GEOENVIRONMENTAL ENGINEERING

Integrated management of groundwater and contaminated land

edited by R. N. Yong and H. R. Thomas

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Preface

This book is a compilation of peer reviewed papers which were presented at the 4th BGA Geoenvironmental Engineering Conference at Stratford-upon-Avon in June 2004. This was the fourth conference in the series, previous conferences being held in Cardiff, London and Edinburgh. Issues associated with Geoenvironmental Engineering continue to be a major preoccupation for Governments, public and private organisations and the general community around the world. This conference brings together people working in industry, acadaemia and the public sector to discuss the latest ideas and developments in Geoenvironmental Engineering and related fields. The papers in these proceedings reflect the work being undertaken across the discipline.

The theme of the fourth conference was Integrated Management of Groundwater and Contaminated Land. The papers in this book are grouped according to the sessions under which they were presented at the conference: Risk Management and Remediation of Contaminated Groundwater and Land; Landfill Processes; Risk Assessment and Modelling; Management of Wastes; Fate and Transport of Pollutants in the Subsurface; Mine Wastes and Waters; and Legislation and Regulatory Control. The papers have been submitted from authors from across the world and reflect the international flavour of the conference.

The conference was organised by the Geoenvironmental Engineering Research Centre at Cardiff University and the British Geotechnical Association. We would like to thank the members of the Organising Committee: Dr M Dyer, Prof S Jefferis, Dr D H Owen, Dr H Potter, Dr R M Reid, Dr D Stewart and Ms C Summers (Secretariat). We would also like to thank the Local Organising Committee at the Environment Agency: Dr H Potter, Mr R Harris, Dr T Kearney, Dr A Hart, Mr J Smith, Dr B Bone and Mr B Barnes. The assistance of the two committees with regard to the paper review process and the arrangements for the conference was invaluable.

R N Yong
H R Thomas

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FATE AND TRANSPORT OF CONTAMINATES IN THE SUBSURFACE

Influence of the unsaturated zone of soil layer on the solute migration

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INTRODUCTION

To design waste containments and retention ponds, low permeability soils or manufactured products are required. It is recommended to use a soil layer of five meter thickness when the coefficient of permeability is 10^{-6} m/s or a layer of one meter when the coefficient of permeability is less than 10^{-9} m/s. But the used earth material permeability is control in the laboratory with the standard permeability tests. These tests are performed on saturated or quasi-saturated soil samples. It is recognised that the coefficient of permeability increases with the degree of saturation of the sample. So the use of the value of the coefficient of the permeability of saturated soil gives an upper value of the barrier leakage. Some authors tried to prove analytically, that the barrier thickness can be reduced when the coefficient of permeability of the barrier material is less than 10^{-9} m/s (e.g. 10^{-10} or 10^{-11} m/s). The use of the saturated soil permeability for liner performance evaluation, does not take into account the fact that the barrier material on site is unsaturated. It is obvious that water and pollutant transfer through the liner is influenced by the degree of saturation because of the moisture retention and sorption phenomenon.

Laboratory infiltration tests are carried out on unsaturated soil columns to observe moisture and solute migration. Two soil materials, clayey sand and clay, are used to compare, according to the infiltrated volume, the solution action on the soil and the saturation duration. The slag lead leachate is used as a percolated liquid. Moisture and solute migration is described with TDR measurements. The change on soil electrical conductivity reveals the depth of the solute migration. So the use of Nadler (1991) relation allows the soil electrical conductivity computing with soil impedance measures. The soil impedance is determined from the TDR signal voltage ratio.

Meddahi et al (1993) have shown that the relative mass of the retained solute can be estimated with soil impedances. So the measurements of the impedance by the TDR method permit the solute relative mass retained monitoring. For given depth, the time to saturate the over soil thickness is determined and compared for the two types of the soils used. This time can characterise the efficiency of the layer thickness to reduce the pollutant transfer.

MATERIALS AND METHODS

To follow water and solute migration, infiltration tests are carried out on compacted soil in column. During a test, infiltrated volume is measured versus time to determine infiltration

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curves and infiltration rate. TDR measurements are performed to get moisture and soil impedance profiles. One of the two soils is chosen to have water coefficient of permeability of 10^{-7} m/s at the dry bulk density of 1.6. The second soil is clay used for waste containment barrier.

Geotechnical characterisation of tested soils

Different laboratory tests were carried out to obtain geotechnical characteristics of the tested soils. Proctor compaction tests gave the optimum water content and dry bulk density. Characteristic values for soil identification are shown in table 1. Size grain distribution and Atterberg limits show that the premier soil is clayey sand (SC) and the second soil is plastic clay.

Table 1 Soil geotechnical characteristics

Soil	Fines (%<80μm) (%)	Clay (%<2μm) (%)	LL (%)	IP (%)	Optimal dry density	Optimal water content (%)
Clayey sand	71	22	30	19	1.77	12.5
Gault Clay	100	69	40	21	1.85	17.5

Standard permeability tests carried out on saturated soil samples gave water permeability coefficient of 2.10^{-7} m/s for the clayey sand and $2.5\ 10^{-10}$ m/s for the clay.

Infiltration test device

Infiltration tests are carried out in soil columns of 550 mm height. Each column is composed with eleven ring of 106mm diameter and of 50mm height. The wetted soil is compacted in each ring at fixed dry bulk density. Before the compaction of the clayey sand in the rings, ten of them are fitted with three rod TDR probe. The TDR probe has 80mm rod length and each rod has a diameter of 3mm. For the clay column, the TDR probes are located at 25, 75, 275, 375, 475mm depth. The infiltration test column is installed as is shown in figure 1.

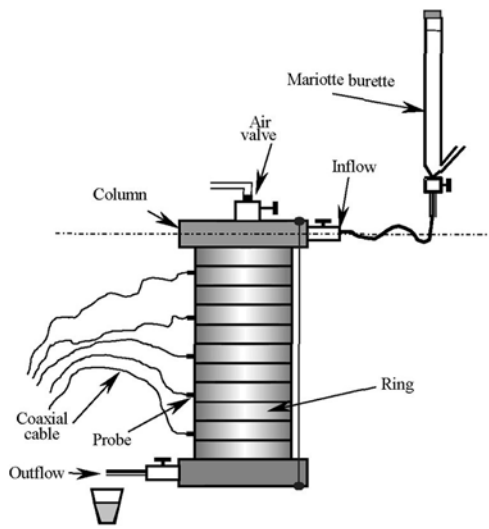

Figure 1 Schematic of soil column used for infiltration tests

Infiltration hydraulic head and infiltrated volume are obtained with Mariotte burette. Infiltration is performed on the clay column at hydraulic head of 980mm of water and zero for the clayey sand column. Cumulative infiltration curve is determined from the infiltrated volume versus time. TDR measurements obtained from Tektronix 1502B, are recorded in computer for further analysis.

TDR measurement theory

TDR method is based on measuring the travel time and the amplitude of an electromagnetic pulse which is propagated along a transmission line embedded in soil. Topp et al. (1980) showed, for many soil materials, a general empirical relation between volumetric water content (θ) and dielectric constant (ε). They proposed the following relationship:

$$\theta = -0.053 + 0.29\varepsilon - 5.5 10^{-4}\varepsilon^2 + 4.3 10^{-6}\varepsilon^3 \quad (1)$$

Dielectric constant (ε) is defined by:

$$\varepsilon = \left(\frac{ct}{2L}\right)^2 \quad (2)$$

where c is the velocity of light in free space and L is the length of the transmission line.

Commercial instruments use the relationship (1) to measure directly volumetric water content (θ). The load of the transmission line (R_L) embedded in the investigated soil can be calculated with the voltage reflection ratio (ρ) defined by:

$$\rho = \frac{R_L - Z_0}{R_L + Z_0} \quad (3)$$

Z_0 is the characteristic impedance of the connecting cable.

The probe's geometric constant K_c is defined by:

$$K_c = \sigma_{ref}(25°C) R_L / f \quad (4)$$

(f, temperature correction)

σ_{ref}(25°C) is the permeant electrical conductivity. K_c is determined by immersing TDR probe into a solution of known electrical conductivity σ_a and by measuring R_L. Kc is then used to calculate soil electrical conductivity, when the voltage reflection ratio (ρ) is measured (Nadler et al. 1991).

Meddahi et al. (1993) have proved that the TDR measurements can be used to obtain the breakthrough curves of non-reactive solute. So supposing a linear relation between the soil electrical conductivity and the concentration of the soil pore water, it is shown that relation between the solute mass and the soil electrical conductivity is linear (Kachanoski et al., 1992). So the relative solute mass ($M_{L,R}(t)$) in the soil at the elapsed time t after solution injection is defined by:

$$M_{L,R}(t) = \left[\frac{R_{L,t}^{-1} - R_{L,t_i}^{-1}}{R_{L,t_0}^{-1} - R_{L,t_i}^{-1}} \right] \quad (5)$$

where

R_{L,t_i} is the initial impedance of the soil of thickness L

R_{L,t_0} is the minimum impedance of the soil of thickness L

$R_{L,t}$ is the impedance of the soil of thickness L at elapsed time t.

The relation (5) can be used for solute accumulation in the soil thickness, when R_{L,t_i} and R_{L,t_0} are determined.

MEASUREMENT RESULTS

To describe the influence of the vadose zone on the solute migration, the soil hydraulic conductivity evolution is determined. The hydraulic conductivity can be computed with the infiltration rate when the depth of the saturated front is known. This depth can be obtained from Green Ampt relation using cumulative infiltration. The accurate value of the saturated depth is provided by the moisture profiles. So the two methods of the evaluation of the saturation front are applied for the calculation of the hydraulic conductivity of the clayey sand and the clay of Gault.

With TDR measurements, moisture profiles and electrical conductivity distribution in soil column are determined. These two profiles show the solute migration during the soil saturation. The profile forms relate the migration modes in the two soils. So comparing electrical conductivity profiles in the clayey sand and Gault clay columns, we can describe migration mode during the soil saturation.

The clayey sand is compacted in each ring with water content of 9.3% and dry bulk density of 1.6. The column of the Gault clay is built after the compaction of the soil in each ring at water content of 17% and dry bulk density of 1.7. The used lead slag leachate is an acid leachate (pH6.3) which electrical conductivity is 53mS/cm.

Description of moisture and solute movement in the tested soils

The TDR signals recorded during the infiltration tests give a dielectric constant using the relation (2). Then relation (1) gives the volumetric water content. The figure 2 shows the moisture profiles in the clayey sand and the Gault clay. It takes 15.5hours to saturate the clayey sand column. But the saturation front just reaches the depth of 250mm after 759 days of infiltration. A saturated zone is observed in the clayey sand column after 1.50hours but 15days is needed in the Gault clay column. In the saturated zone, called transmission zone (Pillip, 1957-2), the water has a convective movement. In the transmission zone, the flow rate is governed by hydraulic head pressure and Darcy law can be applied. That means that the coefficient of permeability can be computed with infiltration rate for soil thickness of 100mm after 1.50hours when the compacted soil is clayey sand and 15days when the compacted soil is the clay of Gault.

This measurement results show that it is not five times the thickness of the clay of Gault is needed if clayey sand layer must be used when the saturation process is taken into account.

It is not sure that the moisture movement describes the solute migration. Solute movement can be referred to soil electrical conductivity. Indeed, the bulk electrical conductivity is a linear function of the electrical conductivity of the pore solution.

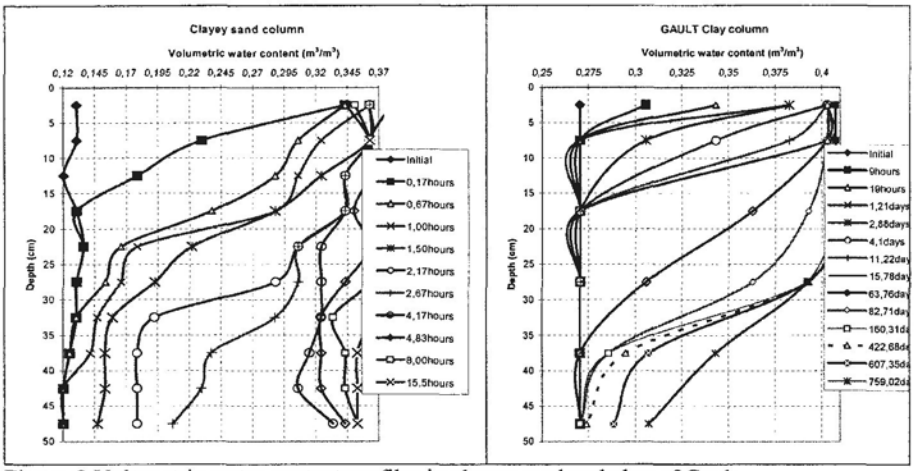

Figure 2 Volumetric water content profiles in clayey sand and clay of Gault

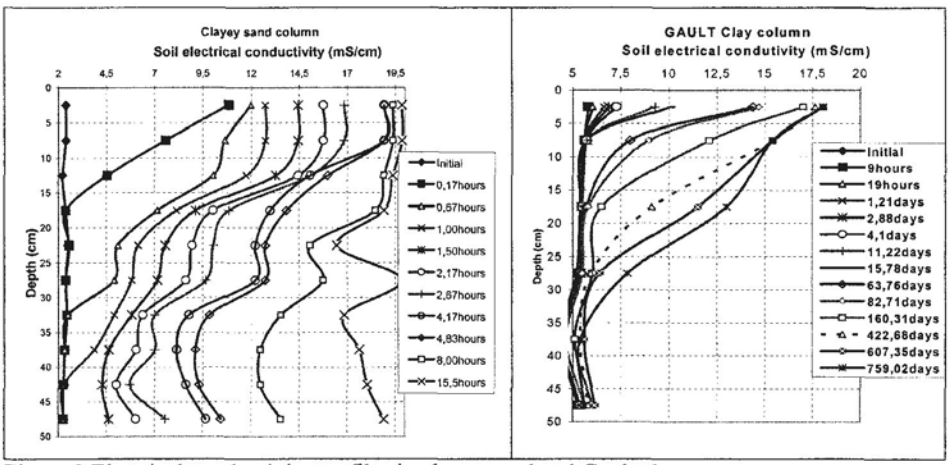

Figure 3 Electrical conductivity profiles in clayey sand and Gault clay

The soil impedance is determined with TDR measurements. Using the probe geometric constant and the relation (4), the soil electrical conductivity is computed. Electrical conductivity profiles in clayey sand and in clay of Gault columns are embedded in figure 3. The form of the electrical conductivity profiles proves that the solute has a dispersive movement in the clay of Gault column. In spite of the hydraulic head pressure of 980mm of water and in spite of the saturation depth of 250mm. The solute migration in clayey sand becomes dispersive-convective after 0.67hours and before transmission zone appears and

before soil saturation. If the unsaturated state of soil is taken into account, it is not only the increase of the thickness of high permeability layer which must recommend but also the reduction of the convection rate by high dry bulk density.

It is noticed that the clayey sand thickness reduces the solute transport during 15.5hours. This reduction stands before the soil thickness saturation. That means the high permeability soil layer thickness can participate to the pollution flux reduction like the low permeability soil layer thickness.

Hydraulic conductivity assessment during Infiltration tests

The pollutant movement in barrier system is described by the coefficient of permeability of the soil material in saturated state. This coefficient is often determined during laboratory tests. Now, many devices are developed for in situ measurements of the coefficient of permeability. For the determination of the permeability of the soil layer on site, one only records the infiltration rate. The depth of the saturation front is give by models as that of Green-Ampt (1911) or determined after the infiltration test. Green and Ampt proposed the following relation to determine the depth of the saturation front:

$$z_f(t) = \frac{I(t)}{\theta_s - \theta_i} \tag{6}$$

where:

$I(t)$ is the cumulative infiltration at the elapsed time t

θ_s is the saturation volumetric water content

θ_i is the initial volumetric water content

Using the infiltration cumulative curve the depth of the saturation front is computed for the clayey sand and clay of Gault. The saturated front depth is also estimated with the moisture profiles. The coefficient of the permeability at elapsed time t, is computed with the infiltration rate and with the thickness of the saturated zone. During the infiltration in the clayey sand column, the outflow rate of the leachate is used to determine the coefficient of the permeability. The results are shown in the figure 4.

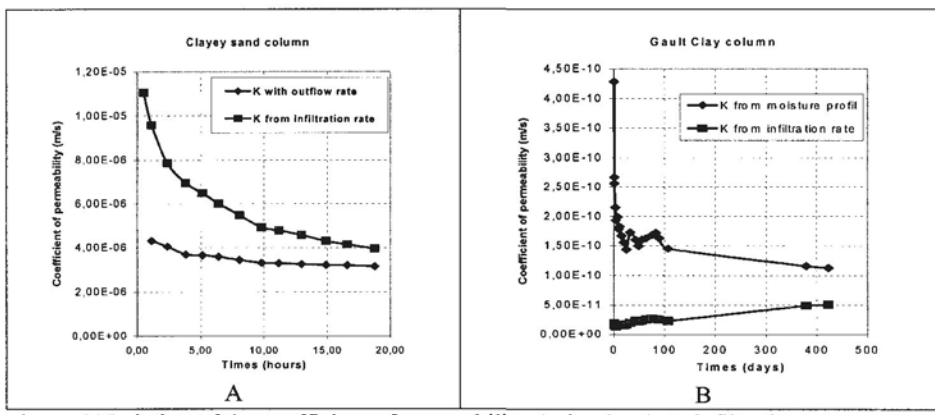

Figure 4 Variation of the coefficient of permeability during leachate infiltration

The coefficients of permeability of the clayey sand computed with the cumulative infiltration and the two methods of the determination of the saturation front are the same. In the figure 4A, the coefficients of permeability K, computed with infiltration rate and with outflow rate are compared. K obtained with the infiltration rate is all time greater than K obtained with the outflow rate. The two values of K decrease to reach K at the saturation of the soil.

In the figure 4B the coefficients K computed with the infiltration rate and the two methods of the determination of the saturation front are compared for the clay of Gault. It is noticed that when the cumulative infiltration is used to determine the saturated front, the computed coefficient of permeability is lower than one computed with the saturated front estimated with the moisture profiles. Indeed, the estimated saturated front with the cumulative infiltration is too low than one gives by the profile at the same elapsed time. It is noticed also that the K obtained with the model of Green-Ampt increases with the elapsed time when the K obtained with the moisture profiles decreases. The two K-values must reach the saturated coefficient of permeability when the clay of Gault column becomes saturated.

Assessment of the soil retention layer during saturation process

From TDR signals and using the relation (3), the soil impedances (R_L) are computed during the leachate infiltration. The initial and the minimum impedance values for the clayey sand the clay of Gault are embedded in table 2. These values are used in the relation (5) to compute the relative mass of solute retained during the leachate infiltration.

Table 2 Initial and minimal values of the soil impedance

Soil material	$R_{L,ti}$ (Ω)	$R_{L,to}$ (Ω)
Clayey sand	150.38	17.91
Clay of Gault	62,67	19,5

The retained relative mass is computed at the depth of 125, 245 and 475mm in the clayey sand column and at 25, 75 and 175mm in the clay of Gault column.

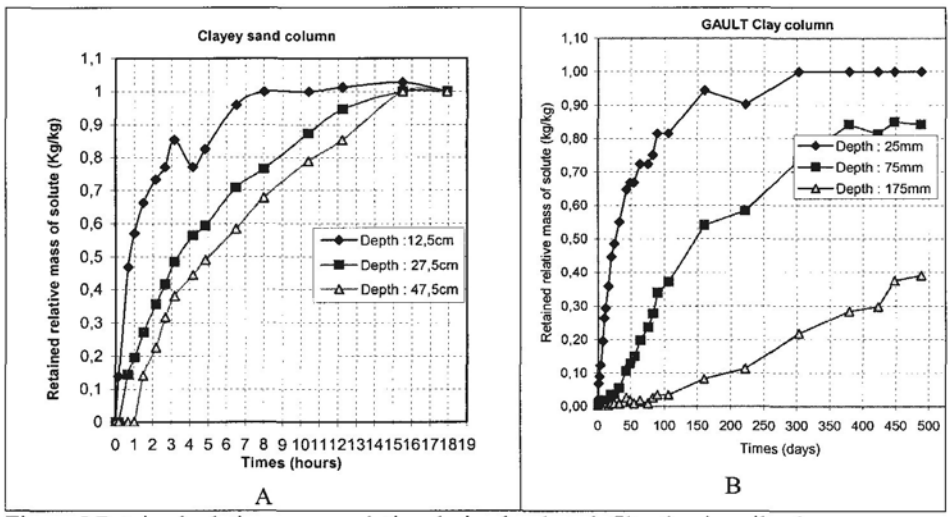

Figure 5 Retained relative mass evolution during leachate infiltration in soil column

The figure 5 presents the change of retained solute mass in the soil column during the leachate infiltration. It is shown that the clayey sand column reaches its retention capacity after 15,5hours (fig.5A). During this elapsed time the soil column becomes saturated. This proves that the solute and the moisture migrate with the same rate. So, the solute has a convective movement in the clayey sand column.

In the figure 5B, the capacity of solute retention of the clay of Gault is reached on 25mm after 300days leachate infiltration. After 500days, the clay of Gault column continues solute retention. These results prove we have to compare 25mm layer of the clay of Gault with 475mm layer of the clayey sand which are saturated, according to their retention capacity. This difference between the thicknesses is very far from one recommends when earth material of permeability of 10^{-6}m/s is used instead of earth material of permeability of 10^{-9}m/s.

According to moisture profiles presented on the figure 2, the saturation front in the clay of Gault is beyond 175mm after 500days of the leachate infiltration. But this thickness of the clay of Gault can still retain solute. That is a delay in solute migration due to sorption phenomenon which do not takes into account when only the coefficient of permeability is retained for barrier design. In the clay of Gault there is the combination of the influence of the unsaturated zone and the sorption phenomenon which increase the solute migration delay.

CONCLUSION

It is recognized that the sealing layer which must limit the flux of pollutants must be qualified by its coefficient of permeability. But the thickness and the saturation state of the liner are never evaluated. With our infiltration tests and TDR measurements it is shown that the layer thickness takes part in pollutant transfer reduction. The two earth materials used show that the difference of the solute migration concerns also the capability of the soil to retain the solute.

The electrical conductivity profiles prove that during the soil saturation the migration mode change. The soil saturation process delays the solute movement even the coefficient of permeability is higher than 10^{-9}m/s. The time need to reach the retention depend on the type of soil and especially the compaction dry bulk density. This time value can be used to evaluate the soil layer efficiency.

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Solute Transport in An Aquifer During Passing of A Single Flood Wave in A Fully Penetrated Stream

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INTRODUCTION

Analytical solution of the advection - dispersion differential equation for the uniforming round water flow has been derived by Ogata and banks (1961). Several other investigators (Bear.1972: Marion 1974:Van Genuchten . 1982: Anand Prakash. 1982) have also analyzed solute transport problems considering advection and dispersion with the assumption of uniform ground water flow. In reality. due to varied boundary condition at flow domain boundaries. the ground water remains in an unsteady state. Besides the flow does not remain unidirectional. Numerical methods have been developed (e.g. Charles. Fraust and James. 1980: Ole and Bruce. 1980: Lapidus et. al. 1982) in which the spatial and temporal variation in the flow velocity are taken into account. When advection dominates dispersion. numerical methods pose problems of instability (Stefan 1981:Javedal. Doughly and Tasng 1984). Solute transport problem has also been solved by carrying out mass balance in thoroughly mixed reservoirs connected in series (Vander Molen. 1979). Bear (1972) has developed a model consisting of an array of small cells with interconnecting channels for the study of one - dimensional dispersion. Cells were assumed to be completely mixed. He found that the longitudinal dispersivity of the medium to be equal to $0.5\ (\Delta l')^2$ Δl. Δl. and $\Delta l'$ being the length between centers of cells and length of a mixing cell. If $\Delta l \sim \Delta l'$ the dispersivity = 0.5 Δl. Glueckauf (1949) has analytically solved the advection dispersion equation which also shows that the dispersivity is half of the mixing length. In the present study considering the flow domain to be thoroughly mixed reservoir connected in series. transport of conservative solute has been analyzed when a flood wave passes in a long reach of a fully penetrated stream. The variation in the flow velocity has been taken into account.

STATEMENT OF THE PROBLEM

A semi infinite homogeneous and isotropic unconfined aquifer is bound by a fully penetrating straight stream. Initially the levels of water surface in the stream and in the aquifer are same. A flood wave passes in the stream. and the stream stage '$\sigma(t)$' varies with time t. Let the flood wave be sinusoidal and let it follow Cooper and Raurbaugh's equation (1963)

$$\sigma(t) = \sigma_{max}\left[\frac{1-\cos\omega t_e}{1-\cos\omega t_e}\right] e^{-\beta(t-t_c)} \qquad \text{for } 0 \le t \le \tau$$

$$= 0 \qquad \text{for } t > \tau \qquad \ldots\ldots\ldots(1)$$

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

in which τ = duration of the flood wave, $\omega = 2\pi/\tau$, σ_{max} = maximum rise at the peak, $\beta = \omega \cot(0.5\ \omega\ t_c)$, t_c = time of occurrence of flood crest. The parameter β determines the asymmetry of the flood wave. Consequent to the passage of the flood wave the water table in the aquifer becomes unsteady and the velocity of flow varies with time and distance from the stream. Prior to the change in stream stage the solute concentration in the ground water as well as in the stream in C_I. With change in stream stage, the solute concentration of the stream water changes from C_I to C_R. The problem is to find the change in concentration in groundwater at various distances from the stream.

ANALYSIS

Analysis for Groundwater Flow

The rate of flow Q (x, t), at a distance x from a fully penetrating stream due to a step rise, σ_o, in stream stage, is given by (Carslaw and Jager, 1959)

$$Q(x,t) = \sigma_o \sqrt{\frac{T\phi}{\pi\phi}} \exp\left[-\frac{\phi x^2}{4Tt}\right] \qquad \text{.....(2)}$$

Let the aquifer be conceptualized to be made up of a number of reservoirs connected in series as shown in Fig. 1(a). The rates of inflow and outflow for a reservoir, which is bounded by x = L_1, and x = L_2, are :

$$Q(L_1,t) = \sigma_o \left[\frac{T\phi}{\pi t}\right]^{1/2} \exp\left[-\frac{L_1^2\phi}{4Tt}\right] \qquad \text{.....(3)}$$

$$Q(L_2,t) = \sigma_o \left[\frac{T\phi}{\pi t}\right]^{1/2} \exp\left[-\frac{L_2^2\phi}{4Tt}\right] \qquad \text{.....(4)}$$

The volume of water at time t in the reservoir is given by

$$V(L_1,L_2,t) = \phi(L_2 - L_1)\,E + \int_0^t Q(L_1,\tau)d\tau - \int_0^t W(L_2,\tau)d\tau \qquad \text{.....(5)}$$

in which E is initial saturated thickness of aquifer. Combining 3, 4 & 5 and integrating the expression for the reservoir volume, V (L_1,L_2,t), is found to be

$$V(L_1,L_2,t) = 2\sigma_o(\pi Tt/\pi)^{1/2}\left[\exp\{-L_1^2\phi/(4Tt)\} - \exp\{-L_2^2\phi/(4Tt)\}\right] - \sigma_o\phi L_1\,\mathrm{efrc}\left[\{L_1^2\phi/(4Tt)\}^{1/2}\right] + \sigma_o\phi L_2\,\mathrm{efrc}\left[\{L_2^2\phi/(4Tt)\}^{1/2}\right] + \phi(L_2 - L_1)E \qquad \text{.....(6)}$$

$\phi(L_2 - L_1)E$ is the initial volume of the reservoir and the remaining is the increament in reservoir volume due to the step rise in stream stage.

Morel Seytoux and daly (1975) have proposed a method for computation of exchange of flow between a stream and an aquifer for varying stream stage. Following this method

$$Q(L_1,n) = \sigma_o K_q(L_1,n) + \sum_{\gamma=1}^{n} \{\sigma(\gamma) - \sigma(\gamma-1)\}\,\delta_q(L_1, n-\gamma+1) \qquad \text{.....(7)}$$

in which $K_q(L_1,n)$ = flow response to a unit step perturbation = $Q(L_1,n)$ for $\sigma_o = 1$. The discrete Kernel coefficient $\delta_o = 1$. The discrete Kernel coefficient $\delta_q(L_1,n)$ is defined as (Morel Seytoux and Daly, 1975) :

$$\delta_q(L_1,n) = \int_0^1 \left\{\frac{T\phi}{\pi(n-\tau)}\right\}^{1/2} \exp\left\{\frac{L_1^2\phi}{4T(n-\tau)}\right\} d\tau$$

Performing the integration

$$\delta_q (L_1, n) = 2\left[\frac{T\phi}{\pi}\right]^{1/2}\left\{n^{1/2}\exp\left[-\frac{L_1^2\phi}{4Tn}\right] - (n-1)^{1/2}\exp\left[-\frac{L_1^2\phi}{4T(n-1)}\right]\right\} + \phi L_1 \operatorname{erf}\left\{\left[\frac{L_1^2\phi}{4T(n-1)}\right]^{1/2}\right\} - \phi L_1 \operatorname{erf}\left\{\left[\frac{L_1^2\phi}{4T(n-1)}\right]^{1/2}\right\} \quad \ldots\ldots(8)$$

Let $K_v(L_1, L_2, t)$ be the unit step response function for volumetric change. From Eq. (6),

$$K_v (L_1, L_2, t) = 2\left[\frac{\phi T t}{\pi}\right]^{1/2}\left\{\exp\left[-\frac{L_1^2\phi}{4Tt}\right] - \exp\left[-\frac{L_2^2\phi}{4Tt}\right]\right\} - \phi L_1 \operatorname{erfc}\left\{\left[\frac{L_1^2\phi}{4Tt}\right]^{1/2}\right\} + \phi L_2 \operatorname{erfc}\left\{\left[\frac{L_2^2\phi}{4Tt}\right]^{1/2}\right\} \quad \ldots\ldots(9)$$

The volume of the reservoir, corresponding to the varying stream stage is given by

$$V(L_1, L_2, t) = \phi (L_2 - L_1) E + \sigma_0 K_v (L_1, L_2, t) + \int_0^t \frac{d\sigma}{d\tau} K_v (L_1, L_2, t-\tau)\, d\tau \quad \ldots\ldots(10)$$

Defining a discrete kernel coefficient $\delta_v (L_1, L_2, t) = \int_0^t K_v (L_1, L_2, n-\tau) d\tau$, the volumne of the reservoir at the end of nth unit time step is expressed as

$$V(L_1, L_2, n) = \phi (L_2 - L_1) E + \sigma_0 K_v (L_1, L_2, n) + \sum_{\gamma=1}^{n} \{\sigma(\gamma) - \sigma(\gamma-1)\}\, \delta_v (L_1, L_2, n-\gamma-1) \quad \ldots\ldots(11)$$

Mass Balance of Solute in the Reservoir

Mass balance of the conservative solute in the reservoir over a period Δt during the rising stage leads to

$$q(L_1,t)\, C(L_1,t)\, \Delta t = q(L_2,t)\, C(L_2,t)\, \Delta t + [v(L_1, L_2, t+\Delta t) - v(L_1, L_2, t)]\, C(t+\Delta t) + v(L_1, L_2, t)\, [C(t+\Delta t) - C(t)] \quad \ldots\ldots(12)$$

in which $q(L_1,t)\, C(L_1,t)$ and $q(L_2,t)\, C(L_2,t)$ are average rates of mass inflow and outflow respectively of the solute during the time interval t to $t + \Delta t$. $C(L_1,t)$ = concentration of the solute in the in flowing water. $C(L_2,t)$ = concentration of the solute in the out flowing water, and $C(t)$ = concentration of the solute in the reservoir at time t.

The average mass inflow and outflow rates during time period t to $t + \Delta t$ are expressed as :

$$Q(L_1,t)\, C(L_1,t) = W_1 q(L_1, t-\Delta t)\, C(L_1, t-\Delta t) + W_2 q(L_1,t)\, C(L_1,t) + W_3 q(L_1, t-\Delta t)\, C(L_1, t+\Delta t) \quad \ldots\ldots(13)$$

$$q(L_2,t)\, C(L_2,t) = W_2 q(L_2, t-\Delta t)\, C(L_2, t-\Delta t) + W_2 q(L_2,t)\, C(L_2,t) + W_3 q(L_2, t-\Delta t)\, C(L_2, t+\Delta t) \quad \ldots\ldots(14)$$

Assuming the temporal variation of mass inflow and outflow to follow a second order polynomial, the weightage factors, W_1, W_2 and W_3 are found using the procedure adopted in the derivation of Simpon's rule of numerical integration (Piskunov, 1969). The factors are : $W_1 = -1/12$, $W_2 = 2/3$, and $W_3 = 5/12$.

Incorporating equations (13) and (14) in equation (12) the following expression is obtained :

$$[W_1 q (L_1, t-\Delta t) C (L_1, t-\Delta t) + W_2 q (L_1,t) C (L_1,t) + W_3 q (L_1, t-\Delta t) C(L_1, t-\Delta t)] \Delta t$$
$$= [W_1 q (L_2, t-\Delta t) C (L_2, t-\Delta t) + W_2 q (L_2,t) C (L_2,t) + W_3 q (L_2, t-\Delta t) C(L_2, t-\Delta t)] \Delta t + [v (L_1, L_2, t-\Delta t) - v(t)] [C (t-\Delta t) - v (L_1, L_2, t) [C (t+\Delta t) - C (t)] \quad \ldots\ldots\ldots (15)$$

For a completely mixed reservoir $C(L_2,t) = C(t)$. Replacing $C(L_2,t)$ by $C(t)$ in equation (15) and rearranging

$$C (t-\Delta t) = C(t) + [W_1 q (L_1, t-\Delta t) C(L_1, t-\Delta t) + W_2 q (L_1,t) C(L_1,t) + W_3 q (L_1, t-\Delta t) C(L_1, t-\Delta t) + W_1 q (L_2, t-\Delta t) C(t-\Delta t) + W_2 q (L_2,t) C(t) + W_3 q (L_2, t-\Delta t) C(t-\Delta t)] \Delta t/V (L_1, L_2,t) + C (t-\Delta t) [v (L_1,L_2,t-\Delta t) - v (L_1,t)]/v (L_1,L_2,t) \quad \ldots\ldots\ldots (16)$$

Let the time domain be discretised by uniform time steps of size Δt. and the flow domain be comprised of series of reservoirs of uniform length Δx as shown in Fig. 2. Defining $t = j\Delta t$. $L_1 = i\Delta x$. $L_2 = (i-1)\ \Delta x$. the reservoir bound by L_1 and L_2 as $(I-1)^{th}$ reservoir. and $v\ (i\Delta x, (i-1)\ \Delta x, t)$ as $v(i-1, j)$. equation (16) alternatively can be written as.

$$C(i-1, j-1) = C (i-1,j) + [W_1 q (i, j-1) C(i, j-1) + W_2 q (i, j) C(i, j) + W_3 q (i, j-1) C(i, j-1) + W_1 q (i-1, j-1) C (i-1, j-1) + W_2 q (i-1, j) C(i-1, j) + W_3 q (i-1, j-1) C (i-1, j-1)]/v (i-1,j) + C (i-1, j-1) [v (i-1, j-1) - v (i-1, j)] / v (i-1, j) \quad \ldots\ldots\ldots (17)$$

Solving for $C (i-1, j-1)$

$$C (i-1, j-1) = [C (i-1, j) + \Delta t/v (i-1, j) \{W_1 q (i, j-1) C(i, j-1) + W_2 q (i, j) C(i, j) + W_3 q (i, j-1) C(i, j-1) + W_1 q (i-1, j-1) C (i-1, j-1) + W_2 q (i-1, j) C(i-1, j)\}] / [\{\Delta t W_3 q (i-1, j-1) C (i-1, j-1)]/v (i-1,j)\}] \quad \ldots\ldots\ldots (18)$$

The concentration can be computed in succession starting from j=0. i=0. j=0 corresponds to the initial time and i=0 corresponds to the reservoir adjacent to the stream.

For a fully penetrating stream the inflow rate to the first reservoir at t = 0 consequent to a step rise in stream stage is infinite. However. as the volume $\int_0^t q\ (o, \tau) d\tau$ is finite. an average inflow rate equal to $[\int_0^{\Delta t} q\ (0, \tau)\ d\tau]\ \Delta t$. can be used in place of q (0.0). The average inflow rate is $2/\sigma\ (T\phi\ \pi)^{1/2}\ \Delta t^{-1/2}$. For the flood wave defined by Cooper and Rourabough q (0.0) = 0.

The temporal and spatial variation of concentration for uniform groundwater flow can be derived starting from equation (16) and it is given by :

$$C(i-1, j-1) = [W_1 C (i, j-1) + W_2 C (i, j) + W_3 C (i, j-1) + W_1 C (i-1, j-1)] - \{\Delta x\phi / (u\Delta t) - W_2\} C (i-1, j) / \{W_3 + \Delta x\phi\ (u\Delta t)\} \quad \ldots\ldots (19)$$

in which u is the constant Darcy velocity.

Equations (18) and (19) are applicable for $j \geq 1$. Concentration at the end of the first time step (j=0) can be obtained substituting $W_1 = 0$. and $W_2 = W_3 = 0.5$. The expression is

$$C(i-1.1) = [C(i-1.0) + \frac{\Delta t}{v(i+1.0)} \{0.5\, q(i.0)\, C(i.0) + 0.5\, q(i.1)\, C(i.1) - 0.5\, q(i-1.0)\, C(i.0) + 0.5\, q(i.1)\, C(i.1) - 0.5\, q(i-1.0)\, C(i-1.0)\}] \left[\frac{0.5\,\Delta t\, 1(i+1.1)}{v(i+1.0)} + \frac{v(i+1.1)}{v(i+1.0)}\right] \quad \text{.....(20)}$$

During recession period the solute concentration is computed as described below.

The flow directions soon after the drop in stream stage will be as shown in Fig. 1(b). The reversal of flow will occur in the first reservoir immediately after the drop in stream stage. Depending upon Δx and Δt the point of reversal will lie within the first reservoir during time t_c to $t_c - \Delta t$, otherwise it will propagate to the adjacent reservoir. Let the time step from t_c to $t_c + \Delta t$ be designated as J. The concentration of the solute has been computed upto $t = t_c$ i.e. for time step j = J-1.

During Jth time step q(0.J) is negative and q(I.J) is positive. Thus the first reservoir during time step J looses water from its storage on either side. Hence, C(1.J) = C(1, J-1). The concentration C(i.J), i = 2....N, can be computed using equation (18).

The point of water divide propogates with time. Flow directions at different sections some time after the drop in stream stage are shown in Fig. 1(c). Let I be the reservoir in which flow reversal takes place during time step j'. Mass balance in the zone of reversal of flow is as follows :

Inflow to the ith reservoir (for $i \leq 1$) during jth time step

$$= -\{W_1\, q(i.j'-2)\, C(i.j'-2) + W_2\, q(i.j'-1)\, C(i.j'-1) + W_3\, q(i\,j')\, C(i-1.j')\}\Delta t \quad \text{..... (21a)}$$

If q (i. j'-1) is –ve. then C (i. j'-1) in above equation is to be replaced by C (i–1. j'-1). Also if q (i. j'-2) is –ve. then C (i. j'-2) is to be replaced by C (i–1. j'-2).

Outflow from the ith reservoir

$$= -\{W_1\, q(i-1.j'-2)\, C(i-1.j'-2) + W_2\, q(i-1.j'-1)\, C(i-1.j'-1) + W_3\, q(i-1.j')\, C(i.j')\}\ \Delta t \quad \text{..... (21b)}$$

If q (i-1. j'-2) and q (i-1. j'-1) are negative then C (i-1. j'-2) is to be replaced by C (i. j'-2) and C (i-1. j'-1) is to be replaced by C (i. j'-1).

$$\text{Change in storage} = \{C(i.j') - C(i.j'-1)\}\, v(i.j'-1) + \{v(i.j') - v(i.j'-1)\}\, C(i.j') \quad \text{..... (21c)}$$

Performing the mass balance and simplifying

$$C(i.j') = [W_1\, q(i.j'-2)\, C(i.j'-2) + \{W_2\, q(i.j'-1) - v(i.j'-1)\ \Delta t\}\, C(i.j'-1) + W_3\, q(i.j')\, C(i-1.j') - W_1\, q(i-1.j'-2)\, C(i-1.j'-2) - W_2\, q(i-1.j'-1)\, C(i-1.j'-1)]\ \{W_3\, q(i-1.j') - v(i.j')\ \Delta t\} \quad \text{.....(21)}$$

Starting from i = 1 to i = I, the concentration in all the reservoirs between the stream and the Ith reservoir can be computed using Eq. (21).

RESULTS AND DISCUSSIONS

Results have been presented for following set of aquifer parameters and hypothetical flood wave characteristics :

$T = 100\ m^2/day$; $\phi = 0.1$; $E = 50$ m; $\tau = 80$ days; $\sigma_{max} = 3$ m; $t_c = 3$ days;
Duration of recession = 17 days; $\Delta t = 0.1$ day; $\Delta x = 1$ m

The time step size Δt has been so chosen that for the assumed flood wave at any section the Current number $(q(x) / (E\phi)\ \Delta t / \Delta x < 1$.

The variations of $(C-C_I) / (C_R-C_I)$, with x are shown in Fig. 2 for an assumed flood wave of 80 days duration. The dimensionless concentration for $C_R = 0$, and $C_I = 1$ pertains to a situation where the aquifer is polluted and the stream, which is free from pollution, cleans the aquifer during the passage of a flood. The cleaning action as seen is slow. At the end of the flood, at x = 10 m, $(C-C_I) / (C_R-C_I) = 0.05$. At x = 5m the solute concentration of the groundwater is nearly zero. The flow has not affected the aquifer beyond 28m. With reversal of flow, the zone which was made free from the solute, again gets polluted. At the end of 90 days, at x = 5m, $(C-C_I) / (C_R-C_I) = 0.22$.

The variations $(C(x.t)_C_I) / (C_R-C_I)$ with time at different distance from stream x are shown in Fig. 3. For $C_R = 0$, $C_I = 1$, the graph demonstrates the flushing action of the pollutant free river. At x = 10 m and t = 63 day $[C(x.t) - C_I] / [C_R-C_I] = 0.05$.

CONCLUSIONS

Based on the study presented, the following conclusions have been arrived at :

(i) Analytical expressions of discrete kernel coefficients for computation of flow rate and cumulative flow at any section in an aquifer have been derived and solute transport in the aquifer due to passage of a sinusoidal wave in a fully penetrating stream has been quantified.

(ii) The flushing action of a stream is limited only to small distance from its bank. If the solute concentration in stream water is zero, during the passage of a flood the solute in an aquifer in the vicinity of the stream is puched into the aquifer, but with reversal of flow, the zone which was made free from the solute again gets polluted. If the stream is polluted and groundwater is free from it, the polluted travels only to limited distance from the stream bank.

(iii) A pollution free aquifer with transmissivity 100 m^2 day, storage coefficient 0.1 and thickness 50 m, receives 18 C_R (mass unit) due to passage of a flood whose duration = 20 days and which attains a peak height of 3m in 3 days. Out of this 18 C_R, 10 C_R returns to the stream after the recession of the flood. If the stream water is free from pollution, i.e. if $C_R = 0$, for the above flood, 3.2 C_I is flushed out from the aquifer per unit length of stream during the reversal of flow.

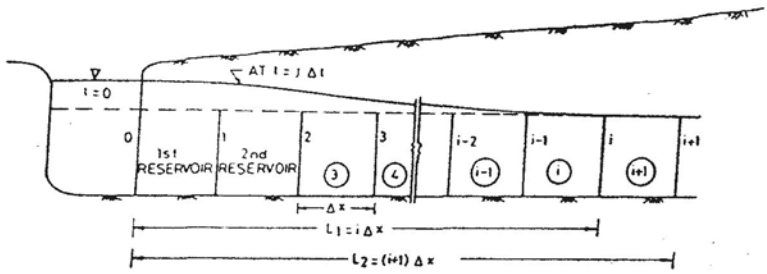

Fig. 1(a) Division of Flow Domain into Reservoir with Uniform Size.

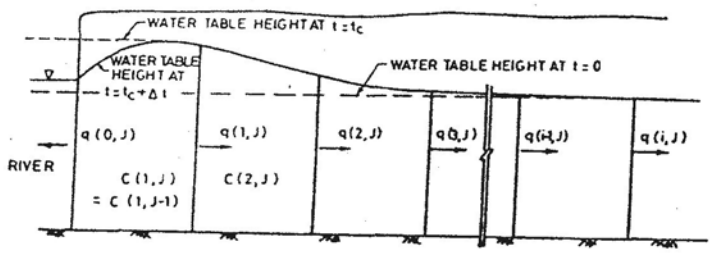

Fig. 1(b) Flow Directions Soon After the Drop in Stream Stage.

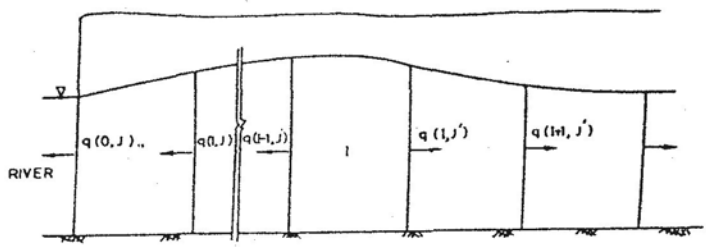

Fig. 1(c) Flow Directions Some Time After the Drop in Stream Stage.

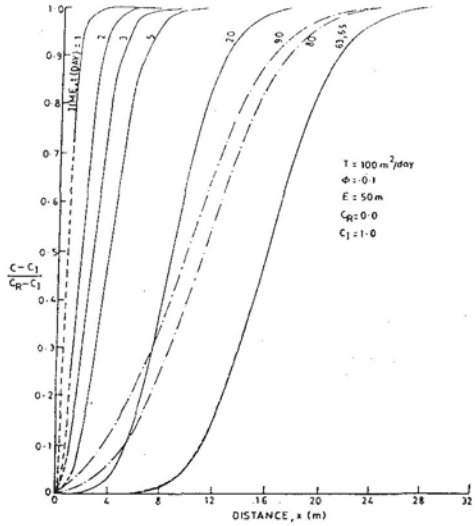

Fig. 2 Variation Of $(C-C_I) / (C_R/C_I)$ With Distance X, For Long Duration Wave

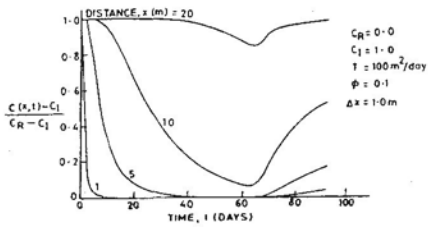

Fig. 3 Variation Of $(C-C_I) / (C/C_I)$ With Time at Some specific distance For Long Duration Flood Wave

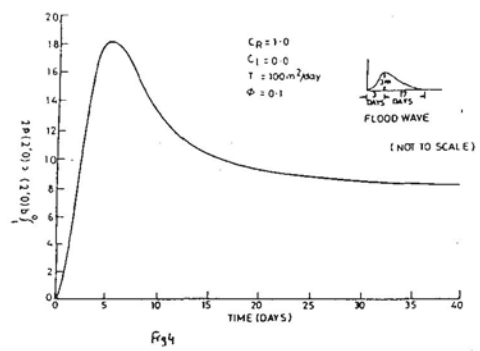

Fig. 4 Solute Exchange Between Stream and Aquifer When Stream is Polluted

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Use of Equilibrium and Initial Metal Concentrations in Determining Freundlich Isotherms for Soils and Sediments

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ABSTRACT
Batch equilibrium tests were conducted to examine Pb and Cd retention by kaolinite, humic acid and mackinawite and mixtures of these soil/sediment materials. All the batch test results were modeled using Freundlich isotherms where the retained metal was plotted both as a function of the equilibrium metal concentration, C_e and as a function of the initial metal concentration, C_i. When the initial metal concentration rather than the equilibrium metal concentration is used, smaller values of K_F and larger values of $1/n$ are obtained and there is no significant difference in goodness of fit for the two types of isotherms based on the coefficient of determination, r^2 and a normalized deviation, Δq. A dimensionless form of a new unified sorption variable K_u, representing the changing slope of the isotherm, is evaluated for all of the isotherms. Since the isotherms for metal uptake as a function of C_i had a steeper and closer to linear slope, the variation in the value of K_u for these isotherms was not as great as for the isotherms for metal uptake as a function of C_e.

1. INTRODUCTION
Industrial discharges to the environment have made removal of metals from wastewater, surface waters and groundwater an important concern. Metal removal from industrial effluents has been primarily by precipitation and secondarily by adsorption, ensuring that removal to water quality guidelines can be achieved (Brown et al, 2000). Since ion exchange resins and adsorbents such as activated carbon are too expensive for widespread use, more economical materials such as peat, clay minerals, laterite minerals, calcareous soils, oxic sediments, natural zeolites, suspended particles of river water, composts and agricultural wastes have been considered (Ho et al, 2002; Mohammad and Najar, 1997).

Metals discharged to the environment are also scavenged in-situ and can be naturally attenuated by sediments and soils (Mulligan and Yong, 2003). Contaminants in surface waters become sorbed to suspended particulate matter, settle, and may eventually become buried, while metal removal from groundwater occurs by the processes of precipitation and adsorption under favourable geochemical conditions (Fiorenza et al., 2000). Soils and sediments can be used to treat wastewaters and contaminated surface waters and groundwater.

Solute or contaminant uptake by an adsorbent is most often measured with batch equilibrium tests (Sparks, 2003). Varying solute concentrations are mixed with an adsorbent until equilibrium is achieved and the contaminant removed from solution is plotted as a function of that remaining in solution (Bohn et al., 1985) or as a function of the initial contaminant

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concentration, it is often modeled using the empirical two-parameter Freundlich isotherm that is widely used in geoenvironmental analysis (Chen et al., 1999).

The distribution coefficient or partitioning of a contaminant between the solid and liquid phases is constant when adsorption is given by the following linear adsorption isotherm

$$q_e = K_d C_e \quad [1]$$

and K_d is the distribution coefficient, C_e is the equilibrium contaminant concentration and q_e is the adsorbed contaminant. The distribution coefficient is important because it is used in transport prediction models (Yong, 2001). The Freundlich isotherm usually describes adsorption behaviour more accurately than a linear isotherm but the Freundlich isotherm is nonlinear and so partitioning of the contaminant between the solid and liquid phases is not constant and its evaluation is more complicated (Chen et al., 1999; Yong, 2001).

Evaluation of the parameters in the Freundlich isotherm is accomplished by obtaining a linear form of the isotherm and the best fitting line for the data is obtained by maximizing the coefficient of determination r^2. The r^2 value indicates the goodness of fit between the data and the isotherm but other error functions have also been in evaluating the performance of adsorption models (Ho et al, 2002; Haghseresht and Lu, 1998; Juang et al., 1996).

In this study Pb and Cd uptake by kaolinite, humic acid and mackinawite and mixtures of these three materials is represented by Freundlich isotherms, given as a function of the equilibrium metal concentration and as a function of the initial metal concentration and these two types of isotherms are analyzed and compared. The initial concentration is useful for comparing contaminant uptake by different materials or uptake of a variety of contaminants on the same graph and Chen at al. (1999) note that with the equilibrium concentration it is more difficult to compare different adsorbents or contaminants since the range of equilibrium concentrations may not correspond. The coefficient of determination and a normalized deviation used by Juang et al. (1996) and Haghseresht and Lu (1998) are employed to evaluate the accuracy of the model in representing the data. Finally the new unified sorption variable of Chen et al. (1999), similar to the distribution coefficient and uniting the two parameters of the Freundlich isotherm, is evaluated.

2. MATERIALS AND METHODS

2.1 Batch Equilibrium Tests

Batch equilibrium tests of 24 hours duration were conducted at room temperature (22°C) with Pb (as $PbCl_2$) and Cd (as $CdCl_2$) and the Pb and Cd solutions were adjusted with HCl to pH 3.6 and 3.9 respectively. Kaolinite, humic acid and mackinawite and mixtures of these three materials were used in the batch tests in the proportions shown in Table 1. The sediment/soil suspensions without mackinawite were pH adjusted while the suspensions with mackinawite were tested at their natural pH and in each case the initial pH value of the suspension is indicated in Table 1. The suspension pH was not controlled and pH decreased during the batch tests in proportion to the concentration of metal added.

For all the mixtures that contained mackinawite, the batch tests were conducted under anoxic conditions obtained by bubbling all solutions and suspensions with high purity nitrogen gas to reach a dissolved oxygen concentration of 0.3 mg/L. The concentration of the

metal solution was adjusted to account for evaporation during de-aeration. A centrifuge tube or nalgene bottle was half filled with the soil/sediment suspension that was de-aerated before the mackinawite was added. The pH of the suspension was measured, and the tube was filled to capacity with the de-aerated metal solution, sealed with parafilm, capped and placed on a roller for 24 hours. The suspension was centrifuged at 6000 rpm for 10 min to separate the solid and liquid phases, the supernatant was acidified to pH 1 with HCl, the metal in solution was measured using a Perkin Elmer 3110 atomic absorption spectrometer, and the pH of the final suspension was measured. The mackinawite was precipitated in the lab and the description of this is given in Coles et al. (2000).

Table 1. Solid and liquid proportions and mixtures used in batch equilibrium tests and approximate initial pH values of soil/sediment suspensions.

Soil/Sediment Mixture No.	Initial pHs	Kaolinite g	Humic Acid g	Mackinawite g	Solution mL
1	4.3	5			50
2	6.1	5			50
3	4.3	5	0.05		50
4	6.2	5	0.05		50
5	4.3		0.03		30
6	6.0		0.03		30
7	6.9	14		0.1	140
8	6.4	14	0.14	0.1	140
9	6.4		0.042	0.042	42
10	6.3			0.042	42

For the batch tests without mackinawite no de-aeration was necessary and there was no need to ensure zero air space in the sample containers. The range of metal concentrations for the oxic batch tests was from 0.241 to 12.0 mmol/L of Pb and from 0.445 to 22.0 mmol/L of Cd. For the anoxic batch tests the lowest metal concentrations of 0.241 mmol/L Pb and 0.445 mmol/L Cd were not tested and in some instances complete metal uptake was observed for the next lowest metal concentrations. Therefore, a greater number of data points were obtained for the oxic batch tests than for the anoxic batch tests.

Flat D kaolinite was obtained from the Dry Branch Kaolin Company in Dry Branch, Georgia. It was crystalline, 75% of its particles were larger than clay sized, its background metal concentrations were negligible, it had a cation exchange capacity of 1.97 meq/100 g, a zero point of charge at approximately pH 2.6, and it appeared to be relatively free of impurities (Coles and Yong, 2002)

The humic acid was extracted from a compost/topsoil in Montreal according to the method of Schnitzer and Preston (1986) except that the ash removal step was not undertaken. The humic acid contained 33.9% ash, had a pH 7 cation exchange capacity of 436 meq/100 g on an ash free basis, and a zero point of charge below pH 0.5. The oxygen-containing functional group content of the humic acid was typical and indicated the presence of both poorly and more fully decomposed fractions (Coles, 1998).

2.2 The Freundlich Isotherm

The Freundlich isotherm model is considered to be appropriate for describing both multilayer sorption and sorption on heterogeneous surfaces (Ho et al., 2002). The Freundlich equation is given by

$$q_e = K_F C_e^{1/n} \quad [2]$$

where q_e is the retained metal at equilibrium (mmol/kg), C_e is the non-retained metal at equilibrium (mmol/kg), K_F is the Freundlich constant ($(mmol/kg)^{1-1/n}$) and $1/n$ is a dimensionless parameter that varies between 0 and 1. The isotherm is linear if $1/n = 1$ and as $1/n$ approaches zero the isotherm becomes more nonlinear. The units for q_e and C_e should be consistent if parameters are to have any practical application (Yong, 2001). Since units for K_F depend on the value of $1/n$, K_F parameters are only comparable when their $1/n$ parameters are the same, and K_F is not analogous to the distribution coefficient K_d (Chen et al., 1999).

In order to reduce the value of K_F to the most simple form, the units for the ordinate (q_e) and the abscissa (C_e) have been selected to be the same and only the actual metal and soil contents are taken into account. Although differences in adsorption during batch tests can occur when different volumes of the liquid phase are used, these differences are small and the liquid component is neglected here.

Other systems have expressed q_e in mg/kg, C_e in mg/L and K_F in units of $mg^{1-1/n}\ kg^{-1}\ L^{1/n}$ or alternately q_e in mmol/kg, C_e in mmol/L and K_F in units of $mmol^{1-1/n}\ kg^{-1}L^{1/n}$. The use of different units, however, has made it difficult to compare values of K_F (Chen et al., 1999).

A linear form of the Freundlich isotherm can be obtained by taking the log of each side of the Freundlich equation to give

$$\log q_e = \log K_F + (1/n)\log C_e \quad [3]$$

and when $\log C_e$ is plotted on the x-axis against $\log q_e$ on the y-axis, $\log K_F$ becomes the intercept of the line and $1/n$ becomes the slope of the line. Investigators have tried to link the Freundlich parameters K_F and $1/n$ to mechanisms of adsorption (Sparks, 2003).

Batch test results are usually plotted with the equilibrium contaminant concentration (C_e) against the retained concentration although are also sometimes plotted with the initial concentration of contaminant (C_i) against the retained concentration (Yong, 2001; Ziper et al., 1988). Adsorption isotherms, on the other hand, have usually been expressed in terms of the equilibrium contaminant concentration. This research will investigate the application of both the equilibrium and the initial metal concentrations in the Freundlich isotherm model.

2.3 Performance Criteria

The coefficient of determination r^2 has been most frequently used as a measure of the goodness of fit between adsorption data and an adsorption isotherm. The better the fit the more closely r^2 approaches 1. A normalized deviation, Δq has also been used to test the fit between adsorption data and the Freundlich isotherm (Haghseresht and Lu, 1998; Juang et al., 1996) and it is defined as

$$\Delta q = \left(\frac{1}{N}\right)\sum_{i=1}^{N}\left|\left(q_{e,i}^{\ calc} - q_{e,i}^{\ \exp}\right)\right| / q_{e,i}^{\ \exp} \quad [4]$$

where N is the number of data points and $q_{e,i}^{\ calc}$ and $q_{e,i}^{\ exp}$ are the calculated and experimentally determined retained metal concentrations. The better the fit between the model and the data, the more closely Δq approaches 0.

2.4 Unified Sorption Variable, K_u

One of the problems in using the Freundlich isotherm model has been related to the difficulty in trying to compare values of K_F when either the $1/n$ values are not the same, or different units of measurement have been used. Therefore, Chen et al. (1999) proposed a unified sorption variable, K_u to represent the constantly changing slope of the Freundlich isotherm ($K_u = q_e/C_e$), and in a linear system $K_u = K_d$. This new variable has the same units as K_d and can be estimated in terms of either C_e or q_e employing the following two equations.

$$K_u = K_F / C_e^{(n-1)/n} \quad [5]$$

$$K_u = K_F^n / q_e^{n-1} \quad [6]$$

The more closely data fits the Freundlich isotherm, the better will be the agreement between equations [5] and [6] for determining K_u. Chen et al. (1999) assigned units of L/kg to K_u but here since units of mmol/kg have been assigned to both q_e and C_e, K_u is dimensionless and in this form might have more universal application. Values of K_u are calculated and evaluated for the data in this research since K_u is a new and relatively untested variable.

Table 2. Freundlich parameters, goodness of fit parameters, and the unified sorption variable for Freundlich isotherms of adsorption data plotted in terms of the initial metal concentration and the equilibrium metal concentration. Units for K_F are $(mmol/kg)^{1-1/n}$ and other parameters are dimensionless.

	With initial Pb concentration					With equilibrium Pb concentration				
No.*	K_F	$1/n$	r^2	Δq	K_u range	K_F	$1/n$	r^2	Δq	K_u range
1	1.62	0.510	0.96	0.071	1.14-0.15	3.76	0.324	0.95	0.075	10.9-0.14
2	2.17	0.457	0.92	0.085	1.63-0.17	6.95	0.183	0.96	0.027	34.3-0.12
3	1.74	0.580	0.96	0.068	1.32-0.25	5.57	0.333	0.98	0.046	28.8-0.29
4	5.79	0.335	0.90	0.025	1.28-0.26	14.2	0.142	1.00	0.005	44.6-0.32
5	28.18	0.408	0.96	0.015	1.25-0.10	112.2	0.255	0.97	0.012	14.1-0.09
6	104.7	0.302	0.74	0.017	0.66-0.12	374.2	0.161	0.58	0.020	3.3-0.10
7	10.35	0.288	0.76	0.023	1.12-0.31	32.35	0.039	0.09	0.024	1.64-0.24
8	2.84	0.678	0.95	0.019	0.98-0.51	27.25	0.240	0.90	0.026	38.9-1.19
9	6.56	0.728	0.91	0.020	1.19-0.66	523.5	0.248	0.84	0.027	242 -2.27
10	41.69	0.510	0.81	0.038	1.46-0.46	1737	0.099	0.59	0.016	66.2-0.54
	With initial Cd concentration					With equilibrium Cd concentration				
No.	K_F	$1/n$	r^2	Δq	K_u range	K_F	$1/n$	r^2	Δq	K_u range
1	1.18	0.427	0.96	0.046	0.72-0.05	1.59	0.370	0.96	0.050	0.93-0.05
2	2.56	0.403	0.97	0.030	1.14-0.09	4.02	0.276	0.91	0.079	1.67-0.07
3	2.06	0.426	0.98	0.027	0.93-0.09	3.71	0.310	0.98	0.026	4.12-0.09
4	2.26	0.486	0.92	0.068	1.26-0.15	4.99	0.336	0.90	0.081	7.82-0.16
5	9.27	0.493	0.87	0.030	0.43-0.07	15.49	0.442	0.86	0.031	0.70-0.08
6	0.482	0.897	0.96	0.015	0.22-0.18	0.759	0.868	0.95	0.018	0.29-0.21
7	2.70	0.462	0.80	0.034	0.32-0.14	4.57	0.371	0.74	0.038	0.49-0.15
8	1.85	0.642	0.97	0.014	0.50-0.27	4.10	0.523	0.96	0.017	0.99-0.36
9	60.26	0.429	0.86	0.017	1.19-0.35	501.2	0.204	0.91	0.012	22.9-0.60
10	151.4	0.365	0.82	0.016	1.34-0.29	1047	0.172	0.85	0.014	27.2-0.39

* Numbering for soil/sediment mixtures same as in Table 1.

3. RESULTS AND DISCUSSION

The Freundlich parameters presented in Table 2 represent the batch test results with the metal retention as a function of the initial metal concentration and as a function of the equilibrium metal concentration and some of these isotherms are plotted in Figures 1 and 2.
Table 2 and Figures 1 and 2 reveal that when the initial metal concentration is used, smaller values of K_F and larger values of $1/n$ are always obtained. With a large proportion of metal uptake at lower metal concentrations, the equilibrium metal concentration is smaller and the x value of the first data point is smaller, giving a larger y intercept and a flatter slope. For complete metal uptake, the equilibrium metal concentration is zero, log of zero is undefined and this data point cannot be used in the linear form of the Freundlich isotherm.

Higher values of K_F and $1/n$ indicate that greater metal uptake is occurring. Since $1/n$ and log K_F represent the isotherm's slope and the intercept, respectively, metal uptake between isotherms with either the same value of $1/n$ or the same value of K_F is easy to compare. If both of the Freundlich parameters differ, the two isotherms may intercept and plotting the isotherms may better reveal how the metal uptake differs.

The values of r^2 and Δq in Table 2 suggest it is better to use more than a single error measurement to confirm the goodness of fit between the data and the Freundlich model, as there are instances where one parameter indicates a poor fit and the other indicates a good fit.

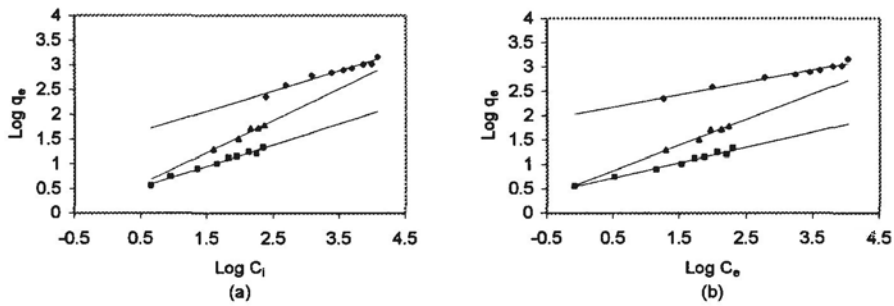

Figure 1. Freundlich isotherms showing the retention of Pb by the pH 4.3 humic acid No. 5 (◆) and retention of Cd by the pH 4.3 kaolinite and humic acid, No. 3 (■) and the mackinawite, humic acid and kaolinite, No. 8 (▲). Metal uptake is given as a function of the initial metal concentration (a) and the equilibrium metal concentration (b).

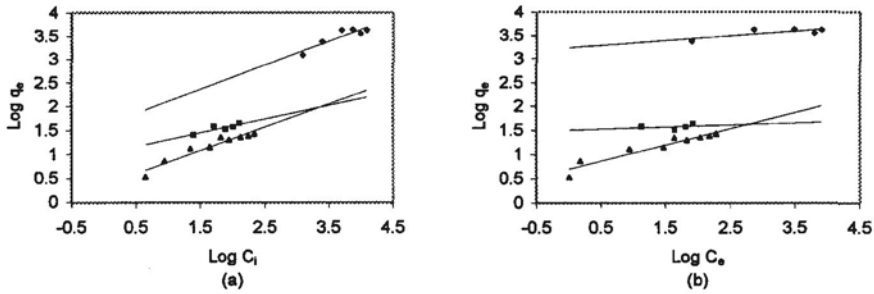

Figure 2. Freundlich isotherms showing the retention of Pb by the mackinawite, No. 10 (◆) and the mackinawite and kaolinite, No. 7 (■) and retention of Cd by the pH 6.2 kaolinite and humic acid, No. 4 (▲). Metal uptake is given as a function of the initial metal concentration (a) and the equilibrium metal concentration (b).

Figure 1 contains pairs of some of the curves where both r^2 and Δq indicate that the isotherms are a relatively good fit for the data and Figure 2 contains pairs of curves where one or both of the values of r^2 and Δq indicate that the curve is not as good a fit for the data as in Figure 1. These two parameters appear to be valid indicators because observation reveals that only 1 of the 46 data points in Figure 1 are not touching the lines whereas 10 of the 38 data points in Figure 2 are not touching the lines and both figures are to the same scale.

The top curve in Figure 2a ($r^2 = 0.81$, $\Delta q = 0.038$) has three points off the line while the top curve in Figure 2b ($r^2 = 0.59$, $\Delta q = 0.016$) has only one point off the line. The top line in Figure 2b appears to be a better fit because the Δq value is better, in spite of the r^2 value being worse. The middle curve in Figure 2a ($r^2 = 0.76$, $\Delta q = 0.023$) looks comparable to the middle curve in Figure 2b ($r^2 = 0.09$, $\Delta q = 0.024$). The seemingly low r^2 values for the two upper curves in Figure 2b may be due to these curves each having one less data point than their counterparts in Figure 2a and this is because at the lowest metal concentrations complete metal uptake occurred. The need for both r^2 and Δq values in determining goodness of fit can be seen from Figure 2.

Table 3. Selected distributions of K_u, calculated in terms of C_e or C_i and q_e.

Pb with Soil No. 4 $r^2 = 1.00$, $\Delta q = 0.005$			Pb with Soil No. 5 $r^2 = 0.97$, $\Delta q = 0.012$			Cd with Soil No. 3 $r^2 = 0.98$, $\Delta q = 0.027$		
C_e	K_u $f(C_e)$	K_u $f(q_e)$	C_e	K_u $f(C_e)$	K_u $f(q_e)$	C_i	K_u $f(C_e)$	K_u $f(q_e)$
0.28	42.2	47.0	18	13.0	15.1	4.41	0.87	0.97
5.36	3.36	2.83	97	3.72	3.04	8.81	0.59	0.55
14.6	1.41	1.25	593	0.96	0.81	22.0	0.35	0.34
25.3	0.89	0.87	1720	0.44	0.57	44.1	0.23	0.24
47.7	0.51	0.58	2840	0.30	0.40	66.0	0.19	0.17
69.7	0.37	0.39	3990	0.23	0.31	88.1	0.16	0.15
92.0	0.29	0.30	6220	0.17	0.18	133	0.12	0.12
			8600	0.13	0.16	176	0.11	0.13
			10600	0.11	0.06	220	0.09	0.09

When the Freundlich isotherms are obtained using the initial metal concentrations, the average r^2 and Δq values are 0.90 and 0.034 respectively and when the Freundlich isotherms are obtained using the equilibrium metal concentrations the average r^2 and Δq values are 0.84 and 0.031 respectively. The lower r^2 values obtained when using the equilibrium metal concentration may be influenced by the fact that some data points are lost when complete metal uptake occurs at the lower metal concentrations. Overall, differences in values of r^2 and Δq for the two types of isotherms may not be significant.

Table 2 also shows how the value of the unified sorption variable, K_u differs when the initial and equilibrium metal concentrations are used to determine the Freundlich isotherms. A narrower range of K_u values is obtained when metal uptake is given as a function of the initial metal concentration because the value of $1/n$ tends to be larger or closer to a linear isotherm, for which a constant value of K_u or K_d would be obtained.

The values of K_u in Table 2 were determined by estimating K_u from equations [5] and [6] and taking the average. Samples of some of the distributions of the unified sorption variable are contained in Table 3. The samples were selected according to how well equations [5] and [6] agreed and this can usually be predicted by a high r^2 value. The K_u values in the left hand columns are for the isotherm with single best fit in terms of both r^2 and Δq. When the r^2 is at least 0.96 or 0.97 or when an r^2 of at least 0.95 is combined with a low Δq, agreement between equations [5] and [6] was generally good. When the Freundlich isotherm is was not a good fit for the data, there was significant variation in the values of K_u and in these instances the values of K_u in Table 2 may not be as representative.

4. CONCLUSIONS

Whether the Freundlich isotherms are determined for metal uptake as a function of the initial metal concentration or as a function of the equilibrium metal concentration, there is no significant difference in the goodness of fit between the data and the isotherms. An advantage of using the initial metal concentration could be that the range of metal concentrations for all of the batch tests is comparable. The reason this is not obvious from the data in this research is because there are differences in the precise ratio of solid to liquid used. If this ratio had been consistent then similar values for C_i would show up in Figures 1a and 2a. This is an area where future research could be undertaken. Another advantage could be that when complete contaminant uptake occurs there is no need to exclude any of the data.

Since in this research the units of mmol/kg were the same for q_e and C_e and C_i, the unified sorption variable K_u became dimensionless and in this form it could possibly have even more widespread application.

For metal uptake as a function of the initial metal concentration compared to metal uptake as a function of the equilibrium metal concentration, $1/n$ is closer to 1 or closer to a linear isotherm, and K_u is closer to being a constant value as occurs when the isotherm is linear. What the implications are of this could be ascertained if it was possible to determine what a normal range of K_d values should be.

Values of K_u are most accurate when the data is a good fit for the isotherm. The results suggest that an r^2 of at least 0.96 or 0.97 or an r^2 of at least 0.95 with a low Δq, will ensure

reasonable agreement between the two equations used for calculating the unified sorption variable.

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Humic Acid Properties and Implications for Treatment of Wastewater Containing Metals

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ABSTRACT
Humic acid (HA) extracted from soil is investigated in terms of its cation exchange capacity (CEC), zero point of charge (zpc), oxygen containing functional group content, scanning electron microscope (SEM) images, and pH. The CEC of HA that was dried was approximately half the CEC of hydrated HA. Metal retention by HA was studied by conducting 24 h batch equilibrium tests with lead (Pb, as $PbCl_2$) and cadmium (Cd, as $CdCl_2$) and HA at pH 4 and pH 6, and with a mixture of HA, mackinawite and kaolinite. The reactivity of the HA towards Pb and Cd was reduced when it was combined with the mackinawite and kaolinite. The mackinawite raised the pH and dissolved some of the HA, until sufficient reactions between the metals and mixture lowered the pH enough for the dissolved HA to solidify and remove more metal from solution. HA bonding with the mackinawite and kaolinite reduced the HA sites available for metal uptake. The functional group content of the HA provided indications regarding the origin of the HA, the extent of humification and the presence of less decomposed fractions. The CEC of the HA could conservatively predict the amount of metal uptake. Low pH conditions are favorable for metal removal from solution by HA because the zpc of the HA was below pH 0.5 and because at higher pHs HA begins to dissolve. HA, especially in the hydrated phase, may represent an important material for metal removal from waters and wastewaters containing metals.

1. INTRODUCTION
Industrial effluents are contributing to increasing concentrations of metals being discharged to the environment. Since these metals are not biodegraded they need to be removed from waters and wastewaters and adsorption onto various media is generally the preferred treatment (Mohammad and Najar, 1997). Organic matter, such as found in sediments and surface soils, has natural and powerful adsorbent properties and because of this, humic acid (HA), which is the most abundant fraction of decomposed organic matter, has been the focus of much research. Sorption interactions of four forms of HA have been studied in depth and they include the dissolved phase, a solid phase coating on another material, a low pH powder (comparable in this study to the dried HA), and a sol-gel (Laor et al, 2002).

The oxygen containing functional groups in HA represent a quarter of the total molecular weight of HAs (Rashid, 1985). The carboxyl (COOH) group increases in abundance with humification (Rashid, 1985), reacts readily with metals (Spark et al, 1997; Barancikova, 1997), and gradually dissociates between pH 2.5 to pH 7 to form the carboxylate (COO^-) group (Buffle, 1988; Spark et al, 1997; Perdue, 1985). The phenolic hydroxyl (OH) group is more abundant in the early stages of decomposition (Yong and Mourato, 1988), is derived from lignin in woody plants (Rashid, 1985), reacts less with

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metals, and dissociates between pH 8 and pH 13.5 (Perdue, 1985). The COOH and phenolic OH groups account for the total acidity of HA (Schnitzer, 1982) while the alcoholic OH group is only weakly acidic and reacts minimally with metals (Yong, et al, 1992).

The carbonyl (C=O) group increases in abundance with humification (Saito and Hayano, 1980; Lavti and Paliwal, 1981), is the main functional group in sediments (Rashid, 1985) and transforms into the COOH group under oxidizing conditions (Pillon et al, 1986) or when exposed to clay (Rashid, 1985).

The pH dependent surfaces of HA cause flocculation at low pH and dispersion at high pH (Flaig, 1971). SEM images of HA reveal smooth, compact shapes at pH 3 and rough, elongated and dispersed shapes at pH 7 (Senesi et al, 1996) and HA also begins to dissolve at higher pHs (Spark et al, 1997). HA may remove metals from solution at low pH but at high pH metal bonding with dissolved HA results in the formation of soluble metal humate species (Hatton and Pickering, 1980). It is also believed that small materials can become trapped inside voids within the HA molecules (Shulten and Schnitzer, 1995).

HAs are highly negatively charged and organic matter contributes towards the lowering of the zero point of charge (zpc) of soils (Van Raij and Peech, 1972; Morais et al, 1976). Kretzschmar et al (1997) show kaolinite with a zpc at ≈ pH 4.8 and the same kaolinite containing only 0.25 wt. % HA with a zpc of ≈ pH 2.0. Approximately 80% of aquatic humus may be electrically neutral between pH 1.2 and pH 1.8 (Gjessing, 1976).

Metal uptake, pH and properties of the HA including CEC, zpc, functional group content and the HA phase are considered. Better understanding of the properties and behaviour of HA may lead to the development of metal removal applications in industry such as in wastewater treatment, in the use of reactive walls to intercept groundwater flow, and in the use of landfill liners.

2. MATERIALS AND METHODS

2.1 HA Extraction, Purification and Ash Content Determination

The HA was obtained from a compost/topsoil from a low-lying area in Montreal. The year old compost had consisted of fertilizer and pesticide free lawn clippings and leaves. The HA was extracted form the soil and purified by removing suspended clays as described by Schnitzer and Preston, (1986). Ash removal was not undertaken as harsh treatments and the use of strong acids can alter the surface chemistry of HA (Yong and Mourato, 1988). Instead the HA was washed for 1 hr with 0.003 mol/L HCl (at pH 2.5) to wash out the soluble potassium that remained from the clay removal step. The HA was centrifuged and air-dried, causing it to shrink and solidify, so it was then ground with a mortar and pestle. The ash content was measured by combusting the HA (Hirata, 1992).

2.2 HA Characterization

The pH 7 cation exchange capacity (CEC) of the HA was determined by the calcium acetate–calcium chloride displacement method (Sheldrick ed., 1984) both for samples that had been dried and for hydrated samples that were only centrifuged. The wet samples were dried and weighed afterwards since any difference in weight resulting from a change in the saturating cations would be negligible. All other characterization (and batch) tests were only conducted on the dried and powdered HA. The total acidity, the COOH groups, the total OH groups and the C=O groups were measured (Schnitzer, 1982). Determination of the zpc of the HA (Van Raij and Peach, 1972) was attempted. 0.035 g of HA was mixed with 20 ml of 1.0, 0.1, 0.01 and 0.001 N solutions of NaCl and the samples were mixed for 1 hour. Subsequently, 2 ml of 0.01 N NaOH or 1.0 N HCl were added every 2 mins and the change in pH was recorded. A Japan Electro-Optics Laboratory (JEOL), model 6T100 scanning electron microscope was used to photograph the HA, and the pH of a mixture of 1 part of HA and 100 parts of distilled water was measured.

2.3 Determination of Metal Retention

Batch equilibrium tests were conducted at room temperature (22°C) in duplicate, triplicate or quadruplicate. The solutions of Pb (as $PbCl_2$) and Cd (as $CdCl_2$) were adjusted with HCl to approximately pH 3.6 and pH 3.9 respectively to ensure that the metals were soluble. Batch tests with the dried HA were conducted under aerobic conditions, and batch tests with the HA, mackinawite and kaolinite were conducted under anoxic conditions.

For the batch tests with the HA and metals only, suspensions of HA and distilled water were adjusted to pH 4 and pH 6. 0.03 g HA was mixed with 30 mL of solution and metal concentrations of 50, 100, 250, 500, 750, 1000, 1500, 2000 and 2500 mg/L were tested. 24 h batch tests were conducted because this is a typical duration (Hatton and Pickering, 1980: Pilarski et al, 1995) and preliminary tests suggested that metal uptake would be approximately 90% complete within this time. The suspensions were centrifuged for 10 minutes at 6,000 rpm and the supernatant metal concentrations were measured with a Perkin Elmer 3110 atomic absorption (AA) spectrometer. Metal uptake was taken as the difference between the metal added and the metal in the supernatant.

For the other batch tests 0.14 g HA, 0.1 g mackinawite and 14 g kaolinite were mixed with 140 ml of solution and the suspensions were tested at their natural pH. The metal concentrations were approximately 500, 1000, 1500, 2000 and 2500 mg/L. The mackinawite was preparared as described by Coles and Yong (2000) and the Flat D kaolinite was obtained from the Dry Branch Kaolin Company. A nalgene bottle that was half filled with distilled water, kaolinite and HA, was bubbled with high purity nitrogen gas to give a dissolved oxygen concentration of 0.3 mg/L. The mackinawite was added, the suspension pH was measured, the de-aerated metal solution was added to give zero air space, and the bottle was sealed with Parafilm, capped and placed on a roller for 24 h. The pH was again measured and the suspension was centrifuged to determine the supernatant metal concentration.

3. RESULTS AND DISCUSSION

3.1 Characterization Tests

The ash content of the HA was 33.9% and the pH of the HA was 3.6. The dry, powdered HA had a CEC of 288 meq/100 g or 436 meq/100 g on an ash free basis, and the hydrated HA had a CEC of 533 meq/100 g or 806 meq/100 g on an ash free basis, while reported CEC values for soil HAs are between 300 and 787 meq/100 g (Lavti and Paliwal, 1981). The CEC of the hydrated HA is almost double that of the dried HA and is greater than typical values, so the hydrated HA appears to be significantly more reactive than the dried HA. Cox et al (2000) observed that Hg adsorption by a wet carbonaceous material was double the Hg adsorption by the same material that had been dried and ground, and they concluded pore shrinkage during drying was inhibiting the entry of Hg^{2+} ions. Mohammad and Najar (1997) reported that undried tea could adsorb more Pb and Cd than dried tea. Shrinkage of the HA during drying could have resulted in less space available for cation exchange reactions.

Air-drying of the HA caused the HA particles to be strongly bonded together. Since water layers closest to a soil surface are the most difficult to remove, and clays can require temperatures in excess of 500° C (Hillel, 1998), this bonding may be due to residual moisture held by the functional groups of the HA. Weak bonding within the hydrated HA could be due to interactions between the functional groups of HA and water molecules.

Overnight mixing of the dried HA with distilled water did not restore the HA to its pre-dried state and Cox et al (2000) did not observe any swelling when their dried carbonaceous material was placed in water. The effects of the drying process do not appear to be readily reversible when the HA is brought into contact with water under moderate conditions of pH and temperature. In addition to the dissolved, powdered, sol-gel and solid coating HA phases, the hydrated HA could become an important adsorbent phase.

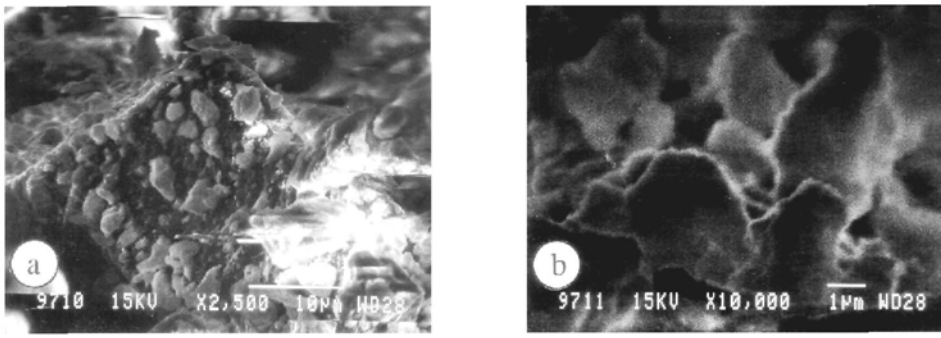

Figure 1. SEM images of HA a) at 2,500 × magnification and b) at 10,000 × magnification.

Table 1. Oxygen-containing functional groups in HA on an ash free basis.

Functional Group	HA, ash free Meq/100 g	Typical soil HA[1] meq/100 g	Range sediment HA[2] meq/100 g
Carboxyl, COOH	472	360	200 – 500
Phenolic OH	330	390	0 – 250
Alcoholic OH	648	260	0 – 300
Carbonyl, C=O	572	290	300 - 600

[1]from Schnitzer (1978)
[2]from Rashid (1985)

The SEM images of the HA (Figure 1) reveal a material of closely packed, non-uniform shapes, ≥ 1µm in size. The final washing of the HA at low pH could be responsible for the compact appearance of the HA and the relatively large, non-uniform shapes may be formed by the HA coating the ash.

The zpc for the HA was found to be below pH 0.5 because the experiment was stopped at this point. Gjessing (1976) reported values for the zpc of aquatic humus of between pH 1.2 and pH 1.8. Therefore, HA will be able to retain metals at very low pHs.

The functional group contents for the HA are reported in Table 1. The alcoholic OH group content is high while the amounts of the other groups are reasonable. Higher COOH and C=O group contents and a lower phenolic OH group content indicate a well humified HA (Lavti and Paliwal, 1981; Yong and Mourato, 1988) whereas a high alcoholic content indicates the presence of poorly decomposed HA (Lavti and Paliwal, 1981). The HA is mostly well-humified but also contains some less decomposed organic matter, which may represent more recently added lawn clippings and leaves.

The COOH group content (312 meq/100g) should be approximately the same as the pH 7 CEC of the HA (288 meq/100g) (Buffle, 1988). The use of different methods to determine these values can account for the small variation. According to the dissociation of the phenolic OH groups (Perdue, 1985) the pH 13 CEC of the HA is 530 meq/100 g, and the expected increase in CEC with pH is observed.

3.2 Batch Equilibrium Test Results and Metal Retention

For all batch tests, solutions Pb as $PbCl_2$ (adjusted to pH 3.6) and solutions of Cd as $CdCl_2$ (adjusted to pH 3.9) were used. For the batch tests with HA only, suspensions of HA and distilled water were initially adjusted to pH 4 and pH 6, and the results of these tests are

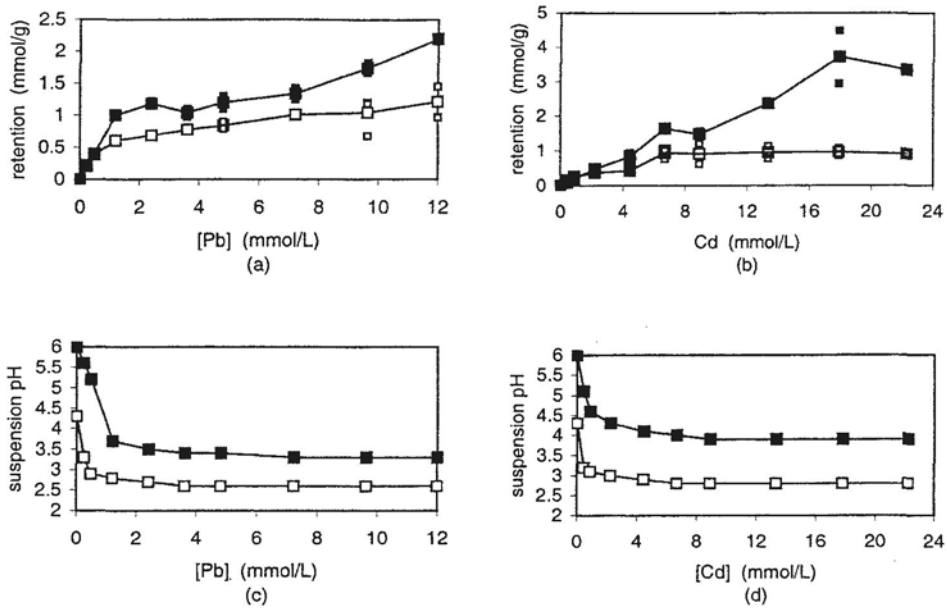

Figure 2. a) Pb retention by HA at pH 4 (□) and pH 6 (■), b) Cd retention by HA at pH 4 (□) and pH 6 (■), c) final pHs of suspensions with Pb and HA, and d) final pHs of suspensions with Cd and HA, with all values as a function of the initial metal concentration.

shown in Figure 2. For the batch tests with mixtures of HA, mackinawite and kaolinite, the mixture was tested at its natural pH, and the results of these tests are shown in Figure 3.

A visual comparison of the Pb and Cd retention can be observed from Figures 2a and 2b where metal is plotted as a function of the initial metal concentration. The greater uptake at the higher pH may be attributed to 1) the greater negative charge of the HA as seen in the increase in CEC with pH, 2) the greater dispersion of the HA at the higher pH, and 3) the reduced quantity of H^+ ions that would otherwise compete for adsorption sites. Properties of the metals which could be effecting metal uptake are 1) the size of their hydrated radii and 2) their speciation.

At the lower metal concentrations, uptake of Pb is greater than uptake of Cd. Metal speciation analysis using critical stability constants from Martel and Smith (1974) reveals that at low concentrations, divalent metal cations are dominant. For metal retention by ion exchange, the greater uptake of the Pb^{2+} ion compared to that of the Cd^{2+} ion (hydrated radius $\approx$ 0.45 nm versus $\approx$ 0.50 nm, respectively) (Dean, 1985) could be due to their relative sizes. At low pH the metals are doubly protonated so chemical bonding might be discouraged (Bowden et al, 1980), but the HA is capable of sequestering metals within its voids, so this is another potential retention mechanism (Schulten and Schnitzer, 1995).

For the HA that was initially adjusted to pH 4, and for metal concentrations above 7 mmol/L, Cd uptake is constant while Pb uptake is increasing. The reasons for this seem to be that 1) Cd, more than Pb is governed by electrostatic forces (Gerritse and Van Driel, 1984), and 2) the HA is more flocculated and compact at the lower pH meaning that steric effects may be preventing further bonding.

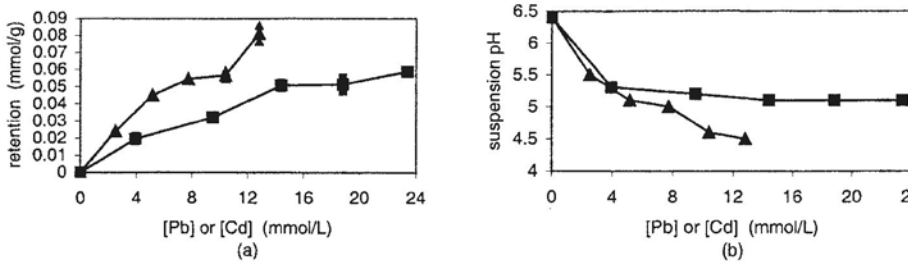

Figure 3. a) Retention of Pb(▲) and Cd (■) by HA, mackinawite and kaolinite and b) final suspension pHs, as a function of the initial metal concentrations.

