, and polymer) with TiO_2 based paints demonstrates that VOC remediation via photocatalysis is not influenced by the substrate (Auvinen and Wirtanen, 2008).

Anti-fog capabilities

When moist air cools down on surfaces of mirrors or glass they form water droplets or fog that impairs visual clarity. TiO_2 - SiO_2 based surface coatings can be hydrophilic under UV illumination (Watanabe *et al.*, 1999; Wang *et al.*, 1997). This means that the water spreads evenly across the surface, substantially improving the visual clarity (Fig. 15.8). Automobile side-view mirrors as well as adhesive plastic films using this technology are manufactured in Japan.



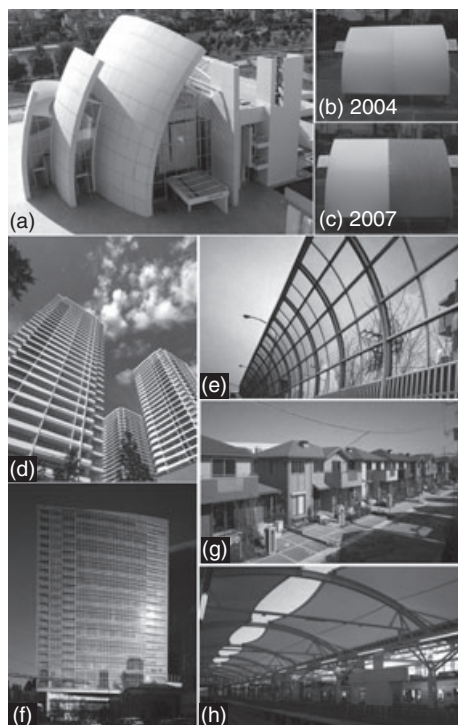
15.8 Antifog glass: (a) hydrophobic surface before UV irradiation; (b) highly hydrophilic surface after UV irradiation; (c) hydrophobic TiO_2 -coated glass with water vapor – the fog or small water droplets impedes the view of the text placed behind the glass; (d) antifog surface after UV irradiation. High hydrophilicity prevents the formation of water droplets, making the text clearly visible (reprinted by permission from Macmillan Publishers Ltd: *Nature* (Wang *et al.*, 1997), copyright 1997).

Self-cleaning capabilities

Because the TiO_2 embedded in the surface can decompose organic contaminants under ultraviolet or visible light, the surface can clean itself. Moreover, the self-cleaning effect of TiO_2 can be enhanced in the presence of water flow, such as natural rainfall (Wang *et al.*, 1998). This enhancing phenomenon is due to the super-hydrophilic property of the TiO_2 surface; more exactly, the water penetrates the space between the contaminant and the super-hydrophilic TiO_2 surface (Fujishima *et al.*, 2008). Even if the light exposure is not sufficient to decompose the surface contaminants by photocatalysis, the surface will remain clean when flowing water is present. Exterior construction materials that are exposed to plenty of sunlight and rainfall would benefit the most from this technology. Materials with self-cleaning capabilities have been commercially available since the late 1990s, mostly in Japan and lately in Italy. They are very attractive because they can be used to mitigate urban air pollution and confer self-cleaning capabilities to structures. Self-cleaning materials do not require the use of harsh chemicals or solvents, giving a clear environmental benefit (Fig. 15.9(b), (c)). They can be found as photocatalytic concrete and other coating materials for architectural walls (Fig. 15.9(a)), self-cleaning tiles (Figure 15.9(d), (g), (h)), photocatalytic paints, and filters. An architectural structure that uses self-cleaning concrete was completed in 2003 in Rome, Italy. The Jubilee Church (or *Dives in Misericordia*) in Rome uses Portland cement with photocatalytic additives with the intention of keeping the building clean. The photocatalytic materials are widely used in Japan; several thousand buildings are covered with self-cleaning tiles; Nagoya International Airport uses self-cleaning glass; there are self-cleaning sunshades in parks, bus and train stations; and eco-life style type houses have been marketed since 2003 (Fujishima *et al.*, 2008). Photocatalytic capabilities are also beneficial to air-cleaning filters, that can kill and decompose bacteria and other organic substances instead of accumulating them (Grinshpun *et al.*, 2007).

Photo-road technology

Photocatalysis of TiO_2 is able to remove NO_x from automobile exhaust, which is becoming a serious source of pollution in urban areas (Ichiura *et al.*, 2003). When colloidal TiO_2 solution is mixed with cement, the nitric acid formed during the oxidation of nitrogen oxides reacts with the cement, forming calcium nitrate, a compound that is easily washed off by rainwater. This 'photo-road technology' has been tested in Japan for more than 10 years (Fujishima *et al.*, 2008). For example, 300 m² on a highway in Tokyo was estimated to remove 50–60 mg of NO_x per day, corresponding to the amount exhausted by 1000 automobiles. This technology is currently being tested by an Italian cement company in Rome and Paris as well.



15.9 Photographs of self-cleaning exterior building materials: (a) the church 'Dives in Misericordia' in Rome built with self-cleaning concrete that incorporates TiO_2 (reprinted from Pacheco-Torgal and Jalali, 2011, copyright 2011, with permission from Elsevier); (b) and (c) self-cleaning test for an outdoor PVC tent material with the left half coated with TiO_2 (manufacturer Taiyo Kogyo) situated in the Photocatalyst Museum, KAST; (d) self-cleaning tiles on MM Towers in Yokohama (courtesy of Toto); (e) self-cleaning glass on Matsushita Denso building (Nippon Sheet Glass); (f) self-cleaning sound-proof wall (courtesy of Sekisui); (g) self-cleaning tiles and glass in eco-life-type housing (courtesy of PanaHome); (h) self-cleaning roof on a train station in Motosumiyoshi (courtesy of Taiyo Kogyo) (b–h reprinted from Fujishima *et al.*, 2008, copyright 2008, with permission from Elsevier).