Retention of Pb and Cd becomes more equal at increasing metal concentrations, and more so for the higher pH HA where steric effects might be less important. As the metal salt concentrations increase, the formation of $CdCl^+$ species exceeds the formation of $PbCl^+$ species. With more of the monovalent species being able to balance the negative charge on the HA, a greater uptake of Cd is possible, and the small hydrated radius of $CdCl^+$ (≈ 0.40 nm) (Dean, 1985) could also be facilitating its bonding with the HA.

For the HA that was initially adjusted to pH 6, data points for metal concentrations of 0.241 mmol/L Pb, 0.482 mmol/L Pb, 0.445 mmol/L Cd and 0.890 mmol/L Cd are missing because these samples could not be centrifuged. The repulsive forces on the HA surfaces at the higher pH were not sufficiently balanced by the low concentrations of acidic cations added so the suspensions remained dispersed.

The final suspension pH values for the batch tests with HA are plotted as a function of the initial Pb and Cd concentrations in Figures 2c and 2d respectively. These figures show a reduction in pH according to the extent of metal uptake and displacement of H^+ ions from the HA surfaces.

Metal uptake by the HA, mackinawite and kaolinite and the final pHs as a function of the initial metal concentration are shown in Figures 3a and 3b respectively. The mackinawite is increasing the pH of the mixture (Coles, 1998), but the inconsistent trend in pH for the Pb contaminated suspension may be due to the presence of the HA. There is a further drop in pH at the highest Pb concentrations and it coincides with a dramatic increase in Pb retention at the maximum metal concentration. It appears that when the pH of the HA, mackinawite and kaolinite was raised by the mackinawite, some of the HA was dissolved. Then as more Pb was retained by the mackinawite and kaolinite, the pH dropped and some of the dissolved HA re-solidified and provided more sites for subsequent Pb uptake from solution. This may not have been observed for Cd because both the metal uptake and the drop in pH were less.

There is an advantage to raising the pH of HA so that metal retention can be increased. Too great a rise in pH, however, causes dissolution of the HA and although the metals may react with the HA by forming soluble metal humate species, the metals will not be precipitated out of solution. So this is one aspect that needs to be considered in treating metal contaminated wastewater.

The approximate maximum metal uptake by the HA and by the HA, mackinawite and kaolinite is 4 mmol/g and 0.08 mmol/g, respectively. These values suggest that interactions between the three sediment components in the mixture are occurring and producing a structure with fewer sites available for metal uptake, and so the total metal uptake by the three components together would be less than the sum of the metal uptake by the three components separately. Barancikova et al (1997) found that HA that is part of the soil had less affinity for

metal ions than HA isolated from the same soil. When the HA is isolated it can be more effective at scavenging metals and it appears that the hydrated HA could be an even better adsorbent than the dry powdered HA.

The pH 4 CEC of the HA would be approximately 190 meq/100 g, meaning the HA could retain 1.90 mmol/g of monovalent cations or 0.95 mmol/g of divalent cations. The maximum Pb and Cd uptakes when the final pH is ≈ 4 are 2.19 mmol/g and 3.71 mmol/g respectively. This is greater than predicted by the CEC but within the same order of magnitude. In this case the CEC is providing a conservative estimate of metal uptake.

4. CONCLUSIONS

Organic matter within the soil matrix is responsible for significant bonding of heavy metals, but metal retention by HA may increase when HA is isolated, and even greater metal uptake by HA may be possible when the HA is not dried but kept in its hydrated state. This was illustrated by the CEC of the hydrated HA on an ash free basis as it was slightly higher than typical values. Since hydrated HA is not widely recognized as a an important phase for reaction with contaminants, it should be considered farther how this phase can be used in applications such as removal of metals from wastewater.

Another important feature of this research is that it indicated that HA could be effective at removing metals at as low as pH 0.5. Metal removal from solution by HA increases as the pH increases as long as the pH increase in not enough to dissolve the HA.

The quantities of functional groups present in the HA provide information about the origin of the HA in terms of whether it was derived form a soil or sediment, the degree of humification of the HA, and the presence of less decomposed fractions

The CEC of the HA may provide a conservative estimate of the potential metal uptake. One of the retention mechanisms proposed for the pH 4 and pH 6 HA over the short term of 24 h is cation exchange and this could be influenced by the sizes of the hydrated radii and the concentrations of divalent and monovalent cations of Pb and Cd. Sequestering of Pb and to a lesser extent Cd may also be occurring.

5. ACKNOWLEDGMENTS

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Fate and transport of bacteriophage in UK aquifers as surrogates for pathogenic viruses

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ABSTRACT
Recent threats to groundwater quality in the UK (arising from leaking sewers and burial pits used during the recent Foot and Mouth Disease epidemic) have highlighted the need to understand the fate and transport of pathogenic viruses in the subsurface so that a robust assessment of their potential threat to environmental and public health can be made. Non-hazardous microbial tracers (phage) that mimic the movement of pathogenic microorganisms through groundwater systems are being used. Bacteriophage have good potential as surrogates to help us better understand the fate and transport of viral pathogens and are discussed here in the light of their injection as tracers into UK aquifers. Specific bacteriophages (MS2, PRD1 and ϕX174) that exhibit good potential as tracers and have properties similar to pathogenic viruses of interest are discussed.

INTRODUCTION
The importance of groundwater in the UK can not be over-stated as it is often the sole available water resource for large population centres. The main aquifers in the UK are the Chalk, Permo-Triassic Sandstone and the Jurassic Limestone. These are all relatively complex aquifers with a high degree of heterogeneity and so the protection of these vital resources is an important, though complex, task. Recent challenges with microbial contaminants entering the subsurface have highlighted a paucity of reliable and useful information needed to assess the fate and transport of pathogens in groundwater systems. Furthermore, enteric virus monitoring in urban areas of the UK has produced evidence to show that, even at depth, slow-moving groundwater systems such as the Sherwood Sandstone aquifer cannot be assumed to be virus free (Cronin *et al.*, 2003). These findings have major implications for public health, especially with regard to groundwater protection and land use management policies relating to sewerage leakage and sewage disposal as well as potential contamination from animal burial sites and cemeteries. There is also a need to be able to understand the survival and movements of pathogenic viruses within the environment as a means of informing microbial risk assessments.
A range of substances have been used to trace groundwater flow. Most of these are dissolved in the water, for example fluoresceine and rhodamine dyes or conservative anions such as bromide. Alternatively, suspensions of particles of polystyrene beads have been used to provide a size effect to the racer experiment. However, none of these can provide a

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comprehensive model for pathogenic viral transport as they do not have the same chemical composition, charge, surface properties or even physical size (Harvey, 1997). Hence, microbial tracers are needed to develop more robust models of microbial transport. Pathogenic viruses can not be released into aquifers due to the immediate threat to public health and consequent liability on the assessor, so robust and reliable surrogates are needed to assess the characteristics of pathogenic viruses in a typical UK aquifer. Bacteriophages (a group of viruses that infect bacterial cells) are an obvious alternative (Armon and Kott, 1996; Metcalf *et al*, 1995) due to their similar characteristics to mammalian viral pathogens, i.e. size, shape, morphology, physiochemistry and isoelectric points (Table 1). Furthermore, they pose little risk to plants, animals or, indeed, people. Bacteriophages are very unlikely to replicate in the environment due to limiting factors; bacteriophages (like any other virus) require a viable host cell to replicate and so the bacteriophage of enteric bacteria are unlikely to replicate in the environment due to low numbers or absence of a suitable host. In addition, the environmental conditions (e.g. low temperature of groundwater) may not be conducive to replication. Finally, methods of bacteriophage isolation (i.e. the double agar method) are easier and cheaper than enteric viruses (i.e. cell culture). Hence, bacteriophages meet many of the necessary requirements of a useful tracer. Commonly used bacteriophage tracers include MS2, PRD1, and ϕX174, are discussed below in more detail.

	Virus / Phage	*Size*	*Symmetry*	*Isoelectric point*	*Genetic material*
Phage	MS2	26	Icosahedral	3.5-3.9	ss-RNA
	PRD1	62	Icosahedral	4.2	ds-DNA
	ϕX174	25-27	Icosahedral	6.6	ss-DNA
Viral path-ogens	Adenovirus	80-110	Icosahedral	N/A	ds-DNA
	Astrovirus	27-30	Polyhedral	N/A	ss-RNA
	Coxsackievirus	28-30	Icosahedral	4.8	ss-RNA
	ECHOvirus	28-30	Icosahedral	5.0-6.4	ss-RNA
	Apthovirus (Foot and Mouth DV)	27-30	Icosahedral	N/A	ss-RNA
	Norovirus	35-39	Icosahedral	5	ss-RNA
	Poliovirus	28-30	Icosahedral	4.5-6.5	ss-RNA
	Rotavirus	80	Icosahedral	3.9	ds-DNA

Table 1: Characteristics of viruses and possible phage surrogates; N/A = Not available.

BACTERIOPHAGES COMMONLY USED AS SURROGATES

Two main bacteriophage groups have been used in survival and tracer studies as surrogates for viral pathogens: somatic coliphages (i.e. bacteriophage that infect *E. coli*), and male specific F-RNA bacteriophages (Table 2). Somatic coliphage attach to the cell wall of the host. F-RNA bacteriophage infects cells through the sex pili (F-pili) produced by some bacteria during the growth cycle.

Phage type	**Family members**	**Host**	**Genetic material**	**Tail type**	**Size (nm)**	**Shape**	**Phage**
Somatic	Myoviridae	*E. coli*, other Enterobacter iacea	Linear ds-DNA	Long contractile	95 x 65	Cubic Capsid (icosahedral or elongated)	T2, T4, T6
	Siphoviridae	*E. coli*, other Enterobacter iacea	Linear ds-DNA	Long non-contractile	54	Cubic capsid (isosahedral)	T5, λ

	Podoviridae	*E. coli*, other Enterobacter iacea	Linear ds-DNA	Short non-contractile	47	Cubic capsid (isosahedral)	T7, T3
	Tectiviridae	*E. coli*, other Enterobacter iacea	Linear ds-DNA		62	Cubic (isosahedral) capsid	PRD1
	Microviridae	*E. coli*, other Enterobacter iacea	Circular ss-DNA	No tail	30	Cubic capsid (isosahedral)	ϕX174, S13
Male specific F-RNA	Leviviridae	*E. coli*, *Salmonella*	Linear ss-RNA	No tail	20-30	Cubic capsid (isosahedral)	MS2, Qβ
	Inoviridae	*E. coli*, *Salmonella*	Circular ss-DNA	No tail	810 x 6	Filamentous or rod-shape	SJ2, fd, M13

Table 2: Groupings and characteristics of bacteriophages. (from IAWPRC, 1991; Havelaar *et al.*, 1986)

MS2

MS2 is an icosahedral f-specific bacteriophage with a diameter of 27nm and a low isoelectric point (pI) of 3.5. MS2 is seen to be less stable than some other enteric viruses (Blanc and Nasser, 1996; Yahya *et al.*, 1993). This bacteriophage is a conservative tracer for enteric virus transport because in the majority of soil types the adsorption of MS2 is relatively low when compared to other viruses (Jin *et al.*, 1997; Schijven *et al.*, 1999). However, similarities of removal rates for MS2, Hepatitis A virus (HAV), poliovirus 1, and echovirus 1 were observed in columns packed with clay loam at a pH of 6-8 (Sobsey *et al.*, 1995).

PRD1

The PRD1 bacteriophage has an icosahedral shape with a diameter 62 nm with an inner lipid membrane (Bales *et al.*, 1991). The pI of PRD1 is between 3 and 4 (Loveland *et al.*, 1996). PRD1 can be considered as a worst case surrogate for survival due to its low rates of inactivation at temperatures between 10 and 23°C, PRD1 is more stable at elevated temperatures than MS2 (Yahya *et al.*, 1993; Blanc and Nasser, 1996). PRD1 has been recommended as a surrogate for rotaviruses and adenoviruses, due to the similarities in size (Sinton *et al.*, 1997). Also, adenovirus has a similar structural design to PRD1 although they may differ in surface charge (Belnap and Stevens, 2000). PRD1 seems to be transported less conservatively than MS2, this may be due to PRD1 being more hydrophobic than MS2 (Bales *et al.*, 1991; Dowd *et al.*, 1998).

ϕX174

ϕX174 is a somatic coliphage with an icosahedral shape, 27nm in diameter and a pI of 6.6 to 6.8. ϕX174 shows the least electrostatic and hydrophobic areas of all the bacteriophages and so is regarded to be a good surrogate virus for transport purposes (Lytle and Routson, 1995). ϕX174 has a high rate of adsorption to columns packed with Ottawa sand (Jin *et al.* 1997). This rate is higher than that of MS2 and this may be contributed to the different pI values of the two bacteriophages. The pI of ϕX174 and poliovirus 1 are similar. However, when ϕX174, poliovirus 1 and reovirus 3 were investigated within 8 different soil types, die-off of ϕX174 was shown to be more affected by residence time and distance as opposed to the two enteroviruses whose die-off was more related to the soil type (Funderberg *et al.*, 1981). Field studies conducted by DeBorde *et al.*, (1998), showed that ϕX174 was very stable and its inactivation was minimal over the period of half a year.

ϕX174 under high hydrophobic conditions would be the surrogate of choice compared to MS2 and PRD1, mainly due to is high stability, and low hydrophobicity. ϕX174 behaviour varies greatly in different pH values (due to change in net surface charge) at pH6 surface charge is positive at pH 8 it is negative.

SURVIVAL AND TRANSPORT OF BACTERIOPHAGE IN AQUIFERS

There are many environmental factors that influence the survival and transport of viruses and bacteriophages in groundwater and aquifers. Conflicting evidence has been reported on the extent of inactivation and immobilisation of viruses by these environmental factors that include:

Temperature and microbial activity

Temperature and microbial activity (i.e. degradation via the production of enzymes and secondary antagonistic metabolites by indigenous microbes) are considered as two of the most influential environmental factors (Yahya *et al.*, 1993; Blanc and Nasser, 1996). Survival of viruses and bacteriophages is enhanced at temperatures below 15°C (Lefler and Kott, 1974). Microbial activity is thought to have a detrimental effect on the survival of viruses and bacteriophages in aquifers (Sobsey *et al.*, 1980), some investigators have found no significant difference between sterile and non-sterile conditions (Yates *et al.*, 1990). Recent work (Gordon and Toze, 2003) suggests that inactivation rates by temperature are indirect and that microbial activity at elevated temperatures is the direct factor involved.

Moisture content and hydraulic conditions

Saturated conditions increase the survival and transport of viruses and bacteriophages through the subsurface (Powelson and Gerba, 1994; Jin *et al.*, 2000; Lytle and Routson, 1995). Although, Lefler and Kott (1974), reported no difference between saturated and unsaturated conditions.

Acidity and salt species and concentrations

Salt species and their concentration and the acidity (pH) of the surrounding environment all play an important role in the survival and transport of viruses and bacteriophage in the subsurface (Sobsey *et al.*, 1980). pH affects the sorption (low pH) and desorption (high pH) of viruses and bacteriophage to the surrounding strata, hence affecting their movement (Sobsey *et al.*, 1980; Moore *et al.*, 1981). Higher ionic concentrations increase the adsorption of viruses to the subsurface (Moore *et al.*, 1981).

Soil properties and organic matter

The extent of virus and bacteriophage adsorption will influence survival times (Sobsey *et al.* 1980; Bales *et al.*, 1991). Greater movement of viruses and bacteriophages is observed in coarse-textured soils while clay soils bind viruses and phages. (Sobsey *et al.*, 1980). Organic matter may bind to air-water interfaces (that may inactivate viruses) within an aquifer therefore decreasing virus and bacteriophage inactivation (Lefler and Kott, 1974). In addition, competition from organic particles for sorption sites within the strata may result in increased movement of viruses and bacteriophages (Zhuang and Jin, 2003).

Virus and bacteriophage type

Different viruses and bacteriophages exhibit different behaviour under various environmental conditions. These differences in behaviour are thought to be due to different electrostatic charge and hydrophobicity of the virus surface (Dowd *et al.*, 1998, Jin *et al.*, 2000). The protein coat, depending on how it is folded, may have hydrophobic parts on the outside or inside (Gerba, 1999). McKay *et al.* (1993) found size differences in attachment when conducting field tracer experiments, although Lance *et al.* (1982) found little evidence to support this when studying column experiments with poliovirus and echovirus.

CURRENT AND FUTURE RESEARCH STRATEGY

Though much progress has been made in understanding how suitable phage are as surrogates for enteric viruses, more research is still needed into the survival and transport characteristics of both bacteriophages and viruses. This is needed both at laboratory scale to understand the generic process but also at field scale as each aquifer has different matrix type, flow regime and hence varying ability to facilitate viral transport. Hence, while much work has been done on sands and gravels in North America (e.g. Harvey, 1997), this is not directly applicable to UK settings and so field-scale tracing work is currently being planned.

Laboratory experiments have examined the survival of poliovirus and MS2 at concentrations of 10^4-10^5 plaque forming units (pfu)/ml in four separate solution types: groundwater (GW); groundwater passed through a UV light on a re-circulating flow cycle (UVGW); phosphate buffered saline (PBS) solution and 1/16 Ringers solution (RS) (Figs. 1 and 2). The virus and bacteriophage were kept at 12°C in dark conditions. Assays for both the virus (cell culture with BGM cells) and bacteriophage (double agar method) (Adams, 1959) were carried out for the first seven days, then once every week for 3 weeks, then once a month up to 2 months. The MS2 bacteriophage (Fig. 1) shows a rapid initial die-off and then a reduced die-off rate to approximately 50% of the initial concentration over the first 77 days. Poliovirus (Fig. 2) also shows a rapid initial die-off that then reduces to approximately 50-80% (for all four water types) over the first 77 days.

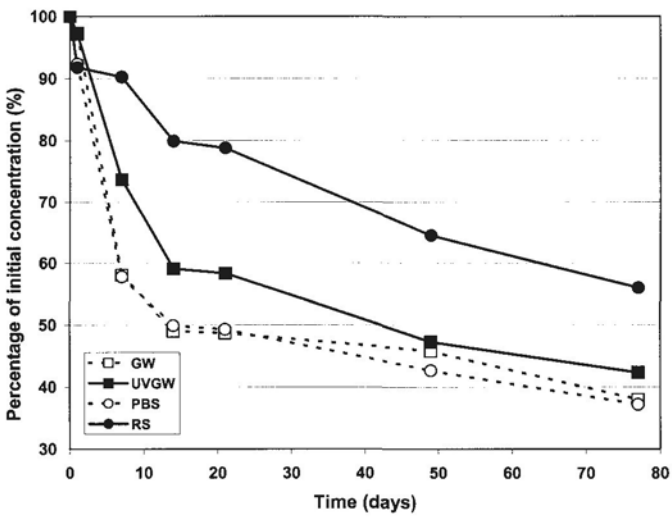

Figure 1: Inactivation of MS2 bacteriophage in four water types.

This phenomenon of rapid initial inactivation followed by a lower rate is often found with viruses and suggests that two or more sub-populations exist that differ in stability (Hurst *et al.*, 1992; Yates *et al.*, 1985). These findings indicate long survival times for poliovirus and MS-2 in all four-water types emphasising the threat they pose to groundwater quality. These findings agree with other research (e.g. Gordon and Toze, 2003; Yates *et al.*, 1985; Schijven, *et al.*, 2003; Sobsey *et al.*, 1980). Long survival rates for both groundwater and UV-sterilised groundwater indicate that microbial activity, at 12°C, has little affect on the viruses (Gordon and Toze, 2003). Hence, viruses at typical UK groundwater temperatures can survive for several months. Initial results show slow inactivation coefficient rates (μ) (Schijven *et al.*, 2003) for both poliovirus and MS2 (Table 3). Current laboratory work by the authors is

focussing on batch experiments looking at the adsorption, de-adsorption and inactivation of bacteriophage and viruses to sandstone aquifer material are currently underway.

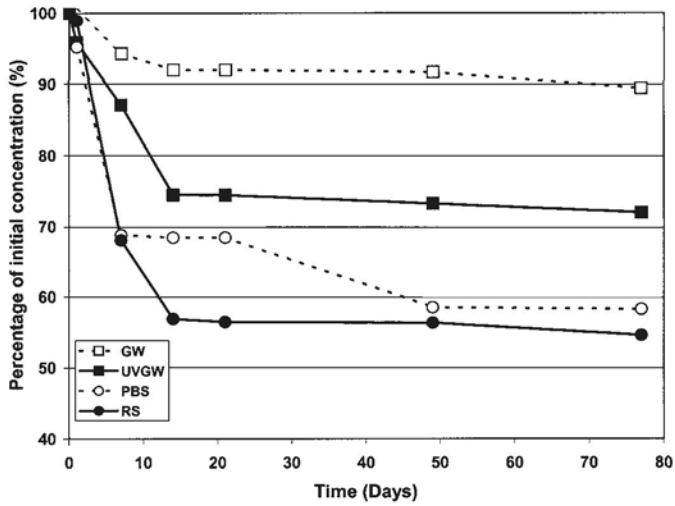

Figure 2: Inactivation of poliovirus in four water types.

Water Type	Average inactivation rate coefficient (μ) for MS2 Phage (day^{-1})	Average inactivation rate coefficient (μ) for Poliovirus (day^{-1})
GW	0.013	0.001
UVGW	0.011	0.004
PBS	0.013	0.007
RS	0.008	0.008

Table 3: Inactivation rate coefficients (day^{-1}) for MS2 bacteriophage and Poliovirus in four water types.

Future fieldwork involves carefully designing, hydrogeologically testing and then establishing infrastructure at a UK field research site. After the characterisation of this field site (including conservative and other tracer work), bacteriophage will be introduced directly into the groundwater so that the fate and transport responses can be monitored over specific time periods. This information will then be used to create a phage reference tool. This will aid in environmental management and future emergency situations or epidemics by allowing quick hypothesis testing of the properties and behaviour of an appropriate bacteriophage in the subsurface to allow inferences is drawn with the pathogenic virus of interest. The project is currently ongoing and due to report in late 2005.

CONCLUSIONS

Groundwater microbial quality in the UK is being threatened by a variety of contaminant risks. Surrogates are needed to carry out tracer work in order to better understand viral transport through these complex aquifers. Bacteriophages have good potential as surrogates for enteric virus movement and survival in the subsurface due to their similarities in size and morphology and the fact that they pose no foreseeable risk to public health. However,

identifying specific individual bacteriophages as adequate surrogates for particular pathogenic viruses is not so simple as there are many varying characteristics to consider. MS2 bacteriophage has the potential to be used as a worst-case surrogate due to elevated survival times and conservative transport when compared to enteric viruses. Other bacteriophages ϕX174 and PRD1 are also considered adequate surrogates for other strongly adsorbed or larger viruses respectively.

Research carried out to date has identified useful surrogates for field trials and confirmed initial low inactivation rates of poliovirus and MS2 bacteriophage, when placed in sterile and non-sterile groundwater. Fieldwork is currently being planned to test these findings.

ACKNOWLEDGEMENTS

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Ground Investigation of Chlorinated Solvent Contamination at a Manufacturing Plant in Southern Italy.

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Valeriano Pastore, and Anna Galigani, Studio Geotecnico Italiano, Italy

Abstract
Past spillages of chlorinated solvents at a factory in southern Italy, which is still in use, have resulted in a localised but highly contaminated zone within the site boundary. The principal pollutants are PCE and TCE. The paper reports on the results from recent ground investigation that measured both aqueous and gaseous concentrations in the subsurface of up to 8540 μg/l and 10,200 mg/m^3 respectively. The ratio of aqueous and gaseous concentrations were found to agree with Henrys constant at standard temperature and pressure (STP).

Keywords. Chlorinated solvents, PCE, TCE, aqueous and gaseous phases, volcanic deposits.

1.0 Introduction

An ongoing site investigation is being carried out at an operational factory in southern Italy, where past spillages of chlorinated aliphatic hydrocarbons (CAHs) have been detected in volcanic deposits of centric sand, ash, pumice and tuff. The principal contaminants are trichlorethene (TCE) and perchloroethene (PCE). Analyses of groundwater samples retrieved from slotted piezometers have recorded aqueous concentrations of up to 8540 μg/l of PCE in shallow piezometers (8-13 m depth) with corresponding gaseous concentrations of 10,200 mg/m^3. The paper presents the results of the recent gas and groundwater sampling.

2.0 Site History

The site is located in Southern Italy and covers an area of approximately 9.8 hectares. It has been occupied by a factory since 1960s, which is still in production. Approximately 3.625 hectares of the site is covered by buildings with 3.032 hectares unpaved and the remainder occupied by roads. There are 3 main buildings on the site. The first was constructed in the 1960s and contains a manufacturing unit, offices and changing rooms. The building is powered by a fuel thermal power station, a substation, a transformation unit and a compressors station. The second building was built in 1970s and houses testing sections, changing rooms, packing units, offices and an infirmary. The sub-basement contains a thermal power station. In addition, a third building was constructed in the 1970s. It currently houses stores (equipment, papers, packing, inflammable products used in the productive unit). Outside there are smaller secure stores for holding hazardous waste materials. This third building also houses a galvanic plant and a wastewater treatment plant for effluent from the galvanic unit itself, which was operated until 1991 and later dismantled in 1995. Nearby the same building there was a cyanides store, which was reclaimed in 1990s and is now used for storing paper. A location plan and layout of the site is shown in Figure 1.

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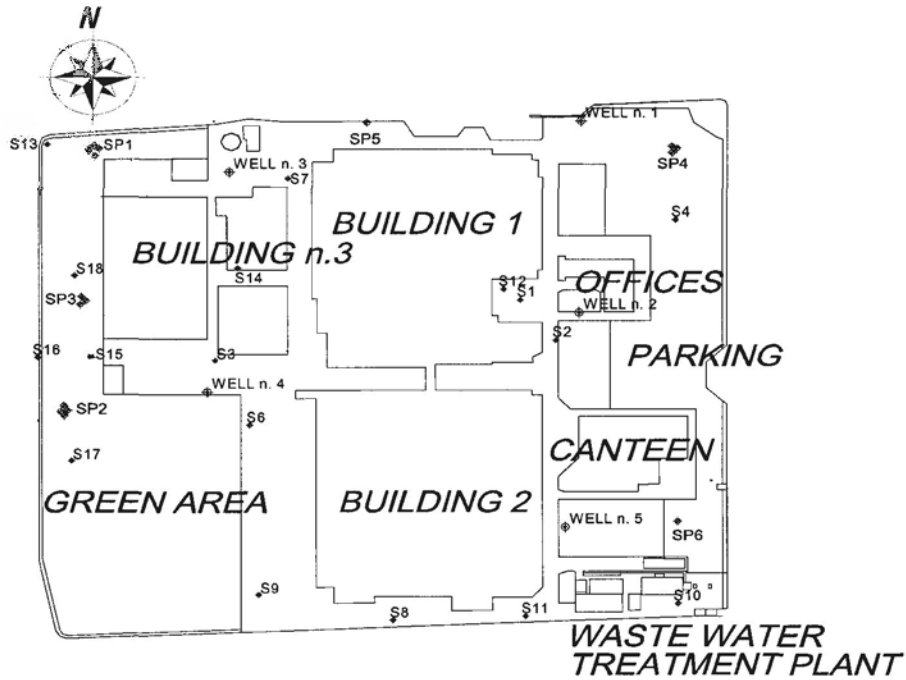

Figure 1 Site layout showing location of boreholes from different phases of the ground investigation as well as principal buildings

A total of five groundwater abstraction wells exist at the site (sunk to a depth of 40m). Two of the wells provide water for the manufacturing process, which generally involves assembly of electronic components . A third well supplies the fire system. And a further two wells are not currently in use. Drinking water is supplied from an external source some hundred kilometres from the plant and is stored in four tanks.

Wastewater is disposed using two sewerage networks; water coming from the cooling system and meteoric water are conveyed into "white network" while water coming from toilets and canteen is treated in a biological treatment plant and then conveyed into "black network". Washing water is used in closed circuits and finally held in tanks and disposed according to Italian regulation.

There are five thermal power stations in the plant; one is working by means of methane while the other are fed by fuel oil, which is stocked in 5 underground storage tanks (UST). The USTs were install before 1970s. and subjected to capacity tests to verify any possible leak, which proved negative.

The main chemicals and auxiliary materials currently used in the plant are: welding paste, silk screen printing compound containing welding power, rosins and aliphatic solvents, flux

containing lead and tin, washing fluids for welding frames and machine tools, ethyl and isopropylic alcohol, technical gases, lubricating oil and grease, diesel oil, acetone, ammonia, detergents and disinfectants for cleaning.

The main waste products from the manufacturing process are industrial waste (washing solution, aqueous solution, exhausted solvents and fluxes, welding paste welding waste, scrap and obsolete components, lead storage batteries and cables, packing (paper, cardboard, plastic and wood), biological mud (originating from biological treatment plant and septic pit) and mixed municipal waste. Where feasible re-usable wastes are recovered, while the remainder are disposed in landfill. Packing and non-dangerous waste are placed in an open asphalt area, while dangerous waste are confined in closed cells with containing basins until final disposal. From this inventory of chemicals for the manufacturing process and waste products, ground investigations have identified spillage of chlorinated solvents into the subsurface (perchloroethylene and trichloroethylene) as being the most problematic.

3.0 Ground Conditions

The ground conditions at the site are principally volcanic deposits from pyroclastic flows, which comprise a homogeneous mixing of coarse gravelly pumice pyroclasts and ashes dating back to local volcanic ignimbritic. The site itself is located on a plain graben, which arose in Plieocene Period and later subsided several thousands meters. The central part consists of alluvial sediments dating back to Holocene Period, which are mainly silty and clayey-silty soil. Locally there are pumice horizons with pyroclastic material and peat lenses. In the lateral part of the plain there are pyroclastic stones with typical tuff lobes.

The ground conditions at the site have been investigated to a depth of 50 m from ground level Past ground investigations have identified following main stratigraphic units:

UNIT 1 (Ground level to 1.0÷2.6 m.) Superficial layer of made ground comprising brown silt and sand in variable proportions with roots, electric cable, bricks bits and building waste. The soil was generally wet because of roots and surface water seepage.
UNIT 2 (1.0÷2.6 up to 2.8÷3.9 m.) Brown grey ochre and hazel sand silt with localised pumice gravel in discontinuous and overlapping lenses
UNIT 3 (2.8÷3.9 up to 5.4÷8.0 m) Tuff horizon comprising loose and weakly silt of varying competence
UNIT 4 (5.4÷8.0 up to 24.5÷26.5 m) Grey-black cineritic sand, generally coarse grain sized occasionally slightly silty including fine or coarse gravel size particles of pumice in decimetric layers
UNIT 5 (24.5÷26.5 up to 40.÷46.1 m) Discontinuous horizons of sand and silt with different gathering rate and colour.

Beneath the volcanic deposits (o÷45 m) area marine deposits comprising shelly silty sand or sandy silt, which acts as an aquitard.

The hydrogeological regime is understood to comprise a superficial unconfined phreatic groundwater table flowing from N-E to S-W with a gradient of 0.2% (industrial wells operating) 0.3% (industrial wells not operating). It is fed laterally by groundwater from carsic massifs. The groundwater level is at 8 m depth beneath the site. Past groundwater pumping from industrial and agricultural wells have locally depressed the groundwater level. Beneath the superficial groundwater table, there is an artesian aquifer with groundwater flowing in the

same direction from N-E to S-W. The groundwater level is from 50 to 60 m deep. Ground investigation have generally only detected the superficial phreatic groundwater table with groundwater levels measured between 8-9 meters depth.

4.0 Ground Investigations and Sampling

Three ground investigations have been carried out at the site for environmental site assessments. The first took place between July and November 2001. The first ground investigation consisted of 18 no boreholes (S1 – S18) sunk using continuous sampling. Slotted piezometers were installed in 12 no of the boreholes from 8 to 12÷20 meters depth below ground level. In addition, 2 no seismic refraction surveys were carried out to investigate the Tuff horizon. A total of 31 no shallow boreholes were also sunk for visual inspection. Laboratory analysis carried out on soil and groundwater samples concentrated on the following range of parameters: pH, heavy metals (e.g. total chromium, chromium VI, cyanides), hydrocarbon fuels (e.g. benzene, ethyl benzene, styrene, toluene, xylene), polycyclic aromatic hydrocarbons(e.g., pyrene) and chlorinated aliphatic hydrocarbons (e.g. trichloroethylene, perchloroethylene and degradative by-products), PCBs, hydrocarbons C<12 and C>12.

Following appointment of Studio Geotecnico Italiano, a second round of groundwater sampling was organised in 2002 (March to June) from piezometers and abstraction wells at the site. On this occasion, laboratory analyses focussed on chlorinated solvents, and in particular trichloroethylene, perchloroethylene, total organic halogenated compounds. In addition, a supplementary ground investigation was commissioned involving (a) constant and variable head permeability tests in existing wells, (b) soil gas survey in the vadose zone using of in situ analysis with colorimetric vials and lab analysis of activated carbons vials with gas extracted from 3 m depth in Geoprobe boreholes, (c) supplementary soil sampling two months later using 17 no Geoprobe (4 m depth). The soil samples were analysed for chlorinated solvents trichloroethylene, perchloroethylene, total organic halogenated compounds. The supplementary boreholes are not shown in figure 1.

In order to comply with Italian environmental regulations (Ministero dell'Ambiente 1999), a third phase of ground investigation was organised in 2003 (May until June). This most recent investigation involved sinking of 6 no. percussion boreholes plus 9 no additional augered boreholes alongside in order to obtain multi-level samples (SP1 – SP6. Note: SPs refer to location not individual boreholes). Slotted HDPE piezometers were installed in each of the boreholes with a gravel surround and sealed using bentonite. As a result 4 no piezometers were installed with a slotted section for groundwater sampling from 8 to 13 m depth, 6 no slotted from 19 to 26 m and 3 slotted from 39 to 43 m below ground level. Soil and groundwater samples were taken from the boreholes (using split spoon sampler for soil, static sampling methods for water). During this phase of the ground investigation, some of the earlier PVC standpipes were found to be destroyed by the high levels of contamination in groundwater.

In addition to sinking conventional boreholes the latest phase of the ground investigation also included (a) in-situ soil gas survey using colorimetric vials, (b) further soil sampling with Geoprobe in 3 shallow boreholes (12 samples), (c) 6 in situ variable head (Lefranc) permeability tests, (d) a second seismic refraction geophysical survey that was unable to differentiate the tuff layer from overlying deposits of slits and sand. The numbers and depths

of piezometers installed in boreholes for the latest phase of the ground investigation are shown in Table 1

Piezometers/Borehole Locations	SP1	SP2	SP3	SP4	SP5	SP6
Shallow (9-13 m)	X	X	X	X		
Intermediate (19-26m)	X	X	X	X	X	X
Deep (39-43m)	X	X	X	X		

Table 1 Array of piezometers installed in boreholes for 3rd phase of ground investigation for borehole locations SP1 to SP6

The Laboratory analysis on soil and water samples concentrated on original contaminants (PCE, TCE) and possible degradative by-products (cis-DCE, VC, ethene) in order to assess the potential for natural biodegradation of chlorinated aliphatic hydrocarbons at the site. The total range of parameters included : chloromethane, trichloromethane, vinyl chloride, 1,2 dichloroethane, 1,2 dichloropropane, 1,1 dichloroethylene, 1,1,2 trichloroethane, trichloroethylene, 1,2,3 trichloropropane, 1,1,2,2 tetrachloroethane, perchloroethylene, cis-1,2 dichloroethylene, trans-1,2 dichloroethylene,

5.0 Results and Discussion

The array of shallow, intermediate and deep piezometers installed in the latest phase of ground investigation allowed a more accurate groundwater monitoring and gas survey to be carried out in the vicinity of the source zone and at the perimeter of the site upstream of the superficial aquifer and in the area of the waste water storage tanks. The analysis of groundwater showed that contamination was largely restricted to the area of the source zone near boreholes SP1, SP2 and SP3 with relatively negligible levels of contamination detected at the boundary of the site at SP4 or in the vicinity of the waste water storage tanks at SP5 and SP6.

At borehole locations SP1, SP2 and SP3, analysis of groundwater samples from piezometers detected seven chlorinated aliphatic hydrocarbons (CAHs). The CAHs were 1,1,2-trichloroethane, 1,1-dichloroethene, 1,2-dichloropropane, chloroform, cis-dichloroethene, trichloroethene, and perchloroethene. The highest aqueous concentrations were detected for shallow and intermediate piezometers at borehole location SP2, where apart from cis-DCE all the CAHs exceeded Italian permitted levels for industrial sites by significant amounts (Ministero dell'Ambiente 1999). In contrast only aqueous concentrations TCE and PCE exceeded permitted levels at the other borehole location SP1 and SP3 as well as the deep piezometer for SP2. The measured aqueous concentrations for PCE, TCE and chloroform are plotted in Figure 2. The greatest aqueous concentration for PCE was measured for piezometer SP2C at 8540 μg/l. Interestingly much lower concentrations were detected for cis-DCE (2.4μg/l) but not the alternative isomer trans-DCE, which would suggest that some limited biodegradation was taking place all be it at a low level of activity.

The results for aqueous concentrations of contaminants indicate that PCE is the principal pollutant. Furthermore the distribution of pollution levels are greatest at shallowest depth which suggest that the down migration of pollutants have been retarded by the layered nature of volcanic deposits but not halted. This feature would need to be borne in mind when

designing future remediation works that could trigger further download migration by for example decreasing viscosity by steam injection.

In comparisons, the results for the gas survey are shown in Figure 3 and 4 for PCE and TCE respectively. The gas samples were retrieved using activated carbon. Results from colormetric vials are not shown because the gaseous concentrations were found to be outside of the range of measurement. The gas samples where taken by pumping gas from 3 m depth inside the piezometer tubing for the groundwater monitoring boreholes. Similar to aqueous concentrations, gaseous measurements for PCE were found to be much higher than other CAHs.

The maximum recorded gaseous concentration for PCE was 10,200 mg/m^3 for borehole S16 located slightly north of the piezometer monitoring borehole SP2 that recorded the highest aqueous concentration for PCE (8540 μg/l). Interestingly if the Henrys constant (unitless value of 1.21 for STP after Weidemeier et al 1999) is used to estimated the gaseous concentration corresponding to an equivalent aqueous concentration, the measured aqueous concentration of 8540μ/l equates to a gaseous concentration of 10,300 mg/m^3. This calculated gaseous concentration agrees very closely with measured maximum gaseous concentration.

6.0 Conclusions

Using standard HDPE slotted piezometers it has proved possible to take reliable measurements of aqueous and gaseous concentrations of CAHs (in particular TCE and PCE) at the site of a manufacturing factory, where past spillages of solvent resulted in a localised and highly contaminated area of soil and groundwater.

The variation of aqueous concentrations of PCE with depth combined with the layered nature of volcanic depth suggests that the majority of the spillage is retained within the upper half of the volcanic deposits (~26 m depth) below and above the groundwater table. This needs to be taken into account when selecting remediation works that could trigger downward migration. A comparison of maximum aqueous and gaseous concentrations for PCE shows a ratio in close agreement with Henry's constant. This agreement provides further support to reliability of contaminant measurements and suggests that the high level of contamination in soil and groundwater has reached chemical equilibrium with gaseous concentrations in the vadose zone. This is not often encountered and suggest that negligible attention of vapours are taken place in the vadose zone that would involve biodegradation, diffusion or advection. Hence the source zone appears at present to be contained and largely immobile both for aqueous, pure product and aqueous phases.

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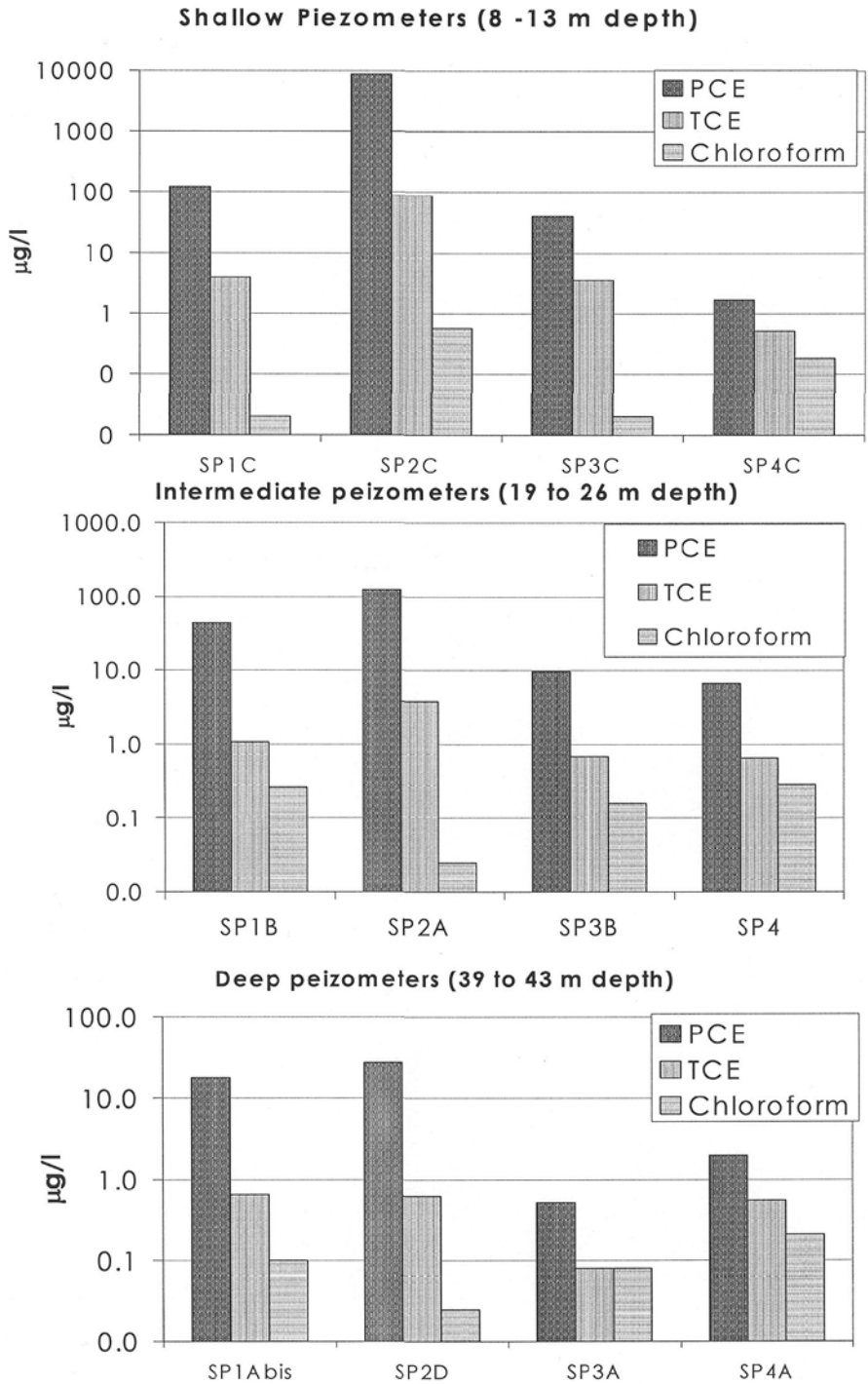

Figure 2 Aqueous concentrations of major CAHs sampled from (a) shallow, (b) intermediate and (c) deep piezometers in boreholes SP1 to SP6

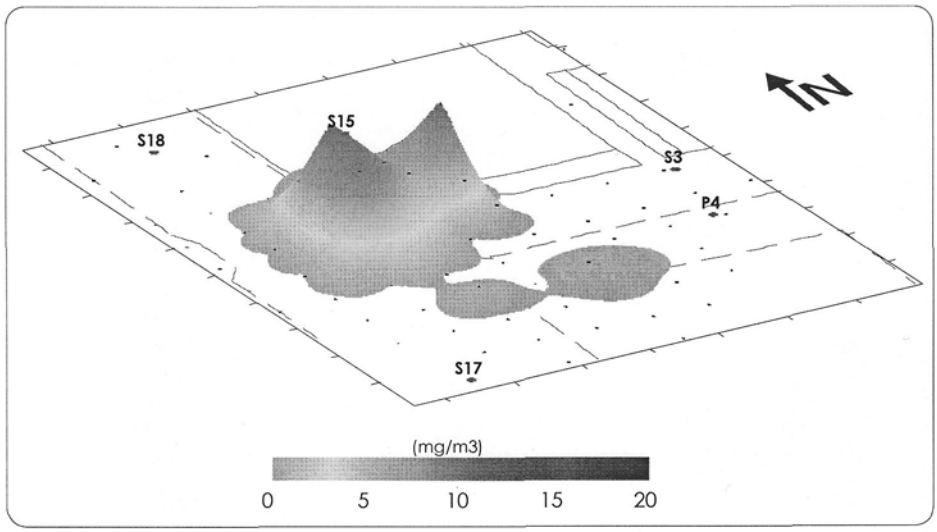

Figure 3 Measured gaseous concentrations for TCE sampled using activated carbon vials

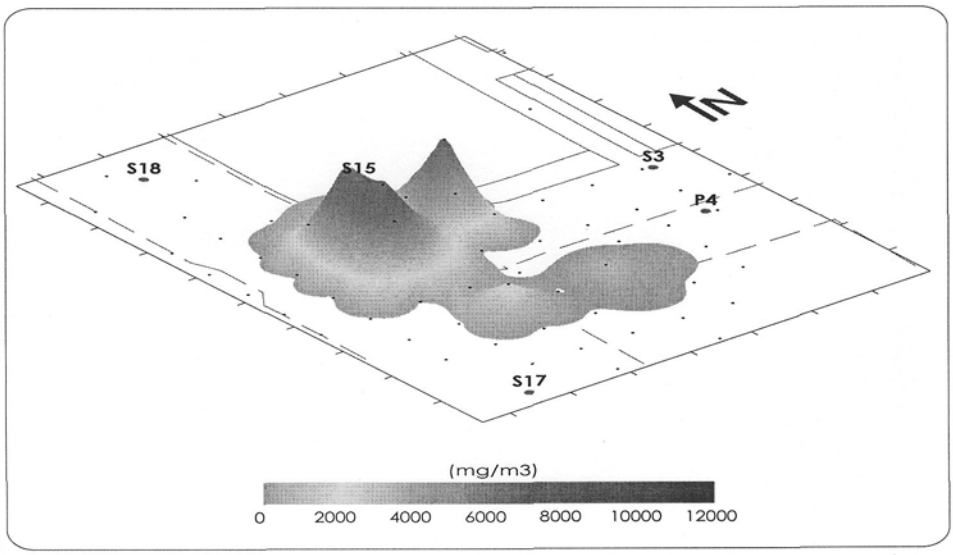

Figure 4 Measured gaseous concentrations for PCE sampled using activated carbon vials

Resistivity Change during Transport of Heavy Metal in Sand

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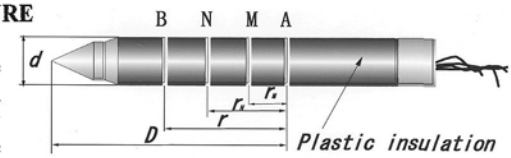
ABSTRACT
A resistivity cone technique was developed to monitor the transport of hazardous substances in soils. Resistivity change during transport of heavy metals, i.e., Pb, Zn, Cu, Ni, was measured using sandy soils and a resistivity cone. The penetration of heavy metal ions into the sandy soils causes the decrease in resistivity of the soil at the first stage. The decrease in the resistivity was dependent on the concentration of heavy metal ions. However, the continuous transport of heavy metal ions gradually increased the resistivity to a quite high value. Therefore, it is possible that soils contaminated with heavy metals have a high resistivity. The remediation works decreases the resistivity of the soils. However, this is unexpected result.

INTRODUCTION
Reliable monitoring technique of hazardous substances in soils becomes a strong device to solve many geoenvironmental problems. The primary object to use the monitoring technique may be to check if the remediation works of soils is being properly done. In the conventional method, number of sampling and chemical analyses, are often omitted, because of the high cost. As a result, some remediation works may fails. Therefore, a low-cost monitoring technique is required to systematize and complete remediation works.

Fukue et al (2003) developed a resistivity cone and examined resistivity change during seepage of solution containing heavy metal ions in their model experiments. The results showed that the resistivity decreased with the increasing concentration of heavy metal ions. They also measured resistivity of sand during seepage of TCE solution, and found that the resistivity of soils increased with increasing TCE concentration ranging 1 to 100 ppm. However, the change in concentration of the TCE solutions without soil particles did not showed any significant change in electrical conductivity. This means that the interactions between TCE and soil particles influence the electrical conductivity, i.e., resistivity.

Electrical measurement is one of the most useful techniques to monitor the change in soil properties, including geoenvironmental properties, such as contamination (Fukue et al, 1998, Fukue et al, 2003). Therefore, electrical properties should be correlated to the geoenvironemntal properties. In this study, resistivity changes are measured during transport of heavy metals in soils.

SOILS AND EXPERIMENTAL PROCEDURE
The soil sample used is commercially available silicate sand. The physical properties of soil sample are shown in Table 1. The resistivity cone used is illustrated in Figure 1. The dimensions of the cone instrument are shown in Table 2. The separation of electrodes was 1 cm. The cone was first installed in the test box as shown in Figure 2, and then the sand was poured in the test box. The sand was relatively in loose state.



A: current electrode
B: grounded electrode
M and N: electrodes for potential measurement

Fig.1 Resistivity cone developed.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

Table 1 Physical properties of soil sample.

	Specific gravity	D_{10} (mm)	Void ratio	Permeability (m/s)	Hydraulic Gradient	Background resistivity (Ωm)
sample	2.64	0.11	1.16	4×10^{-4}	0.2	238-310

Prior to the test, fresh water was poured in the inlet and allowed to flow toward the outlet. The coefficient of permeability was measured using a constant hydraulic gradient and the volume of water flow. However, because the seepage is affected by the cone installed in the center of the sand sample, the coefficients of permeability obtained are not actual value, but apparent.

AC current of 0.1 mA or 1 mA with a frequency of 1 kHz was applied through the electrodes, and the electric potential developed in the sand was measured. It is noted that the difference of this range in AC current does not affect the electric potential. The resistivity was obtained using the following equations derived by Fukue et al (1998).,

$$\rho=\pi^2\Delta V/(CI) \quad (1)$$

where, ΔV: potential difference
I: AC current applied
And C is given by

$$C=1/(d+r_M)-1/(d+r-r_M)-1/(d+r_N)+1/(d+r-r_N) \quad (2)$$

Table 2 Dimensions of the cone.

d (cm)	D (cm)	spacing (cm)
4.2	25	1

After a steady state flow was obtained, the heavy metal solution was poured into the inlet and allowed to infiltrate into sand. 20 L of heavy metal solution was gradually poured into the inlet. After all the heavy metal solution was poured, fresh water was poured again.

RESULTS AND DISCUSSION

General pattern

A typical result of resistivity change during transport of fresh water and heavy metal solution is shown in Figure 3. The initial resistivity of the sand sample was 238 Ωm. The test was started by infiltrating fresh water. Five minutes later, the mixed heavy metal solutions of Cu, Pb, Ni and Zn were poured into the inlet. The concentration of each heavy metal was 2 ppm and totally 8 ppm.

After a few minute, the resistivity starts decreasing, because heavy metal ions act as electrolytes. However, the resistivity starts increasing after about 30 minutes. The minimum resistivity is 160 Ωm. The minimum resistivity is indicated as RL in this study. After 20 L of heavy metal solution was infiltrated, the fresh water was continuously infiltrated. During the

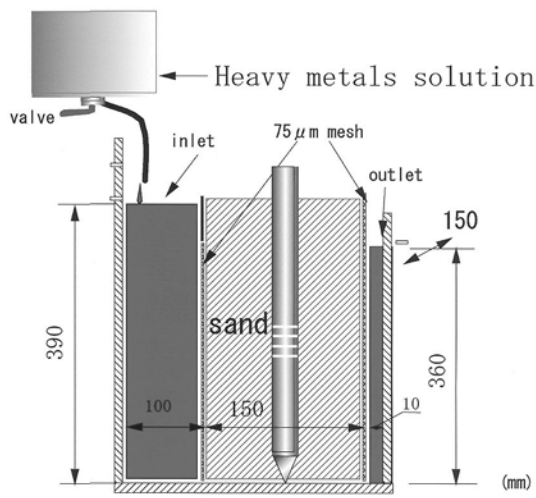


Fig.2 Apparatus for infiltration experiments.

infiltration, the resistivity continues to increase to some extent, but it turns to decrease after 180 minutes. Thus, the resistivity has the maximum value which is greater than the initial value.

Effect of concentration

As electrical conductivity of soils increases with the concentration of electrolyte in the pore water, it is expected that the penetration of heavy metal ions decreases the resistivity of the soils. This is true for a short performance of infiltration of electrolytes (Fukue et al, 2003). However, a long infiltration performance of heavy metal ions shows an unexpected phenomenon. In Figure 3, the rapid increase in the resistivity after 100 minutes occurs by the penetration of fresh water again. It is noted that the dilution of heavy metal solution makes the RH value higher beyond the background value.

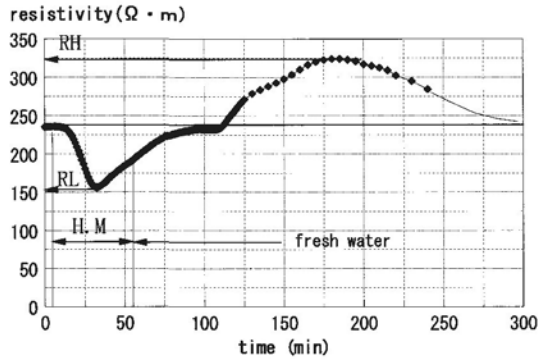


Fig.3 A typical pattern of resistivity change during penetration of heavy metal ions into sand layer. (continuous 0.1 mA and 1 kHz)

The general trend of resistivity change can be described as follows.

a) constant resistivity during fresh water infiltration(stage 0),
b) gradual or abrupt drop in resistivity due to electrolyte effect, depending on concentration (stage 1), usually to the minimum resistivity,
c) anti-electrolyte effects (stage 2), i.e., increasing of resistivity,
d) back to the background value due to washing effect by fresh water (stage 3).
e) dilution effect by fresh water (stage 4), increase in resistivity if concentration is relatively high, but decrease in resistivity if the concentration becomes extremely low.

Figure 4 shows four infiltration performances of heavy metal solutions into the sand sample. The solutions used were a mixture of Cu, Pb, Ni and Zn. The concentrations indicated in the figure show the value for each element. The effects of the penetration of heavy metal solution appear after 13 minutes, as seen in Figure 4. This time lag is due to the permeability of the sand sample. The changes in resistivity due to the penetration of the heavy metal solutions are quite different with the concentrations of ions. The higher concentration provides the lower resistivity (stage 1). If the low concentration of solution s penetrated into the sample, the initial decrease in the resistivity (stage 1) cannot be seen. In this case, the resistivity will increase. In Figure 4, the

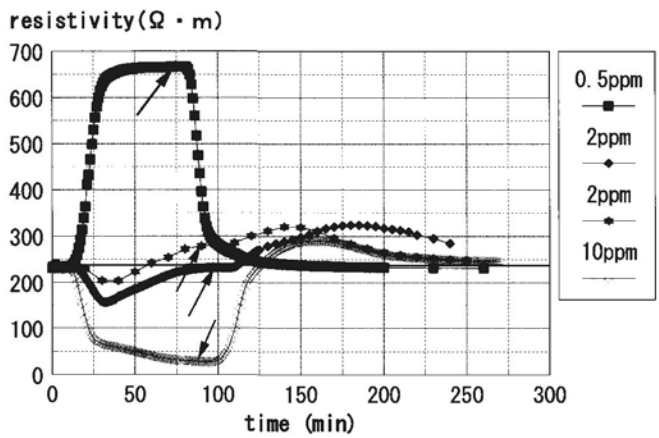


Fig. 4 Changes in resistivity during penetration of heavy metal ions.

switch from the solution to fresh water is indicated by the arrow. The pore water with ions is diluted with fresh water. The dilution will decrease the resistivity, if the concentration of pore water is very low. On the other hand, if the concentration is relatively high, the dilution will increase the resistivity. However, the further dilution will decrease the resistivity. Finally, the resistivity returns to the background, i.e., the original value, as shown in Figure 4.

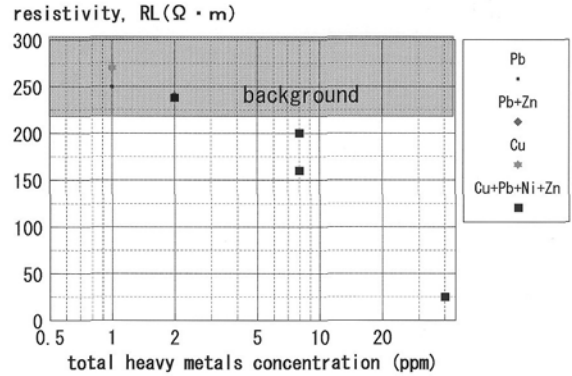


Fig.5 RL values for various total concentrations.

Although it is suspicious that the stage 2 is due to the precipitation of hydroxides, it is denied from the calculation that hydroxides can hardly be formed under the measured pH values.

RL value

The effects of ions can be described in terms of electric conductivity. In general, the higher the concentration of electrolyte, the higher the electric conductivity is. Therefore, the higher concentration will provide the lower resistivity. The effects can be seen as the RL value defined in this study. Figure 5 shows the minimum resistivities, i.e.,RL values, caused by the infiltration of the heavy metal ions. The initial (background) resistivity varies from 230 to 300 Ωm for each performance. The results show that the RL value is lower for the higher concentration under a similar initial concentration, where the concentration used is total amount of the each heavy metal ions. Figure 5 also shows that the significant drop of resistivity cannot be seen if the concentration is low.

RH value

Electrical conductivity of electrolyte solutions is well defined in electrochemistry. In general, for monocharged ions, it is expressed by Onsager's limiting law or the modified law, if the solution is very thin. However, it is well known that theoretical approach becomes difficult in the case of multicharged ions.

As shown in Figure 4, the electrical properties and behaviour of soils with heavy metal ions are somewhat complicated. In particular, the increase in resistivity beyond the background value at low concentration can hardly be explained.

The RH value, i.e., the maximum resistivity during penetration of heavy metal ions, seems to be dependent on the total concentration of heavy metal ions, as shown in Figure 6. The RH value may be greater than the background value and it is higher for lower total concentration of ions. For example, 1 ppm of Pb solution provides

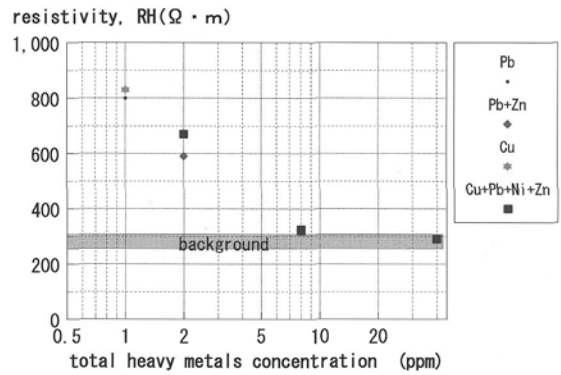


Fig.6 RH value versus total concentration.

a RH of 800 Ωm. The similar result was obtained for 1 ppm of Cu solution. The RH values of these cases are more than 2 times of the background. The unknown effect was examined as follows.

a) precipitation of hydroxides ? The precipitation of hydroxides was denied from the calculation of the concentration and pH value. For example, the production of hydroxide of Pb requires very high concentration under the corresponding pH.

b) effects of the AC current applied ? AC current was applied and the frequency was 1 kHz. Under the condition, the ions cannot be attracted to the cathode or anode. In order to examine the effect of electrical fields, the AC current was applied only when the electric potential was measured. The result was similar to the case that the current was applied continuously during the infiltration experiment, as shown in Figure 7. Figure 7 was obtained at conditions similar to those used in the experiment shown in Figure 3, except the time of the current applied. The AC current was applied for a few second at every 10 minutes, when the electric potential was measured. However, the result shown in Figure 7 is very similar to that in Figure 3. Therefore, it is no significant effect to apply AC current. It may be concluded that AC current of 1 kHz may not affect the transport of ions.

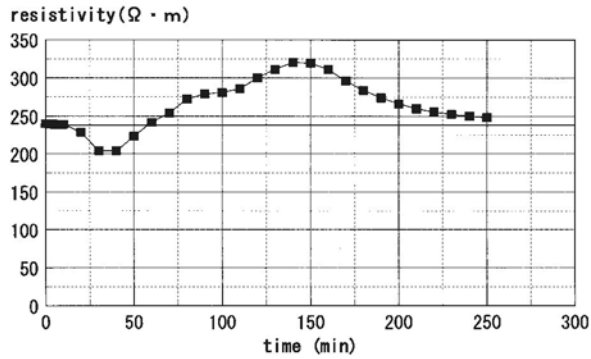


Fig. 7 Change in resistivity with AC current discontinuously applied.

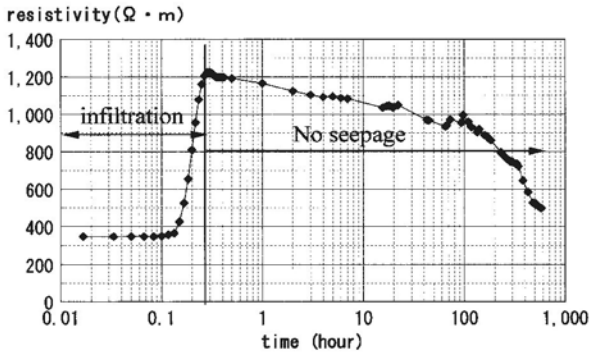


Fig. 8 Long period measurement of resistivity under a very low constant concentration of heavy metals.

Resistivity change for long period

The resistivity change of soils during the transport of heavy metal ions is complicated in terms of the concentration of ions. From the engineering point of view, next interest may be "what is the initial resistivity of soils with heavy metals ?" and "how will the remediation change the resistivity of the soils ?".

Figure 8 shows a long period measurement of resistivity for smaller sands than that shown in Table 1. The solution used is mixture of 0.1 ppm standard solutions of Cu, Pb, Ni and Zn, respectively. The result shows the initial rapid increase in resistivity, because the concentration used is very low. The RH is 1200 Ωm for a total concentration of 0.4 ppm. These values are comparable to the relation shown in Figure 6, though the soil samples used are different.

In this experiment, fresh water was not infiltrated, but the heavy metal solution infiltrated was left in the

sand sample, by stopping the seepage after about 20 minutes from the beginning. Then, the electric potential was measured for 600 hours. The measurement shows that after the rapid increase in resistivity, it turns to decrease and continues to decrease with time, as shown in Figure 8, although the concentration of ions in the sand sample is kept constant.

At present, the ultimate resistivity is unknown, but it seems to return to the background or near background, because of low concentration of heavy metals.

CONCLUDING REMARKS

The resistivity of soils was measured during the transport of heavy metals. The results show that the change in resistivity measured with the resistivity cone is very complicated.

The penetration of heavy metal ions may cause a rapid decrease in resistivity, but the opposite change, an increase in resistivity, may occur after the rapid decrease. After the resistivity reaches the maximum value, it may start to decrease to an ultimate value in a long time.

Spills of hazardous substances may provide a variety of chemical conditions, such as concentration, pH, etc. Therefore, it is often difficult to know what happens to soils, unless all the information needed is obtained.

ACKNOWLEDGEMENT

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Sensitivity of Predicted DNAPL Source Zone Longevity to Mass Transfer Correlation Model

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ABSTRACT
Despite significant research into the topic for 20 years, the interrelationship of DNAPL source zones and downgradient aqueous-phase contaminant concentrations is poorly understood. A number of experimentally derived correlation models have been published to describe mass transfer from the non-aqueous to the dissolved phases. This study examines the sensitivity of DNAPL migration, dissolution and transport simulations in homogeneous and heterogeneous porous media to the choice of mass transfer expression using six published, experimentally derived correlation models. One-dimensional simulations illustrate the sensitivity of predicted effluent concentrations to the employed dissolution model. This sensitivity is observable in the magnitude of dissolved phase concentrations, the length of time during which contaminated groundwater effluxes through the column, and the pattern of dissolved phase concentrations observed over time. Two-dimensional simulations of a realistic DNAPL release into a heterogeneous porous medium illustrate that the dissolution model employed significantly impacts predicted behaviour. Source zone life spans were observed to vary by greater than an order of magnitude, and maximum observed aqueous-phase concentrations were observed to vary from the solubility limit to less than one-third that value. This study suggests that attempting to infer DNAPL source configuration from downgradient concentrations or to predict site remediation times remains uncertain until such time as a comprehensive mass-transfer expression is derived and validated.

INTRODUCTION
Groundwater contamination is present throughout the industrialised world. The most ubiquitous class of organic compounds polluting groundwater are Dense Non-Aqueous Phase Liquids (DNAPLs), which includes polychlorinated biphenyl (PCB) oils, creosote, coal tar, and chlorinated solvents (Pankow and Cherry, 1996).

A conceptual model of groundwater contamination by DNAPLs is presented by Kueper and Frind (1991a). Following the release of DNAPLs at ground surface, DNAPLs *migrate* in intricate patterns through the subsurface as a separate fluid, creating a complex *source zone* composed of vertical trails of immobile *residual* blobs and horizontal accumulations of non-aqueous phase *pools*. *Dissolution* of both DNAPL residual and pools results in the evolution of dissolved-phase contaminant plumes. *Transport* of toxic, dissolved-phase constituents to environmentally sensitive receptors is the primary hazard associated with DNAPL contamination scenarios.

Numerical modelling is an effective tool for designing laboratory and field-scale experiments and can be used to perform sensitivity and uncertainty analysis in the study of DNAPL

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migration and remediation. Numerous multiphase flow models have been developed for use in a contaminant hydrogeology context including Lujan (1985), Faust (1985), Abriola and Pinder (1985a,b), Osborne and Sykes (1986), Kuppasamy *et al.,* (1987), Forsyth (1988), Faust *et al.,* (1989), Kueper and Frind (1991a,b), Gerhard (1995), and others. Most such models account for the migration but not the dissolution of the nonaqueous phase. Transport of aqueous-phase contaminants dissolved in groundwater is described by the Advection-Dispersion equation. Numerous transport models solving the Advection-Dispersion equation have been developed, including MT3D (Modular 3-Dimensional Transport, Zheng, 1990). However, the majority of these models do not incorporate the effects of immobile DNAPL presence or transient DNAPL flow. Some numerical models are capable of simulating multiphase flow, dissolution and contaminant transport. These include *compositional models* such as Corapcioglu and Baehr (1987), Forsyth and Shao (1991), Sleep and Sykes (1993), Huyakorn *et al.,* (1994a), Slough *et al.* (1999) and Reynolds and Kueper (2001) and decoupled flow and transport models such as Reeves and Abriola (1988). With the exception of Reeves and Abriola (1988), these models have extremely large data requirements and are therefore of limited use for simulating field-scale scenarios.

To simulate DNAPL dissolution, numerical models rely on mathematical representations of the complex physio-chemical phenomena involved. Numerous experiments have been conducted to examine these phenomena (Miller *et al.,* 1990; Powers *et al.,* 1992; Imhoff *et al.,* 1994; Powers *et al.,* 1994; Saba and Illangasekare 2000; Nambi and Powers, 2003). Correlation models have been developed using data from these experiments to describe the process of mass transfer from the non-aqueous phase to the aqueous phase.

This study examines the sensitivity of DNAPL migration, dissolution and transport simulations in homogeneous and heterogeneous porous media to the choice of mass transfer expression using six published, experimentally derived correlation models.

NUMERICAL MODEL

A split operator (SO) approach (Barry *et al.*, 2002) was used to integrate the two-phase flow model DNAPL3D (a 3-Dimsneional, 2-Phase flow model) developed by Gerhard (1995, 2001) with the dissolved-phase transport code MT3D (Zheng, 1990). The computationally efficient numerical model developed - capable of simulating two-phase flow, dissolution, and dissolved-phase transport - will be referred to as DNAPL3D-MT (DNAPL3D with multiple species transport). The migration and transport sub-models are linked through a mass transfer expression, which takes one of three forms: (1) no dissolution, (2) equilibrium dissolution (i.e., mass is transferred from the non-aqueous phase to the aqueous phase instantaneously at the solubility limit of the DNAPL) and, (3) rate-limited mass transfer.

Rate-Limited Mass Transfer

A variety of models exist to describe mass transfer between phases in a multiphase system (Miller, 1990). Most assume that the rate of transfer is a function of a driving force and the interfacial area between the two phases. The mass transfer relationship is often expressed as:

$$J = k_{la} a_{na} (C_s - C) = K(C_s - C) \tag{1}$$

where J is the solute mass flux from the non-aqueous phase to the aqueous phase, k_{la} is an average mass transfer coefficient for the DNAPL-water surface, a_{na} is the interfacial area between the DNAPL and the aqueous phase, C_s is the aqueous phase solubility concentration, and C is the aqueous phase solute concentration in the bulk solution. To avoid the need to quantify entrapped DNAPL geometry, a lumped mass transfer coefficient (K=$k_{la}a_{na}$) is often used in equation (1) (Miller *et al.*, 1990). The value of K, incorporating the unspecified

specific surface area between phases, is typically determined from laboratory measurements that employ a modified Sherwood number:

$$Sh = Kd_p^2 D_m^{-1} \tag{2}$$

where Sh is the Sherwood number, d_p [L] is the mean particle diameter, and D_m [L^2T^{-1}]is the molecular diffusion coefficient for the soluble constituent (Miller *et al.*, 1990). Experimental determinations of the Sherwood number are usually presented in the form of traditional dimensionless groupings such as Schmidt, Peclet, and Reynolds numbers (Sale and McWhorter, 2001).

Table 1 presents six experimentally derived correlation models and the conditions under which they are valid. In general, the expressions are only valid for residual source zones and small groundwater velocities. However, the applicability of the expressions is further limited by the experimental conditions under which they were derived. For example, each expression assumes an immobile DNAPL phase. With the exception of Saba and Illangasekare (2000) and Nambi and Powers (2003), the expressions neglect to account for the effects of flow dimensionality. With the exception of Imhoff *et al.* (1994) and Saba and Illangasekare (2000), the expressions ignore the fact that the average value of K for a source zone decreases with an increase in the length of the source zone, thus, limiting the validity of the expression to source zones with the same lengths as the laboratory columns from which they were derived (Saba and Illangasekare, 2000). With the exception of Nambi and Powers (2003), the expressions were developed from experiments conducted in homogeneous porous media. However, recent studies have indicated that the choice of dissolution rate correlation has greater influence on DNAPL dissolution in heterogeneous systems than uncertainty in DNAPL distribution or spatial heterogeneity (Unger *et al,* 1998).

Table 1. Dimensionless Sherwood Number Correlations for Interphase Mass Transfer

Experimental System	Correlation	Valid Conditions	Reference
1-D	$Sh = 12\,\mathrm{Re}'^{0.75}\,\theta_n^{0.6}\,Sc^{0.5}$	$0.016<\theta_n<0.07$ $0.001<Re'<0.1$ (steady state dissolution)	Miller *et al.*, 1990
1-D	$Sh = 57.7\,\mathrm{Re}^{0.61}\,d_{50}^{0.64}\,U_i^{0.41}$	θ_n = constant $0.012<Re<0.2$	Powers *et al.*, 1992
1-D	$Sh = 340\theta_n^{0.87}\,\mathrm{Re}'^{0.71}\left(\frac{d_{50}}{x}\right)^{0.31}$	$0<\theta_n<0.04$ $0.0012<Re'<0.021$ $1.4<x/d_p<180$	Imhoff *et al.*, 1994
1-D	$Sh = 4.13\,\mathrm{Re}'^{0.598}\,\delta^{0.673}\,U_i^{0.369}\left(\frac{\theta_n}{\theta_{n0}}\right)^{\varphi}$	$0.015<Re<0.23$	Powers *et al.*, 1994
2-D	$Sh = 11.34\,\mathrm{Re}'^{0.2767}\,Sc^{0.33}\left(\frac{d_{50}\theta_n}{\pi L}\right)^{1.037}$	-	Saba and Illangasekare, 2000

2-D	$Sh = 37.15\mathrm{Re}^{0.61} S_n^{1.24}$	$0.1<S_n<0.35$ $0.018<Re<0.134$	Nambi and Powers, 2003

Definition of terms and variables are as follows: 1-D, one-dimensional; d_{50}, mean particle diameter [L]; *Re*, Reynolds number; *Sh*, Sherwood number; *Sc*, Schmidt number; U_I, uniformity index of the porous media; θ_n, volumetric content of DNAPL; θ_{n0}, initial volumetric NAPL content; *x*, distance from the dissolution cell entrance [L] for Imhoff *et al*,(1994); δ, normalised grain size ($=d_{50}/0.05cm$); ψ, fitting parameter which can be correlated to grain size distribution for Powers *et al.* (1994); τ, tortuosity of sand; *L*, path length inside a contaminated zone [L]; and, S_n, DNAPL saturation.

Numerical Simulations

The first suite of numerical simulations investigate the influence of correlation model selection on source zone life span and downgradient dissolved-phase concentrations in a one-dimensional (1-D) horizontal column. The column was 5 cm long, divided evenly into 18 nodes, characterized by a homogeneous sand (absolute permeability = 5.0 x 10^{-11}, porosity = 0.3). The first two nodes were assigned an initial amount of residual DNAPL ($S_n^{node\ 1} = 0.09$, $S_n^{node\ 2} = 0.05$) while constant head boundary conditions were employed to give a hydraulic gradient of 8.77×10^{-3} across the column.

The second suite of numerical simulations employed a two-dimensional heterogeneous porous medium to further examine the influence of correlation model selection on source zone life span and downgradient dissolved-phase concentrations. The simulation domain (representing a laboratory flow cell) was 2m wide, by 1m high, by 0.02m deep discretised into 5000 0.02m x 0.02m nodes. The top and bottom boundaries of the domain were no flow boundaries, and the left and right boundaries were constant head boundaries to give a hydraulic gradient of 0.01 across the domain. A 1,2-DCE constant flux source (200 ml input in 1 hour) was placed along the top boundary, 0.5m from the left end of the domain. The source was turned off after 1 hour and the simulation was allowed to continue until the source zone was completely dissolved. The heterogeneous permeability field employed is spatially correlated both horizontally (20 cm) and vertically (4 cm) with a mean ln(permeability) = -23.47 m^2 (variance = 0.4714 m^2). The porous medium has a porosity of 0.32 and has constant relative permeability parameters throughout: residual wetting saturation = 0.13; emergence wetting saturation = 0.92; ratio of terminal to displacement pressure = 0.6; maximum DNAPL relative permeability = 0.85; maximum residual DNAPL saturation = 0.09: main drainage DNAPL relative tortuosity exponent = 1.70: and, an imbibition DNAPL relative tortuosity exponent = 0.20 (Gerhard and Kueper, 2003a,b). Other parameters used in the simulations include: mean particle diameter = 0.5 cm; uniformity index = 1.0; Leverett dimensionless pressure coefficient = 0.18557; '*x*' for Imhoff *et al.* (1994) = 0.02m; and, 'Ψ' for Powers *et al.* (1994) = 0.667.

Throughout this study, the DNAPL considered was dichloroethane (1,2-DCE), a common chlorinated solvent. 1,2-DCE has a density of 1260 Kg/m^3, a viscosity of 0.000887 Pa.s, solubility of 8520 mg/L, a free diffusion coefficient (in water) of 9.908×10^{-10} m^2/s, and an interfacial tension with water of 0.02 N/m.

For each of the 1-D and the 2-D investigations, seven simulations were conducted. Each of the first six simulations employed one of the correlation expressions presented in Table 1 for all mass transfer phenomena occurring during that simulation. The seventh simulation in each suite employed the equilibrium assumption. It is acknowledged that a single relationship may not be appropriate for all mass transfer situations within a realistic DNAPL

source zone. Nevertheless, more comprehensive correlation models do not exist; furthermore, employing this assumption permits investigation into the sensitivity of predicted downgradient dissolved phase concentrations to the mass transfer function employed in the source zone.

RESULTS AND ANALYSIS

One-Dimensional Breakthrough Curve Analysis

Figure 1 is a plot of relative 1,2-DCE concentrations vs. time (logarithmic scale) at the downgradient end of the 1-D homogeneous column. This figure clearly illustrates the variability in maximum dissolved phase concentration, and length of time during which contaminated groundwater effluxes through the column, between the correlation models. The equilibrium mass transfer assumption is the only simulation that results in greater than 8% of the solubility limit at the downgradient end of the column; the dissolved phase concentrations for this simulation approach the solubility limit (8520 mg/L) of 1,2-DCE while the maximum concentration observed for any of the rate-limited mass transfer models is approximately 610 mg/L (using Miller *et al.*, 1990). For the equilibrium assumption simulation, the source has been completely dissolved and all contaminated groundwater has exited through the downgradient boundary within approximately 2.8 hours. However, the rate-limited mass transfer models all require significantly more time to achieve the same affect, with the model of Nambi and Powers (2003) requiring the longest amount of time; in excess of 1,000 hours (approximately 42 days).

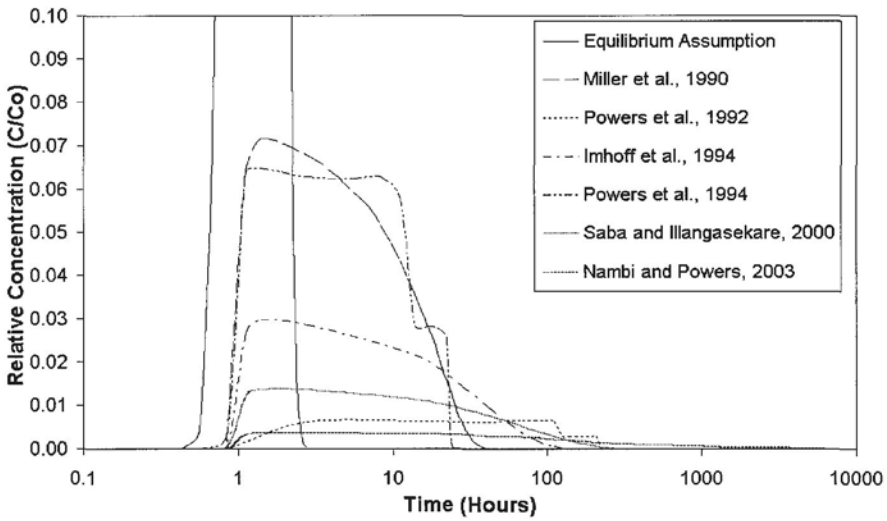

Figure 1. Simulated breakthrough curve comparison at the downgradient boundary of the one-dimensional model domain from emplaced residual DNAPL source.

Figure 1 reveals that the maximum effluent concentration for all simulations exits the domain after approximately 1.4 hours with the exception of Powers *et al.* (1992). In that latter, the maximum occurs near the end of the simulation, just after the DNAPL has completely dissolved, because this function is independent of DNAPL saturation. This correlation model exhibits an increase in mass transfer rate constant with a decrease in DNAPL saturation as a

result of an increase aqueous phase velocity. The remaining correlation models were derived under non-steady state conditions (with respect to DNAPL saturation) and therefore account for the observed decrease in mass transfer rate constant as DNAPL saturations decrease. As a result, the BTC's show an increase in effluent concentration to a maximum at early time, followed by a slow decline or 'tailing' of effluent concentrations until the source zone has been completely dissolved.

Another feature observable in two of the plots (Power *et al.,* 1992 and Powers *et al.,* 1994) is a step-wise decrease in concentration near the end of curve. This feature is again a function of correlation model formulation and appears as the DNAPL input in Node 2 of the model domain is completely dissolved prior to complete dissolution of the DNAPL input in Node 1 of the domain.

Transient DNAPL Release in a Two-Dimensional Heterogeneous Porous Medium

Figure 2 was generated from data collected from the simulation employing the equilibrium assumption mass-transfer model. This figure shows the DNAPL source zone after 10 hours of migration, and illustrates the variability of aqueous phase concentrations throughout the domain.

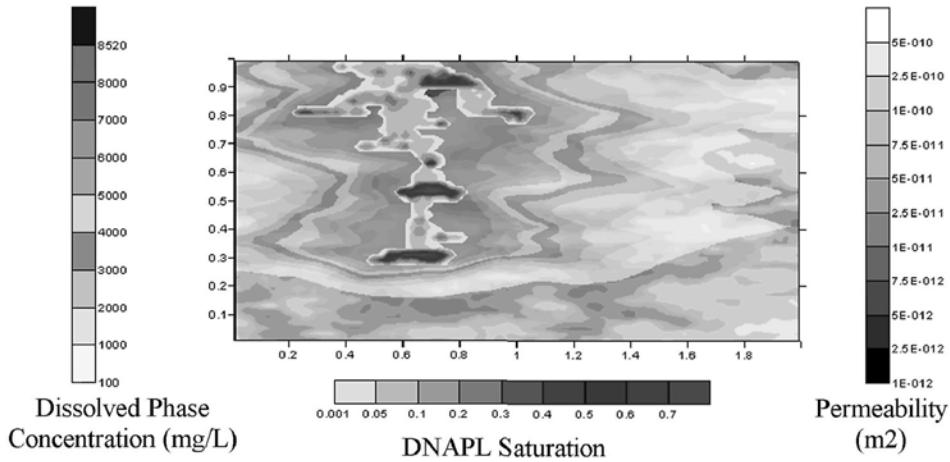

Figure 2. DNAPL saturations and aqueous-phase concentrations employing the equilibrium mass-transfer model in the simulation domain at time = 10 hours.

Figure 3 illustrates the length of time required for complete source zone dissolution as well as the maximum aqueous-phase concentration observed in the domain in the 2-D simulations. Source zone life spans range from approximately 9 days for the equilibrium dissolution model, to approximately 221 days for Powers *et al.* (1992), representing more than an order of magnitude uncertainty resulting from the choice of mass transfer model utilised in the simulation.

As illustrated in figure 3, source zone life span appears to be related to the maximum aqueous-phase concentration observed in the simulation domain. The highest maximum concentration observed corresponds to the equilibrium dissolution model at 8520 mg/L (i.e. the solubility limit of 1,2-DCE), whereas the lowest corresponds to Power *et al.* (1992) at approximately 2800 mg/L. In general, the higher the maximum aqueous-phase concentration,

the shorter the source-zone life span. An exception to this pattern is observed for Saba and Illangasekare (2003), where the source zone life span is disproportionately long relative to the maximum observed dissolved phase concentration. However, the aqueous-phase concentration varied significantly over time in this simulation, changing from less than 250 mg/L during the first hour, to the maximum concentration observed at approximately 1 week, to less than 400 mg/L for the remaining 40 days. Therefore, the maximum dissolved phase concentration during the majority of the simulation was significantly lower than the overall maximum concentration observed, and, as a result, the time for complete source zone dissolution was increased.

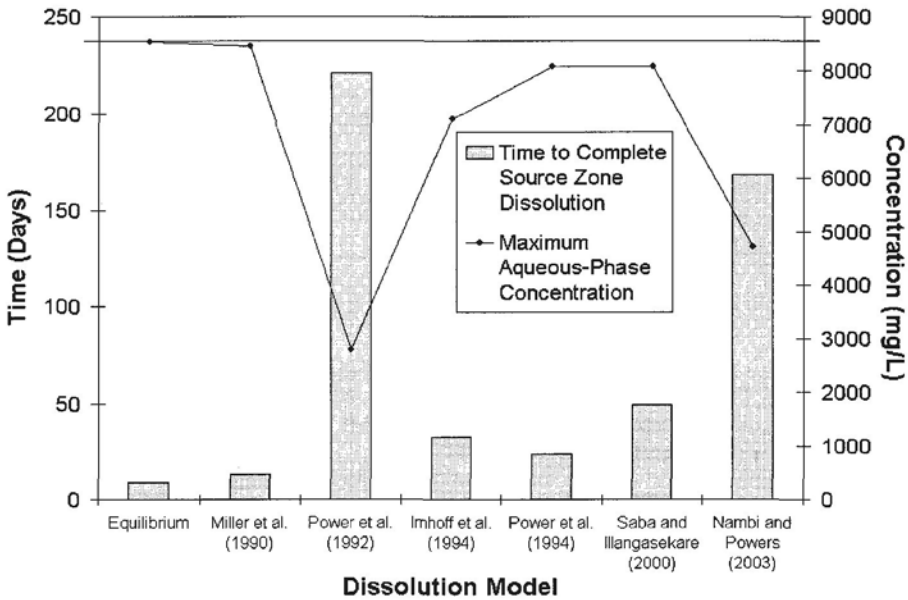

Figure 3. Time to complete source zone dissolution as well as maximum aqueous-phase concentration observed in the 2-D heterogeneous porous medium simulations for each of the dissolution models. The horizontal line in the plot indicates the solubility limit of 1,2-DCE.

CONCLUSIONS

Numerous experimentally derived correlation expressions exist to describe mass transfer from the non-aqueous phase to the dissolved phase. The validity of most is limited to simple, specific circumstances and no comprehensive correlation model exists for simulating the range of dissolution phenomena expected in complex and evolving DNAPL source zones.

One-dimensional simulations in a homogeneous medium illustrate the sensitivity of predicted effluent concentrations to the employed dissolution model. This sensitivity is observable in both the magnitude of dissolved phase concentrations, the length of time during which contaminated groundwater effluxes through the column, and the pattern of dissolved phase concentrations observed over time. Two-dimensional simulations of a realistic DNAPL release into a heterogeneous porous medium illustrate that the dissolution model employed significantly impacts predicted behaviour. Source zone life spans were observed to vary by greater than an order of magnitude, and maximum observed aqueous-phase concentrations in the domain were observed to vary from the solubility limit to less than one-third that value.

Two of the practical implications of this study are that (i) predicted dissolved phase concentrations downgradient of a realistic DNAPL release are quite sensitive to the chosen mass transfer expression, and (ii) a more robust and comprehensive correlation model is likely necessary for accurate simulations.

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Conceptual Model and Mathematical Formulation of NAPL Transport in Unsaturated Porous Media

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ABSTRACT
As the first step in theoretical development of a fully coupled mathematical model for transport of immiscible contaminants in unsaturated soils, a conceptual model is introduced. The conceptual model is an expression of what happens in the nature. In this paper, the conceptual model, different components of the system and principal factors governing their interaction have been specified based on available theoretical and experimental works. Mathematical description of this conceptual model in term of suitable state parameters is then presented and a numerical solution for the model is performed by the finite element method using weighted residual approach.

INTRODUCTION
Unsaturated soils, which have covered vast areas of the earth, are too important in the field of manmade damages to the environment and specially study of contaminant transport in soils. In fact, the superficial layer of the earth including the unsaturated soil acts as a transit for crossing contaminants down to groundwater and acts as a pathway for crossing their vapors in inverse direction, up to the atmosphere.

The first step of simulating NAPL flow in unsaturated porous media is introducing a 'conceptual' model for the phenomena. To initiate the conceptual model, it is necessary to identify the different components of the system and major mechanisms governing the behavior of the system.

The next step is to establish a mathematical model. In this step the dominant mechanisms are stated in the form of mathematical relations. For the purpose of initializing the mathematical model, selecting proper state parameters has a great degree of importance and mathematical equations and constitutive relations are to be presented in term of state parameters. In order to solve the set of partial differential equations of the mathematical model, the finite element method, based on Galerkin's weighted residual approach, is implemented as the numerical solution method.

CONCEPTUAL MODEL
The dominant mechanism governing the transport of all NAPLs in unsaturated soils is the same, regardless of their molecular structures and chemical properties. NAPL migration in the subsurface is affected by: volume of released NAPL, area of infiltration, duration of release, properties of the NAPL, properties of the media and groundwater flow conditions. In

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the following sections, the mechanism and principal factors influencing the NAPL flow in unsaturated zone are explained.

The mechanism of NAPL migration in the subsurface

When entering the subsurface layers, due to gravity forces, NAPL migrates downward through the unsaturated zone as a distinct liquid. This vertical migration also is accompanied by lateral spreading due to the effect of capillary forces [1] and medium spatial variability. When NAPL flows downward in the unsaturated zone, it leaves residual liquid trapped in the pore spaces. This entrapment is because of surface tension effects [2]. In addition to migration of NAPL, some of the immiscible fluid may volatilize and form a vapor extending beyond the NAPL. When reaching to the groundwater, NAPL spreads on the groundwater surface (LNAPL – Lighter than water Non-Aqueous Phase Liquid) or flows through it down to low permeability layers (DNAPL – Denser than water Non-Aqueous Phase Liquid), regarding to its density. Similar to unsaturated zone, in both cases there will remain some residual NAPL in the saturated zone.