Antibacterial applications

Due to their antimicrobial properties, paints or tiles with photocatalytic abilities can be used on the floors and walls of hospitals, operating rooms, childcare centers and food processing centers where sterile conditions are very important (Fujishima *et al.*, 2008). Antibacterial tiles on the walls lead to decreased bacterial counts not only on the walls but in the surrounding air. Antibacterial tiles are already used in Japan in hospitals, hotels and

restaurants, among others. Using surfaces with TiO_2 as antibacterial agent has the advantage of passive operation, without the need for electrical power or chemical agents, the already available light and oxygen being sufficient. In addition, it will not result in environmental pollution from using harsh chemicals.

Anticorrosion properties

It was found that TiO_2 coatings have a protective anticorrosive effect on steel (Ohko *et al.*, 2001). After UV irradiation, the TiO_2 coating injected electrons into the steel, this process giving a protective effect against corrosion. The photo-generated holes also play a role in decomposing organic contaminants and provide a self-cleaning function. Later it was observed that TiO_2 coupled with WO_3 maintained an anticorrosion effect even in the dark for a period of time, due to the energy storage capabilities of WO_3 (Tatsuma *et al.*, 2002; Fujishima *et al.*, 2008).

The issues regarding photocatalytic compounds include concerns on the generation of more than just water and carbon dioxide, but pollutants harmful to human health; the lifetime of photocatalytic ability, and last but not least, the possibility of airborne nanoparticulates that can be inhaled and cause significant toxicity.

15.3.5 Antimicrobial coatings

Several types of nanoparticles (Ag, Cu, ZnO, and TiO_2) exhibit high toxicity to a broad spectrum of pathogens and can be used as antimicrobial agents. Silver nanoparticles can be incorporated into paints (Lansdown, 2002) and fabrics (Li *et al.*, 2011) and confer them antimicrobial properties.

Silver-based compounds are able to reduce the growth of several kinds of bacteria, including *Escherichia coli*, *Staphylococcus aureus*, *Leuconostoc mesenteroides*, *Bacillus subtilis*, *Klebsiella mobilis*, and *Pseudomonas aeruginosa* (Marambio-Jones and Hoek, 2010). In addition, silver nanoparticles have a biocidal activity against other organisms, such as fungi and algae (Marambio-Jones and Hoek, 2010). They were found to have antiviral activity as well, inhibiting the replication of Hepatitis B virus (Lu *et al.*, 2008) and respiratory Syncytial virus (Sun *et al.*, 2008) and HIV-1 virus (Mastro *et al.*, 2010). Ag, Cu, and Ag–Cu nanoparticles strongly inhibit the replication of the HIV-1 virus, not only preventing it from attaching to host cells but by denaturing the resulting proteins of the target organisms by binding to reactive groups and inactivating them (Mastro *et al.*, 2010). An excellent review on the biocidal activity of silver can be found in Marambio-Jones and Hoek (2010).

Silver-based antimicrobial agents are important due to the low toxicity of Ag ions to human cells, having a long-lasting biocidal activity and low volatility, and being thermally stable (Williams *et al.*, 1989). However, studies of Ag nanoparticle toxicity revealed that silver nanoparticle aggregates are more toxic than asbestos (Soto *et al.*, 2005, 2007). Hence, much attention must be paid to the careful incorporation of silver nanoparticles into paints and active surfaces in order to avoid their release into the environment and their uptake by humans.

15.3.6 Insulating materials

Nanomaterials used in insulations are aerogels, made of nanofoam with nano-bubbles or nano-holes. Aerogels are probably the most promising thermal insulation materials for building applications, with a potentially large impact on energy consumption and greenhouse gas emission due to heating (Fig. 15.10). First discovered in the 1930s (Kistler, 1931), aerogels are slowly being developed for commercial applications (Baetens *et al.*, 2011). Aerogels, also known as ‘solid smoke’, are composed of a very small amount (0.2%) of silica (or other material) and 99.8% air (Pacheco-Torgal and Jalali, 2011). With the lowest thermal conductivity of any solid, down to 13 mW/mK, and a high transmittance in the solar spectrum, aerogels are of particular interest in the construction sector for the construction of future high-insulation windows (Baetens *et al.*, 2011).

15.3.7 Nanosensors and actuators

As a result of fatigue and environmental effects, concrete structures suffer damage in the form of cracks. Continuous health monitoring of concrete structures is needed to make decisions regarding their maintenance and repair. The development of nanotechnology opens the avenue for their use



15.10 Aerogel cube (courtesy NASA/JPL-Caltech).

as smart advanced sensing materials that can be used for *in situ* monitoring of the health condition of structures. A conductive network of carbon fibers embedded in concrete will change its resistivity as a function of strain (piezoresistivity) and will act as *in situ* sensors for the wireless detection of damage in concrete structures. Experimental results indicate that wireless measurement of the resistance of CNTs to change makes possible the early detection of structural damage, such as cracks (Saafi, 2009). In addition to CNTs (Saafi, 2009; Han *et al.*, 2010b), other conductive particles have been researched as cement nanocomposite components with piezoelectric properties, such as Ni (Han *et al.*, 2009, 2010a) and carbon black (Li *et al.*, 2006a; Xiao *et al.*, 2011).