Principal factors affecting the NAPL flow in unsaturated zone

Parameters influencing the subsurface migration of NAPL determine its distribution in the media from start of release to sometime after passing immiscible contaminant through unsaturated zone. These parameters include interfacial tension, wettability, capillary pressure, residual saturation, effective permeability, water solubility and density [2].

Interfacial tension is stated as difference in mutual attraction between molecular particles within a fluid and mutual attraction between molecules of two different immiscible fluids across their interface.

Wettability is a competition between two fluids in spreading over solid particles, in this competition the wetting fluid tends to cover surface of soil particles and to fill smaller pores and pore throats, while non-wetting fluid tends to fill larger pores. In a four-phase medium (soil, water, NAPL and air), water is wetting fluid, air is non-wetting fluid and NAPL is intermediate wetting fluid [3].

Capillary pressure is tendency of the system to draw in the wetting fluid and repel the non-wetting fluid [4]. In static condition, capillary pressure is defined as:

$$P_c = \frac{2\sigma Cos\ \varphi}{r} \tag{1}$$

in which, r is radius of the pore that is full of wetting fluid and is to be filled by non-wetting fluid, σ is wetting – nonwetting fluid interfacial tension and φ is contact angle.

When fluids start to flow in porous media, capillary pressure is expressed as the difference of non-wetting fluid pressure and wetting fluid pressure. In this condition, if the capillary pressure is greater than displacement pressure (Pc>Pd), the non-wetting fluid displaces wetting fluid and fluid starts to flow.

Generally speaking, displacement pressure (Pd), at each point of the porous medium, is given by equation (1) but it has been modified for different conditions such as hydrostatic and hydrodynamic flows and more complicated relations are presented. In a heterogeneous porous medium, smaller pores and pore throats have larger displacement pressures, so they can make a diaphragm obstructing the non-wetting fluid flow.

Experimental observations have shown that capillary pressure is in a relation with degree of saturation; however the capillary pressure-degree of saturation relation in the imbibition and drainage processes is inherently hysteretic. The capillary pressure-saturation relation is one of the fundamentals in most of the mathematical models for multi-phase flow in porous media.

When the fluid looses its continuity and becomes immobilized due to presence of capillary forces, the proportion of trapped fluid volume to the total void volume of porous medium is called residual saturation.Residual NAPL is a steady source for water contamination and its amount depends on permeability and moisture content [5]. Pore size distribution, contact angle and hydraulic gradient are other effective parameters on residual NAPL degree of saturation.

Effective permeability is one of the most important mechanical properties of the media influencing the migration, distribution and fate of contaminants in porous medium.In the study of one-phase fluid flow, effective permeability is defined as below:

$$k = K_{in}.\frac{\rho g}{\mu} \tag{2}$$

where k is effective permeability (Darcy permeability coefficient), K_{in} is intrinsic permeability, μ is dynamic viscosity and ρ is density of the flowing fluid.

While more than one fluid is present in the medium each fluid compete other fluids to fill more pore space. As a result, effective permeability of each of present fluids in the system reduces. In the unsaturated zone (two-phase flow condition) the effective permeability of water and air depends on moisture content and void ratio. Generally speaking, for the multi-phase flow in porous media, each fluid has its own effective permeability and it is a function of pore size distribution, the wetting ability and saturation history; therefore, equation (2) turns to generalized form:

$$k_{\alpha} = k_{rel-\alpha}.\frac{\rho_{\alpha} g}{\mu_{\alpha}}.K_{in} \tag{3}$$

in which, k_{α} is effective permeability of the α–phase in multi-phase flow, K_{in} is intrinsic permeability and $k_{rel-\alpha}$ is relative permeability of the α–phase and ρ_{α} and μ_{α} are density and viscosity of the α–phase in multi-phase flow in porous media. Relative permeability is a dimensionless ratio and can be stated as the ratio of the effective permeability of a fluid at a fixed saturation to the intrinsic permeability. Relative permeability is a function of saturation and there is a hysteresis effect in their relation.Many investigations have been performed to state relative permeabilities of different phases, consequently some experimental methods [6] and theoretical models ([7], [8] and [9]) have been presented.

MATHEMATICAL MODEL

Similar to study of moisture transfer in unsaturated soils , in the study of multiphase flow in porous or fractured-porous media, a set of nonlinear partial differential equations including the balance equation of solid particles and continuity equations of all fluid phases are considered. The multiphase flow equations can be written in term of pressure variables or pressure/saturation variables [10]. The multiphase pressure differential equations, including the continuity equations combined with Darcy's law, are widely applied for formulating hydrological problems [11] and in combination with balance equation for solid particles can be a complete formulation for simulating the multiphase flow in unsaturated deformable porous media. This formulation is the generalized form of the formulation studied in

unsaturated soil mechanics and considers the coupled effect of flow and deformation in the medium.

As one of the first attempts in modeling of multiphase flow-deformation coupled behavior, [12] presented a model for simulating the two-phase flow in deformable porous medium. The model was based on mass conservation equation as a function of intrinsic phase velocities and the solid and liquid equilibrium equations for a unit element of porous medium. In 1993, in order to study the three-dimensional three-phase flow in deforming saturated oil reservoir, Lewis & Sukirman [13] established a numerical model based on Biot's three-dimentiosional consolidation theory. In their model an elostoplastic soil behavior on the basis of the Mohr-Coulomb yield surface has been considered. Schrefler et al. [14] presented a general model for analysis of pollutant transport in partially saturated deforming soils. They assumed soil as multi-phase porous system where the interstitial voids of solid matrix are filled with water, an inert gaseous phase and the contaminant which may be miscible or immiscible with the existing fluid phases. Rahman & Lewis [15] developed a fully coupled numerical model to describe multiphase fluid flow through soil. Their model, which simulates immiscible fluid flow in unsaturated media, generalizes the two phase flow model of Brooks & Corey [16] and expresses the nonlinear saturation and relative permeability in term of capillary pressure. The mathematical model presented in this paper, is based on the model developed by Rahman & Lewis [15] with some modifications. In the present model, the elastic linear behavior for soil is considered, creep behavior of solid phase is ignored and fluids are assumed to be uncompressible; also isothermal condition has been assumed for the system.

State parameters

In order to describe the phenomena mathematically, selecting proper state parameters is crucially important. In this regard, σ-$m\boldsymbol{P}$, P_{cgw}, P_{cnw} are considered as state parameters; while σ is total stress, m is $[1\ 1\ 0]^T$, $\boldsymbol{P}$ is effective fluid pressure on the solid particles, P_{cgw} is air-water capillary pressure and P_{cnw} is NAPL-water capillary pressure.

Effective fluid pressure ($\boldsymbol{P}$) has been stated in different ways, Ertekin & Ali [17] utilized the NAPL pressure as the effective pressure exerted on the soil particles; Tortike & Ali [18] assumed the water phase covered the soil particles totally, and effective pressure is equal to water-phase pressure. In present paper referring to [13] and [15], effective fluid pressure is defined as below:

$$\boldsymbol{P} = S_w.P_w + S_g.P_g + S_n.P_n \tag{4}$$

in which, S_n, S_w and S_g are NAPL, water and air saturation and P_n, P_w and P_g are NAPL, water and air pressure respectively.

Governing equarions & Constitutive laws

In order to have a fully coupled model of unsaturated porous media, the effect of capillary pressure changes on the skeleton deformation and fluid-phase permeabilities should be taken into account. On the other hand the influence of stress level and induced-strain on degree of saturation and pore pressure dissipation should be considered too [19]. The mass conservation equations of water, NAPL and air and the equilibrium equation of skeleton associated with water, NAPL and air flow equations and constitutive relations form a complete set of field equations.

Water, NAPL and air flow:
Mass conservation equations of water, NAPL and air phases can be written as:

$$\phi\frac{\partial}{\partial t}(\rho_\alpha S_\alpha)+\rho_\alpha S_\alpha[(m^T-\frac{m^T D_T}{3K_s})\frac{\partial\varepsilon}{\partial t}+(\frac{(1-\phi)}{K_s}-\frac{m^T D_T m}{(3K_s)^2})(P_1\frac{\partial P_n}{\partial t}+P_2\frac{\partial P_g}{\partial t}+P_3\frac{\partial P_w}{\partial t})]$$
$$+div[\rho_\alpha.v_\alpha]=0 \quad , \quad \alpha=w,\ n,\ g \tag{5}$$

When water, NAPL and air flow are assumed to be governed by Darcy's law:

$$v_\alpha=-\frac{Kk_{r\alpha}\rho_\alpha}{\mu_\alpha}\nabla(P_\alpha+\rho_\alpha gh) \tag{6}$$

in which, ρ_α, S_α and $k_{r\alpha}$ are fluid density, fluid saturation and fluid relative permeability, respectively; K is intrinsic permeability of the medium, K_s is bulk modulus of solid skeleton, ϕ is porosity and D_T is the stiffness matrix of solid phase and represents the elastic linear behavior of soil. In the equations (5), the factors which contribute to the rate of fluid accumulation of each flowing phase are [15]: change of total strain due to variations in effective stress, change of solid particle volume due to pressure change, change of the fluid saturation and change of solid particle size due to effective stresses changes.

Water, NAPL and air relative permeabilities depend on capillary pressures. As stated before, in order to express relative permeabilities, some empirical expressions have been presented by several authors. In the present model, the expressions suggested by Lujan [8] have been utilized:

$$k_{rw}=S_{ew}^{(2+3\lambda)/\lambda},\quad k_{rn}=(S_{te}-S_{ew})^2(S_{te}^{(2+\lambda)/\lambda}-S_{ew}^{(2+\lambda)/\lambda}) \text{ and } k_{rg}=(1-S_{te})^2(1-S_{te}^{(2+\lambda)/\lambda}) \tag{7}$$

Where, λ is pore size distribution factor [16] and S_{te} and S_{ew} are effective saturations and are calculated from Brooks & Corey capillary pressure equations ([15], [16]). Effective saturations are expressed as:

$$S_{ew}=(S_w-S_{rw})/S_{\max} \quad , \quad S_{te}=(1-S_g-S_{rw}-S_{rn})/S_{\max} \tag{8}$$

when,

$$S_{\max}=1-S_{rw}-S_{rn}-S_{rg}$$

Solid phase deformation

The total deformation of the porous medium can be evaluated by using the equilibrium equation of skeleton with a constitutive law. The equilibrium equation for the soil phase is written using the principle of virtual work:

$$\int_v\delta\varepsilon^T.d\sigma.dv-\int_v\delta u^T.db.dv-\int_s\delta u^T d\bar{t}\,ds=0 \tag{9}$$

in which, σ is total stress should be written in term of effective stress and effective pore pressure, ε is total strain of solid skeleton and, b and $\bar{t}$ are body force vector and boundary traction vector respectively. On the other hand, according to the effective stress equation, the total stress can be expressed as:

$$\sigma=\sigma'-m\boldsymbol{P} \tag{10}$$

when $\boldsymbol{P}$ is effective pore pressure and fluid pressures are assumed to be compression positive.

The effective stress – strain relationship is the constitutive law in the modeling of solid skeleton behavior [13]:

$$d\sigma'=D_T(d\varepsilon-d\varepsilon_p) \tag{11}$$

while, ε_p represents the volumetric strain caused by uniform compression of solid particles due to pore fluid pressure and D_T is the stiffness matrix of solid phase. Substituting the equations (10) and (11) into (9), we obtain the equilibrium equation of solid skeleton:

$$\int \delta\varepsilon^T D_T \frac{\partial \varepsilon}{\partial t} dv - \int \delta\varepsilon^T m \frac{\partial \overline{P}}{\partial t} dv + \int \delta\varepsilon^T D_T m \frac{\partial \overline{P}}{\partial t} \frac{1}{3K_s} dv - \int \delta u^T \frac{\partial b}{\partial t} dv - \int \delta u^T \frac{\partial \overline{t}}{\partial t} ds = 0 \qquad (12)$$

Initial & boundary conditions

The initial conditions of the system identify the determined values of independent variables, u, v, P_w, P_n and P_g, of the model in each point of the medium at the time $t = 0$, or:

$$u_i = u_i^\circ \quad , \quad P_\alpha = P_\alpha^\circ \quad , \quad \text{when} \quad \alpha = w,\ g,\ n \qquad (13)$$

The Dirichlet and Neumann boundary conditions of the model are:

$$\begin{cases} \underline{\underline{\sigma}}.\underline{n} - \overline{\underline{\underline{\sigma}}} = 0 \\ u_i = \overline{u_i} \end{cases} \quad \text{on} \quad \begin{matrix} S_1 \\ S_2 \end{matrix} \quad \text{and} \quad \begin{cases} q_\alpha.\underline{n} - Q_\alpha = 0 \\ P_\alpha = \overline{P}_\alpha \end{cases} \quad \text{on} \quad \begin{matrix} S_1^\alpha \\ S_2^\alpha \end{matrix} \quad , \quad \alpha = w,\ g,\ n \qquad (14)$$

Numerical solution

Assuming the nodal displacements (u, v) and nodal fluid pressures to be the independent variables, numerical solution of the mathematical model is performed. The spatial discretization of set of partial differential equations and conversion into matrix form has been done by utilizing the finite element method based on weighted residual approach; and, for each element, strains, displacements and fluid pressures are calculated from nodal values by:

$$\varepsilon = B\,U \quad , \quad u = N^T U \quad , \quad p^\alpha = N^T P_\alpha \qquad (15)$$

while, N is shape function, B is linear operator and, U and P_α are nodal values of displacement and fluid pressures respectively. Four nodded isoparametric elements with bilinear shape functions have been used in the finite element procedure.By substitution of equations (15) in equations (5) and (12) and weak formulation, discretized form of equations is resulted. Time discretization is performed using the single step integration in time domain which is defined by:

$$\int_0^t u.dt = [(1-\theta)u_0 + \theta u_1].\Delta t \qquad (16)$$

where, θ indicates the type of interpolation and is set equal to 0.66 in the present model. The set of governing equations in matrix form can be written by:

$$\begin{bmatrix} K_{uu} & K_{uw} & K_{ug} & K_{un} \\ K_{wu} & K_{ww} + \theta\Delta t S_w & K_{wg} & K_{wn} \\ K_{gu} & K_{gw} & K_{gg} + \theta\Delta t S_g & K_{gn} \\ K_{nu} & K_{nw} & K_{ng} & K_{nn} + \theta\Delta t S_n \end{bmatrix} \cdot \begin{Bmatrix} U^i \\ P_w^i \\ P_g^i \\ P_n^i \end{Bmatrix} = \qquad (17)$$

$$\begin{bmatrix} K_{uu} & K_{uw} & K_{ug} & K_{un} \\ K_{wu} & K_{ww} - (1-\theta).\Delta t S_w & K_{wg} & K_{wn} \\ K_{gu} & K_{gw} & K_{gg} - (1-\theta).\Delta t S_g & K_{gn} \\ K_{nu} & K_{nw} & K_{ng} & K_{nn} - (1-\theta).\Delta t S_n \end{bmatrix} \cdot \begin{Bmatrix} U^{i-1} \\ P_w^{i-1} \\ P_g^{i-1} \\ P_n^{i-1} \end{Bmatrix} + \theta\Delta t. \begin{Bmatrix} F_u^i \\ M_w^i \\ M_g^i \\ M_n^i \end{Bmatrix} + (1-\theta)\Delta t. \begin{Bmatrix} F_u^{i-1} \\ M_w^{i-1} \\ M_g^{i-1} \\ M_n^{i-1} \end{Bmatrix}$$

In order to calculate coefficients of equation (17), Gaussian quadrature rule over quadrilateral region is utilized. After determination of coefficients and terms incorporating in equation (17) for each element, the global matrix is assembled. The required conditions of stability

and accuracy of the solution algorithm is acquired by specifying a time step criterion based on the type and the shape of elements of the model [20].

VALIDATION & APPLICATION

The model has been validated in the study of one-dimensional consolidation in a fully saturated fine sand column and verificated in comparing to an experimental model of NAPL transport [3]. Furthermore, for two different time intervals, the model is utilized to solve a NAPL flow problem in unsaturated porous media. The fully coupled numerical model has been used to simulate the NAPL flow in an unsaturated deformable porous medium in two different time intervals. As shown in figure 1, an undetected continuous leaking NAPL source is located on the top surface of the simulation domain containing fine sand. The width of the NAPL source is 1m and it contains 1000 litres of NAPL. Also, release rate of NAPL is equal to 320 liter per day. In this example, NAPL cosidered to have a density (ρ_n) of 957 kg/m^3, a viscosity (μ_n) of 48 cP, an air-NAPL interfacial tension (σ_{gn}) of 22 mN/m and an NAPL-water interfacial tension (σ_{nw}) of 30 mN/m. Linear variation for the air-water capillary pressure in height has been assumed; and based on Brooks & Corey equations [16], the initial unsaturated profile of the medium has been determined. Figure 2 (Case I) shows variations of water saturation, in height.

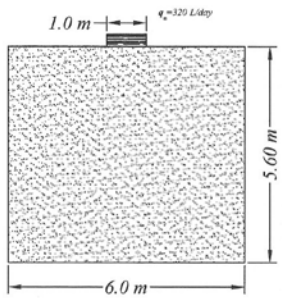

Figure 1: Simulation area

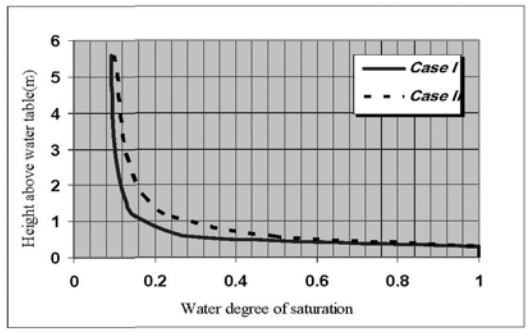

Figure 2 : Water saturation profile at t = 0

Other properties of the medium used in establishment of initial saturation profile of the model are a pore size distribution index (λ) of 1.59, a displacement pressure (P_{dgw}) of 3943 Pa and a residual water saturation (S_{rw}) of 0.087. Furthermore, the NAPL-water capillary pressure is assumed to be zero before NAPL starts to penetrate in the medium. Boundary conditions of the model have been set as:

for top surface: $q_w = 0$ and $P_a = 10^5$ Pa;

Lateral surfaces: u = 0 and $q_w = q_g = q_n = 0$; and

Bottom surface: u, v = 0 and $P_w = P_g = P_n = 10^5$ Pa.

While, q_w, q_g and q_n are rate of water, NAPL and air infiltration, respectively; and water table is assumed to be at depth of 5.6 m. The mechanical and hydraulic properties of the fine sand are an Elastic modulus of 10^7 N/m², a poison's ratio (ν) of 0.3, a porosity (ϕ) of 0.3, an intrinsic permeability (K) of 4.2×10^{-12} m² and a bulk modulus (K_s) of 6.1×10^8 N/m². Other properties selected for the simulation are the water viscosity of 1 cP, the NAPL-water displacement pressure (P_{dnw}) of 2717 Pa and the NAPL residual saturation of 0.02. In presence of NAPL, the water residual saturation is assigned equal to 0.08 and pore size distribution index is set equal to 1.95.

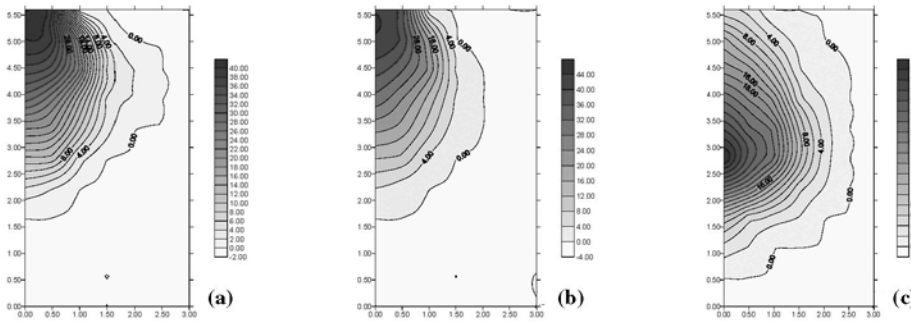

Figure 3: NAPL distribution for (a) Case I and (b) Case II of two initial unsaturated profiles; (c) NAPL distribution two months after start of the release

Inasmuch as simulation domain is axis-symmetric in geometry and loading, half of the zone has been contributed in the numerical solution and has been discretized in 60 elements. In order to study the short-term behavior of the system, the results of the model immediately after completion of release of the 1000 liter of NAPL in the medium are calculated. Figures 3(a) and 3(b) show the distribution of NAPL for cases I and II of initial saturation in the medium instantly after end of release. As it can be observed, an increase in degree of saturation of water in initial saturated profile cause the horizontal and vertical propagation of NAPL to decrease and the maximum concentration of NAPL to increase. In the study of long-term behavoiur of the system, the results of the model have been calculated for two months after the NAPL starts to release. The long-term distribution of NAPL in modelling area is displayed in figure 3(c) which is compatible with experimental results derived from centrifuge tests [3]. In order to study the effect of changes in permeablity of the medium on NAPL distribution, two other values for permeabilities have been considered. Figures 4 (a), (b) and (c) show the changes in long-term distribution of NAPL due to changes in the intrinsic permeability of porous medium.

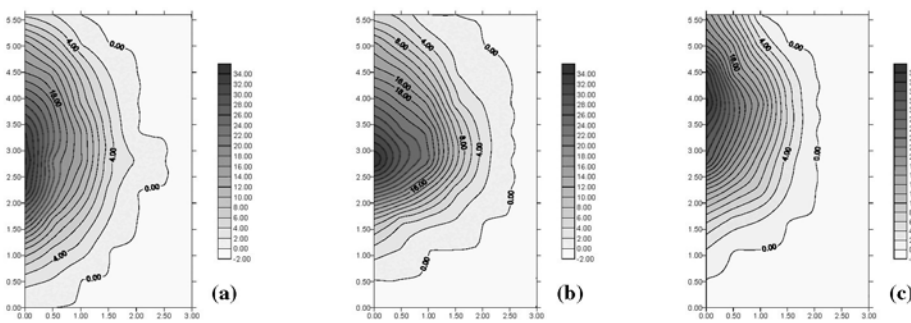

Figure 4: NAPL distribution 2 months after the start of release when, (a) K= 8.4×10^{-12} m², (b) K= 4.2×10^{-12} m² and (c) K= 2.1×10^{-12} m²

CONCLUSION

In regard to the dominant mechanisms of NAPL transport in the subsurface layers, the conceptual model and major factors influencing the migration of NAPL in unsaturated soil have been discussed. Then, based on the conceptual model and existing theoretical models, a mathematical formulation for NAPL transport phenomena in deformable unsaturated porous medium has been presented. The Galerkin's method with weighted residual approach then has been utilised to solve the set of nonlinear partial differential equations. The numerical model has been validated against well-known simple problems and then has been used in

solving a NAPL flow problem. The short-term and long-term results of the model have been compared to the results of an experimental model and good agreements have been observed.

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Leather tanneries hazardous waste dumping on open land in Pakistan

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ABSTRACT

Bentonite has been studied as an adsorbent for Cr(III) and Cr(VI) ions for its possible use for cleaning the waste effluents from the leather tanneries. The chemical and structural properties of bentonite were determined. The sorption of Cr(III) and Cr(VI)from aqueous solutions on bentonite has been studied by batch technique. Distribution coefficients (K_d) were determined for the sorption systems at different temperatures. Sorption data has been interpreted in terms of Freundlich, Langmuir and Dubnin-Raduskevich equations. Thermodynamic parameters for the sorption systems have been determined at different temperatures. The sorption of Cr(III)on bentonite is exothermic in nature while of Cr(VI) is an endothermic process. The heat of sorption, ΔH^o values for Cr(III)and Cr(VI) were -51.94 KJ/mol at 298 K and 5.619 KJ/mol at 293 K respectively. The mean free energy of sorption, E for Cr(VI) is 10 KJ/mol which shows that chromate ions from aqueous solutions having 10^{-5} to 10^{-3} M concentrations are predominantly sorbed on bentonite by an ion-exchange process. The sorption data for Cr(III) do not fit in the D-R equation. Negative values of ΔG^o show the spontaneity of the sorption processes; ΔG^o values of Cr(III) become less negative at higher temperatures which shows that sorption is less favoured at higher temperatures, while the increase in the negative values of ΔG^o of for Cr(VI) with the increase in temperature indicates that sorption is favoured at higher temperatures

INTRODUCTION

Uncontrolled industrialization in Pakistan since its creation in 1947 (Directory of Industrial Establishments, 1988; Khan, 1989) has resulted in the degradation of the environment. The waste water effluents from industrial establishments containing all types of hazardous substances including heavy metals are being disposed off either onto the open land or put into the natural water bodies directly or through the municipal sewage system (Hanif, 1990). These substances enter into the life cycle through various routes and have given rise to various types of diseases including cancer (Hussain et al., 1990, Hussain et al., 1992, Khan and Hussain, 1992). Disposal of industrial waste effluents containing heavy metals is a very big problem in Pakistan.

Many leather tanning units, varying from the cottage scale to big industrial units, are in operation in and around many big cities of Pakistan. They use big quantities of chromium salts for leather tanning. They are producing good variety of exportable leather, but only a few units have the facilities for the treatment of their waste water effluents containing chromium (VI) salts by the conventional method of reducing Cr (VI) into trivalent state followed by alkaline precipitation of Cr $(OH)_3$. The waste water effluents from most of these

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

tanneries are discharged onto the open land or put into the sewage system. These leather tanneries are one of the big source of chromium pollution in the environment.
Adsorption of soluble metallic species by clays, oxides and other colloidal matters appears to be an important means of controlling the soluble metal ions concentration in heterogeneous systems(Huang et al., 1974). Many adsorbents, are of mixed oxide type, and variation in composition profoundly influences their behaviour. Adsorption of Chromate ions on a single adsorbent (Panday et al., 1982), mixed adsorbent (Panday et al., 1984) and 1 : 1 mixture of Fly ash - wollestonite has been studied by Panday and Coworkers, 1984. Chromate ions adsorption on MnO_2 has been studied by Bhutani and Coworkers, 1992. No much work appears to have been done on the adsorption of Cr(III) and Cr (VI) on natural clays and sediments.

Bentonite because of its physical and chemical properties is considered as one of the most promising natural material as an adsorbent. The soil and clay minerals from different localities, because of the variations in their composition may behave differently, therefore, each soil or clay deposit, if it is to be used as an adsorbent for metals from aqueous solutions requires specific studies (Bangash et al., 1992, Khan, 2003).

To evaluate the feasibility of local soil and clays as an adsorbent for the industrial waste water effluents containing heavy metals, adsorption behaviour of Cr (III) and Chromate ions on local bentonite has been studied from aqueous solution at different temperatures. Adsorption isotherms have been analysed in terms of Freundlich, Langmuir and D-R equations. Thermodynamic parameters such as enthalpy of adsorption ΔH°, free energy change, ΔG°, entropy change, ΔS° and mean free energy of adsorption, E, have been calculated and are interpreted.

EXPERIMENTAL

Various bentonite samples were obtained through local clay contractors. The samples were picked up at random from individual big lots of bentonite collected by contractors from various localities. The samples were individually processed. This was done by first crushing the bentonite sample in a thoroughly cleaned jaw crusher. A steel roller was then used to homogenise the sample. It was then subjected to sampling by coning and quartering. Finally it was pulverised in a ball mill and sieved through - 250 mesh screen. Various physical, chemical and other structural properties of all the samples were determined.

Table No.1. Chemical analysis of bentonite from Shina Bagh.

Metal Oxides	Chemical Analysis (%)
Silica (SiO_2)	70.68
Alumina (Al_2O_3)	16.22
Lime (CaO)	4.62
Iron Oxide (Fe_2O_3)	3.21
Magnesia (MgO)	3.00
Potassium oxide (K_2O)	1.05
Sodium Oxide (Na_2O)	0.71
Titanium Oxide (TiO_2)	0.33
Chromium Oxide Cr_2O_3)	0.01
Vanadium Oxide (V_2O_5)	0.17
	100.00

On the basis of XRD, chemical analysis (table 1) and other characteristic properties (table 2) bentonite from Shina Bagh, Kala Chita Forest, Attock, Pakistan which contained montmorillonite as a major constituent and also contained some quartz was selected for sorption studies. All other samples were found to contain either mixed clays or were having

more sandy contents. Bentonite was used without any heat or chemical treatment for the sorption studies reported here.

Table No.2. Characteristics data of the bentonite.

Particle Size	:	ranged between 1.29 to 37.87 microns. Fifty percent were having 7.52 microns size.
Texture	:	Sand - 2% Silt - 74% Clay - 24%
Surface Area		
i) Normal Sample	:	34.027 m^2/g
ii) Sample heated at 110°C	:	27.446 m^2/g
Intrusion data summary (normal sample)		
Total Intrusion Volume	=	0.4923 mL/g
Total Pore Area	=	34.027 sq-m/g
Median Pore Diameter (Volume)	=	1.0091 μm
Median Pore Diameter (Area)	=	0.0060 μm
Average Pore Diameter (4V/A)	=	0.0579 μm
Porosity	:	49.23 %
Cation exchange capacity	:	151.96 m mol/100 g
Bulk density	:	0.75
Carbonate (Alkalinity)	:	6.5 (wt. %)
pH (20 : 1 solution/bentonite)		7.3
Organic matter	:	1.59%
Moisture content (heated upto 150°C)	:	14.00%
Major minerals	:	Montmorillonite and Quartz

1.0 Molar chromium (III) Stock solution was prepared by dissolving 40.015 g of $Cr(NO)_3.9H_2O$ (Merck) into 0.01 M HNO_3 solution and making the volume to 100 cm^3. 1.0 Molar chromium (VI) stock solution was prepared by dissolving 48.550 g of potassium chromate (Merck) into 0.1 M HNO_3 and making the volume to 250 cm^3. Chromium-51 ($t_{1/2}$ = 27.8 d) was supplied separately in oxidation states (III) and (VI) by the Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad. Radiotracer $^{51}Cr^{3+}$ was in 16 cm^3 of 0.1 HNO_3 solution, the metal content in the solution was 70 mg and its total activity was 74 MBq. Radiotracer $^{51}Cr^{6+}$ was supplied as Sodium Chromate containing 70 mg of Chromium in 5 cm^3 of 0.1 M HNO_3 solution, the total activity of the solution was 55.5 MBq.

Various spiked solutions of Cr (III) and Cr (VI) were prepared by taking known aliquots of the appropriate stock solution, adding a known volume of the radioactive tracer solution and making the volume to a known volume.

The pH of the solution was measured using microprocessor pH meter model H18417 by "Hanna instruments". The shaking was carried out in a thermostated shaker bath "Precision USA" model 25. The centrifugation was done with a Wirowka Type WE-1 Centrifuge machine at 4500 rpm. NaI (Tl) detector crystal size 3"*3", coupled either with a complete

counting assembly or 2 K multichannel γ - spectrometer and an IBM computer from EG & G ORTEC USA, was used for gamma counting.

The sorption of Cr(III) and Cr (VI) on bentonite was studied radiometrically by batch technique. The general method used for these studies is described below:
A known weight, i.e. 0.5g of the bentonite was equilibrated with 10 cm^3 of the metal spiked solution of known concentration in a stoppered Pyrex glass flask at a fixed temperature in a thermostated shaker water bath for a known period of time. The flasks containing the weighed amounts of bentonite and of metal spiked solutions were separately kept in the thermostated bath before mixing for a sufficient period of time to attain the desired experimental temperature. After equilibration the suspension was centrifuged in a stoppered tube for 15 minutes at 4500 rpm. Gross Gamma activity in 1 cm^3 of the supernatant was determined by scintillation counter. The activity of 1 cm^3 of reference solution was also recorded at the same time. The counting of the sample solutions was always done for a period of time to have counts which lie within 1-2% of statistical accuracy. The solution to solid ratio in all these experiments were 20:1. The pH of the solution was that of the supernatant which was obtained after equilibration. The amount of metal adsorbed, x, and the equilibrium concentration of Cr(III) or Cr(VI) in the solution, C_e, was always determined radiometrically, i.e. on the basis of the initial activity in the reference solution and the activity left in the solution after equilibrium. Adsorption of Cr(III) and Cr(VI) on the walls of glass flasks and centrifuge tubes were determined separately by running the blank experiments, this was found to be negligible. Sorption of these metals on bentonite were determined in terms of distribution coefficients, K_d or amount sorbed per unit weight of the sorbent, x/m. These are described below:
In the present study K_d values were determined radiometrically by using the following equation:

$$K_d = \frac{A_i - A_e}{A_e} \times \frac{V}{W} \ (cm^3/g) \qquad (1)$$

Where A_i and A_e are the activities of radionuclide in solution at the beginning and at the end of sorption respectively, V is the volume in cm^3 of the solution used for equilibration and W is the weight of adsorbent in grams.
Amount adsorbed per unit weight of the bentonite, x/m, was calculated radiometrically from the initial (known metal concentrations) and final activities of the solutions.

RESULTS AND DISSCUSION

Adsorption Isotherms

The adsorption isotherms for Cr(III) and Cr(VI) sorption on bentonite were obtained at three different temperatures by varying the metal bulk concentration in the solution from 0.01 to

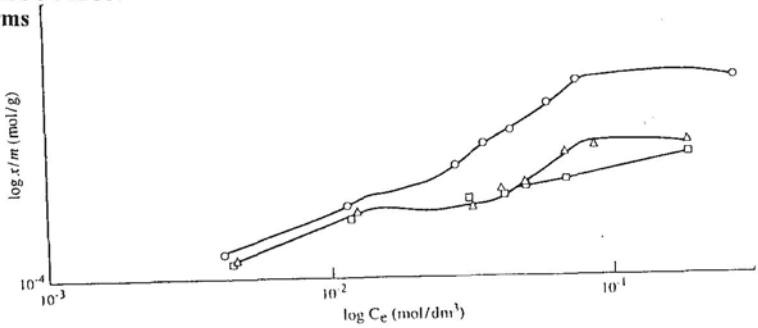

Figure 1. Sorption isotherms of Cr (III) on bentonite at different temperatures 298 K (O), 303 K (Δ) and 308 K (□) .

0.3 mol/dm^3 for Cr (III) and from 10^{-5} to 10^{-3} mol/dm^3 for Cr (VI), while keeping all other parameters i.e. solution to solid ratio 20:1, shaking time 30 minutes, and pH 3.5 for Cr(III) and pH 2 for Cr (IV). Figs. 1 and 2 show these results for Cr(III) and Cr(VI) respectively. The sorption results are analysed in terms of Freundlich, Langmuir, and Dubinin-Radushkevich (D-R) isotherms.

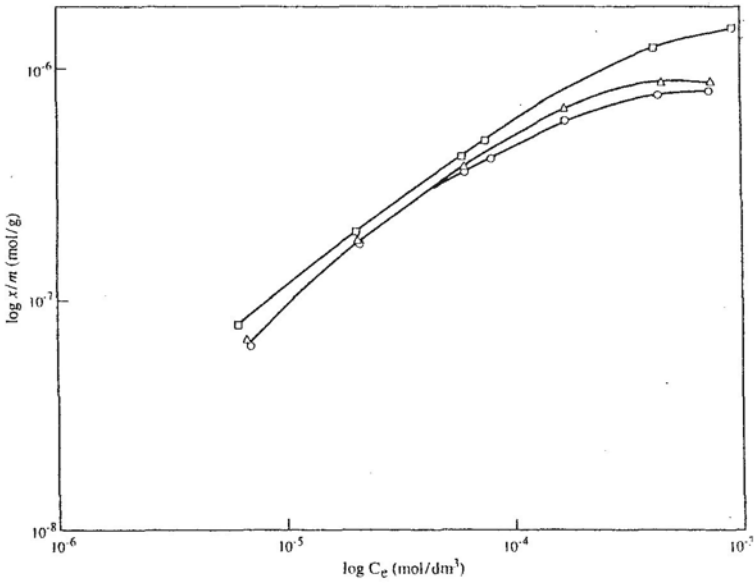

Figure 2. Sorption isotherms of Cr (IV) on bentonite at different temperatures 293 K (O), 303 K (Δ), and 313 K (□).

Data obtained for the sorption of metal ions in the concentration range from 10^{-8} to 10^{-2} mol/dm^3 for Cr (III) and 10^{-5} to 10^{-3} mol/dm^3 for Cr(VI) were fitted to Freundlich isotherm. The following linearized form of the Freundlich equation, was used for this purpose:

$$\log x/m = \log K + 1/n \log C_e \quad (2)$$

Where x/m is the amount of Cr(III), Cr(VI) sorbed per unit weight of the sorbent, C_e is the equilibrium metal concentration, 1/n is the constant for the system and K is a constant dependent on the temperature. A plot of log x/m against log C_e gives a straight line, the slope and intercept of which correspond to 1/n and log K respectively. Freundlich plots for Cr(III) and Cr(VI) are shown in Figs. 3 to 4. Linear regression gives a slope of less than 1 for all the three plots, indicating a concentration dependent sorption of Cr(III), and Cr(VI) on bentonite in the concentration range used. These results are similar to the sorption of some metal ions on illitic soil (Bangash et al., 1992). and various other adsorption systems.

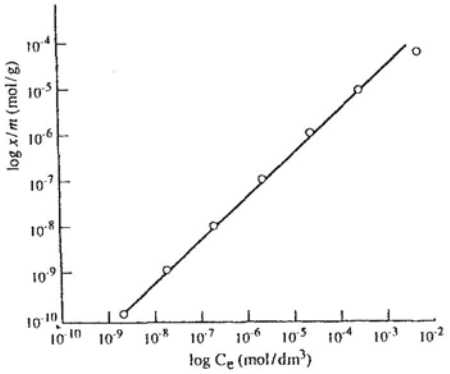

Figure 3. Freundlich plot for Cr (III) sorption on bentonite.

The sorption data for Cr^{3+} and Cr^{6+} in the concentration range used do not fit in the Langmuir equation.

Thermodynamic parameters

Thermodynamic parameters, i.e. heat of adsorption, ΔH^o, and entropy change, ΔS^o, for the sorption of Cr(III) and Cr(VI) on bentonite were calculated for each system by using the

following equation(Saleem et al., 1992).

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

The plots of ln K_d Vs 1/T for Cr^{3+} and Cr^{6+} are shown in Figs. 5 to 6 respectively. The values of ΔH° and ΔS° are obtained from the slope and the intercept of each plot. The free energy for the specific adsorption, ΔG°, was calculated by using the following well known equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

The values of the thermodynamic parameters for the sorption of Cr(III) and Chromate ions on bentonite are given in tables 3 to 4.

These results show that sorption of Cr^{3+} on bentonite is an exothermic process. The value of ΔG° for these processes becomes less negative with increasing temperature, which shows that sorption is less favoured at high temperatures. The decrease in the entropy, ΔS° in both these processes (tables 3) show that the sorbate ions are stable on the solid surface. Association, fixation, or immobilization of Cr^{3+} ions as a result of adsorption is attributed to a decrease in the degree of freedom of adsorbate ions which give rise to a negative entropy change.

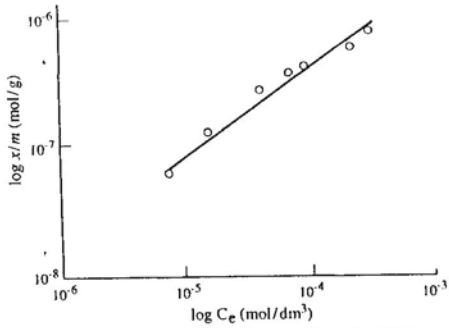

Figure 4. Freundlich plot for Cr (VI) sorption on bentonite.

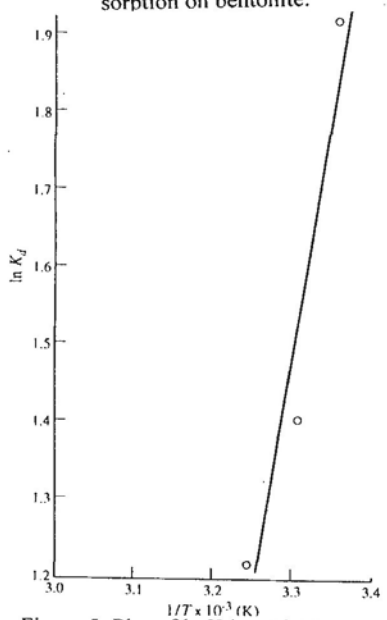

Figure 5. Plot of ln Kd vs 1/T for Cr (III) sorption on bentonite.

Table 3. The Values of the Thermodynamic Parameters for Cr^{3+} Sorption on Bentonite.

Temperature (K)	ΔH° (KJ/mol)	ΔG° (KJ/mol)	ΔS° (KJ/mol)
298	-51.94	-4.706	-0.1585
303	-51.94	-3.913	-0.1585
308	-51.94	-3.121	-0.1585

The positive values of ΔH° (table 4) show that the sorption of Chromate ions on bentonite is an endothermic process. The values of ΔG° becomes more negative with increasing temperature which indicates the spontaneity of the process, it further shows that the sorption is favoured at higher temperatures. For an endothermic process the entropy of the system must increase and the value of $T\Delta S^\circ$ should be more positive than the value of ΔH°, if the process is to occur spontaneously. The value of ΔS° for the sorption of Cr (VI) from 8×10^{-4} mol/dm^3 potassium chromate solution on bentonite is positive. The reason for the positive value of ΔS° in the sorption process of Cr(VI) is probably due to the increase in the translational entropy of the ions displaced from the bentonite compared with the entropy decrease due to the removal of Chromate ions from solution and their sorption on the solid.

This behaviour is different than what has been reported (Bhutani et al., 1992) for Cr(VI) sorption on MnO_2, but is similar to the sorption behaviour of some metal ions on various other materials(Saleem et al., 1992).

Table 4. The Values of the Thermodynamic Parameters for Chromate Sorption on Bentonite.

Temperature (K)	ΔH° (KJ/mol)	ΔG° (KJ/mol)	ΔS° (KJ/mol)
393	5.619	- 0.241	0.020
303	5.619	- 0.441	0.020
313	5.619	- 0.641	0.020

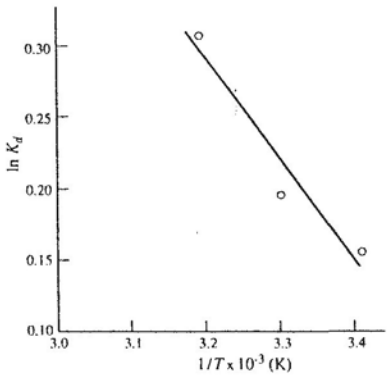

Figure 6. Plot of ln Kd vs 1/T for Cr (VI) sorption on bentonite.

The adsorption mean free energy, E, was calculated by using the following equation (Hobson,1969;Cerofolini, 1971).

$$E = (-2K)^{-1/2} \quad (5)$$

The value of K was calculated from the D-R equation.

$$\ln X = \ln X_m - K \epsilon^2 \quad (6)$$

Where X is the amount of solute adsorbed per unit mass of solid (mol/g). X_m is the sorption capacity per unit mass (mol/g). ϵ is polanyi potential = RT ln (1 + 1/C). C is the equilibrium solute solution concentration (mol/dm^3). R is the gas constant (Kj/deg mol). T is temperature (k). K is a constant related to the sorption energy (mol^2/kj^2).

The sorption data for Cr(III) in the concentration range studied, do not fit in the D-R equation. The plot of ln X against for Cr (VI) sorption on bentonite is shown in Fig.7. The D-R Parameters, X_m and K are calculated from the intercept and the slope of the line in Fig. 7. The values of these parameters and the value of E calculated from K value are given in table 5.

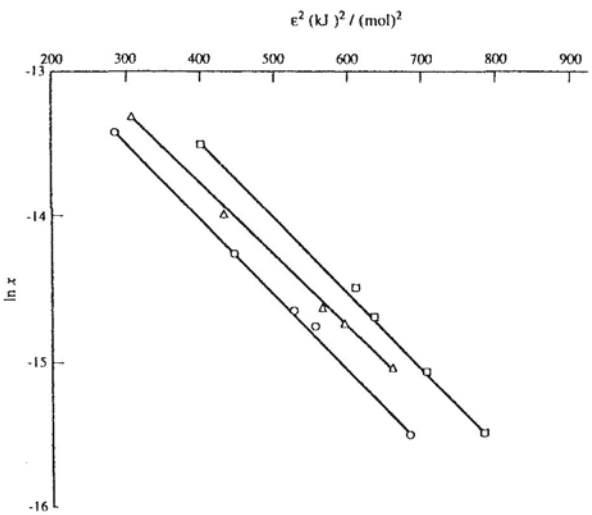

Figure 7. D-R plots of Cr (VI) on bentonite at different temperatures 293 K (O), 303 K (Δ) and (□) 313 K.

The value of E for Chromate sorption on bentonite (table 5) is about 10 KJ/mol at all the three temperatures studied, this is within the energy range for ion-exchange processes (Helferrich, 1962; Rieman and Walton, 1970) i.e., 8-16 KJ/mol. The adsorption capacity, X_m, of the bentonite for Cr(VI) sorption at 20 °C is 0.635 m mol/100 g which increases to 1.10 m mol / 100 g at 40°C.

These results show that bentonite can effectively be used for the removal of Chromate ions from the waste water effluents if the metal concentration is low and the pH of the waste effluents is adjusted to about 2.

Table 5. The Values of the D-R Parameters for Chromate (VI) Sorption on Bentonite.

Temperature (K)	K (mol^2/KJ^2)	E (KJ/mol)	X_m (KJ/mol)	(r)
293	-5.02×10^{-3}	9.98	6.35×10^{-6}	0.99
303	-4.81×10^{-3}	10.19	7.16×10^{-6}	0.99
313	-5.08×10^{-3}	9.91	1.10×10^{-5}	0.99

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Mass flux behaviour of DNAPL sources after insitu surfactant flushing remediation

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ABSTRACT
Past field studies have shown that complete removal of DNAPL by insitu remediation technologies is not possible in most cases. Accepting such limitations, there is a need to evaluate the risk of groundwater contamination after source remediation. To perform the evaluation, the mass transfer processes on DNAPL sources, which have undergone remediation must be known. It is considered that a better control of mass flux coming out of the remediated source zone leads to a better plume management including natural attenuation processes. The mass transfer processes are governed by various factors such as source geometry and morphology, NAPL saturation, and groundwater condition including local flow around the source zone. In this study, both soil column and tank experiments were conducted to quantify the dissolution behaviour of residual DNAPL sources of different geometries. Different levels of source zone removal were achieved by flushing surfactants in stages and the mass fluxes generated from the sources were measured at each stage of remediation. The experimental results show that the decrease in mass flux values are not proportional to the degree of DNAPL removal and the relative importance of source zone geometry and local groundwater flow condition on mass flux values is highlighted.

INTRODUCTION
Chlorinated solvents (such as TCE and PCE) used in industrial operations are one of the major causes of groundwater contamination. These compounds are slightly soluble in water and tend to exist as a separate organic phase called non-aqueous phase liquids (NAPLs). Since the density is often higher than that of water, they are known as dense non-aqueous phase liquids (DNAPLs). DNAPLs tend to exist as a separate phase below the water table in the subsurface (source zone as shown in Figure 1.). However, they slowly dissolve into the groundwater creating a contaminant plume and this dissolved concentration is often more than sufficient enough to exceed the maximum acceptable levels in consumption water. Therefore, a remediation method has to be applied to either remove the pure phase non-aqueous phase liquids (NAPLs) from the subsurface or control the contaminant plume.

Enhanced flushing technologies, based on flushing the DNAPL source zone with chemical agents such as cosolvents, surfactants and complexing agents, have been identified as an alternative to the basic pump and treat method. Addition of solubilisation agents to the flushing solution can remove DNAPL by increasing the apparent solubility of the DNAPLs as well as by mobilising the free phase due to decrease in the interfacial tension (Fountain et al., 1991).

Most past studies on surfactant flushing remediation focused on the degree of DNAPL removal and used the total percentage removal as the measure of its effectiveness. However,

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

the results of these studies have shown that 100% removal is highly unlikely in a reasonable time frame even in homogeneous one dimensional column cases. It is almost impossible to completely remove NAPL source in real ground by surfactant flushing (or perhaps any insitu methods) because of its complex subsurface condition (Soga et al., 2003). Therefore, the percentage removal is not a suitable index to assess the system efficiency.

In this study, the effectiveness of surfactant flushing is assessed by the change in the mass flux coming out from the NAPL source zone (see Figure 1) as the level of source removal was varied. The paper describes the laboratory experimental results that quantify the changes in mass flux before and after surfactant flushing of DNAPL sources. Different geometries and morphologies of DNAPL sources were created in 1-D soil columns and 2-D soil tanks. The mass flux values were measured at different groundwater flow velocities.

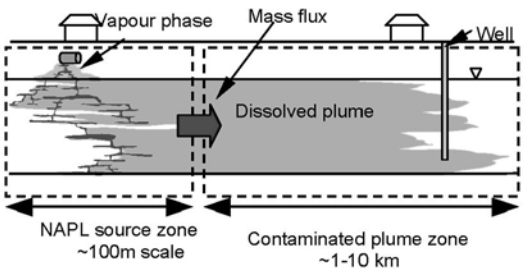

Figure 1: Source and plume zones of NAPL

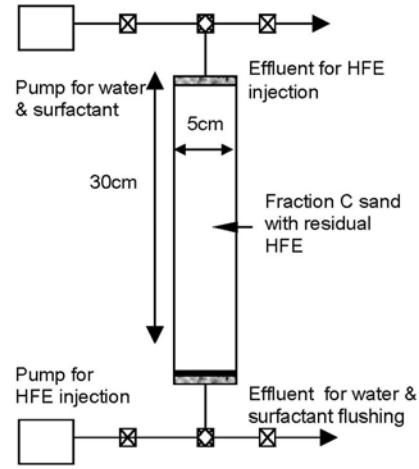

Figure 2: Experimental column setup

EXPERIMENTAL DETAILS

A typical experiment consists of (1) placing a DNAPL source in a soil column or sand tank, (2) measuring mass flux from the source zone at different groundwater flow velocities, (3) removing the source mass partially by injecting surfactant solution, and (4) measuring mass flux at different groundwater flow velocities after flushing out the surfactant solution. Stages (3) and (4) were repeated to obtain the relationship between mass flux and the amount of mass removed. Soil columns were used to simulate one dimensional flow, whereas sand tanks were used to achieve more realistic two dimensional flow condition (to allow flow bypass around the source zone) and to examine different geometries and morphologies of DNAPL source.

Soil column experiments

30cm long borosilicate glass columns with 5cm internal diameter were used for 1-D column experiments as shown in Figure 2. The column was filled with dry British Standard Fraction C sand (d_{50}=0.5 mm) in incremental steps to obtain uniform bulk density. In order to achieve a better water saturation CO_2 was injected before saturating the column with water. The column was then slowly saturated with deionised water from the bottom using a flow pump (flow rate = 0.25 ml/min). A model DNAPL, Methoxynonafluorobutane (HFE 7100), was then injected at a flow rate of 2ml/min from the bottom of the water saturated column until free phase HFE came out from the top. HFE, which is safe to be used in laboratory

experiments, has a density of 1.52g/cm^3, a molecular weight of 250.1 g/mol, and an aqueous solubility of 20 mg/l at 25°C. The column was then flushed with water from the top to obtain a residual NAPL saturation. The column was flushed with water initially at a slower velocity, 0.25ml/min, for 2 pore volumes and then at a higher velocity, 3 ml/min, for about 7-8 pore volumes. The residual NAPL saturation achieved was 18.2%.

After creating a residual saturation state in the column, the steady state aqueous HFE concentration (or mass flux) was measured at two different Darcy's velocities (0.5m/d and 1.5m/d). Aerosol 80 supplied by the Cytec Industries BV was used as the surfactant solution to remove the HFE entrapped in the sand column. One soil column was flushed with the surfactant solution at Darcy's velocity of 1.5m/d in 3 stages in 30 hours cycles. The other column was flushed at 0.5m/d for the same surfactant pore volumes as in the first surfactant cycle of the previous column. Each surfactant stage was followed by water flushing to remove the remaining surfactant from the column and then water flushing was continued at 0.5m/d and 1.5m/d to obtain the steady state aqueous HFE concentrations or mass flux values.

Two dimensional flow soil tank experiments

For the 2-D flow experiments, a soil tank with dimension of 175 cm (length) x 120 cm (height) x 8 cm (width) was used as shown in Figure 3. The tank is made of a steel frame. The front panel of the tank is made of glass while the back panel is made of Perspex to allow installation of sampling ports. Two wells were installed at both sides of the tank to inject and extract surfactant solutions. The bottom of the each well was connected to a constant head moving reservoir for controlling the groundwater flow rate inside the tank. On the backside of the tank, there are 180 sampling ports that can be used for aqueous phase sampling during surfactant flushing as well as water flushing. The sampling points are arranged in fifteen rows and thirteen columns.

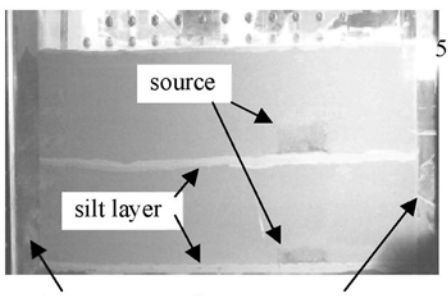

Figure 3: View of the soil tank

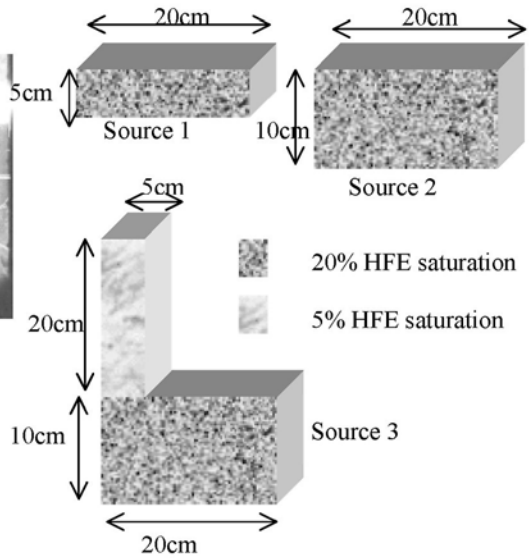

Figure 4: Source zone geometries used for 2-D tank experiments

Three DNAPL sources with different geometries (pool or pool+finger) and NAPL saturations (20% saturation for pools and 5% saturation for fingers) were created in the sand tank as shown in Figure 4. The sources were prepared externally by thoroughly mixing of predetermined amount of dyed HFE and damp Fraction C sand according to the geometry of the source zone; a similar technique was used by Brusseau et al. (2000). The source zones were placed on top of a less permeable silt layer. The tank was then filled with sand under water to achieve a fully saturated condition.

To measure the mass flux coming out from the sources, a water flow at Darcy's velocity of 0.5m/d was created across the tank. Aqueous phase samples were collected from all the sampling points when the flow reached the steady state condition. A water soluble dye was injected from the upstream well to evaluate the local groundwater flow condition inside the tank (flow bypass around the sources in particular), which allowed to quantify the mass flux generated from the sources using the measured steady state concentration values.

The tank was then flushed with Aerosol surfactant at 1.5m/d for 30hours. Similar to the column experiments, three surfactant flushing cycles were applied for each tank experiment. Each cycle consists of water flushing at 1.5m/d to remove the remaining surfactant from the tank followed by water flushing at 0.5m/d to obtain the steady state aqueous HFE concentration. During the surfactant flushing, liquid samples were collected from selected sampling ports to track the mass removed, whereas during the water flushing stage samples were collected at every sampling ports to obtain the spatial distribution of aqueous phase HFE concentration. At the end of the experiments, soil samples were collected to evaluate the final distribution of remaining DNAPL within the soil model.

RESULTS AND DISCUSSION

Soil column experiments

Various degrees of mass removal were achieved by injecting the surfactant in different rates and pore volumes. For example, Figure 5 shows the changes in the effluent HFE concentration with the amount of surfactant injected described in pore volumes. In the experiment, three cycles of 19PV surfactant injection were applied. In the first cycle, the effluent HFE concentration increased with injected surfactant volume and reached to a steady state. The effluent concentration remained constant for about 12PV of surfactant injection. When approximately 65% of total HFE was removed from the column, the effluent concentration started to decrease because the surface area of HFE in contact with the flowing aqueous phase decreased leading to limited mass transfer. Similar behaviour of effluent PCE concentration during surfactant flushing was observed by Pennell et al. (1994), Abriola et al. (1995), and Taylor et al. (2001). The effluent concentration behaviour during the second and third surfactant flushing cycles show that limited amount of HFE was removed; the HFE mass removed from the column during the third surfactant flushing cycle was only 0.17% of total mass.

Figure 6 shows the steady state HFE mass flux with different HFE removal levels. In the figure, the vertical axis is the normalised mass flux, which is the measured aqueous phase HFE concentration divided by the solubility limit, whereas the horizontal axis is the average HFE saturation, which is calculated from the remained HFE mass and the original source volume. At the residual saturation state before remediation, the normalised mass flux values were 0.80 and 0.88 at water flows of 1.5m/d and 0.5 m/day, respectively. The flux value decreased with the increase in aqueous flow velocity, indicating rate limited dissolution behaviour. These measured values are similar to the reported values. For example, Power et

al. (1992) measured a normalised mass flux of 0.85 for 16.5% residual Styrene saturation, whereas Miller et al. (1990) measured a normalised mass flux of 0.9 for 13.2% initial Toluene saturation at the same Darcy's flow (0.5m/d). They also observed the rate limited behaviour of dissolution.

The normalised mass flux decreases with HFE removal, but the decreasing rate is rather gradual until the average saturation becomes approximately 4%. The results show that 50% mass remove will not reduce mass flux to 50% of the pre-remediation mass flux. After reaching the average HFE saturation of approximately 4%, the aqueous HFE mass flux shows a sharp reduction even with small reduction in the average NAPL saturation.

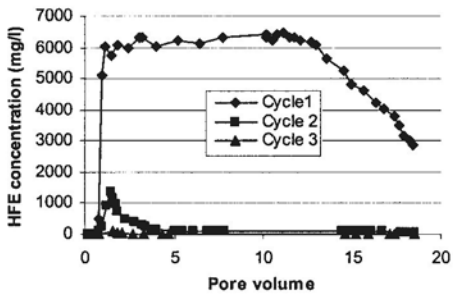

Figure 5: HFE break through curve during surfactant flushing at 1.5m/d

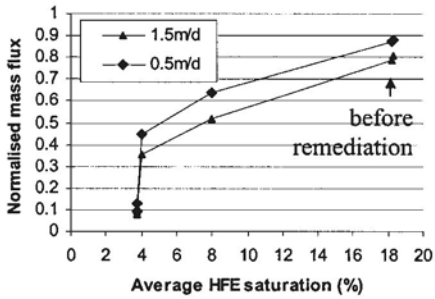

Figure 6: Normalised mass flux at different water flow velocities with average HFE saturation for column experiments

Tank experiments

Figure 7 shows that the mass removal rate during surfactant flushing for Source 3. Similar to the 1-D experiments, the HFE concentration initially increased with injected surfactant volume and remained at the steady state. The mass removal rate started to decrease after removal of 55% of the initial HFE mass and further injection of surfactant gave very low effluent concentration. The behaviour is similar for all three source cases.

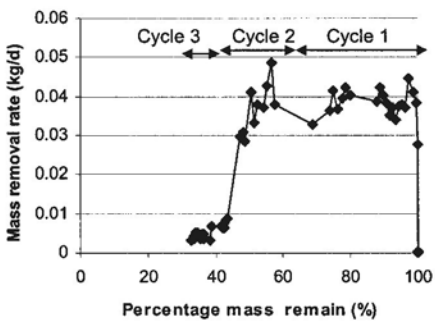

Figure 7: HFE brake through curve during surfactant flushing for source 3

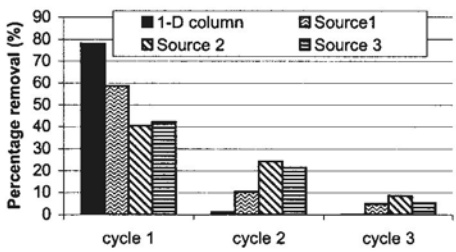

Figure 8: Percentage mass removed during each surfactant flushing cycle

In the 2-D tank experiments, 73.94%, 73.42% and 68.96% of the original HFE DNAPL were removed from Sources 1, 2 and 3 respectively after three cycles of 30PV surfactant flushing. Figure 8 shows that the percentage removal in each cycle for both 1-D and 2-D cases. The

results of the first cycle show that the removal efficiency for the two dimensional cases were smaller than that of the one dimensional case even though larger pore volumes of surfactant were injected in the two dimensional cases. The loss of NAPL-aqueous phase contact area due to remobilisation of free phase HFE and flow bypass around the source zone are contributing in deceasing the rate of removal. Within the two dimensional cases, the Sources 2 and 3, which had a thicker pool than Source 1, gave lower removal efficiencies. The finger in Source 3 had less effect on the removal efficiency than the thickness of the pool.

Figure 9 shows the steady state aqueous HFE concentration contours for Sources 1 and 2 before and at the end of each surfactant flushing cycle. The dissolution plume concentration distribution depends on the source height.

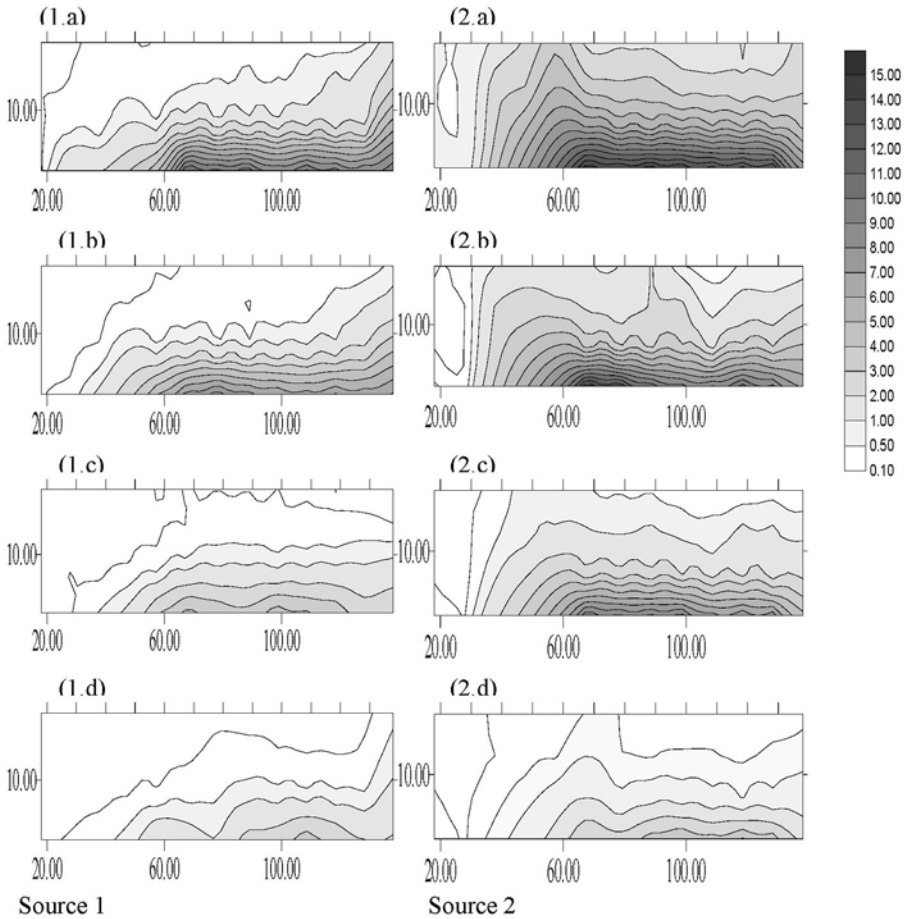

Figure 9: HFE aqueous concentration contours for source 1 and source 2 (a) Before surfactant flushing (b) After first surfactant cycle (c) After second surfactant cycle (d) after third surfactant flushing cycle.

Figure 10 shows the variation of the normalised HFE mass flux with the change in average NAPL saturation. To follow the same normalisation procedure used for the column experiment data, the following normalised mass flux (*NMF*) is proposed.

$$NMF = MF/(Cs \times FV \times A)$$

where *MF* is the measured mass flux (mg/day), *Cs* is the solubility limit (mg/m^3), *FV* is Darcy's velocity (m/day = 0.5 m/day in this case) and *A* is the cross sectional area of the source zone perpendicular to the groundwater flow (m^2).

Similar to the 1-D column data, the normalised mass flux reduces with HFE saturation. The mass flux value depends on source zone geometry. Source 3 shows lower mass flux values because of the finger makes the cross sectional area large. Sources 1 and 2, which simulated pool only, show similar mass flux behaviour after normalising the measured mass flux with the cross-sectional area. Similar to the 1D experimental data, the reduction in mass flux is not proportional to the NAPL removal; that is, 50% removal did not reduce mass flux 50%. A noticeable reduction in mass flux is achieved only when the average NAPL saturation becomes approximately 8%.

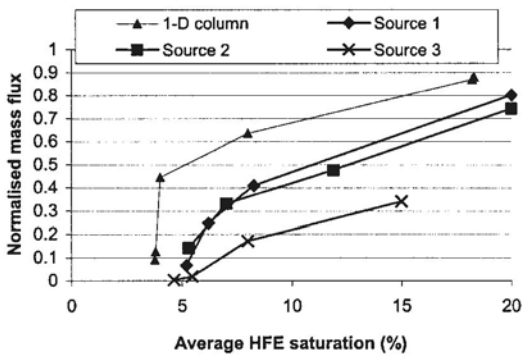

Figure 10: Variation of normalised mass flux with average HFE saturation

For a given NAPL saturation, the 1-D column data gives a higher normalised mass flux comparative to the 2-D source zone data. In the 1-D experiments, the water flow is forced through the column, whereas in the 2-D experiments, the flow can bypass the source zone due to smaller water permeability in the source zone compared to the surrounding non-source zone and hence the water travels through less resistant paths. Hence, it is expected that the 1-D condition gives a higher mass flux than that in more realistic 2-D flow conditions at the same NAPL saturation conditions.

CONCLUSIONS

In this study, it is proposed that the effectiveness of source zone remediation should be based not on the percentage removed, but on the reduction of mass flux achieved. Mass flux behaviour of residual DNAPL sources of different geometries and morphologies was investigated by 1D column and 2D tank experiments. After measuring the mass flux at different groundwater flow conditions, the DNAPL sources were subjected to partial removal by surfactant flushing remediation. Different levels of mass removal were achieved and mass flux values were measured at different removal stages. Both 1-D and 2-D results show that

the mass flux reduced with the removal of contaminant from the source zone. However, the mass flux reduction was not proportional to the mass removed and the rate of mass flux reduction with mass removal increased when the NAPL saturation was approximately 4% for the 1D column case and 8% for the 2D sand tank cases. For a given NAPL saturation, the mass flux in the 1-D flow condition was higher than that in the 2D flow condition. This is due to flow bypass of local groundwater around the source zone, reducing the contact area between NAPL and groundwater. The results show that the mass flux also depends on the groundwater flow rate, indicating rate limited behaviour. Although the findings are limited to DNAPL sources of simple geometry, the present data shows the importance of source geometries and morphologies as well as local groundwater flow on mass flux behaviour and possible relationship between source mass removal and mass flux. Further study is needed to upscale the current findings to more realistic field conditions.

ACKNOWLEDGEMENT
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Fate and Transport of Lead Pollution Along a Highway Corridor

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ABSTRACT
Annual source indicators for lead have dropped drastically with the phasing out of tetra ethyl lead as a fuel additive more than 15 years ago. Deposited lead concentrations along highway corridors continue to exceed the standard set in the B.C. Contaminated Site Regulation. The Ministry of Transportation and Highways is obliged to mitigate risks, without consideration of the mobility of the contaminant. This project was to determine whether it is acceptable to leave lead-contaminated roadside soil in place. Lead accumulations up to 1628 mg/kg were found in the highway soils. Lead contamination was found mainly in the top 0.3 m surface soil, with Pb concentrations rapidly decreasing to the background level at a depth of 0.6 m. The top 0.3 m contains more organic material and has a high adsorption capacity. Highway soils were found to have 3-10 times higher adsorption capacity for lead than the amount currently deposited on site. Therefore, it is unlikely that adsorption capacity will be saturated in the near future. Batch desorption tests using H_2O at pH 5.5 and a HNO_3 solution of pH 4.0 as leaching solutions indicated leachant concentrations below 2 ppm with a detection limit of 0.1 ppm. Despite the high total Pb concentration found in the soil, all sample leachants were below the B.C. Environmental Drinking Water Standard (10 ppm in solution). These results suggest that Pb has very limited mobility in highway soil and leaving the Pb contaminated soil in place may be acceptable.

KEYWORDS
Lead, mobility, highway, environment

INTRODUCTION
The main source of lead in roadside soils is vehicle emissions. In the early 1920s it was discovered that lead additives overcame the problem of incomplete combustion of gasoline in automobile engines and leaded-fuel gasolines quickly became standard. Leaded fuel in Canada was phased out in the early 1990s. However large accumulations of Pb remain in roadside soils worldwide. Even today, vehicles contribute lead to the environment, albeit at much reduced volumes, in the forms of lead in paint, lead release from tire and brake wear and naturally occurring lead in today's "unleaded" fuels (US Federal Highways 1998). Elevated soil Pb concentrations have been reported near roads in numerous studies worldwide. The most convincing direct evidence is derived from several studies of Pb

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isotope ratios, which conclude that car exhausts are the main source of the Pb contamination near roads (Alloway, 1995).

Lead is a very toxic element, which causes a variety of health effects at low dose levels. Chronic (long term) exposure to lead in humans results in adverse effects on the blood (anemia), central nervous system, blood pressure, kidneys and vitamin D metabolism. Children are particularly at risk because they absorb lead more readily than adults (ATSDR, 1993). The US EPA also classifies lead as a probable human carcinogen (EPA, 1993). Recent tests have shown that soil lead concentrations in excess of the provincially determined standard are present at a number of highway construction sites. British Columbia's Ministry of Environment, Lands and Parks uses the Contaminated Sites Regulation (CSR) to deal with the Ministry of Transportation and Highways' highway construction projects. In order to comply with the Contaminated Sites Regulation the Ministry of Transportation and Highways (MoTH) is required to conduct a site assessment whenever there is a possibility of disturbing contaminated soils. If soil lead concentrations within the construction limits of a project are above the CSR standard, risk mitigation is required. Presently, MoTH is obligated to mitigate risks by excavating and disposing of the contaminated soil present at each highway project at considerable cost. This is being carried out without consideration of a significant risk-determining factor, the mobility of the contaminant. The mobility of lead in the contaminated soils of the Willingdon and TransCanada Highway Interchange, Burnaby was studied. If the mobility is sufficiently low, leaving the contaminated soil in place may be acceptable. The legal requirement for risk mitigation would be met without the costly excavation and disposal of contaminated soil.

This study is focused on the evaluation of the mobility of lead in the roadside soils along a high traffic volume highway. It included: (1) the extent of current Pb contamination in surface and subsurface soils with respect to distance from roadside, depth and longitudinal distribution along the highway; (2) the leaching potential of samples; (3) optimum adsorption capacity of lead. The results are compared to the estimated remaining capacity against current input rates to determine whether soil will continue to sorb Pb in the future. The relationships between estimated soil adsorption capacity and the current Pb concentration (total Pb by aqua regia digestion), soil pH and total carbon content (Leco analysis) are observed.

MATERIALS AND METHODS

The selected site for this study is a high traffic highway section along the TransCanada Highway located at the Willingdon Interchange exit on Highway 1 in Burnaby, British Columbia. The sampling locations are shown in Figure 1. Sampling was carried out in mid-June, 1999. A track-mounted drilling rig supplied by MoTH was used to drill thirty-four boreholes at seventeen different points. All the drilling of boreholes was done by Mud Bay Drilling Co. Ltd., using a Marl Technologies truck and Geoprob technique. All boreholes were drilled to depths of 2.4 m, using the same drilling technique. The core diameter for all boreholes was 41 mm. Samples were taken every 0.1 m. A total of 139 soil samples were subjected to total metal analyses using Inductively Coupled Plasma (ICP) to determine the metal concentrations in highway roadside soils. Four borehole samples were selected for detailed study of their soil characteristics to provide a good overall representation of the site in question.

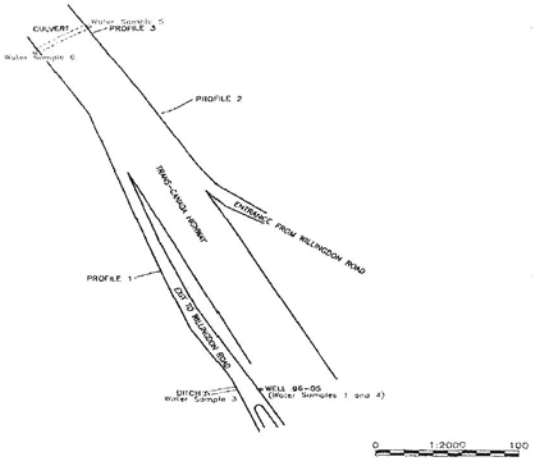

Figure 1 Sampling locations

Characterisation of Surface and Subsurface Soils

X-ray diffraction (XRD) was employed for mineralogical characterization. The fine fraction, particle-size <74 μm, was subjected to XRD analysis. The slides were prepared as described in Kittrick and Hope (1963). The XRD analysis was then conducted over a range of 3-70° 2θ with CuKα radiation on a standard Siemens D5000 Bragg-Brentan Diffractometer and the Siemens Kristalloflex (Germany). Combined analyses were used – sieve analysis for measuring particles coarser than 53 μm and a SediGraph for particles finer than 53 μm. Surface areas of samples were determined using the B.E.T. method for the external area of soil and ethylene glycol monoethyl ether (EGME) method for the total surface area (Sheldrick, 1984). The organic content in the surface and subsurface soil was determined by means of a Leco induction furnace equipped with a carbon analyzer.

Batch Adsorption Capacity Determination

The batch equilibrium test (USEPA 1987) with 1 g : 10 ml soil:solution ratio was used to determinate the heavy metal adsorption isotherms of the soil. Lead nitrate solutions of various concentrations at pH 3.6 were used to ensure that no precipitated forms of lead were introduced in the adsoption process. Duplicate samples were prepared for each concentration to verify reproducibility, and a kaolinite sample of known adsorption properties was also analysed to verify the accuracy of the test and for QA/QC. The nominal Pb^{2+} ion concentrations (expressed in ppm, i.e. mass/vol) in each set of solutions were 0, 50, 100, 150, 250, 500, 750, 1000, and 2000 ppm for all samples from boreholes BH2, BH5, BH13 and BH16 at depths from 0 to 2.2 m. Samples were shaken for 24 hours for equilibration, and then centrifuged for 15 minutes at about 2000 r.p.m. in a Beckman GS-6 centrifuge to separate the solids and supernatant in order to determine lead concentrations using a Video 22 Thermo Jarrell Ash aa/ae Spectrophotometer - Model 957 (AAS) and pH using an Orion model 1 420A pH meter.

The heavy metal sorption concentration for the sorbent is calculated from the equation:

$$q_a = \frac{(C_i - C_f) * V}{M} \qquad (1)$$

where q is the lead sorption concentration (mg/kg) obtained from a batch adsorption test, C_i is the initial concentration of prepared lead nitrate solution measured by AAS for its actual concentration (ppm), C_f is the equilibrium (final) lead concentration in solution after 24 h of shaking (ppm), V is the volume of lead nitrate solution (L) in the batch test, and M is the equivalent dry mass of the soil sample (kg).

Batch Leaching (Desorption) Test

Batch equilibrium tests were adopted to evaluate the mobility of the lead. This test involves a more aggressive extraction technique than the column leaching test because the soil is in suspension, with each grain in direct contact with lead solution. The results from this test are therefore more conservative than those from a column leaching test. The other advantage of a batch-leaching test is that it requires a relatively short time to achieve optimum leaching information. All batch desorption tests followed the same procedures as the batch adsorption test (USEPA, 1987). Distilled water (pH 5.5) and nitric acid (HNO_3) at pH 4 were used as the leaching solutions to simulate normal precipitation and acid rain conditions, respectively. Lead concentrations leached out in the desorption tests were compared with the total lead content in the soil to determine the availability and mobility of lead under different leaching conditions.

RESULTS AND DISCUSSION

Nature and Extent of Lead Contamination

A typical distribution of Pb in relation to depth in the field situation can be observed in Figure 2. The Pb is deposited mainly in the top 0.3 m of the soil along the highway corridor, consistent with the past records from MoTH. Pb concentrations in all boreholes dropped to background levels by 0.6 m depth. The average abundance of Pb in the earth's crust is 15 ppm. The pH values were uniform – almost all between pH 5.0 and 6.5. The borehole samples show an increase in moisture content at depths below 0.5 m. The moisture content is high at the surface horizons. In the borehole set, the carbon content is highest in the surface horizons and decreases with depth. This top 0.3 m of soil contains comparatively high carbon contents, primarily due to organic carbon. The decrease in concentration of Pb found at depths below 0.3 m drops to background level at a depth of 0.6 m. This trend may be due to the fact that the soils have an adsorption capacity that is much higher than the accumulated soil lead concentration found on the site. It also indicates that Pb is strongly bound to the soil.

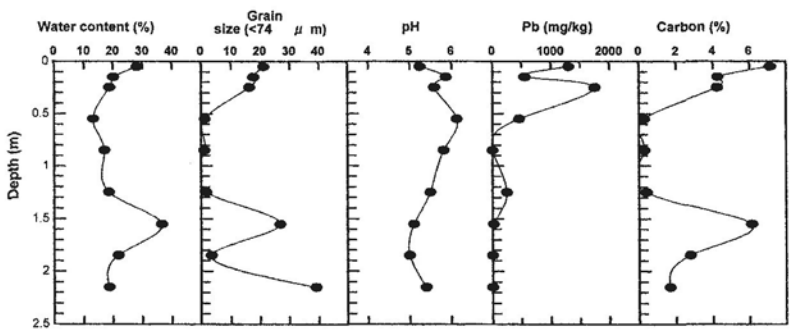

Figure 2 Typical borehole profile for Pb retained on site and soil properties as a function of depth

Retention capacity of roadside soil

The typical batch adsorption isotherm results for the top 0.3 m samples are shown in Figure 3. The maximum Pb adsorption values of the soil samples are summarized in Table 1 under the column "spiked[(2)]". The highest value under the field[(1)] column represents the accumulation of all Pb deposits between the construction of the interchange in 1963 to the present, an estimated 26 years of leaded gasoline emissions. Compare these two columns (field and spiked), the adsorption capacity values ranged from 3 to 10 times the highest 1628 mg/kg soil Pb concentration found on the site. With final phase-out of leaded gasoline in the late 80s in Canada, source inputs have decreased dramatically. Therefore it is unlikely that sorption capacity will be reached in the near future.

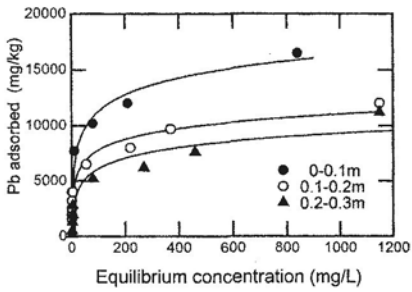

Figure 3 Typical batch adsorption isotherm for the top 0.3m samples

Table 1 Summary results of batch adsorption and desorption tests

Sample #	Soil pH	Field [(1)] Pb (mg Pb/kg soil)	Spiked [(2)] Pb sorbed (mg Pb/kg soil)	H_2O at pH 5.5 Pb conc. in solution (ppm)	H_2O at pH 5.5 Leachated (mgPb/kg soil)	H_2O at pH 5.5 Equil. pH	HNO_3 at pH 4.0 Pb conc. in solution (ppm)	HNO_3 at pH 4.0 Leachated (mgPb/kg soil)	HNO_3 at pH 4.0 Equil. pH
L2- 0.0-0.1	5.82	1393	9784	0.33	4.38	5.74	0.34	4.51	5.80
L2- 0.1-0.2	5.65	755	7958	0.70	9.19	5.99	0.35	4.59	5.82
L2- 0.2-0.3	6.52	100	2469	0.01	0.11	6.71	0.15	1.73	6.44
L5- 0.0-0.1	5.89	1423	10292	0.41	5.21	5.96	0.32	4.04	5.91
L5- 0.1-0.2	6.31	1170	7367	1.01	11.87	6.30	0.61	7.22	6.11
L5- 0.2-0.3	6.40	279	4174	0.52	6.07	6.44	0.33	3.80	6.22
L13-0.0-0.1	5.25	1150	9704	0.01	0.14	5.37	0.20	2.86	5.35
L13-0.1-0.2	5.88	575	7949	0.61	7.62	5.98	0.50	6.30	5.98
L13-0.2-0.3	5.73	1628	3940	2.04	25.04	5.86	1.29	16.12	6.13
L13-0.5-0.6	6.14	460	2461	0.90	10.32	6.26	0.96	11.16	6.09
L16-0.0-0.1	4.96	978	5896	0.25	3.28	5.10	0.31	4.07	5.14
L16-0.1-0.2	6.30	449	4378	1.15	13.05	6.40	1.16	13.11	6.40
L16-0.2-0.3	5.44	439	4782	0.15	2.03	5.53	0.37	5.00	5.37

Note: [(1)] Original field concentration of Pb

[(2)] Spiked condition: maximum adsorption of Pb from adsorption isotherm

Relationship of soil properties and Pb adsorption capacity

To what extent does adsorption capacity correlate with total Pb concentration, soil pH, silt and clay, and total carbon content? Figure 4 shows that absorption capacity equilibrated with 100 ppm solution is significantly correlated with the carbon content. The 100 ppm

level for the equilibrium concentration is chosen based on the B.C. Environment Water Standard for Livestock (100 ppm).

To remove the retained Pb, the energies of interaction with the soil must be weakened or overcome; or another agent must compete with the soil for sorption of the Pb (e.g. the use of organic ligands, which have a high affinity for heavy metals). To demonstrate the potential of Pb release in the rainy season and an acid rain situation, the batch equilibrium test was used to determine the desorption of Pb.

Leachability and mobility of Pb in roadsoils

These tests were conducted with soil in suspensions shaking for 24 hours. This permits one to determine how strongly the Pb is held by the soil. The results of batch desorption test on the originally Pb-contaminated soils are shown in Table 1. In all 13 samples tested using H_2O at pH 5.5 and HNO_3 at pH 4.0, the leachant concentrations were below 2 ppm. The results indicate that none of the samples has lead leaching resulting in equilibrated solution concentration higher than the B.C. Environmental Drinking Water Standard (10 ppm in solution). This is in spite of the high total Pb concentration found in the soil, as high as 1628 mg Pb per kg soil. Thorough mixing and low soil:solution ratio in the leaching test likely overestimated leaching. More soil surface (surface charge) sites were available for attack by the nitric acid and Na-exchange of Pb than would occur in the field (EPA 1999, Harter and Naidu 2001). The results suggest a low likelihood of significant leaching, even under aggressive acid conditions and with a conservative test. Removing lead from soil requires high energy to overcome or weaken the energies of interaction (Li et al 2001). Even strong acid may not be effective in removing Pb from a certain soil fraction (Li and Li 2000).

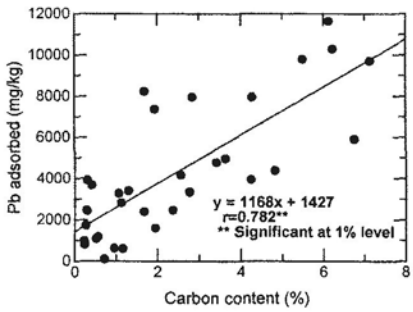

Figure 4 Relationship of organic carbon and Pb adsorption

Batch equilibrium testing is a simple and quick method of acquiring desorption-based information. The results suggest that leaving the Pb contaminated soil in place may be acceptable.

CONCLUSIONS

- Significant Pb accumulations of up to 1600 mg/kg were found in the soils along the highway corridor of Willingdon and Highway 1 interchange site. The distribution of Pb contamination followed the characteristic distribution from the literature. Soil Pb concentration rapidly decreased to background level at a depth of 0.6 m. Soils at the top 0.3 m contained more organic soil materials and they have high adsorption capacity.

- Estimated adsorption capacities of 13 samples from 4 borehole locations subjected to the batch adsorption test ranged from 2500-10000 mg of Pb/kg of soil. Estimated capacities are 3 to 10 times higher than the soil Pb concentrations found on the site. Given that leaded gasoline was the primary source of Pb contamination, it is unlikely that the sorption capacity of the soil for Pb will be reached in the near future.
- The batch desorption tests on 13 samples using H_2O at pH 5.5 and HNO_3 at pH 4.0 indicate that leachant concentrations were below 2 ppm, with a detection limit of 0.1 ppm. Despite the high total Pb concentration (up to 1628 mg Pb per kg soil) found in the soil, all samples' leachants are below the B.C. Environmental Drinking Water Standard (10 ppm in solution).
- Soil organic materials have a significant positive correlation with Pb retention. Therefore, addition of organic matter is recommended as a remedial or preventive measure to help deal with lead contamination.

AUTHORS CONCERNS AND COMMENTS

Concern over exposure to lead is certainly justified. Roadside soil has been identified as a significant source. However, a risk is only present when there is an operable pathway between the source and the receptor. There are chain-link fences and right-a-way land running along both sides of the highways. No residential activities, commercial activities or sensitive ecological species are expected, especially in the vicinity of the busy highway interchange. Therefore, oral ingestion and dermal contact of soil is not considered to be a real risk. Any inhalation of roadside soil would be negligible compared to inhalation of the source vehicular emissions present when traffic conditions make the interchange a virtual parking lot. The remaining pathway to ecological and human impact is leaching. Leaching of Pb from soils is controlled by its sorption behaviour. Unfortunately, in many countries in Asia and South America, there are commercial, residual and farming activities immediately adjacent to the highways due to limited land uses. In such cases, oral ingestion and dermal contact of soil will be a real risk. The uptake of heavy metals by plants, worms, birds and other animals could also be a risk. Plants can adsorb and translocate available Pb from nutrient solution (Jaworski 1978). Pb absorbed by a plant tends to accumulate in the roots. The amount of Pb adsorbed by a plant relative to the concentration of Pb in soil solution is known as bioavailability. One approach to estimate the environmental impact of Pb in soils is to determine the bioavailability of the Pb in contaminated soil. Even when ingested, only a portion of the total Pb in soil is absorbed by the receptor of concern.

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Lead transformation in the environment of small-arms firing ranges.

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ABSTRACT

Toxic levels of lead (Pb) are often found in soils of army training facilities. This is a result of bullet build-up in and around impact areas. This study was performed in order to assess Pb contamination in the soils of six firing ranges located in California and New Jersey. The soils tested have differences in pH and they range from acidic (pH~4.5) to alkaline (pH~8.75). In some samples, total Pb values were as high as 49,228 mg/kg. Toxicity characterization leaching procedure (TCLP) experiments were conducted to examine Pb mobility. The results from these experiments showed that the soil leached more Pb than acceptable under EPA regulations. TCLP-Pb in surface samples was as high as 594 mg/L. The metallic Pb present could have been transformed into different weathering products, which would determine Pb solubility and bioavailability. Sequential extractions of the different berm soils will determine the amount of readily available Pb as well as the amount of potentially available Pb and Pb that has been transformed to non-labile forms. The following phases were identified: exchangeable, carbonate, iron and manganese oxides, organic matter and sulfides and residual bound- Pb. The majority of Pb in most locations was found in the carbonate phase of the soils. Soils with a high buffering capacity did not follow this pattern and released the majority of Pb with the Fe-Mn oxides phase of soils. In two of the ranges tested up to 20% of the leached Pb was associated with the exchangeable phase, which indicates that Pb is highly bioavailable in the soils. Remediation techniques such as phytoremediation and chemical washing are recommended for some of the ranges based on the results of this study.

INTRODUCTION

Lead (Pb) is an essential commodity in the modern industrial world. With properties such as a low melting point, ease of casting, high density, low strength and chemical stability, Pb has many uses in every day applications such as in storage batteries, ammunition, pigments plumbing etc. However, as a result of Pb's adverse health effects, even at low levels of exposure, many of the traditional uses of Pb have been phased out in recent decades (Scheuhammer and Norris, 1995).

Lead is deposited at firing ranges as spent Pb bullets in soil berms. Since Pb is not insoluble in a soil environment, Pb concentrations, in firing ranges around the world, have been measured at levels greater than 10,000 mg/kg (Rooney, 2002). While some bullets may remain intact upon impact, a considerable amount of metal particulates is generated as a result of the shock and abrasion with the soils.