15.3.8 Possible future applications

Among the many applications of CNTs in construction, there are three main areas where CNTs are very promising: their incorporation in existing construction materials (composites), CNT-based cables, and heat transfer systems (Makar and Beaudoin, 2003). The application of CNTs in ropes and cables is currently restricted due to the limited lengths of CNTs. With advances in nanotechnology, if longer CNTs can be fabricated they could be woven into ropes and cables and used for bridges, elevators, etc. CNT aligned composites could be applied in the heating of buildings, taking advantage of the differences in thermal conductivity across and along the tubes, in a new system for heated floors.

15.4 The uptake of nanoparticles and their toxicity

Nanoparticles are ubiquitous on Earth and beyond. The Earth and the Solar System are believed to have formed by the contraction of clouds of molecules and nanoparticles, their condensation into larger particle seeds, and finally the accretion of these seeds. Life on Earth has been exposed to nanoparticles since its beginnings. Several billion years of life on Earth and 7 million years of human evolution have led to specific evolutionary adaptations of humans and other life forms to nanoparticle and microparticle intruders. For instance, in humans, any inhaled particle encounters just to cite a few defense mechanisms: (1) at the cellular level the mucociliary escalator, performed by specialized cilia of the respiratory epithelium moving particles away from the lungs towards the upper respiratory tract; (2) at the molecular level, the labeling of non-self nanoparticles with immunological molecules – opsonins (e.g. antibodies or complement molecules) – existing in the lung-lining fluid; labeling facilitates the recognition of nanoparticles by phagocytes – cells specialized in the ingestion and sequestration of foreign intruders by the process of phagocytosis; and (3) phagocytosis by

phagocytes and other cells with phagocytic abilities, occurring both in the lungs and throughout the body. Under normal circumstances, the success of these defense mechanisms will depend on the amount, size, and composition of the inhaled nanoparticles. When phagocytosis is impaired, the nanoparticles accumulate and generate oxidative stress and cellular damage. Oxidative stress plays a significant role in the etiopathogenesis of various diseases, such as cancer, cardiovascular, and neurodegenerative diseases. Tissue damage provoked by oxidative stress at the cellular level may evoke acute and chronic inflammation. Inappropriate immune stress is a well-recognized player in complex cardiovascular and respiratory illnesses, such as asthma and chronic obstructive pulmonary disease (COPD).

Currently, our belief is that the main molecular mechanism by which oxidant or transition metals in nanoparticle form elicit their deleterious effects is by shifting the redox balance towards oxidation (Buzea *et al.*, 2007; Unfried *et al.*, 2007). Due to their small size, nanoparticles are able to enter cells by phagocytosis and other mechanisms, such as passive uptake or adhesive interactions mediated by Van der Waals forces, steric interactions, and electrostatic charges (Peters *et al.*, 2006; Geiser *et al.*, 2005). Their uptake can thus occur even in the absence of specific cell surface receptors, and associated subcellular structures. Depending on their intracellular localization, nanoparticles can produce oxidative stress or damage DNA. It is also accepted that nanoparticles may modulate the immune response (Zolnik *et al.*, 2010). Studies have reported that some nanoparticles can enhance the expression of specific viral receptors and lead to excessive inflammation, while others can decrease the expression of certain viral and bacterial receptors, leading to lower resistance to some microorganisms (Lucarelli *et al.*, 2004).

Just how toxic each type of nanoparticle is remains a controversial subject (Schierow, 2008). We do know that the toxicity of nanoparticles depends on several factors, amongst which are chemical composition, crystalline structure, size, and aggregation. Since at nano level the basic physicochemical properties of materials can change with small variations in size, it is virtually impossible to extrapolate their adverse effects from their bulk properties. Very often, a material that is considered nontoxic in bulk form might be extremely toxic at the nanoscale (Buzea *et al.*, 2007). Indeed, much research is needed in order to assess the toxicity spectrum of each material at the nanoscale.

Chemical composition

Nanoparticle composition is important in their chemical interaction with cells. Depending on their composition, nanoparticles may have different cellular uptake mechanisms and intracellular localization and may or may

not induce oxidative stress. Studies comparing the toxic effects of various nanoparticles to those of particles with known toxic effects, such as asbestos, indicate that silver nanoparticle aggregates are more toxic than asbestos (Soto *et al.*, 2005, 2007); carbon nanotubes are extremely toxic, having more detrimental effects to the lungs than carbon black or silica nanoparticles. Contrastingly, titanium oxide, iron oxide, and zirconium oxide are less toxic than asbestos (Soto *et al.*, 2005). These effects are summarized in Table 15.1. Once inhaled, some metallic dusts are known to cause respiratory diseases such as asthma, pulmonary fibrosis, or lung cancer (Nemery, 1990). Some metallic dusts are found in the brain matter of patients affected by neurological diseases such as Alzheimer's and Parkinson's disease (Wang *et al.*, 2009; Antonini *et al.*, 2006; Weiss, 2006). Furthermore, the exposure to certain dusts containing silica or asbestos is linked to autoimmune diseases, including rheumatoid arthritis and systemic lupus erythematosus (Noonan *et al.*, 2006).

Crystalline structure

The toxicity of nanoparticles varies greatly with the crystalline structures for particles with the same composition. While nanoparticles with specific crystalline structures are benign, other allotropes can prove very detrimental to health. For instance, titanium dioxide allotropes – rutile and anatase – have different levels of toxicity (Soto *et al.*, 2005). Rutile nanoparticles induce oxidative DNA damage in the absence of light, while anatase nanoparticles of the same size (200 nm) do not (Gurr *et al.*, 2005). Other studies demonstrated that 10–20 nm nanoparticles of TiO₂ stimulated reactive oxygen species production even in the absence of UV light (Long *et al.*, 2006). When inhaled, TiO₂ dust has been classified by the International Agency for Research on Cancer (IARC) as a substance possibly carcinogenic to humans (Markowska-Szczupak *et al.*, 2011).

Size

Size is a very important factor in determining nanoparticle toxicity. In general, smaller nanoparticles of the same composition are able to pass in an easier manner through physiological barriers and reach organs than their larger counterparts. In addition, nanoparticles with sizes smaller than 100 nm are not effectively phagocytized compared to larger nanoparticles, and are therefore able to evade this defense mechanism. Experiments on animal models suggest that smaller nanoparticles produce higher inflammatory reactions in rat lungs than larger nanoparticles (Oberdorster *et al.*, 1994). The larger surface area of a given volume of small nanoparticles

causes more oxidation and DNA damage than an equal volume of larger particles (Buzea *et al.*, 2007).

Shape

As previously mentioned, shape is also an important determinant of the uptake and cytotoxicity of nanoparticles. The internalization rate of a particle will change depending on the aspect ratio if the composition and size are kept constant (Huang *et al.*, 2010). CNT pulmonary exposure results in the biopersistence of CNTs within the lungs for up to several months (Deng *et al.*, 2007; Elgrabli *et al.*, 2008). The higher the aspect ratio, the higher the toxicity of a material tends to be, as shown in Table 15.1.

Aggregation

Experimental studies indicate that a higher concentration of nanoparticles resulting in aggregates is not as toxic as smaller concentrations of the same nanoparticles that fail to coalesce. Nanoparticles in small concentrations have a higher probability of being distributed to the circulatory system and organs, while a high concentration of nanoparticles leads to the formation of larger aggregates that can be phagocytized more efficiently (Takenaka *et al.*, 2001). However, a very large concentration of nanoparticles is likely

Table 15.1 Relative cytotoxicity index (RCI) of nanoparticles with different composition on murine macrophage cells (after Soto *et al.*, 2005)

Material	Mean particle size (nm)	Mean aggregate size (μm)	RCI(at 5 μg/ml)	RCI(at 10 μg/ml)
Ag	30	1	1.5	0.8
Ag	30	0.4	1.8	0.1
Al ₂ O ₃	50	0.7	0.7	0.4
Fe ₂ O ₃	50	0.7	0.9	0.1
ZrO ₂	20	0.7	0.7	0.6
TiO ₂ (rutile)	Short fibers 5–15 nm diameter	1	0.3	0.05
TiO ₂ (anatase)	20	2.5	0.4	0.1
Asbestos chrysotile	Fibers 20 nm diameter, up to 500 aspect ratio	7	1	1
Carbon black	20	0.5	0.8	0.6
SWCNT*	100 nm diameter	10	1.1	0.9
MWCNT*	15 nm diameter	2	0.9	0.8

* SWCNT = single-walled carbon nanotubes; MWCNT = multi-walled carbon nanotubes.

to produce lung injury, due to the higher rate of accumulation than clearance. Depending on nanoparticle type, the clearance can occur within months or years, while some nanoparticles might never be eliminated. Longer residence times of nanoparticles within the lungs, circulatory system, and organs result in greater occurrence of negative health effects; this is particularly relevant for nanoparticles with mutagenic potential.

Surface chemistry

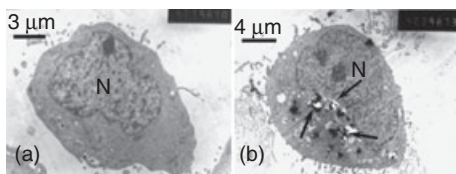
Nanoparticle surface chemistry is a major factor affecting the response of biological systems to nanoparticle exposure, and largely determines particle distribution within the body (Araujo *et al.*, 1999) as well as their compatibility with the immune system (Dobrovolskaia and McNeil, 2007). The toxicity profile of a material in nanoparticle form can be drastically affected by its surface functionalization, which can render toxic nanoparticles nontoxic and vice-versa.

15.5 Diseases associated with nanoparticle exposure

The dimensions of nanoparticles are similar to those of viruses and some small bacteria, and analogous to these microorganisms, they have the ability to affect cellular processes and cause disease. Their minute size allows them to translocate to organs (Sonavane *et al.*, 2008) and undergo cell uptake (Buzea *et al.*, 2007). An example of cellular internalization is shown in Fig. 15.11. The potential effects of nanoparticle exposure on cellular processes are diverse, ranging from uncontrolled cell proliferation, as occurs in cancer, to premature cell death, as seen in neurodegenerative diseases. Many nanoparticles have a significant genotoxic effect (Landsiedel *et al.*, 2009).

Responses to nanoparticle exposure vary greatly between individuals, as both epigenetic and genetic factors as well as pre-existing diseases contribute to the severity of the ensuing health effects. Pre-existing diseases, such as asthma or diabetes, may facilitate the uptake of nanoparticles and increase their translocation to organs (Buzea *et al.*, 2007). The adverse health effects associated with nanoparticle exposure can take anywhere from several hours up to many years to manifest clinically.