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Bullets fired from different kinds of weapons (shotguns, pistols, rifles) will make impact with berm soils at different velocities (Batelle, 1997). Rifle bullets, which are fired at the highest velocity, generate the greatest amount of fine particulates, while low velocity shotgun shots generally cause no fragmentation (Batelle, 1997). Due to its instability in soil environments, metallic Pb will become oxidized. As it oxidizes, corrosion products and crust materials form on Pb particles. These crusts are composed of various Pb compounds, predominantly cerussite, hydrocerussite ($Pb(CO_3)_2(OH)_2$) and small amounts of anglesite. Lin et al. (1995) found that 4.8% of the metallic Pb in deposited pellets had been transformed to Pb carbonate and Pb sulphate, within a period of 20-25 years. Finer metallic Pb particles that have a greater surface area will transform even faster. Lead compounds show the greatest aqueous solubility within the acidic (pH <4) and alkaline (pH>11) ranges (ITRC, 2003; Scheuhammer and Norris, 1995). Therefore, acidic soils and surface waters will enhance the process of chemical weathering and increase the amount of dissolved Pb. Areas with high annual precipitation rates will enhance the transport of dissolved and particulate Pb. Low organic carbon content will have a similar enhancing effect since organo-complexes trap Pb, thus limiting its mobility and availability. Sequential extraction techniques are an important tool for the operational characterization of the different chemical pools, which contribute to Pb immobilization and determine its fate and transport in the soil and in surface and groundwater. A sequential extraction technique was applied to soils from six different firing ranges, which receive a variety of weapons and have a different texture and chemical composition. The main objective of this study is to determine the effect of those parameters on Pb partitioning and the fate of Pb in these soils. The chemical "pools" that effectively or ineffectively bind Pb in these soils will determine possible remediation practices for the effective reuse or safe disposal of these soils. Some of the modern remediation alternatives used in range soils are phytoremediation and soil washing technologies, which involve physical and/or chemical extraction.

SAMPLING AND METHODS

Soil samples were taken from the surface of the berm (backstop) at 6 different firing ranges. The firing ranges are located in 2 different geographical areas (California and New Jersey, USA) and their parent soils have different geotechnical and chemical characteristics. The ranges sampled were: Goldstone and Range 5 (Mojave Desert, California) and several New Jersey army training facilities: the Armaments Technology Facility (ATF) and Marine Range (indoor facilities, Picatinny Arsenal) and Range 15 and Range 26 (Fort Dix). Soil pH was measured using the ASTM standard (ASTM D4972-89). Total metal concentrations were measured according to USEPA methods 3050B and 6100. Lead leachability from the soil samples was determined using the Toxicity Characteristic Leaching Procedure (TCLP), EPA method 1311. Lead speciation in the soils was determined using the sequential extraction method (SEQ) of Tessier et al., 1979 (Table 1). The samples were finally analyzed by ICP-OES (Varian Vista-MPX).

Table 1. Summary of "Tessier" method.

Hypothesized soil fraction attacked	**Reagents used**	**Reaction time**
loosely adsorbed such as on clays	1 M $MgCl_2$, pH 7, room temp. 8mL	1 hour
carbonate some hydroxides	1 M CH_3COONa, pH 5, room temp., 8 mL	5 hours
Mn and Fe oxides	0.04M $NH_2OH{\cdot}HCl$, in 25% (v/v) CH_3COOH, 96°C, 20mL	6 hours
Organics and sulfides	30% H_2O_2, pH 2 with HNO_3, 85°C, 1.2M NH_4COOH, room temperature 20mL	5 hours 30minutes
Residual	EPA method 3050B	

During SEQ, the different fractions of the soil attacked are "operationally" defined as: exchangeable, carbonate, Fe-Mn oxides, organic matter and sulfides and the residual phase. At each step of this procedure, the same soil aliquot is treated with progressively more aggressive chemical reagents. Lead's bioavailability will decrease with the order of the extraction sequence. Hence, the first step will bring into solution metals that are readily dissolved by mild extractants such as a neutral salt solution (1M $MgCl_2$ used here). The next three steps will bring into solution the potentially available metals. Though not immediately available, these metals may become available through shifts in pH and redox potential. The second step extracts metals bound to carbonates and specifically adsorbed phases that become mobile upon a pH decrease. The remaining three fractions are generally strongly held and are normally not available to plants (Li et al., 1995). If fresh metallic Pb is present in the soil, it is expected to leach at the last, residual phase.

Soils from Range 5 and Goldstone were also sieved and segregated according to different particle sizes. The particle size groups were as follows: -#4+#10, -#10+#40, -#40+#200, -#200+#400 and -#400. These groups correspond to the following designations: coarse sand, medium sand, fine sand, silts and clay size soils. This was done in order to examine the association of Pb with the various "operationally" defined groups of Pb partitioning relative to soil particle size.

Soils from the other firing ranges were not separated into different particle size groups, and were examined as a whole either as -#4 or -#10 material. The exact processing method was chosen based on the quantity of metallic pieces that passed through each screen. If a significant amount of bullet remains were identified in the #10 material, this particular screen was used as the starting point of the soil testing. Otherwise, the #4 material was used. Any bullet remains were removed from the soils before chemical extraction.

All the soils tested were divided in two groups. One group was processed after mechanical pulverization whereas the second as is, with no additional pulverization. This way any artifacts caused by applying the SEQ to fine particle size soils could be determined. Also metallic Pb of different particle sizes from coarse to fine was subjected to SEQ. The effect of the particle size of metallic Pb on Pb leachability at each step of the SEQ were quantified. The different particle size of metallic Pb tested were: Lead shot (1-3mm), lead granules ~30mesh, lead shot <0.5mm, lead powder (-100 mesh), and lead powder (-325).

RESULTS AND DISCUSSION

Table 2 presents the pH, water content and the concentration of major elements (Al, Ca, Mg, Fe, Mn) in the soil.

Table 2. Selected chemical and geotechnical properties of the range soils

Firing Ranges	Water content (%)	Soil pH (1:1) water to soil	Al mg/kg	Ca mg/kg	Fe mg/kg	Mg mg/kg	Mn mg/kg
Range 5	2	8.3	9440	10609	11320	3165	171
Goldstone	6	7.5	22009	12249	24920	7487	509
ATF	4	8.7	10644	3511	15638	1385	148
Fort Dix R 15	1	4.4	2407	203	1978	60	6
Fort Dix R 26	2	4.8	6350	307	6047	68	5
Marine Range	0	7.3	2247	235044	5562	17010	252

The pH of the soils ranged from 4.4 to 8.7. It is expected that Pb mobility will be affected by soil pH. Concentrations of Ca and Mg were very high, 235,044mg/kg and 17,010mg/kg, respectively, in Marine Range relative to the other locations where concentrations of Ca and Mg were less than

12,249mg/kg and 7,487mg/kg respectively. This occurrence is probably related to the presence of calcite ($CaCO_3$) dolomite ($Ca,Mg)CO_3$ in Marine Range soils. As a result of the high dolomite content, the buffering capacity of these soils is expected to be high. Soils from the Goldstone range had the highest concentration of Fe and Mn, 24,920mg/kg and 509mg/kg respectively. High levels of Fe and Mn oxides and hydroxides will also limit Pb availability in the environment because of the high sorption capacity of these substrates. Goldstone soils also had the highest water content, which is attributed to the high clay mineral content in these soils (Dermatas et al., 2003).

The acidic soil pH in Fort Dix soils may result in the dissolution of Pb precipitates, thus increasing the bioavailability of Pb. Lead concentrations in all soils ranged from 1,025 to 49,228 mg/kg and TCLP Pb concentrations ranged from 10 to 594mg/L. The results presented in Table 3 indicate that Pb concentration in all sampled soils was above the New Jersey standard of 400mg/kg for soil intended for residential use. Lead concentrations were also above the 1000mg/kg limit of California's Code of Regulations for the Total Threshold Limit Concentration (TTLC) in soils in Range 5 and Goldstone (Table 3).

Table 3. Total Pb (mg/kg) and TCLP Pb (mg/L) in berm soils from different firing ranges.

Firing Ranges	Pb (mg/kg)	TCLP Pb (mg/L)	TCLP to total Pb ratio (%)
Range 5	10542	420.6	79.8
Goldstone	3530	81.9	46.4
ATF	27417	594	43.3
Fort Dix R 15	1025	50.2	97.9
Fort Dix R 26	3196	117.8	73.7
Marine Range	49228	10.0	0.4

The ratio of TCLP Pb to total Pb could reflect the mobility of Pb in the firing range soils (Cao et al. 2003). In the soils sampled, this ratio ranged from 0.4 to 97.9%. The lowest ratio was observed in the soils with the most elevated Pb concentration (Marine Range), which indicates that Pb leachability is a complicated process and not solely related to a high total Pb concentration. At Ranges 15 and 26 in Fort Dix, New Jersey, where soil pH was below 5 (Table 3), the ratio of TCLP to total Pb was the highest among the ranges studied herein.

In size fractionated samples from Range 5 and Goldstone the majority of Pb was found in the carbonate pool of the soils (Figures 1 and 2). This is more evident in Range 5 (Figure 1) than in Goldstone soils (Figure 2).

Pb partitioning was similar in both pulverized and non-pulverized soils at the particle size fractions that passed through the #40 sieve. However, differences were observed among the coarser fractions. These differences are not only in the chemical association of Pb in the soil but in the mass balance of Pb in each soil fraction. In Range 5, total Pb concentration in the coarse sand fraction (-#4+#10) of the pulverized samples was 637mg/kg, but only 34 mg/kg in the non-pulverized samples. Pb concentration in the medium sand fraction (-#10+#40) was 12865mg/kg in the pulverized samples and only 4589mg/kg in the non-pulverized samples. The distribution of Pb in the pulverized samples of the medium sand fraction is as follows (in descending order of Pb concentration): carbonate, Fe+Mn oxides, organic matter & sulfides, residual. Lead distribution in the non-pulverized soils, however, is more balanced with the organic matter pool dominating. This is considered irregular since Range 5 soils are sandy soils of low moisture and low organic matter content (Dermatas et al., 2003).

Similarly, the soils tested from the Goldstone range did not exhibit any differences between pulverized and non-pulverized soils for the particle size groups finer than the #40 sieve. The majority of Pb in the fine sand fraction is associated with the carbonate phase of the sediment. However, in the finer particle size fractions Pb is also scavenged by the Fe and Mn oxides and hydroxides present in the soils. Iron and manganese are present with high concentrations in these soils, probably as either coating to the finer particles or as particulates. The coarse sand fraction of the same soils had elevated Pb concentration in the pulverized soils (6,516mg/kg) relative to the non-pulverized soils (1,010mg/kg).

The differences in the results between pulverized and non-pulverized samples can be attributed to the irregularity in the Pb particle distribution within the soil samples following bullet breakup and weathering.

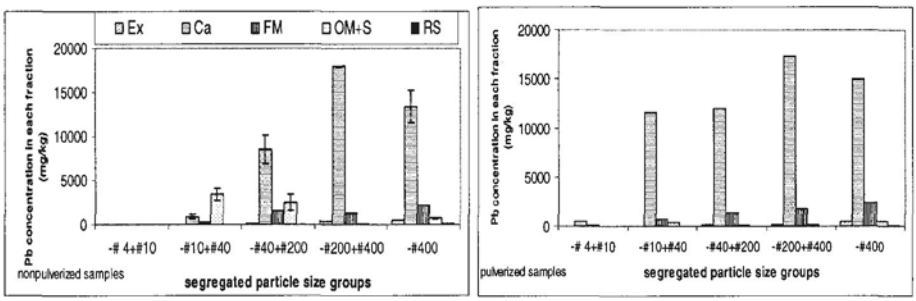

Figure 1. Lead distribution in different sequential extraction steps in the size fractionated soils size from the surface of the berm in Range 5., Fort Irwin, California. EX, exchangeable; CB, carbonate; FM, Fe-Mn oxides; OM+S, organic matter and sulfides; RD, residual.

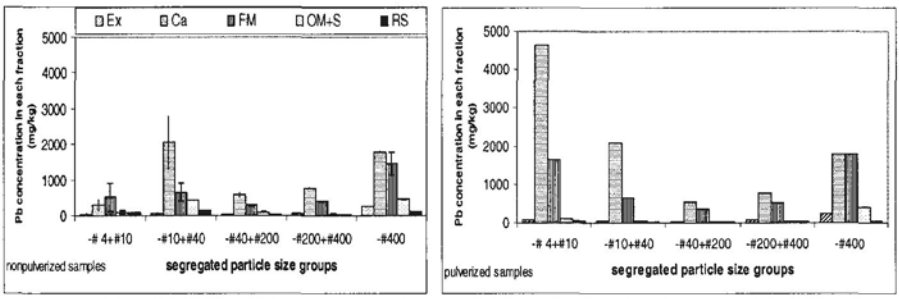

Figure 2 Lead distribution in different sequential extraction steps in the size fractionated soils size from the surface of the berm in Goldstone, Fort Irwin, California. EX, exchangeable; CB, carbonate; FM, Fe-Mn oxides; OM+S, organic matter and sulfides; RD, residual.

The majority of Pb appears to originate from a carbonate sink (weathering of metallic Pb results in the formation of secondary Pb carbonates) or specific adsorption on Fe-Mn oxides or organic matter. Specific adsorption is the chemical interaction with functional groups at the solid surface rather than electrostatic adsorption (Tessier et al., 1982). The predominance of the carbonate phase in the soils as a pool for Pb is also consistent with the XRD data from the material that was separated from bullets found in the Range 5 and Goldstone soils (Dermatas et al., 2003). This result is in agreement with that of Cao et al. (2003), who found that the carbonate phase was dominant in firing range soils. Soils from the other ranges also showed the importance of the

formation of secondary Pb carbonate minerals, cerussite and hydrocerussite. In these soils, Pb was observed to be predominantly in the carbonate phase (Figures 3-4).

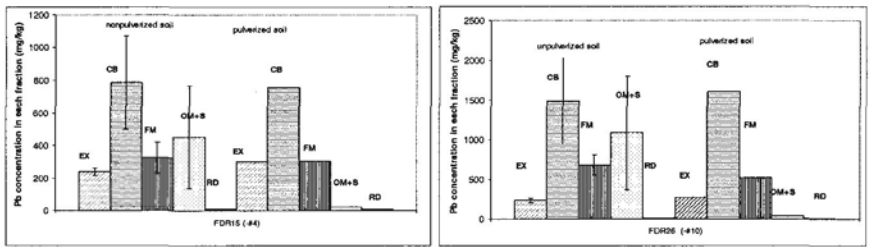

Figure 3. Lead distribution in the different sequential extraction steps in pulverized and non pulverized soils from the surface of a berm of Range 15, and Range 26, Fort Dix, NJ. EX, exchangeable; CB, carbonate; FM, Fe-Mn oxides; OM+S, organic matter and sulfides; RD, residual.

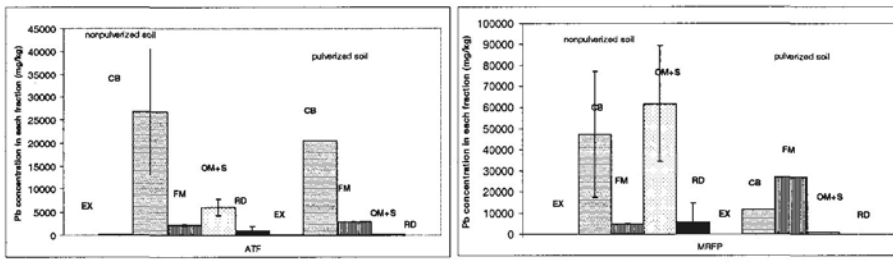

Figure 4. Lead distribution in the different SEQ steps in pulverized and non pulverized soils from the surface of a berm of ATF, Picatinny Arsenal, and Marine Range (indoor range) NJ. EX, exchangeable; CB, carbonate; FM, Fe-Mn oxides; OM+S, organic matter and sulfides; RD, residual.

Lead partitioning in these soils, which were not fractionated, was similar between pulverized and non-pulverized material. The non-pulverized material in most of the cases presented a wide range of values that resulted in high standard deviations as can be seen in the graphs (Figures 3-4). This wide range in the non-pulverized samples is attributed to the presence of Pb particles that may skew the results in the unhomogenized (non-pulverized) samples. Non-pulverized samples showed higher mass balance total Pb concentrations than the pulverized ones. The final results are shown in table 4.

Table 4. Mass balance of Pb extracted at the different fractions of the sequential extraction and % difference with Total Pb (mg/kg) from EPA method 6100.

Firing Ranges	Mass balance SEQ Pb (mg/kg)	Mass balance : Total Pb Ratio (%)
ATF	23892	87.1
Fort Dix R 15	1401	137
Fort Dix R 26	2248	76.6
Marine Range	39577	80.4

As can been seen from the figures 3 and 4, the difference in the results is mainly created by the amount of Pb associated with the organic matter and sulfides fraction of the sequential extraction procedure. In the pulverized samples, Pb association with the organic matter was negligible. However, this association contributes significantly to the final results in the non-pulverized

samples. The association of Pb with the organic matter in the non-pulverized fractions is probably an artifact of the sequential extraction procedure related to metallic Pb leaching. To demonstrate this, metallic Pb particles of different size were also subjected to sequential extraction using the different reagents. The results are shown in Figure 5.

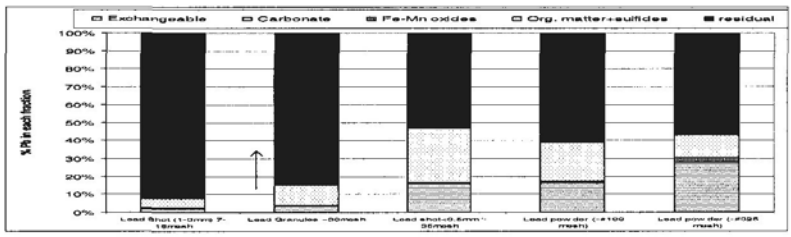

Figure 5. Pb distribution in the different sequential extraction steps of different size metallic Pb particles from coarser to finer. The arrow shows the progress of the sequential extraction.

These results indicate that metallic Pb leachability is affected by Pb particle size, i.e. as the size of metallic decreases, a larger amount of Pb leached with the non-residual phases of the soil. Also, coarser fractions tend to leach at later steps. Therefore, the Pb that leached in the organic matter phase of the berm soils may actually be fine size metallic Pb leaching due to the acidic conditions (pH~2) imposed by H_2O_2. An overestimation in the content of Pb associated with carbonates in pulverized samples may have occurred, because finer fractions could leach up to 30% Pb at the second (carbonate) step, as can be seen in figure 5. This information must be taken into account when attempting to interpret these results.

A large percentage of Pb is held in the exchangeable phase in the acidic soils of Fort Dix (Range 15 and Range 26) (Figure 6). More specifically, 11% of total Pb in Range 26 and more than 20% in Range 15 was present in this phase.

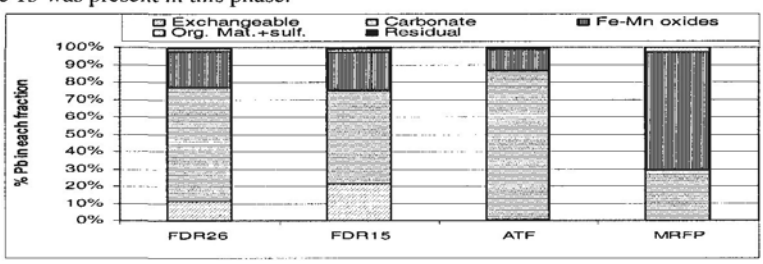

Figure 6. % Pb distribution in the different fractions from the east coast ranges.

The species of exchangeable Pb are probably hydrated Pb^{2+} and adsorbed via outer-sphere surface complexation. Li et al. (1995) have demonstrated that the plant uptake of Pb significantly correlates with the amount exchangeable Pb found in contaminated soils from mining and smelting areas. This is a major concern because the climate conditions in the general area of the berms (Ft. Dix), favor frequent rain events. Such events would enhance leaching and exchange of Pb as well as the transport of dissolved Pb into streams and the groundwater in the general area.

Soils from the indoor range (Marine Range) showed that Pb is sensitive to changes in redox conditions since the majority (68 %) of Pb was found to be associated with the Fe-Mn oxides fraction of the soils. Manganese oxides in particular are considered to be good scavengers of Pb.

Large tunnels in Mn oxides such as hollandite (a-MnO_2) could accommodate large cations such as Pb (Ma and Wren, 1998). The TCLP results from the same soils were low relative to the high total concentration. This indicates that the acidic conditions, which would be encountered in a landfill, would not affect metal leaching.

CONCLUSIONS

From the results presented herein the following conclusions could be drawn:

- Lead is mainly found as Pb carbonate in most army firing ranges soils, which indicates that Pb mobility in these soils is controlled by the solubility of Pb carbonates. If soil washing was determined to be a feasible way of treating these soils, chemical washing would be successful in removing the majority of Pb.
- Soils with a high buffering capacity (Marine Range) resisted leaching under the mild acidic conditions imposed at the second step of the SEQ and released Pb in subsequent steps. This resistance indicates that chemical washing with a mild acidic medium will not be efficient.
- High Pb bioavailability is expected in soils where more than 10% of total Pb is present in its ionic form (Fort Dix Ranges). This occurrence facilitates the application of a phytoremediation technique for soil cleanup.
- SEQ of metallic Pb proved that metallic Pb present in the soil as fine particles is affected by acid leaching. Lead present at sizes less than 35mesh leached almost 30% with the mild acidic solution used in the second step of the SEQ. It is possible that fine metallic Pb in the soils exaggerates the amount of Pb associated with the carbonate phase.
- SEQ results from non-pulverized soils showed a large standard deviation within different aliquots of the same sample. This can be attributed to the presence or lack of metallic Pb in each soil aliquot.

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Influence of dynamic flow on the degree of saturation and matric suction relations

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ABSTRACT

Many geotechnical and geoenvironmental problems, involving unsaturated soils, require an understanding of the hydraulic relations between degree of saturation and matric suction head. For example, in modeling the flow of contaminants in unsaturated soils and coupled flow and stress-strain behavior of unsaturated soils, information about hydraulic relations is essential. In this paper, the results of the relationship between degree of saturation and matric suction head are presented under static equilibrium and during dynamic flow of water using Buchner funnel and fully instrumented 2-D tank. Several scanning loops were simulated by varying the water level between predetermined levels to achieve the objectives of each test. The major influences of the dynamic flow on hydraulic relations are highlighted and discussed.

INTRODUCTION

Several geoenvironmental problems, such as migration of contaminants through unsaturated soils require a sound understanding of parameters that control the flow of such contaminant. Contaminants such as Non-Aqueous Phase Liquids (NAPLs) pollute the subsurface environment and pose a serious risk to groundwater aquifers, which are the main source for domestic water in Europe and United States. The pathways of NAPLs involve layers of unsaturated and saturated ground. Migration of NAPL in a subsurface is influenced by the initial water distribution (degree of saturation of water), matric suction head and the spill conditions (see, for example, Mercer & Cohen, 1990 and Sharam & Mohamed, 2003). Furthermore, geotechnical problems such as buildings on unsaturated expansive soils and design of earth retaining structures require an understanding of the mechanical behavior of unsaturated soils. Recent efforts have proposed that the mechanical behavior of unsaturated soils should be linked with the hydraulic relations involving degree of saturation and suction head (see, for example, Sharma, 1998, Wheeler, et al., 2003 and Gallipoli, et al., 2003).

In any ground, water could be in an equilibrium condition (stable) within the pore voids if there are no external influences such as external loading and fluctuation of ground water table are applied. However, dynamic (transient) flow of water could occur for example as a result of fluctuations of water table (Lambe & Whitman, 1969). This would result in the occurrence of unsaturated/saturated conditions. Fluctuation of groundwater table is common natural phenomenon. The behavior of NAPLs is significantly different under dynamic flow of water

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and during static equilibrium. One way of analyzing and quantifying the effects of fluctuations of groundwater table on NAPL distribution is to examine the nature of the relationship between matric suction and degree of saturation under static equilibrium and during dynamic flow. An elaborated experimental investigation, aimed at developing a new understanding of the relationships between matric suction and degree of saturation under various flow conditions, is the focus of this paper.

Many researchers have investigated and suggested models for the flow of water and contaminants through unsaturated zones (see, for example, Bear, 1979 and Parker & Lenhard, 1987, Fenwick & Blunt, 1998). The key parameter in all proposed models of unsaturated soils is the degree of saturation and/or matric suction head, which affects the value of unsaturated hydraulic conductivity (see, for example, Lenhard & Parker, 1987 and Sharma, 2000). The relationships between matric suction, degree of saturation and unsaturated hydraulic conductivity are different during drying and wetting processes. This difference is attributed to a phenomenon called "hydraulic hysteresis". Recently, researchers have tried to model the flow of NAPL in unsaturated porous medium considering the influence of hydraulic hysteresis, which could be due to fluctuations of groundwater table. It was observed that the modeling results were improved considerably when the effect of hysteresis is taken into account (see, for example, Steffy et. al., 1998). This requires that sufficient data for the relationships between matric suction head/degree of saturation and unsaturated hydraulic conductivity should be available which in some case is difficult and time consuming. An alternative way is by measuring the relationship between matric suction head and degree of saturation. Then the value of unsaturated hydraulic conductivity could be calculated using the measured relations (see, for example, Van Genuchten, 1980, Lenhard & Parker, 1987).

In this paper, results for the relationship between degree of saturation and matric suction are presented and discussed, for water-air system under static equilibrium and during dynamic flow of water. Two setups were used in this experimental investigation involving Bucher funnel and a fully instrumented 2-D tank. The major influences of the dynamic flow on hydraulic relations are highlighted and discussed.

MATERIALS AND TESTING PROGRAM

Buchner funnel was used for measuring the relationship between degree of saturation and matric suction under static equilibrium of water in the pore voids (see, Mohamed & Sharma, 2000). In addition, a fully instrumented 2-D tank with dimensions of 120 cm x 120 cm x 10 cm (see, Sharma & Mohamed, 2003) was used to simulate various scanning loops. In 2-D tank, a drainage system, comprising manifold, gravel filter, fine fiber mesh, a well and a water tank, was used to ensure a uniform distribution of water and to control the water level inside the tank. In addition, a peristaltic pump was used to keep a constant rate of discharge and recharge into the 2-D tank. It should be noted that although 2-D tank was used in this investigation, the flow of water is only in 1-D (vertical direction). The degree of saturation and matric suction head were electronically measured using TDR and pressure transducers respectively. These transducers were inserted from the back of the 2-D tank using special fitting.

Saturated samples were prepared by pouring sand into a partially water-filled container (Buchner funnel and 2-D tank) while the water level was always kept above the sand level. Furthermore, the samples were left for 24 hours to ensure that the samples were thus initially fully saturated. In Buchner funnel, the samples were then subjected to varying value of matric suction according the test objectives. This could be achieved by lowering or raising the

burette to a given height to obtain drying or wetting curves. The degree of saturation was calculated in each step as explained in Sharma & Mohamed, 2003. In 2-D tank, the water level was varied between predetermined heights to produce the intended scanning loops.

In this investigation, fine silica sand was used. The index properties of this sand are $C_u = 1.23$ and $C_c = 0.98$ with D_{50} of 0.35 mm. All sand samples were classified as poorly graded fine sand. The porosity of all the samples was found to vary in a narrow band, 41 (+/- 1) %.

Test 1 was carried out using Buchner funnel to obtain the main drying and wetting paths as well as to produce a scanning loop. Two experiments were performed using the fully instrumented 2-D tank to investigate the relationship between matic suction and degree of saturation under dynamic flow of water. In test 2, the water level was varied between 120 cm and 20 cm to produce three full cycles of drying and wetting whereas in Test 3 the water level was varied in such way to produce different scanning loops. It should be noted that the numbers given in the following figures denote the test progress.

RESULTS

The results of matric suction head and degree of saturation under static equilibrium are shown in Figure 1. It can be seen from Figure 1 that during the drying path, water started to drain out of the sample after reaching a value of suction head of 23 cm. This head is called the bubbling pressure head. Additionally, once the value of suction head increased slightly above the bubbling pressure head, considerable amount of water drained out of the sample. This is because the sand sample has a narrow band of pore-size distribution. Eventually, a minimum degree of saturation of 13.7 % was reached at a value of suction head of 30 cm. This degree of saturation is marked by no further reduction in degree of saturation is obtained even with further increase in matric suction head.

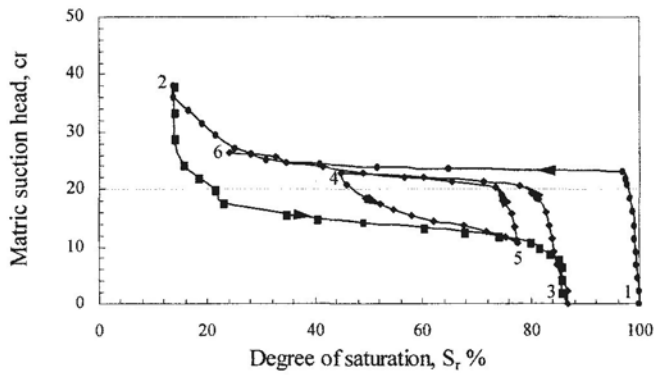

Figure 1: Matric suction versus degree of saturation (under static equilibrium)

During the wetting path, the degree of saturation reached 87 % although the matric suction head had dropped to zero. This suggested that 13.0 % of air was trapped inside the sample. It is clear from these results that there is a hysteresis in the relation between matric suction and degree of saturation. The amount of hysteresis is described here by the difference between the values of matric suction head in drying and wetting respectively at a given value of degree of saturation (conventionally, at a degree of saturation of 50 % or average value between two

reversal degrees of saturation). The amount of hysteresis is 10 cm. Additionally, a reduction in the amount of hysteresis with subsequent drying and wetting cycles was obtained. It should be noted that the secondary drying curve almost passed through the reversal point from drying to wetting (see, point 4) and then almost coincided with the main drying curve.

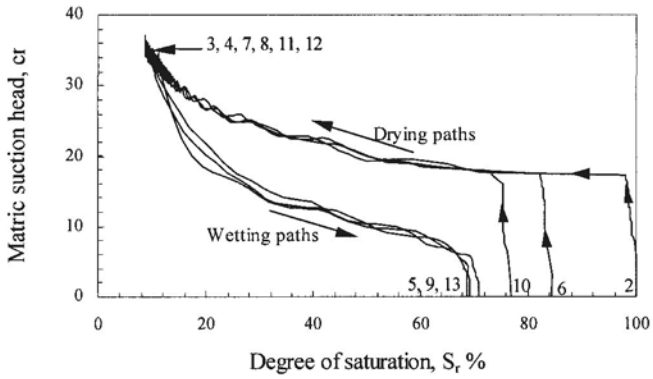

Figure 2: Matric suction head versus degree of saturation during dynamic flow of water

The results of the relationship between matric suction head and degree of saturation during dynamic flow of water was electronically recorded using pressure and TDR transducers respectively. In test 2, three full cycles of drying and wetting are performed. Figure 2 shows the relationship between degree of saturation and matric suction head for three full cycles. It can be seen from Figure 2 that the value of the bubbling pressure head was 17.5 cm. The results of bubbling pressure head measured at different levels were between 17.5 and 20 cm (with mean value of 18.5 cm). It is clear from Figure 2 that once the matric suction head became slightly higher than the bubbling pressure head (note the slope of the part of the curve after reaching the bubbling pressure head), a considerable amount of water drained out of the pores, which is consistent with the results obtained from Buchner funnel (see, Figure 1). The gush of water at a slight increase in the matric suction head is because about 70 % of the grains have the same diameter resulting in a narrow band of pore-sizes. So that a relatively flat transition between 100 % degree of saturation and close to residual degree of saturation was recorded. Eventually, a residual saturation of 11.5 % was obtained at matric suction head of 35 cm or higher.

Upon the completion of the wetting path reaching a zero suction head value, the degree of saturation reached a value of ~ 70 % (see, point 5 in Figure 2). This means that the value of trapped air was ~ 30 % during the dynamic flow of water. It should be noted that there was an increase in the value of the degree of saturation by ~ 13 % when the matric suction head became negative (positive water pressure head relative to the measuring level) as indicated by point 6 in Figure 2. This indicates that after elevating the water level to 120 cm the degree of saturation of trapped air was ~ 17 % with an average value of all measured values degree of saturation of trapped air of ~ 20 %.

The amount of hysteresis measured for the main cycle was between 8 ~ 10 cm which is very close to that measured from Buchner funnel tests. It can be seen from Figure 2 that in both cycles, the primary and secondary drying curves jumped towards the main drying curve

although the starting degree of saturation was not the same or not close to 100 % at zero matric suction head. This is because the suction head is controlled by the menisci at the pore throats, which have not suffered any change (fixed structure of pores) although air might be trapped in the pore voids. The influence of trapped air was found minor and almost identical or very close paths were obtained after passing the bubbling pressure head. The primary and secondary wetting curves almost coincided with the main wetting curve resulting in almost the same amount of hysteresis.

Test 3 was devoted to investigate the influence of reversal degree of saturation on the amount of hysteresis and the characteristics of the inner scanning loops. Figures 3 and 4 show the results of the relationship between matric suction head and degree of saturation measured at two different heights (103 cm and 78 cm respectively). The value of the bubbling pressure head was found to vary between 18 and 19 cm. The residual degree of saturation was 10.5 % and was reached at a value of matic suction head of 35 cm (see, for example, point 7 in Figure 3). The amount of trapped air at zero matric suction head was between 22 to 33 % during dynamic flow of water. These values are very close to those obtained from test 2.

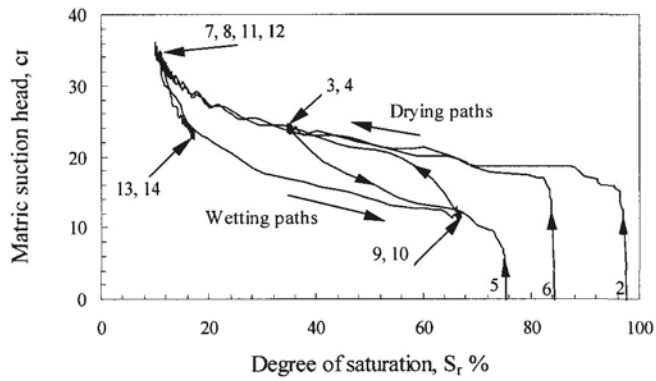

Figure 3: Matric suction head versus degree of saturation during dynamic flow of water

The scanning loops obtained at 103 cm level are shown in Figure 3. After lowering the water level to 80 cm, an incomplete path of the main drying curve was obtained (path 2-3-4). A degree of saturation of 35 % was obtained at a value of matric suction head of 23 cm. Wetting the sand from this degree of saturation yielded 24.5 % trapped air (see, point 5 in Figure 3). However, the amount of trapped air reduced by 8.5 % (path 5-6) under the effect of elevating the water level above the level of the transducers (imposing positive water pressure head). The primary drying curve rejoined the main drying curve at a degree of saturation of 55 %. With further increase in the value of matric suction head, the primary drying curve passed through the reversal degree of saturation (point 4) from drying to wetting. Then it yielded a continuation of the main drying curve as shown in Figure 3. The continuation curve appears to be an extension of the main drying curve reaching a residual degree of saturation at matric suction head of 35 cm. This means that closed loop was formed and the new scanning curve rejoined the previous one. With wetting of the sample, the path 8-9 was formed. Points 9 and 10 located very close to the wetting path 4-5 indicating that path 8-9-10 would rejoin path 4-5. Subsequent drying shows that the scanning drying path (path 10-11) rejoined the main drying curve.

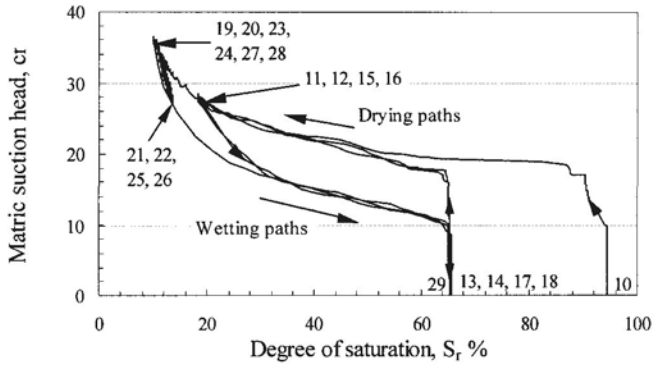

Figure 4: Matric suction head versus degree of saturation during dynamic flow of water measured at level B

Variation of the water level between 80 cm and 50 cm produced an intermediate scanning loops between values of matric suction head of – 2 cm up to 28 cm measured by transducers installed at 78 cm as shown in Figure 4. The results show that there was no increase in the degree of saturation of water when the matric suction head had dropped to –2 cm. Additionally, closed loops and coincided paths resulted as shown in Figure 4. In other word, there was no decrease in the amount of hysteresis over two cycles of drying and wetting provided that the reversal degrees of saturation were very close to residual and at zero suction head.

DISCUSSION

The experimental results of the relationships between matric suction and degree of saturation under static equilibrium and during dynamic flow of water show clearly that the main drying and wetting paths are different. This means that there is hysteresis in the relationship, which is consistent with published results (see, for example, Parker & Lenhard, 1987, Sharma, 1998 and Sharma & Mohamed, 2003). The relationship between matric suction and degree of saturation under static equilibrium and during dynamic flow of water takes the form of S-Shape curve as suggested by Van Genuchten, 1980. It should be noted that the mean value of bubbling pressure obtained during the dynamic flow of water (18.5 cm) was lower than that obtained from Buchner funnel (23.0 cm). This difference demonstrates that there is an impact of the dynamic flow on the measurements of bubbling pressure head. This means that the sand sample could sustain higher bubbling pressure head when the suction head is applied with small increments and given the time to reach an equilibrium condition, which would cause water to redistribute itself withdrawing into smaller pore voids. It is recorded that the degree of saturation of water increases as positive water head is imposed on the sand sample resulting in decreasing the amount of trapped air. The reduction in the amount of trapped air would occur due to various reasons such as:

1. Movement of air bubbles from the saturated soil as a result of the difference in fluid density and with the help of upward flow of water.
2. Compression of air bubbles under the influence of ambient water pressure.
3. Diffusion of air in the water.

The reduction in the amount of trapped air is more likely to be due to the compression and diffusion of air bubbles in the pore water as air bubbles were not observed at the top of water level. The reduction in the amount of trapped air was found to be relatively related to the head of water above the transducers level. Although the average amount of trapped air was decreased to 20 % after elevating the water level, it is as high as 1.5 that obtained at static equilibrium (from Buchner funnel). This suggests that there is an influence of dynamic flow on the continuous entrapment of air during the wetting path.

The residual degrees of saturation measured under static equilibrium and during dynamic flow of water are almost the same indicating that there is slight influence of dynamic flow on the amount of water remained as a meniscus water at the particle contacts. Careful inspection of 2-phase results illustrates that the amount of hysteresis obtained during subsequent wetting and drying cycles depends upon the saturation history and the reversal degree of saturation. The results show that when a scanning path starts from either end of the relation (from a degree of saturation corresponding to zero suction head or from a residual saturation), the scanning path follows respectively the previous one (main drying or main wetting curve). This means that the amount of hysteresis would remain constant. The reason behind that is because the sand sample is practically non-deformable and therefore, the pore voids structure (grains arrangement) remains fixed over subsequent cycles of wetting and drying.

In addition, the scanning drying and wetting curves from intermediate reversal degree of saturation took the shape of convex and concave curves respectively. They passed through the reversal degrees of saturation forming closed loops. It seems reasonable to suggest that any drying or wetting curve can be divided into two parts called transition and parallel or coinciding curve to the main one. The transition curve from wetting to drying would take the shape of convex whereas it would take the shape of concave in case of wetting from drying. The transition curves were found to be dependent upon the saturation history and the value of the reversal degree of saturation. It was concluded that sharp transition from wetting to drying occurs when the reversal degree of saturation is at zero matric suction head. The parallel part of the curve occurs generally after passing through the previous reversal degree of saturation and it usually coincides with the main path.

Employing the definition of two parts of each scanning curve explains why in one test a decreasing hysteresis is obtained while in the other one the hysteresis remains constant. For example, if the inner scanning curve starts from an intermediate reversal degree of saturation to a degree of saturation, which is less than that originally reversed from drying to wetting, a decreasing hysteresis would occur and the hysteretic loop appears to be closing. Furthermore, if the scanning curves occurred between maximum and minimum degree of saturation, almost the same curves are obtained for the main and inner scanning wetting and drying curves with no decrease in the amount of hysteresis. This suggests that the amount of hysteresis and the shape of curve representing the relationship between matric suction head and degree of saturation depend upon the saturation history and the value of the reversal degree of saturation.

CONCLUSIONS

Modeling the flow of contaminants such as Non-Aqueous Phase Liquids (NAPLs) in unsaturated soils and coupled flow and stress-strain behavior of unsaturated soils, require accurate information about the relationship between matric suction head and degree of saturation to be known. The amount of water within the pore voids would either be constant (in equilibrium) or varying according to external conditions such as rainfall and fluctuations of water level (dynamic flow). An experimental investigation was carried out to obtain the

relationships between matric suction and degree of saturation for water-air system under static equilibrium and dynamic flow of water. Two different setups including Buchner funnel and 2-D tank were used in this investigation to address the impact of dynamic flow on the drying and wetting scanning curves.

Following are the main conclusions from the experimental investigation:

1. The bubbling pressure head measured during dynamic flow of water is between 17.5 cm and 20 cm, which is less that obtained from Buchner funnel. This could be due to the impact of the dynamic flow on the measurement of degree of saturation and matric suction head.
2. The residual degrees of saturation during static equilibrium and during dynamic flow are ~13.0 % and ~11.0 % indicating that there is slight influence of the dynamic flow of water on the residual saturation.
3. When a secondary drying path commences from zero suction head (not necessarily to be at 100 % degree of saturation), it jumps to the main drying curve resulting in a very close value of bubbling pressure head.
4. The average amount of trapped air inside the sand sample is 20 % measured at zero matric suction head during a dynamic flow of water. The amount of trapped air obtained during dynamic flow of water is almost 1.3 ~ 1.8 that trapped in Buchner funnel during static equilibrium. This indicates that there is significant impact of the dynamic flow of water on the entrapment of air during the wetting path.
5. The amount of hysteresis measured at 50 % degree of saturation is about 8 ~ 10 cm which is almost identical to that obtained from Buchner funnel tests. The results suggested that if the inner drying and wetting scanning curves started from full saturation and residual saturation respectively, the amount of hysteresis would not decrease significantly. Furthermore, each path jumps sharply to the previous one and then follows it respectively. However, it appears that when the sand sample is wetted or dried from an intermediate degree of saturation ($0 < S_r < 100$ %), the drying and wetting curves would follow intermediate paths (transition curves) between the main ones up to the reversal degree of saturation then rejoin the main ones. Furthermore, the results suggested that the transition curve depends upon the reversal degree of saturation with sharp transition belongs to drying from near full saturation condition.
6. It was found that for most of simulated loops, the scanning path passes through the reversal point forming a closed loop and then forming a continuation of the previous path. In other words, once a drying or wetting scanning path has closed the scanning loop, the previous drying or wetting path is respectively followed. Results of 2-phase system show that the hydraulic relation is not only a function of the reversal degree of saturation but is also a function of the saturation path history.
7. Employing the principles of two parts scanning curves illustrates that the results from Buchner funnel are consistent with those obtain electronically from 2-D tank. For example, if the direction of inner scanning curves is changed during the transition parts, a decreasing hysteresis is obtained.

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Desorption Response and Degradation of Buffering Capability of Bentonite, Subjected to Heavy Metal Contaminants

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ABSTRACT:
Changes in pore fluid chemistry due to leachate intrusion will change the physico-chemical properties and the attenuation performance of clay barrier material. In the field, changes in the pore fluid chemistry will occur as a direct result of leachate intrusion from waste streams, discharges, leaking underground storage facilities, and waste disposal facilities – to name a few. This study investigates bentonite-contaminant interaction at different pH levels and heavy metals concentrations, with particular attention paid to the effect these have on the chemical behaviour of the bentonite soil. For chemical performance, the sorption characteristics of these specimens in relation to different pore fluid chemistries were studied. A series of batch equilibrium tests were performed at different concentrations of Zn^{2+} and Pb^{2+} and different pH levels to study the sorption properties of bentonite.

INTRODUCTION

Although the primary interests in the field of soil-contaminant interaction in the last decades have focused on investigating the attenuation capability of soil material, there is a need to make mention of the problems of contaminants present in the soil on desorption response and degradation of buffering capability of bentonite, subjected to heavy metal contaminants. To do this is to recognize one of the key areas of concern in the use of soil materials as contaminant barriers- the degradation of the physical and chemical properties of the material when it is subjected to all the forces resulting from chemical interactions (Yong, 2001). By and large, heavy metal retention and attenuation characteristics in soils are particularly dependent on soil composition, structure and the environmental condition of pore fluid. In montmorillonite-rich clays (such as bentonite), as might be expected, the relatively high CEC of montmorillonite is responsible for the favorable heavy metal retention capacity of the soil, especially at lower pH levels (Yong 2001). It has been shown that at low pH levels most heavy metals become mobile and adsorption onto clay particles becomes less effective (Yong et al. 1993, Yong and Phadungchewit 1993, Yong 2001). In addition, although the presence of the other clay elements such as oxide/hydroxide, carbonates and organic matters enhance the soil retention capacity of heavy metals, it is shown that the mechanism and process involved in heavy metal retention, including precipitation as liquid phase, ion exchange and complexation reaction are made most affective by the reduction of the pH level or by increasing acid input (Yong et al. 1993, Yong 2001, Ouhadi and Sedighi 2003). Furthermore, changes in environmental properties of the soil water-system due to such things as heavy

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metal existence or pH reduction -not only affect the attenuation and retention capability of bentonite (Yong et al. 1993), but a clay system may exhibit a dynamic mechanical and rheological behaviour due to the physico-chemical response of clay particles to changes in pore fluid characteristics. By exposing bentonite to heavy metal contaminants, several changes may occur in pore fluid characteristics (Sedighi, 2003), and these changes subsequently affect the mechanical or physical properties of the soil (Ouhadi & Sedighi 2003).

The objective of this study is to conduct an investigation of the bentonite- heavy metal interaction at different concentrations and various pH levels on the chemical, desorption response and degradation of buffering capability of bentonite subjected to heavy metal contaminants. The chemical performance studied includes sorption capability, pH variation, and ion exchange properties. An attempt is made to relate and investigate the impact of heavy metals in the pore fluid of soil, and the resulting micro- and macro-structural changes on the chemical response of bentonite.

MATERIAL AND METHOD

Physical and Chemical Properties

Bentonite soil provided by "Iran Barit Co." was used in this study. Physical properties including specific gravity, particle size distribution, Atterberg limits, organic content and moisture content were determined according to ASTM methods (ASTM, 1992). For chemical analysis, bentonite was air-dried and sieved through mesh No. 200 and chemical analysis was continued according to laboratory manual of the Geotechnical Research Center of McGill University. CEC was determined by the $BaCl_2$ replacement method (Handershot & Duquette, 1986). XRD analysis was performed based on the method suggested in the works of -Moore and Reynolds (1989), and Ouhadi and Yong (2003). Specific surface area was measured by ethylene glycol-monoethyl ether (EGME) method, according to the procedure described by Elthantaway & Arnold (1973). The carbonate content of the soil was determined by the titration method (Hess, 1977). Soil pH was measured in 1:10 soil solution. The physical and chemical properties of bentonite are given in Table 1 and Table 2.

Sample Preparation and Experimental Methods

To investigate heavy metal (HM) interaction with bentonite from the physico-chemical point of view, soil samples were prepared by adding solutions of lead nitrate ($Pb(NO_3)_2$) and zinc nitrate ($Zn(NO_3)_2.6H_2O$) in the range of 0.001 to 0.1 mol/l to the bentonite sample. The suspensions of soil-electrolyte were prepared at a 1:10 soil-solution ratio. In addition, suspensions of soil-electrolyte were prepared in a solution of 0.001 and 0.005 mol/l of lead or zinc nitrate and sufficient nitric acid to decrease the pH of the soil-electrolyte system. This made the amount of each HM applied to bentonite equal to 1.0 and 5.0 cmol/kg soil with the amount of acid input ranging from 0 to 200 cmol H^+/kg soil. To evaluate the chemical process of HM interaction with bentonite, a series of batch equilibrium tests were performed according to EPA (1983). The soil suspension samples (prepared by the aforementioned method) were equilibrated (shaken for 24 hrs.) after the solution was applied to the soil. Then, samples were centrifuged at 5000 rpm for about 10-15 min. The amounts of HM and alkaline exchangeable cations including Na^+, Ca^{2+} and Mg^{2+} remaining in the supernatant were analyzed using atomic absorption spectro-photometer (GBC 932 AB Plus).

The amounts of HM retained in the soil or exchangeable cations released by the replacement of heavy metals with and without acid input to free liquid phase were compared to later acid input and changes in soil solution pH.

RESULTS AND DISSCUSSIONS

A part of Figs. 1 and 2 present the variation of retained zinc and lead, in the bentonite soil system, and desorbed alkaline cations from bentonite sample in different concentrations of heavy metals (HMs) in pore fluid, respectively. At a concentration of up to approximately 0.01 molar of HM concentration, relatively all the HM cations were retained by the clay-electrolyte system. As the concentration of HM increased, a part of HMs remained in the soil pore fluid, however, the total retention still increased. These results indicate that the sorption performance of the bentonite sample is better in the case of lead cations than zinc cations. The selectivity orders of different HMs show that lead has a higher-ranking place than zinc in the case of montmorillonite clays (Yong, 2001), and as has been reported previous, the selectivity order appears to be Pb>Zn in illite and montmorillonite rich clay soils (Yong et al. 1992, Yong 2001, Ouhadi et al. 2003).

Another part of Figures 1 and 2 shows the variation of initial HMs concentration mixed with the bentonite sample versus the variation of different released alkaline metals from bentonite. Following the equilibrium concentration of the HM and bentonite sample, the concentration of alkaline metals desorbed from soil samples were measured in the pore fluid of soil. It can be seen from the results that as the initial concentration of HM increases, more alkaline metals are desorbed from the soil surface to the free electrolyte of system. In addition, these results show that the rate of the release of sodium ions to the free electrolyte of the clay system is much faster than that of calcium and magnesium ions. This behaviour can be attributed to the fact that a sodium ion is desorbed from a clay surface easily due to its lower valence. Even after the release of all adsorbed sodium ions to the pore fluid, the release of Mg^{2+} and Ca^{2+} ions continues. This replacement can be attributed to the higher energy level of HM cations because of their concentration, valence and ionic radius. In addition, it seems that the hydrolysis of HM in the electrolyte system primary aggravates the process of alkaline metals release. Based on the hydrolysis equation (Elliot et al., 1986), by releasing HM cations into pore fluid, the pH will decreases because of the increase in hydrogen ions concentration in pore fluid according to the following equation:

$$M^{2+}(aq.) + nH_2O \leftrightarrow M(OH)_n^{2-n} + nH^+ \qquad (1)$$

As has been previously reported, the presence of different heavy metals in soil pore fluid, affects the pH variation of a soil-electrolyte system (Yong et al. 1992, Yong and Phadangchewit 1993). Figure 3 shows the pH variation of the bentonite-pore fluid versus the added heavy metal concentrations. While the reduction of pH, following the increase of HMs concentration, can be attributed to the hydrolysis phenomenon, the higher rate of pH reduction in the presence of zinc ions may have a subsequent rheological effect on bentonite behaviour. As can be seen, the rate of reduction in soil pH due to the addition of zinc ions is relatively higher than that in the case of the addition of Pb^{2+} ions at the same level of concentrations. This process is consistent with the ranking series for pK constants of hydrolysis equation (Yong, 2001).

Two mechanisms, carbonate dissolution and the breaking of the carbonate bridge over the clay mineral surface, cause the higher concentration of the Ca^{2+} measured by replacement of HMs – in contrast to that measured by the replacement of Barium Chloride for CEC determination. These mechanisms cause an increase in reactive surfaces for exchange and an increase in the sorption of HM. Selective sequential extraction studies (Yong et al., 1993) also showed that by lowering the pH down to a specific level, the sorption of HM cations increased in the exchangeable phase. By further decreasing the pH level, a decreasing trend of

Characteristic	Quantity Measured
Clay	76%
Silt	23%
Sand	1%
Liquid Limit, %	314.5
Plastic Limit	31.2
P.I. %	283.3
Activity	3.73
Soil Classification	CH
Water Content (Air-dried)	5.9
Water Content (Oven-dried)	7.1
Gs	2.79

Table 1. Characteristics of bentonite sample.

Characteristic	Quantity Measured
Mineral composition in decreasing abundance	Montmorilonite, Illite, Kaolinite, Calcite, Quartz
Carbonate content%	8
Organic content%	1.4
CEC, (cmol/ kg soil)	68.2
Exchangeable Na^{+}	48.5
Exchangeable Ca^{2+}	14.2
Exchangeable Mg^{2+}	3.4
Exchangeable K^{+}	2.1
Specific Surface Area ($m^2/kg\ 10^{-3}$)	413
pH (1:10, soil-water ratio)	9.5

Table 2. Geo-environmental characteristics of bentonite sample.

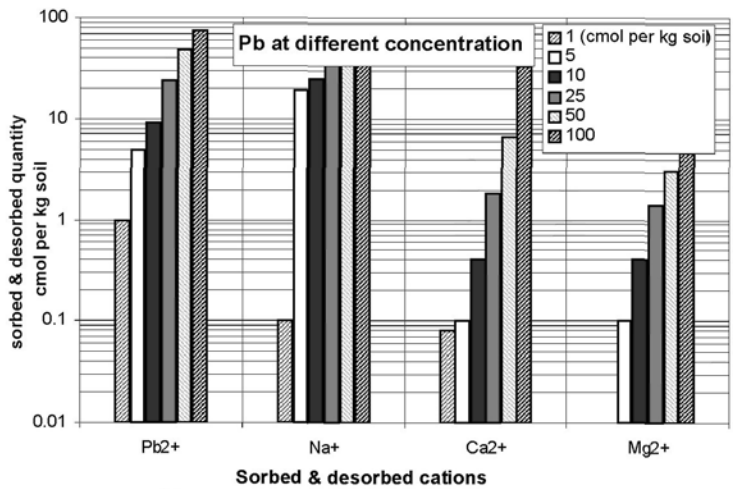

Figure 1. Sorption of Pb^{2+} and desorption of alkaline cations in different concentrations of lead nitrate.

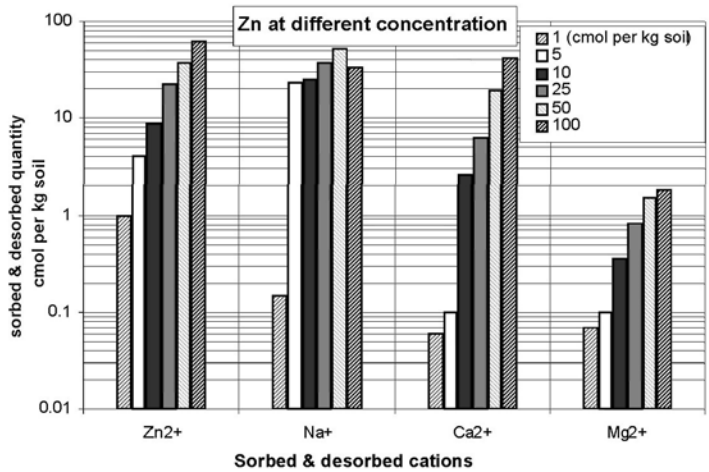

Figure 2. Sorption of Zn^{2+} and desorption of alkaline cations in different concentrations of zinc nitrate.

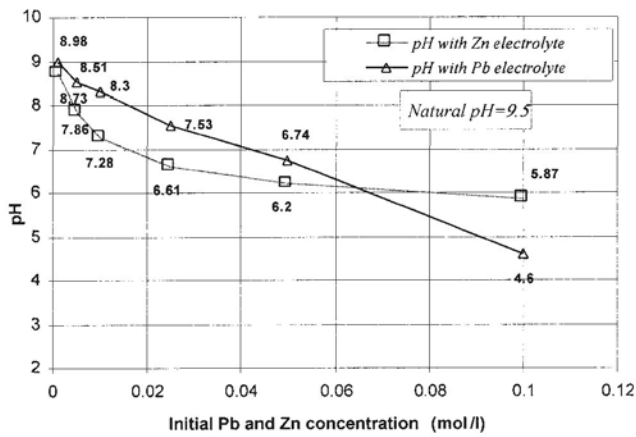

Figure 3. pH variation of bentonite-pore fluid versus the added HM concentrations.

HMs adsorption has been affected. A similar exchange trend for the release of Mg^{2+} cations was observed by increasing the concentration of HMs (Figures 1 and 2). A part of this cation exchange can be related to the replacement of H^+ ions for Mg^{2+} in the silicate crystal. Consequently, this caused an increase of adsorption of Mg^{2+} on to the clay surfaces and provided the possibility of replacing H^+ or HM cations with the sorbed Mg^{2+}. This process is similar to those reported by Chen et al. (1990), in their explanation for the rheological behaviour of Na-montmorillonite at different concentrations of NaCl.

To distinguish between the effects of the presence of heavy metals in the pore fluid -- including the pH effect due to the addition of HMs and the similar acidic condition due to the addition of hydrogen ions (i.e. in the absence of HMs)-- another series of experiments were performed. Figure 4 shows the variations of alkaline cation desorption with the addition of acid to the blank soil samples. The trend observed in this Figure indicates that the presence of acid in the soil pore fluid causes the release of alkaline ions into the free electrolyte of the soil system. It is noted that with the addition of hydrogen ions in the range of 40 cmol/kg soil, more than 95% of sodium ions were desorbed from the bentonite sample. The trend of releasable Ca^{2+} and Mg^{2+} ions in these experiments correlates with the results presented in Figs. 1 and 2.

Figures 5, shows the variation of adsorbed HMs and desorbed alkaline metals of the bentonite samples for samples prepared by a mixture of specific concentrations of heavy metals of lead nitrate-- with pH levels varied by addition of concentrations of hydrogen ions similar to the concentrations reported in Fig 4. As can be seen in Fig 5, the presence of 1 cmol/kg-soil Pb^{2+} ions in the pore fluid speeds up of the release of alkaline ions by adding acid concentration. As an example, though the addition of 20 cmol/kg-soil hydrogen ions releases less than 1% of sodium ions from clay surface, the presence of 1 cmol/kg-soil of Pb^{2+} ions at the 20 cmol/kg-soil hydrogen ion concentrations increases the release of sodium ions almost one order of magnitude. In addition, once the quantity of added acid is more than 20 cmol/kg soils, the quantity of exchangeable alkaline ions is not noticeably a function of heavy metal concentration in the pore fluid. In this condition, the decrease of pH is responsible for the exchange properties of bentonite soil. Such behaviour can highlight the important role of ion exchange in the phenomenon of HMs-soil interaction in comparison with the pH effect in this process. The rest of the results presented in Figure 5, further supports this conclusion. A similar behaviour was observed when zinc nitrate was used as the source for HMs in the soil pore fluid. The relatively high release of alkaline ions in the presence of zinc nitrate from the clay surface in comparison with that of lead nitrate can be attributed to a lower pH in the soil-system once zinc nitrate is present in the pore fluid (Fig. 3). The results show that by increasing of H^+ concentration in the soil-electrolyte system, the HM retention capability of soil decreases. The highest adsorption occurs at pH levels higher than 6. In addition, at pH<4, the retention potential of soil decrease as much as 50%. These results correlate with the results presented by Yong & Phadangchewit (1993).

CONCLUDING REMARKS

The results obtained from this study indicate that in the assessment of the degradation of buffering capability of the bentonite sample, the desorption behaviour is sensitive to the pH levels of the environmental conditions. The presence of different heavy metals in soil pore fluid, affects the pH variation of a soil-electrolyte system. While the reduction of pH, following the increase of HMs concentration, can be attributed to the hydrolysis phenomenon, the higher rate of pH reduction in the presence of zinc ions may have a subsequent rheological effect on bentonite behaviour. The formation of a flocculated structure at this pH level may

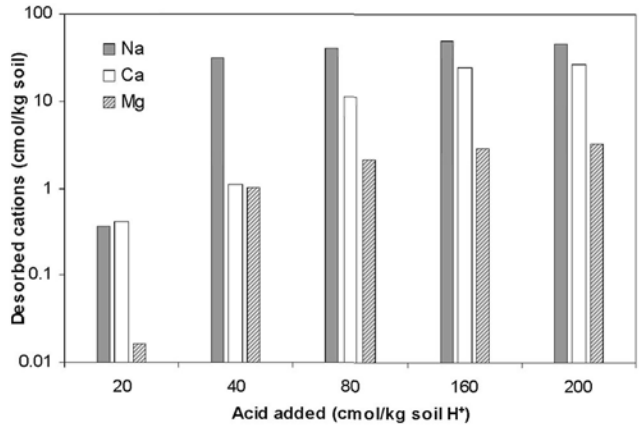

Figure 4. Variations of alkaline cations desorption with the addition of acid to the blank soil samples.

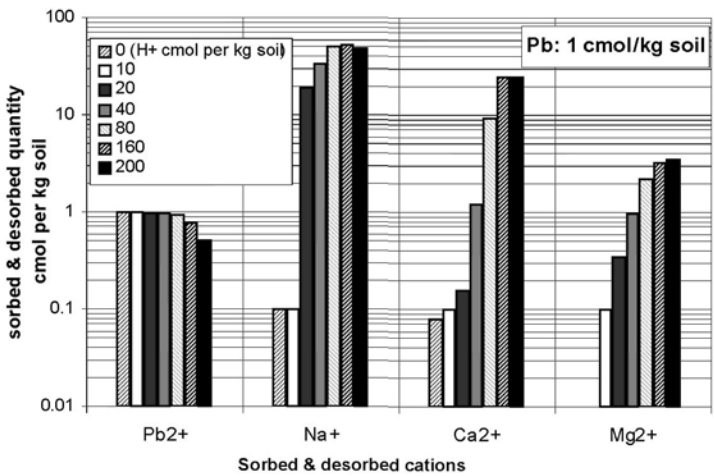

Figure 5. Sorption of Pb^{2+} and desorption of alkaline cations, different concentrations of acid added with 1 cmol/kg soil of lead nitrate.

intensify the possibility of contaminant movement in clay soils if it is used as a clay barrier and exposed to such an HM concentration. Furthermore, between the two mechanisms responsible for the release of alkaline metals from soil surface, i.e. exchangeable and pH phenomena, it seems that variation of replacement and the release of alkaline ions are controlled primarily by the process of pH reduction in the clay-water system, due to the presence of HM in the soil pore fluid.

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Enhanced Electrokinetic Remediation of Contaminated Manufactured Gas Plant Soil

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INTRODUCTION

There are over 3,000 to 5000 former manufactured gas plant (MGP) sites across the United States(US EPA 2000). Contaminants such as PAHs as well as heavy metals sorb strongly to soil, making remediation at these contaminated sites more difficult. In situ electrokinetic remediation has been proposed as a possible remediation technology for the soil contaminated with heavy metals, radionuclides, and selected organic pollutants. This technique involves applying a low-level DC electric potential through electrodes, which are placed into the contaminated soil. If the contaminants are ionic compounds, they can be transported to the oppositely charged electrode by electromigration. In addition, electroosmotic flow (EO flow) provides a driving force for the movement of contaminants. Therefore, soluble contaminants may be removed by EO flow. However, it is difficult to apply the electrokinetic remediation method to remove hydrophobic and strongly adsorbed contaminants especially from the low permeability soils. The use of solubilizing additives that enhances the mobility of such contaminants often has a large impact on the effectiveness of electrokinetic remediation and can significantly improve removal of hydrophobic contaminants (Maturi 2003).

The objective of this study is to develop an effective electrokinetic remediation system for the removal of hydrophobic PAHs from the field soil obtained from actual manufacturing gas plant site. Several flushing solutions, specifically two different surfactants (5% Igepal CA-720 and 3% Tween 80), a cosolvent (20% n-butylamine), and a cyclodextrin (10% HP-β-CD), were examined for their potential use in the removal of hydrophobic PAHs from the field soil. A series of bench-scale electrokinetic experiments were conducted using these different flushing solutions to assess the extent of contaminant migration and removal.

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EXPERIMENTAL APPROACH

Soil Characterization

Contaminated soil used in this study was obtained from a former manufactured gas plant (MGP) site in Chicago, Illinois, USA. The homogenized soil sample was analyzed by standard EPA method for metals, BTEX, and PAHs and there respective concentrations found in the MGP soil are presented in Table 1.

Table 1. Contaminants Found in the Manufactured Gas Plant Soil

(a) Metals		(b) Polynuclear Aromatic Hydrocarbons	
Chemical	**Concentration (mg/kg)**	**Chemical**	**Concentration (mg/kg)**
Aluminum	3800	2-Methylnaphthalene	230
Arsenic	11	Acenaphthene	25-40
Barium	38	Acenaphthylene	84-120
Calcium	38000	Anthracene	69-92
Chromium	8.3	Benz(a)anthracene	66-82
Cobalt	4.9	Benzo(a)pyrene	59-62
Copper	13	Benzo(b)fluoranthene	31-33
Iron	15000	Benzo(g,h,i)perylene	4.8-33
Lead	25	Benzo(k)fluoranthene	23-30
Magnesium	15000	Chrysene	39-75
Manganese	440	Dibenz(a,h)anthracene	9.1
Nickel	14	Dibenzofuran	7.7
Potassium	700	Fluoranthene	92-130
Sodium	88	Fluorene	92
Thallium	1.8	Indeno(1,2,3-cd)pyrene	12-21
Vanadium	12	Naphthalene	600
Zinc	66	Phenanthrene	260-350
		Pyrene	130-210

Electrokinetic Test Variables and Testing Procedure

The electrokinetic test setup used for this study and has been described in detail by Reddy and Chinthamreddy (2003). The contaminated field soil was placed in the electrokinetic cell in layers and compacted uniformly using a hand compactor. Flushing solutions examined to enhance solubilization of PAHs were: two different surfactants (5% Igepal CA-720 and 3% Tween 80), a cosolvent (20% n-butylamine), and a cyclodextrin (10% HP-β-CD) and these particular types of flushing solutions and their concentrations were selected on the basis of results from several series of previous batch and electrokinetic experiments (Maturi, 2004). All of the experiments were conducted at a constant voltage gradient of 2.0 VDC/cm and hydraulic gradient was found to be approximately 1.4, and is not significant enough to generate substantial hydraulic flow because of the characteristic low permeability of the soil. The flushing solution was circulated from anode reservoir and the electroosmotic flow from the cathode reservoir was

collected periodically. Each test was terminated when the current value, flow rate, or contaminant concentrations in effluent was significantly reduced.

After the completion of each test, aqueous solutions from the anode and cathode reservoirs and the electrode assemblies were collected and the volumes were measured. Then, the reservoirs and the electrode assemblies were disconnected, and the soil specimen was extruded from the cell using a mechanical extruder. Each of the extruded soil specimens was sectioned into three or five equal parts to determine the final distribution of pH values across the soil specimen. Each soil section was weighed and preserved in a glass bottle. Representative samples of reservoir solutions, soil sections, and the initial soil for each test were analyzed for total metals and PAHs.

RESULTS AND DISCUSSION

The results of the electrokinetic experiments were analyzed to assess the electric current, electroosmotic flow, and contaminant removal during the electric potential application as well as pH and residual contaminant distribution in the soil after the experiments were terminated. The results showed that the current density values fluctuated with time for all tests conducted with surfactants, cosolvent and HPCD and remain less than 1 mA/cm^2. In all the tests, the electroosmotic flow at the cathode increased with an increase in the operating duration, i.e. elapsed time (Figure 1). It can be seen that electroosmotic flow behavior was dependent on the type of flushing solutions. Maximum electroosmotic flow was observed within the cosolvent system, while the lowest flow was observed with Tween 80 surfactant system. The electroosmotic flow variation is found to be consistent with their respective trend as observed for the variation in current densities in all the tested systems. These results showed that the electric current varies significantly with elapsed time, and were attributed to the physico-chemical processes, such as the electromigration of ionic species and the electrolysis reactions. These processes affect the surface charge of the soil particles (zeta potential) and the pore fluid properties, such as dielectric constant and viscosity, with time, and hence influence the electroosmotic flow. Initially, during the beginning of the test, when the current is high (electromigration is high), the transfer of momentum to the surrounding fluid molecules may be substantial. This often corresponds to a significant volume of electroosmotic flow. A high ionic strength of the pore fluid can also be detrimental for electroosmotic flow, because it reduces the thickness of the diffuse double layer and, thereby, constricts the electroosmotic flow.

Figure 2 shows the pH distribution across the soil after the completion of the experiments. Considering that the MGP soil had a pH of 6.9 before the experiments, the soil pH after the experiment was analyzed for each soil specimen of all the tests. Generally, the electrolysis of water results in the formation of H^+ ions (low pH solution) at the anode and OH^- ions (high pH solution) at the cathode, and, primarily due to electromigration, these ions tend to migrate towards the oppositely charged electrode(s).

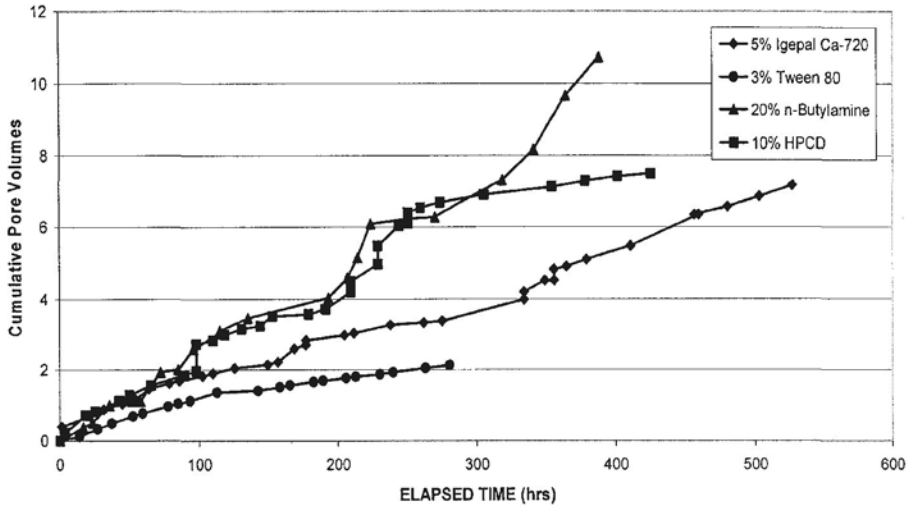

Figure 1. Measured electroosmotic flow

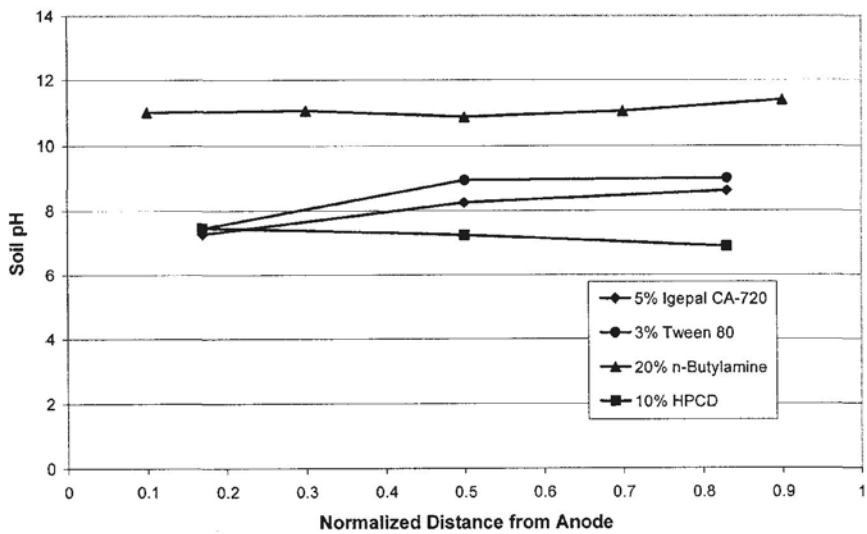

Figure 2. Soil pH variation

Because of high acid buffering capacity of the MGP soil, the H^+ ions are neutralized and are not migrated through the soil. However, OH^- migrate through the soil towards the anode. Thus, Figure 2 illustrates that a weak acidic front of solution was generated by the electrolysis reaction at the anode and pH slightly decreased in the first section near the anode in the surfactant and HPCD enhanced systems. In the second section the difference in the pH behavior becomes more pronounced as it increases for surfactant enhanced systems while remains approximately the same as initial pH in the HPCD enhanced systems. The third section, which is closest to the cathode, high soil pH was observed in the surfactant enhanced systems while remain constant to the initial pH in the HPCD system. In the 20% n-butylamine system, the soil pH remains maximum for all the soil section specimens. This reflects that the basic front is strong in the cosolvent enhanced systems and covers almost entire soil.

After the completion of experiments the soil samples were sectioned into three equal parts: S-1 (near anode), S-2 (middle), and S-3 (near cathode). However, the soil sample of 20% n-butylamine enhanced system was sectioned into five equal parts ranging from S1(near anode), S2, S3 (middle), S4, S5 (near cathode). The contaminant concentrations determined for each of these sections are plotted together in order to elucidate the migration behavior of the contaminants through the soil. Figures 3 show the residual distribution of PAHs concentrations respectively, in the MGP soil treated with 5% Igepal CA-720. This plot show that Igepal CA-720 have strong affinity to remove a wide array of PAH from the MGP soil. It also indicates that all the PAHs from the MGP soil was significantly removed near anode i.e. section S1 and middle section i.e. section S2.

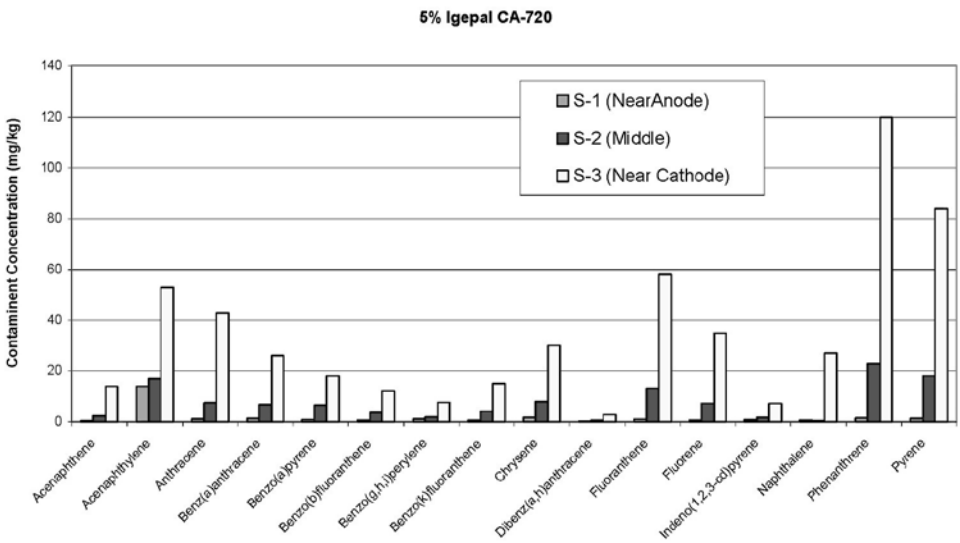

Figure 3. Distribution of PAHs in Soil using 5% Igepal CA-720 surfactant

Comparatively higher concentration of PAHs is found to be accumulated at cathode end i.e. section S3. This reflects the migration behavior of PAHs from anode towards cathode.

Similarly Figure 4 to 6 show the residual PAHs concentrations in different sections for tests conducted with 3% Tween 80, 20% n-butylamine, and 10% HPCD, respectively. It is found that the efficiency of the tested system decreases in the following order: 10% HPCD system > 5% IgepalCA-720 system > 3% Tween80 system > 20% n-Butylamine system. In general the concentration of PAHs increased from section S-1 to Section S-3 in all the studied systems. This shows that PAHs migrated towards the cathode. It is also observed that surfactant enhanced removal of PAHs depends upon the micelle formation at appreciable CMC and this may be responsible for the differences between the efficiency of 5% Igepal 720 and 3% Tween 80 for the removal of PAH compounds from the soil. HPCD enhanced system was found to be more effective for the solubilization of low polarity PAHs. This partial solubilization of low-polarity PAHs is attributed to the formation of inclusion complexes within the relatively non-polar cavity of the HPCD. These results show that Igepal CA-720, Tween 80 and HPCD systems are effective for solubilization of the PAHs from the MGP soil (under investigated conditions). However, metals removal remains insignificant in all the tests. This indicates that flushing solutions used were not effective for desorption and/or dissolution of metals in the soils (Maturi, 2004). This may be due to significant amount of organic matter that strongly adsorbed metals. In addition, the high buffering capacity of the soil may have caused some metals to precipitate.

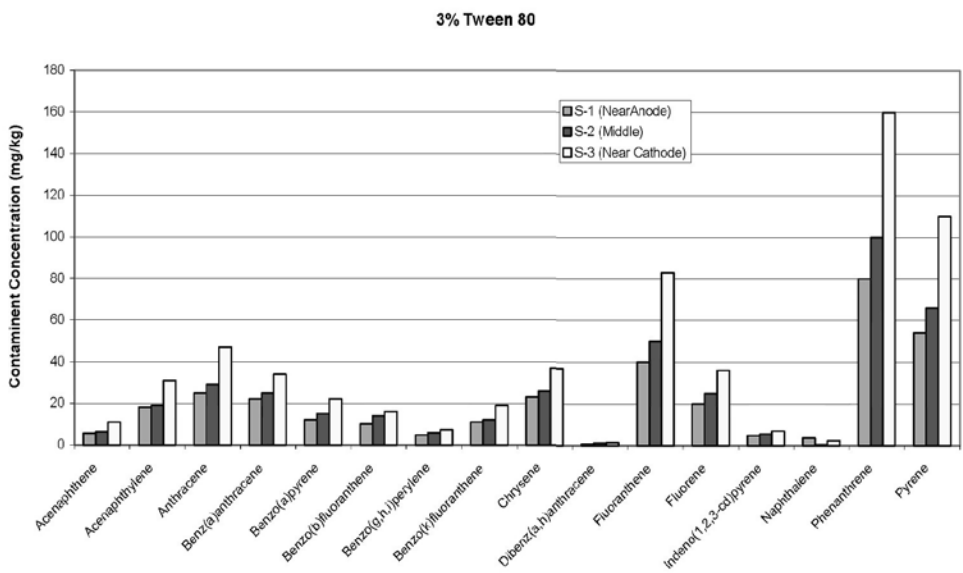

Figure 4. Distribution of PAHs in Soil using 3% Tween 80 surfactant

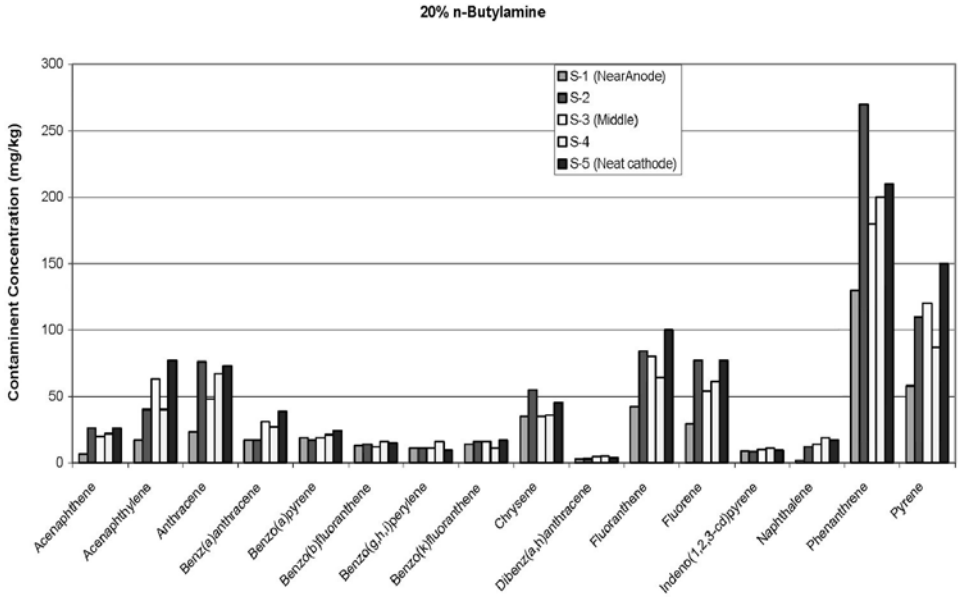

Figure 5. Distribution of PAHs in Soil using 20% n-Butylamine cosolvent

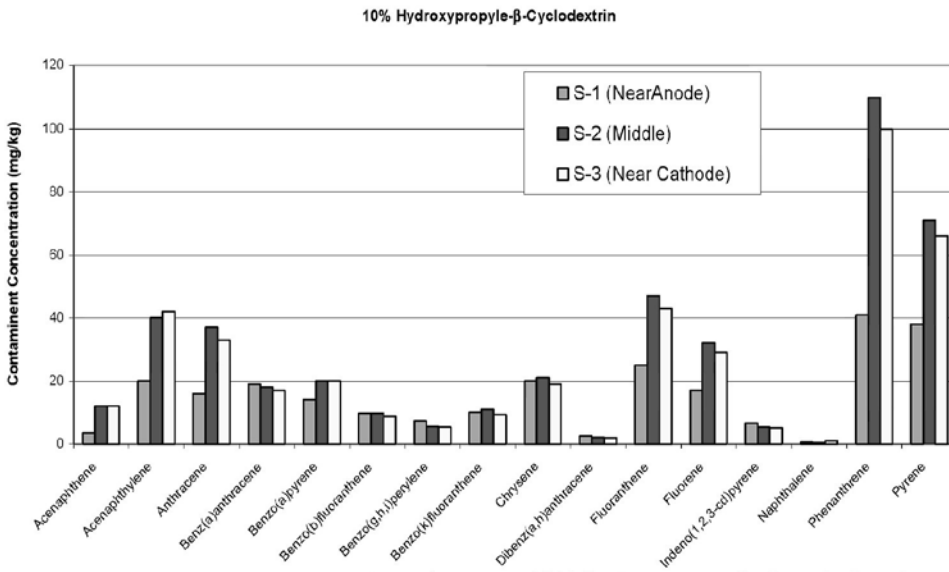

Figure 6. Distribution of PAHs in Soil using 10% hydroxypropyle-β-cyclodextrin

CONCLUSION

This study indicates that substantial electroosmotic flow can be induced in the MGP soils using different flushing solutions resulting in the appreciable removal of PAHs from the MGP soil. PAHs were solubilized in the surfactant and HPCD enhanced systems more efficiently even at low concentration as compared to cosolvent system resulting in significant removal. The mechanism of PAHs solubilization in HPCD enhanced system was found to be partial solubilization. The removal of PAHs in n-butylamine enhanced system was attributed to desorption phenomenon, while the solubilization of surfactant enhanced systems depends upon the stability and number of the micelles formed during the test. It is also believed that longer durations and different applied voltage gradient and higher concentrations of the flushing solutions may also results in the better contaminant removal efficiency.

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Relevance of multi-component NAPL dissolution to source zone longevity

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ABSTRACT
Lab column experiments have been used to determine processes controlling multi-component NAPL (non-aqueous phase liquid) dissolution, in particular the re-equilibration of aqueous dissolved-phase and Raoult's Law (solubility analogue) applicability. Bi-component mixtures of dichloromethane (DCM) and trichloroethene (TCE) have been studied in a multi-port column that samples the aqueous phase present along the NAPL length. Results to date suggest that Raoult's Law provides a reasonable, but not perfect description of behaviour. Re-equilibration of aqueous and NAPL of varying composition, that evolves even within an initially homogeneous multi-component NAPL, occurs over short length and time scales with the result that high-solubility components in the NAPL will be preferentially dissolved from the whole length of NAPL. The relevance of this research and recent field research by the authors to the longevity of multi-component NAPL source zones is summarized.

INTRODUCTION
NAPL (non-aqueous phase liquid) sources often occur as complex multi-component mixtures of compounds, common examples include hydrocarbon fuels, coal tars and chlorinated solvents used for degreasing operations. The composition of a multi-component NAPL fundamentally controls its dissolution. Under ideal conditions, typically applicable when organic components are structurally similar, an analogue of Raoult's Law holds and equilibrium effective solubility (S_i^e) may be estimated from (Broholm and Feenstra, 1995):

$$S_i^e = X_i.S_i^0 \quad (1)$$

where S_i^0 is the pure-phase solubility of solute i and X_i its mole fraction within the NAPL. Dissolution with time becomes complex as X_i and hence S_i^e temporarily and spatially vary within a NAPL source as it dissolves. Groundwater entering the upstream boundary of a NAPL source may come to equilibrium with respect to the particular X_i composition of the upstream NAPL, however, that same dissolved-phase groundwater may be at dis-equilibrium with respect to the differing NAPL composition further downstream within the source. Timeframes for re-equilibration of aqueous phase flowing through a NAPL source that has varying X_i composition along its intra-source groundwater flowpath is hence critical. If fast, high-S_i^e components such as MtBE (methyl tertiary-butyl ether) and benzene within fuels will be rapidly and sequentially flushed from a length of NAPL, i.e. "chromatographic dissolution" occurs. If re-equilibration is slow, such soluble components will persist in sources and cause longer-term plume generation. Limited data from multi-component NAPL dissolution studies is suggestive that the former, relatively fast re-equilibration, is more likely. For example, a lab study of Geller and Hunt (1993) and the NAPL dissolution field

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experiment of Rivett and Feenstra (*in subm.*) (Feenstra, 1997) at Borden indicated that the most soluble component trichloromethane (TCM) was completely flushed from the source (within experiment error) (Frind et al., 1999). However, the long path-length of that source (50 cm) and NAPL-groundwater contact time (~20 days) meant elucidation of re-equilibration time- and length-scales was not feasible.

We report on lab-based research into the dissolution of multi-component NAPL source zones. The objectives of this paper are: to determine processes controlling multi-component NAPL dissolution, in particular the re-equilibration of aqueous dissolved-phase and Raoult's Law applicability; and, more generally discuss the relevance of multi-component NAPL dissolution to source zone longevity. On the latter, we briefly link our lab-scale results to the larger field-scale findings of Rivett and Feenstra (*in subm.*) obtained from their NAPL dissolution study at the Borden, Canada research site. The lab-based research is in-progress and as such conclusions are preliminary. Further modeling work is planned to interpret the lab data using the numerical code of Frind et al. (1999).

PRELIMINARY MODEL PREDICTIONS

The effective solubility model of Feenstra (1997) assumes Raoult's Law behaviour and usefully demonstrates the impact of different re-equilibration times on multi-component NAPL dissolution (Fig. 1). The model assumes Raoult's Law equilibration occurs within a domain sub-cell. As the NAPL domain modelled may be sub-divided into varying numbers of sub-cells the model is able to quasi-represent the re-equilibration process. Fast re-equilibration of aqueous-phase and multi-component NAPL may be represented by the sub-division of the NAPL domain into a large number of cells where re-equilibration successively occurs in each cell. Slow attainment of equilibrium or re-equilibration may be represented by a NAPL domain containing a single-cell or few cells. Fig. 1 predicts the dissolution of a X_{DCM} : X_{TCE} 0.6:0.4 mole fraction ratio bi-component DCM-TCE NAPL. Where the number of cells is large, i.e. re-equilibration is fast, DCM profiles steeply decline as DCM is abruptly flushed from the NAPL zone due to DCM being successively removed from each down-gradient cell. Where cells are few, the DCM decline is slow and tails as DCM in the down-gradient portions of the NAPL zone is more slowly removed.

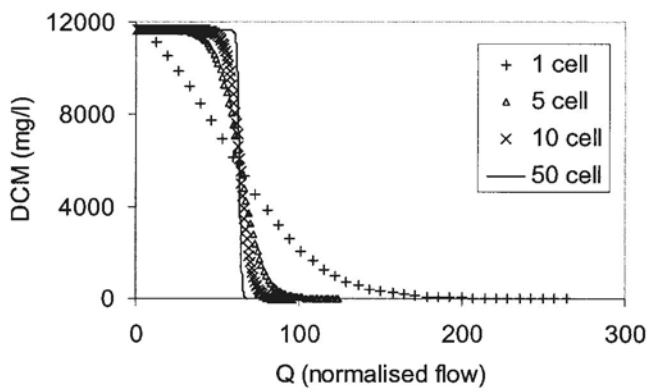

Figure 1. Effective solubility model (Feenstra, 1997) prediction of DCM concentrations from a X_{DCM} : X_{TCE} 0.6:0.4 mole fraction ratio bi-component DCM-TCE NAPL with Raoult's Law equilibration in varying numbers of sub-cells within the NAPL source zone.

COLUMN METHODS

Most column experiments have used single-component NAPLs rather than multi-component NAPLs and monitored concentrations exiting a column's NAPL zones rather than aqueous concentration variation throughout the NAPL source region. Both of these omissions are addressed in our study. Multi-component NAPL dissolution was studied in 1-D column experiments. Glass columns (2.5 cm i.d.; 20 cm length) were constrained between two stainless steel end plates sealed with Viton o-rings. The upper end-plate was fitted with a stainless steel multi-level sampler containing 3 ports that monitored water at points distributed along the NAPL source zone. A fourth port was located at the column effluent. Distances of the ports from the start of the initial NAPL zone was: port 1 at 2 cm; port 2 at 7 cm; port 3 at 12 cm; port 4 at 14.5 cm. End plates were lined with either Teflon screen or Whatman-42 paper filter. The former facilitated organic-wetting, i.e. NAPL entry, the latter permitted water passage and prevented NAPL breakthrough. Columns were packed with oven-dried uniform quartz sand (0.25 – 0.71 mm, Bardon Aggregates) under slight vibration and then flushed with CO_2 to aid air displacement during the 1 ml/min water saturation. NAPLs used in experiments reported here were the chlorinated solvents dichloromethane (DCM) and trichloroethylene (TCE) containing 0.05% Sudan IV dye to aid NAPL visualization.

A uniform distribution of residual NAPL was achieved over a 14.5 cm column length via initial upward invasion of the NAPL followed by downward aqueous displacement. NAPL residual saturation of pore space (R_s) typically achieved was on the order of 15%. NAPL dissolution was monitored under downward water flow with water samples being collected in 2-ml Teflon-capped vials by opening the valve of the port to be sampled and shutting all the other valves. Samples were analyzed within 24 hours via liquid-liquid extraction into pentane containing an internal standard. Analysis was via GC-FID with detection limits ~1 mg/l. Table 1 shows the initial conditions of the three experiments reported with S_i^e values (Equn. 1) based on S^0_{DCM} of 20,000 mg/l (Schwille, 1988) and S^0_{TCE} of 1400 mg/l (Broholm and Feenstra, 1995). Flow control was achieved via a multi-channel digital pump. All reported experiments had a flow of 0.051 ml/min, which at the measured column porosity of 0.33 yields a specific discharge of 0.01 cm/min, pore velocity of 0.03 cm/min (45 cm/d) and residence time in the initial 14.5cm length of NAPL of 460 min (0.32 d).

Table 1. Initial conditions of experiments reported.

Exp. No.	X_{DCM} (-)	X_{TCE} (-)	S^e_{DCM} (mg/l)	S^e_{TCE} (mg/l)
3	0.78	0.22	15600	310
4	0.61	0.39	12200	550
5	0.39	0.61	7800	850

LAB RESULTS AND DISCUSSION

Fig. 2 shows concentrations of DCM and TCE monitored in experiment 4 from all four ports. Initial mole fraction of DCM was relatively high at X_{DCM} 0.61 yielding a predicted effective solubility of S^e_{DCM} of ~12000 mg/l (Table 1). Fig. 2a indicates all ports initially exhibited DCM concentrations in the ~10-14000 mg/l range consistent with the above effective solubility estimate. These data hence imply Raoult's Law applicability and/or the literature-based pure-phase solubility of DCM, S^0_{DCM} of 20,000 mg/l (for which there are limited data) are reasonable for this relatively high solubility component when present at relatively high mole fraction.

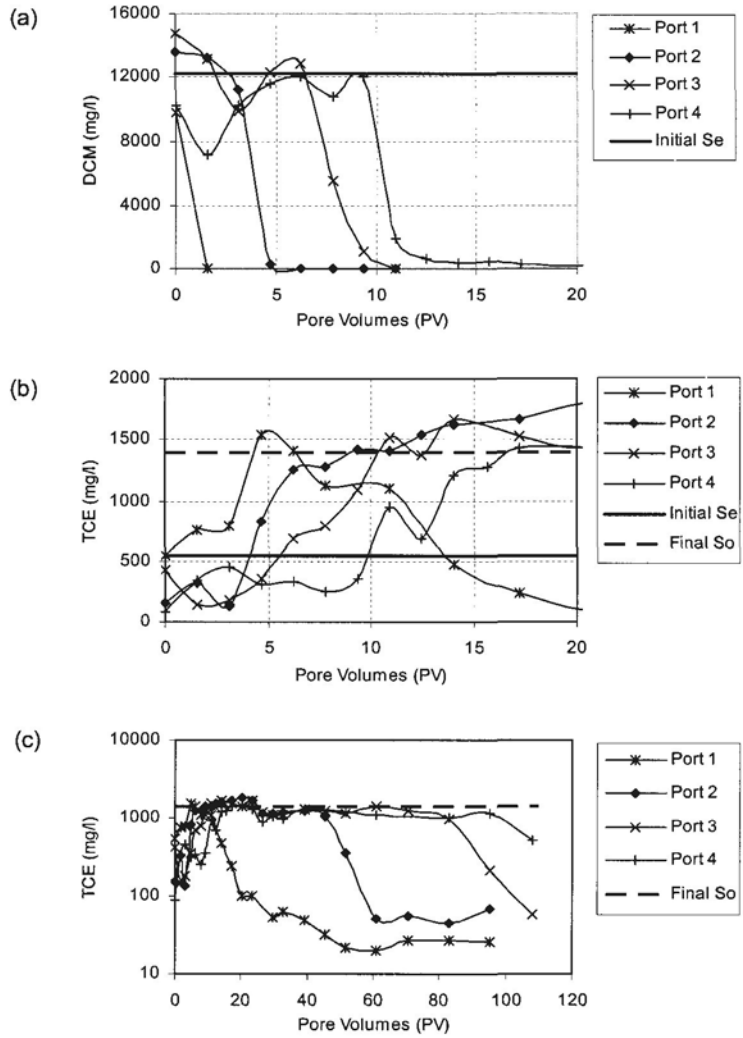

Figure 2. DCM and TCE concentrations from all four-column ports in Experiment 4.

Fig. 2a suggests rapid flushing of the DCM component from the NAPL as all ports sequentially show a rapidly declining DCM concentration front from port 1 initially and finally port 4 downstream of the NAPL. Indeed flushing was so rapid that port 1, at only 2 cm into the NAPL, has a poorly defined profile with concentrations at low values by < 2 PV (column pore volumes). The ratio of the distance the port extends into NAPL to pore volumes flushed by the mid-point of each port's sharply declining DCM concentration front (~6000 mg/l), was relatively constant for the well-defined profiles (ports 2, 3 and 4) at 1.4 to 1.8, suggesting that a relatively uniform flushing of DCM proceeded along the length of NAPL. Although some tailing was evident at low concentrations, e.g. port 4, the sharp decline in concentrations at the ports suggested DCM was efficiently swept from the entire

column with a DCM dissolution front propagating from the upstream to the downstream end of the NAPL. The applicability of literature-based pure-phase solubility data are also seen in the TCE data. Once DCM is essentially flushed from the column, inferred to be ~12 PV from Fig 2a, the NAPL comprises near single-component TCE and it would hence be anticipated that near pure-phase TCE solubility concentrations occur if equilibration times are sufficient. Fig. 2c indicates all ports by 10-20 PV demonstrate concentrations around the depicted S^0_{TCE} of 1400 mg/l (Broholm and Feenstra, 1995) line, maintained until ~ 100 PV for the most downstream port (port 4). Our data support the correctness of the S^0_{TCE} value of Broholm and Feenstra (and others), rather than the lower, often historically-accepted value of 1100 mg/l.

Raoult's Law applicability to the Experiment 4 data is less clear. Fig. 2b shows port 1 initially exhibits a concentration close to the initial predicted S^e_{TCE} of 550 mg/l (line shown) and rises to the S^0_{TCE} of 1400 mg/l in accordance with Raoult's Law and associated depletion of DCM. The other ports tend to initially show concentrations somewhat lower than the initial predicted S^e_{TCE}. It is also apparent from the relative comparison of Figs 2a and 2b that the rise in TCE concentrations is more gradual than the sharp declines already noted in the DCM profiles that would predict a concurrent steep rise in TCE if dissolution followed Raoult's Law ideal behaviour. The TCE appears to generally lag at lower-than-expected concentrations based on an ideal Raoult's Law extrapolation of the DCM data and may signify a combination of non-ideal and pore kinetic effects. All ports do, however, broadly follow a Raoult's Law based profile with TCE concentrations steadily rising sequentially at ports as the mole fraction of TCE steadily enriches along the column during DCM flushing.

Fig. 3 shows dissolution profiles for the three experiments listed in Table 1. The DCM data in Fig. 3a (normal scale) each show concentration profiles that sharply decline around 7-10 PV in spite of the different initial X_{DCM} in the various columns. The similarity in the PV number for each of the dissolution profiles tends to support Raoult's Law applicability in that a linear relationship between X_{DCM} and S^e_{DCM} would yield similar overall dissolution times (PV), i.e. a bi-component NAPL with a factor of 3 greater X_{DCM} than a similar bi-component NAPL would have a factor of 3 greater DCM mass present, but also a factor of 3 greater dissolution rate (S^e_{DCM} value) and hence similar dissolution time overall. The log-scale DCM data (Fig. 3a inset) indicated that when concentrations are monitored to low values, ~1 mg/l, relative to S^0_{DCM} then tailing appeared to be variously present, e.g. some profiles sharply dropped to <1mg/l others more slowly tailed. Single-component NAPL columns are currently being monitored to better distinguish pore-scale kinetic tailing effects from influences related to multi-component re-equilibration issues.

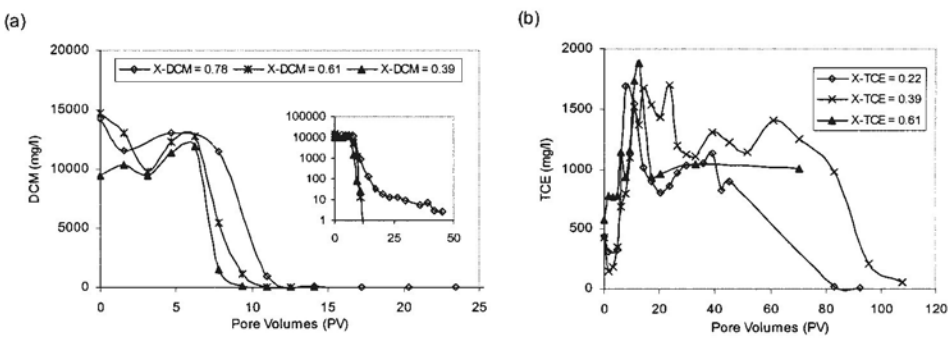

Figure 3. DCM and TCE data from port 3 (d=12cm) for experiments 3,4 and 5 (Table 1).

In relation to TCE, Fig 3b (and Figs 2b and 2c) suggests that dissolved TCE near the end of, or shortly after, DCM removal was occasionally higher than S^0_{TCE} of 1400 mg/l reaching 16-1900 mg/l. This difference is greater than analytical error and appears to show some consistency across columns. The reason at present is not clear and is being investigated further. The timeframes (PV) for flushing of TCE (Fig 2c, Fig. 3b) were approximately an order of magnitude slower than DCM, and anticipated as TCE is around an order of magnitude less soluble than DCM (compare S^e_{DCM} (Table 1) with S^0_{TCE} of 1400 mg/l). The TCE decline is more gradual than for DCM (Fig. 2a) and presumably relates to kinetic effects, e.g. shrinking size of NAPL droplets etc, and will be elucidated further by the on-going single-component TCE study and future modeling using the kinetic dissolution code of Frind et al. (1999).

Fig. 4 depicts dissolved concentrations normalized to solubility (e.g. C_{DCM} / S^0_{DCM}) with distance along the NAPL zone for Experiment 4 in which X_{DCM} was 0.61 and X_{TCE} was 0.39. Data are shown at PVs corresponding to depletion of DCM from the NAPL demonstrated by DCM dissolved concentrations eventually declining to below detection by 10.9 PV with the exception of the most down-gradient port. Initially, C_{DCM} / S^0_{DCM} should equate to the X_{DCM} value of 0.61 if Raoult's law is valid, Fig. 4 shows values around this for 0, 4.7 and 7.8 PV. As X_{DCM} declines along the NAPL zone, X_{TCE} is anticipated and indeed observed to rise as evidenced by increased C_{TCE} / S^0_{TCE} values. Minimum values for the latter should be around the initial X_{TCE} of 0.39 and it should rise to 1.0 once all DCM has depleted. Such behaviour was generally observed although TCE concentrations tend to be a little lower than predicted by Raoult's Law. The total equivalent mole fraction may be back calculated from the dissolved concentrations observed in Fig. 4 and solubility values in accordance with Equn. 1 for each pair of DCM and TCE values. If Raoult's Law is valid, this "X_{total}" (triangle symbols in Fig. 4) should be ~1.0. Fig. 4 indicates values are ~0.75-1.0, i.e. slightly on the low side. At present it is not possible to conclude whether this relates to non-idealities in relation to Raoult's Law or pore-scale kinetic effects.

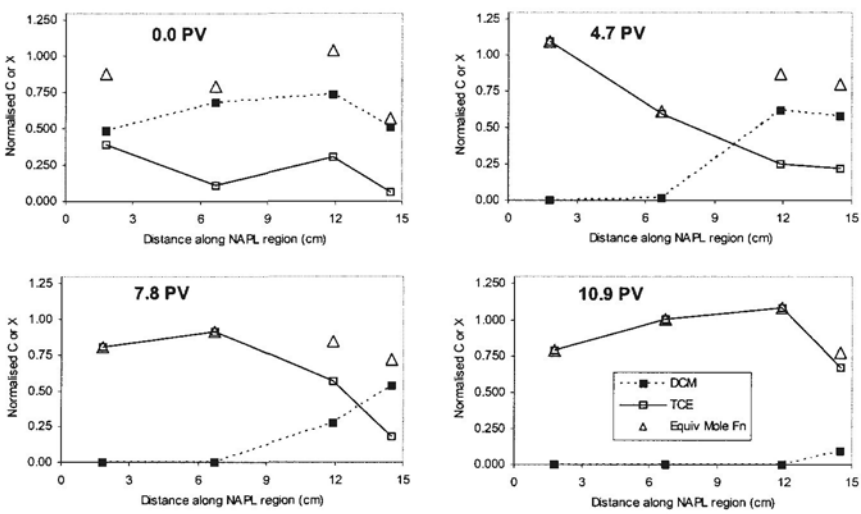

Figure 4. Dissolved DCM and TCE concentrations normalized to solubility (S^0) with distance along the NAPL source zone for Experiment 4 (Table 1); total equivalent mole fraction equivalent to each pair of concentrations is also shown.

Fig. 4 provides very good evidence for re-equilibration occurrence with TCE dissolved in up-gradient portions of the NAPL being re-partitioned back to DCM-enriched NAPL in down-gradient NAPL portions. For example the 7.8 PV data indicate: at 6 cm into the NAPL, dissolved DCM was below detection and TCE near solubility; compared to 12 cm into the NAPL, TCE concentrations were ~0.6 of TCE solubility and DCM at ~0.3 of DCM solubility. Travel time between those 6-cm spaced ports was ~200 minutes giving an indication of the timeframes and distances over which (part) re-equilibration is occurring. These scales are commensurate with those observed for equilibration of water with single-component NAPLs, e.g. Imhoff et al. (1994) provide compelling evidence that equilibration may occur over ~1-2 cm of NAPL contact at a higher velocity than used herein.

LAB EXPERIMENT CONCLUSIONS

The lab-based research is in-progress and hence, as stated at the outset, conclusions are preliminary. The multi-port column provided useful insight to multi-component NAPL dissolution behaviour in the simple bi-component NAPL studied. Chromatographic dissolution behaviour was apparent with a dissolution front of the more soluble component DCM observed to propagate down the NAPL source resulting in a near single-component NAPL, TCE, that displayed a slower moving and more dispersed dissolution front reflecting its order of magnitude lower solubility compared to DCM. When the bulk of DCM was present, DCM exhibited concentrations that approximately accorded with Raoult's Law predictions based on initial mole fractions present. The latter combined with preferential removal of DCM at all mole fractions tested suggested re-equilibration of NAPL and aqueous phases. This includes re-partitioning of dissolved TCE to down-gradient NAPL still enriched in DCM. Re-equilibration appears relatively rapid and shown to occur over scales of ~6 cm NAPL length or ~ 200 minute contact times and quite possibly lower. Raoult's Law was not a perfect predictor of concentrations with dissolved TCE being typically lower than expected and its concentration slower to rise than anticipated from the declining DCM values. Supporting batch solubility experiments are in progress using the method of Broholm and Feenstra (1995) to confirm Raoult's Law ideality in a static (non-column) setting. The provisional conclusion from the column studies to date is that dissolution of TCE-DCM mixtures (that are both chlorinated organics, but of around an order of magnitude difference in hydrophobicity) may be approximated by Raoult's Law. Re-equilibration (at least in part) of NAPL and aqueous phases does occur over relatively short time and length scales and hence chromatographic dissolution occurs with more soluble components sequentially swept from the entire path-length of NAPL.

RELEVANCE TO SOURCE ZONE LONGEVITY

The current lab-based research usefully compliments (and indeed was motivated by) the findings of the 3-year field-scale NAPL dissolution study of Rivett and Feenstra (*in subm.*) who examined the dissolution of a multi-component TCM, TCE and PCE (perchloroethylene) NAPL at Borden, Canada. Brief consideration of their findings in conjunction with this work usefully leads into discussion of the relevance of the research to source longevity.

The relatively long NAPL path-length of the Borden source (50 cm) and residence time (20 d) meant that opportunity for initial aqueous-NAPL equilibration and subsequent re-equilibration was significant causing preferential removal of the soluble TCM from the source with limited kinetic tailing in evidence (Frind et al., 1999). Our current data support re-equilibration occurrence on short length and time-scales and should be assumed to occur in multi-component NAPL sources exceeding a few cm in length. Layered heterogeneities at sites that cause lateral spreading of spilt NAPL as well as the size of typical spill/release

points will typically cause source area path-lengths to be on the order of 1-10 m scales where there is plenty of opportunity for equilibration and re-equilibration in multi-component NAPLs. Our findings suggest that soluble components will be swept from the entire lengths of the NAPL preferentially with re-partitioning of less soluble component in downstream NAPL that previously dissolved into the aqueous phase in upstream portions of the NAPL. Re-equilibration and preferential flushing of soluble components observed suggests that modeling tools, such as the example shown earlier (Fig. 1), should allow for re-equilibration to occur, i.e. a many-celled approach in Fig. 1. More rapid re-equilibration will lead to less tailing of the more soluble components. We would hence anticipate that soluble components, for example MtBE and soluble aromatics, e,g, benzene, would be relatively efficiently removed from the entire length of a NAPL fuel spill that would eventually contain only the lower solubility, e.g. alkane, components. Although more testing is needed on the relevance of Raoult's Law to organic components of contrasting hydrophobicity, our data suggest it is reasonably applicable to fairly similar organic components. The errors introduced by assumption of such ideal behaviour are likely small compared to other uncertainties in NAPL contaminant hydrogeology.

The field study of Rivett and Feenstra indicated other significant controls on NAPL source-zone longevity not apparent in lab column studies. In particular, bypass flow that may arise at the scale of "dissolution fingers", due to preferential flow-paths through a source, that arise from micro-scale heterogeneity, or else bypass of source zones as a whole that may arise from the less permeable nature of the source due to say high NAPL saturations, or its presence in a comparatively low permeability horizon surrounded by more permeable pathways. Such bypass flow will dilute contaminated groundwater emerging from NAPL zones and cause fluxes to tail with time. Bypass effects may cause tailing that is extremely lengthy compared to that produced from pore-scale dissolution effects (only likely important when NAPL path-lengths become very short in the final stages of dissolution of most source zones) and slow re-equilibration within multi-component NAPLs considered herein.

ACKNOWLEDGEMENTS

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Mobility of Arsenic in Saturated, Laboratory Test Sediments under Varying pH Conditions

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ABSTRACT

Experimental studies of arsenic movement in sediments are extremely limited and the interactions between arsenic and the various reactive sites within a soil matrix are poorly understood. This paper reports on a series of laboratory experiments studying the mobility of arsenate (As^{+5}), the oxic arsenic oxyanion, in a saturated laboratory test sediment under varying pH conditions.

A selective sequential extraction showed that very little arsenic was retained in the weakly-sorbed or carbonate fractions. Approximately one quarter of the arsenic was retained in the strongly-sorbed fraction. This is interpreted as non-specifically sorbed arsenic. Approximately 60 % of the arsenic was retained by manganese oxides, amorphous iron oxides and clay minerals. This is interpreted as ligand exchange of the arsenate oxyanion on the sediment surfaces. The remainder of the arsenic is associated with the residual fraction, indicating strong bonding in the sediment mineral lattice.

The leaching column tests showed that arsenic is most stable under neutral conditions (pH 7). Under acidic (pH 4) or alkaline (pH 10) conditions the arsenic becomes more mobile with pronounced effects seen with the acidic permeant. The arsenic became mobile due to changes in speciation brought about by the altered pH. The resulting change in anion charge caused release of electrostatically-bound arsenic.

INTRODUCTION

Arsenic is potentially harmful element. Elevated concentrations of arsenic in sediments can occur due to natural processes or due to anthropogenic causes such as mining and industrial neglect. Contamination of sediments and groundwater from natural and anthropogenic sources pose a significant hazard as a large proportion of the world's population relies on groundwater for domestic and industrial uses.

Mass poisonings due to arsenic have been well documented in the past. People have been affected in areas associated with metalliferous mining, such as in Canada, Ghana, Thailand and the USA (BGS and DPHE 2001). Elevated concentrations of arsenic, which far exceed the World Health Organisation recommended potable water limits (WHO 1994), have been identified in drainage water and groundwater in mining areas of Malaysia, Thailand and the Philippines (Williams 2001).

Reports of naturally-occurring arsenic contamination of groundwater supplies in non-mined areas have historically been less common. However, contamination has occurred in

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

geothermal areas, volcanic regions, aquitards or clay-rich lenses of aquifers containing arsenic-rich minerals, or aquifers containing iron and manganese oxides (Schreiber et al. 2000). Extensive arsenic contamination of groundwater in alluvial sediments has more recently been identified in areas such as Bangladesh, Nepal, USA, Vietnam, and West Bengal (BGS and DPHE 2001). The number of people potentially at risk from the consumption of high-arsenic groundwater water in these regions runs into the hundreds of millions. These cases represent some of the largest incidences of human poisoning that have ever been recorded.

In oxygenated waters, inorganic arsenic acid (arsenate) species are stable. Under mildly reducing conditions, inorganic arsenious acid (arsenite) species become stable. Under normal soil and natural water redox conditions, arsenate exists as an oxyanion ($H_2AsO_4^-$ or $HAsO_4^{2-}$). Arsenite is most often in a neutral form ($H_3AsO_3^0$) and is more mobile (Cullen and Reimer 1989). Because of relatively slow redox transformations and persistence of speciation, both arsenite and arsenate are often found in either redox condition (Raven et al. 1998; Smedley and Kinniburgh 2002).

There has been little experimental investigation of the movement of arsenic through whole soil samples. Gulens et al. (1979) conducted a series of column leaching tests to study arsenic mobility through sand. More recently, Kuhlmeier (1997a) studied the mobility of arsenic-contaminated groundwater in sandy soils taken from a former arsenical herbicide plant in Texas, USA. Kuhlmeier (1997b) furthered the work by conducting column leaching tests on arsenic contaminated silty soils collected from beneath former wastewater ponds. This demonstrates that experimental studies of arsenic mobility are limited. It was therefore decided to conduct a series of leaching column tests to assess the retention and movement of arsenate in a laboratory test (surrogate) sediment.

MATERIALS AND EQUIPMENT

Surrogate Sediment

A 'surrogate' sediment was developed for conducting a series of leaching column tests to assess the mobility of arsenic. The manufacture of 'sediment' allowed control over the physical characteristics and removed some of the inherent variation found when using natural sediments. Two separate sources of material were used. The first was a selection of dried, washed, graded sand (Leighton Buzzard, UK), and the second was a milled shale from a South Wales colliery waste tip, used to provide the clay content of the sediment. Before leaching tests commenced, a characterisation of the surrogate sediment was performed. This included physical and chemical tests as well as Batch Equilibrium Tests (BET's) and a selective sequential extraction to assess the adsorption of arsenic in the sediment and the distribution of the arsenate between the various sediment fractions, respectively.

Leaching Columns

The leaching columns were manufactured from acrylic tubing 150 mm long with an internal diameter of 75 mm. Permeant was stored and delivered from Marriott Tubes. Due to the opening to the atmosphere in the side of the Marriott Tube, the pressure head does not change with the quantity of permeant, i.e. a constant pressure head is applied to the sample.

METHODS

Leaching Column Preparation

Dry surrogate sediment samples were mixed with 8.3 % (by mass) distilled, deionised water in order to achieve the optimum moisture content for compaction. The soil was then

compacted into the leaching columns in 6 separate layers, each layer receiving 8 drops of a 2.3 kg rammer from a height of approximately 200 mm (Shaw 2003). This procedure of compaction was found to give consistency throughout the column.

The samples were saturated from the base upwards using distilled, deionised water, allowing any trapped air to escape through the top of the column. The pore volume of the leaching columns was assumed to be equal to the mass of the saturated sediment minus the mass of dry sediment. Following saturation, leaching was conducted using distilled, deionised water to assess the initial falling head permeability of the samples (Craig 1997).

Table 1 Summary of Leaching Column Properties

Leaching Column	Dry Density (Mg/m^3)	PV (ml)	Initial Permeability (m/s)	pH of desorption Permeant
1	1.90	162	1.09×10^{-07}	-
2	1.90	183	3.79×10^{-07}	-
3	1.90	180	2.24×10^{-07}	4
4	1.92	168	8.51×10^{-08}	7
5	1.92	172	5.35×10^{-08}	10

Artificial Contamination of the Leaching Columns

Following preparation, each column was artificially contaminated with arsenic. This was achieved by permeating 250 ppm arsenate solution through the sediment. Column 1 received 3 PV of solution and was analysed using a selective sequential extraction procedure. The remainder of the columns were permeated with approximately 5.5 pore volumes of arsenate solution. Column 2 was the control column. This column was prepared and artificially contaminated, and subsequently dismantled and the sediment analysed following an Aqua Regia digestion (Shaw 2003), to provide a measure of the 'initial conditions' prior to the use of desorption permeants. 250 ppm arsenate solutions were prepared in distilled, deionised water using reagent grade Na_2HAsO_4. The solution was then adjusted to pH 7.0 using 0.1M HNO_3.

Batch Equilibrium Tests

Batch Equilibrium Tests, following the procedure of Yong et al (1992), were conducted in order to assess the equilibrium adsorption of arsenate onto the surrogate soil. The adsorption mass ratio (q) was calculated from:

$$q=(C_0-C)V/M$$

Where C_0 is the initial concentration, C is the supernatant equilibrium concentration, V is the volume of solution and M is the mass of soil.

Selective Sequential Extraction

In order to determine which phases of the sediment the arsenic was associated with during the leaching experiments, a 5-step selective sequential extraction was performed on column 1. Two samples were analysed, one from each end of the leaching column (inlet and outlet).
Sample preparation and handling followed that of Tessier et al. (1979). The extraction stages were as follows:

i) Weakly Sorbed - Sediment was extracted at room temperature for 1 hour with 8 ml of 1M $MgCl_2$, pH 7.0, with continuous agitation.
ii) Strongly Sorbed - Residue from (i) was mixed with 8 ml of 0.05M $(NH_4)H_2PO_4$ and shaken for 24 hours.

iii) Bound to Carbonates - The residue from (ii) was leached at room temperature with 8 ml of 1M NaOAc adjusted to pH 5.0 with Acetic Acid (HOAc). Continuous agitation was performed for 5 hours.
iv) Bound to Amorphous Compounds and Manganese Oxides - The residue from (iii) was extracted with Acid Ammonium Oxalate.
v) Residual - Aqua Regia extraction was performed on the residue from (iv).

Arsenic Mobility Experiments

Following contamination of the leaching columns, a series of tests studied the effect of varying pH on the retention of arsenic. Column 3, 4, and 5 were leached with approximately 5 pore volumes of permeant, adjusted to pH 4, 7 and 10 respectively. Desorption permeants were prepared from distilled, deionised water, adjusted to the required pH (4, 7 or 10) using 0.1M HNO_3 or 0.1M NaOH.

At regular intervals, 20 ml of leachate was collected from each leaching column. These samples were acidified with 0.5 ml of concentrated HNO_3 (to pH <2) and refrigerated at <4 °C until analysis. The leachate samples were analysed for total arsenic concentration by ICP OES.

RESULTS AND DISCUSSION

Characterisation of the Surrogate Soil

Physical and Chemical Characterisation

XRD analysis showed predominantly quartz with smaller quantities of microcline, aluminium, iron, and clay minerals. Analysis of the clay-size fraction showed predominantly illite with smaller amounts of kaolinite.

The total organic carbon content of the soil was 0.7 % by weight. The soil pH (BS 1377) was 8.36. Particle size distribution of the surrogate soil can be seen in Table 2. Using an EGME adsorption technique (Carter et al., 1986), the estimated specific surface area of the soil was 23.5 m^2/g. The estimated cation exchange capacity of the soil, as determined from the four major ammonium acetate-extractable cations (MAFF/ADAS 1987) (Ca, K, Mg, and Na), was 5.6 meq/100g.

Table 2 Particle-size distribution of surrogate sediment

% Sand			% Silt			% Clay
>600 μm	212-600 μm	63-212 μm	20-63 μm	6-20 μm	2-6 μm	(<2 μm)
12.1	35.1	19.5	2.6	11.9	11.2	7.8

Aqua Regia extraction (Shaw 2003) was performed in order to assess the total element concentration of the surrogate sediment (Table 3).

An acid ammonium oxalate (AAO) extraction (MAFF/ADAS 1987) was performed in order to determine the 'chemically active' fraction of the sediment (Table 3). This extraction characterises the upper limit of potentially mobile elements which could occur under changing geochemical regimes. During the extraction process there was precipitation of calcium oxalate and therefore the calcium values have been omitted.

The high quantity of iron and manganese indicates a large amount of amorphous Fe oxides and Mn oxides. These iron oxides account for 72 % of the total Fe content of the soil. The extractable manganese is 82 % of the total Mn. The results indicate that all the arsenic

present in the sediment before being contaminated is associated with acid ammonium oxalate-extractable phases and could become mobile under varying geochemical regimes.

Table 3 Chemical analysis of surrogate sediment

Extraction	Element Concentration (mg/kg)									
	Al	As	Ca	Fe	K	Mg	Mn	Na	P	S
AAO	212	37	-	13265	466	907	380	189	93	46
Aqua Regia	418	33	660	18515	2116	15675	464	249	195	297

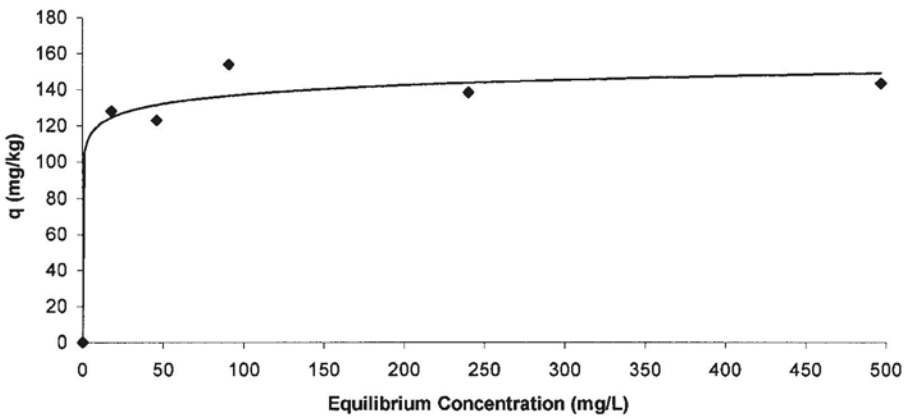

Figure 1 Plot of adsorption mass ratio (q) against equilibrium concentration

Batch Equilibrium Tests

Figure 1 shows that the maximum possible sorption of arsenate on the surrogate sediment was approximately 150 mg/kg. At the concentrations used in the leaching tests (250 mg/L), the maximum sorption of arsenate was approximately 140 mg/kg. The results can be modelled by a Langmuir isotherm. The Langmuir isotherm indicates short-range interactions requiring contact between the adsorbate and adsorbent, and a finite number of adsorption sites available in the sediment for the arsenic. A plot of initial concentration/sorbed concentration against initial concentration (Figure 2) yields a straight line where the sorption constant (K) is equal to the slope of the line divided by the intercept. For this sediment, K was equal to 7.84×10^4 L/mol.

Selective Sequential Extraction

The selective sequential extraction results showed that very little arsenic was retained in the weakly-sorbed or carbonate fractions. Approximately one quarter of the arsenic was retained in the strongly-sorbed fraction. This is interpreted as non-specifically sorbed arsenic which is held in the sediment by electrostatic attraction with the amphoteric surfaces of the amorphous compounds present, and also with broken clay edge surfaces. The arsenic could become mobile under conditions where electrostatic forces of the system alter or where anion exchange reactions occur.

Approximately 60 % of the arsenic was retained by manganese oxides, amorphous iron oxides and clay minerals. This is interpreted as ligand exchange of the arsenate oxyanion on the surfaces of the metal oxides and clay minerals as well as diffusion of arsenic into the metal

oxide minerals present in the surrogate sediment. Ligand exchange and diffusion result in a much stronger retention of arsenic than non-specific adsorption. Release of arsenic from these fractions would require diffusion of the arsenic out of the mineral structures and/or dissolution of the minerals which would subsequently release the sorbed load of arsenic to solution.

The residual arsenic concentration indicates strong bonding of a small quantity of the arsenic in the sediment mineral lattice. Significant changes in groundwater chemistry over long periods would be required to allow this arsenic to become mobile.

Table 4 Selective sequential extraction results showing arsenic concentrations as % of total arsenic

Sample	Weakly Sorbed	Strongly Sorbed	Carbonates	Mn and Amorphous Fe Oxides	Residual
1	BDL	28%	BDL	61%	11%
2	BDL	22%	BDL	61%	17%

BDL – Below detectable limits

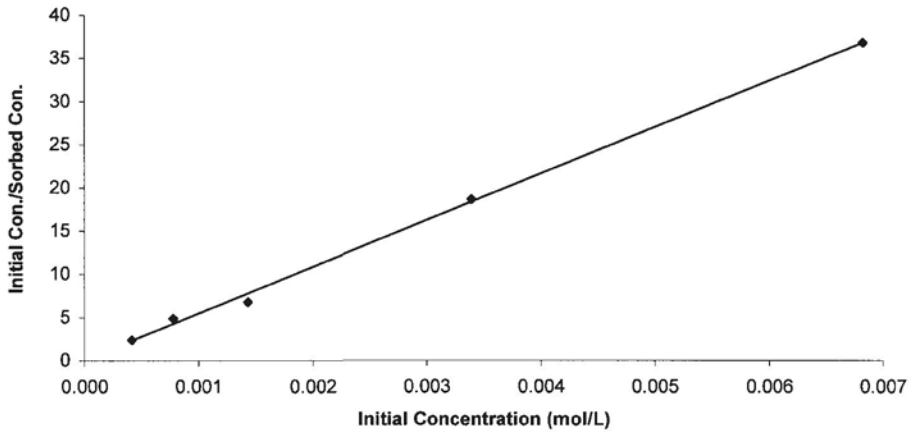

Figure 2 Plot to determine the sorption constant (K)

Effect of pH on Arsenic Mobility

Figure 3 shows a plot of leachate arsenic concentrations for columns 3, 4 and 5 during leaching with permeants of different pH values. These observations are supported by the results of loss of total arsenic from the leaching columns, which was determined by Aqua Regia digestion of the sediment. Column 3 showed the greatest desorption of arsenic, with 28 % removed after 5 pore volumes of pH 4 permeant. Next is Column 5 with 17 % desorption over 5 pore volumes of pH 10 permeant. Column 4 indicates only an 8 % loss of total arsenic even after 5 pore volumes of pH 7 desorbing fluid have passed.

The data show that the acidic permeant (pH 4) introduced to column 3 resulted in the greatest removal of arsenic from the artificially contaminated sediment. Considering the speciation of arsenic with respect to ambient pH and Eh conditions, under the oxic conditions of these experiments and a pH value of 4, there will be conversion of arsenate into arsenite (H_3AsO_3)

(Ferguson and Gavis 1972; Masscheleyn et al. 1991). This is a neutrally-charged ion which is retained much less strongly at low pH values than arsenate. The results would therefore suggest that conversion of the arsenate to arsenite released the majority of the strongly-sorbed arsenic from the soil due to loss of electrostatic attraction. There may also have been loss of some of the arsenic bound to metal oxides and clay minerals.

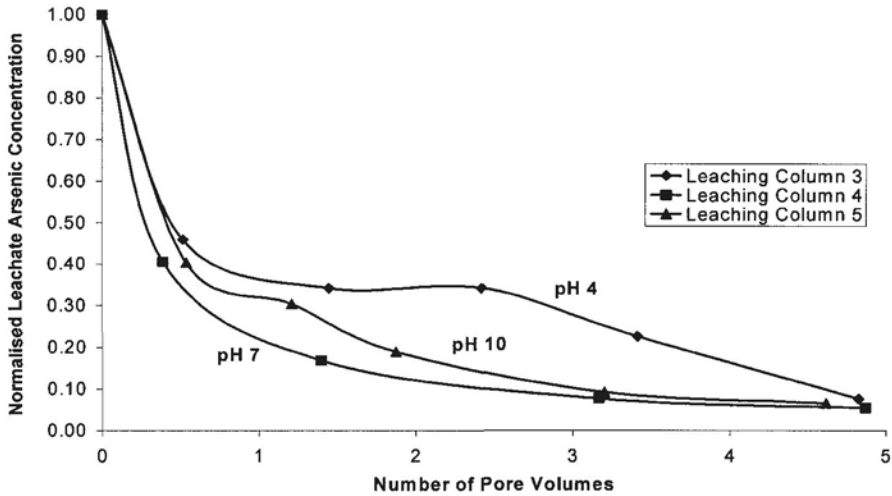

Figure 3 Leachate arsenic concentration

The use of pH 10 permeant also showed significant desorption of arsenic from the sediment. At these higher pH values, arsenate is of the form $HAsO_4^{2-}$. The sediment was contaminated at pH 7 where the arsenate would have been of the form $H_2AsO_4^-$. The BET's indicated that adsorption of arsenic on the surrogate sediment was limited by the number of adsorption sites available. If the sediment was 'saturated' with electrostatically-bound arsenate then approximately half of this would be released due to the doubling of the charge of the arsenate anions as the pH changed from 7 to 10. The results of the selective sequential extraction and the leaching tests therefore correlate well. These observations are supported by various studies (Frost and Griffin 1977; Bowell 1994; Darland and Inskeep 1997; Manning and Goldberg 1997; Raven et al 1998; etc,) which have shown that at high pH values such as 10, metal oxides and clay minerals show a significant reduction in the quantity of arsenate they can retain compared to lower pH values.

When neutral permeant (pH 7) was used, only a small amount of arsenic became mobile. This indicates the relative stability of the arsenic under continuing pH 7 conditions.

CONCLUSIONS

A laboratory (surrogate) sediment was created and used in a number of tests to assess the retention and mobility of arsenic. Batch equilibrium tests showed that the sediment could retain a maximum of 150 mg/kg of arsenate and that adsorption could be modelled by a Langmuir isotherm.

A selective sequential extraction showed that the majority of the arsenic was retained by manganese oxides, amorphous iron oxides and clay minerals. A significant quantity was also held in the sediment by electrostatic attraction. The remainder of the arsenic was found in the residual fraction. No arsenic was associated with weakly-sorbed or carbonate fractions.

Under oxic conditions, arsenate present in sediment is most stable under the influence of neutral permeant. If acidic or alkaline permeant flows through a contaminated soil it will result in greater mobility of arsenic. More pronounced effects are seen with acidic permeant. The release of the arsenic appears to be related to the speciation of the contaminant with changes in the ambient pH conditions causing changes to the arsenic anions and a reduction in affinity of the arsenic for the sediment.

The results imply that even simple changes in pH of a groundwater system can result in groundwaters far exceeding recommended standards for arsenic. These mechanisms could become very important in regions of the world where there are substantial quantities of arsenic in sediments and where changes in groundwater compositions or regimes could occur.

ACKNOWLEDGEMENTS

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Sorption of chlorinated benzenes on alluvial clays beneath a landfill site

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ABSTRACT
Sorption of hydrophobic contaminants commonly present in landfill leachates (chlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene) onto alluvial clays was studied by means of batch experiments. The alluvial clays, which constitute a naturally occurring low permeability barrier to leachate migration, were physically, chemically and mineralogically characterised. Sorption isotherms of chlorobenzene and 1,2,4-trichlorobenzene were adequately described by a linear model while 1,4-dichlorobenzene isotherm showed an appreciable non-linearity. 1,2,4-trichlorobenzene was found to be the compound most retained in the clay, followed by 1,4-dichlorobenzene and then chlorobenzene. The increased sorption of chlorobenzene with the organic carbon content of the alluvial clays indicates that sorption is controlled by the naturally occurring organic carbon. The sorption coefficients obtained in this study were up to 5 times smaller than the values calculated using empirical correlations and values typically reported for sediment and soil samples. This suggests a slightly less lipophilic character of the organic matter in the alluvial clays. The sorption coefficients followed a linear relationship to the indicators of hydrophobicity of the chlorinated benzenes.

INTRODUCTION
Nonionic, hydrophobic organic chemicals such as chlorinated benzenes are common pollutants in landfill leachates (Knox et al., 2000; Kjeldsen et al., 2002). Chlorinated benzenes are widely used as intermediates in the manufacture of dyestuffs and pesticides and are often formed from the degradation of other organochlorine compounds. Because of their toxicity, strict surface water and groundwater quality regulations are enforced to limit their concentrations in the environment. In Europe, chlorinated benzenes cannot be discharged to groundwater (EC Groundwater Directive 80/68/EC). Leakage of leachate from landfill sites to the subsurface is a potential risk both at old landfills without containment systems, and at modern landfills where containment systems may fail in the long term. Knowledge of the transport and fate of hydrophobic organic contaminants in the underlying material of the landfill site will lead to a more accurate assessment of risks arising from failure of the containment systems. The high organic loading of leachate plumes usually leads to anaerobic conditions beneath landfill sites. Under these conditions, the fate of chlorinated benzenes is primarily determined by sorption and the microbial reductive dechlorination of higher chlorinated benzenes to dichlorobenzenes and chlorobenzene (Christensen et al., 2001).

An understanding of the sorption behaviour of hydrophobic organic contaminants is an important key to describing their fate and transport in the subsurface. In addition to slowing down the diffusion and advection of contaminants, sorption may reduce their bioavailability

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

by sheltering the pollutants from direct uptake by microorganisms. The natural sorbents may also affect the chemical reactivity of contaminants by altering the microscale chemical environment around reactive species or by providing a reactive surface (Karickhoff et al, 1979; Pignatello, 1998).

The sorption of hydrophobic organic contaminants has been extensively evaluated for surface and aquifer sediments and a mechanistic understanding of the processes has evolved (Karickhoff et al., 1979; Schwarzenbach and Westall, 1981). Many studies have shown that, for natural sorbents with an organic carbon content greater than 0.1%, sorption is controlled by partitioning into the soil organic matter. General equations for estimating sorption of hydrophobic contaminants have been developed and applied to a large number of soils and sediments (Karickhoff et al., 1979; Schwarzenbach and Westall., 1981; Allen-King et al. 1997; Xia and Ball, 1999). Typically, a linear relationship of the following form is used:

$$\log K_1 = a \log K_2 + b \quad (1)$$

where, K_1 is a sorption coefficient, K_2 is a measure of the hydrophobicity of the chemical (aqueous solubility or octanol/water partition coefficient), and a and b are constants.

Although sorption of hydrophobic compounds has been the topic of considerable study for the past 20 years, most studies have investigated sediments and surface soils. Because naturally occurring clays of low permeability are used to protect underlying groundwater resources it is relevant to understand sorption mechanisms in such materials. Little research to date has focused on sorption mechanisms of chlorinated benzenes in natural clays.

The general objectives of this study were (i) to investigate the sorption of low chlorinated benzenes (chlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene) to natural clay materials which have been used as barriers to leachate migration, (ii) to determine sorption coefficients for use in contaminant fate and transport models and (iii) to investigate the reversibility of the sorption processes. A specific objective was to assess if the sorption coefficients derived in this study for chlorinated benzenes in clays can be determined using empirical correlations and sorption coefficients found in the literature for sediments and surface soils. In this paper, only the sorption processes are described. Further tests are being carried out to ascertain the extent of desorption.

MATERIALS AND METHODS

Test compounds

The hydrophobic compounds used in this sorption study are given in Table 1 together with their selected physicochemical properties. Analytical-grade chlorobenzene (CB) and 1,4-dichlorobenzene (1,4-DCB) were supplied by Sigma Aldrich Chemical (UK) and 1,2,4-trichlorobenzene (1,2,4-TCB) by Fisher Scientific (UK).

Table 1. Physicochemical properties of the hydrophobic compounds used in this study

Compound	log K_{ow}	K_{oc} (ml/g)	H (atm.m^3/mole)	S (mg/l)
chlorobenzene	2.64	268	3.4×10^{-3}	400.5
1,4-dichlorobenzene	3.28	434	1.4×10^{-3}	90.2
1,2,4-trichlorobenzene	3.93	718	2.2×10^{-3}	20.0

Notes: K_{ow}-octanol-water partition coefficients; K_{oc}- sorption coefficient on the soil organic carbon, H-Henry's constant (25°C); and S-aqueous solubility (25°C)
Source: Estimation Program Interface, US Environmental Protection Agency

Alluvial clays

The study landfill site (UK) is underlain by up to 15 m in depth with alluvial clays which have been deposited on Flood Plain Gravels. The alluvial clays contain peat layers which comprise up to 20% of the thickness of the alluvium sequence. Samples of the alluvial clay were collected from several locations at the study site and characterised with respect to organic carbon content, cation exchange capacity (CEC) and bulk and clay mineral content. The organic carbon content was determined by dry combustion (800°C) using a Rosemount Analytical Dohrmann DC-190 Carbon Analyser. CEC analysis was performed using the Barium chloride-triethanolamine method (Environment Agency, 2000). X-ray diffraction analysis (Philips PW 3040/60 X-ray Diffractometer) was used to establish the bulk and clay fraction (<63μm) mineral contents of the alluvial clay samples.

Table 2. Physico-chemical characteristics of the soils selected for this study

Soil properties	Clay 1	Clay 2	Clay 3
Organic carbon content, f_{oc} (%)	1.4	1.6	6.5
CEC (meq/100g)	26.3	25.4	22.5-30.2
Bulk mineral content (%)			
Clay	50.3	52.0	40.0
Quartz	24.0	23.3	19.0
Calcite	10.7	7.7	11.0
Clay mineral content (%)			
Smectite	71.5	75.0	72.0
Illite	16.0	13.0	15.0
Kaolinite	8.5	9.0	9.5
Chlorite	4.0	3.0	3.5

Sorption batch experiments

Synthetic leachate augmented with a spike sample of the chlorinated benzene at selected concentrations was used in the sorption tests to ensure consistency. The composition of the synthetic leachate was intended to mimic the major ion and ammoniacal nitrogen contents and pH value of the landfill leachate observed at the study site: pH 7.7, Ca^{2+} 193.6 mg/l; Mg^{2+} 230.7 mg/l; Na^{+} 2381.6 mg/l; K^{+} 359.6 mg/l; SO_4^{2-} 120.3 mg/l; NH_4^{+} 737.9 mg/l; Cl^{-} 4810.2 mg/l; total organic carbon 953.6 mg/l and hardness 1429.6 mg/l $CaCO_3$.

Batch tests were carried out using the chlorinated benzenes as solutes and alluvial clays as sorbents. A total of 10g of air dried alluvial clay, followed by synthetic leachate were added to glass crimp-top bottles (122 ml internal volume, Sigma Aldrich UK). Air bubbles were removed by completely mixing the soil suspensions for 3 minutes and allowing the bottles to sit overnight before being finally filled and spiked with the contaminant. Synthetic leachate and appropriate volumes of methanol containing the chlorinated benzene were added to the bottles to give initial aqueous-phase concentrations of 0.3% to 22.2% of the compound's maximum aqueous solubility. Sodium azide (100 mg/l) and mercuric chloride (25 mg/l) were also added to the bottles to inhibit biological activity. Each bottle was filled to the top with synthetic leachate and then quickly sealed with aluminium caps with Teflon®–coated septa (Sigma Aldrich UK) to avoid volatilisation of the organic compounds. The small amount of methanol added to the bottles (<0.2% by volume) has been shown to have no measurable effect on sorption (Rao et al., 1990). The effectiveness of sodium azide and mercuric chloride in inhibiting biological activity was assessed by comparing the sorption bottles with control bottles that went through identical processing but contained no biological inhibitors.

The sorption bottles were mixed by horizontal rotary agitation (bottle roller, Fisher Scientific UK) for 5 days at 20±2°C. Preliminary tests with sorption times up to 17 days indicated that

less than 1 day was required to achieve equilibrium conditions. At the end of each contact time investigated, the solid and liquid phases were separated by a centrifuge (Wifug 2000E) at 2000 rpm for 5 minutes. Samples of the supernatant liquid were collected from each bottle for determination of the solute concentration. Blank experiments in which no clay material was added to the bottles containing the chlorinated benzene and biological inhibitors were also carried out. These were used to account for solute losses to the headspace, glass wall and caps. The amount of chlorinated benzene sorbed to the alluvial clay was determined using the equation:

$$C_s = \frac{C_i - C_w}{M} V(1000) \tag{2}$$

where, C_s is the concentration of chlorinated benzene in the alluvial clay at equilibrium (μg chemical/g clay), C_i and C_w are the concentrations of chlorinated benzene in the synthetic leachate at the beginning of the test and at equilibrium, respectively (mg/l); M is the dry weight of alluvial clay in each bottle (g), and V is the internal volume of each bottle (litres).

Analytical techniques

The chlorinated benzenes were quantified by headspace gas chromatography using a Varian Star 3400 CX Gas Chromatograph (GC) connected to a CombiPal Headspace Autosampler. The GC was equipped with a BPX5 megabore column 0.53 mm by 30 m (SGE Ltd) and a flame ionisation detector under the following conditions: column flow rate (hydrogen) 6 ml/min, 50°C initial temperature (ramped at 4°C/min to 60°C and then ramped at 5°C/min to a final temperature of 130°C), injector temperature 150°C and detector temperature 250°C.

RESULTS AND DISCUSSION

Sorption isotherms on alluvial clays

Sorption tests were carried out with alluvial clays of varying organic carbon content (1.4 to 6.5%). Sorption of the chlorinated benzenes was rapid with equilibrium being reached within the first few hours of the test. A specific objective of this study was to check the linearity of the sorption isotherms for aqueous concentrations up to 15 mg/l. In contaminant fate and transport modelling, linearity is often used for reasons of mathematical convenience. The linearity of sorption isotherms for hydrophobic organic contaminants on soil organic matter is so widespread in the literature that it is now too often assumed without verification. Unless curvature is pronounced, which it usually is not, an intrinsically non-linear isotherm can easily be mistaken for linear (Pignatello, 1998).

The equilibrium sorption data of the chlorinated benzenes were fit by two sorption models, the linear model (equation 3) and the Freundlich model (non-linear model, equation 4). These models are widely used for describing sorption of contaminants by natural sorbents (Pignatello, 1998). The Freundlich model becomes linear at low concentrations, but how dilute the system has to be to show linear isotherm varies depending upon the nature of the sorbent and the type of sorption interaction.

$$C_s = K_d C_w \tag{3}$$

$$C_s = K_F C_w^n \tag{4}$$

where, K_d is the linear sorption coefficient (ml/g), K_F and n are the Freundlich sorption coefficient ($\mu g^{1-n} ml^n/g$) and the dimensionless index of site energy distribution, respectively, and C_s and C_w as in equation (2).

Both models were tested with respect to the fit to the equilibrium sorption data of the chlorinated benzenes. The sorption isotherms are plotted in Figure 1 and model parameters are given in Table 3. Least squares linear regression analysis was carried out to obtain the sorption parameters of the linear isotherm and the linearised logarithmic Freundlich isotherm.

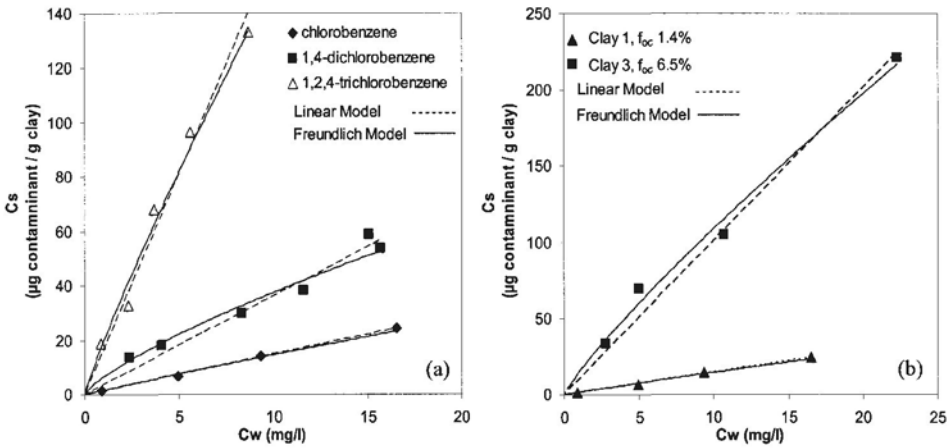

Figure 1. (a) Sorption isotherms of chlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene on alluvial clays, f_{oc} 1.4-1.6% (C_s and C_w as in equation 2) (b) Sorption isotherms of chlorobenzene on alluvial clays of different composition (C_s and C_w as in equation 2)

The slope of the Freundlich isotherm, given by the parameter n, is a measure of isotherm linearity. The closer n is to 1, the more linear is the isotherm. As seen from Table 3, isotherm non-linearity was most notable for 1,4-dichlorobenzene (n=0.76), while chlorobenzene and 1,2,4-trichlorobenzene isotherms had values of n closer to 1 (n>0.89). The model that best describes the sorption data of 1,4-dichlorobenzene varies depending on the circumstances. It may be appropriate to assume linearity for diluted leachate plumes away from the landfill but for larger contaminant concentrations within landfill liners or the unsaturated zone beneath the landfill, the amount sorbed could easily be overestimated by assuming the Freundlich isotherm to be linear.

Table 3. Parameters of the Linear and Freundlich Models fit to the experimental sorption data

Compound	Alluvial clay	Linear Model		Freundlich Model		
		K_d (ml/g)[a]	R^2	Log K_F ($\mu g^{1-n} ml^n/g$)[a]	n	R^2
CB	Clay 1 f_{oc} 1.4%	1.48±0.03 (1.40-1.55)	0.99	0.22±0.04 (0.04-0.39)	0.95±0.06	0.99
	Clay 3 f_{oc} 6.5%	10.18±0.18 (9.69-10.68)	0.99	1.14±0.06 (0.95-1.33)	0.92±0.05	0.99
1,4-DCB	Clay 2 f_{oc} 1.6%	3.61 ±0.15 (3.23-3.99)	0.96	0.81±0.06 (0.66-0.97)	0.76±0.06	0.98
1,2,4-TCB	Clay 2 f_{oc} 1.6%	16.11±0.63 (14.37-17.86)	0.98	1.29±0.05 (1.12-1.47)	0.89±0.09	0.97

Notes: [a] 95% confidence intervals given in parenthesis
R^2- correlation coefficient

Correlation of sorption with the hydrophobicity of contaminants

Sorption of hydrophobic compounds is controlled by the preference of the non-polar hydrophobic compound to partition out of the polar aqueous solvent into the hydrophobic soil organic carbon matter. The repulsive interactions between hydrophobic compounds and the polar aqueous solvent increases with the hydrophobicity of the compound, for which the octanol/water partition coefficient (K_{ow}) and aqueous solubility (S) are common indicators (Karickhoff et al., 1979; Schwarzenbach and Westall, 1981). These hydrophobicity indicators and the sorbent organic carbon content have been used to estimate sorption capacities. A number of empirical correlations of the form given by equation (1) have been established for a range of hydrophobic compounds in sediments and surface soils. For the sorption data derived in this study, a correlation between sorption coefficients and both K_{ow} and S was also obtained (Figure 2). 1,2,4-trichlorobenzene was the most strongly sorbed chlorinated benzene followed by 1,4-dichlorobenzene and then chlorobenzene, which reflects the different hydrophobic character of the chlorinated benzenes, as predicted by the empirical correlations.

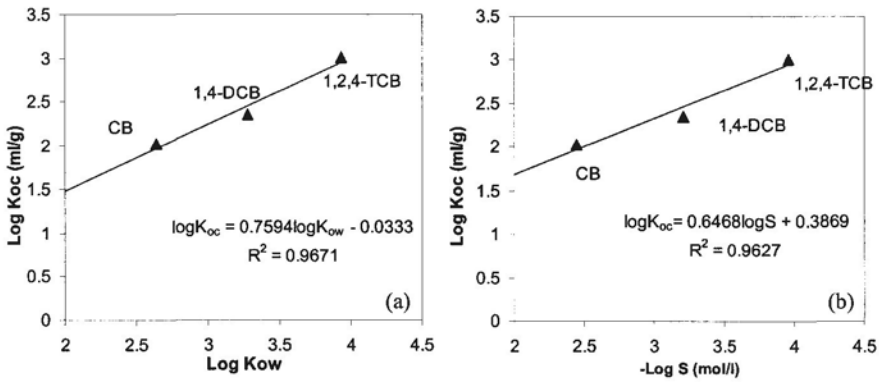

Figure 2. Relationship between the sorption coefficients on the soil organic carbon, K_{oc} ($=K_d/f_{oc}$) and (a) the octanol/water partition coefficient (K_{ow}) and (b) the molar aqueous solubility (S)

The linear sorption coefficients K_d for the chlorinated benzenes were estimated using two empirical correlations of the form given by equation (1). These correlations were developed by Schwarzenbach and Westall (1981) and Xia and Ball (1999) for chlorinated benzenes in a range of sediments and surface soils. The calculated K_d values were up to 5 times greater than those derived in this study (Table 4). Sorption data reported by Walton et al. (1992) and Chen et al. (2000) for surface soils and aquifer sediments with similar organic carbon content to the alluvial clays also overestimated the K_d values obtained in this study (Table 4).

Sorption coefficients different to those predicted by empirical correlations have been attributed to a variety of factors including sorption onto soil mineral fraction and differences in soil organic mater composition (Southworth and Keller, 1986; Allen-King et al., 1997). Many studies have shown that for sorbents with an organic carbon content greater than 0.1%, a significant correlation exists between the sorption coefficient of the hydrophobic compounds and the organic carbon content of sediments. On the basis of the organic carbon content of the alluvial clays used in this study (f_{oc} 1.4 to 6.5%), sorption is expected to be controlled by organic matter. The increase in sorption of chlorobenzene with the organic carbon content of the alluvial clays is in agreement with this (12% sorbed to Clay 1, f_{oc} 1.4% compared with 48% sorbed to Clay 3, f_{oc} 6.5%). One possible explanation for the

overestimation of K_d values is that the organic matter in the alluvial clays is less non-polar (less sorptive) than that found in surface soils and sediments tested by other investigators. The diversity in composition and structure of the organic matter can give a variation in the sorptivity of organic compounds, due to the presence of different fractions such as humic and fulvic acids, lipids and oxidation state (Allen-King et al., 1997).

Table 4. Linear sorption coefficients, K_d, for chlorinated benzenes in natural sorbents: experimental values, estimated values using empirical correlations and literature values

Source	Sorbent	K_d values (ml/g)		
		CB	1,4-DCB	1,2,4-TCB
This study	Alluvial clays f_{oc} 1.4-1.6%	1.48±0.03	3.61±0.15	16.11±0.63
Correlation[a] [1]	River, lake and aquifer sediments f_{oc} 0.04-5.8%	3.44 (2.3)[c]	11.37 (3.1)[c]	33.40 (2.1)[c]
Correlation[b] [2]	Silt loam soil f_{oc} 1.49%	2.89 (1.9)[c]	15.99 (4.4)[c]	79.29 (4.9)[c]
[3]	Silt loam soil f_{oc} 1.49%	4.67	-	-
[4]	Soil f_{oc} 1.2%	-	3.39	10.72
[5]	Aquifer sediment f_{oc} 1.5%	-	-	39.5
[6]	Silt loam soil f_{oc} 1.9%	0.91	3.01	9.55

Notes: a- $\log K_d = 0.72 \log K_{ow} + \log f_{oc} + 0.49$ (correlation coefficient=0.95)

b- $\log K_d = 1.07 \log K_{ow} + \log f_{oc} - 0.51$ (correlation coefficient=0.97)

c- Ratio between estimated and experimental K_d values are given in parenthesis

References: [1]-Schwarzenbach and Westall, 1981; [2]- Xia and Ball, 1999; [3]- Walton et al., 1992; [4]- Southworth and Keller, 1986; [5]- Chen et al., 2000; [6]- Chiou et al., 1983

CONCLUSIONS

Sorption of chlorinated benzenes to alluvial clays from beneath a landfill site was relatively rapid with equilibrium being reached within the first few hours of the test. Sorption isotherms of chlorobenzene and 1,2,4-trichlorobenzene were adequately described by the linear model (Freundlich parameter n>0.89) while 1,4-dichlorobenzene isotherm showed an appreciable non-linearity (Freundlich parameter n=0.76). It may be appropriate to assume linearity for diluted leachate plumes away from the landfill but for larger contaminant concentrations within landfill liners or the unsaturated zone beneath the landfill, the amount of 1,4-dichlorobenzene sorbed could easily be overestimated by assuming the Freundlich isotherm to be linear. Sorption was found to increase with the hydrophobicity of the chlorinated benzene. This indicates that as leachate moves through the alluvial clay, 1,2,4-trichlorobenzene will be the compound most retained, followed by 1,4-dichlorobenzene and then chlorobenzene. Sorption seems to be controlled by the naturally occurring soil organic carbon.

For the chlorinated benzenes and alluvial clays studied, a correlation was found between the sorption coefficients K_d and the hydrophobicity indicators of the chlorinated benzenes (octanol/water partition coefficient and aqueous solubility). Empirical correlations found in the literature for chlorinated benzenes overestimated the K_d values obtained in this study by up to a factor of 5. The K_d values reported in the literature for sediments and soils with similar organic carbon content to the alluvial clays were also higher than the values obtained

in this study. These results suggest that the alluvial clay contains an organic matter phase less lipophilic (less sorptive) than the surface soils and sediments studied by those investigators. Thus, both the concentration and nature of the organic matter in the alluvial clays seem to control sorption. The overestimation of the sorption coefficients using empirical correlations emphasises that correlations may only be valid under similar experimental conditions and only for compounds and sorbents similar to those used in deriving the correlations.

ACKNOWLEDGEMENTS

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Preliminary Results of Tests to Investigate Effects of Hydraulic Gradient and Leaching Time in Column Leaching Tests on Sorption Behavior of Zinc in Illite Clay

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ABSTRACT

The capacity of soil to attenuate pollution is an important parameter to be considered in designing liners of waste containment systems. The attenuation is done through sorption, where a portion of the concentration of the contaminant in the pore fluid is retained in the soil particles. Sorption is quantified by the partitioning coefficient which relates the concentration of the solute sorbed to the equilibrium concentration in solution. To be able to predict the behavior of contaminant in soil accurately, contaminant transport parameters such as dispersion coefficients as well as the partitioning coefficient have to be well-defined. One method of determining the partitioning coefficient is through the use of column leaching tests where a contaminated solution is made to leach through a normally consolidated layer of clay. The amount of contaminant retained through the profile is used to estimate the retardation factor. There are several factors to consider in the design of the experiment, one of which is the leaching time, or the length of time the soil particles were exposed to the contaminant. Another factor to investigate is the effect of the hydraulic gradient. Five column leaching tests were conducted with varying leaching times and hydraulic gradients using illite clay. A fixed concentration of zinc solution was used as the leachant for all tests. The amounts of solute retained in the layers were determined after the leaching procedure using acid digestion. The amount of solute retained in the layers decrease with depth, with most of the solute retained at the topmost layer. Results show that the two factors being investigated do not have a significant effect on the determination of the partitioning coefficient.

INTRODUCTION

Sorption is a term used to describe the process in which solutes are partitioned between the liquid phase and the soil particle interface. Sorption data is important for several reasons: a) to study soil sorption and attenuation of contaminants, b) to estimate the length of time to achieve breakthrough of a contaminant, c) to determine the partitioning

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

coefficient, and d) to estimate the other transport parameters such as the dispersion and diffusion coefficients (Yong et al., 1992). Sorption data is determined empirically using laboratory methods or from field studies. One way of determining sorption characteristics is the use of batch equilibrium tests where all soil particles are made to interact with the contaminant simulating a completely dispersed soil system. Another way is the use of column leaching tests with intact soil samples with a definite matrix and soil structure. The condition in the latter method is a better representation of field conditions. If we are to use the column leaching test as a procedure to determine the partitioning coefficient, its reliability should be ascertained. Specificially, we want to investigate the effects of the hydraulic gradient and the testing time on the partitioning coefficient. Rowe et al. (1995) conducted column tests under a hydraulic gradient very close to field conditions. Equilibrium conditions can be assumed for their study since the flow rate is low enough to reach equilibrium conditions. In our study on the other hand, higher hydraulic gradients are used to make the testing time shorter, thus, the need to ascertain whether equilibrium conditions are met.

MATERIALS AND METHODS

Zinc was chosen as the contaminant to be used since it is a common element found in municipal landfill leachate. Several studies have reported that zinc can be found in the leachate with concentration ranging from as low as 0 to as high as 1000 mg/L (Steiner, et al., 1971; Genetelli and Cirello, 1976; Bedient, 1994).

Zinc used was from the compound zinc nitrate hexahydrate supplied by Kaso Chemical Co. Ltd. Tokyo (Dog Brand Pure Chemicals). The properties of the compound used are shown in Table 1.

Illite clay was chosen as the clay to be studied since its physical characteristics are similar to the marine clay used in off-shore waste disposal sites. Its characteristics are shown in Table 2, with the values in ranges based on the figures reported in Reddi and Inyang (2000). The plastic and liquid limits were measured by the main author. The clay used was supplied by Hayashi Kasei Corporation. Illite is bonded together by potassium ions. The potassium ions, fixed between the layers, prevent swelling of the mineral and provide little interlayer surface area for cation exchange. The combination of the high specific surface area and the significant surface charge make clay important in the development of contaminant attenuating process or contaminant accumulation mechanism in soils.

Experimental Set-up

The column test used was developed by the Soil Mechanics Laboratory of the Tokyo Institute of Technology (Ozawa et al., 2000). The column test system is illustrated in Figure 1. The column is made of translucent acrylic resin material, has an inner diameter of 150 mm and a height of 500 mm. It is attached to a base plate and sealed

Compound used	Zinc nitrate hexahydrate
Formula	$Zn(NO_3)_2 . 6 H_2O$
Molecular Weight	297.49 g
Density	2.065 mg/L
Solubility	0.5 part water
pH (100 g/L, 25 °C)	3.5 – 5.4

Table 1: Properties of zinc

Specific gravity	2.6 – 3
CEC (mEq/100g)	10 – 40
Liquid limit (%)	87
Plastic limit (%)	32

Table 2: Properties of Illite Clay

with a top lid with a hole for the piston of the air cylinder. An air cylinder is placed on top to supply the vertical loading to apply the pressure directly on the clay layer. The vertical pressure applied was 30 kPa which approximates the stress condition at a depth of 7.5 meters of soft clay deposit in natural sea bed assuming the unit weight of the saturated soil is 14 kN/m^3. Hydraulic loading is applied by introducing air pressure through an opening at one point on the column wall 150 mm from the top. To make vertical load distribution and seepage uniform across the clay layer, a porous plate is placed on top of the clay layer. The porous plate has three hundred holes of 2 mm diameter and has a thickness of 5 mm. At the neck of the piston, a plastic plate is inserted. The tip of the settlement gauge is placed on this plate to measure settlement. The settlement gauge is used to establish that the layer has been fully consolidated (Tanchuling et al., 2000). The clay slurry was mixed and de-aired for 30 minutes using a vacuum pump. The column walls were lined with a silicone-seal bond to prevent water from flowing along the side walls. A round filter paper with a thickness of 0.2 mm was placed on top of the bottom plate. Using bare hands, the clay slurry was then placed inside the column. Another round filter paper was placed on top of the clay layer, on top of which was lain the upper porous plate.

Consolidation

The clay layer was normally consolidated using an applied vertical loading (σ'_p)of 30 kPa and hydraulic loading (σ_{cell}) ranging from 30 to 100 kPa creating the vertical effective stress shown in Figure 2. To consolidate the clay, force is applied through a loading plate which is attached to a piston which is being pushed by air pressure through a bellofram cylinder. The ambient temperature in the testing room was kept constant at 20°C.

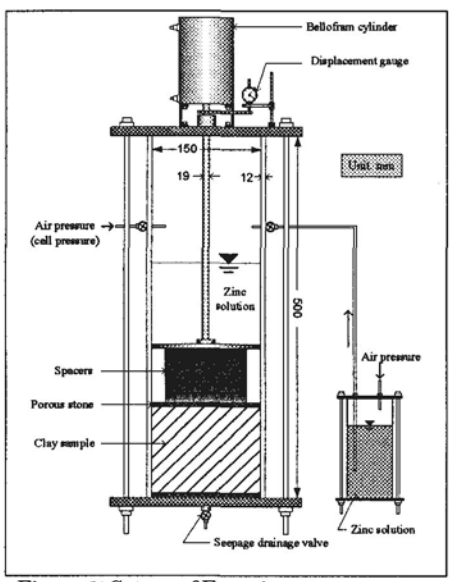

Figure 1: Set-up of Experiment

Leaching

After the consolidation was completed, the clay layer was leached with the zinc solution. The remaining water on top of the porous plate was drained by using a suction pipe. A solution was prepared to make an input zinc concentration of 475 mg/L. The input contaminant was placed inside the column through an opening on the upper part of the column. Leaching was commenced. After a pre-determined number of pore volumes, the test was stopped.

Sampling Procedure

After leaching, the top plate was unfastened, and any remaining liquid was drained using a suction pipe. Core samples were taken

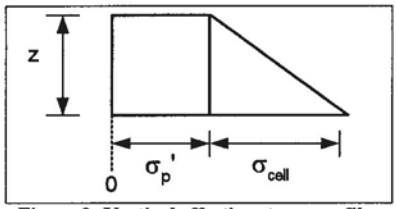

Figure 2: Vertical effective stress profile

using a boring apparatus made up of a 10 mm in diameter stainless steel pipe. A wooden rod is used to push the clay out of the pipe. Three core samples were taken from each test, once from the center and one each for each side opposite each other. For three test cases (I6, I7, and I8), the length of the partitions was 5 mm for the upper 30 mm, and 10 mm, for the rest of the length of the sample. For I2 and I5, all partitions were 10 mm long. With a spatula, the sample was partitioned along its depth, weighed and dried in the oven for 24 hours. After drying, the weight of the samples was taken, and the moisture content was computed for each partition of the sample.

Acid digestion

The amount of solids retained in the layers was determined by extraction of the zinc content through acid digestion. After drying, the samples were manually ground into fine powder. In a beaker, 0.5 g of the powder was mixed with 2 mL of nitric acid and 4 mL of hydrochloric acid and placed in a hot plate at a temperature of 120 °C for 2 hours. A watchglass covered the beaker to keep the liquid from evaporating. The supernatant was diluted, then filtered using a microfiltration system. Blank samples were also prepared to determine background concentrations and were used to adjust the concentrations that were determined by the Inductive Coupled Plasma-Atomic Emission Spectrometer (ICP-AES).

RESULTS AND DISCUSSION

Five column tests were conducted, labeled as I2, I5, I6, I7, I8. The measured parameters for each test are shown in Table 3. The height of clay layer was measured from the core sample taken after the leaching test. The hydraulic gradient, i is computed as hydraulic head/height of clay layer. Porosity, n was based on the assumption that the specific gravity of the soil is 2.65 g/cm^3. For each test case, the moisture content is the mean moisture content for all partitions of all samples.

Steady state flow

The flow rate was measured by weighing the amount of fluid collected at the outlet from the bottom plate. The graph in Figure 3 shows that the volumetric flow rate is constant for all test cases. The large variation in flow rate of I7 can be attributed to the leakage at the bottom plate, making it difficult to collect all effluent at all times. The hydraulic gradient was graphed against the Darcy velocity and illustrated in Figure 4. (Another column case was included to make this graph). From the linear relationship, v = ki, where v is Darcy velocity and computed as, v = Q/A where Q is the measured flow rate and A is the cross-sectional area of the column, a value of k (permeability coefficient) can be inferred. For the illite clay used in all tests, k is equal to

	I2	I5	I6	I7	I8
Final height of clay layer (mm)	122.5	68	63	65	65
Hydraulic gradient	83.3	105.04	48.59	109.89	109.89
Porosity	0.61	0.634	0.635	0.63	0.646
Leaching time (days)	33.90	10.03	31.02	14.32	12.62

Table 3: Measured parameters of all test cases

6.047×10^{-10} m/s. For the testing time used, the introduction of the contaminant did not have any effect on the hydraulic conductivity.

Amount of solute retained in the layers

The total amount of solute retained was computed as $C_{total} = C_{measured}$*volume of dilution/mass of soil where $C_{measured}$ is the concentration from the acid digestion procedure. The total amount of zinc retained in the layers in the core samples of one testing case (I2) are shown in Figure 5.

Three samples were taken, one from the center and two at the sides. The side samples were collected very near the walls. The graph shows the mean value and the range of values, covering the mean minus one standard deviation to mean plus one standard deviation. From the spread of values taken from the three samples in each layer, we can say that there is no significant difference between samples taken from the center compared to those taken from the sides. The other cases show the same trend. This indicates that flow is one-dimensional and uniform across the cross-section. Since the testing time is not long enough for the contaminant to travel a long distance, most of the concentration measured was limited to, for most of the cases, the upper 20 mm.

Estimating the partitioning coefficient

Using the profile of the concentration of the zinc in the layers that were retained as input data, the retardation factor and the dispersion coefficient were estimated from the analytical solution to the advection dispersion equation using the non-linear least squares fitting method within the software package MATHEMATICA. The analytical solution used was developed by Ogata and Banks (1961) and is expressed as

$$C(x,t) = \frac{C_o}{2}\left[erfc\left(\frac{Rx - V_x t}{2\sqrt{RD_x t}}\right) + \exp\left(\frac{v_x x}{D_x}\right) erfc\left(\frac{Rx + V_x t}{2\sqrt{RD_x t}}\right)\right]$$ given the following boundary conditions: C (0,t) = Co; C (x,0) = 0; C (∞, t) = 0; and where C is concentration in porewater, Co is initial concentration, R is retardation factor, x is distance from the origin along the flow, V_x is the porewater velocity, D_x is the hydrodynamic dispersion coefficient, and t is time. Since this equation is expressed in porewater concentration C, and experimental data is in terms of the total concentration C_{total} which includes the concentration of the solids sorbed and the concentration in the porewater, we need to express the equation in terms of C_{total}. For linear relationship between sorbed amount and concentration in solution, $C^* = K_d C$, where C^* is amount of solids sorbed, and K_d is the

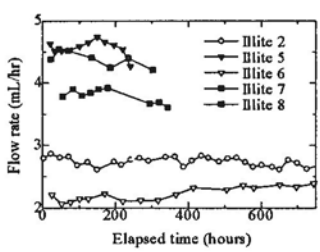

Figure 3: Flow rates

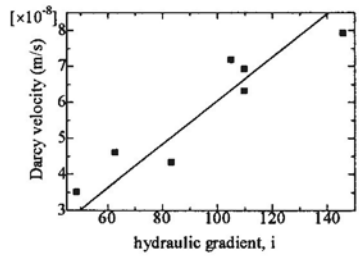

Figure 4 : Permeability coefficient

partitioning coefficient.

Since mass is conserved in the system, $C_{(total)}\, m_{(total)} = C^*\, m_{(soil)} + Cm_{(water)}$. Then, $C_{(total)}\, m_{(total)} = K_d\, C\, m_{(soil)} + C\, m_{(water)}$. Also, since $m_{(total)} = m_{(soil)} + m_{(water)}$, then, $C = \dfrac{C_{total}}{m^*_{soil} K_d + m^*_{water}}$ where $m^*_{soil} = m_{soil}/m_{total}$ and $m^*_{water} = m_{water}/m_{total}$. For linear sorption, $R = 1 + \dfrac{\rho_b K_d}{n}$ where ρ_b is dry density and n is porosity. Thus, $C_{total}(0,t) = \left(m^*_{water} + m^*_{soil}\dfrac{n}{\rho_b}(R-1)\right)C_o$ and finally,

$C_{total}(x,t) = \left(m^*_{water} + m^*_{soil}\dfrac{n}{\rho_b}(R-1)\right)\dfrac{C_o}{2}\left[erfc\left(\dfrac{Rx - V_x t}{2\sqrt{RD_x t}}\right) + \exp\left(\dfrac{v_x x}{D_x}\right) erfc\left(\dfrac{Rx + V_x t}{2\sqrt{RD_x t}}\right)\right]$. Using this equation, R and D were computed with the results summarized in Table 5. One test case (I2) is shown with the experimental and analytical data (Figure 6). Pore volume (PV) was computed as $PV = V_x{*}t/L$, where L is the height of the clay layer. I2 and I6 are based on the mean values per layer. I5 was based on one sample taken from the side while I8 was based on the center sample. I7 used the mean of two samples. The hydraulic conductivity that was used was uniform for all cases (6.047×10^{-10} m/s), based on the slope of the line relating the Darcy velocity and hydraulic gradient (Figure 4). Likewise, porosity used for all cases was based on the average value of 0.63.

The partitioning coefficients that were computed are close to each other with a mean of 8.982 cm^3/g and a coefficient of variation of 10.53%. This confirms the reliability and replicability of the procedure based on the small coefficient of variation in values obtained.

Using the computed partitioning coefficient, K_d, the total concentration was divided into the two components of the solids and porewater concentration (Figures 7 and 8 respectively). The concentration profile of all cases show a similar trend and are very close to each other since the variation of pore volumes used is not large.

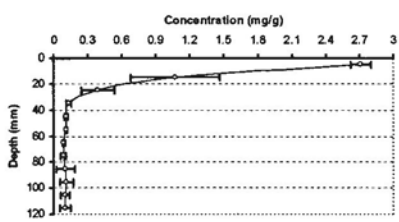

Figure 5: Concentration profile of I2

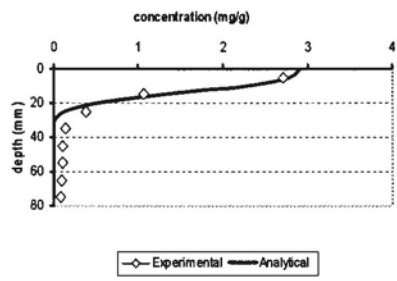

Figure 6: Results for I2

	I2	I5	I6	I7	I8
Pore volume	1.840	1.280	1.980	2.01	1.77
Retardation factor	15.88	12.56	15.58	16.26	15.22
Partitioning coefficient (cm^3/g)	9.561	7.427	9.374	9.804	9.135
Dispersion coefficient (x 10^{-10} m^2/s)	1.094	1.211	2.605	3.229	1.176
Estimated variance	.0260	.0080	.1745	.1873	.0837

Table 5: Computed values of retardation factor and dispersion coefficients

Effect of hydraulic gradient and leaching time on the sorption behavior

From Figure 9, we can see that the partitioning coefficient, Kd remains constant over the range of hydraulic gradient that was tested. Thus, we can say that the hydraulic gradient within the range tested does not affect the partitioning coefficient that can be obtained using the column leaching test. However, since the hydraulic gradient in the field is much lower than the ones used in the test we should be able to find a partitioning coefficient that is applicable to the field. From centrifuge experiments using a range of gravities from 1300 to 5280 over a 3-mm thick clay layer (Antoniadis and McKinley, 2000), it was shown that lower hydraulic gradient gives higher retardation factors caused by longer contact time between the soil and the contaminant. We can not show the same results in this study since the range of hydraulic gradient from 48 to 109 used was not large. Similarly, from Figure 10, it is evident that the leaching time expressed in pore volumes does not affect the value of partitioning coefficient obtained. Since the range of pore volume used is quite narrow (1.28 to 2.01), more tests are being conducted using higher pore volumes to check whether the partitioning coefficient remains constant. The mobility of zinc in illite clay can be quantified by the velocity of the zinc solution with one-half of the starting concentration (V_c) using the equation, $V_c = V_x/R$. Based on the results of this study, V_c of zinc in illite clay is $0.0662V_x$.

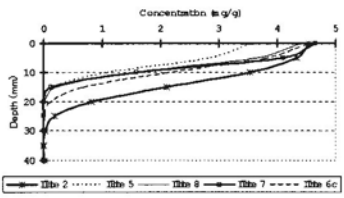

Figure 7: Amount of solids sorbed

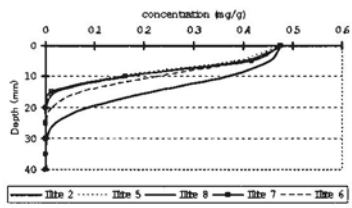

Figure 8: Porewater concentation

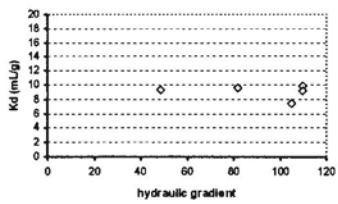

Figure 9: Effect of hydraulic gradient

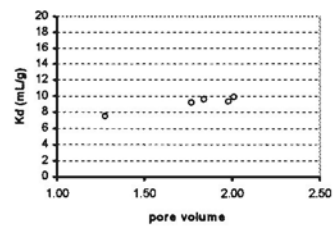

Figure 10: Effect of pore volume

Comparison with batch equilibrium tests

Batch equilibrium tests were conducted to be able to compare results with those from the column leaching tests. The concentration that was used in the column tests when done in batch tests would give a partitioning coefficient of 17.56 cm^3/g which is almost twice the mean of the partitioning coefficients obtained from the column tests. The partitioning coefficient to be used in the advection dispersion equation to predict contaminant transport should have been obtained from conditions similar to the field. Batch equilibrium tests are applicable to completely dispersed systems where all the soil particles are exposed to the contaminant.

CONCLUSIONS

From this study, we can conclude the following points:

1. The column leaching test has been shown to be a reliable method in determining the partitioning coefficient.
2. There is no significant effect of hydraulic gradient and testing time on sorption for the range of values that were used.
3. Partitioning coefficients obtained from batch tests if used directly in contaminant transport models overestimate attenuation capacity of clay.
4. The mobility of zinc in illite clay is retarded by a factor of 15.1.

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Non-equilibrium Fate And Transport Of Cd In Saturated Soils: Temperature Effect

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ABSTRACT
Two surface soils were investigated with the miscible displacement technique to analyse the effect of temperature on nonequilibrium transport of cadmium through the saturated homogeneously packed soil columns. The columns were fed with non-sorptive bromide and sorptive cadmium. The breakthrough curves were curve fitted with equilibrium and non-equilibrium models using the nonlinear least squares optimization program, CXTFIT version 2.1. The equilibrium model successfully described the BTCs of Br, indicating the appropriateness of the two-site nonequilibrium model in describing the observed nonideality in Cd BTCs. The nonideality prevailed in BTCs at 283 and 294K but not in BTCs at 308K. Less tailing of BTCs at 308K also evidenced the approach from nonequilibrium to equilibrium transport prompted by increasing temperature. The sorption distribution coefficients increased slightly with increasing temperature. This is probably because the transport was under equilibrium condition at higher temperature (308K) while it was under nonequilibrium condition at lower temperature (283 & 294K). Increasing temperature elevated the sorption rate constant but imposed no effect on the fraction of instantaneous sorption. The ascending sorption rate constant therefore specifies the approach towards equilibrium transport. The value of activation energy of sorption, which was calculated using Arrhenius' equation with the sorption rate constants, probed that the rate limitation causing nonequilibrium transport might be intra-organic matter diffusion.

INTRODUCTION
The nonequilibrium behaviour, manifested as early breakthrough and long tailing, occurring in pollutant transport in soils has been extensively observed and investigated in laboratory and field studies over the last two decades, while the temperature dependence of solute transport received little focus. Piatt et al. (1996) investigated the effect of temperature (277 and 299K) on the hydrophobic organic chemicals (HOCs) sorption and transport in soils and observed the rate constant increased with increasing temperature. Heron et al. (1998) showed thermally enhanced remediation of trichloroethlyene (TCE) could significantly reduce the tailing of sorption observed at normal temperature. Carroll et al. (1994) demonstrated high-temperature (383K) pretreatment of the sediment substantially increased the fraction of instantaneous desorption from the sediment, which could not be raised upon bar-milling that reduced particle size and increased surface area. This study aims to quantify the effect of temperature (283-308K) on Cd transport in saturated soils with miscible displacement technique.

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METHODS

Soil Characteristics

The surface soil samples were taken from 25-50 cm below ground surface at the campus of Hong Kong University of Science and Technology (UST soil) and Clearwater Bay (CWB soil) in Hong Kong. The soils were air-dried and passed a 2-mm sieve. The particle size distribution was obtained by sieving and hydrometer methods. The soil pH was measured in 1:2 soil-to-water ratio (Dane and Topp 2002). The organic matter contents of the soils were indexed by the organic carbon contents, which were determined by dry combustion (Sparks 1996). The specific surface area was measured by a nitrogen adsorption BET method (Dane and Topp 2002). The cation exchange capacity (CEC) of the soils was determined by NH_4-Na exchange (USEPA method 9081). The clay fractions of the soils were separated by pipette method (Dane and Topp 2002). Of the clay fractions, the most abundant minerals were analysed with X-ray diffraction (XRD) method (Tan 1993).

Miscible Displacement Experiments

The miscible displacement experiments were conducted using vertical columns with internal diameter of 3.6 cm and length of 10 cm, in which UST and CWB soils were homogeneously packed. The packed columns were weighted to calculate the bulk density and porosity, which were 1.508 g/cm^3 and 0.433 for the UST soil columns, and 1.242 g/cm^3 and 0.532 for the CWB soil columns. O-rings were used to seal the end plates against the interior of the glass column. The porous stainless steel plates were attached at both ends of columns to promote a radial distribution of the influent solution and reduce hydrodynamic dispersion of moving solution at or near column exit. The columns were saturated by feeding background electrolyte of 0.03M $NaNO_3$ from bottom with peristaltic pumps at low pore-water velocity (~2 cm/h). The background electrolyte solution was adjusted to pH 5 by HNO_3. The non-sorptive Br (by NaBr) and sorptive Cd (by $Cd(NO_3)_2$) solutions were prepared in the presence of background electrolyte. The average input concentrations of Br and Cd were approximately 10 mg/L and 2 mg/L, respectively. Upon saturation of the columns, the Br and Cd pulses were individually injected to UST and CWB soil columns at pore-water velocities of roughly 8 cm/h (UST soil) and 6 cm/h (CWB soil) accordingly. Six columns in total were implemented at 283 ±0.5, 294 ±0.5 and 308 ±0.5K (10 ±0.5, 21 ±0.5 and 35 ±0.5 °C), in which three for UST soil and three for CWB soil. The tracer pulses were applied to the columns until the effluent concentration approximately equalled the input concentration during adsorption. Then the columns were fed with background solution again until the effluent concentration was close to zero during desorption. Effluent samples were collected from the top exit of columns periodically. The effluent Br was analysed by Ion Chromatography (Dionex DX-500). The effluent Cd was measured by Atomic Absorption Spectrometry (Hitachi, Z-8200).

Data Analysis

The dimensionless concentration (effluent concentration/input concentration) was plotted against dimensionless time (pore volume) to construct the breakthrough curves (BTCs), which were analysed using the nonlinear, least-squared, optimization program CXTFIT version 2.1 (Toride et al. 1999), employing the equilibrium transport equation and the two-site nonequilibrium transport equations.