Exposure pathways together with the most severe adverse health effects associated with nanoparticle exposure are summarized in Fig. 15.1. The range of pathologies associated with nanoparticle exposure encompasses respiratory, cardiovascular, lymphatic, autoimmune, gastro-intestinal, and nervous system diseases. Interestingly, specific nanoparticles seem to be linked to some diseases with unknown etiology, such as autoimmune (Noonan *et al.*, 2006), Crohn's (Gatti, 2004; Lomer *et al.*, 2002), Alzheimer's and Parkinson's disease (Weiss, 2006; Kawahara, 2005; Miu and Benga, 2006;



15.11 Uptake of Fe_2O_3 nanoparticles by human aortic endothelial cells (reprinted from Zhu *et al.*, 2011, copyright 2011, with permission from Elsevier).

Quintana *et al.*, 2006). Scanning electron microscopy has identified micro- and nanoparticle debris in organ tissue and circulating blood of patients with worn orthopedic implants (Gatti and Rivasi, 2002), blood disease (Gatti *et al.*, 2004), colon cancer, Crohn's disease, ulcerative colitis (Gatti, 2004), and idiopathic diseases (Gatti and Rivasi, 2002). Autopsy results revealed that coal workers have an increased amount of particles in the liver and spleen compared to non-coal workers (Donaldson *et al.*, 2005). Animal studies with inhaled stainless steel welding fumes indicate that manganese accumulates in the blood and liver (Donaldson *et al.*, 2005). Experiments in rats have shown that following inhalation exposure with 4–10 nm silver nanoparticles, within 30 min the nanoparticles enter the circulatory system, and after one day can be found in the liver, kidney, and heart (Takenaka *et al.*, 2001).

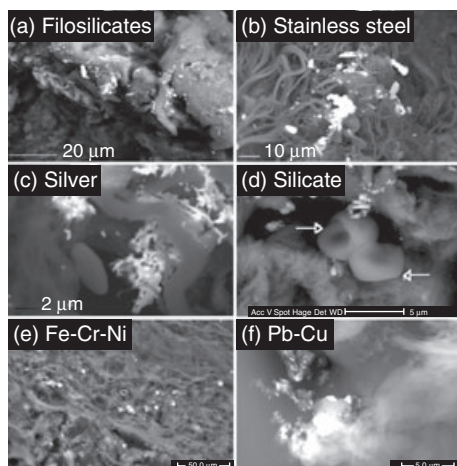
Experimental studies have demonstrated that inhaled nanoparticles with diameter smaller than 30 nm can reach the brain via the olfactory nerves or blood–brain barrier (Borm *et al.*, 2006). Multiple studies suggest that the accumulation in the brain of a high concentration of metals (such as copper, aluminum, zinc, manganese, and iron), together with oxidative stress, may initiate and promote the development of neurodegenerative diseases such as Alzheimer's and Parkinson's disease (Buzea *et al.*, 2007; Weiss, 2006; Kawahara, 2005; Miu and Benga, 2006; Quintana *et al.*, 2006). Epidemiological reports indicate possible association between manganese dust inhalation and the earlier than expected occurrence of neurological diseases in miners (Weiss, 2006) and welders (Antonini *et al.*, 2006). Currently, it is unknown if the high concentration of metals in the brain of patients with neurodegenerative diseases is due to the migration to the brain of nanoparticles themselves, or their soluble components followed by aggregation. Nonetheless, studies on animals and autopsy reports indicate that exposure to particulate pollution produces chronic brain inflammation and pathological findings similar to those of the early stages of Alzheimer's disease (Peters *et al.*, 2006). The number of deaths caused by Alzheimer's disease shows a linear increase in recent years, from less than 1.9% in 1999 to 3% in 2006 of the total number of deaths per year in the United States

(Anderson, 2001, 2002; Anderson and Smith, 2003, 2005; Heron and Smith, 2007; Heron, 2007; Kung *et al.*, 2008).

Nanoparticles that reach the lungs and are not removed via mucociliary clearance or phagocytosis will accumulate and/or pass into the circulatory and lymphatic systems. Inhalation of nanoparticles is associated with respiratory diseases such as asthma, pulmonary fibrosis, emphysema, mesothelioma, and lung cancer (Buzea *et al.*, 2007). A large body of epidemiological research supports the role of particulate pollution in causing these adverse effects. In general, exposure to pollution nanoparticles with various compositions, aggregations, and sizes, is associated with pulmonary and cardiovascular diseases (Buzea *et al.*, 2007). Elevated levels of particulate pollution are linked to higher numbers of hospital admissions for respiratory illnesses, such as pneumonia, bronchitis, and lung cancer (Iwai *et al.*, 2005), and to increased mortality due to either cardiopulmonary failure or lung cancer (Pope *et al.*, 2002). Indeed, hospital admissions for cardiovascular illness increase on days with higher levels of particle pollution (Schwartz and Morris, 1995). There is significant correlation between inhalation of nanoparticulate matter and various cancers (lung, breast, endometrium, and ovary) (Iwai *et al.*, 2005; Knox, 2005).

Due to their small size, inhaled nanoparticles can cross physiological barriers and enter the circulatory system. Experimental evidence suggests that inhaled metallic nanoparticles smaller than 30 nm pass easily into the circulatory system (Geiser *et al.*, 2005; Takenaka *et al.*, 2001; Donaldson *et al.*, 2005; Oberdorster *et al.*, 2005). Within the circulatory system nanoparticles can interact with blood and endothelial cells, potentially leading to circulatory diseases such as arteriosclerosis and thrombus formation. Within 30 minutes of exposure, intra-tracheally instilled 30 nm gold nanoparticles have been found within pulmonary platelets in rats (Oberdorster *et al.*, 2005), indicating a possible connection between nanoparticles and the experimental formation of thrombus. It is interesting to note that nanoparticles of various compositions such as gold, silver, cobalt, titanium, tungsten, nickel, zinc, barium, iron, chromium, silicon, glass, talc, and stainless steel have been collected from explanted *vena cava* filters of patients deemed to be at risk of developing thrombo-emboli (Fig. 15.12(e), (f)) (Gatti *et al.*, 2004). Furthermore, the same study reported that nanoparticles were present within microthrombi trapped at the vertex of the implanted *vena cava* filters. Human aortic endothelial cells have been shown to release inflammatory mediators upon the uptake of Y_2O_3 or ZnO nanoparticles (Gojova *et al.*, 2007). A large body of literature supports the notion that nanoparticles with their pro-inflammatory properties may lead to the induction of heart arrhythmia and cardiac failure (Vermylen *et al.*, 2005).

The size of nanoparticles entering the circulatory system and organs is partly determined by the junction sizes of the endothelial cells lining the



15.12 Nano- and microparticles found in colon cancer tissue from human biopsies: (a) ceramics (filosilicates); (b) stainless steel; (c) silver and (d) silicate (reprinted from Gatti, 2004, copyright 2004, with permission from Elsevier); and debris entrapped inside tissue formed around a filter inserted in the *vena cava* for 156 days: (e) debris of Fe-Cr-Ni; (f) debris of Pb-Cu (with kind permission from Springer Science+Business Media: Gatti *et al.*, 2004).

vascular system. These junctions range between 2 and 100 nm in size, depending on the organ or tissue (Hussain *et al.*, 2001; Schwab and Pang, 2000). However, capillary permeability considerably increases in the presence of inflammation and in subjects with pre-existing respiratory and circulatory diseases, allowing more and larger nanoparticles to enter into circulation. Inhaled nanoparticles have been shown to reach organs, translocating from lungs to blood (Geiser *et al.*, 2005; Takenaka *et al.*, 2001; Donaldson *et al.*, 2005; Oberdorster *et al.*, 2005), liver, kidneys (Takenaka *et al.*, 2001; Gatti and Rivasi, 2002; Ballestri *et al.*, 2001), spleen (Jani *et al.*, 1990), brain (Peters *et al.*, 2006; Takenaka *et al.*, 2001), and heart (Takenaka *et al.*, 2001). *Ex vivo* experiments using a human placenta perfusion model have shown that polystyrene particles with diameter smaller than 240 nm are able to cross the fetus–placental barrier, establishing the potential risk of nanoparticle exposure *in utero* (Wick *et al.*, 2010). Experiments on mice demonstrate that intravenously injected 70 nm silica and 35 nm titanium dioxide nanoparticles, respectively, are associated with pregnancy complications in pregnant mice (Yamashita *et al.*, 2011). These nanoparticles cross the placental barrier, being found in the fetal liver and fetal brain (Yamashita *et al.*, 2011).

In addition to inhalation, nanoparticles can also be ingested. Common sources of exogenous nanoparticles in the gastro-intestinal tract are food

additives and colorants (such as titanium dioxide), pharmaceuticals and cosmetics (toothpaste and lipstick), dental prosthesis wear, and inhaled nanoparticles (Buzea *et al.*, 2007). Contaminants may also be an important source of ingested nanoparticles (Gatti *et al.*, 2009). Experiments on animals performed by Jani *et al.* showed that oral uptake of polystyrene microspheres results in systemic absorption and size-dependent localization to organs, including the liver, spleen, blood, and bone marrow (Jani *et al.*, 1990). The length of stay of particles can also become a determinant factor on their toxicity. Indeed, nanoparticles have been found consistently in the gastro-intestinal tract, blood, and organs of patients with Crohn's disease, ulcerative colitis, and colon cancer (see Fig. 15.12(a–d)) (Gatti, 2004). It is remarkable that the nanoparticles found in diseased subjects have various chemical compositions (carbon, ceramics, silicon, stainless steel, silver and zirconium, among others) and are not toxic in bulk form (Gatti, 2004). The sources of nanoparticles in the gut of patients with Crohn's disease are both anthropogenic and natural, and include titanium dioxide from food additives, aluminosilicates from natural clay, and environmental silicates (Powell *et al.*, 1996). Taking into account the possible adverse health effects that nanoparticles may elicit in the gastro-intestinal tract and their lack of nutritional value, the commercialization of dietary nanoparticles should be strictly regulated.