The equilibrium model for a linear sorption reaction is given as (notations in appendix),

$$R\frac{\partial c}{\partial T} = \frac{1}{P}\frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial x} \qquad \text{(Eq 1)}$$

where, $c = C/C_o$, $T = \frac{vt}{L}$, $x = z/L$, $P = \frac{vL}{D}$, $R = 1 + \frac{\rho K_d}{\theta}$ (Eqs 2a-e)

The dimensionless equations of the first-order, two-site nonequilibrium model for linear sorption are given as (notations in appendix),

$$\beta R \frac{\partial c_1}{\partial T} + (1-\beta) R \frac{\partial c_2}{\partial T} = \frac{1}{P} \frac{\partial^2 c_1}{\partial x^2} - \frac{\partial c_1}{\partial x} \quad \text{(Eq 3)}$$

$$(1-\beta) R \frac{\partial c_2}{\partial T} = \omega (c_1 - c_2) \quad \text{(Eq 4)}$$

where, $c_1 = C/C_o$, $c_2 = S_2/(1-F)K_d C_o$, $T = \frac{vt}{L}$, $x = z/L$, $P = \frac{vL}{D}$,

$R = 1 + \frac{\rho K_d}{\theta}$, $\beta = \frac{\theta_m + F\rho K_d}{\theta + \rho K_d}$, $\omega = \frac{\alpha(1-\beta)RL}{v}$ (Eqs 5a-h)

The curve fitting of experimental data to the equilibrium model involves optimization of two parameters (R and D), while to the nonequilibrium model involves optimization of three parameters (R, ω and β). The values of P, K_d, F and α are calculated using Eqs 2d-e and 5e-h, and the rest parameters (C, C_o, v, L, ρ and θ) are experimentally measured.

RESULTS

Soil Characteristics

The properties of the soils are listed in Table 1. CWB soil contained much higher silt and clay contents, which contributed to larger surface area, in comparison with UST soil. The CEC of CWB approximately doubled that of UST, both of the values lay in the common range of CEC reported for surface soils (Sposito 1989). The organic carbon contents of about 0.6% in the two soils were expected for surface soils. The most abundant mineral in the clay fractions of the two soils was kaolinite, 1:1 layer clay.

TABLE 1. Soil Characteristics.

	UST	CWB
Particle density (kg/L)	2.666	2.652
Sand (%)	75	25
Silt (%)	16	42
Clay (%)	9	33
Soil Classification	Sandy Loam	Clay Loam
Soil pH	7.6	4.3
Organic Carbon (%)	0.616	0.644
Surface area (m^2/g)	4.57	36.37
CEC (mmol/g)	0.14	0.31
Clay mineral	Kaolinite	Kaolinite

Miscible Displacement Experiments - Non-sorptive Br Transport

Table 2 lists Br concentrations and pore-water velocities used, and optimized values of retardation factor and dispersion coefficient of BTCs of Br with equilibrium model. The nonequilibrium model was also attempted but the CXTFIT program rejected nonequilibrium model optimizations automatically. The BTCs of Br (not shown) were symmetrical in shape and well described by equilibrium model, indicating the adequate use of two-site

nonequilibrium in describing the transport of sorptive solute (Kookana et al. 1994) (Nelson et al. 2003). The Peclet number determined by Eq. 2e from non-sorptive Br test (Table 2) was used to calculate the dispersion coefficient of the sorptive Cd transport (Brusseau 1993).

TABLE 2. Fitted and Calculated Parameter Values with Equilibrium Model for Br Transport.

				Equilibrium			
Expt. No.	Soil	C_{Br} (mg/L)	v (cm/h)	R	D(cm^2/h)	P	r^2
1	UST	10.12	8.155	0.942	5.526	14.76	0.990
2	UST	11.29	8.134	0.945	4.230	19.23	0.985
3	UST	10.12	8.788	0.970	8.878	9.90	0.967
4	CWB	10.12	6.925	1.370	5.531	12.52	0.989
5	CWB	10.07	7.335	1.377	6.537	11.22	0.992
6	CWB	10.12	7.045	1.308	5.759	12.23	0.991

Miscible Displacement Experiments - Sorptive Cd Transport

Breakthrough curves (BTCs) for the Cd in UST and CWB soils at 283, 294 and 308K are shown in Figure 1. At 283 and 294K, nonequilibrium model fitted the observed shape of BTCs much better than equilibrium model in UST soil and comparatively better than equilibrium model in CWB soil. However, at 308K, equilibrium model described the BTCs of the two soils well. The nonequilibrium model was also attempted but failed to curve fit the BTCs as the optimized parameters were indicating equilibrium model. These findings illustrated that the Cd transport in both soils was under nonequilibrium condition at 283 and 294K, while it was under equilibrium condition at 308K. Table 3 summarizes the applied Cd concentrations, pore-water velocities, equilibrium and nonequilibrium parameters calculated by Eqs. 2d&e and Eqs. 5e-h.

TABLE 3. Fitted and Calculated Parameter Values of Equilibrium and Two-site Nonequilibrium Models for Cd Transport.

						Equilibrium		
Expt. No.	Soil	T(K)	C_{Cd} (mg/L)	v (cm/h)	D(cm^2/h)	R	K_d (cm^3/g)	r^2
1	UST	283	1.949	7.162	4.852	64.62	18.27	0.968
2	UST	294	2.038	8.134	4.230	66.31	18.75	0.950
3	UST	308	1.960	8.732	8.820	73.39	20.79	0.994
4	CWB	283	1.944	6.562	5.241	26.60	10.97	0.983
5	CWB	294	1.967	6.374	5.681	30.35	12.57	0.991
6	CWB	308	1.955	6.596	5.393	42.86	17.93	0.997

		Nonequilibrium						
Expt. No.	Soil	R	β	ω	K_d (cm^3/g)	F	α (h^{-1})	r^2
1	UST	71.21	0.730	0.552	20.16	0.726	0.021	0.998
2	UST	69.69	0.737	0.843	19.72	0.734	0.037	0.995
3	UST	-	-	-	-	-	-	-
4	CWB	28.00	0.907	0.098	11.57	0.904	0.025	0.986
5	CWB	31.62	0.877	0.240	13.12	0.873	0.039	0.997
6	CWB	-	-	-	-	-	-	-

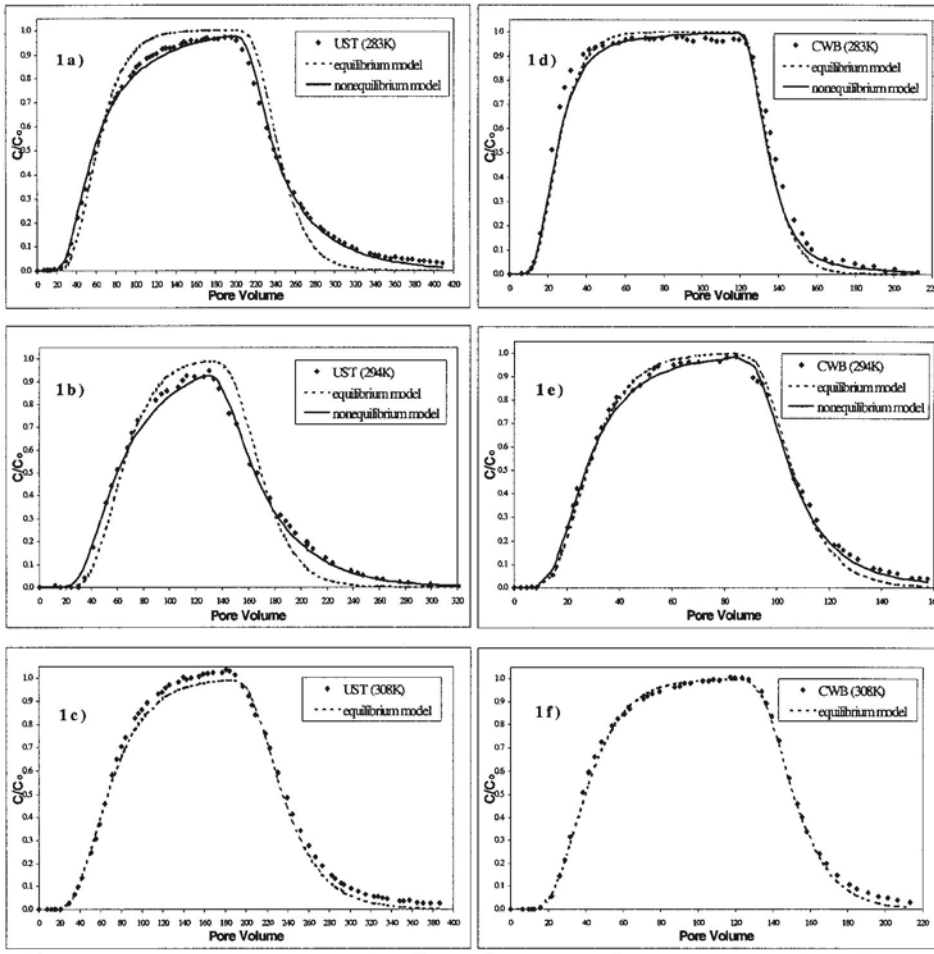

FIGURE 1. Breakthrough curves (BTCs) of Cd in: (a) UST soil at 283K; (b) UST soil at 294K; (c) UST soil at 308K; (d) CWB soil at 283K; (e) CWB soil at 294K; (f) CWB soil at 308K. The input Cd concentrations were about 2 mg/L and the pore-water velocities were about 8 cm/h (UST soil) and 6 cm/h (CWB soil).

The retardation factor (R) and sorption distribution coefficient (K_d) increased as the temperature increased from 283 to 308K (Table 3). This trend is ascribed to the fact that the transport is approaching from nonequilibrium towards equilibrium conditions with increasing temperature. Under equilibrium condition, all sorption is instantaneous and complete during the residence time in column. In contrast, under nonequilibrium condition, part of sorption is instantaneous and complete, and the rest is kinetic and incomplete within the residence time associated with the transport. Conceptually, equilibrium condition should possess higher sorption than nonequilibrium condition has. Then, there is no surprise that higher equilibrium distribution coefficient is obtained under a situation that is relatively closer to equilibrium at higher temperature.

The sorption in nonequilibrium transport is conceptually divided into two types: one is equilibrium sorption; the other is kinetic sorption, which is probably rate-limited by chemical reaction, film diffusion or intra-sorbent diffusion, in which the slowest process is rate-limiting. The higher value of fraction of instantaneous sorption (F) indicates the larger portion of sorption is under equilibrium. Table 3 shows the observed fraction of instantaneous sorption (F) has weak relationship with the temperature change (283-294K), which conforms to the findings of other studies. Brusseau et al. (1991) and Piatt et al. (1996) found that the fraction of instantaneous sorption did not change much with temperature. With the three possible rate-limiting processes leading to kinetic sorption, the fraction of instantaneous sorption should be more or less invariant to temperature change. The fraction of sites associated with slow chemical reaction is determined by characteristics and interaction between solute and sites. The fraction of sites covered by thick film that limits diffusion, or the fraction of sites located at interior of soil component that is less accessible, are both structurally destined. Brusseau et al. (1991) suggested that the physical and chemical characteristics of the sorptive domains and thus the fraction of kinetic sorption associated with the interior of the soil organic matter should not change appreciably with a 20K change in temperature. In this study, the kinetic sorption is believed to associate with the soil organic matter, because intra-sorbent diffusion is the rate-limiting process as discussed later, and the most abundant clay minerals of the two soils are kaolinite, in which only external planar surface sites are available for sorption and intra-sorbent diffusion would be insignificant.

The transport in the two soils was under equilibrium condition at 308K, implying all sorption was instantaneous. Jardine and Sparks (1984) illustrated similar results in batch kinetic study, in which one fast reaction and one slow reaction were revealed in potassium adsorption kinetics at 283 and 298K while only one reaction was revealed at 313K. As for this study, in the absence of an obvious relationship between the fraction of instantaneous sorption and temperature, the disappearance of fraction of rate-limited sorption at 308K would be ascribed to an increase of sorption rate constant instead of the structural change of soil components.

As the temperature increased from 283 to 294K, the sorption rate constant increased roughly 1.8 and 1.6 times in UST soil and CWB soil (Table 3). Such a large increase in sorption rate constant might reasonably account for the observed shift from nonequilibrium to equilibrium condition with further increase in temperature. The rate constants at 308K were not reported in Table 3 and 4, because the transports were under equilibrium and all sorption were instantaneous.

The nonequilibrium model approximates the rate-limited sorption with first-order kinetic reaction, which is a widely adopted approach due to its simplicity and sufficiently high accuracy. The sorption rate constant in nonequilibrium model is fundamentally apparent that lumps several possible mechanisms in the first-order reaction. The sorption rate constants are dependent on system parameters such as pore-water velocity, length-scale, and residence time (Maraqa 2001). Jardine and Sparks (1984) suggested the apparent rate constant is comprised of film diffusion rate, intra-sorbent diffusion rate, and chemical reaction rate. Although all of the chemical rate and the two diffusion rates would increase with rising temperature, the response to temperature change should be more substantial for chemical rate than for diffusion rate. Hence, calculating of the energy of activation of kinetic sorption might provide clues for deducing the corresponding rate-limiting mechanism. The integrated form of Arrhenius' equation is used to calculate the activation energy (E_a) from the sorption rate constant (α) at different absolute temperature (T) (Sparks 1989),

$$\ln \alpha = (\ln A) - E_a / RT \qquad \text{(Eq 5)}$$

TABLE 4. Sorption Rate Constant and Activation Energy.

		ln α	
T (K)	1/T	UST	CWB
283	0.003534	-3.8873	-3.7010
294	0.003401	-3.2834	-3.2365
E_a (kJ/mol)		37.98	29.21

Table 4 lists the calculated activation energy with sorption rate constants at different temperatures obtained from nonequilibrium model. The values of activation energy of sorption in UST soil and CWB soil were 38 and 29 kJ/mol, respectively. The activation energy measures the magnitude of the forces to be overcome during the reaction process (Sparks 1989). The values of activation energy of the sorption less than 42kJ/mol indicate diffusion-controlled sorption; higher values indicate chemical exchange-controlled sorption (Ogwada and Sparks 1986). Of the diffusion-controlled processes, the intra-sorbent diffusion process is characterized by activation energies between 21 and 42 kJ/mol whereas the film diffusion process exhibits activation energies of less than 21 kJ/mol (Jardine and Sparks 1984) (Werth and Reinhard 1997). Thus, the values of activation energy of sorption in UST soil and CWB soil suggest that the kinetic sorption in nonequilibrium would probably be rate limited by the intra-organic matter diffusion, as the soil organic matter is probably associated with the kinetic sorption.

CONCLUSIONS

There are two major findings about the dependence of Cd transport on temperature in this study. First, a moderate enhancement in temperature from 283 to 308K would be sufficient to bring the Cd transport in saturated soils from nonequilibrium to equilibrium conditions. Thus elevating temperature relieves the deviation from ideal equilibrium model, and most importantly, lessens the long tailing, implying an increase in effectiveness of cleanup with in-situ pumping system. Second, the intra-organic matter diffusion is the rate limitation in sorption, indirectly indicated by sorption rate constant and Arrhenius' equation. Such rate limitation in sorption leads to nonequilibrium transport. Further experiments by removing organic matter from soil would directly confirm whether the soil organic matter is the predominant cause of nonequilibrium sorption and transport.

APPENDIX

C effluent solute concentration (mg/L)
C_o influent solute concentration (mg/L)
c dimensionless solution concentration
c_1 dimensionless solution concentration of total liquid phase
c_2 dimensionless sorbed concentration for kinetic sites
S_2 sorbed concentration for kinetic sites (mg/kg)
z distance (cm)
x dimensionless distance
L column length (cm)
t time (h)
T dimensionless time (number of pore volumes) in transport models, or absolute temperature in Arrhenius' equation (K)
v average pore-water velocity (cm/h)
D hydrodynamic dispersion coefficient (cm^2/h)

P	column Peclet number (dimensionless)
ρ	bulk density of soil column (g/cm^3)
θ	porosity of soil column (dimensionless)
ω	dimensionless mass transfer coefficient
β	dimensionless partition coefficient
R	retardation factor (dimensionless)
K_d	sorption distribution coefficient (cm^3/g)
F	fraction of instantaneous sorption (dimensionless)
α	first-order sorption rate constant (h^{-1})
E_a	activation energy of reaction (kJ/mol)
R	gas constant (8.314 J/mol-K)
A	Arrhenius' constant

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Mass Transfer Behaviour After Air Sparging Remediation of LNAPL Source Zone – 2D Tank experiments

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ABSTRACT
Complete source zone removal by insitu remediation is often difficult due to subsurface heterogeneity. It is therefore necessary to adopt the concept of risk reduction evaluation at the receptor after the termination of source zone remediation process. To perform such an evaluation, it is essential to understand mass transfer behaviour from NAPL source both before and after remediation. In this study, soil tank experiments were performed to investigate the mass transfer process after applying air sparging remediation to toluene NAPL sources. Results show that both pre- and post- mass transfer processes from NAPL to gas and aqueous phases depend on NAPL source entrapment condition as well as the texture of soil where NAPL is trapped. Both gas and aqueous concentrations increased after remediation from the values at the end of the air sparging process; the gas phase concentration reached to a steady state level, whereas the aqueous phase concentration continuously increased towards the maximum solubility value of toluene.

INTRODUCTION
Past studies show that none of the currently available in situ source zone remedial techniques is capable of removing nonaqueous phase liquid (NAPL) contaminant mass completely from the subsurface. The limited removal efficiency is primarily due to subsurface heterogeneity (Waduge, 2003 and Waduge et al., 2004). Therefore, remediation technologies should be evaluated based on the degree of reduction in risk achieved after an incomplete mass removal instead of the degree of mass removed (Soga et al., 2002 & 2003). For instance, a clean-up technology may remove 70% of the contaminant mass, but the process of remediation can change the characteristics or morphology of the remaining 30%, which results in elevated downstream risk. Alternatively, a 20% reduction in NAPL mass could be sufficient to change its subsurface distribution into a condition of significantly reduced mass transfer (such as a greatly reduced NAPL surface area) with a corresponding reduction in receptor risk.

Three possible scenarios of changes in contaminant concentration at the receptor after remediation are illustrated in Figure 1; that is, spatial or down gradient concentration to increase (scenario 1), stay constant (scenario 2) or decrease (scenario 3) following the termination of source zone remediation. Scenario 1 is often observed in incomplete source removal conditions; the NAPL source continues to produce contaminant flux by increasing or continuous mass transfer processes and the risk values consequently increase with time. On the other hand, Scenario 3 can be considered as a successful remediation because the

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concentration decreases with time. A typical example of this is when the mass flux produced from the incompletely removed source is small enough so that natural attenuation processes overrides. Considering that complete removal is not possible, it is therefore necessary to understand the mass transfer behaviour from remaining NAPL source after remediation so that the site can undergo natural attenuation processes in a favourable condition. Hence, combined temporal mass flux evaluation with estimates of natural attenuation capacity is needed to develop meaningful risk-based source-plume management strategies.

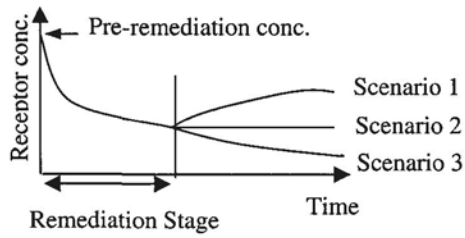


Figure 1 Possible scenarios after source remediation

This study examines pre-and post-remediation mass transfer processes of LNAPL pool entrapped in heterogeneous soils. 2D tank experiments were performed for the investigation. In the experiment, mass transfer behaviour from LNAPL was investigated by measuring the variation of gas and aqueous concentrations after air sparging remediation was applied. A total of five tank experiments were performed for the investigation. However due to page limitation, this paper reports three experiments; two soil models have a coarse sand lens in the fine sand matrix, whereas the other has a fine sand lens in a coarse sand matrix.

EXPERIMENTAL MATERIALS AND METHODS

A soil tank with internal dimensions of 1.2 m (length) x 0.8 m (height) x 0.15 m (width) was utilised to conduct LNAPL source zone remediation experiments by air sparging (see Figure 2). The tank is built by aluminium except the front surface, which is made of toughened glass to achieve the visibility of subsurface during testing. Two wells were placed at the lateral sides of the tank; one is used as an extraction well, where as the other is opened to the atmosphere. The bottom of the tank was connected to a water tank through a moving reservoir to maintain the necessary height of the water table.

There are 77 sampling ports of 10 mm diameter on the backside of the tank (see Figure 3). These ports are used to obtain gas or aqueous phase samples before, during and/or after air sparging or to install resitivity probes for continuous measurements of water saturation in unsaturated soil region. The sampling ports consist of a rubber septum held in brass fittings.

The soil vapour extraction system has a pump, vacuum gauge, regulator and flow meter, whereas the air sparging system consists of a compressor, regulator, pressure gauge, flow meter and sparger. A plastic silencer (RS components Ltd, UK) of 38.5 mm diameter and 123.5 mm effective length is used as a sparger to inject air into the soil model.

Toluene (Fisher Scientific International Company), a major constituent of gasoline and other petroleum products, was used as the model LNAPL. Toluene, which has high volatility and toxicity, was mixed with non-volatile, organic soluble Red Oil O (Aldrich Chemical Company Inc.) (0.5 g of dye in one litre of toluene) to achieve the visibility in the migration through the porous media.

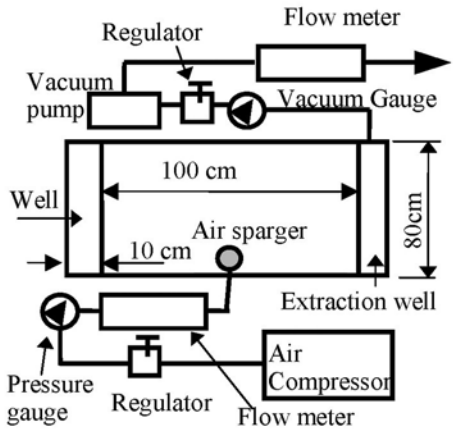


Figure 2. Set up of the 2D air sparging/SVE system

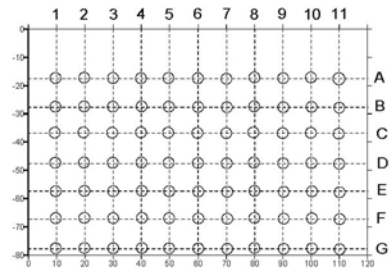


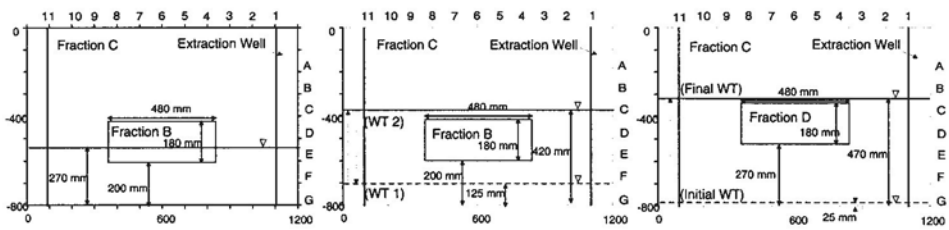
Figure 3. Layout of 77 grid sampling ports

Three different unconsolidated sands were used in the experiments; Fraction B (particle size ranging from 0.6 mm to 1.18 mm), C (particle size ranging from 0.3 mm to 0.6 mm) and D (particle size ranging from 0.15 mm to 0.3 mm), according to the British Standard. Fraction B and C were provided by WBB Minerals (UK) and David Ball Group plc, England provided Fraction D.

TESTING PROGRAMME

Soil Model Preparation

The results of three tank experiments are reported in this paper. The experiments were performed considering two extreme scenarios; a coarse sand lens in a fine sand matrix and a fine sand lens in a coarse sand matrix. Two tests were conducted with a coarse sand lens and the height of the water table was varied to create two different LNAPL pool entrapment conditions. The other test was carried out with a fine sand lens. The soil model geometries with the water table location are shown in Figure 4.



(a) Test 1 (b) Test 2 (c) Test 3

Figure 4. Soil models

The soil tank was filled with sands under water (wet packing). The wet packing gives a uniform, homogeneous and almost fully saturated soil conditions. More detailed description of soil model preparation is reported in Waduge et al. (2003 a & b). The mass of dry soil and

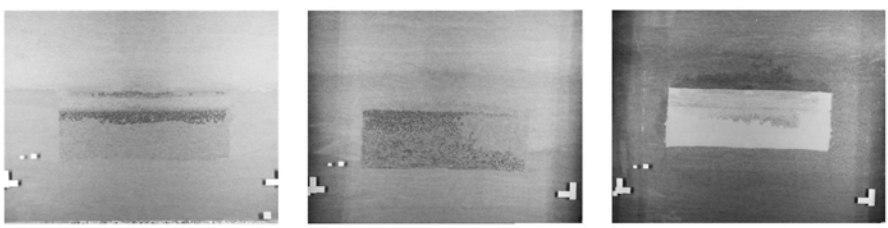
the volume of the sand packs were measured to calculate the porosity of each sand after placement. The average porosities of Fraction C sand matrix, and B and D sand lenses were 0.4, 0.44 and 0.38, respectively.

After creating a fully saturated soil model, the water table was lowered gradually to a predetermined level to create different LNAPL entrapment conditions. The resistivity probe readings confirmed that the model was in a hydrostatic condition at the end of water drainage. Prior to the spill or injection of toluene into the model, a rubber membrane was placed over the entire soil model to ensure that all contaminated vapour would go into the extraction well. The system was then sealed by placing a lid on top of the tank.

NAPL Spill

In Test 1 and 2, toluene was spilled from the top of the sand model using a line source. The line source, which has 145 mm length, 25 mm diameter and 2 mm split at the bottom over complete length, was used to achieve a 2D spill over the entire tank width. A total of 8×10^{-4} m^3 (687 g) of toluene was spilled at an average rate of 8000 mm^3/s. In Test 3, toluene was directly injected into the unsaturated zone of the finer lens through three syringes with 100 mm long needle using a flow pump. A total of 600 g of toluene was injected at a rate of 155 mm^3/s.

Once the spill or injection of toluene was completed, the model was left for LNAPL redistribution until the movement of LNAPL ceased. In Test 1, the height of the water table was set such that a part of the coarse sand lens was below the water table as shown in Figure 4(a). Consequently, a majority of spilled toluene was trapped in the upper part of the coarse sand lens as shown in Figure 5 (a). In Test 2, the majority of spilled toluene was entrapped below the saturated zone, as shown in Figure 5 (b), due to fluctuation of the water table. Test 3 had a fine sand lens as shown in Figure 4(c). Since the water table was raised after the completion of toluene injection, the majority of toluene was inside the fine sand lens, as shown in Figure 5 (c).



(a) Test 1 (b) Test 2 (c) Test 3

Figure 5. Final distribution of toluene

Pre-remediation monitoring of mass transfer processes from the NAPL source to gas and aqueous phases was performed for 70 to 140 hours. The gas samples were collected at selected sampling ports using a 100 µL gas-tight syringe. The size of the gas sample was 50 µL and it was directly injected into an Agilent 6850 Series II gas chromatography with a flame ionisation detector (FID). The headspace method was used to measure the aqueous toluene concentration at different sample locations in the saturated region of the model.

Air Sparging Remediation

At the end of the pre-remediation monitoring, air sparging process was initiated to remove the LNAPL source trapped in the soil models. Air was injected at a flow rate of 0.005 m^3/min from a sparger placed at the mid-bottom location of the tank and the contaminated air was extracted at a flow rate of 0.012 m^3/min from the extraction well. Ten cycles of 10 hour operational periods followed by 14 hours of shutdown period were conducted. In Test 2, the water table was lowered before initiating AS/SVE and was increased step by step every other day during AS/SVE until it came to the level as shown in Figure 4(b) at the end of the air sparging.

Post-remediation monitoring of the mass transfer behaviour was performed after the completion of air sparging remediation. The monitoring period was approximately 240 hours.

DISCUSSION

Mass Removal Efficiency

The mass removal efficiency is defined as the amount of NAPL mass removed compared to the initially spilled or injected mass. As shown in Figure 6, the mass removal efficiencies of Tests 1 and 2 were 82% and 86%, respectively. The mass removal efficiency in Test 3, where there was a fine sand lens in a coarse sand matrix, was 44%. The results clearly show that mass removal efficiency decreases nearly by 40% when NAPL is trapped inside a fine sand lens. This is because of the bypass of injected air around the source zone due to the low permeability fine sand lens, resulting in loss of air-NAPL contact area through which mass transfer is occurring.

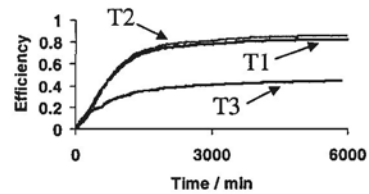


Figure 6. Mass removal efficiency

Changes in Concentrations Before and After Remediation

The temporal variation of toluene gas concentration at different sample locations in Tests 1, 2 and 3 before and after remediation are shown in Figure 7. In general, prior to air sparging remediation, toluene gas concentration increased gradually with time and reached towards a steady state gas concentration. However, the steady state gas concentration varies according to the sample location. For example, the toluene gas concentrations at the sample locations close to the source zone rapidly increased to the equilibrium gas concentration of 140 mg/L (B7 and C6 in Test 1 and A6 and B5 in Test 2). The rate of change in gas concentration decreased when the sample locations were away from the source zone (A2, A4 and B9 in Test 1 and A2, B2 and B9 in Test 2). This is due to the diffusion driven mass transport within the soil models.

The gas concentration values varied according to different entrapment conditions of toluene. The measured gas concentrations in Test 1 are the highest since the majority of toluene is in the unsaturated zone and there is an exclusive interaction between NAPL and air, resulting higher mass transfer. In Test 2, although most of the spilled toluene was trapped below the saturated zone, the contribution of entrapped toluene in the unsaturated zone during spilling increased the NAPL-air mass transfer. Therefore, relatively high toluene gas concentrations were measured. In Test 3, toluene was trapped in the fine sand lens below the water table. Hence toluene had to dissolve in water first and then volatilise into the gas phase.

Consequently, the gas concentrations were low values even at the locations close to the source zone as shown in Figure 7(c) (A6 and A7).

The gas concentration after remediation increased gradually with time from the level at the termination of remediation and reached towards a steady state value as shown in Figure 7. In Tests 1 and 2, the final gas concentrations at the end of the monitoring process were much smaller than those in the pre-remediation monitoring stage. On the other hand, in Test 3, the gas concentrations after remediation are much higher than those measured in Tests 1 and 2. This is primarily due to the differences in mass removal; the mass removal in Test 3 was much lower than that in Tests 1 and 2. This suggests that mass transfer rate is governed by the amount and texture of the soil where NAPL is entrapped.

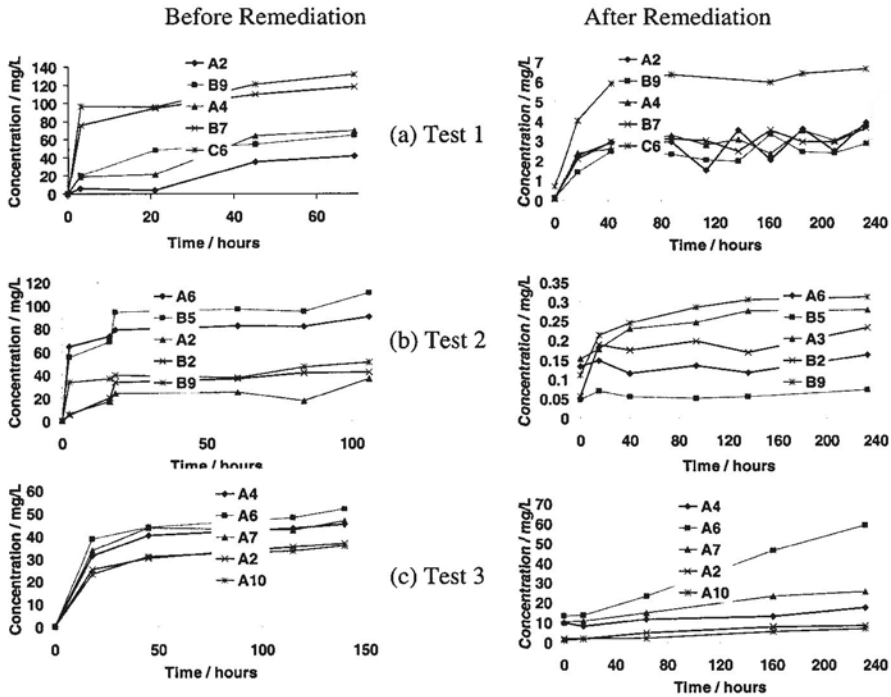


Figure 7. Variation of Gas concentration before and after air sparging

Figure 8 shows the spatial and temporal variation of toluene aqueous concentrations before and after remediation. In the pre-remediation stage, the dissolved toluene concentration at all sample locations increased gradually with time. The aqueous phase concentration also varied according to the sample location of the soil model. At the locations that are close to or within the possible NAPL source, the aqueous concentrations rapidly increased towards the solubility limit of toluene (530 mg/L) (C5 in Test 2 and D3 and C9 in Test 3).

The aqueous concentration after remediation increased with time from the value at the end of the air sparging remediation. As shown in Figure 8, the aqueous concentrations continuously increased towards the maximum solubility without reaching to a smaller steady state value. This is primarily due to the dissolution of remaining NAPL source in the saturated zone. The

slow dissolution of NAPL provides contaminant mass continuously into the aqueous phase. However, the rate of increase in dissolved concentration depends on the distance from NAPL source (e.g. E6 has a higher rate compared to C3). In general, the post-remediation aqueous concentrations in Test 3 are higher than those in Tests 1 and 2. Again, this is primarily because less NAPL was removed in Test 3.

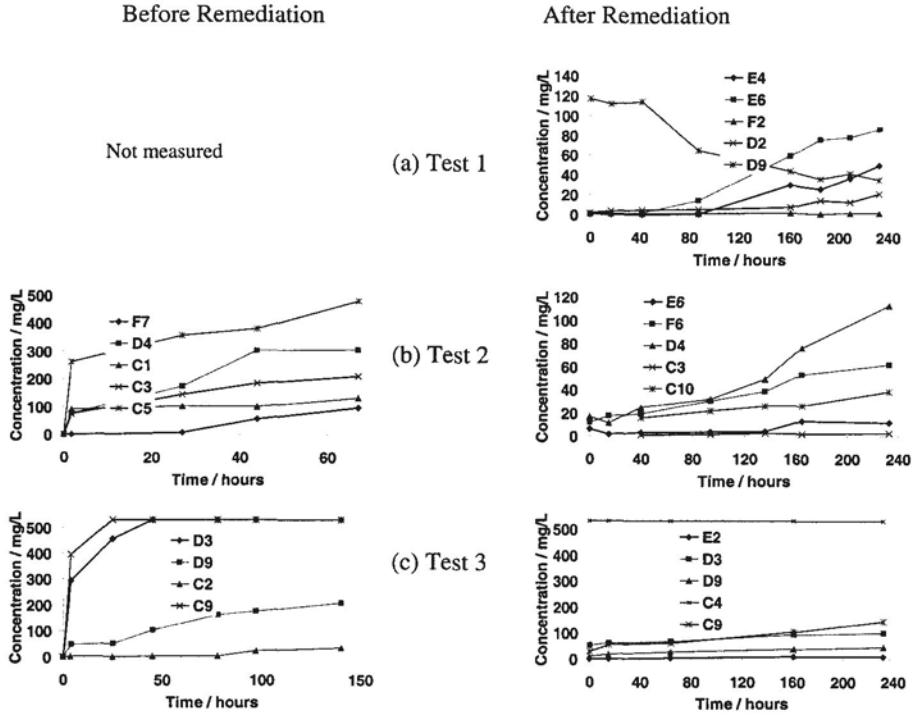


Figure 8. Variation of aqueous phase concentration before and after air sparging

Mass Transfer Modelling

In this study, the contaminant movement within the soil models is entirely due to diffusion. It was assumed the effect of absorption is negligible since pure sand was used in all these experiment. The possible mass transfer mechanisms within the soil model are (a) NAPL to gaseous, (b) NAPL to aqueous and (c) aqueous to gaseous phase. Hence, the mass balance equation for the gaseous and aqueous phases in a rigid, non-deforming porous medium can be expressed as follows.

$$nS_\alpha \frac{\partial C_\alpha}{\partial t} - nS_\alpha . \nabla\left(D_\alpha \nabla C_\alpha\right) = k_{n\alpha}\left(C_e - C_\alpha\right) \pm k_{wg}\left(HC_a - C_g\right) \qquad (\alpha = gas, aqueous)$$

where n is porosity, S_α is fluid phase saturation, C_α is fluid phase concentration (M/L^3), D_α is effective diffusion coefficient (L^2/T), S_α is phase saturation, C_α is phase concentration, D_α is *effective diffusion coefficient*, $k_{n\alpha}$ *is* NAPL- α *phase mass transfer coefficient*, k_{wg} is aqueous-gaseous mass transfer coefficient, C_e is equilibrium gas concentration, C_a is aqueous phase concentration and H is Henry's constant.

A finite element program, FEMLAB, was used to model the mass transfer and transport processes before and after air sparging remediation. By matching numerically produced concentration variation with the experimentally measured values, it is possible to evaluate the mass transfer coefficients k_{ng} and k_{na} for the conditions before and after remediation. Waduge (2003) reported typical mass transfer rate coefficients, which are listed in Table 1, for the three NAPL source entrapment conditions.

Table 1. Mass transfer coefficient rates before and after remediation (Waduge, 2003)

	Test 1		Test 2		Test 3	
	Before	After	Before	After	Before	After
k_{ng} / day^{-1}	240	2.2 x 10^{-3}	72	0.0024	36	0.48
k_{na} / day^{-1}	24	0.24	48	0.24	48	24

According to the mass transfer coefficient values given in Table 1, a significant decrease in the mass transfer rates for NAPL-gas and NAPL-aqueous states was achieved by air sparging when the NAPL was trapped inside the coarse sand lens. When the NAPL was trapped inside fine sand lens, source removal was limited and hence the decrease in the mass transfer rates was also small.

CONCLUSIONS

Complete removal of NAPL source by insitu remediation technologies such as air sparging is difficult in the field mainly due to heterogeneous subsurface conditions. Accepting this limitation, it seems that integrated modeling and measurement of both mass flux from the post-remediation source and natural attenuation capacity of the subsurface environment is needed. In this study, the mass transfer behaviour before and after air sparging remediation of toluene was investigated using a two-dimensional laboratory soil tank. The results of this study show that both gas and aqueous concentrations increased from the level at the termination of remediation process because of the continuous mass transfer processes from the partially removed source. According to the measured gaseous and aqueous concentration values, the gaseous concentration after remediation increased gradually and reached to a steady state value, whereas the aqueous concentration increased continuously with time towards the maximum solubility. The mass transfer rates evaluated from the finite element simulations of the tank experiments varied according to the texture of the soil where NAPL is trapped.

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LANDFILL PROCESSES

Population dynamics in *Asellus aquaticus* as modified by chronic leachate stress

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ABSTRACT

In the past, many landfill sites were constructed and operated without engineering containment, and from which leachate is likely to arise over the next several decades. Landfill leachate can contain high concentrations of toxic substances, which may pose a threat to the surroundings. In the worst cases, leachates may seep through the underlying substrata causing contamination of groundwater, of surface water drains, and ultimately of the rivers into which they discharge. As a consequence, the diversity and species richness of benthic communities are often degraded.

The chronic toxicity of a landfill leachate was investigated in this study, with respect to determining the 'environmentally safe' concentration in which the long term survival of an *Asellus aquaticus* population is assured. The leachate was from a disused site known to contain industrial wastes, and samples were collected from a surface drain. The leachate used in the toxicity tests had a 600 mgl^{-1} BOD and 1200 mgl^{-1} COD.

Sub-lethal toxicity tests were carried out at concentrations that were lower than the acute toxicity threshold of *Asellus aquaticus*. The toxicity was judged on the basis of offspring produced and the growth rate of newly born individuals. Tests showed that even a dilution of 1:20 would affect the size of the breeding colony of *Asellus*. A 30 mgl^{-1} COD concentration was judged to be the 'environmentally safe' leachate dilution in which the number of offspring, birth frequency and juvenile length would not be affected. At this concentration the integrity of an *Asellus* population would be protected.

KEY WORDS

Leachate, landfill, toxicity testing, sub-lethal (chronic) toxicity

INTRODUCTION

Current landfill engineering practice and regulatory control have gone a long way in protecting the environment through reducing pollution loads by the use of leachate treatment

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

systems, and by controlling leachate migration. There are, however, a considerable number of closed landfill sites that were constructed and operated without engineering containment, and from which leachate is likely to arise over the next several decades. At these sites consideration needs to be given to methods for reducing environmental impacts and the development of appropriate evaluation techniques. Chemical analysis, although useful in characterisation of leachate does not illustrate the toxic effects, which may result from the leaching out of chemicals from the landfill. As a result, greater attention is focused on the incorporation of toxicity tests performed on leachates with aquatic organisms.

Wastes are currently one of the most acute problems facing mankind. The majority of generated wastes are disposed of at landfills, of which the UK has 11,300 sites (some 6,100 licensed as operational in 1993/94), (DEFRA, 2003). The environmental impacts of this disposal technique, include amongst others, the generation of leachate, which is a consequence of various available chemicals leaching from the landfill following precipitation events. The amount of leachate generated, its toxicity, hydrological pathways and environmental impacts depend on a number of factors, including the climate, geomorphology of the area, geochemical, mineralogical, petrological properties of the prevalent ores, the landfill's engineering layout, and the geological properties of the surrounding landscape.

The diversity and species richness of benthic communities are often degraded by the impacts of toxic discharges. The restricted community fauna, which does survive, consists of high numbers of a few adaptable species. *Asellus aquaticus* (*isopoda*) is one such species (Mulliss et al., 1994). Understanding the impact of leachate on the dynamics of the hydrobiota may ultimately help us to optimise the engineering design of landfills, depending on the geology of the area. The objective of this study was to establish the dose response relationship of *Asellus aquaticus* to sub-lethal concentrations of leachate. A future part of the work will be to relate this information to the makeup of the freshwater ecosystem that receives a direct discharge of the leachate.

The principle aim of aquatic toxicology is to preserve the integrity of aquatic habitats by preventing or minimising the impact of episodic and continuous pollution. It is necessary to determine what concentrations of a particular substance have a toxic or sub-lethal effect on an organism so that standards for the protection of the aquatic ecosystem can be developed (Bloor and Banks, 2003c). In the past, interest focused on acute toxicity tests to preserve the integrity of natural systems, and in the case of aquatic habitats to preserve ecological diversity by reducing levels of pollutants to a point where their impact is negligible (Buikema et al., 1982). Acute toxicity tests assess the effect of concentration of a pollutant (or mixture of pollutants), on a test organism under controlled conditions that can be measured and replicated. Estimates of acute toxicity, such as the median lethal concentration (LC_{50}), are derived from these short-term tests. In this type of conventional toxicity test the concentration of a toxicant is raised until immobilisation, death or some other defined response occurs.

However, nowadays sub-lethal (chronic) responses provide more relevant information to develop water quality standards, as some substances will not be at lethal concentrations but may interfere with normal life. Chronic toxicity often arises by accumulation (Hellawell, 1986) of the toxicant. Sub-lethal effects may be biochemical, physiological (Pascoe et al., 1991), behavioural (Macleod and Smith, 1966) or at life-cycle level (Sprague, 1971; Christensen et al., 1977; McCahon et al., 1987; Taylor, 1993). The assessment of toxicants is

complicated by the need to integrate the toxic action with dissolved oxygen, temperature and other environmental parameters including possibly the presence of other toxicants (Sprague, 1971). The principle purpose of chronic toxicity tests is to establish 'environmentally safe' concentrations in which the long term survival of a population is assured by observing growth, development, fertility and behaviour, or physiological and biochemical functions (Pascoe and Edwards, 1989).

MATERIALS AND METHODS

Leachate

Leachate samples were taken from a French drain which collected together a number of diffuse sources of leachate and surface drainage water from around the perimeter of an undisclosed landfill site. The full chemical composition of the leachate is unknown but it was shown to be of variable strength at the sampling point depending on rainfall. The sample taken for use in the current experiments had a BOD of 600 mg l^{-1} and COD of 1200 mg l^{-1}.

Chronic toxicity tests

These were set up in a series of six 10-litre tanks that contained dilutions of leachate at predetermined sub-lethal acute toxicity levels (90, 70, 50, 30 and 10 mgl^{-1} COD concentrations and a deionised water control). Thirty juvenile *Asellus aquaticus* (two week old) were added to each tank; they were fed on conditioned alder leaves and subjected to partial 'water' changes on a weekly basis. The test animals were obtained from a laboratory based breeding programme. For a 4-month period, daily observations were made on the animals ability to reproduce. Offspring were retrieved from the tanks and placed in 350 ml test pots, containing the same leachate dilution from which they were extracted. For one month, the animals growth patterns were measured on a weekly basis. After this period, the juveniles were transferred back into their original tanks (Bloor and Banks, 2003a; 2003b; 2003c).

RESULTS

Chronic toxicity tests were carried out over a 4-month period, during which the test animals were exposed to acutely sub-lethal concentrations of the leachate. The main criteria of assessment was the number of offspring born and the frequency at which offspring were produced. As a further assay the growth rate of the newly born offspring was measured by recording the length of individuals over a period of four weeks whilst maintaining them in the same leachate strength, but away from the parents to prevent cannibalism.

The data was handled using Microsoft Excel and SPSS software. The Kolmogorov-Smirnov test was used to check the assumption of normality for the data. Were the data was not normally distributed, the Mann-Whitney test was applied, whilst, the Dunnett test was used for normally distributed data.

For example, application of Kolmogorov-Smirnov test indicated that there was no significant departure from normal distribution for either the number of *Asellus aquaticus* offspring produced or frequency of births (Figure 1).

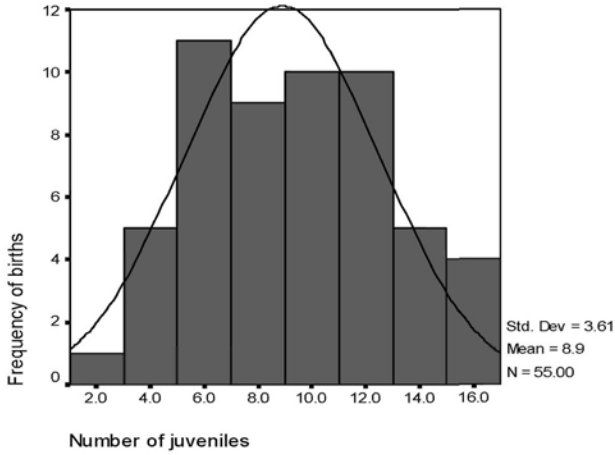

Figure 1. An example of the SPSS output showing the fit of normal curve for the number of *Asellus aquaticus* offspring produced and frequency of births in deionised water (control). Test statistics Z = 0.721, P = 0.676, indicating that there is no significant departure from normal distribution

The statistical analysis revealed that in 90, 70 and 50 mgl^{-1} COD concentrations the number, and frequency of *A. aquaticus* births was significantly reduced in comparison to the deionised water control (P<0.001), (Table 1 and Figure 2).

Table 1. Dunnett test comparison of births in deionised water (control) with those in chronic tank dilutions 90, 70,50, 30 and 10 mgl^{-1} COD

COD concentration (mgl^{-1})	Test comparison	Mean difference	Significance
90	Deionised water	-7.9692*	0.000
70	Deionised water	-6.6264*	0.000
50	Deionised water	-5.8942*	0.000
30	Deionised water	-1.5692	0.163
10	Deionised water	-0.7692	0.507

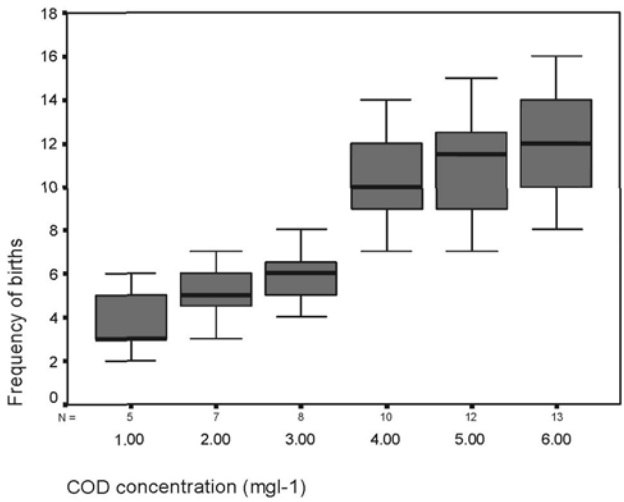

Figure 2. Box plot graph showing the differences in statistical characteristics of *Asellus aquaticus* birth frequency in relation to the leachate strength. It should be noted that the frequency of births in lower concentrations of leachate (i.e. 10 and 30 mgl^{-1} COD) did not significantly differ from those obtained in deionised water – see table 1 for exact Dunnett test results

Furthermore, the offspring's growth rate was also significantly reduced at 90, 70 and 50 mgl^{-1} COD concentrations ($P<0.001$), which proved non parametric distribution (Figure 3).

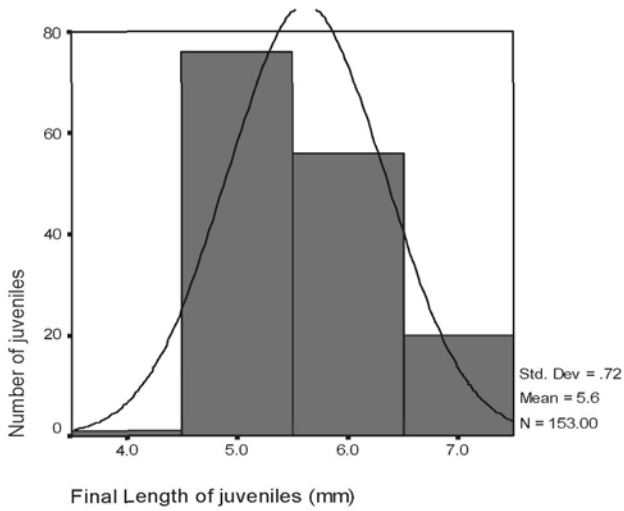

Figure 3. An example of the SPSS output showing the fit of normal curve for the final length of *Asellus aquaticus* juveniles born in deionised water (control) after a four week monitoring period. Test statistics $Z = 3.837$, $P = 0.000$, indicating a significant departure from normality

As the data was not normally distributed, the Mann-Whitney test was applied. Test results show that after four weeks of monitoring, there was a significant difference between the final length of juveniles born in 90, 70 and 50 mgl^{-1} COD concentrations compared to the control but not for those born at 30 or 10 mgl^{-1} (Table 2).

Table 2. Mann-Whitney test comparison of final length in deionised water (control) with that in chronic tank dilutions 90, 70, 50, 30 and 10 mgl^{-1} COD (threshold $P < 0.01$, this accounts for Bonferoni correction)

	Comparison of final length in deionised water (control) with that in chronic tank dilutions 90, 70, 50, 30 and 10 mgl^{-1} COD				
	90 mgl^{-1} & control	70 mgl^{-1} & control	50 mgl^{-1} & control	30 mgl^{-1} & control	10 mgl^{-1} & control
Mann-Whitney U	368.50	1322.000	2666.000	7452.500	9634.000
Asymp. Sig (2-tailed)	0.000	0.000	0.004	0.513	0.465

DISCUSSION AND CONCLUSIONS

The tests were carried out using individuals which had been taken from naturally clean river conditions and then cultured in laboratory tanks as breeding populations giving rise to new generations. As such none of the animals used in the test programme had been exposed to leachate or other pollutant within their life history (Bloor and Banks, 2003a; 2003b; 2003c). This could have affected the result as it is well known that the sensitivities of animals to toxic stress vary both within and between populations. Animals from already contaminated areas may be less vulnerable than those from 'clean' sites (Maltby, 1995), whilst juveniles are considered more susceptible than adults (McCahon and Pascoe, 1988).

The toxicity of a pollutant can be altered by many factors, with temperature, pH, hardness and dissolved oxygen being of particular importance (Voyer and Heltshe, 1984). In addition, a number of other water quality parameters (e.g. conductivity, alkalinity, transparency, turbidity, salinity, chemical composition etc.) may influence the exact speciation. In a natural environment, the specific combination of these parameters would result from a multivariate interplay of geological, ecological, metrological, geochemical and landfill engineering factors. In this study, however, environmental conditions such as temperature and levels of dissolved oxygen were controlled as far as possible, but no attempt was made to acclimate either of the test species to leachate over a number of generations. The obtained results, therefore, provide an estimate of the relationship expected between leachate toxicity and the resulting environmental impact.

Many studies have used acute toxicity testing to establish the impact of environmental pollution on the receiving waterbodies. The acute toxicity test, however, is of limited value where exposure of a population may be over a much longer time span than for the period of the test. This would certainly be the case for leachate discharge into a receiving water course, and, although concentration may vary as a result of surface water dilution, components of the leachate will always be present. Acute testing is more suited to assessing the impact of occasional or intermittent pollutant entry into the receiving water. Allowing discharge even at

concentrations below the known acute toxicity threshold limit, unfortunately does not offer protection to animals from the risk of sub-lethal effects, which often arise from toxin accumulation (Buikema et al., 1982). Taking into account the limitations of acute toxicity testing, the present study may provide a valuable alternative for monitoring the environmental impacts of landfilling on far-field aquatic environments.

The chronic toxicity tests showed that even a dilution of 1:20 would affect the size of the breeding colony of *Asellus*. The results illustrate that the 'environmentally safe' leachate dilution, which may protect the integrity of an *Asellus* population was a 30 mgl^{-1} COD leachate concentration. At this concentration, neither the number of offspring produced , birth frequency or juvenile length was significantly affected, in comparison to those individuals born in the control. The immediate conclusion that can be drawn is that the leachate contains fertility and growth inhibiting toxins. Further research is needed to identify which leachate components were inhibiting fertility and growth, and to ascertain if the animals sex ratio was disrupted.

The presented results have clearly shown the response of the studied biota to the landfill leachate used. This response should be born in mind, whilst trying to estimate the environmental impacts of landfill sites or other industrial applications, which involve the generation of large quantities of polluting substances and / or considerable changes to the surrounding geographical landscape and underlying geological strata. The results of this research may, therefore, be of use to studies related to landscape engineering, landfill design, pollution control and environmental impact assessment.

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The Service Life of Polyethylene Geomembrane Barriers

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INTRODUCTION

Legislation recently introduced in the UK, including the Groundwater Regulations 1998; Pollution Prevention and Control Regulations 2000; the Landfill Regulations 2002 and forthcoming legislation to implement the Water Framework Directive, requires that groundwater is protected from pollution and that remediation is undertaken where this is necessary. A risk-assessment and management approach is commonly adopted in the UK (DETR *et al.*, 2000) in determining whether there is likely to be an unacceptable risk of pollution, and in designing mitigation measures.

Although many of the technical issues of landfill design are longstanding, the new regulatory regime is such that quantitative understanding of landfill design and leachate control has assumed a much higher priority within the Environment Agency. This is particularly true where groundwater is sensitive or landfill gas would present risks to local receptors (Environment Agency, 2003a). Many modern landfill sites include synthetic geomembranes, typically high-density polyethylene (HDPE), as part of a basal liner system. As manufactured, HDPE is impermeable to liquid flow, and movement through intact HDPE is limited to diffusive processes, which are normally very slow. In field situations, however, a number of other factors including quality of installation, stresses caused by slope instability, contact with aggressive chemicals and the depletion of antioxidants may affect the properties of HDPE, which can give rise to defects or cause failure.

A thorough review of polyethylene geomembrane degradation processes and defect frequency has been undertaken (Environment Agency, 2003b, in prep). The results provide the basis on which guidance and assumptions on medium to long-term landfill liner performance can be formulated in the UK. The results of this study will be of direct application in environmental risk assessments for landfills (Environment Agency, 2003a) and within a LandSim performance assessment (Environment Agency, 2003c).

Studies of landfill leachate chemistry and degradation processes suggest that landfills managed using typical current approaches will take hundreds, if not thousands, of years to stabilise (Hall *et al.*, 2003). It is only after this period that they will no longer pose a pollution hazard to their surrounding environment. The durability of engineering containment and control measures is therefore critical in assessing the long-term pollution potential.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

GEOMEMBRANE LINER SERVICE LIFE

The service life of a geomembrane liner can be defined as the length of time the liner continues to act as an effective hydraulic barrier for the purposes of the site under consideration. Clearly, this will depend upon the circumstances at the site and, for groundwater quality, the acceptable amount of leakage of specific contaminants. The main factors influencing this are:

- The number and sizes of holes in a geomembrane liner overlain by leachate;
- The type of liner (single, composite, or double liner);
- In a composite liner, the quality of contact at the geomembrane mineral liner interface;
- Persistence of leachate source (e.g. rate of declining source concentrations);
- Leachate head and the nature and concentrations of contaminants in the leachate;
- Site sensitivity with respect to groundwater quality (e.g. groundwater vulnerability).

A geomembrane may have a certain number of holes, with a range of sizes. At one site the resultant leakage may be deemed acceptable yet at another, more sensitive site, the leakage may be considered unacceptable. The generation of holes in geomembrane liners, whether by physical damage mechanisms, stress cracking or material degradation is only one factor in the prediction of the service life of that liner.

PHYSICAL DAMAGE

Most damage to geomembranes, causing holes or non-penetrative defects, has been found to occur during the installation and seaming of the liner, and as a result of the placement of the overlying drainage or cover material. The causes of geomembrane liner damage have now been extensively reported from the results of electrical leak location (ELL) surveys, (e.g. Nosko *et al.* (1996); McQuade and Needham (1999); Rollin *et al.* (1999); and Nosko and Touze-Foltz (2000)). The surveys have been undertaken using mobile and fixed ELL systems. Mobile ELL surveys are carried out on completion of liner construction after placement of the cover material but are unable to detect holes after waste disposal commences. Surveys using fixed (or "permanent") ELL systems can be performed at any time after the system installation, continuing well into the operational and post-closure phases of the landfill. Where ELL surveys are not conducted, then it must be expected that holes of the types identified will be present in these liners. Little data have been published specifically identifying holes found by fixed ELL surveys after commencement of waste disposal. Nosko *et al.* (1996) report that only 2% of the total number of holes identified occurred in the post-construction phase during waste filling.

Data have been reviewed from an ELL survey company on their fixed ELL surveys conducted on 17 commercial sites with a total liner area of about 800,000m^2. The maximum period of monitoring for leaks after liner installation was 6 years. Of the holes detected, 42% occurred during the site operation, a much higher proportion than the 2% found by Nosko *et al.* (1996). For the holes occurring during the operational phase, the causes related to physical damage and not to deterioration in the geomembrane liner material. Results were also reviewed from a second ELL survey company from surveys using fixed ELL systems over the 7-year period 1996 – 2003. The data were obtained from 88 cells and 18 leachate lagoons at 55 landfill sites in Eastern Europe, Belgium and the UK. The total area monitored was approximately 1,022,000m^2. The number of fully penetrating defects was 1460, with 74% located during the initial leak survey at the end of liner construction and 26% being located in subsequent monitoring surveys. The most common cause of damage (78%) found

in the later surveys was stone puncture resulting from traffic movement over empty cells. None of the damage was attributed to a lack of durability of the geomembrane material.

A fixed ELL system has been installed at Sandy Lane landfill, UK since 1995. The ELL system monitors the entire site throughout the construction, landfilling and post-closure stages. The extensive monitoring has so far revealed that:

- 27% of the defects have been detected after completion of the liner (i.e. during the period before waste disposal commenced in the cell or after landfilling commenced);
- Only two holes remain unrepaired in the liner due to their inaccessible location and no detectable leakage has been identified by the ELL system;
- The sizes of holes found after liner completion ranged from pinholes in welds to major rips caused by plant movement;
- Almost all new holes detected after the commencement of waste disposal resulted from the early activities of landfilling (e.g. puncture by waste materials and plant movement);
- Frequent (quarterly surveys) allowed the early identification of defects and their repair.
- There has been no evidence of the gradual development of holes.

Double liner systems are commonly used in the USA. The leakage detection layer between the primary and secondary liners is monitored to ensure the leakage does not exceed the permitted rate. Reviews of leakage rates measured over periods of up to 10 years have been summarised by Rowe (1998) and Koerner *et al.* (2000) and have concluded that the leakage rate consistently decreases from the start of the landfill to well into the post-closure period. This again suggests that significant damage does not develop in the geomembrane liners for periods of at least 10 years.

The principal findings from the review of physical damage are:

- If no ELL survey is undertaken, holes will likely be present in liners at the start of their operational life from imperfect manufacture and installation damage;
- Of all holes created during the construction and operational stages of a landfill, approximately 30 - 35% may be estimated to occur during the latter period;
- The installation and regular monitoring of a fixed ELL system can enable the identification of these holes and, in most cases, their repair;
- The locations experiencing the greatest frequency of defects are exposed or poorly protected liner at the margins of a cell, on bunds and benches, and on slopes;
- Once a liner is covered by several metres of waste, the agents for the future development of holes in the liner are limited. The evidence to date from ELL surveys and monitoring of leakage detection layers shows that holes are unlikely to develop for at least the first decade of the service life of the geomembrane liner, and probably much longer.

GEOMEMBRANE LINER DURABILITY

The degradation process that has the greatest detrimental effect on buried HDPE geomembranes is thermal oxidation. Oxidation is temperature dependent with the rate of oxidation increasing rapidly as temperature rises. As oxidation proceeds, the physical and mechanical properties of the polymer start to change eventually leading to failure of the geomembrane as an effective hydraulic barrier. Oxidation of polyethylene can be delayed by the addition of suitable stabilisers called antioxidants to the resin, which function by interrupting the various oxidation reactions. There are various types of antioxidants and they protect the polymer in different ways and over different temperature ranges. A package of

antioxidants is added to HDPE geomembranes to provide a broad spectrum of resistance both during the manufacturing process and for the service life of the material.

Hsuan and Koerner (1995) describe the oxidative degradation of polyethylenes with antioxidant stabilisers as a three-stage process. The first stage is the depletion of the antioxidants caused either by their consumption as a result of chemical reactions and/or to their physical loss by extraction or volatilisation (Luston, 1986). The oxidation reactions then start very slowly in an initial induction period during which there is minimal observable geomembrane degradation. This is followed by the final stage where oxidation causes significant loss of material properties.

Three long-running research projects into the long-term oxidative degradation of HDPE geomembrane liners have been reported by Hsuan and Koerner (1995), Sangam (2001) and Müller and Jakob (2003). The findings of these extensive projects form the basis of the current understanding of antioxidant depletion and, to some extent, subsequent oxidative degradation of HDPE geomembranes under laboratory conditions. From these projects, several factors have been identified as having a key influence on the outcome of the laboratory ageing tests and, therefore, also on the estimation of the long-term durability of the HDPE geomembranes. These are:

- the characteristics of the HDPE resin and antioxidant package;
- the test duration;
- the exposure medium – air, water, leachate or soil (saturated and dry);
- the availability of oxygen;
- the ageing temperature(s); and,
- the activation energy of the antioxidant depletion process.

The activation energy (E_a) reflects the necessary minimum energy of the antioxidant depletion process and will depend on the characteristics of the HDPE resin, the antioxidant package and the exposure conditions in which the antioxidant loss is occurring. As the rate of antioxidant depletion is exponentially dependent upon the activation energy, it is important to assess the appropriate value to use in the estimation of antioxidant depletion times.

The antioxidant depletion rates recorded by oxidative induction time (OIT) tests (ASTM D3895) determined by the three teams for the different geomembranes, exposure conditions and ageing temperatures are shown on Figure 1. It can be seen that:

- Reducing the exposure temperature caused a marked decline in the depletion rate;
- Leachate immersion gave a much higher depletion rate than the other exposure media;
- The much longer duration testing by Müller and Jakob (2003) showed a two-stage depletion process with the second being very slow.

High initial OIT values need not correlate with long-term oxidation stability. Certain antioxidants will markedly increase the initial OIT value but are ineffective below about 150°C and do not contribute to long-term oxidation stability at normal operating temperatures. Thus, polyethylene geomembrane specifications should stipulate not only the initial OIT value but also require a minimum retention of the OIT value following a standard oven ageing test (GRI GM13, 2003). Müller and Jakob (2003) expected that activation energies relevant to the second, slow antioxidant depletion stage found in their long-term tests would be higher than found by Hsuan and Koerner (1995). As the antioxidant depletion is controlled by the rate of diffusion, then the use by Müller and Jakob (2003) of relatively high activation energy values derived from studies of antioxidant diffusion appears justified.

This tentative antioxidant depletion / activation energy model for each individual geomembrane formulation depends on the actual composition of the antioxidant package used and the polyethylene resin characteristics.

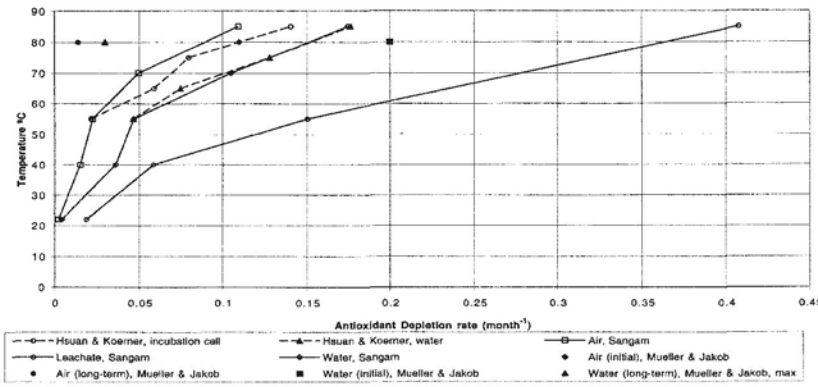

Figure 1: Comparison of antioxidant depletion rates by different researchers

All three research projects provide valuable results which, when considered together, give a technical basis for the derivation of a reasonable estimate of HDPE geomembrane durability in landfill conditions. The estimate is based on:

- Slow long-term OIT depletion rates from Müller and Jakob (2003);
- The increased rate of depletion for leachate exposure found by Sangam (2001);
- The effects of a confined sample under comprehensive stress sandwiched between saturated sand and dry sand, as investigated by Hsuan and Koerner (1995);
- Measuring laboratory durability of the geomembrane in terms of the tensile test.

Using the OIT depletion rate derived from this approach, estimates of geomembrane material durability can be derived from an Arrhenius equation on the temperature dependence of antioxidant depletion (Müller and Jacob, 2003). Typical results for different temperatures and activation energies are given in Table 1 below:

Table 1 Estimates of HDPE geomembrane liner durability in landfill conditions derived from laboratory research projects

Average landfill temperature (°C)	Activation energy (kJ/mol)	Estimated durability (years)
20	60	450 - 650
20	70	900 - 1300
35	60	140 - 200
35	70	220 - 320
35	80	370 - 530

The durability estimates refer only to the complete depletion of the antioxidants and do not directly relate to the continuing ability of the geomembrane to act as an effective hydraulic barrier.

LINER EXPOSURE CONDITIONS

The temperature of a buried polyethylene liner will be a controlling influence on its rate of degradation. Rowe (1998) reviewed landfill temperatures reported in the literature and

reported a clear correlation between the temperature at the base of a landfill and the leachate head above the base (Figure 2).

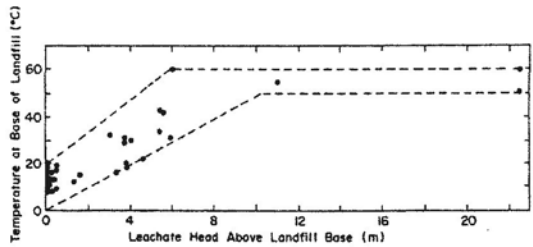

Figure 2 Variation in basal landfill temperatures with leachate head (from Rowe, 1998)

Koerner and Koerner (1995) report on temperature data at a "dry" cell (no additional liquids added or recirculated) at a Pennsylvania landfill, with additional data recorded on the Geosynthetics Institute (GRI) website. After 9 years, an average temperature of 27°C was recorded. Temperatures measured at a "wet" cell at the same landfill operated as a bioreactor gave a liner temperature of 25°C from the start of filling (5°C higher than for the dry cell). Over a 2.5 year monitoring period, the average temperature had risen to 40°C (10°C higher than at the dry cell). An experimental study at Beddington bioreactor landfill in the UK starting October 2000 included temperature measurements (Knox, 2003). Readings of leachate head and temperature were recorded on 19 piezometers and thermocouples. Placement of MSW began in October 2000 with recorded temperatures of 14° - 21°C and by May 2003, the temperature range had climbed to 24° - 30°C with no reduction in the rate of temperature increase (0.25° - 0.4°C) per month evident.

The considerable variability in temperatures recorded at the liner complicates the prediction of an average service temperature to use in estimating the long-term degradation of HDPE geomembranes. No records have been seen which show the rise and eventual fall towards ambient values of basal temperatures, so the duration of elevated temperatures is also difficult to predict. Sites that are active bioreactors, practise leachate recirculation and/or have elevated leachate levels are likely to have temperatures at the higher end of the range. A reasonable long-term average for such landfills is estimated as between 30°-35°C. For "dry" landfills or those with a low biodegradable content, a long-term average temperature of 15° - 20°C may be appropriate.

Oxygen is an essential component of oxidation reactions but is not necessary for antioxidant depletion. If the methanogenic phase of a landfill is complete and aerobic conditions re-established before all antioxidants are removed, then oxidation should not be hindered by a lack of oxygen. However, if methanogenic conditions persist, the absence of oxygen available to the upper surface of a geomembrane would prevent oxidation of that surface, increasing the durability of the geomembrane. On the underside of the geomembrane, oxygen availability is likely to be very small where there is good geomembrane to mineral liner contact. This will retard both the antioxidant depletion and oxidation induction stages.

HDPE geomembranes are recognised as having excellent chemical resistance against leachates derived from municipal, industrial and commercial wastes, as well as co-disposal

waste sites in the UK. Leachate quality from co-disposal sites has been well characterised by studies over many years and has been shown to be similar in most respects to the leachate quality from MSW landfills.

The Landfill Directive requires member states to reduce the quantity of biodegradable MSW sent to landfill to 35% of the 1995 level and to deposit pre-treated hazardous wastes in separate landfill areas. From research undertaken by Bone et al. (2002a and 2002b), three main factors influencing HDPE liner degradation were evident:

- The reduction in the biodegradable fraction should result in lower temperatures ;
- Leachates from mechanically and biologically pre-treated (MBP) and hazardous wastes have elevated metal concentrations compared to untreated MSW or co-disposal sites. This may be instrumental in accelerating polyethylene degradation;
- The timescale before wastes complying with the Landfill Directive reach final storage quality is likely to be as long as that of current UK landfills.

STRESS CRACKING

Stress cracking of HDPE geomembranes has been well reported (e.g. Peggs, 1997). Normal stress rupture curves derived using the NCTL stress crack test (ASTM D5397) show ductile and quasi-brittle failure modes, with the break-in-slope (or "knee") defining the ductile/brittle transition point. Durability research in Germany (Hessel, 1990) identified a third stage (Figure 3) in which the curves at different test temperatures showed a second knee followed by an even steeper, almost vertical, slope. The second knee was defined as the stage at which all antioxidants had been consumed and any applied stress would cause cracking.

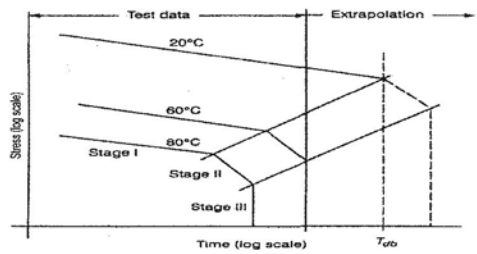

Figure 3: Three-stage stress rupture curve as a function of temperature (from Hessel, 1990)

Thus, when a geomembrane is under stress at the same time as oxidation is occurring, the degradation process is more complex than the simple models used in laboratory studies using unstressed samples. Even when the antioxidants have been fully depleted and oxidation commences, a geomembrane liner remains in place as an effective hydraulic barrier unless physically damaged or holes develop. Setting aside physical damage, holes through the liner should only develop or enlarge as a result of stress cracking unless stresses are so high as to cause ductile tensile failure. Oxidative degradation embrittles geomembranes making them much more susceptible to stress cracking so where low tensile stress is present, it is likely that stress cracks will occur. Where tensile and shear stresses in the liner can be avoided, the liner should remain intact, for all practical considerations, indefinitely.

The service life of the geomembrane liner will end once excessive leakage for that site occurs. If physical damage can be limited to acceptable levels, then the service life of the

geomembrane liner as an effective hydraulic barrier depends on the development of stress cracks in locations that allow excessive leakage to occur.

STAGES OF HOLE GENERATION

The development of holes in HDPE geomembrane liners may be seen to occur in six stages, as proposed by the following conceptual model. The model is a simplification of a much more complex process as a geomembrane liner will be deteriorating at different rates and will be subjected to various stress levels at different locations across a cell.

Stage 1: The first stage is the number and sizes of holes remaining in the liner after construction of the liner and placement of the cover material and drainage system. Where an ELL survey has been properly carried out, then the detected holes can be repaired and zero or a very small number of holes may be considered to remain at the end of Stage 1.

Stage 2: This represents the holes caused before or during waste filling operations by physical damage mechanisms resulting in either new damage or the opening of latent defects. Where a fixed ELL system is in place and regularly monitored, and detected holes repaired, then only a small number of holes may remain at the end of Stage 2.

Stage 3: Present evidence shows that holes are not seen to develop for at least the next 10 years after liner completion. As there is generally no agent to cause holes, it is reasonable to predict that Stage 3 would comprise a 10 to 50 year period during which no further holes develop. The range in duration reflects different geomembrane material properties, efficacy of liner protection, design quality and standard of installation.

Stage 4: A gradual development of stress cracks within the stressed areas of the geomembrane occurs. The number of cracks depends on the estimated extent of areas under stress. The levels of stress, the stress crack resistance (SCR) of the geomembrane and the prevailing liner temperature control the time to the initiation and growth of stress cracks.

Stage 5: This stage occurs once oxidation of the geomembrane liner is in progress (following the loss of antioxidants and the induction period of oxidation). The geomembrane will become brittle and further stress cracking damage occurs relatively rapidly at all locations in the geomembrane remaining under tensile stress.

Stage 6: It is predicted that further generation or extension of holes in the geomembrane will be slow. The geomembrane will be a "leaky", degraded barrier with the geomembrane away from cracks and other holes remaining intact and, for all practical purposes, permanent.

The length of Stage 4 may be estimated from the material durability assessment procedure outlined earlier. The duration of Stage 5 depends upon the rate of oxidation in the service environment. No data are available to estimate of this period, although Koerner and Hsuan (2003), Sangam (2001) and Rowe (1998) have made widely differing estimates. From laboratory studies presented by Müller and Jakob (2003), it is apparent that Stage 5 will be quite short relative to the length of Stage 4 and, on this basis, a period of 50 years is proposed as being a reasonable estimate. In Stage 6, the geomembrane liner may remain as a partially effective hydraulic barrier. Depending upon the environmental sensitivity of the site and the residual hazard of the waste, the acceptability of the leakage through the degraded geomembrane will control whether the liner has reached the end of its service life.

SUMMARY

The service life of an HDPE geomembrane liner is the length of time the liner continues to act as an effective barrier for a particular site. Less sensitive sites will be able to accept a

greater amount of leakage; other factors being equal, the service life at a less sensitive landfill site will be longer than at environmentally vulnerable sites. Physical damage, material degradation and stress cracking will generate holes in the liner leading to leachate or gas escape where the holes are subject to a leachate head or gas pressure.

A conceptual model of hole generation from these causes has been presented. The holes generated in each of the six stages, and the duration of each stage, can be estimated for use in environmental risk assessments of the long-term performance of landfills.

Physical damage to the liner can be readily identified by mobile or fixed electrical leak location surveys, fixed systems being able to monitor for defects during and after waste disposal, as well as at the end of liner construction. Identified holes can then usually be uncovered and repaired. High standard installation and CQA will not only reduce the number and size of holes but also the frequency of non-penetrative defects, which would eventually develop into holes.

From long-term laboratory research projects, it is seen that degradation of the HDPE material by oxidation is controlled by the liner temperature, the activation energy of the antioxidant depletion process and the OIT performance of the material under ageing conditions. Specifying a geomembrane with superior stress crack resistance will increase the delay before the initiation and development of stress cracks, improving the service life of the geomembrane liner.

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Calculating hydraulic conductivity of fine-grained soils to leachates using linear equations

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ABSTRACT
This article proposes the linear equations obtained from correlations between laboratory-measured values of hydraulic conductivity and of some geotechnical properties of Portuguese fine-grained soils for selecting, in a preliminary phase of waste landfill studies, the natural soils that are likely to result in low hydraulic conductivity liners. These linear equations are suggested as an useful alternative to guidelines proposed in the bibliography and in current use for the two main reasons as follows: a) the laboratory-measured values of hydraulic conductivity were obtained in permeability tests carried out on specimens permeated directly with demineralised water, on specimens permeated with acid leachate after percolation with demineralised water, and on specimens permeated directly with acid leachate; b) the permeability tests were performed on natural fine-grained soils covering a wide range of mineralogical, chemical and physical properties. It is supposed that the linear equations developed in this study, may be satisfactorily used in a large number of waste landfill studies to select, in a preliminary phase, the soils that are likely to be adequate for constructing compacted soil liners with a hydraulic conductivity equal to 1×10^{-9} m/s or less.

INTRODUCTION
The hydro-geochemical performance of compacted soil liners (bottom and talus liners and final cover) present in waste landfills is particularly relevant in controlling the transport of pollutants from those infra-structures to the environment. Its significance in the leachate flow rate that may seepage through compacted soil liners is illustrated by the values of the hydraulic conductivity as follows: a) if $k = 1 \times 10^{-8}$ m/s, the leachate flow rate per hectare (ha) and per day (d) will be 10 m^3; b) if $k = 1 \times 10^{-9}$ m/s the leachate flow rate will be 1 m^3/ha/d; c) if $k = 1 \times 10^{-10}$ m/s the leachate flow rate will be 0.1 m^3/ha/d (a unit hydraulic gradient is assumed).

Either the fine-grained soils or the clayey soils are the most adequate natural materials to constructing compacted soil liners and to protect both the soils and the water resources. The procedure most commonly used in assessing the hydro-geochemical performance and the compatibility of soils to leachates is to conduct permeability and diffusion tests. Nevertheless, in low permeability soils these tests are complex, time-consuming and expensive.

Therefore, in the preliminary phase of the waste landfill projects, the procedures adopted should be simple, quick, non-expensive and reliable enough to make it possible to select the soils that are likely to be adequate for constructing compacted soil liners.

Several authors, as a result of the experience acquired (since the beginning of the 80s), have estimated the variation ranges the most adequate for the index properties (grain-size distribution and plasticity) of the soils with a view to construct low permeability compacted soil liners ($k \leq 1 \times 10^{-9}$ m/s). The main disadvantage of the criteria proposed in the bibliography is associated with the fact that these do not make it possible to estimate a potential value for the hydraulic conductivity of the material. In fact, they only permit to

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indicate semi-quantitatively if the hydraulic conductivity is potentially higher or less than 1×10^{-9} m/s (requirement established for hazardous-waste and nonhazardous-waste landfills).

A comprehensive experimental laboratory programme developed in LNEC and INSA de Lyon (Roque, 2001) has made it possible to gather important conclusions and it is likely to contribute to overcome the limitations imposed by the known semi-quantitative criteria. In fact, the results obtained make it possible to propose that, in the preliminary phase of the waste landfill projects, the assessment of the hydraulic conductivity of fine-grained soils will be done based on linear equations developed in this experimental programme resulting from the correlation between the hydraulic conductivity k measured on laboratory permeability tests and the percentage of fines of the soils studied. The main advantages of that procedure are as follows: a) the values of k used to define the linear equations resulted from permeability tests conducted on specimens of natural fine-grained soils, which were permeated directly with demineralised water, permeated with acid leachate (pH = 4.6) after percolation with demineralised water, and permeated directly with acid leachate; b) the permeability tests were performed on natural fine-grained soils covering a wide range of geotechnical properties; c) the quantitative assessment of k, even though approximate, is preferable to the semi-quantitative assessment.

SELECTION OF SOILS BASED ON SEMI-QUANTITATIVE CRITERIA

This section presents the variation intervals recommended by different authors for the index properties of the soils potentially favourable to the construction of compacted soil liners with $k \leq 1 \times 10^{-9}$ m/s.

Daniel (1990), Shakoor and Cook (1990), Benson *et al.* (1994) and Daniel and Koerner (1995) indicated either the minimum or maximum percentages, or both, which were the most adequate for the grain-size distribution of soils.

Benson *et al.* (1994) stressed the influence of the percentage of clay size on the hydraulic conductivity of soils. According to the relation obtained between the clay size and k, the percentage of clay size in the soils must be higher than 10-20% to make it possible to construct compacted soil liners with $k \leq 1 \times 10^{-9}$ m/s.

The percentage of fines is also an indicator of the possibility, or not, of constructing compacted soil liners with $k \leq 1 \times 10^{-9}$ m/s.

Benson *et al.* (1994) observed that a percentage of fines higher than 50% may be enough for constructing liners with $k \leq 1 \times 10^{-9}$ m/s. On the other hand, Daniel (1990) recommended a percentage of fines of at least 30%.

Shelley and Daniel (1993) emphasised the influence of the percentage of gravel on the hydraulic conductivity of kaolinite and of mine spoil. It was observed that $k < 1 \times 10^{-9}$ m/s, when the mixtures gravel-kaolinite and gravel-mine spoil, compacted for different water contents, were formed by a percentage of gravel less than 60%. With percentages of gravel higher than 60%, the hydraulic conductivity increased significantly.

Shakoor and Cook (1990) compacted mixtures of poorly plastic soils with gravel, by varying the percentage of gravel and the water contents (slightly less than the Standard Proctor optimum water content). The results indicated a slight increase in k when the gravel percentage was less than 50% and a significant increase for higher percentages.

The researches done by Shelley and Daniel (1993) and by Shakoor and Cook (1990) suggest that for gravel percentages less than 50%, the fines fill the voids between gravels and control the hydraulic conductivity of the mixture.

Other authors (Daniel, 1990; Benson *et al.*, 1994; Daniel and Koerner, 1995) tried to define the variation intervals the most adequate for the consistency limits of soils with a view to construct compacted soil liners with $k \leq 1 \times 10^{-9}$ m/s.

Daniel (1990) suggested that the soils with a plasticity index I_P higher than or equal to 10% are likely to permit the construction of compacted soil liners with $k \leq 1 \times 10^{-9}$ m/s. Nevertheless, that author also mentioned that some soils with $I_P < 10\%$ also made it possible to construct liners with $k \leq 1 \times 10^{-9}$ m/s. For the purpose, he quoted Albrecht and Cartwright (1989) who obtained values of k *in situ* equal to 8×10^{-10} m/s with a soil of $I_P = 7\%$.

Benson *et al.* (1994) stressed the variations of k in function of w_L and I_P: k tends to decrease when w_L and I_P increase. In particular, k decreases significantly when w_L increases from 20 to 50%, subsequently showing an almost constant value. It has also been observed that k decreases significantly when I_P increases from 10 to 30%. For values of I_P higher than 30%, the value of k is almost constant. According to these authors, the soils with $w_L \geq 20\%$ and $I_P \geq 7\%$ are potentially adequate for constructing compacted soil liners.

Daniel and Koerner (1995) concluded that the soils with 7-10% > I_P > 30-40% are not adequate for constructing compacted soil liners. The soils with I_P < 7-10% contain irrelevant percentages of clay size and clay minerals and have a low plasticity. The contribution of the compaction of such type of soils becomes marginal for constructing compacted soil liners with $k \leq 1 \times 10^{-9}$ m/s. The soils with I_P > 30-40% have the tendency to form hard clods when dry and soft clods when wet, which creates workability problems in earthworks.

Table 1 shows a synthesis of requirements collected in the bibliography for the index properties of soils, so as to pre-select the soils potentially adequate for constructing compacted soil liners.

Table 1
Semi-quantitative criteria to preliminary selection of soils potentially adequated for constructing compacted soil liners

Parameter	Semi-quantitative criteria						
	1	2	3	4	5	6	7
Clay size (%)	>25	—	>25[(c)]	—	—	>20	>15
Fines (%)	—	—	>30-50	>20	>30	—	>30
Gravel (%)	—	—	—	<10	<10-20	<10[(d)]	—
w_L (%)	>35 e <60	<90	>30	—	—	—	>20
I_P (%)	>15 e <30	>12[(b)] e <65	>15	>10 e <30-40	>7-10 e <30-40	>10 e <30-40	>7
A_c[(a)]	—	—	—	—	—	—	>0.3

1 - MATRECON (1980); 2 - NRA (1989); 3 - Gordon *et al.* (1990); 4 - Mitchell and Jaber (1990);
5 - Daniel (1990), Daniel and Koerner (1995); 6 - Monjoie *et al.* (1992); 7 - Benson *et al.* (1994).
(a) - Skempton activity coefficient; (b) - Added by Murray *et al.* (1992); (c) - $\varnothing < 0.005$ mm; (d) - $\varnothing < 2.5$ mm.

SELECTION OF SOILS BASED ON QUANTITATIVE CRITERIA

Bases of the study

The study of the correlation between the hydraulic conductivity and the geotechnical properties of Portuguese fine-grained soils, presented in this work, has been done on the basis of results obtained in a comprehensive experimental laboratory programme. The main objective of the programme was to contribute to improve the knowledge about the hydro-geochemical performance of natural soils (advective transport, diffusive transport and retardation capacity of pollutants) usually considered as the most potentially adequate for constructing compacted soil liners.

With a view to obtain a comprehensive sampling of the hydro-geochemical performance of Portuguese fine-grained soils, the procedures adopted were as follows:

a) preparing multi-specie synthetic leachate, acid (pH = 4.6) with the composition and chemical concentration (electrical conductance EC ≅ 14 mS/cm) the most representative as possible of those observed in real leachates;

b) collecting thirty samples in different Portuguese clayey formations and studying their geotechnical characteristics;
c) selecting representative samples of the collected population;
d) assessing the long-term integrity of soils.

The study of the hydro-geochemical performance has been done on seven representative samples of the collected population. Their selection was done on the basis of the statistical treatment of results obtained in the geotechnical characterisation of materials by the Principal Components Analysis method.

As regards the study of the hydraulic performance, the compaction of six specimens was performed on all seven samples statistically selected as follows: a) two with a water content 2% less than the Standard Proctor optimum water content ($w_{opt-2\%}$); b) two with a Standard Proctor optimum water content (w_{opt}); c) two with a water content 2% higher than the Standard Proctor optimum water content ($w_{opt+2\%}$). The three specimens of a first set were sequentially permeated with demineralised water and acid leachate (i.e., the specimens were permeated with acid leachate after initial permeation with demineralised water) and the three specimens of a second set were permeated directly with acid leachate.

The author designed a permeameter, usually designated as rigid-wall permeameter, to assess the hydraulic performance of materials. Even though the methodologies used in the tests are identical to those of the classic permeability tests, there are a few significant differences, namely the need to extend the tests until establishing the steady state of chemical conditions.

The mean hydraulic conductivities k_{Ad} (in specimens permeated directly with demineralised water), $k_{La/Ad}$ (in specimens permeated with acid leachate after percolation with demineralised water), k_{La} (in specimens permeated directly with acid leachate) were calculated after the conditions, in the sequence as follows, have been observed:
a) volume of the effluent solution proportional to the time;
b) flow rate of the effluent solution proportional to the hydraulic gradient;
c) pH and CE of the same order of magnitude in the influent leachate and in the effluent solution (in the stage of permeation with demineralised water, the condition to be observed was the total eluviation of soluble salts in the natural soil);
d) approximately constant hydraulic conductivity.

Reference must be made to the fact that not always has been possible to fulfil all these conditions, particularly as regards: i) the positive linear relation between the flow rate and the hydraulic gradient (point b); the measurement of the same pH on the effluent solution and on the influent leachate (point c); and, lastly, the complete eluviation of soluble salts in the natural soil (point c).

Geotecnhical characteristics of Portuguese fine-grained soils
Tables 2 to 5 show the main mineralogical, chemical, physical and hydraulic characteristics of the seven samples statistically selected.

Linear correlation between hydraulic conductivity and geotechnical characteristics of Portuguese fine-grained soils
In view of the significant number of permeability tests performed and the wide range of geotechnical properties of soil materials selected, the linear correlation between the hydraulic conductivity and the following geotechnical properties of Portuguese fine-grained soils was studied: a) montmorillonite content; b) percentage of clay size; c) percentage of limon; d) percentage of fines; e) liquid limit; f) plastic limit; g) shrinkage limit; h) plasticity index; i) Skempton activity coefficient; j) free swell index.

Table 2
Semi-quantitative mineralogical composition of Portuguese fine-grained soils

Sample	Total fraction (%)				Clay size (%)					
	Quartz	Feldspar	Calcite	Phyllosilicates	Montm.[te]	Micas		Kaolinite	Quartz	Others
						Musc.	Illite			
Cs.3	20	1	—	79	71	9		7	13	—
SR.5	40	18	2	40	100	—	—	—	—	—
MP.8	47	4	—	49	45	22		20	12	1
MP.12	21	2	3	74	7	60	—	20	13	—
Ji.19	28	2	—	70	—	86		—	7	7
Js.28	69	14	1	16	—	51		29	20	—
Ci.29	41	1	—	58	21	13	—	55	11	—

Table 3
Chemical characteristics of Portuguese fine-grained soils

Sample	pH of soil. 25 °C (Sorensen scale)	EC of soil solution. 25 °C (mS/cm)	S_t (m^2/g)	CEC meq/100g
Cs.3	8.1	475	283.18	58.43
SR.5	8.6	53	179.58	42.05
MP.8	7.7	818	117,00	21.95
MP.12	8.3	277	181.46	28.8
Ji.19	8.6	282	41.65	12.3
Js.28	9.4	153	27.00	6.5
Ci.29	5.1	51	102.56	20.55

EC - Electrical conductance; S_t - Total specific surface area; CEC - Cation exchange capacity.

Table 4
Physical characteristics of Portuguese fine-grained soils

Sample	G_s	Consistency limits			Grain-size distribution			USCS Classification	Compaction		I_S (%)
		w_L (%)	w_P (%)	w_S (%)	Sable (%)	Limon (%)	Clay (%)		w_{opt} (%)	γ_{dmax} (kN/m^3)	
Cs.3	2.8	51.2	31.1	12.9	—	47	53	MH	25.4	15.3	150
SR.5	2.66	47.7	37.2	21.8	50	32	18	ML	20.8	15.5	45
MP.8	2.77	39.3	21.2	15.4	2	71	27	CL	17.8	16.9	85
MP.12	2.78	55.0	29.5	14.7	5	41	54	MH	23.8	15.9	150
Ji.19	2.84	24.7	18.2	12.6	46	41	13	CL-ML	14.0	19.4	50
Js.28	2.73	25.7	17.1	12.7	22	66	12	CL	9.8	19.7	40
Ci.29	2.73	59.0	26.7	14.5	1	55	44	CH	18.4	16.8	140

G_s - Specific gravity of solids; w_L - Liquid limit; w_P - Plastic limit; w_S - Shrinkage limit;
w_{opt} - Standard Proctor optimum water content; γ_{dmax} - Maximum dry unit weight; I_S - Free swell index.

Table 5
Hydraulic conductivity of Portuguese fine-grained soils

Sample	Specimen permeated directly with demineralised water (Dw) and after with acid leachate (La)						Specimen permeated directly with acid leachate (La)		
	$w_{opt-2\%}$		w_{opt}		$w_{opt+2\%}$		$w_{opt-2\%}$	w_{opt}	$w_{opt+2\%}$
	k_{Dw}	$k_{La/Dw}$	k_{Dw}	$k_{La/Dw}$	k_{Dw}	$k_{La/Dw}$	k_{La}	k_{La}	k_{La}
	x 10^{-9}		x 10^{-9}		x 10^{-9}		x 10^{-9}	x 10^{-9}	x 10^{-9}
Cs.3	0.062	0.13	0.013	0.015	0.016	0.016	4.2	0.016	0.035
SR.5	5.3	16.0	2.3	11.0	0.53	0.92	50	13	2.5
MP.8	0.092	0.13	0.048	0.05	0.042	0.053	0.47	0.17	0.047
MP.12	0.018	0.015	0.012	0.013	0.022	0.028	0.018	0.017	0.052
Ji.19	0.43	1.5	0.38	0.53	0.33	4.7	33	0.55	0.68
Js.28	0.087	0.13	0.058	0.072	0.055	0.058	1.2	0.37	0.14
Ci.29	0.078	0.085	0.022	0.03	0.023	0.028	0.055	0.058	0.033

1.5 $k > 1 \times 10^{-9}$ m/s; ne - Not realized.

Table 6 shows the values of the coefficient of linear correlation R between the hydraulic conductivities k_{Ad}, $k_{La/Ad}$ and k_{La} and the clay size percentage (%clay), the fines percentage (%fines), the plasticity index I_P and the free swell index I_e. The values of the coefficient of linear correlation R, between k (i.e., k_{Ad}, $k_{La/Ad}$ and k_{La}) and the other geotechnical properties formerly mentioned, are not presented since they are not satisfactory. From among the correlations presented in Table 6, the one obtained between k and the %fines has almost invariably been the highest and the correlation between k and I_P the lowest.

Table 6
Linear correlation between k_{Dw}, $k_{La/Dw}$ and k_{La} and geotechnical properties (%clay, %fines, I_P and I_S) of Portuguese fine-grained soils

Properties	Hydraulic conductivity								
	$w_{opt-2\%}$			w_{opt}			$w_{opt+2\%}$		
	k_{Dw}	$k_{La/Dw}$	k_{La}	k_{Dw}	$k_{La/Dw}$	k_{La}	k_{Dw}	$k_{La/Dw}$	k_{La}
%Clay	0.64	**0.82**	0.64	**0.9**	0.7	**0.82**	**0.8**	**0.81**	0.72
%Fines	**0.85**	**0.87**	0.79	**0.9**	**0.91**	**0.87**	**0.97**	**0.96**	**0.98**
I_P	0.58	0.79	**0.81**	**0.82**	0.64	0.68	0.76	0.76	0.75
I_S	0.68	**0.86**	0.69	**0.93**	0.75	**0.85**	**0.85**	**0.85**	0.79

0.97 - Linear correlation coefficient R with very high value ($R \geq 0.95$).
0.82 - Linear correlation coefficient R with high value ($0.80 \leq R < 0.95$).

For the specimens compacted with $w_{opt+2\%}$, the values of the coefficient of linear correlation between k_{Ad}, $k_{La/Ad}$ and k_{La} and the %fines were higher than or equal to 0.96. Figs.1a to 1c illustrate these results, which suggest that the hydraulic conductivity of fine-grained soils may be approximately estimated from the linear equations presented in those figures.

Based on the operation of a waste landfill, it is considered as adequate to use the linear equation presented in:

a) Fig. 1a to estimate the hydraulic conductivity of the compacted soil liner that comprises the final cover, considering that the most likely situation is its direct permeation by rainfall water;
b) Fig. 1b to estimate the hydraulic conductivity of the compacted soil liner that comprises the talus liner system, considering that the most likely situation is that the permeation of rainfall water will occur in the initial stage of landfill operation and the one of the leachate in the intermediate and final stages of the landfill operation;

c) Fig. 1c to estimate the hydraulic conductivity of the compacted soil liner that comprises the bottom liner system, considering that the most likely situation is its direct permeation by leachates (the use of the expressions indicated in Figs. 1a and 1b could lead to overestimating the hydraulic performance of materials).

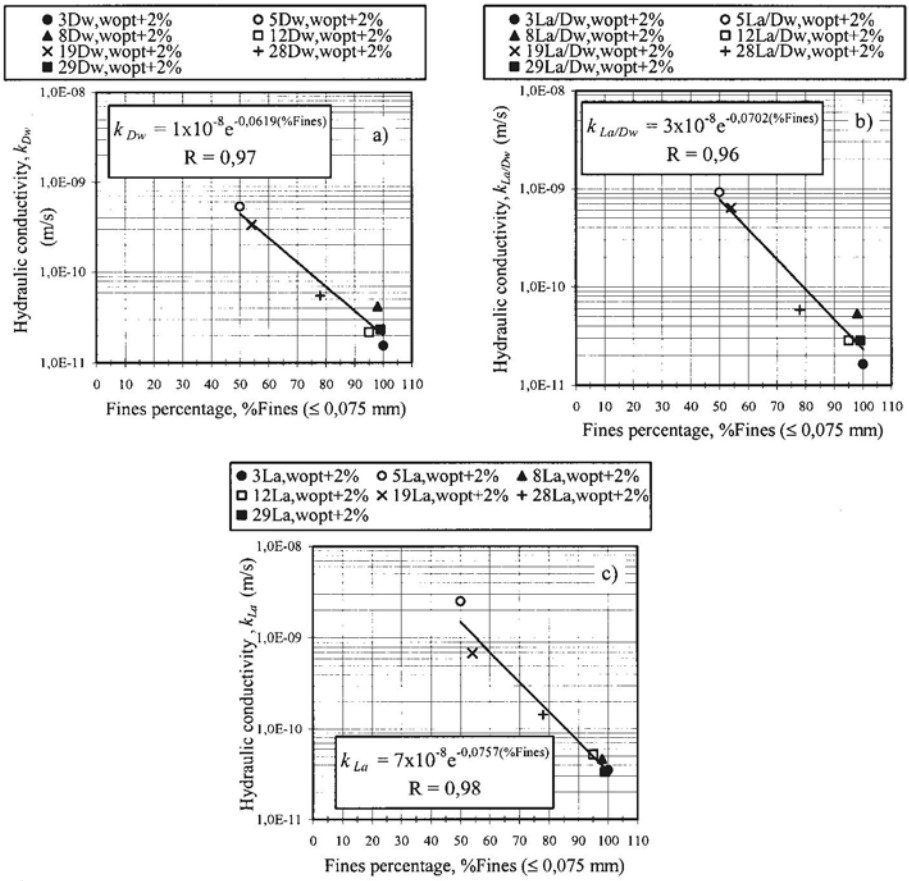

Fig. 1 – Linear correlation between the hydraulic conductivity k obtained on compacted specimens at $w_{opt+2\%}$ and the fines percentage: a) hydraulic conductivity k_{Ad} of specimens permeated with demineralised water; b) hydraulic conductivity $k_{La/Ad}$ of specimens permeated with acid leachate, in the same specimen permeated with demineralised water; c) hydraulic conductivity k_{La} of specimens permeated with acid leachate.

PRACTICAL APPLICATIONS

The laboratory evaluation of the hydro-geochemical performance of soils is a very long process that requires significant human and financial resources. Therefore, it becomes interesting and desirable to have the tools that will make it possible to carry out - in a simple, quick, non-expensive and sufficiently reliable way - the selection of the soils the most potentially favourable to the construction of compacted soil liners in the preliminary stage of the projects of waste landfills. The main advantage of that preliminary selection is represented in a reduction of the soils to be characterised from the point of view of hydro-geochemical performance, through permeability and diffusion tests.

Based on the results mentioned in the previous section, we suggest to replace the known semi-quantitative criteria by the quantitative criteria represented by the linear equations presented in this paper from correlations between the hydraulic conductivity of specimens compacted with $w_{opt+2\%}$ and the %fines, in the preliminary phase of the waste landfill study. The latter procedure seems to be the most adequate because: a) several studies have shown that the lowest hydraulic conductivity of a soil is reached when the latter is compacted with a water content about 2% higher than the Standard Proctor optimum water content; b) a potential value of k is obtained rather than a semi-quantitative indication that k is potentially less than or equal to 1×10^{-9} m/s; c) the parameters necessary for the application of the linear equations developed are less than those necessary for the semi-quantitative criteria: the percentage of fines for the procedure proposed and the percentage of clay size, the percentage of fines, the percentage of gravels, the liquid limit, the plasticity index and the Skempton activity coefficient for the semi-quantitative selection criteria.

The fact that the linear equations obtained result from permeability tests performed on natural fine-grained soils with a significant range of geotechnical properties, and with a pure solution (demineralised water) and a concentrated solution (acid leachate), leads us to assume that these can be satisfactorily applied to a large number of different cases.

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Risk Management Solutions for Contaminated Land in the UK: Selection, Feasibility, Efficiency and Impact.

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INTRODUCTION

Pragmatic and efficient management of risks arising from historically contaminated sites is a key prerequisite for successful redevelopment of brownfield sites. The risk management framework comprises identification and assessment of potential hazards, estimation of the risks posed by these hazards and evaluation of their importance (e.g. source-pathway-receptor analysis and identification of significant pollutant linkages). Where the identified risks are deemed unacceptable suitable risk management solutions are developed for their mitigation. The general objective for these solutions, also known as remedial measures, is risk reduction through breaking the pollutant linkage. This can be achieved by source reduction, pathway management, control of the receptor exposure, or by a combination of these controls.

Careful selection of remediation methods is critical if resources are not to be wasted and environmental risks are to be minimised. However, despite the growing number of remedial solutions available many risk management decisions are still largely intuitive and impulsive, driven by the experience, or lack of it, of key stakeholders (land owner, consultant, regulator).

Although the range of process-based remediation technologies is steadily growing only a limited number have been tested on the commercial scale or have a proven track record or the necessary licences to operate. Remediation technologies that are currently commercially available in the UK are summarised in Table 1.

Table 1. Potential remediation technologies available in the UK; not an exhaustive list.

Type	Location	Technology
Biological	In-situ	Monitored Natural Attenuation, Bioventing, Biosparging, Enhanced Bioremediation, Phytoremediation,
	Ex-situ	Landfarming, Windrow turning, Bio-piles, White rot fungi, composting, Treatment beds, Bioreactors
Chemical	In-situ	Soil flushing, Chemical oxidation, Oxygen release compounds (ORC), Permeable reactive barriers, Dechlorination
	Ex-situ	Solvent extraction
Physical	In-situ	Air sparging, Soil vapour extraction, Dual phase extraction, Hydrofracturing, Electroremediation, Pump and treat, Soil washing, Solvent extraction, Electrokenesis, Stream stripping

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	Ex-situ	Soil washing, solidification and stabilisation,
Thermal	Ex-situ	Thermal desorption, Incineration, Vitrification
Containment	In-situ	Stabilisation, Impermeable barriers
	Ex-situ	Stabilisation, Capping

This paper summarises the procedures involved in the decision making process for contaminated land management and presents a tiered approach to selection of appropriate risk management solution using a case study by way of example.

DECISION MAKING FRAMEWORK

In the UK the risk management decisions involve four key stages: selection of appropriate solution, implementation, performance monitoring and validation and reassessment. This paper primarily focuses on the selection of risk management solutions or *options appraisal* as termed in the recent draft UK guidance on the model procedures for management of land contamination (Environment Agency 2003, CLR 11). Although the recent guidance document (CLR 11) does attempt to define the main requirements of the options appraisal, the guidance tends to be generic and hence there is still a need for transparent guidance on the selection of risk management solutions.

General Objectives

The implementation of risk management solutions in the UK is primarily driven by a combination of regulatory requirements and business needs. The most common objectives are summarised in Table 2.

Table 2. General objectives for risk management in the UK

Objectives	Key drivers
Protection of Human Health and the environment (controlled waters, ecological systems, property)	Environmental Protection Act 1990 & Water Resources Act 1991
Facilitate redevelopment (satisfy regeneration criteria and render land suitable for the intended use)	Town and Country Planning Act 1981
Economic investment (improve asset value, limit potential future liabilities)	Divestment or acquisition of property, business and/or reputational risk
Repair of unsuccessful or insufficient remedial works	Any of the above

Regardless of which of the above general objectives is driving the remediation, the chosen strategy must incorporate site specific objectives. In this process the solutions available for achieving the general goal are considered in the light of additional factors such as stakeholder satisfaction, cost effectiveness and sustainability (Bardos et al. 2002).

Examples of relevant stakeholders, in addition to those directly involved in the risk management (e.g. landowner, consultant, regulator), can be site workers and users, financial bodies, neighbours, campaigners and technical peers in the scientific community. This stakeholder diversity necessitates careful planning and early consultations when considering remedial solution with potentially significant impact.

Cost benefit considerations involve the assessment of the relative gain from each solution in terms of monetary value, balancing, among others, benefits achieved, impacts incurred and resources used up. Cost benefit analyses are notoriously difficult due to the variety of factors involved and the many non-generic issues that are likely to be specific to a particular site. In the UK, the Environment Agency issued a framework for comparison of remedial alternatives utilising multicriteria analysis (Postle et al. 1999, Hardisty & Ozdemiroglu 1999).

The necessity for sustainable development has to be considered in every risk management solution, and indeed, key principles are included in the above cost benefit framework. Here it should be noted that many impacts, both positive and negative in terms of sustainable development, can not be easily defined in monetary terms. The impacts are socio-economic as well as environmental. The primary environmental considerations include the energy efficiency of the solution, renewability of the materials used, use of landfill resources and impact on soil and landscape value. Socio-economic issues may include loss of revenue to site owner, impact on local businesses, impact on the local community (infrastructure, employment, leisure) or public perception of the risk management approach.

The selection of appropriate solution must consider all of the above issues albeit in the knowledge that their individual significance will vary from site to site. Some of the more common issues are discussed below, complemented with real life examples, loosely based on a recent remediation of chemical works.

Information requirements

The type and quality of information necessary for an effective and efficient risk management is generally given by the complexity of the site and the requirements of the risk assessment. As a general rule, staged environmental assessment comprising preliminary investigation (desk-top, reconnaissance), detailed site investigation and risk assessment would be carried out. Often additional investigations, particularly aimed at the properties of pathways and the behaviour of potential contaminants in time and space are also undertaken (e.g. groundwater investigation, monitoring of groundwater, ground gas etc.). It is essential that the data available is reviewed and a gap analysis is undertaken to identify any further requirement that may be specific to a particular remedial solution.

A critical element for efficient decision making is an accurate conceptual model of the site. General guidelines for the preparation of the conceptual model are given by Fookes (1997), ASTM (2000), McMahon et al. (2001), Nathanail et al. (2002).

Based on the conceptual model, significant pollutant linkages are assessed and the risks to each receptor are quantified during a site-specific risk assessment. Where a linkage is deemed to pose an unacceptable risk to any associated receptor, the primary risk management objective is to reduce the risk to an acceptable level. To achieve this a remediation strategy is prepared including site specific remediation objectives. Examples of such objectives include 'site specific target levels' (SSTLs) as criteria for reduction of a particular source, thickness of a cover layer or performance of an in-ground barrier.

TECHONOLOGY SELECTION

The process of selection of the appropriated solution is illustrated using a recent case study of a large industrial facility in north England. A conceptual site model is shown in Figure 1. The significant pollutant linkage identified for the site was:

Source
Shallow groundwater contaminated with Tri Chloro Ethylene (TCE) and break down products.

Pathway
Migration through groundwater.

Receptor
River bordering site.

Site specific objectives

Specific objectives were formulated on the basis of the risk assessment and discussions with the client and the regulator:

1. Take action to remove credible risk of regulatory action due to historic contamination;
2. To take action to remove credible risk of third party liability;
3. To carry out the exercise without harm to personnel or neighbours;
4. Avoidance of adverse publicity resulting from the project; and
5. Ensure professional, timely and cost effective approach.

Review of available solutions

The purpose of the primary screening was to identify technologies that were technically suitable for the treatment of the subject site. In general, a single technology can rarely remediate an entire site. Consequently, two or more treatment technologies are usually combined at a single site to form what is known as a treatment train or treatment combination. For our case study site, where soil and groundwater was contaminated from a single source, one or two technologies should be sufficient. The following treatments and treatment combinations that were available in the UK at the time were found to be suitable for the geological and hydrogeological conditions identified on the site. The potential suitability of each technology was assessed as shown in Table 3.

Table 3. Suitability of remedial methodologies for achieving remedial objectives.

Technology	Code	Suitability for achieving objectives*					Comments
		1	2	3	4	5	
Monitored Natural Attenuation	MNA	?	✓	✓	✓	×	As yet there is no evidence of the contaminant plume shrinking; SSTLs may not be achieved within a reasonable timescale.
Enhanced Natural Attenuation	ENA	?	✓	✓	✓	?	Introduction of oxygen or hydrogen and nutrients into the contaminated zone could accelerate natural degradation to acceptable levels, however, it is difficult to control the treatment once introduced.

Enhanced Natural Attenuation combined with Pump & Treat	ENA/ PT	✓	✓	✓	✓	✓	The employment of Pump & Treat would accelerate the process and will enable control of the treatment whilst operating.
Air Sparging and biosparging	AS/BS	×	?	✓	✓	×	The effectiveness would be compromised by the presence of DNAPL. Injection rates would be crucial not to enlarge the plume.
Bioremediation ex situ (Biopiling)	ExBio	×	✓	✓	✓	×	May be feasible but is there sufficient storage space within the site for biopiling.
Containment Hydraulic containment & product recovery	CB/ CH&PR	?	?	✓	✓	?	May adversely affect hydrogeology of site.
Excavation and Disposal combined with temporary Pump & Treat	ExcD/ PT	✓	✓	✓	✓	×	Not a sustainable solution. Unnecessary use of landfill space. Total cost of this approach was estimated around three times the amount of the next most expensive scheme.

Note: * for individual objective refer to text; ✓ – suitable; × – unsuitable; **?** – suitability uncertain.

It is apparent from Table 3 that one technology combination was found to be suitable, and a further two technologies or technology combinations were considered to be potentially suitable, for the remediation of the site. At this stage appropriate service providers were contacted on a pre-tender basis in order to obtain information regarding technical feasibility, potential restrictions, timescales and costs. This information along with site specific issues and client's requirements were used for the selection of the most suitable methodology.

Assessment of suitable solutions

The purpose of this assessment is to evaluate the risks associated with the employment of the proposed technologies at the subject site and rank these according to their suitability. Generally, risks associated with site remediation can be divided into four categories:

- Operational (technical feasibility, result uncertainty);
- Environmental (impact on ambient environment, including properties and public);
- Commercial (cost implications, time-scales, necessary statutory consents); and
- Legal (regulatory compliance, e.g. Mobile Plant Licence, Waste Management Licensing Regulations, Duty of Care, health and safety, off-site contaminant migration).

Table 4 presents an assessment of risks posed by the employment of treatment technologies or technology combination identified in the previous section for specific factors within these categories. The assessment is semi-quantitative whereby each factor is allocated a suitability ranking from 0.1 to 1.0, with 0.1 denoting the lowest suitability (highest risk) and 1.0 denoting highest suitability (none or negligible risk). This way, technical feasibility, for example, would be rated 0.9 for enhance natural attenuation, comprising drilling treatment wells and provision of oxygen source, but only 0.7 for hydraulic containment and product recovery as the installation of treatment wells, ducting, vacuum pump, scrubber unit etc. is far more elaborate.

Table 4: Risk assessment for the employment of individual treatment technologies.

Risk Factor	Weighting	Suitability Ranking		
		ENA	ENA/PT	CB/CH&PR
Operational				
Technical Feasibility	1	0.9	0.9	0.7
Result Uncertainty	2	0.5	0.8	0.7
Environmental				
Environmental Impact	1	0.9	0.8	0.6
Commercial				
Capital Cost	2	0.8	0.7	0.5
Operation/Maintenance Cost	1	0.9	0.8	0.6
Monitoring Cost	1	0.9	0.7	0.8
Treatment Duration	2	0.2	0.6	0.8
Statutory Consents, Negotiations	1	0.2	0.8	0.8
Effect on Development Programme	2	0.9	0.9	0.2
Legal				
Regulatory Compliance	1	1.0	0.8	0.8
Health Liability	2	1.0	0.8	0.8
Off site migration	2	0.3	0.7	0.7
Average rank score*		68%	77%	65%

* ranking coefficient 1 corresponds to 100%

In this case study the rating was done qualitatively based on experience, however, once sufficient data is obtained on each technology, semi-quantitative scores can be derived for a particular solution. Each risk factor is given a weighting from 1, 2 or 3, corresponding to low, medium or high importance, respectively, which are allocated following discussions with key stakeholders, in this case the statutory authorities, residents representative and the client. The resulting average rank score for each individual treatment technology is calculated as a weighted average of all risk quotients and expressed in percentage of maximum possible score. The most suitable technology is then indicated by the highest score.

Evaluation and selection of preferred solution

Following the above assessment enhanced natural attenuation combined with pump and treat system was selected as the appropriate solution for managing ground and groundwater contamination risks in the subject site.

CONCLUSIONS

Despite the plethora of innovative remediation technologies arriving at the UK market the number of effective and reliable remedial solutions is growing slowly. The introduction of novel techniques is being hampered by the lack of trial data, unproven reliability, licensing difficulties and not least by the pessimism or conservatism of key stakeholders.

This naturally limits the number of solutions available for formulation of efficient, effective and flexible remediation strategies. A careful analysis is needed at this stage in order to incorporate a variety of factors including stakeholder satisfaction, sustainability and cost-effectiveness.

The selection of the appropriate remedial solution should be carried out in a staged assessment of available techniques. The two stage system proposed in this paper comprises technology screening, based on: technical feasibility, availability in the UK and their suitability to achieve all site specific objectives, followed by a suitability ranking which judges the potentially suitable solution on their operational, environmental, commercial and legal risks.

The basis for this decision making framework is currently fully qualitative. Much more information is needed before more objective assessment can be made, perhaps drawing from an industry-wide information sources and databases.

As the variety of remediation technologies available in the UK market increases, the need for an integrated approach in the decision making on remedial solutions becomes an essential prerequisite for successful risk management of contaminated land. First step has been made in the Environment Agency's consultation draft on the model procedure for the management of land contamination (Environment Agency 2003).

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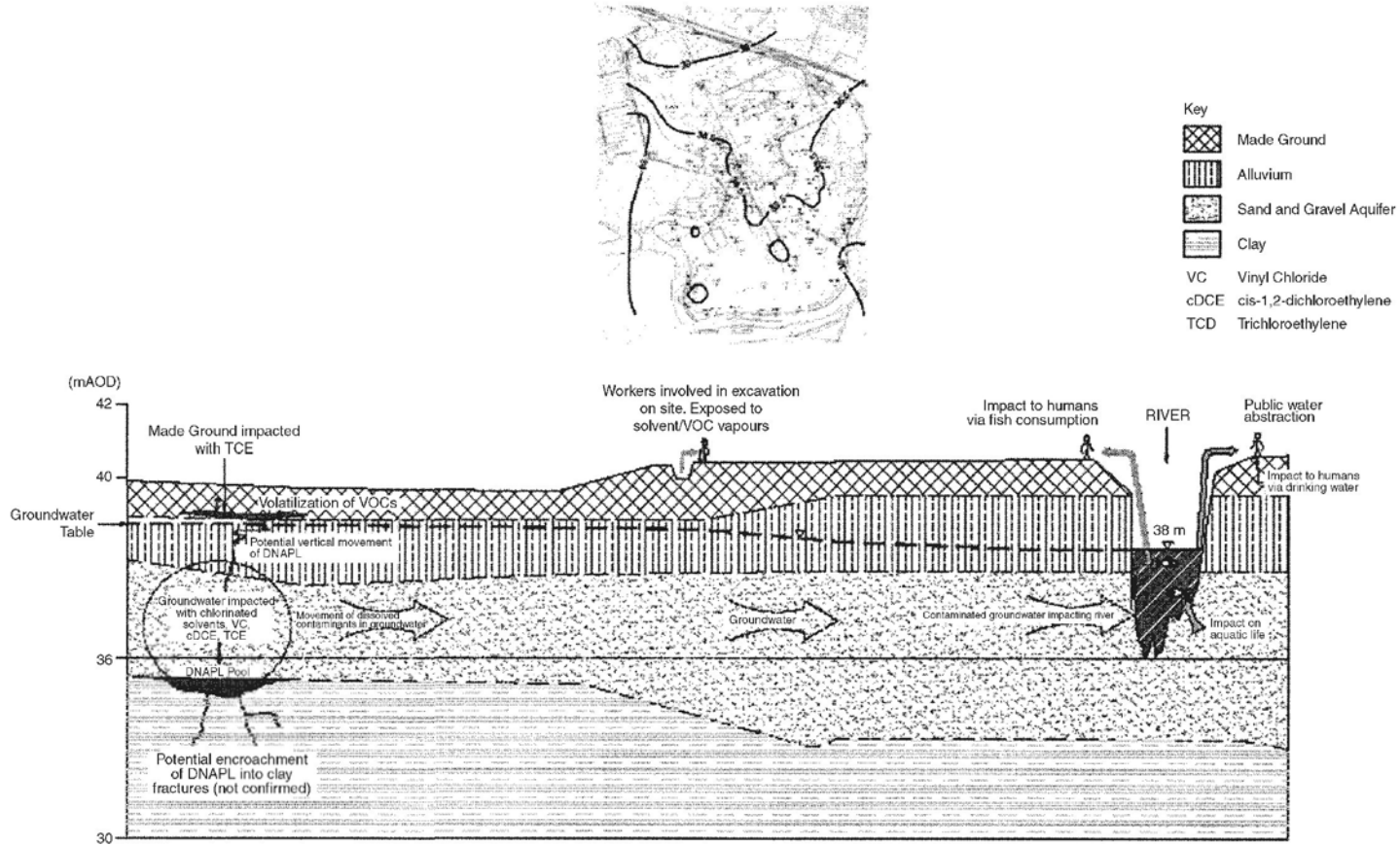

Figure 1. Simple conceptual model showing indicative groundwater contours and a generalised cross section through the site.

LEGISLATION AND REGULATORY CONTROL

A Regulatory Perspective

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INTRODUCTION

Remediation of land affected by contamination can involve:

- excavation or abstraction of the contaminant source and disposal off site
- treatment of the contaminated soil or polluted water and / or
- civil engineering solutions.

Prior to deciding on the remediation technique the processes of site investigation and risk assessment have to be undertaken. The site investigation and remediation process involves the potential to cause pollution and both may be caught by environmental regulations.

Whilst most geoenvironmental engineering projects will be going ahead to correct an environmental wrong, this does not mean that specific regulatory requirements do not have to be met. Prior to starting any engineering project you should carefully consider what regulations apply to it. It is highly likely that an environmental permit is needed for one or more aspects of the project.

The United Kingdom (UK) has an industrial legacy which has over the centuries resulted in contamination of large tracts of land. Activities have previously been carried out with scant regard to the environmental impact and some waste disposal practices have been found wanting. This has lead to the steady introduction of new and increasingly sophisticated regulatory controls. There are those originating from Europe, such as the Integrated Pollution Prevention and Control Directive and those in domestic legislation, the Contaminated Land regime – Part IIA of the Environmental Protection Act 1990, being a prime example. The regulatory requirements discussed in this paper relate specifically to England. Similar, but slightly different requirements may relate to Wales and Scotland.

Most modern environmental regulatory regimes are preventative in nature. They also contain provisions allowing the enforcing authorities to require action of the polluter and in some cases third parties, such as the landowner or occupier. Other statutory regimes have been designed to be more interventionist when pollution occurs.

This paper briefly summarises the regulatory controls that can trigger remediation and those that are needed to be complied with during the remediation process. Reference to the actual regulations and supporting guidance is needed to ensure that the proposed geoenvironmental project is compliant with the law. More often than not advice from suitably qualified and experienced practitioners will be needed, including the appropriate enforcement authority.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

TRIGGERS FOR REMEDIATION

There are a number of statutory instruments that require remediation to be carried out. These include:

Town and Country Planning
Building Regulations
Part IIA – Contaminated land regime
Anti- pollution Works Regulations - Work Notices
Surrender of a Pollution Prevention and Control (PPC) permit or Waste Management Licence.

Alternatively remediation may be conducted on a voluntary basis.

Town and Country Planning

The Town and Country Planning legislation[1] is the vehicle under which most remediation activities take place in the UK. The redevelopment of land that is affected by contamination often involves geoenvironmental solutions.

Redevelopment of a site for a new use is often the most economic way of remediating land that is affected by contamination. The costs of remediation are off set by the increased value of the land. However, this is not the case at every site.

An environmental impact assessment[2] may be required, resulting in the development of an Environmental Statement, which is submitted in support of a planning application. The presence or potential presence of contamination is a "material consideration" in the planning process[3]. Where planning permission is granted it will normally have conditions attached relating to the remediation activity and requirements to deal with unsuspected contaminants that were either not detected during the site investigation or are present in greater quantities than originally thought.

The remediation objectives for the site, or different parts of the site, should be related to the use that the site is to be put to. The resultant quality of the land should be "suitable for use".

Building Regulations[4]

The standard of remediation will be driven in part by the need to ensure that the building materials, namely foundations, floors and services, are chemically and physically compatible with the resultant geoenvironment following remediation.

Control measures to prevent the subsequent users of the buildings coming into contact with the resultant contaminants can be built into the structure. Provided that the design life of the materials used, within the site specific geoenvironment have been carefully considered. Long term maintenance, particularly in relation to active control systems, should also be considered.

"Approved Document C: Resistance to moisture" has been updated to take into account contamination during the building design and construction phase. A draft was consulted on in

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[1] Town and Country Planning Act 1990
[2] The Town and Country Planning (Environmental Impact Assessment) (England and Wales) Regulations 1999, Detailed guidance is provided in Circular 2/99.
[3] PPG23 Planning and Pollution Control
[4] Building Regulation 2000

December 2002 and emphasised the need for appropriate site investigation, risk assessment and remediation.

Engineering measures do provide satisfactory solutions allowing the safe development of building on sites where contaminants remain. However, the actions of the subsequent occupiers may accidentally, or deliberately, breach those control measures. In the author's opinion this should feature strongly in the risk assessment and overall design of the remediation process and building.

Building on land affected by contamination is a specialist task and should be undertaken with great care.

Contaminated Land - Part IIA[5]
Local Authorities are under a duty to inspect their area, from time to time, to identify land that meets the definition of contaminated land as defined in Part IIA of the Environmental Protection Act 1990. Where the definition of contaminated land[6] is met and a pollution source is affecting a specified receptor[7], via a pathway this is referred to as a "significant pollution linkage" (SPL). The person who caused or knowingly permitted the contamination (referred to as a Class A appropriate person)[8] is required to break the SPL. If a Class A person can not be found then the owner or occupier of the land (Class B appropriate persons) may then, subject to certain restrictions, be required to break the SPL.

In carrying out a geoenvironmental engineering project careful planning and implementation is needed to ensure that the works, or intrusive investigation, do not establish the significant pollution linkage. For example drilling or piling operations may breach a natural containment layer allowing mobile contaminants to flow downwards into an underlying aquifer. Placement of low permeability covers to prevent water ingress in order to mitigate groundwater pollution may lead inadvertently to ground gases migrating laterally off site, whereas previously the gases had vented to atmosphere. Alternatively contaminants may not be affecting any receptors, that is until following the completion of an engineering project when new receptors may be introduced on to the site. If the remediation measures are found not to be adequate, or fail, then the developer may, subject to the specifics of the legislation, be considered the appropriate person.

Anti-pollution Regulations - Works Notices
Where pollution of water is occurring or is likely to occur, the Environment Agency has the power to serve a Works Notice[9] on a person to prevent pollution and / or to remedy any pollution which has occurred. Prior to serving the notice the Agency will have carried out an investigation, conducted a risk assessment and considered the various options.

The notice will specify what works are to be done and by when. Normally the remediation objectives will be related to the water quality prior to the pollution incident. Under certain circumstances the Agency may carry out the works themselves and recovery the costs from the relevant person.

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[5] Section 57 of the Environment Act 1995 inserted a new Part IIA to the Environmental Protection Act 1995
[6] Section 78A (2) EPA 1990 Part IIA
[7] Circular 4/2000 "Contaminated Land – see Tables A and B (pages 73 and 75)
[8] Section 78K EPA 1990 Part IIA
[9] The Anti-Pollution Works Regulation 1999. (Water Resources Act 1991, Section 161 A – D)

Surrender of a PPC Permit or Waste Management Licence
A PPC permit is required to carry out specified activities as set out in the 2000 Regulations. A Waste Management Licence[10] is required when carrying out waste disposal or recovery operations. When such activities are brought to an end an operator can surrender the permit or licence. However, this is only where the Environment Agency accepts the surrender.

Prior to formally accepting the surrender the operator or holder of a permit or licence may be required to remediate the site. Generally, the remediation will be focussed on the contamination caused during the operation of the permit or licence, not historical contamination.

Voluntary Action
Voluntary remediation may be carried out, for example, to mitigate against legal action by the enforcing authority, to divest the land or reduce possible liabilities. However, in carrying out that remediation an environmental authorisation of one kind or another will probably be needed. The specific type of environmental authorisation will be dependant upon the remediation technique proposed and the anticipated residues from that process.

REGULATIONS CONTROLLING THE REMEDIATION PROCESS

Waste Management
The contaminants within the soil or water have effectively been discarded. Treatment of the contaminated soil or water should be carried out under the provisions of a waste management licence issued by the Environment Agency. Currently, Mobile Plant Licences (MPL) are used. This involves applying for a MPL, supported by a generic working plan, which sets out how generally the plant is utilised at a site. Prior to starting work at a site a site specific working plan has to be submitted and approved by the Environment Agency in the area that the site is located. The site specific working plan sets out the detailed procedures that will prevent or mitigate emissions to the environment during the remediation.

Site licences are required where waste is disposed of on site. This includes the development of on site disposal facilities such as repositories or placing waste below containment layers.

Site investigation and remediation often entails the generation of contaminated waste materials, as well as non-hazardous waste. The Duty of Care system requires that the waste is transported by a registered waste carrier and is accompanied with transfer notes that adequately describe the waste. Hazardous waste has to be accompanied with special waste consignment notes. Disposal of any waste from the site must be to an authorised site that is specifically licensed to accept that type of waste.

Groundwater Regulations
The Groundwater Regulations are designed to protect groundwater. They prohibit the direct discharge of List I substances and control the disposal of List II substances[11] to an aquifer such that pollution of the groundwater is prevented.

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[10] EPA 1990 Part II
[11] See "Guidance on the Groundwater Regulations 1998" (DETR 2001). Annexes A and B detail the substances in each list.

Prior investigation to assess the hydrogeology, the purifying powers of the rocks and soil and risks the discharged substances would have on the quality of the groundwater, is a pre-requisite before an authorisation is issued.

A specific exemption relates to the prohibition of the direct discharge of List 1 substances that are re-injected to groundwater in the aquifer where it originated during civil engineering works.

Notices may be served by the Agency in relation to the storage, manufacture or use of listed substance and there is a risk that a discharge to groundwater may occur. The notice may prohibit the activity or impose conditions that have to be complied with.

Groundwater authorisation or notice provisions may relate to the discharge of substances following remediation or where such substances are being stored or treated at a site, respectively.

Discharge Consent

A discharge consent may be required where the geoenvironmental project results in the collection and disposal of effluent to a water course[12] or sewer[13]. The classification of the watercourse will have a bearing on the acceptability of the effluent. The chemical composition of the effluent needs to be determined and the risks associated with the proposed discharge on the receiving water body have to be assessed.

In discharging to a sewer the impact the effluent may have on the actual sewer has to be considered as well as the ability of the receiving sewage works to effectively treat the effluent. The company operating the sewage works has to comply with its own discharge consent following treatment of all the different sewage effluents that it has received.

Any soakaways should be strategically located such that they do not result in additional water flowing through soluble contaminants that may remain following the remediation project The location of soakaways should be agreed with the Environment Agency.

Water Abstraction Licences[14]

Civil engineering work often involves de-watering of the ground. The affect that this may have on other water abstractors or hydraulically connected water features normally has to be determined. Where such affects are unacceptable the application may be refused.

Drilling method statements, particularly in water sensitive areas may have to be agreed with the Environment Agency to prevent contamination from fluids associated with the chosen drilling technique. Casing may be required to prevent artesian leakage. In some circumstances geo-physical logging may be required.

From a remediation point of view abstraction licences are normally associated with "pump and treat" schemes. In areas of greatest groundwater demand it may be the case that an abstraction licence would not be issued. Alternative treatment methods would then need to be considered, such as permeable reactive barriers that treat the contaminated groundwater in-situ.

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[12] Water Resources Act 1991

[13] Water Industry Act 1991

[14] Water Resources Act 1991 – see section 24(1) and section 32(3)

Habitats Regulations
These regulations[15] implement the Habitats and Birds Directives. They provide protection to designated sites. These sites are Special Protection Areas (SPAs) and Special Areas of Conservation, including candidate sites. These are known as European Sites and form the Natura 2000 Network. Similar protection is provided to Sites of Special Scientific Interest (SSSIs)[16].

In addition to protected sites the Habitat regulations provide special status to "European Protected Species". These include certain bats, butterflies, some marine animals, newts, snakes and the otter. Specified flora is also protected.

Competent authorities are required to consult with English Nature (Countryside Council of Wales, in Wales) if the project or plan could have a significant affect on the European site prior to issuing an authorisation. The affect of other additional projects or plans are taken into consideration.

The timing of certain aspects of the project or plan may be influenced. Alternative proposals may have to be put forward because of the potential significant affect on the site, at a particular time.

OTHER REGULATION ASSOCIATED WITH REMEDIATION

Oil Storage Regulations
These regulations[17] apply when more than 200 litres of oil is stored in one or more containers at a site, including bowsers. They require the bunding of storage areas. Additional requirements relate to the capacity, permeability, strength, location of associated pipes and valves. The regulations do not relate to waste oil.

Statutory Nuisance[18]
Local Authorities are under a statutory duty to inspect their area from time to time. Where activities are found that are prejudicial to health or causing a nuisance they can serve a notice prohibiting the activity or requiring works or steps to be taken to abate the nuisance or restricting it so that it does not occur or reoccur. The notice will normally specify by when the required works or steps have to be achieved.

A nuisance can arise from such thing as smoke, fumes, gases, dust or odour. All of which can if not managed properly and dependant upon the specific process, result from site investigations or remediation activities.

CONCLUSION
Geoenvironmental engineering projects and the site investigations that precede them can and do have an environmental impact. Regulations to mitigate those impacts will apply. Which

[15] The Conservation (Natural Habitats & c.) Regulations 1994
[16] The Countryside and Rights of Way Act 2000 (amending section 28 Wildlife and Countryside Act 1981)
[17] The Control of Pollution (Oil Storage) Regulations 2001
[18] sections 79 to 82 of the Environmental Protection Act 1990

regulations, and to what extent, they apply is dependant on the actual activity proposed. It is unlikely that one or more of the above regulations would not apply to geoenvironmental engineering projects.

The views expressed within this paper are those of the author and do not necessarily reflect those of the Department, Government or the Environment Agency.

LANDFILLING – THE ROAD LESS TRAVELLED

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ABSTRACT
Landfilling is about to change. Targets for the progressive reduction of the landfilling of biodegradable municipal waste, together with waste acceptance criteria that prescribe stringent limits for the organic content of inert and hazardous wastes suggest significant changes in waste composition and the landfill gas and leachate it produces. The paper discusses the issues surrounding landfilling according to sustainable development principles.

INTRODUCTION
The Landfill Directive (European Council (1999)) came into force on 16th July 2001. The Directive and the associated Council Decision (European Council (2002)) will have a huge impact on waste management in European Union (EU) member states, like the UK, that rely heavily on the landfilling of untreated wastes. Those member states that have a waste management infrastructure based on incineration are not subject to the same disruption. Many of the requirements of the Directive were reflected in the UK Waste Strategy (Department of the Environment, Transport and the Regions (2000)) but most sectors of the waste management industry will be affected by the requirements of the Directive as set out below.

- Landfills must be classified as inert, non hazardous or hazardous.
- Only hazardous waste will be accepted at a hazardous waste landfill.
- Non-hazardous waste sites will only be able to accept hazardous waste that is stable and non-reactive.
- the landfilling of liquid wastes is to stop.
- Waste acceptance procedures have been set for all landfills and generally, all wastes must be treated prior to landfilling after specific dates.
- Waste acceptance criteria (WAC) that restrict the biodegradable content and limit the leachability of many inorganic components have been set for inert waste sites, for hazardous waste sites and for the cells in non-hazardous waste sites that accept stable, non-reactive hazardous wastes.
- Stringent targets have been set for the diversion of biodegradable municipal waste (BMW) from landfill.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

Inert Waste Sites
The Landfill Directive definition of inert waste is very strict and can be considered to be given by the WAC set for inert waste landfills. These, together with the requirement to treat wastes prior to landfilling, indicate that, once these requirements are implemented, there are likely to be very few inert waste landfills and most existing sites will require reclassification as non-hazardous waste sites.

Hazardous Waste Sites
The ban on the co-deposit of hazardous and non-hazardous wastes, together with the ban on liquid waste landfilling signals the end of co-disposal in the UK, which has served as the main disposal route for hazardous wastes. There appears to be an understandable reluctance on the part of the UK waste management industry to opt to reclassify current co-disposal sites as hazardous waste sites or to provide hazardous waste treatment plants. It seems likely that this will lead to a short-term shortage of disposal facilities for hazardous wastes. The problem that this poses for waste producers is exacerbated by the stringent nature of the WAC for those hazardous waste sites that will exist and the even more stringent criteria for the placement of stable, non-reactive hazardous wastes in non-hazardous sites.

Non-hazardous Waste Sites
Although no criteria have been set for non-hazardous waste accepted at non-hazardous sites at present, it is the diversion targets for BMW that are likely to have the greatest impact on the nature of these sites in the future. In the UK, by 2020 at least 16 m tonnes/annum of MSW will have to be dealt with in ways other than by landfilling. At sometime before then, as the amount of biodegradable waste going to landfill decreases in response to the targets, it may be sensible to sub-divide non-hazardous landfills into biodegradable and non-biodegradable waste sites. This will allow the biodegradable sites to be run in the conventional 'wet' way applying measures that enhance degradation and the flushing of degradation products from the site, while non-biodegradable sites are run in a different way. This might be 'dry tomb' or some other method that allows enhancement of the rate at which the waste within the site approaches stability.

SUSTAINABLE DEVELOPMENT

The EU Strategy for Sustainable Development (European Union (2001)) outlined the long-term vision of a society that is more prosperous, more just, which promises a healthier environment and which delivers a better quality of life for us and for our descendants. In practice this requires that economic growth supports social progress and respects the environment, that social policy underpins economic performance and that environmental policy is cost-effective. The Commission proposed that the strategy should focus on a small number of problems that present severe threats to the future well-being of European society.

The inexorable growth in waste production was identified as one of those threats and an objective was set to break the link between resource use and economic growth i.e. between the growth in waste production and gross domestic product (GDP). This was addressed in the 6th Environmental Action Programme (European Union (2002)) and has resulted in the recent publication of the EU white paper on the development of a thematic strategy on the prevention and recycling of waste (European Union (2003)).

In the UK, sustainable development has become one of the major planks of government policy, as set out in A Better Quality of Life (Department of the Environment, Transport and the Regions (1999)). However, for the Agency it is one of those rather nebulous concepts,

like the very closely linked Best Practicable Environmental Option (BPEO), where, although all can see that the philosophy is sound, there is little in the way of either legislative or financial instruments with which to promote it. The revision of ministerial guidance under S4 of the Environment Act 1995 on the Agency's objectives and contributions to sustainable development (Defra (2003)) has lent some weight to Agency actions in this area. The four pillars of sustainable development are:

- social progress which recognises the needs of everyone;
- effective protection of the environment;
- prudent use of natural resources; and
- maintenance of high and stable levels of economic growth and employment.

However, the fact remains that to simultaneously observe the four pillars requires compromise that can generate uncertainty.

Pollution Potential

Although the Landfill Directive waves an arm at sustainable development and will no doubt push UK waste management practices some way down the road towards it, there is not one single reference to sustainable development in the Directive. This is probably because the Directive was published in 1999, before the Strategy for Sustainable Development. Also because the Directive was so long in gestation – having been started in 1990 - much of the text originated from that time. However, there are very few activities that retain their pollution potential for as long as landfilling and therefore have the capacity to have a detrimental effect on future generations. One thing that can be said with some certainty is that the majority of landfilling conducted today in the UK and in several other EU member states does not meet sustainable development criteria.

The most obvious offender is the biodegradable waste site. Several workers have, over a period of time, predicted that the pollution potential of sites will exist for centuries rather than decades (e.g. Knox (1990), Harris et al. (1994), Heyer & Stegmann (1995)). The current estimate is greater than 500-1000 years (Hall et al. (2004)). In 1995 Hjelmar surprised many of us by demonstrating that those sites that take mainly inorganic wastes are also far from reaching stability within decades; the reason being the slow leaching of inorganic components from the sites. So the problem posed is four-fold:

- what is the endpoint to aim for?
- what are the relevant sustainable development criteria for landfill?
- what wastes should be excluded from landfill?
- where should sites be located?

Endpoints

There are separate surrender tests for landfills in the Environmental Protection Act 1990, the Pollution Prevention and Control (England and Wales) Regulations 2000 (the PPC Regulations) and the Landfill Regulations (England and Wales) 2002. Nevertheless, these tests are compatible, as the objectives are the same - to ensure that the landfill remains under regulatory control until it no longer presents a risk of harm to health or the environment. The basic completion criterion for determining whether the surrender of a landfill authorisation can be accepted is that the undisturbed landfill will not pose a pollution risk.

In practice, once active pollution control systems have been switched off, then if emissions:

- are not unacceptable; and
- are unlikely to increase;

surrender of the landfill permit can be accepted. The determination of what is acceptable is not easy but is not impossible. For a biodegradable waste site, the determination of the likelihood of increased emissions depends to a considerable extent on a knowledge of the amount and the degree of waste biodegradation that has occurred. Probably one of the best ways of ensuring that the majority of the waste in a site has the opportunity to degrade, is to actively operate the site using accelerated stabilisation techniques. Also required is a well-developed conceptual model for the site and good long-term monitoring data.

It seems that the attainment of the completion criterion is equivalent to having reached equilibrium status. A current working definition of equilibrium status is:

> *when emissions of contaminants are at a rate that allows full natural attenuation without further intervention or management beyond a post-closure period that is measured in decades rather than centuries.*

This proposed definition (Hall et al. (2004)) raises the issue of institutional longevity and takes a precautionary approach by suggesting that the post-closure management period should span a relatively short time. (Institutional longevity can be regarded as the length of time regulatory and financial bodies or their successors exist, are able to recognise the need to remediate the site and are able to access the financial provisions for the aftercare of the site.) On the other hand, the proposed definition also implies that at completion, the contents of the site might be quite far from stabilisation and the achievement of final storage quality. Also, when controls cease, regard needs to be taken of the likely increase of emissions resulting from uncontrolled leachate levels. The criteria for determining landfill completion have been relaxed since the drafting of the first guidance on licence surrender in 1994. The endpoint is no longer the point at which leachate concentrations reach background water quality. Nevertheless the ability to achieve the criteria within the lifetime of a generation seems no nearer.

Criteria

Government has provided ten principles and approaches that reflect key sustainable development themes. Those most relevant when considering landfill are:

- taking a long term perspective;
- taking account of costs and benefits;
- respecting environmental limits;
- the precautionary principle;
- using scientific knowledge;
- making the polluter pay.

These do not appear to help much in determining the criteria, but do perhaps set the boundaries and provide a checklist of considerations. The sustainable landfill working group of the Institute of Wastes Management (IWM (1999)) provided the following objectives for sustainable landfilling:

- the contents of the landfill must be managed so that outputs are released to the environment in a controlled and acceptable way;
- the residues left in the site should not pose an unacceptable risk to the environment and

the need for aftercare should not be passed on to the next generation;
- future use of groundwater and other resources should not be compromised.

These objectives appear to have stood the test of time and are compatible with the suggestion that achieving landfill completion within a generation is a definition of sustainable landfill. It has to be said that not all members of the group were able to agree the second objective. Some were of the view that a landfill that leaks to the environment at an acceptable rate could be seen as sustainable. The monitoring and maintenance requirements for such a site need not be considered as a burden to future generation(s) provided that financial resources are made available for the purpose. The issue then turns on the longevity of institutional control and the availability of financial provisions for monitoring and maintenance in the long-term. Perhaps this is where the Agency should take the precautionary approach, indicated by Defra's sustainable development principles, until more is known.

Wastes

Results of ongoing benchmarking studies (Hall et al. (2004)) have identified a number of key species that are likely to limit the rate of achievement of equilibrium status for conventional municipal solid waste (MSW) sites. It is important to note that the study showed that the species likely to take the longest to reach equilibrium status are not usually included in routine leachate and groundwater analyses, e.g. Antimony, Barium and Molybdenum.

Recent work by Knox and Robinson (2004) has shown that many landfills taking mechanical biological pretreatment (MBP) wastes will pose risks to groundwater, and require aftercare periods similar to current conventional MSW sites. Pretreatment processes do have the potential to reduce both the concentration and the mass of contaminants released but the timescales over which the resulting leachates would continue to require management, remains uncertain (Bone et al. (2003a)). This brings us back to the issue of longevity of institutional control.

The hazardous waste landfills considered in a European study by Knox et al. (2004) were at liquid:solid (L/S) ratios of less than 0.3 - it is clear that they were nowhere near final storage quality, despite the lack of biological activity. For current landfills it will be necessary to achieve an L/S ratio of 2-4 for mobile species and possibly as high as 10 for less mobile ones, in order to bring leachate concentrations down to levels that would require no further intervention (Hall et al. (2004)). This indicates the need for active leachate flushing measures.

The impact of WAC on leachate quality will not be known until several years after implementation. However, many of the input criteria at the landfills studied by Knox et al. (2004) were similar to the WAC set in the Directive. For many parameters such as Total Organic Carbon (TOC), Ammoniacal Nitrogen (NH_4-N) and heavy metals, the leachate quality data in the study are likely to be a guide to what may be expected from landfills operating the WAC. The high salinity of the leachates indicated the possible need to limit discharges into non-saline water bodies without the use of separation techniques such as reverse osmosis. The level of NH_4-N and heavy metals found in leachates in the study suggests that they are likely to require treatment prior to discharge (Bone et al. (2003b)).

One of the most worrying aspects of the current studies by Hall et al. (2004)) is that initial work has indicated that when using the concentration values set as acceptance criteria for hazardous waste sites, virtually all species required a time period of greater than 1000 years to reach equilibrium status and 50% required in excess of 2000 years. So, although there is a

view that the proposed waste WAC are difficult to achieve, even they do not appear to provide input parameters that will give rise to sustainable landfills.

Sites

Sites that provide the greatest potential for unmanaged natural attenuation will probably be in similar locations to those preferred in Regulatory Guidance Note 3 (RGN3) (Environment Agency (2003)). Obviously, the Water Framework Directive (European Parliament & Council (2000)) will have come and gone in a thousand years time, meanwhile, it must be remembered that the priority substances, the definitions of groundwater bodies and the criteria by which harm will be judged will be modified by that directive.

One of the consequences of the Landfill Directive will be the concentration of wastes prior to disposal. This may cause a rise in leachate salinity to an extent that is likely to exceed discharge consents. Dilution or concentration are the only treatments available and this may influence the optimum location of such sites – coastal sites offering a potential advantage.

Current studies show that the pollution potential of sites taking wastes that meet WAC compatible with the Landfill Directive may exist for far longer than any containment system or institutional control can be expected to survive. Risk assessments need to include the phenomena that may occur during that time – that is geological processes, the next ice age and global warming. Seismic activity may further weaken the site containment and change the groundwater regime; the next ice age is likely to disperse the contents of a site in a southerly direction; and the most likely impact of global warming is flooding. All three may cause population migration. Coastal locations that might be favoured for higher salinity wastes might be more vulnerable to flooding during global warming episodes.

CONCLUSIONS

Given the evidence before us, it appears that we must be pro-active if we are to ensure that landfilling leaves no unacceptable legacy. It seems that there are 4 main factors:

- to locate sites in least vulnerable positions;
- to set a sensible site aftercare period;
- to provide limit values that are closer to equilibrium status;
- to require accelerated stabilisation at sites.

The definition of a sustainable landfill can probably be agreed. Perhaps the aftercare period over which we might be comfortable with institutional integrity might legitimately be extended to say 100 years rather than 50. The Bank of England has existed for 310 years but not many other institutions have lasted that long. At present, it is difficult to envisage extending aftercare beyond this time.

There is already an indication of the leachate constituents that are responsible for extending the aftercare period. We should perhaps concentrate on these and set WAC that reduce this time period. Part of the sustainable development dilemma is ensuring that the cost of doing so would also be acceptable.

Finally, there is accelerated stabilisation, both during filling and after closure. The IWM sustainable landfill group (IWM 1999) came to the conclusion that the additional cost of accelerated stabilisation would hinder any significant uptake of the activity. It concluded that it would only occur if legislation or financial incentives were introduced. The financial

provisions requirements of the PPC Regulations do supply a vehicle for such incentives – provisions could be justifiably lower where measures were taken to reduce liability.

It is clear that investigation of the use of aerobic stabilisation of landfills and contaminated land is undergoing a revival. It would be useful to review the work of, e.g. Heyer et al. (2003), Hantsch et al. (2003) and Cossu et al. (2003) to take a view on its value in contributing to the measures required to ensure that landfilling becomes a sustainable activity.

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Protocols for the Use of Alternative Materials in Construction

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ABSTRACT
As part of its policy on sustainable development, the UK government encourages the use of alternative materials in construction in place of primary aggregates. However, the use of these materials is sometimes hindered by complex specifications and requirements for both engineering and environmental performance. Engineering specifications for alternative materials have developed considerably in recent years, but the environmental requirements are less well defined, and the two sets have largely developed independently of each other. A set of protocols has therefore been developed to guide potential users through the engineering and environmental requirements for the use of a number of alternative materials in a range of common construction applications. The protocols, which are in the form of a series of linked flow charts, can be downloaded from the web site www.viridis.co.uk. The protocols are described and possible future developments of the system are discussed.

INTRODUCTION
The UK government supports the principle of sustainable development and has put in place a number of policy documents and fiscal measures to encourage this. Part of this policy is to encourage the use of alternative materials, such as recycled and secondary aggregates, as an alternative to primary aggregates. This meets the goals of prudent use of natural resources and protection of the environment (Department of the Environment, Transport and the Regions, 2000). The Aggregates Levy, introduced on 1 April 2002 at £1.60 per tonne, supports this principle, as it applies to primary aggregates but recycled and secondary aggregates are excluded. Government and other clients are increasingly setting targets for the use of these materials as a factor in tender assessment.

There are therefore powerful economic and environmental drivers for greater use of recycled and secondary aggregates. However, there are still a number of factors that can potentially inhibit the use of these materials (Reid and Chandler, 2001). One of these factors is the complex situation with regard to specifications for these materials, for both engineering and environmental performance. The requirements that have to be satisfied can include:

- Inclusion on a list of permitted materials
- Compliance with the engineering properties specified for the application
- Changes to design procedures or methods of working to accommodate the alternative materials
- Assessment of risks of pollution of controlled waters or harm to human health
- Compliance with the Waste Management Regulations

These requirements can be more onerous for recycled and secondary aggregates than for primary aggregates, which, for example, do not fall within the remit of the Waste

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

Management Regulations. Equally important is the perception that there are more barriers for the use of alternative materials than for primary aggregates. Confusion about what the requirements are and fear of additional paperwork, delay, expense and potential liabilities can lead to the loss of opportunities to use these materials.

The requirements fall into two broad categories: engineering and environmental. Engineering requirements are generally expressed in the form of Specifications, which list the permitted materials for given applications and the properties they must possess to give satisfactory performance. Environmental requirements include the Waste Management Licensing Regulations and concerns about pollution and risk to human health. The two categories have very different objectives and have largely developed independently of each other. Thus, a material might satisfy all engineering specifications for a given application but if used could cause pollution of surface or ground water. Equally, a material might be inert chemically but not have the required engineering properties for the application. There is thus a need for a system that takes into account all these aspects and guides the user through the questions that have to be answered before a recycled or secondary aggregate can be used in a given situation.

An attempt to meet this need has been made by Viridis. A set of protocols has been developed in a project funded by the RMC Environment Fund under the Landfill Tax Credit Scheme with third party contribution from Tarmac Limited. The protocols, and an accompanying report, are available as free-to-download pdf files on the Viridis web site at www.viridis.co.uk.

MATERIALS

A large number of alternative materials are potentially available for use in construction. The principal interest is in granular materials - sand and gravel sized - which can be used directly in construction. Fine-grained materials were only included if they have potential for use in construction and are produced in large quantities. Manufactured aggregates, such as expanded clay or pulverized-fuel ash, were not included. A list of the materials considered in the protocols is shown in Table 1.

Table 1. Alternative Materials Covered by the Protocols

Recycled aggregate	Unburnt colliery spoil	Foundry sand
Recycled concrete	Spent oil shale	Recycled glass
Recycled asphalt	Furnace bottom ash	Incinerator bottom ash
Blast-furnace slag	Pulverized-fuel ash	Recycled plastic
Steel slag	China clay sand	Recycled tyres
Burnt colliery spoil	Slate aggregate	Cement kiln dust

ENGINEERING SPECIFICATIONS

This is an area where there have been significant developments in recent years, and lack of engineering specifications is no longer an obstacle to the use of alternative materials in many applications. The main concern is lack of awareness of the specifications by clients, contractors and specifiers. However, the rate of development has been more rapid in some areas than others. In particular the Specification for Highway Works (Highways Agency et al., 2001) was updated in May 2001 with a number of amendments that greatly increase the potential for use of alternative materials. This is probably the most widely-used specification in the construction industry in the UK, particularly for infrastructure projects, and is very influential. Other specifications that have developed to allow the use of alternative materials include BS 8500: 2002 for concrete and the Specification for the Reinstatement of Openings

in Highways, 2nd edition, 2001. Specifications in other areas, such as railways and airports, are less well developed. The main specifications that were used for the protocols are listed in Table 2. A number of British and European Standards were also consulted for the use of alternative materials in particular applications, but are not listed in Table 2.

Table 2. Engineering Specifications Covered by the Protocols

Specification for Highway Works, May 2001 amendments (The Stationery Office)
Civil Engineering Specification for the Water Industry, 5th edition, 1998 (UKWIR)
BR 392: Quality Control – the production of recycled aggregates (CRC Ltd)
BRE Digest 433: Recycled Aggregates (CRC Ltd)
BS EN 8500: 2002 Concrete, Parts 1 & 2 (British Standards Institution)
Highway Authorities and Utilities Committee Specification for the Reinstatement of Openings in Highways (2nd edition, 2002) (The Stationery Office)
National House Building Council Standards
Railtrack and MoD Specifications
Highway Authorities Standard Specification (Autumn 1999) (CSS)
BS 6543: Guide to the use of industrial by-products and waste materials in building and civil engineering

The inclusion of alternative materials in lists of permitted materials in specifications has been accompanied by a requirement for quality control procedures to ensure that the materials are consistent and fit for purpose. The use of recycled aggregates in the Specification for Highway Works, for example, is dependent upon the materials being produced under the quality control procedure set out in BR392 (Anon, 2000). These measures give the client confidence that use of alternative materials will not lead to inclusion of unsuitable material in the works and unsatisfactory performance.

ENVIRONMENTAL CONSIDERATIONS

The situation in the environmental area is much less well defined than for engineering performance, and there is much greater scope for confusion, uncertainty and loss of opportunity to use alternative materials. There are three main areas that need to be addressed:

- The regulatory position; is the material a waste and how should it be controlled?
- The potential for harm to human health during construction and in the long term
- The potential for pollution of surface or ground water during construction and in the long term.

Discussions were held with the Environment Agency to establish the position on these areas, and the protocols are based on the situation in the summer of 2003.

Waste Management Licensing

This is an area where there have been developments in recent years in response to cases in the European Court relating to the definition of waste, and in particular when a material has been recovered such that it is no longer a waste but a product. The current situation is that a recycled or secondary material remains a waste until it is placed in an engineering structure. For bound materials, such as concrete and asphalt, this occurs at the batching plant. However for unbound materials, such as capping or sub-base for roads, it does not occur until the material is placed in its final position on site. Previously, a material would be regarded as a product once it had been reprocessed such that it could be used in the same way as a primary aggregate, that is before it left the recycling centre or treatment plant.

With the new interpretation, any site using recycled or secondary aggregates in unbound form becomes subject to the UK Waste Management Licensing Regulations (1994). The site therefore either needs a Waste Management Licence or to register an exemption from the Regulations. The use in construction of many of the more common recycled and secondary aggregates, such as construction and demolition waste and slag is covered by the exemptions from the Regulations. However, some materials, such as recycled tyres, are not covered, and a waste management licence will be required if they are to be stored or used on site.

Harm to Human Health

The presence of certain substances may lead to the possibility of significant harm to human health if the concentrations exceed critical levels. A first assessment of whether the material is likely to cause harm to human health may be made by comparing the total concentrations of key contaminants to Soil Guideline Values (SGVs) published by the Department for Environment, Food & Rural Affairs (DEFRA) and the Environment Agency (EA) (2002). The SGVs have been derived by using the Contaminated Land Exposure Algorithm (CLEA) model for a range of scenarios including residential, allotments and commercial/industrial. For most construction applications the commercial/industrial scenario will be appropriate, but each situation should be examined to select the most appropriate scenario. For contaminants for which no SGVs have yet been published, it is suggested that the Upper Threshold Concentrations in the EAs Interim Guidance on the Disposal of "Contaminated Soils" (3rd edition, 2001) be used as interim guideline values. These threshold values are used to identify "soils" suitable for use on exempt sites. If plants are to be grown on the materials, the Lower Threshold Concentrations should be used.

During construction, the exposure of workers to materials will be much greater than the subsequent exposure of the public to the materials in the completed works. Where the materials contain contaminants, there may be a risk of inhalation of dust or dermal contact. If the materials are to be used as aggregate in asphalt, there may be a risk of emissions of toxic gases from the mixing plant. The potential hazards should be identified and monitoring carried out for particular substances where necessary. These should generally be with respect to the Occupational Exposure Limits (OEL) and Maximum Allowable Concentrations (MAC) published annually by the Health and Safety Executive (HSE) as EH40.

Pollution of Surface and Ground Water

There are no specific guideline values for pollution of controlled waters. However, a rapid assessment may be made by comparison with two indicative sets of guideline values. The first are the acceptance criteria for inert wastes at landfill sites, as given in the Environment Agency's Regulatory Guidance Note 2 (version 4.0, November 2002) for the Landfill Directive. Table 1 of this document gives a list of materials that may be accepted at an inert waste site without testing. The list includes uncontaminated concrete, bricks, tiles and ceramics, glass, soil and stones, excluding topsoil and peat. For materials that are not on the list in Table 1, limit values are given in Tables 2 and 3. The values in Table 2 are for leaching tests using the CEN standard two part batch test BS EN 12457-3. The values in Table 3 are for the total content of organic parameters.

For the specific situation of the use of unbound industrial by-products in road construction, CIRIA Report 167 (Baldwin et al., 1997) provides guidance on water quality effects. On the basis of laboratory leaching tests, materials are grouped into one of three categories depending on the degree of dilution required to bring the concentrations in the leaching tests

within Environmental Quality Standards or Water Quality Standards for List I and II substances. Group 1 is considered to be equivalent to natural aggregates such as limestone, and materials in this category should have no restrictions on their use based on the potential to affect water quality. Group 2 materials may need some restrictions, and Group 3 materials will need restrictions based on their potential to affect water quality. The CEN 2 stage batch leaching test (BS EN 12457-3) is recommended as the preferred laboratory leach test.

THE PROTOCOLS

The protocols are in the form of a series of linked flow charts, which are accessed from the initial slide, titled 'all applications' (Figure 1).

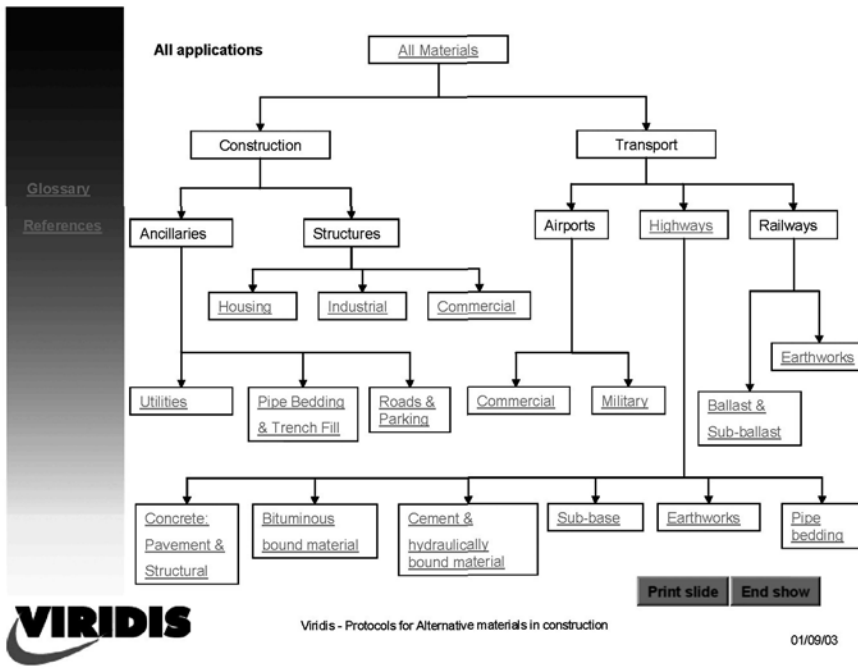

Figure 1. The first page of the protocols, the "All Applications" slide

To use the protocols, click on an application and it will open to reveal a flow chart which goes through the relevant questions for the use of a material in that application. The questions fall into three broad categories:

- Selection: which materials are permitted for the application?
- Environmental: what considerations have to be addressed?
- Engineering Properties: can the material perform the required function?

At every question, there is a link to slides that provide the detail to answer the questions. At the selection stage there are a series of matrices showing the permitted constituents for the relevant applications under existing specifications. The matrix for use in concrete is shown in Figure 2. At the environmental stage, questions such as waste management permitting, harm to human health and pollution of controlled waters are addressed and references given to appropriate publications and legislation. The flow chart for unbound applications is shown in

Figure 3. For engineering properties, the relevant test methods, limiting values and references to specification clauses are given. Where more detail is required, a further layer of slides is provided. The aim has been to keep the overall process clear, with the detail available in further slides as required.

Permitted materials for Concrete Aggregates

	SHW Structural Concrete	SHW Pavement Concrete	SHW Cement Bound Material	BS 8500: Concrete 2002	House Building* NHBC Standards	Water Industry CESWI
Recycled Aggregate	No	No	Yes	Yes	No	No
Recycled Concrete Aggregate	No	Yes	Yes	Yes	No	No
Blast-furnace Slag	Yes	Yes	Yes	Yes	Yes	Yes
Steel Slag	No	No	No	No	No	No
Burnt Colliery Spoil	No	No	No	No	No	No
Unburnt Colliery Spoil	No	No	No	No	No	No
Spent Oil Shale	No	No	No	No	No	No
Pulverised Fuel Ash	Yes	Yes	Yes	Yes	Yes	Yes
Furnace Bottom Ash	No	No	No	Yes	Yes	Yes
China Clay Sand	No	No	No	No	No	No
Slate Aggregate	No	No	No	No	No	No
Cement Kiln Dust	No	No	No	No	No	No
Foundry Sands	No	No	No	No	No	No
Recycled Glass	No	No	No	No	No	No
Incinerator Bottom Ash	No	No	No	No	No	No
Recycled asphalt	No	No	No	No	No	No
Recycled Tyres	No	No	No	No	No	No
Waste Plastics	No	No	No	No	No	No

* Note: Written permission required from NHBC

SHW Specification for Highway Works, May 2001 amendments

CESWI Civil Engineering Specification for the Water Industry, 5th edition, 1998

NHBC National House Building Council

Blast-furnace Slag must comply with the requirements of BS 1047

The composition of Recycled Aggregate and Recycled Concrete Aggregate must comply with the requirements of the SHW or BS 8500 respectively

01/09/03 Viridis - Protocols for Alternative materials in construction Print slide Back

Figure 2. Selection Matrix for Concrete

The protocols can also be accessed via the "All Materials" button on the Applications slide (Figure 1). This leads to a list of the materials covered by the protocols (see Table 1). Click on the material you are interested in, and this takes you to a list of applications for which it is a permitted constituent. Clicking on the application takes the user to the relevant flow chart in the lower half of the applications slide, where the selection-environmental-properties route is rejoined. This facility allows users to determine rapidly the applications for which a particular material may be suitable.

The intention is not to supersede existing specifications, regulations and legislation, but to provide a guide for users to navigate the system with respect to alternative materials. The information is based on the latest available versions, which are indicated in the text. The information is necessarily somewhat simplified, and users should refer to the original documents for full details and the most up-to-date information.

FUTURE DEVELOPMENTS

The protocols are based on current versions of specifications and interpretations of legislation, but this is an area where there is rapid change. The protocols will thus need updating at regular intervals to maintain their usefulness; the next challenge will be the introduction of harmonised European Standards for aggregates and the withdrawal of the existing British

Standards in 2004. Among other changes, the European Standards will require the use of Factory Production Control systems for all aggregates, not just recycled and secondary ones, and will probably lead to the widespread use of CE marking. These developments will generally favour the use of recycled and secondary aggregates.

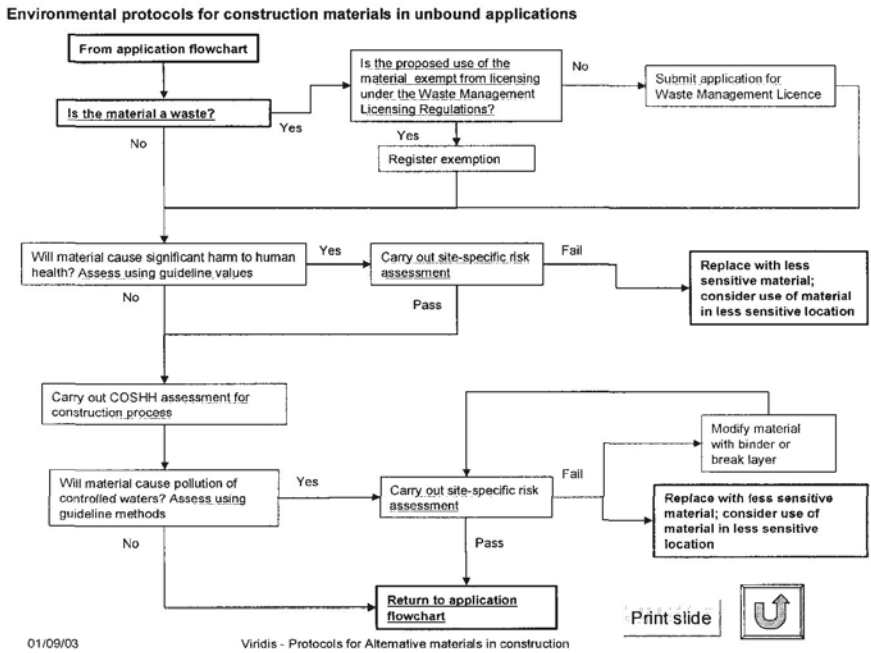

Figure 3. Flow Chart for Environmental Aspects of Unbound Materials

On the environmental side, discussions have taken place between the Environment Agency, Government, industry and the Waste and Resources Action Programme (WRAP) to resolve the 'definition of waste' issue. The discussions have focussed on the development of the existing protocol for recycled aggregates, BR 392. If a recycled aggregate was produced in accordance with this document, it would be classed as a product rather than a waste, and could be used in unbound form without the requirement to either register an exemption or obtain a waste management licence for the site. It is hoped that the revised document will be published for recycled aggregates early in 2004, and extended to secondary aggregates during the first quarter of 2004.

There are, of course, a number of other factors that affect the use of recycled and secondary aggregates, not least the economics compared to use of primary aggregates. Many clients are now including the proportion of recycled materials as a factor in tender assessment. These and other factors will determine which materials are used on a case by case basis, as every project has its own unique circumstances. However, it is hoped that the provision of clear guidance on existing specifications and environmental issues will help to reduce the confusion surrounding the use of recycled and secondary aggregates, and so encourage their greater use in construction.

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UK Contaminated Land Reports (CLR 7–11): Their Application in the Real World.

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INTRODUCTION

In March 2002 the Department for Environment, Food and Rural Affairs (DEFRA) and the Environment Agency (EA), published a series of Contaminated Land Reports (CLR 7-10), which provided a framework for the assessment of risk to human health from land contamination (DEFRA and Environment Agency 2002a, b, c, d). A further report, CLR 11, setting out general procedures for the management of land contamination has been published in consultation draft (Environment Agency 2003).

The guidelines were introduced as operating tools for the implementation of Part IIA of the UK's Environmental Protection Act enacted in April 2000 with the intent of raising the standards of contaminated land investigation, assessment and management in the UK.

The first 18 months saw variable success in the implementation of the new guidelines. In this paper we discuss some implications as seen by a consultant in the UK market. In addition, we present an initial view on the potential pitfalls that may be generated by the proposed CLR 11 guidance (Environment Agency 2003).

CLR 7–10

The guidelines represent a UK framework for the assessment of the risk to human health from soil contamination. The key products of the guidance are generic screening levels for soil contamination, the Soil Guideline Values (SGV). SGV are derived using Contaminated Land Exposure Assessment Model (CLEA) for generic land use scenarios.

The guidelines present a selection of potential contaminants that the UK government is covering in its research work on land contamination (DEFRA and Environment Agency 2002b). The general objective is to focus on substances which are most likely to be of concern. The potential contaminants are selected on two criteria: the substance is likely to be present in the UK environment in sufficient concentration to cause harm and it is known or suspect to pose significant risk of harm to humans, ecosystems, building or building materials, or it is known or suspected to pose a significant risk to the water environment. One of the above criteria is deemed sufficient for selection, eg high toxicity and low abundance or low toxicity and high

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

abundance, although some highly toxic rare substances have been excluded. The list of potential contaminants contains 48 substances or group of substances with most notable absentees including ammonia, thiocyanide, phthalates and some pesticides.

Potentially harmful substances are grouped according to their toxic action into two categories: those for which there is considered to be a threshold below which they fail to induce any discernible adverse health effect, and those for which a threshold cannot be assumed (DEFRA and Environment Agency 2002c). The first group of chemicals generally comprises non-carcinogens and non-genotoxic carcinogens, ie carcinogens that operate through chronic cell damage. The second group comprises mutagenic and genotoxic carcinogens which have the potential to affect DNA and initiate genetic mutations or cancer.

For some substances a threshold for the onset of adverse health effects can be assumed. Consequently, a tolerable daily intake (TDI) is determined for these chemicals. It is derived from no observed adverse effect level (NOAEL) or lowest dose at which an adverse effect is observed (LOAEL). An exceedance of TDI is undesirable although it does not inevitably lead to increased health risk. The implications of exceedance need to be assessed on a case-by-case basis. For chemicals for which a threshold of adverse health effects cannot be presumed, an index dose is determined. It represents the level of exposure at which the associated risk is considered minimal. Index dose is generally based on a nationally or internationally agreed exposure standard from a single source. An exceedance of index dose indicates an increased risk to health with general consensus over 10^{-4} as the upper bound of "acceptable" additional lifetime risk from exposure to environmental contamination from any one source, such as, for example, a contaminated site (DEFRA and Environment Agency 2002c).

The CLEA model is a probabilistic assessment tool utilising Monte Carlo simulation with three key modules:

- Human exposure to contaminants in the soils system
- Fate and transport of contaminants in soil system
- Evaluation of the risk to human health arising from the exposure

SGV are derived for three generic conceptual models which are detailed in DEFRA and Environment Agency (2002d): residential land use with or without consumption of home-grown vegetables, allotments and commercial/industrial land use.

Key Implications

The key implication of the CLR 7-10 guidelines for the UK industry is its replacement of the ICRCL Guidance Note 59/83 (ICRCL 1987) which has been widely used in the industry during the past 15 years. The ICRCL guidance note set out a number of Trigger Values (threshold and action concentrations) for contaminants in soil including ten metals, cyanides, sulphates, PAHs and phenols.

The Trigger Values were intended to provide an indirect method of assessing the risk from levels of contamination in soil according to land-use. For each contaminant three possible concentration zones were set out – namely, areas of acceptable and unacceptable risk separated

by a zone for further investigation or professional judgement. In theory, threshold and action values based on the total concentration of the contaminant in soil would establish the boundary between these zones. In practice, for many of the common metal contaminants only the threshold values were established which, over time, have often been misinterpreted as remediation standards.

In contrast, the CLEA package deals with the direct assessment of risks to human health from soil contamination based on toxicological criteria that establish a level of unacceptable human intake of a contaminant derived from soil and estimates of human exposure to soil contamination based on generic land-use (DEFRA 2002).

This approach is much more complex and technically challenging than the previous blanket application of the ICRCL values putting increasing demands not only on landowner, developers and their consultants but also on the regulators, the Local Authorities. It is particularly the inconsistency applied by the consultants and the Local Authorities across England and Wales that has hampered the application of the new guidelines. This has been exacerbated by slow release of supporting guidance and material by DEFRA and the Environment Agency and lack of the support given to local regulators.

In our experience some important issues frequently encountered across the UK industry include:

- Difficulties associated with the use of the guidelines within the context of the planning regime.
- Lack of toxicological data released by DEFRA and the Environment Agency.
- Lack of guidance on site characterisation and understanding of sampling and field assessment techniques.
- Inflexibility of CLEA model for utilisation of site specific data.
- Bioaccessibility of key contaminants (ie the fraction of a substance available for absorption by an organism/human).
- Lack of guidance on elevated background concentration (either naturally occurring or industrial).

All the above issues are open to interpretation and, indeed, are interpreted in different ways by various stakeholders. In the following section we will discuss the common pitfalls and misinterpretations affecting the industry.

Use of CLR 7-10 within the planning context

Despite the enactment of the Part IIA of the Environmental Protection Act 1990 over 3.5 year ago the main driver, by an overwhelming majority, for the management of land contamination in the UK is the Town and Country Planning Act 1981. The planning authorities and their consultees are advised to use the guidance to aid their planning decisions while facilitating adequate management of land contamination.

In practice the Planning Authority usually imposes conditions on development which are to be satisfied prior to any site construction activities. The conditions generally require the developer to assess the land in accordance with current standards and guidelines, often stating CLR 7–10 as

the key documentation. However, as the site is being developed the potential risk to human health generally comprises risk to construction workers, generally managed under various Health and Safety regulations, and risk to *future* site users.

The CLR 7–10 guidelines, designed for the assessment of historical contamination, use assumptions which would be satisfied under the future, ie as built conditions of the site. Here it is imperative that there is a clear consensus between the developer and the planning authority as to how the potential risks will be managed during this time lag. This is not always the case as there is still the tendency, as with ICRCL values, to use SGV as blanket remedial target values.

Rather, the principles of the CLR guidelines should be used to agree a risk management strategy during construction to include a robust monitoring and verification programme, particularly when engineering sites for sensitive use such as nurseries, schools and private housing.

Lack of toxicological data

Out of the 48 substances or group of substances listed in CLR8 only 10 have had their toxicological information published to date. This is clearly insufficient for the assessment of potential risk to human health arising from soil contamination. The current advice from DEFRA is that Local Authorities are to request assessment of risk to human health to be carried out in accordance with the toxicological criteria and principles published in CLR 7–10. This puts the onus on the land owners, developers and their consultants to derive toxicological data including appropriate safety factors to be input into the contaminated land exposure model (CLEA). Apart from enticing the industry into "doing the Government's job" this introduces potentially dangerous uncertainty into the risk management of land contamination as the risk assessment itself is then assessed and potentially approved rather ad hoc by a Local Authority without centralised government guidance.

Sampling and field assessment

Although there has been significant advances in the guidelines for site characterisation and field assessment (Steeds et al 2000a, 2000b, BSI 2001) the general level of ground contamination characterisation remains poor in the industry, which further complicates the application of the new guidelines.

The new CLR regime is based on the principle of "averaging area" which represents a body of soil that forms a source in the source-pathway-receptor framework. The term "area" is used as in most cases human exposure to contaminated soils occurs via a surface boundary and therefore the corresponding source is a shallow body of soil.

Naturally, the key objective in assessing the human health risks is to identify the appropriate area and accurately estimate the concentrations of potentially harmful contaminants within it. This is achieved by developing an appropriate conceptual site model including appropriate averaging areas and by estimating the concentration of a particular contaminant as the upper 95th percentile of the sample mean representative for each particular averaging area.

This is a robust approach which should ensure accurate and consistent regulation. However, it is not uncommon that the whole site is used as averaging area despite variable land use within it.

In addition, sampling frequency only rarely takes into consideration the likely size of potential anomalies, ie areas with localised elevated concentrations which ought to be evaluated separately.

Although insufficient sampling is generally driven by financial constraints we believe that many poor investigations can be avoided with better understanding of sampling design and data analysis. Guidance published by the UK government in 1994 (Department of the Environment 1994) is more suited to investigation than to assessment of land contamination and the real life benefits of different sampling strategies remain ambiguous.

CLEA model

The main drawback with the use of the CLEA model is its inflexibility. Given the paucity of workable SGV and only three generic conceptual models (residential, allotments and industrial) available it is imperative that the industry can utilise a flexible tool to model non-standard scenarios. It is ironic that its main strength, probabilistic modelling, is offset by fixing many site specific variables, most notably the exposure characteristics, to a single value.

This can be partially addressed by the production of further generic conceptual models for sensitive land uses. The obvious candidates are schools and nurseries where the accuracy and transparency of the risk assessment is an essential pre-requisite in dealing with perceived risks almost always associated with these land uses.

Bioaccessibility

The assumption used for derivation of SGV is that 100% of the contaminant present in soil is available to uptake into the human system. Although there is a provision for the assessment of bioaccessibility in the guidelines (CLR9) there has been limited guidance on how this assessment should be carried out. Despite recent advances in the research of bioaccessibility (Cave et al. 2002, Wragg and Cave 2002) it appears to be a complex subject difficult to regulate (Nathanail and McCaffrey 2003).

Background concentrations

Part IIA of the Environmental Protection Act 1990 makes no distinction between risks from naturally occurring and anthropogenic sources. This is undoubtedly correct but further guidance is needed on the management of risk from contaminants in areas where the background concentration of such contaminant is above the generic screening levels. Examples of such areas include naturally elevated arsenic in granite based soils, mainly in the southwest England and anthropogenically elevated concentrations of some polyaromatic hydrocarbons in urban topsoils.

Current recommendations require detailed risk assessment and potential remediation to be carried out for each individual site or property. If not handled carefully this could lead to escalated development costs and potentially unnecessary land blight.

CLR 11

In Autumn 2003 the Environment Agency issued a draft version of their proposed Model Procedures for the Management of Land Contamination (CLR11). Responses had to be made by

21 November. The following comments therefore refer to the consultation draft document, which may or may not have been subsequently updated.

The assessment and management of the contamination of land is necessary in a diverse range of circumstances. The Model Procedures therefore need to be simple and flexible and should clearly define the key principles which need to be applied to ensure that land is safe to use and unlikely to pollute. We believe the consultation draft fails to satisfy these basic requirements as the rigid compartmentalisation of the procedures is unlikely to be compatible with the majority of projects encountered in the real world.

Potential Implications

Overall the draft procedure obscures the key principles that should be adopted in the assessment and management of land contamination. It introduces numerous, overlapping and unnecessary stages which, if followed, would produce a mass of data that would obscure information of real importance. In addition, it is likely to lead to radical and unnecessary increase in costs of land redevelopment.

The procedure is open-ended without provision for demonstration in a Completion Report that the site is safe for its proposed use and is unlikely to cause pollution.

Further potential concerns are detailed below:

- There is insufficient emphasis on describing the site before identifying potential linkages.
- At higher tiers of assessment, there is too much emphasis on "criteria" (i.e. contamination target values) rather than an holistic assessment of risk.
- There is no description of the process of determination of whether significant pollutant linkages under Part IIA of Environmental Protection Act 1990 are present.
- The remediation option section ignores the treatment of landfill gas, soil combustibility and soil expansivity, all of which may cause harm to humans or property as defined in DETR circular 02/2000 (DETR 2000).
- Much of the content of the remediation strategy sections forms part of normal engineering design development and does not need to be defined in this prescribed manner. The essential principle is that the implementation should embrace the principles of the remediation strategy and the elimination of the significant pollutant linkages.
- The full process of detailed consideration of options is usually unnecessary for practicable reasons. Provided the solution is compatible with the key criteria and eliminates the significant pollutant linkages the only area which is likely to be in dispute is relative cost. This is a matter for economic design, a concept which is well understood within the industry.
- Remediation should not be seen as a combination of options. An experienced environmental engineer will develop a remediation strategy which achieves a satisfactory solution to all significant pollutant linkages and is consistent with the key criteria (objectives and constraints). When producing a jigsaw the full picture is created first. You do not make the individual pieces and then try to fit them together.
- The need for risk assessment of the implementation process as part of validation is not identified.

An Outline of Procedures for Use in the Real World

The procedure for the investigation, assessment and management of land which may be contaminated can be summarised in only 10 steps.

1. Adequately describe the site.
2. Identify potential pollutant linkages (hazards).
3. Eliminate linkages by risk assessment to demonstrate that they are not significant (i.e. they do not represent an unacceptable risk to use of the site or the environment).
4. Identify the key criteria and constraints to be applied to the remediation processes.
5. Identify appropriate remediation processes which will eliminate each of the identified significant pollutant linkages.
6. Identify an appropriate remediation strategy that satisfies the key criteria and constraints. This should include validation and may include monitoring and maintenance.
7. Test the strategy by risk assessment to demonstrate that there are no significant pollutant linkages after remediation.
8. Test the remediation process itself to ensure that additional linkages are not created by the process.
9. Implement the remediation in accordance with the strategy.
10. Validate the remediation carried out including a final risk assessment to demonstrate that the resulting condition of the site contains no significant pollutant linkages.