Skin constitutes a third portal of entry for nanoparticles into organisms. Though a controversial subject, experimental evidence indicates that specific nanoparticles are able to penetrate skin, with their cytotoxicity dependent on their composition. Skin uptake of soil nanoparticles has been shown to result in the impairment of the lymphatic system, due to inadequate fluid drainage in podonconiosis (Blundell *et al.*, 1989). *In vitro* experiments have evidenced the uptake of multi-wall carbon nanotubes by human epidermal keratinocytes (Monteiro-Riviere *et al.*, 2005). Both *in vitro* and *in vivo* experiments suggest that sun-illuminated titanium dioxide nanoparticles from sunscreens catalyze DNA damage, and produce inflammation in human endothelial cells (Serpone *et al.*, 2001; Dunford *et al.*, 1997). Additionally, silver nanoparticles, used in pharmaceuticals as antibacterial wound dressings, are not only bactericidal but may also be toxic to keratinocytes and fibroblasts (Poon and Burd, 2004).

The relationship between nanoparticle exposure and the immune response is not well understood. Exposure to silica and asbestos dusts is linked to autoimmune diseases with unknown etiology, such as rheumatoid arthritis and systemic lupus erythematosus (Noonan *et al.*, 2006; Pfau *et al.*, 2005). Recent research indicates that, depending on the material, size, and physico-chemical properties, various nanoparticles can either suppress or stimulate the immune response (Dobrovolskaia and McNeil, 2007; Zolnik *et al.*, 2010), and inhibit (Ryan *et al.*, 2007) or exacerbate allergic reactions

(Dobrovolskaia and McNeil, 2007; Dwivedi *et al.*, 2009). For instance, fullerenes have antiallergic properties, inhibiting allergic responses *in vitro* and anaphylaxis *in vivo* (Ryan *et al.*, 2007). Carboxyfullerenes were found to enhance the ability of neutrophils to destroy specific *Streptococcus pyogenes* (Dobrovolskaia and McNeil, 2007). Functionalized polylactic-glycolic acid nanoparticles reduce inflammation in arthritis animal models (Dobrovolskaia and McNeil, 2007). One must note that while some nanoparticles could be used to suppress the immune response in the treatment of inflammatory diseases, some undesirable immunosuppression could be detrimental in managing cancer and infections.

The composition, size, and other physico-chemical properties of nanoparticles, determine their ability to penetrate cells, affect organelles, and influence basic cellular processes, such as the cell cycle and cell death. Experimental evidence shows that nanoparticles are internalized by a variety of cell types, ranging from alveolar macrophages (Takenaka *et al.*, 2001; Hoet *et al.*, 2004), platelets (Nemmar *et al.*, 2002), red blood cells (Peters *et al.*, 2006; Rothen-Rutishauser *et al.*, 2006), and endothelial cells (Gojova *et al.*, 2007), to nerve cells (Hutter *et al.*, 2010). Nanoparticles have been found at different locations within cells, such as the cytoplasm, mitochondria (Xia *et al.*, 2006), and nucleus (Porter *et al.*, 2006). The cytotoxicity varies with a multitude of factors, including the cell type, nanoparticle composition, size, surface chemistry, and aggregation. In general, the cytotoxic effect emerges with increasing dose and length of exposure, in a manner which varies with nanoparticle composition. Associated increases in cell death are related to cell internalization and subsequent generation of reactive oxygen species. There is not clear evidence whether nanoparticles can interact with surface or intracellular receptors. We consider that it is reasonable to speculate that some nanoparticles may interact with pattern recognition receptors (PRRs) such as the toll-like receptor (TLR) family of genes at the cell surface, or once internalized they may also interact with the NOD-like receptor (NLR) family of genes triggering cytotoxic pathways (Martinon *et al.*, 2009). It is also plausible that danger-associated molecular patterns (DAMP) released from injured cells inflammasomes, as observed with microparticles of asbestos and silica, may amplify and perpetuate the inflammatory response.

Beneficial effect of some nanoparticles

It is important to note that while most nanoparticles may be potentially toxic, there are significant exceptions (Buzea *et al.*, 2007; Connor *et al.*, 2005; Goodman *et al.*, 2004). Indeed, some nanoparticles appear to have antioxidant properties, and hence are beneficial to human health (Buzea *et al.*, 2007; Bosi *et al.*, 2003; Schubert *et al.*, 2006). Examples include

functionalized fullerenes (Bosi *et al.*, 2003) and nanoparticles of non-stoichiometric rare earth oxides (CeO_2 and Y_2O_3) (Schubert *et al.*, 2006), which are neuroprotective and exhibit consistently anti-apoptotic activity in various cell types due to their antioxidant properties.

Surface functionalization has been used to render toxic nanoparticles nontoxic, making them valuable tools for use at the molecular level. This technique is currently used to fabricate contrast agents in molecular imaging and designing artificial molecular receptors (Asiyanbola and Soboyejo, 2008). Further possible applications of this technique include targeting specific malignant cells or microbes. Nanoscale drug delivery systems targeting cancer are used to deliver chemotherapy drugs with lower systemic toxicity, improved selectivity and specificity (Malam *et al.*, 2009). The toxicity of some nanoparticles to specific microorganisms makes them important antiseptic nanotools (Lara *et al.*, 2010). Silver, titanium dioxide, zinc oxide, and magnesium oxide nanoparticles all exhibit antibacterial activity, while fullerenes and silver nanoparticles have antiviral activity. In addition, sea-salt aerosols resulting from water evaporation are probably among the few natural nanoparticles with beneficial health effects, helping restore the mucociliary clearance in patients with respiratory diseases (Ballard *et al.*, 2006).

15.6 Detection of occupational nanoparticles and remedial action

Airborne nanoparticles may pose a health risk to workers as well as to consumers of products containing nanoparticles that may be released into the environment. The National Institute for Occupational Safety and Health (NIOSH) developed a 'Nanoparticle Emission Assessment Technique' (NEAT) that uses a combination of measurement techniques and instruments able to assess the inhalation exposure to nanoparticles (Methner *et al.*, 2010a, 2010b). They used NEAT to assess potential inhalation exposure of nanoparticles in facilities producing and handling nanomaterials, such as CNTs, fullerenes, metal oxides, and quantum dots (Methner *et al.*, 2010a). It was found that occupational exposure to CNTs occurs during their handling and transportation. Precautions should be taken during the weighing, mixing, collection, manual transfer, cleaning operations, drying, spraying, chopping, and sonication of CNTs (Methner *et al.*, 2010a; Stella, 2011).

Unfortunately, currently there are no laws or regulations to impose occupational exposure limits to most nanoparticles (Hallock *et al.*, 2009). This is mostly due to the swift commercialization of products containing nanoparticles and a slower pace of research into their toxicity mechanisms. In order to avoid possible inhalation of nanoparticles, much care should be taken



15.13 Technician cleaning plastic sheets with ink containing SWCNTs (courtesy Mary Schubauer-Berigan and Matt Dahm, NIOSH).

during all the fabrication stages involving nanoparticle composites and coatings, and the wearing of protective equipment and filters should be mandatory (Fig. 15.13). In addition, Material Safety Data Sheets (MSDSs) should be developed and provided for the most hazardous nanoparticles (van Broekhuizen and van Broekhuizen, 2009).

Until toxicology information becomes available for all types of nanoparticles, workers using nanoparticles should prevent inhalation, dermal and ingestion exposure (Hallock *et al.*, 2009). Studies show that airborne nanoparticles can stay suspended in air for days or weeks and if inhaled about 35% will be deposited into the lungs (Maynard and Kuempel, 2005). Best practices in preventing nanoparticle exposure are summarized below (Hallock *et al.*, 2009):

- Inhalation exposure prevention: handling of nanoparticles in a fume hood; the use of HEPA filters; transport in sealed containers.
- Dermal exposure prevention: use preferably disposable gloves or double gloves, laboratory coats and eye protection.
- Cleaning procedures: wet-wipe surfaces after use; do not sweep or use compressed air for cleaning; use HEPA vacuum cleaners for spills.
- Disposal: dispose of nanomaterials and nanomaterial-contaminated laboratory materials as hazardous waste labeled as nanoparticles.
- Toxicity information: obtain current toxicity information on nanomaterials because MSDSs most often report health effects of micron-sized materials, while nanoparticles are more toxic.

15.7 Sources of further information and advice

Several excellent reviews on the application of nanotechnology in constructions are Fujishima *et al.* (2008), van Broekhuizen and van Broekhuizen

(2009), Raki *et al.* (2010), Allen *et al.* (2005), Hochmannova and Vytrasova (2010), Lee *et al.* (2010), Mann (2006), Bystrzejewska-Piotrowska *et al.* (2009), Makar and Beaudoin (2003), Sanchez and Sobolev (2010), Steyn (2009), and Pacheco-Torgal and Jalali (2011). Some excellent reviews regarding nanoparticle toxicity are Borm *et al.* (2004, 2006), Buzea *et al.* (2007), Bystrzejewska-Piotrowska *et al.* (2009), Crosera *et al.* (2009), Dobrovolskaia and McNeil (2007), Donaldson *et al.* (2005), Fubini *et al.* (2010), Hoet *et al.* (2004), Oberdorster *et al.* (2005), Sharma (2010), Shvedova *et al.* (2010), Simko and Mattsson (2010), Sioutas *et al.* (2005), Stone *et al.* (2007), Vermeylen *et al.* (2005), Warheit *et al.* (2008), Xia *et al.* (2009), and Peralta-Videa *et al.* (2011).

15.8 Conclusion and future trends

We are just discovering the wonderful properties of materials at the nanoscale, and bottom-up approaches will allow the fabrication of novel nanostructures and nanotechnologies that will likely be implemented in all the areas of our life. There is no doubt that nanotechnology will revolutionize the construction industry, with lighter and stronger materials, and smart sensing structures, with self-cleaning antimicrobial surfaces, that improve energy conservation and remediate pollution in the cities of the future. However, without rules and regulations for the handling and disposal of nanomaterials they might have an adverse impact on our society. The pace at which nanomaterials find their way to new applications does not parallel the pace of research that should be directed towards ensuring their safety before they reach the hands of consumers. Current research indicates that many nanoparticles are toxic to living organisms. Their toxicity depends on various physico-chemical characteristics whose relative importance is still unknown. Nanoparticles are associated with a wide range of diseases that can manifest themselves immediately following exposure or up to many years later. While today the main focus of criticism is on engineered nanoparticles due to their toxicity and potential environmental impact, we must emphasize that particulate pollution from vehicle exhaust and from incomplete combustion of various fuels currently constitutes the majority of anthropogenic nanopollutants associated with adverse health effects. Because it is impossible to extrapolate the toxicity of a nanomaterial from the properties of the bulk material, a case-by-case approach is required in order to identify hazardous nanomaterials. Thus, sustained research programs are needed to determine the toxicity spectrum of newly developed materials in nanoparticle form. Each type of nanoparticle has to be treated as a unique material, and its toxicity investigated prior to its use in consumer products or as medicine. It is not only

the responsibility of the industry, but ours as society, to ensure that the safety of all materials is assessed prior to their commercialization and the appearance of deleterious effects.

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