Adequately describing the site requires sufficient information for the level of risk assessment that is being applied. For this reason supplementary information may need to be obtained about specific linkages where more detailed analysis is needed. Such an approach ensures that unnecessary costs are avoided in obtaining data that are not required.

The fundamental requirement for characterisation of a site is its subdivision into zones, layers and anomalous features. Each can be then be described in more or greater detail as required in order to provide the basic information to be used in assessment. Only when this has been done can consideration be given to identifying potential hazards (pollutant linkages). The production of a conceptual model comprising linkages without first properly describing the site, as proposed in the draft procedure, is unlikely to provide either clarity or a correct result.

The risk assessment step is a tiered process in which linkages are eliminated as not significant, initially by simple techniques, but with increasingly more sophisticated assessment applied to those remaining. At any level a decision can be taken to accept a linkage as being significant. A suggested approach is shown in Fig 1.

Pollutant linkage matrix:

Source	Receptor X	Receptor Y	Receptor Z
A	1	2	
B	3	4	
C		5	6

Assessment matrix:

Assessment		Potential Linkage 1 A-X	2 A-Y	3 B-X	4 B-Y	5 C-Y	6 C-Z
1	Screening	Not Eliminated	Not Eliminated	Eliminated	Not Eliminated	Not Eliminated	Not Eliminated
2	Generic	Not Eliminated **SIGNIFICANT**[a]	Not Eliminated		Eliminated	Not Eliminated	Not Eliminated
3	Simple Site Specific		Eliminated			Not Eliminated	Not Eliminated
4	Detailed Site Specific					Eliminated	Not Eliminated
5	Greater Detail Site Specific						Not Eliminated **SIGNIFICANT**[b]

[a] cost-effective remedial solution available (eg cover layer)

[b] further risk management necessary (eg monitored natural attenuation)

1 – **Screening:** comparison with values so low that they cannot harm or pollute (e.g. site water is cleaner than required at the receptor.

2 – **Generic Assessment:** comparison with generic values for exposure scenarios at least as sensitive as the site.

3 – **Simple Site Specific Assessment:** allow for differences from standard scenarios (e.g. allow for soil cover), allow for natural attenuation (eg Marsland and Carey 1999, Carey et al. 2000).

4/5 – **Detail (/Greater Detail) Site Specific Assessment:** increasingly more detailed modelling and use of site specific parameters and calculation of risk.

Figure 1: An example of a systematic approach to the assessment of land contamination. Pollutant linkages determined in pollutant linkage matrix are systematically assessed within project specific constraints.

The process of establishing objectives and constraints (key criteria) in order to choose an appropriate design solution is well understood by designers in many fields. This process will satisfactorily deliver a remediation strategy (which is essentially a design concept), without the need to adopt the tortuous and impracticable procedures described in the consultation draft document. The key principle is that the strategy (and also the detailed remediation design when it is produced) should be tested to against the key criteria. This will include checking that the strategy will eliminate significant pollution linkages, will not create new ones, will provide a site that is suitable for its proposed use and will not cause pollution. Provided this is done and the principles of economic design are embodied within the process, there is no reason to document the method by which it is achieved other than for the purpose of quality management.

CONCLUSIONS

In this paper we attempted to highlight key issues which are currently slowing down the implementation of the new contaminated land management framework in the UK. It is our view that more concise guidance, training, more transparency and regulatory consistency is required to enable efficient management of land contamination.

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Implementing the Landfill Regulations - A Scottish Perspective of Engineering Aspects

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Abstract:

To comply with the requirements of the Landfill Directive, a total of 257 landfill sites in Scotland were required to submit conditioning plans by mid July 2002. By 2007 approximately 110 of these existing sites will have made an application to operate under a PPC permit with the remainder required to close. Those sites staying open face the challenge of meeting the technical requirements of the Landfill (Scotland) Regulations (SSI 2003/235) including containment measures, gas management and monitoring. The sites closing are required to meet the aftercare monitoring requirements of the regulations as well as capping and restoring the site in an appropriate manner. This process is to be completed by 2007, a timescale which poses demands on all the landfill industry including operators, regulators, consultants and contractors.

A overview of the implementation process and consequent effects on landfill provision in Scotland is presented in this paper. The challenges facing the Scottish Waste Management Industry in terms of meeting the containment and capping provisions on the Landfill Regulations are reviewed with a focus on the key engineering issues and the scale of the activities necessary on a national level to provide Scotland with a Landfill infrastructure capable of meeting the new legislative requirements.

1 INTRODUCTION AND LEGISLATIVE BACKGROUND

The implementation of the Landfill Directive (1999/31/EC) in Scotland has been achieved via separate legislation from England & Wales. The Scottish Executive carried out two consultations on the implementation of the Landfill Directive. The first from February 2001 (Scottish Executive, 2001) and the second, which included draft regulations, from August 2002 (Scottish Executive, 2002). The Landfill (Scotland) Regulations (SSI 2003/235) were approved by the Scottish Parliament and came into force on 11 April 2003.

During this process SEPA was required to introduce the requirements of the Directive under 3 separate provisions:

1/ The Scottish Executive wrote in August 2001 instructing that SEPA implement the Directive as far as possible using existing legislation;
2/ The Landfill (Scotland) Direction of 21 June 2002 required SEPA to classify hazardous sites, exclude hazardous waste from non-hazardous landfill sites and require site-conditioning

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

plans from the operators of all operational landfills by 16 July 2002. SEPA achieved this by the service of notice on operators of 257 sites by 5 July 2002;
3/ The Landfill (Scotland) Regulations 2003 took effect on 11 April 2003 and introduced provisions for SEPA to serve notices closing landfill sites or requiring PPC permit applications by a specified date.

As of September 2003, 187 landfill sites have returned Site Conditioning Plans. The remainder includes 63 landfill sites that have already ceased receiving waste for disposal.

2 ESTIMATES OF LANDFILL NUMBERS

Based on the review of SCPs it is currently anticipated that in the region of 70 to 100 landfills will remain open after 2007. Figure 1 shows a lower bound estimate of the number of existing inert and non-hazardous sites that will remain open in years to come. This plot assumes that those sites operating after 2007 will apply and receive a PPC permit to operate and does not take into account permits, for new sites and extensions to sites that may be issued between 2003 and 2007. This data is skewed by the inclusion of 25 sites (only 3 which were non-hazardous sites) that did not report a closure date in their SCP, rather then omit these from the chart they have been included with an assumed closure date of 2007. However permit applications may be made by these sites and they may remain open after 2007, which would mean more available capacity in the medium term. However, this skew is primarily in relation to inert landfill sites.

Whilst it is not possible at this stage to exactly quantify the number of non-hazardous landfills that will remain open after 2007 a rough estimate is around 50 to 60 such sites. The remaining sites will comprise inert landfills, totalling around 20 to 50. The reduced confidence in estimating inert landfill numbers is due to operators of these landfills not estimating site life when returning their SCP.

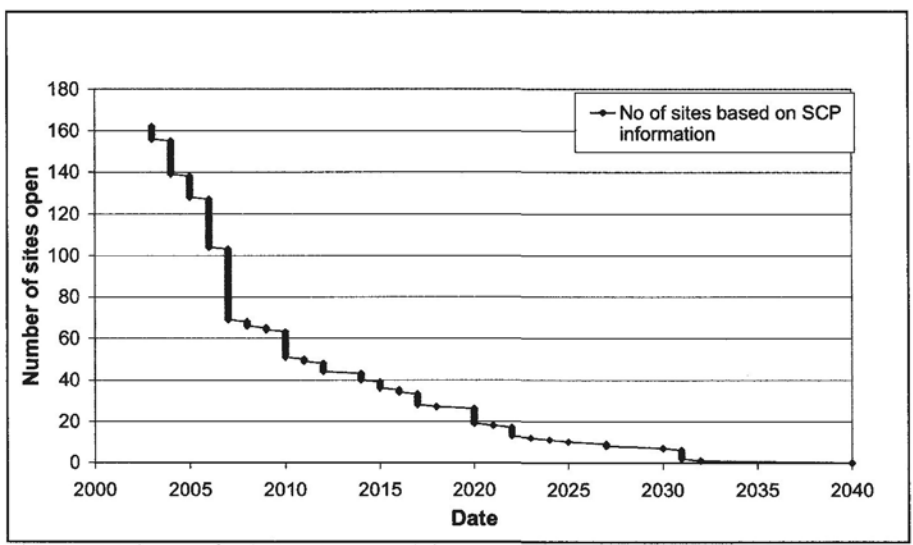

Figure 1: Estimate of existing sites remaining open

It is difficult to conclusively establish the numbers of sites that will be available in the long term, as operators will be required to consider their landfill capacity in the context of the new legislative requirements, and this will be primarily carried out when applying for a PPC permit. The data is however presented as an early indication of likely landfill numbers and clearly indicates the need for continued development of landfill provision. Greater accuracy and confidence in these predications will be gained over the next few years as the existing sites apply for and, where compliant with legislative requirements, receive a permit.

3 IMPLICATIONS TO SITES REMAINING OPEN

Of the estimated 50 to 60 non-hazardous landfill sites that may remain open, less than half currently provide containment measures. Sectors of those landfills that do not comply with the requirements of the Landfill (Scotland) Regulations will be required to close and future sectors will need to be constructed to a compliant standard (SEPA, 2003(a)). In essence this means constructing new lined areas. The timescales for this process are challenging, with all disposal of biodegradable waste being on compliant lined areas by 31st March 2007 at the latest.

A principal constraint is that disposal in noncompliant sectors will be required to cease as soon as possible and thus the footprint for new lined areas in many existing sites will be constrained by existing waste deposits. This inevitably leads to some form of piggyback lining on the flanks of existing waste deposits to separate non-compliant and compliant sectors of the landfill.

Based on 2001 data, 8.91Mt of waste was disposed to landfill (SEPA, 2003(b)) which at that time was going to 257 operational landfill sites. As of 2003 approximately 160 sites remained operational and by 2007 this will be reduced to around 110 sites. Only 50 to 60 of these sites will be able to accept non-hazardous wastes in suitably lined cells. The remainder will be able to accept a restricted list of inert waste. On the basis that 2.1 Mt per annum (industrial C&D) waste will be suitably inert to be disposed of at inert landfills, some 6.8 Mt per annum will require disposal in non-hazardous landfill, at 2002 landfilling rates (SEPA, 2003(b)). The waste strategy for Scotland (Scottish Executive, 2003) aims to significantly reduce landfilling of biodegradable municipal waste and this accounts for a reduction of landfilled household waste from 2.94 Mt/a to 1.36 Mt/a by 2020. There therefore remains a long term requirement for appropriately engineered landfill disposal capacity. Accounting for the waste strategy reduction, non-hazardous disposal capacity of 6.8Mt/a will be required in the short term and this reduces to 5.22 Mt/a (assuming only diversion of BMW) by 2020. The reduction in landfill numbers and capacity will put significant pressure on other waste streams and subsequently increase the focus on waste reduction, reuse, recovery and ultimately diversion from landfill which should in itself further reduce the amount of waste going to landfill.

Post 2007 the disposal of 6.8M t/a of waste is likely to be distributed between 60 non-hazardous landfills and this gives an average requirement of 113,000 t/a new disposal capacity each year per site. However as shown in table 1 (SEPA, 2003(b)) few sites currently have this licensed tonnage capacity and therefore it is likely that the main bulk of the capacity will be provided by a smaller number of large landfills.

Licensed capacity (tonnes)	Number of licences
150,000 and above	14
75,000 to <150,000	49
25,000 to <75,000	40
0 to <25,000	154
Total	257

Table 1: Number of sites by tonnage capacity

At this stage it is not possible to identify specific site capacities pending submission of PPC permit applications. However on a national level, assuming 6.8Mt/a of non-hazardous waste being landfilled at an average waste depth of 30 m (density 1t/m^3), a new area of 227,000 m^2/year of containment works will be required in Scotland each year. This could be viewed as a 500x500mx30 m deep cell required each year. This has implications of resource provision in Scotland. Assuming a standard landfill directive construction profile the following materials would be required each year for such a 'cell':

Top soil cover: 227,000 m^3 (circa 500,000 t /a of top soil)
Drainage layer: 113,500 m^3 (circa 250,000 t/a of drainage gravel)
FML cap: 227,000m^2 of HDPE
Clay cap: 227,000 m^3 (circa 500,000 t /a of clay for a 1m clay cap)

Leachate collection layer: 113,500 m^3 (circa 250,000 t/a of drainage gravel)
Leachate sealing liner: 227,000m^2 of HDPE
Mineral liner: 227,000 m^3 (circa 500,000 t /a of clay for a 1m clay liner)

In total this equates to 2 M tonnes per annum of construction materials (clay, aggregates and soils) and approx 500,000m^2 of membrane liner to landfill 6.8Mt of non-hazardous waste in any one year. Whilst this is a rather theoretical estimate, as it is based on an assumed 30m average waste depth, it does illustrate the significant construction material requirements to meet the landfill regulations engineering requirements. In addition to this gas abstraction and utilisation/ flaring systems and leachate management works will also add to the pressure on engineering resources. The above example indicates a real need to consider alternative site specific arrangements to optimise the use of minerals to achieve the landfill directive requirements especially for capping and closure of landfills. If virgin materials are used in rote adherence to the regulatory recommendations, a ratio of nearly 1 tonne of primary virgin minerals to 3 tonnes waste disposed is achieved. Even by doubling the average depth to 60m of waste (which is unrealistically high as an average) a ratio of 1:6 is achieved. Without refining and optimising landfill designs on a site specific basis so that the regulations are still met with optimal use of materials, a significant pressure will be placed on raw aggregate supplies. In certain areas of Scotland the availability of quarried products may be limited and within a landfill site boundary suitable engineering materials may not be present. This will pose a constraint that will require consideration for the design options available for lining and capping works at sites

Most of the landfills remaining open have previous areas of waste deposition that do not include containment measures compliant with the Landfill Regulations. For these sites the process of remaining open involves an upgrade plan whereby future landfilling will be carried out within phases that are lined and constructed in accordance with the Regulations (SEPA, 2002(a)). Inevitably this will involve lining between the interface of existing waste deposits and future waste disposal activities. This poses a number of engineering challenges to the further development of the landfill.

Construction of a lining system on a waste formation requires an assessment of the likely settlement behaviours of the underlying waste and the effects on the integrity of lining system. Anticipated differential settlements as well as rotational movement of the interface slope due to varying waste depths from toe to crest of slope require quantification. Another key area of consideration is the detail where the interface lining system ties in with the basal lining system of the new compliant phases. There is the potential for significant differential stains to occur in this area due to the interface lining system being on a waste and the basal liner being on a firm foundation. Slope reinforcement to smooth out any sharp stain differentials may be required in these areas and attention to detail of drainage blankets and pipe work is necessary.

The aforementioned constraints will limit the extent to which a piggyback liner can be installed along a waste interface. The need to retain a slope of sufficient gradient to allow collection and drainage of leachate along the interface lining will limit piggybacking to side slopes /flanks of existing waste deposits. The design life of interface lining systems will also need to be taken into account within the risk assessment for the landfill (SEPA, 2002(b)) as the strains and hence induced stresses in the lining components will serve to reduce the service life of materials used. However, on a steep interface lining where leachate head is not anticipated to build up to any extent, the risk assessment can account for increased defects and reduced service life. Similarly the Landfill Regulations do not specify what materials or products should be used for a mineral layer and a leachate collection and sealing system. There are a variety of products including GCLs, geocomposites and geodrains which could be used with an interface lining system and designs will require assessing the performance of these systems when used in this fashion.

4 IMPLICATIONS TO SITES AND PARTS OF SITES CLOSING

The closure of landfill sites will take place in a phased process leading up to a point where the sites are ready for definite closure. The ultimate effect of the legislative provisions is to require that all landfills and sectors of landfills that do not comply with the regulations close as soon as possible. Non compliant sectors of landfill sites required to apply for PPC permits must cease to import waste for disposal in such sectors by 31 March 2007 and will be required to cap such sectors as soon as possible and site specific, time limited conditions of the PPC permit will ensure that appropriate capping and pollution control measures are put in place as soon as possible (SEPA, 2003(a)).

Landfill site operators not required to apply for PPC permits will be required to cease importing waste subject to the regulations by 30 October 2007 at the latest, and to cap such sectors as soon as possible and site specific, time limited conditions of the waste management licence will ensure that appropriate capping and pollution control measures are put in place as soon as possible.

In most cases it is likely that the standards of closure/ capping and aftercare of previously completed sectors will be appropriate, however the onus is on the operator to demonstrate this. Where standards of closure, capping and aftercare are insufficient, works may be required in order to ensure compliance with the regulations.

The standard of cap required is to be based on site-specific assessment (SEPA, 2002(c)). The regulations require that soil, groundwater and surface water are protected by the geological barrier and a top liner following closure. The regulations then go on to provide recommendations for capping but these can be established on a site-specific basis by risk assessment considering the whole life cycle of the landfill site. To allow full life cycle analysis of a landfill the performance of the cap is of crucial importance as the degree of infiltration of rainwater through the cap dictates the leachate generation from the waste.

An artificial sealing liner (such as LDPE) may well be required at a non-hazardous site in order to act as a seal for gas collection purposes or to minimise rainfall infiltration. This would be overlain by a drainage layer, either a blanket of drainage stone, a herringbone network of field drains or a drainage geocomposite systems, or a combination of all of these.

Restoration and topsoil cover will need to be established on a site specific basis depending on restoration and after use proposals. A difference is drawn between the terms 'Top soil' used in the Regulations and 'topsoil' used as a soil classification. The regulations appear to mean a top layer of soil as a cover rather than a 1m thickness of topsoil material.

The closure, capping and restoration at landfills will place demands on the waste management industry due to timescales introduced by the legislation. This capping and closure work will be required at the same time as new complaint lining systems are being put in place for future disposal cells. By 2007 at the latest the non-compliant landfills and parts of landfills will have been closed and capped. It is estimated that around 140 sites will close and an application for a PPC permit will not therefore be made. The exact scale of work required will be site specific in nature but there is no doubt that this will increase the pressure on resources both in terms of construction materials and on the as work load of operators, consultancies and contractors. Whilst many sites are restored on a phased basis during landfilling there are others where substantial works are required to be undertaken on large areas of the site to close, cap and restore the landfill. This work is in addition to that required for the construction of new containment cells discussed in section 3 above. Operators have been required to develop and submit closure, restoration and aftercare plans to SEPA to detail the site specific operations and this should enable a quantification to be made of the levels of work required across Scotland.

5 CONCLUSIONS

A significant challenge faces the Scottish Waste management industry. The commencement of the Landfill (Scotland) Regulations in April 2003 heralded sweeping changes to the engineering standards of landfill sites in Scotland and set a timescale that will have resource implications across the industry. By March 2007, some 4 years after commencement of the regulations, all biodegradable landfills will either be closed and undergoing capping works or continuing disposal on engineered cells. Currently around 25 sites have containment of some form and only a handful have lining works that may be compliant with the regulations. By 2007 the estimated 60 remaining biodegradable sites will all require compliant containment

systems. Not only do the noncompliant sectors of landfills require replacement with new engineered disposal capacity but also the year on year demand for appropriately engineered landfill capacity requires to be provided.

This effect will have major implications on resource demand for the construction of the new facilities. Raw materials for the provision of clay liners, capping works and drainage systems will be required in significant quantities putting pressure on natural quarry products, hence the location and geological settings of sites will become a key constraint in order that site won materials can be used in the development. Innovative use of existing waste streams, in such a way that the environment remains protected (i.e. whole used tyres in drainage systems; recovered aggregates from grading), will prove an important tool in providing both the new infrastructure required and the capping/closure of old non-compliant phases. It is likely that the use of synthetic products in place of natural materials will become more predominant. Greater use of GCLs and BES is already been noticed in areas of Scotland where there are limited deposits of natural low permeability clay.

The consultancy and construction industry will also be faced with the amount of lining projects nearly doubling at the same time as a programme of capping and closure at landfills is underway. This increase in workload comes attendant with the problems of skills shortages within the design, construction and CQA of landfill containment systems. The risks here are that inexperienced staff are involved with design & CQA leading to sub-standard works. This aspect is accentuated in landfill design as it is an area of design that is not heavily enshrined in design codes but is based primarily on a detailed knowledge of industry standard practice and founded on basic geotechnical principals.

With the increase in work load a skills migration from other engineering areas is likely to occur. This increases the risks of inappropriate use of other engineering practices to the landfill application (i.e. embankment compaction criteria vs. clay liner compaction criteria). In addition, operating in a lined facility introduces numerous operational constraints both in order to protect the lining system and deposit wastes in an appropriate manner, control leachate, manage surface water, ensure stability etc. This will be a new area of consideration at more than half of the non-hazardous sites planning to remain open after 2007. Again there is a risk, due to site operators inexperience (all site staff, not necessarily site management), of post construction damage to containment systems (i.e. compactor damage, plant running over unfilled lined cells, etc) and inappropriate site operations for a contained landfill especially with relation to leachate management.

In conclusion it is clear that the next few years offer as many opportunities as challenges to the waste management industry in Scotland. This is particularly true in terms of the Geoenvironmental Engineering aspects of landfill development where innovative uses of both natural and synthetic materials will be required to provide the future infrastructure. It is fundamentally important that those involved ensure that the design of these materials is correctly applied and that this is followed through to construction under appropriately experienced staff and then operated in accordance with the constrains incumbent with an engineered landfill. In an area where theory and practice are evolving at a significant rate the need for a quantified and studied design founded on established geoenvironmental principals has never been more acute. To the uninformed landfill design can appear simplistic. To the informed it requires the application of some of the most advanced geoenvironmental aspects developed and is a high risk area both from a design and operational perspective. Organisations involved in this area will have to strive to control the risks to them from using

staff inexperienced in engineered/contained landfill design and operation. This is an inevitable consequence of the sudden, significant increase in workload to the Scottish industry and will require training of all parties from site operatives, to membrane installers, to contractors, designers and landfill operators.

6 DISCLAIMER

The opinions expressed in this paper are those of the author and do not necessarily reflect the view of the Scottish Environment Protection Agency.

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MANAGEMENT OF WASTES

Mechanical Properties of MSW: Development of a Classification System

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Why is another waste classification system needed?

To ensure stability of a construction both the properties and mechanical behaviour of its components have to be well known. In a landfill, waste presents the largest structural element and often controls both the stability and integrity of the lining system (Jones and Dixon 2003). However, in spite of this critical role there is a dearth of knowledge on behaviour of waste as an engineering material. It is proposed that a rigorous classification system is required to help explain mechanical behaviour of waste bodies, to group wastes with similar mechanical properties and to facilitate the exchange and interpretation of measured properties. Given the significant variation in waste materials, and the limited number of researchers and practitioners engaged in measuring mechanical properties of waste, a classification system is deemed crucial to development of a unified framework for waste mechanics, and hence of our ability to design and operate landfills that represent a minimal risk to the environment. Past experience is a poor guide to future behaviour. Life style changes and the introduction of new legislation (e.g. reductions in biodegradable waste given by the EC Landfill Directive (1999)) and pre-treatment are resulting in significant changes to waste components. Knowledge of the properties of waste components is required to evaluate future changes in waste mechanical properties and hence landfill behaviour.

Waste bodies are heterogeneous with anisotropic physical and biological properties. To enable the assessment of mechanical behaviour of waste bodies (e.g. compressibility and stability) it is necessary to investigate the properties of its components. A first step is to develop a classification system that groups components according to their physical and mechanical properties, including an assessment of their potential to influence mechanical behaviour of the waste body. The second step is to describe in situ component assemblages (e.g. structure of the waste body) and mechanical properties (e.g. compressibility and shear strength). In proposing a framework for classification and description of waste materials it is appropriate to follow those developed for soils, although additional properties will also have to be considered (e.g. degradation and compressibility of components). Whitlow (1983) justifies the need for a classification system and describes the principles for classifying soil as follows.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

"The system adopted needs to be sufficiently comprehensive to include all [...] deposits, while still being reasonable, systematic and concise. [...]. Without the use of a classification system, published information or recommendations on design and construction based on the type of material are misleading, and it will be difficult to apply experience gained to future design. Furthermore, unless a system of conventional nomenclature is adopted, conflicting interpretations of the terms used may lead to confusion. [...] A classification system must satisfy a number of conditions:

a) It must incorporate as definitive terms that are brief and yet meaningful [...].

b) Its classes and sub-classes must be defined by parameters that are reasonably easy to measure quantitatively.

c) Its classes and sub-classes must group together soils having characteristics that will imply similar engineering properties."

This paper describes a framework for classifying waste components.

Review of existing waste classification systems for mechanical behaviour

A number of the existing classification systems are simply based on materials groups (Siegel *et al.* 1990) or on the distinction between soil-like and non soil-like, or fibrous, appearance (Manassero *et al.* 1997; Thomas *et al.* 1999). These existing classification systems do not fulfil the requirements of a rigorous classification framework as outlined above. Table 1 provides a summary of existing classifications systems including the parameters defined.

Author	Key Classification Issue	Parameters
Turczynski, 1988	Waste type	Density, shear parameters, liquid/plastic limit, permeability
Siegel *et al.*, 1990	Material groups	Part of composition
Landva and Clark, 1990	Organic, inorganic materials	Degradability (easily, slowly, non) Shape (hollow, platy, elongated, bulky)
Grisolia *et al.*, 1995	Degradable, inert, deformable material groups	Strength, deformability, degradability
Kölsch, 1996	Material groups	Size, dimension
Manassero *et al.*, 1997	Soil-like, other	Index properties
Thomas *et al.*, 1999	Soil-like, non soil-like	Material groups

Table 1: Overview of existing classification systems

Key elements of these classification systems are considered further. Landva and Clark (1990) proposed a classification system that differentiates between **organic** and **inorganic components**. They subdivided these into putrescible and non-putrescible within the organic components, and degradable (corrodible) and non-degradable within the inorganic components. Additionally, void-forming constituents within each subdivision, excluding the putrescible group, are highlighted. This system provides detailed information on degradation and compressibility potential of components but does not consider component shape or material properties (e.g. tensile strength).

Grisolia *et al.* (1995) defined **degradable, inert** and **deformable** component groups and classified wastes by plotting the percentages of each group in a triangular diagram. This

allows comparison of the composition of different wastes. A strength of this system is that it provides information about compressibility and degradability of components. However, it is possible for a component to fit into more than one group (e.g. food residues are biodegradable and highly deformable) and again particle shape is not considered.

Kölsch's (1996) classification system includes **material groups, size** and **dimension of components**. The advantage of this system is the possibility for a more detailed examination of component properties, which is consistent with the known large variability of waste component form and properties. The disadvantage is the large amount of data required and the omission of information on degradation potential. Such a detailed system is more appropriate for research purposes than regular practical use. None of the existing systems fulfil the requirements for a rigorous waste mechanics classification. However, they provide useful criteria. The information required to classify waste components can be summarised as:

- Knowledge of component shape is required to distinguish between soil-like (3-dimensional e.g. granular) and non soil-like (2-dimensional e.g. sheets) components. This allows classification of components in relation to their potential for influencing mechanical behaviour of the waste mass (e.g. shear strength).
- Grading by size is required for each group of components.
- A distinction is required between the material groups (i.e. based on material properties), with dominant groupings established, in conjunction with information on the proportion (e.g. by weight) of the material groups in relation to the size and mechanical properties of components.
- An assessment of compressibility and potential for components to change shape.
- An assessment of degradation potential for both organic and inorganic components.

Elements of a classification system

Description of the components

The starting point for a classification system is identification of the main waste components by material type. Due to the large variety of materials present in waste, a practical approach is to identify major groups of materials. For example, an American waste composition survey done by the DEQ (1998) used the following groups: Organic, paper, wood, polymer/plastics, metal (FE/non-FE), soil-like, ceramic, glass, inerts and rubber. Waste composition is defined by measuring the percent by mass of each material group present in a sample. A significant barrier to the sharing of information on waste behaviour is the use of different groups of materials by those classifying samples used in experimental programmes. In many instances the reasoning behind selection of specific groupings is not explained, and hence the factors influencing measured behaviour can not be fully understood.

Mechanical properties of material groups

Selection of appropriate groups requires consideration of component mechanical properties. It is proposed that components be considered in the condition they have on delivery to the landfill site. Definition of this initial state is required because mechanical properties, shape and size of components will change as a result of placement conditions (i.e. compaction)and stresses due to burial, due to the compressibility of some particles, and in the longer-term due

to degradation processes. The classification system must provide the possibility for components to change group. Moreover the groupings should be appropriate for every type of waste. The following properties of each component can be considered as a basis for producing groupings:

- Shear strength
- Tensile strength
- Compressive strength
- Elongation at break (at given strain)
- Compressibility
- Modulus of elasticity

Figure 1 shows indicative shear and tensile strengths, elongation at break, compressive strength and modulus of elasticity for the material groups proposed by DEQ (1998). This information can be used to identify those groups of materials that could be amalgamated to simplify the classification. In addition, it provides an indication of the groups that could influence specific aspects of waste mechanical behaviour (e.g. compressibility, shear strength). However, this is also dependant on the composition of the waste body, for which information is given in Figure 1, and on the in situ density, structure and stress state. The data for the mechanical properties derive from various sources and databases and show significant variability. Only average values for components are presented. A more detailed examination of these properties would contribute to the accuracy of the dataset.

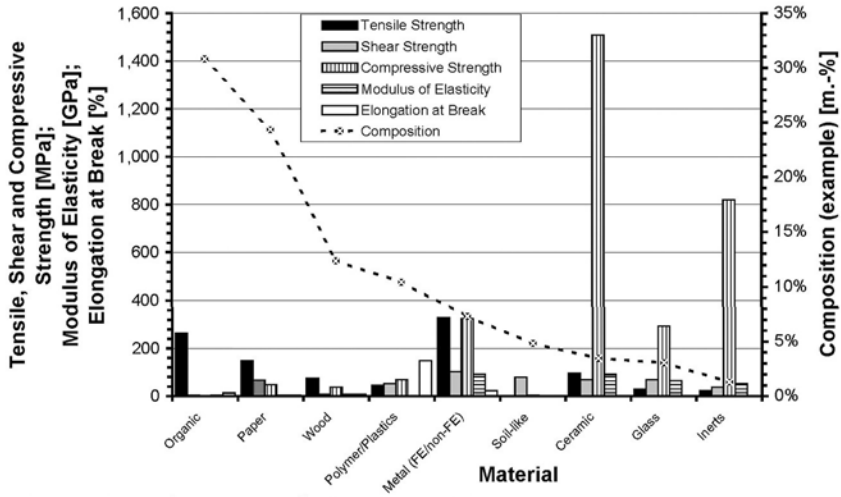

Figure 1: Mechanical properties of selected material groups

For tensile strength, organic matter and paper are the dominant materials. The high tensile strength of the metals has only limited influence due to the low percentage present in this sample of waste. Considering compressive strength, possible groupings of materials could be: ceramics and inerts with a very high compressive strength; glass and metals with a high to medium compressive strength; and paper, wood and polymers/plastics with a low compressive strength. Figure 1 indicates that the organics and soil-like material posses almost no compressive strength. In the case of soil this is thought to be misleading as individual soil grains (i.e. waste components) may have a relatively high compressive strength. It is important that the properties of only the components are considered here and not of assemblages of components (i.e. a quantity of soil).

Shape of components

Kölsch (1996) proposed that the shape of waste components could be characterised by one of three basic groups based on both size and shape:

- DIM 0 - particles smaller than 40 mm, all shapes
- DIM 1/2 - particles larger than 40 mm with 2-dimensional shapes (e.g. fibres, sheets or foils)
- DIM 3 - particles larger than 40 mm with three-dimensional shapes (e.g. boxes, spheres etc). These can be further sub-divided into:
    - 3a. Hollow and easily compressible
    - 3b. Hollow and difficult to compress
    - 3c. Solid and incompressible

The sub-division of hollow 3-D components in terms of compressibility is necessary for assessing changes in classification resulting from placement activities and overburden stresses. It is possible that a similar sub-division should be carried out for the DIM 0 fraction. Stressing these components could lead to shearing and crushing of components (i.e. grains/particles), with weak organic particles most likely to behave in this way. However, at present there is insufficient experimental data to enable such a sub-division to be made.

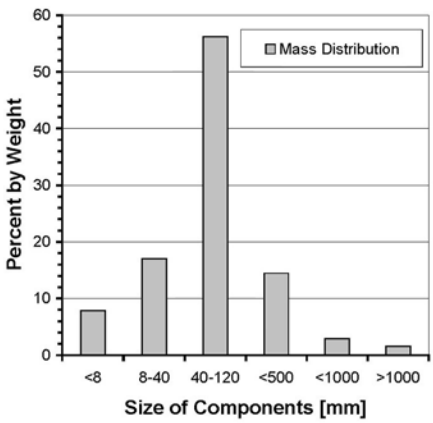

Figure 2: Mass distribution regarding size of the components

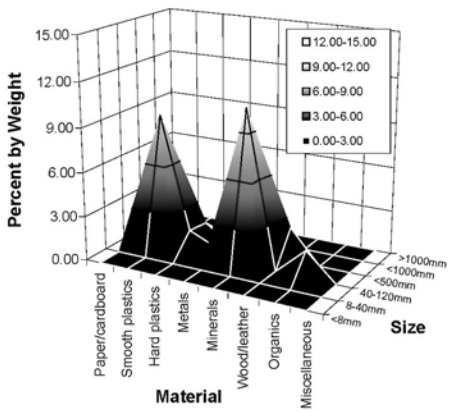

Figure 3: Mass distribution for DIM 3

Size of components

A key element of a classification is information on grading. Data from Kölsch (1996) is used to demonstrate a mass distribution for waste components with a range of sizes. The data shown in Figure 2 is for a fresh domestic refuse from an urban district. Due to a separate bio-waste collection the organic content was reduced. The waste components were sorted using three different criteria: material type, dimensions and size. The material groups used were: paper/cardboard; smooth and hard plastics; metals; minerals; wood/leather; organics and miscellaneous <40mm. Although there are some similarities with the groups used by DEQ (1998) there are also significant differences that make it difficult to compare waste types. This is justification for producing a standard classification system. Each material group was subdivided based on dimensions (i.e. the fraction greater than 40 mm was subdivided into 2-

dimensional, DIM 1/2, and 3-dimensional, DIM 3, groups and the 'miscellaneous' fraction, less than 40 mm, was placed in DIM 0). The final step was to grade the components in the material groups of DIM 1/2 and 3 into the following size ranges: 40-120mm, <500mm, <1000mm, >1000mm. The 'miscellaneous' group (DIM 0) was subdivided into the sizes 8-40mm and <8mm. From Figure 2 it can be seem that the components forming the largest proportion by weight in this sample are those with sizes in the range 40-120mm, presumably these are heavy components such as broken glass, soil etc. The fine fraction, <40mm, would be higher in areas without pre-treatment to reduce organic materials (i.e. due to the presence of coffee grounds, tea bags, food residues, etc.).

As an example of subdivision of material groups based on component dimensions, Figure 3 shows the material and size groups for 3-D components larger than 40 mm (DIM 3). Two clear peaks for minerals and smooth plastics, and a small peak for organic material, are shown within the range of 40-120mm. A peak for wood/leather is located in the range of <500mm. It should be noted that this data is for the waste in its initial, pre-placement, condition. Figure 2 and Figure 3 demonstrate how detailed information on material group, size and dimensions of components can be presented.

Degradation potential

In order to be able to represent changes in classification that occur due to degradation of components, it is necessary to provide information on degradation potential. The subdivisions proposed by Landva and Clark (1990), and discussed above, are considered to be an appropriate approach.

Outline of proposed classification framework

Figure 4 shows the framework of waste classification discussed above. Components of a waste sample are examined to obtain information on: material type (and hence properties), size and shape. This would typically be achieved through a combination of measurement, use of published information (e.g. on waste properties) and estimation. Based on this data components are grouped by material properties in order to minimise the number of material categories.

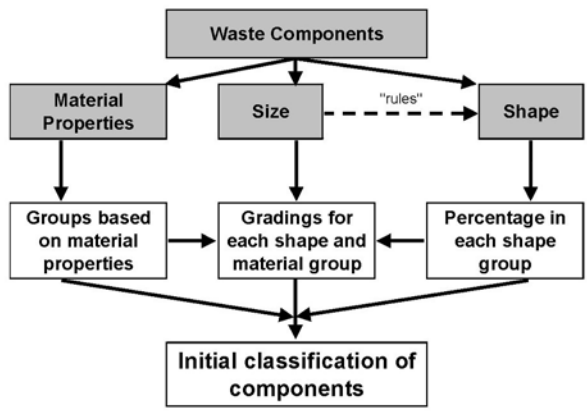

Figure 4: Classification framework

The shape information, supported by size data, is used to group components according to whether they are 2-dimensional, 3-dimensional or smaller than 40 mm. A grading is obtained for each dimension group, with information provided on the grading of each material group

present in the shape group. Finally, the percentage of degradable components in each shape, by material group, is defined. The data produced by Kölsch (1996) is used to demonstrate data analysis and presentation. Information for components in the 3-dimensional, larger than 40 mm, dimension group (DIM 3) is presented in Figure 5. This includes: the selected material groups, a grading for all components, gradings for each material group, organic content of each material group and an average compressive strength for each range of component sizes. Values for compressive strength are derived from weighting component material strengths based on the percentage mass present. The information on organic content enables an assessment of potential mass reduction of specific components due to degradation, and thus the reduction in proportion of the entire waste sample composed of each shape group. This information can be used to revise the classification of the waste for the long-term condition when degradation is complete.

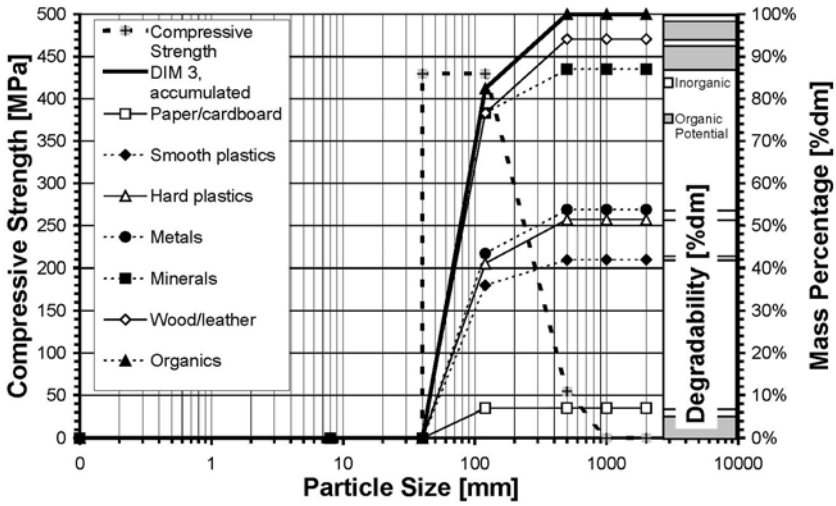

Figure 5: Material groups, gradings, organic content and compressive strength for the 3-dimensional shape group

The data produced by Kölsch (1996) can be used to classify the waste based on percentages of the three shape groups (Figure 6). In addition, this diagram can be used to demonstrate changes in classification resulting from waste placement, which results in compression of components, and in the long-term following degradation. In Figure 6 the initial state is derived directly from the original shape data. For the potential state after placement it has been assumed that the percentage of the 2-dimensional components (DIM 1/2) increases due to the compression of 3-dimensional components (DIM 3a and 3b) such as plastic packaging, organics and paper/cardboard packaging. The potential final state has been calculated based on the percentage of degradable organic materials in each dimension group. A loss of mass was assumed due to methane and carbon dioxide generation and the alteration of organic into mineral matter. From the location of the states within the ternary diagram (Figure 6) a change in the classification of the waste is obvious, although this is based on a number of assumptions. A more detailed classification of the placement and long-term conditions

requires a more detailed investigation of changes in grading, shape and mechanical properties.

In summary, a framework for classifying components of waste has been presented. It is proposed that it can be used to provide information on the state of components as delivered to site, following placement and in the long-term following degradation. The data presented above demonstrates an approach for presenting the relevant information. The method is likely to be of use to researchers involved in sharing and interpreting experimental data on mechanical properties of waste.

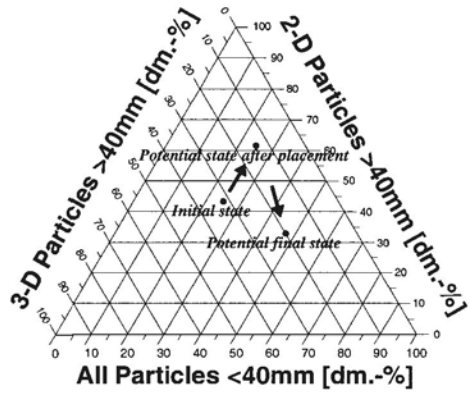

Figure 6: Classification based on ratios of dimension groups

The classification system is currently incomplete. Research is ongoing to define classification groups that can be used to categorise waste materials in relation to their potential mechanical behaviour (e.g. in relation to shear strength, compressibility). Work on protocols for describing undisturbed waste bodies is also ongoing.

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Groundwater contamination plume monitoring in sealed waste dumps

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KEY WORDS: Sealed waste dumps; data integration; monitoring; kriging; dynamic models

ABSTRACT

With the approval in 1997 of the Strategic Plan for Municipal Waste, Portugal took a step towards the implementation of a sustainable waste management policy. One of the main purposes of the plan was to seal and close 300 waste dumps.

Nevertheless, sealing waste dumps does not mean that they are no longer an environmental hazard, since almost of them were constructed many years ago, without taking into account the present legislation. Therefore, after being closed a monitoring plan should be implemented and, when necessary, characterization studies must be undertaken to avoid unforeseen problems.

To design monitoring plans for these areas, it is very essential to have knowledge of local geology and hydrogeology, since potential contamination of soils and groundwater depends essentially on the physical characteristics of the area (porosity and permeability) and local dynamic of fluids (water level, flow direction).

This paper presents a methodology for monitoring the surrounding area of sealed waste dumps in Portugal and for determining the presence of contamination in groundwater.

INTRODUCTION

With the closure of the totality of the waste dumps in Portugal, there is a need to follow the environmental evolution of these structures, because simply sealing the site does not

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guarantee the removal of risks to the environment. The implementation of an effective monitoring survey appears to be the most efficient solution for space-time control.

Data provided by monitoring studies give indications on the quality of the seal and, in situations where dispersion of the contamination is observed it is possible to characterize lateral and depth extension, in order to produce contamination plumes images. For example, leachate quantity should decrease gradually after sealing because rainwater is diverted. The result provides technical support for decision-making in remediation programs and mitigation of unexpected scenarios.

This operational methodology described has been demonstrated to be well-adjusted and produced satisfactory results.

METHODOLOGY

The methodology consists of several stages. Firstly, a preliminary investigation of the area is necessary to characterize local geological and hydrogeological conditions. Secondly, an investigation in the field with a physical survey of the site is undertaken. In third place, integration of all the collected information in a GIS database is required. Following these tasks, geophysical surveys are carried out to determine the position and the extent of contaminating plumes and chemical analyses of groundwater are undertaken, to characterize groundwater both upstream and downstream. Finally, all the information is gathered to build a dynamic hydrogeological model, which enables present and future scenarios of contaminant migration in space and time to be developed.

Preliminary investigation

This first stage enables the collection up of important data of the studied area with low financial costs. Through topography maps and digital orthophotos it is possible to characterize the relief and the occupation of the area, but also to identify the main geological and morphological structures and streamlines. Geological maps supply regional information concerning the geology of the place (scale 1/50000 or higher), but in order to validate this or to obtain more detailed geological mapping, field surveys may also have to be performed. The lithological descriptions resulting from monitoring wells also supply in-depth detailed geological information, complementing data collected from geological maps and fieldwork.

Previous studies of the area (such as sealing projects and installation of the waste dumps) should be consulted. The study of the region should also include an investigation of all previous activities to obtain information on other possible sources of contamination.

Field investigation

After the preliminary retraction of information, a physical reconnaissance of the study area must be undertaken to obtain additional data and to confirm or correct results from the preliminary investigation. This survey should include information obtained from nearby residents, who usually possess knowledge of the region that can pass unobserved to the occasional visitors.

A detailed survey of superficial geology must now be made, including examination of natural ditches, slopes, indications of faults and lithologies, concerning the confirmation and add information gotten from the geological maps. It is necessary to carry through a hydrogeological inventory in the area to identify springs and other points of water and to determine groundwater flow direction. In order to predict areas potentially affected by lateral contaminant dispersion, surface flow direction must be determined.

Integration of information in a GIS database

As the majority of the data collected is spatially referenced, such as altimetry in the different phases of the project (initial, before closing and after sealing), surface geology, water levels measured on a network of monitoring wells, chemical analyses, geophysical surveys, lithological description of monitoring wells and field observations, all this is structured and classified, becoming information layers of a GIS project. This geographical database is the kernel of all the collected information, and is an excellent tool to execute this function.

All used information comes from one of two sources: digital information such as altimetry or aerial photographs, and information collected in the field with GPS receivers (Global Positioning System), such as location of water wells, the study area perimeter, and sample collection locations (geophysical and analytical surveys).

With the baseline information and the fieldwork results, a conceptual model of the under study site can be built. This model is a virtual simplified image of the reality, in the sense that only aspects relevant to the resolution of the project/problem are retained in a scale or detail that will help to achieve the intended results. In this case study, the conceptual model includes a 3D representation of the geology (with different layers), hydrogeology (water levels) and the localization and volume of the waste dump in a TIN model type (triangular irregular network) based in two surfaces (top and base). The three-dimensional visualization allows easy in-depth interpretation of the various layers. Figure 1 shows a simplified three-dimensional model of the case study.

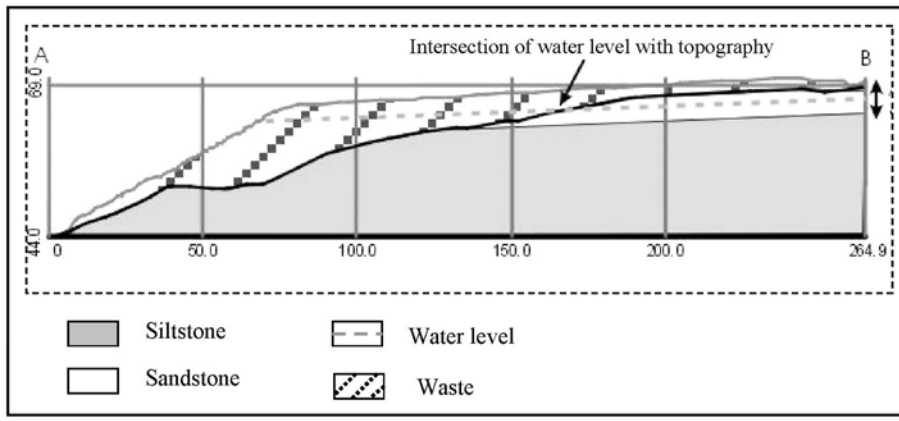

Figure 1 – Conceptual model of the case study waste dump

The integration of the information in a GIS project is an important task that occupies an important part of the consumed time of the project. This effort is widely compensated, because the GIS project constitutes an historical spatial database of all information, which can be consulted and updated during the project. The observation of important spatial trends crossing the different types of information (for example, verification that a contamination plume has the same orientation as a pre-existing streamline, that can only be observed in topographical surveys previous to the deposition of the waste dump) is an extremely important result and can only possible be produced, in useful time, with a system of this type. Figure 2 illustrates an example of integration of information of the case study.

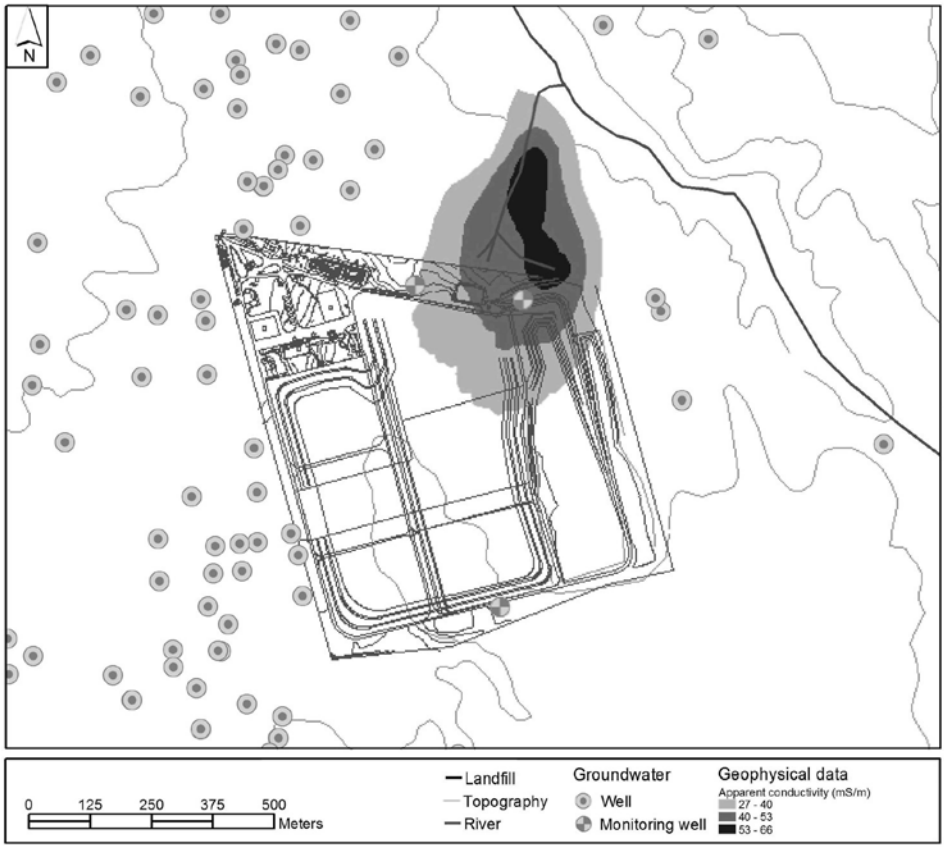

Figure 2 – Integration of different layers of information

Another advantage of the use of a GIS is the derivation of information directly from the sampled values, using spatial analysis and geostatistical techniques. In figure 2, a geostatistical model of kriging interpolation is shown. Kriging is an optimal linear estimator that takes into consideration the spatial structure of the variables through variograms or experimental spatial covariance. The resulting maps are instruments for visualizing the average dispersion behaviour of the parameter under study.

Geophysical surveys

Geophysical methods are appropriate for environmental studies as they do not harm natural or artificial waterproofing covers, and they are non-invasive, low cost and fast. These methods are also very useful for locating additional collection of hard data (particularly preferential location of additional wells), which could be carried out at a later stage.

In this type of study, geophysical survey results are used to characterize the extent of the contamination plume, and to determine of the saturated zone, the flow direction and depth of the bedrock (or clayey strata levels that help to sustain the contamination). Geophysical methods can also provide information on the occurrence of faults, the interface between different geological units, the identification of different materials in the dumping zones and the definition of the waste deposit thickness and structure. The results obtained supply very useful information for the monitoring and remediation measures that must be implemented in the contaminated area.

The most commonly used methods are electrical resistivity and electromagnetic (especially EM-34). This electromagnetic method involves the propagation of low frequency electromagnetic fields. The data obtained enables the production of maps of apparent conductivity at different depths, and determine the location and extent of the contamination plume (since contaminant substances generate liquids with high concentrations of salts, thereby inducing a conductivity increase) and can also supply to information on groundwater flow direction.

Analytical characterization of leachates (source), aquifers and streamlines (receivers)

Chemical analyses of leachates provide accurate information on residue diversity. The analyzed parameters provide information of the contaminating potential of leachates for both soil and groundwater and surface waters, taking as reference the legislation that governs landfill operations. The chemical composition of the leachate varies with the type and the age of the residues, but it is generally characterized by a high organic load (COD and BOD), high hardness, and high concentrations of salts (chlorides and sulphides).

In order to determine water quality in the region it is recommended to sample superficial and groundwater both upstream and downstream of the waste dump site. The monitoring and remediation measures to be implemented will therefore depend on the baseline conditions determined by this procedure.

Dynamic hydrogeological model

The final step of the proposed methodology is the production of a dynamic flow model designed to mathematically represent the natural hydrogeological and chemical conditions of the study area. It is thus to predict different scenarios of the system's evolution over time and to assess environmental risks (e.g. changes in contaminant concentration, time taken to reach a receiver), as well as to test different remediation and mitigation techniques.

The required information to produce these models is acquired during field surveys; some of the most important data are in-depth and lateral geological descriptions, and hydraulic parameters (information on water levels, aquifer recharge and groundwater chemical analyses). Among hydraulic parameters, the hydraulic conductivity as determined with pumping or slug tests is the most important.

The construction of a hydrological model is based on the need to predict fluid movement (dispersion of the contamination plume). It is also convenient to make use of experimental information in space and time, without which it is not possible to properly calibrate the plume movement a real time scale simulator.

CONCLUSIONS

This paper presents a simplified form of a possible methodology for the study of sealed waste dumps. The implementation of this methodology will lead to a significant reduction in costs during the study. For example, the production of a conceptual model anticipates the most likely localization of the contamination plume, and offers target areas for geophysical surveys carried out to confirm the conceptual model. Furthermore, a groundwater sampling campaign carried out with a better knowledge of the problem saves a series of unnecessary analyses in places that did not have a high probability of contamination.

The use of new technologies, combined with existing tools, facilitates the production of dynamic images that allow the introduction of new data, keeping scenarios of the problems in question updated.

Special attention must be given to the monitoring of sealed waste dumps, because the leachates produced inside these structures will continue to be released and contaminate soil and groundwater for many years to come.

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Leachability of Metals from Municipal Solid Waste Fly-ash and Bottom-Ashes at Different pH

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ABSTRACT
The generation of municipal solid waste (MSW) has reached 50 million tonnes per year since 1985 due to the growing economy in Japan. Due to limited availability for land space, this huge amount of waste is reduced by incineration, with the residue of fly ash and bottom ash disposed in controlled landfills. A compacted low hydraulic conductivity of $<1x10^{-8}$ m/s and chemical compatible clay liner is in place under the polyethene liner in the landfill site. The focus of this paper is the leachability of heavy metals from MSW fly ash and bottom ash at different pH to simulate the worst situation such as acid rain. This work investigates the elements present in the MWS fly ash and bottom ash, and the leachibility of heavy metals from both fly-ash and bottom ash. XRF, XRD and ICP are used to characterize the ashes. The leachability of metal ions and anions is evaluated using repeated batch-leaching and column-leaching tests. The results are used to estimate the short- and long-term environmental impact of MSW fly ash in landfill sites and to provide information for the design of thickness and required hydraulic conductivity of landfill soil liners. The results of this study indicate that the fly ash and bottom ash consist of mostly of Si, Na, Ca, Mg, Fe, Zn, Cu, and Pb. The leaching activity to some degree depends on the pH of the leaching solution. Repeated batch leaching tests indicate that the leachabilities of MSW flyash at pHs from 3 to 6 were very similar. Heavy metals such as Pb, Zn, Cu leached at low concentrations. The MSW ashes have high buffer capacity. The pH of leachates for the washing solution of pH 3, 4, 5, and water were between 10 and 11, except for the pH of the leachate for a pH2 washing solution, which dropped from 11 for the first washing to 3.5 for the 80th washing. Column leaching tests of fly-ash and bottom-ash indicate that the concentrations of leached Pb>Zn>Cu in water leaching and effluent pH remain as high as 11. With the pH 2 leaching solution, as the buffer capacity of the ashes decreased Zn and Cu leached much more than Pb.

KEYWORDS
MSW fly ash, bottom ash, heavy metals, leaching, pH

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

INTRODUCTION

The generation of municipal solid waste (MSW) has increased rapidly since 1985 due to the growing economy in Japan, reaching 50 million tonnes per year (Hanashima and Furuichi, 2000). Due to limited availability for land in Japan, it is extremely difficult to secure new landfill sites. To reduce this huge amount of waste, one of the options is to burn it. Incinerators now handle almost 80 percent of all municipal solid waste in Japan. The remaining solid residue, called fly ash, containing heavy metals, dioxins and other toxic contaminants, normally ends up in controlled landfills. Even controlled or engineered landfills have the potential to contaminate subsurface groundwater supplies through the migration of leachates from land-based waste sources down to the water table and into groundwater aquifers, despise the use of polyethene liners (Freeze 2002). The same problems occur with leachate collection systems such as drains clog. One might argue that perhaps the worst contaminants are flushed out of the landfill in the first few years, and the landfill leachates may become more benign as years pass. However, there is evidence that landfill leachates continue to deliver contaminants to the environment at unacceptable concentrations for periods much longer than the apparent life spans of the protective barriers. The engineered landfill site, the performance of soil liner is based on retention capacity and low hydraulic conductivity, which could be affected by the MSW fly ash leachate composition and pH.

Over the past twenty years, MWS incineration has been developed considerably by chemical engineers to reduce air pollution, and to stabilize the fly ash and bottom ash (Chandler et al 1997). However, there are limited studies on the pollutants and the leachability of the fly ash that might impact the environment. Osako et al. 2001 studied the leaching of bottom ash for Pb using the JLT-13 and pH-stat test. Ecke et al. 2002 used titration methods at pH 8.5 and 4.5 with an initial liquid/solid (L/S) ratio of 40, with pH adjustment with L/S of 40 to determine the leaching of Cd, Cr, Pb and Zn for fly ash. Kida and Sakai 2001 investigated the leachability of Pb from fly ash adopting the JLT-46 test, which involved a 6-hour shaking test with deionized water with L/S of 10 and a pH4-stat test of 6-hour mixing with HNO_3 to maintain L/S of 10. Most of the work was done using batch tests, with few studies using column leaching tests, which are more similar to the landfill situation. There is also a lack of comprehensive and consistent study regarding the leachability of metals from both MSW fly ash and bottom ash for a wide range of pH. At present the hydraulic conductivity of soil liner is $\sim 1 \times 10^{-6}$ cm/s. With tightened environmental standards in Japan, issues regarding the contaminants/soil interactions constitute a large topic in contaminated site remediation and might extend to landfill environment in the foreseable future.

Since fly ash and bottom ash are co-disposed in landfill sites, this work comprehensively determines the pollutant components of fly ash and bottom ash, and systematically examines the leaching of heavy metals (Pb, Zn and Cu) from ashes for a wide range of pH, in order to simulate acid rain or other possible worst acidic situations using batch leaching tests and column leaching tests.

MATERIALS AND METHODS

Source and Process of Incineration

Fly and bottom ashes were collected from a MSW Incineration Plant in a city at Kyushu, Japan. The MSW waste was incinerated in a Stoker furnace at a temperature of 850 to 950°C using wet quenching. The burned wastes were composed of combustibles such as plastics as well as crushed combustibles from bulky wastes and incombustibles. Air pollution was

controlled using $Ca(OH)_2$ as a semi-dry treatment, blowing of activated carbon powder, then bag-filtered with $DeNO_x$ as catalyst for NO_X removal, and an electrostatic precipitator, then wet scrubbing for HCl-SOX removal. The residue wastes were separated into fly ash and bottom ash.

Characteristics of fly ash and bottom ash

The collected ashes were semi-wet containing 14.1% and 20 to 50% moisture content for fly ash and bottom ash, respectively. For the sample preparation, bottom ash was air-dried to 7.65% moisture content and then passed through a 2 mm sieve. X-ray diffraction (XRD) was used for crystallized phase mineralogical characterization. The fine fraction, particle-size <74 μm, was submitted for XRD analysis. A qualitative total chemical analysis of ash was also performed using inductively coupled plasma mass spectrometry (ICP-MS) on samples decomposed with HNO_3 (APHA, AWWA, & WEF, 1995).

Multiple Batch Leaching Tests

The batch equilibrium test (USEPA 1987) was used for determination of ion leached from fly ash and bottom ash. Distilled water (pH 6.8) and nitric acid (HNO_3) solution at four different pHs 2, 3, 4, and 5 were used as leaching solutions to simulate normal rain fall, acid rain and extreme acid conditions. A 1:10 solid:solution ratio with approximately 4 g (equivalent dry weight) of ash and 40 ml of solution were placed into a 50 ml polypropylene centrifuge test tube. Samples were shaken for 24 hours, and then centrifuged. The concentrations of heavy metals of Pb^{2+}, Zn^{2+} and Cu^{2+} were measured using an atomic adsorption spectophotometer – SOLAAR m, Nippon Jarrel-ash Co., Ltd., Japan. The supernatant pH was also measured. The same procedures were repeated on the same sample with the same pH solution for a maximum of 100 washings.

Batch equilibrium tests were adopted to evaluate the leachability of fly ash and bottom ash. This test is a more aggressive extraction technique than the column leaching test because the soil is in suspension, with each soil grain directly in contact with the lead solution. The results from this test are therefore more conservative than those from a column leaching test. The other advantages of using a batch-leaching test are that it is easy to carry out and handle the samples to achieve optimum leaching information.

Column Leaching Tests

The leaching cell test was used to determine ash leachability, simulating the field situation where ashes are placed on the landfill and then compacted to reduce the storage space. In addition, this result would be used with the batch leaching results to estimate the ions generated during operation of the landfill site. No standardized method exists for rigid-wall leaching cells; however, the hydraulic conductivity results of Daniel (1995), showed good agreement between the flexible-wall, and rigid-wall leaching cells. The fly ash was compacted directly in the leaching cell in one layer using static compaction. Static compaction was used because it was able to produce more consistent results (Weber 1991, and Cabral 1992), and it provides a more conservative estimate for leaching cell hydraulic conductivity tests (Yong 2000). Figure 1 illustrates the leaching cell test setup. The leaching cell has a diameter of 5.95 cm and is 2.15 cm deep. 45 g of bottom ash and 40 g of fly ash were compacted to dry densities of 0.75 g/cm^3 at 7.65% moisture content and 0.66 g/cm^3 at 14.06% moisture content, respectively, in the leaching cells. A micro tube pump at 10 mL/min was used to feed the influent to the leaching cell to ensure a constant flow rate. All equipment was made of materials that are non-reactive with heavy metals. As the pH solution

permeated through the leaching cell, the time and volume of discharge was noted periodically. In addition, the discharge was analyzed for concentrations of heavy metals Pb^{2+}, Zn^{2+} and Cu^{2+}, and measured for the pH of the effluent.

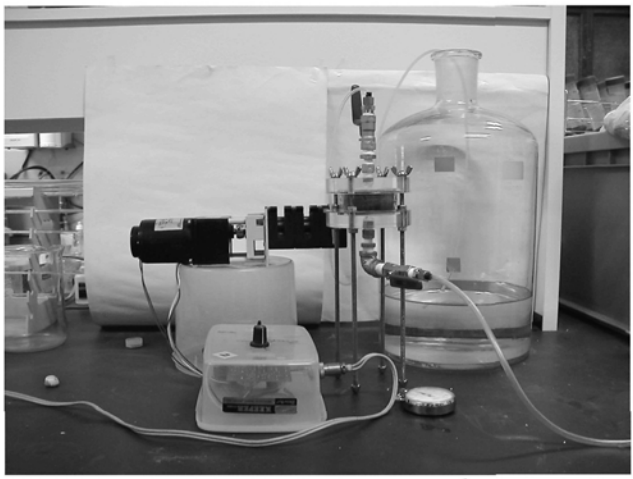

Figure 1 Leaching cell test setup

RESULTS AND DISCUSSION

Elemental Composition and Mineralogical Composition of Fly Ash and Bottom Ash

The elemental analyses of fly and bottom ash using XRF indicates that they were composed of Ca, Si, Al, Fe, Na, K, Ti, Mg, Cu, Zn, Pb, Mn, Fe, and Cr metals. Cl and S were also detected in significant amounts. Quantitative analysis of metals by XRF was not performed in this work. Total digestion of fly ash and bottom ash using ICP was used to further characterize the ash samples as shown in Tables 1 and 2. Results in Table 1 indicate that SiO_2, Al_2O_3 and CaO are dominant among the determined elements expressed in oxide forms. The geochemical analysis in Table 2 shows that Cu, Pb and Zn are present in significant amounts. The crystalline phases were studied by means of X-ray diffraction (XRD). The X-ray diffraction pattern shows that fly ash contains sylvite, halite, calcite, gypsum, anyhydrite and possible hydrotalcite. While, bottom ash contains significant amount of calcite, minor amount of quartz, possible anhydrite and peaks assigned to halite and hydrotalcite are tenuous. Fly ash and bottom ash resulting from MSW incineration contains hazardous components, as demonstrated in Tables 1 and 2. However, the availability of pollutants depends more on surface accessibility and surface solubility than on the total content.

Table 1 ICP total ashes analysis*

Sample#	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	CaO %	Na_2O %	K_2O %	TiO_2 %	P_2O_5 %	MnO %	Cr_2O_3 %	Ba ppm	Ni ppm	Sc ppm	LOI %	Sum %
Fly ash	17.21	10.47	1.24	2.55	16.59	5.54	5.79	1.53	1.42	0.06	0.04	525	142	3	34.6	97.1
Bottom ash	29.73	14.24	6.00	2.28	20.88	2.49	1.94	1.33	2.41	0.11	0.04	576	200	3	17.5	99.0
Standard	61.65	13.83	5.85	2.35	4.68	4.12	1.40	0.60	0.99	0.53	0.44	401	41	23	3.4	99.8

Table 2 Geochemical analysis of Group 1DX

Sample#	Mo ppm	Cu ppm	Pb ppm	Zn ppm	Ni ppm	As ppm	Cd ppm	Sb ppm	Bi ppm	Ag ppm	Au ppm	Hg ppm	Tl ppm	Se ppm
Fly ash	11.5	886.2	3655.3	13044	26.9	16.4	122.8	511.0	10.6	39.9	18.2	4.46	0.3	2.9
Bottom ash	7.1	1594.6	779.0	3530	53.8	3.6	5.9	70.4	0.9	3.5	48.0	2.38	<0.1	<0.5
Standard	6.4	126.6	31.9	158	34.7	23.7	5.2	4.9	5.3	0.3	27.3	0.28	1.1	1.3

Multiple-Batch Leaching Tests

During landfilling, pH is a major factor that affects metal mobility. In the long term, the environment of MSW landfills can change from highly alkaline to lower pH due to increasing atmospheric CO_2 proton activity or acid rain contributed by industrial air pollution. Normally, MSW fly ash and bottom ash are co-disposed with 20% of other wastes (Hanaashima and Furuichi 2000), including organic-wastes. In this case, microbial activities might increase proton activities and reduce pH of the landfill leachate to even lower values such as pH 3-5.

The results of multiple-batch leaching tests using varies pH solutions are shown in Figures 2 and 3 for fly ash and bottom ash, respectively. The alkalinity of the fly ash and bottom ash was controlled by Ca compounds such as CaO and $Ca(OH_2)$, as identified by ICP and XRD. The leaching activity to some extent depends on the pH of the leaching solution. Repeated batch leaching tests indicated that the leachabilities of MSW fly ash at pH 3-6 were very similar where the pH of water is around 6. Heavy metals (Pb, Zn, Cu) leached at low concentrations during each repeated leaching. This could be due to the high initial pH of MSW ashes, which provide a high buffering capacity. The final pH of leachates of the washing solution (for an initial pH of 3, 4, 5, and water) were between 10 and 11, except for the pH of the leachate of the pH2 washing solution, which dropped drastically after the first 10 washings. The results indicate the Pb has mobility at high pH (see Figures 2b and 2d) compared to very low concentrations of Zn and Cu. At pH 8, the leachabililty of Pb was 2 to 3 orders of magnitude lower than at pH 12. In the alkaline between pH 8 to 12, the leachability of Zn was low. At low pH of 4 to 5, considerable leaching of Pb, Zn and Cu occurred. Total leached concentrations are similar to the abundance in the fly ash (Table 3), i.e. Zn>Pb>Cu. Bottom ash has much less leached metals than fly ash, and the Pb leached concentration was slightly higher than for Zn and Cu.

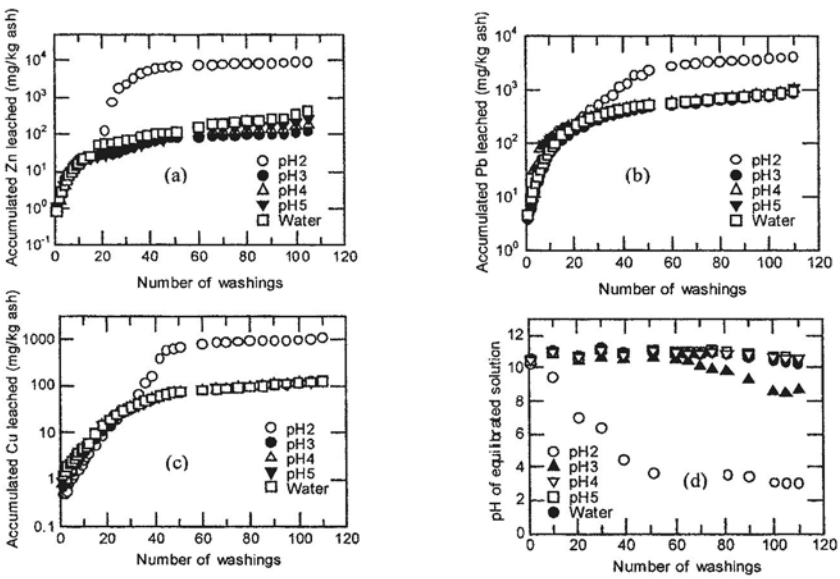

Figure 2 Accumulated concentrations of metals leached from fly ash (a) Zn, (b) Pb, (c) Cu and (d) pH of the equilibrated solution

Column leaching tests of fly-ash and bottom-ash indicate that the concentrations of leached Pb>Zn>Cu in water leaching and effluent pH remain as high as 11. With the pH 2 leaching solution, as the buffer capacity of the ashes decreased, Zn and Cu leached much more than Pb for fly ash, while Zn, Cu, and Pb were very similar for bottom ash. These results agree with the multi-batch leaching results.

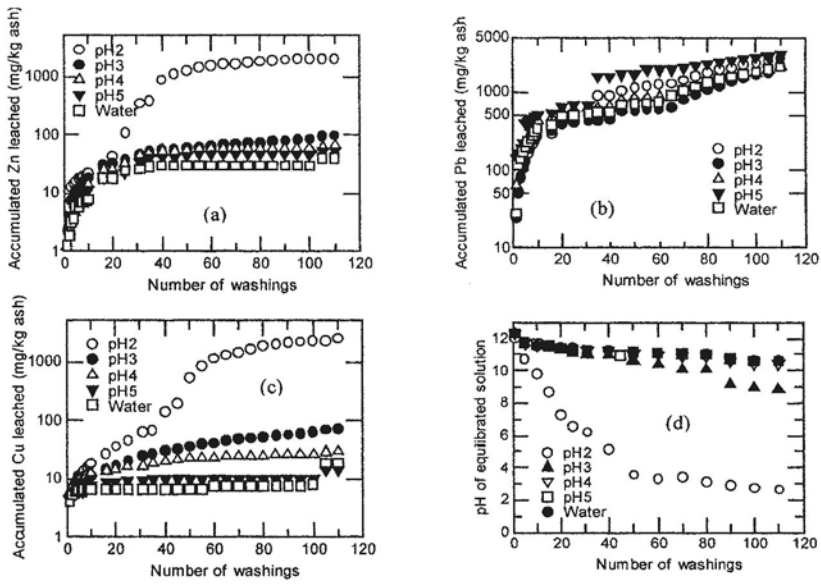

Figure 3 Accumulated concentrations of metals leached from bottom ash (a) Zn, (b) Pb, (c) Cu and (d) pH of the equilibrated solution

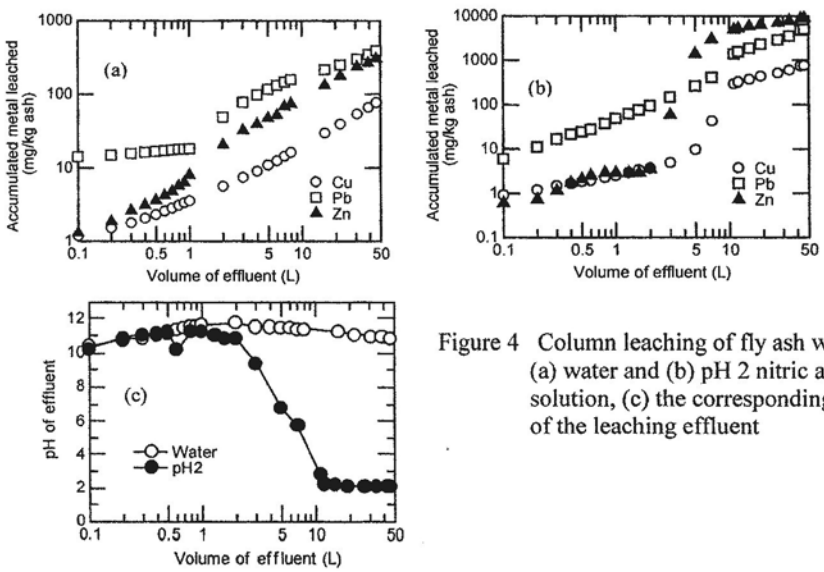

Figure 4 Column leaching of fly ash with (a) water and (b) pH 2 nitric acid solution, (c) the corresponding pH of the leaching effluent

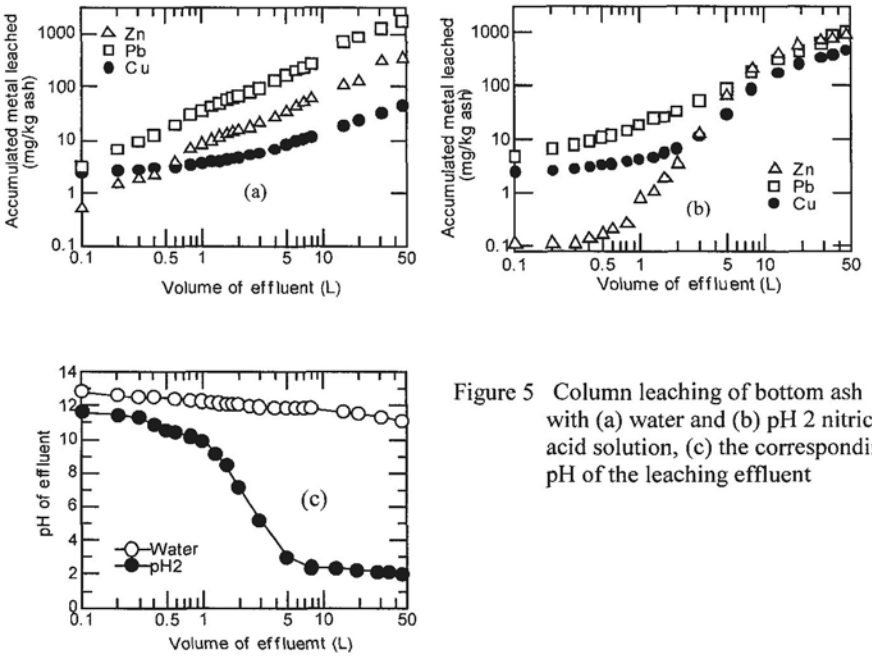

Figure 5 Column leaching of bottom ash with (a) water and (b) pH 2 nitric acid solution, (c) the corresponding pH of the leaching effluent

CONCLUSIONS AND RECOMMENDATIONS

This investigation has shown that fly ash and bottom ash from municipal solid waste incineration (MSW) could generate heavy metal contaminated leachate. Treatment is required for high pH and the mobile fractions of Pb, Zn, and Cu.

Cations and salts leached from MWS could be in high concentrations as indicated in the elemental analyses. These cations and the high pH of the ash leachate might affect the performance of clay liners due to exchange of cations, which might affect the adsorption of metals onto clay. It is expected that the generation of leachates with high loading of salts and cations will continue for decades. Our on-going study will examine the effect of ions on the adsorptivity of clay liners.

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Mining science – the Environment Agency's science programme for mining waste and minewater

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ABSTRACT

The legacy of coal and metal mining in the UK will be a significant barrier to achieving Water Framework Directive goals since mine waters are the major cause of pollution in many catchments, especially in Wales, and the north and west of England. The Environment Agency is working closely with the Coal Authority to deal with priority coal minewater impacts and has invested significant capital in the remediation of metal mining impacts (e.g. £20M at Wheal Jane Tin Mine, Cornwall). Environment Agency Wales has published a strategy for dealing with metal mine impacts and identified 50 priority sites, however there is no equivalent strategy for abandoned metal mines in England. Previous remedial solutions for coal and metal mines have been ad-hoc, are not necessarily sustainable and may not employ best science and technology.

The Agency's Air Land & Water Science Group is now taking a strategic approach to mining pollution with a nationally co-ordinated science and research programme. This is focussed around the newly created *Environment Agency Research Fellowship for Mine Waters and Wastes* at the University of Newcastle. The overall research priorities for the Agency are to understand the hydrological and geochemical processes associated with minewater rebound and mine spoil weathering/leaching, place these within the context of diffuse pollution at both local and catchment scales, and promote the sustainable management of mining wastes. Working with universities, industry and other key players, the Agency is engaging with external national/international initiatives and centres of excellence, disseminating learning across the Agency and providing the sound underpinning to decision-making in this area.

INTRODUCTION

The legacy of coal and metal mining in the UK will be a significant barrier to achieving Water Framework Directive goals since mine waters are the major cause of pollution in many catchments, especially in Wales, and the north and west of England. It has been suggested that "the environmental impacts resulting from the underground mining of minerals presents perhaps our greatest global contamination challenge, with an estimated cost of $ trillions to remedy pollution from abandoned metal mines alone" (Sir Robert Wilson, chairman of Rio Tinto plc, 16th May 2002). Inappropriate management of coal mines, both during operations and after abandonment, can also give rise to serious pollution (Parker, 2002). The main environmental concerns are contaminated water from the rebound of formerly depressed groundwater and leaching from spoil heaps, and the residual spoil and other solid wastes from the extraction and smelting processes. The main pollutants from mining activities are metals, primarily iron, but also manganese, aluminium, lead, zinc, cadmium and copper (Younger, 2002) that cannot be destroyed (e.g. by biodegradation). Furthermore the areal and

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temporal (many centuries) extent of mining activities means that in addition to point sources of pollution (e.g. discharges from discrete adits), there are also more diffuse discharges that may affect aquifers (e.g. the Magnesian Limestone in East Durham) or an entire catchment (River Swale/Humber Estuary; Jickells et al., 2002).

Managing mine waters and wastes therefore requires a thorough understanding of hydrogeology, hydrology, geochemistry, microbiology, civil engineering, and not least, mining practices. Moreover it should be noted that mining remediation schemes offer the opportunity to involve, and engage, the local community and so break down the traditional split between "technical experts" and "the public". Successful engagement with the local community can be critical to successful remediation since many schemes will require regular maintenance, and the avoidance of vandalism, over several decades before the remedial objectives are achieved. Notable examples of public engagement are at Quaking Houses, Durham (Younger et al., 1997) and at the National Coal Mining Museum for England.

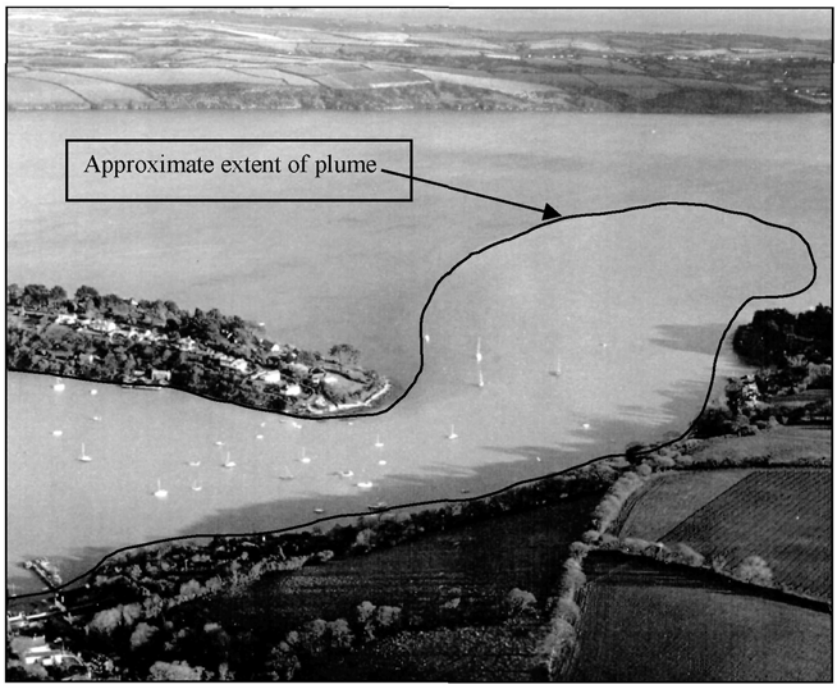

Figure 1. Restronguet Creek , Cornwall after discharge from Wheal Jane Tin Mine.

Throughout the world, significant environmental disasters associated with mines occur on an annual basis, but usually only reach our attention when they occur in Europe, such as the catastrophic failure of tailings dams at Aznalcóllar, Andalucia in 1998 and Baia Mare, Romania in 2000 (Council of the European Communities, 2003). As outlined in the proposed EC Mining Waste Directive (Council of the European Communities, 2003), the UK has not avoided such accidents with the 1966 Aberfan tip catastrophe in which 144 people, mostly children, were killed being the most catastrophic example. The British Isles can also record

some serious minewater pollution issues in a number of river catchments (National Rivers Authority, 1994), with some high profile incidents over the past 10 years or so, including:

- release of acidic minewater from the abandoned tin/zinc mine at Wheal Jane in 1992, resulting in a highly visible plume of acidic, metal-laden water in the Carnon River and Restronguet Creek (Figure 1);
- significant concerns over risks to human health and livestock, for example at various spoil sites in mid-Wales, and Snailbeach, Shropshire; and
- contaminated groundwater rebound in Durham coalfield predicted to pollute public water supply from Magnesian Limestone aquifer in Sunderland and an aquatic SSSI unless urgent preventative measures are implemented.

The Environment Agency's approach has tended to be highly reactive utilising "end-of-pipe" treatment only when polluting discharges to surface waters appear at the surface (e.g. Wheal Jane, Bullhouses Colliery) even after they have been predicted for some time. Although, by working with the Coal Authority, this operationally driven approach has so far been relatively successful in coping with problems with individual sites (Tate, 2002), at least in the short term, it has not tackled the problem at source, i.e. before the pollution reaches the river or the related ecosystem.

"End-of-pipe" treatment also requires long-term management, including disposal of waste sludges. The handling and disposal of sludges from alkali dosing pump-and-treat systems can account for 25-50% of treatment costs (Younger et al., 2002). Factors affecting the overall cost of sludge management include sludge density (often as low as 5% weight/weight solids) and the concentration and type of metal contaminants.

The implementation of the Landfill Directive (Council of the European Communities, 1999) will severely limit the disposal of sludges to landfill as low density sludges may be classed as liquid wastes, and the availability of landfill for hazardous wastes will be severely restricted. The cost of landfill is also likely to significantly increase as a consequence of implementation of the directive. It is therefore imperative that research into alternative strategies for sludge disposal or utilisation, including sludge densification, and remediation techniques that produce less waste is encouraged and extended.

The last 10 - 15 years has seen a move toward research and installation of passive treatment systems for mine waters, utilising natural attenuation processes and natural energy sources in constructed systems to remove metal contaminants from, and adjust pH of, the discharged mine water (Younger et al., 2002). Such passive methods range from traditional aerobic wetlands to combined aerobic/anaerobic systems with multiple components. Passive systems tend to have a high capital cost, but are designed to be low (not no!) maintenance.

Despite the large number of passive systems now in operation in North America and Europe, there is often a poor understanding of the natural processes involved in treating mine water. The current multidisciplinary research being carried out to understand these processes more fully (e.g. Hallberg and Johnson, 2002) should be encouraged and extended, and ultimately lead to the design of more efficient passive systems that perhaps will require less land. An example of the latter is the development of permeable reactive barrier technologies (Environment Agency, 2002) and their application to mine water treatment (e.g. Amos and Younger, 2002; Benner et al., 1997; Benner et al., 1999).

Other important, and little addressed, issues for passive treatment systems include the disposal of sediment and the potential need for decommissioning. There is therefore a need to understand the long-term fate of contaminants with particular regard to their potential to be re-released into the aquatic environment.

STRATEGIC APPROACH

A recent report to the EU (Amezaga and Younger, 2002) highlighted some of the drawbacks of the Agency's approach to mine waters, particularly the lack of a national strategy for metals mines, which undermine the Agency's ability to obtain environmental improvements. Despite spending over £20M on remedial works at the Wheal Jane site alone, the Agency has not had a national strategic approach for dealing with pollution from metal and coal mining. Working with the Coal Authority at a national level has enabled prioritisation for remediation of discharges from coal mines to be agreed (Tate, 2002). However it is only relatively recently that a national approach has been taken to coal mining at an operational level, whilst work on a national strategy for metal mines in England has only recently begun (a strategy for Wales was published in 2002). In the absence of a national science strategy, research has been undertaken on an ad-hoc basis that has led to duplication and an inability to influence the wider research community. This has undermined the Agency's ability to ensure that the UK is prepared for the challenges posed by the Water Framework Directive (Council of the European Communities, 2000) and proposed directive on the management of mining wastes (Council of the European Communities, 2003), and inhibited the efficient exchange of information across the country.

Following the creation of the Agency's Science Group in October 2003, a greater emphasis has been placed on an integrated strategic approach to many key science challenges such as mining pollution, considering contaminant fluxes across different media, and at both the catchment and local scales. To enable the Agency to develop its strategy for mining pollution, a senior Research Fellowship for Mine Waters and Wastes has been created in collaboration with the University of Newcastle. Although the Fellowship is based at Newcastle, the Agency seeks to encourage collaboration with other parties (universities, industry, consultancies etc.) to promote multi-disciplinary investigation of mining pollution. This will facilitate the development of the Agency's science-based strategy for mining pollution and support research to underpin the Agency's current and future regulatory responsibilities.

The overall research priorities for the Agency are to understand the hydrological and geochemical processes associated with minewater rebound and mine spoil weathering/leaching, place these within the context of diffuse pollution at both local and catchment scales, and promote the sustainable management of mining wastes. This research will support:

- the development of sustainable policy and operational support for dealing with groundwater rebound in mining areas especially in relation to interactions with overlying aquifers;
- the effective use of operational resources in capital projects where the Agency or Defra bears the cost of remediation;
- developing an understanding of mining impact assessments in terms of controlled waters, ecosystems, livestock and human health;
- the effective management of catchment-scale issues in mine-impacted catchments under the Water Framework Directive; and

- identification of sustainable remediation technologies for dealing with abandoned mine sites and their discharges, particularly in light of the future directive on the management of mining wastes.

One of the main goals of this strategic science programme will be to increase the transfer of knowledge on mining pollution between academia, practitioners, the Coal Authority, and industry within the UK. This will be achieved by participating in existing research activities, and also obtaining external funding to initiate new research projects with support being sought from research councils, the European Union Framework 6 Programme, industry and others. The Agency will develop new guidance (or promote existing work) to ensure that all remediation schemes are designed to best practice, and that the regulatory approach is scientifically-based and ensures the environment is protected.

CONCLUSION

The Environment Agency has created a three year *Research Fellowship for Mine Waters and Wastes* in collaboration with the University of Newcastle which will form the focus for a new strategic approach to mining pollution by implementing a nationally co-ordinated science and research programme. This will benefit the Agency and the UK by developing knowledge pertaining to the prevention and remediation of mining pollution from groundwater rebound, spoil heaps and the management of wastes from treatment technologies. In conjunction with the Agency's Air Land & Water Science Group, the Research Fellow will forge links between groups within the UK and in the rest of the world and provide expert support to the Agency's operational staff and policy development. The overall research priorities for the Agency are to understand the hydrological and geochemical processes associated with minewater rebound and mine spoil weathering/leaching, place these within the context of diffuse pollution at both local and catchment scales, and promote the sustainable management of mining wastes. Working with universities, industry and other key players, the Agency is engaging with external national/international initiatives and centres of excellence, disseminating learning across the Agency and providing the sound underpinning to decision-making in this area.

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Characterization of Fresh and Landfilled Cement Kiln Dust for Reuse-In-Construction Applications

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ABSTRACT

Significant quantities of cement kiln dust (CKD), a by-product of the cement manufacturing process, are generated every year in the US. Despite improvements in kiln operations and efforts that have gone into finding re-use applications, considerable amounts of CKD continue to require disposal through stockpiling or landfilling every year. Due to the variability in the chemical and physical properties of cement kiln dust, its utilization in construction has been to this day quite limited. In addition, the work performed so far has been for the greatest part focused on freshly generated CKD, while the issue of reusing stockpiled or landfilled material remains mostly unexplored.

The paper presents the preliminary work performed to characterize both the freshly generated CKD produced by a US plant as well as the material sampled from the adjacent landfill facility. At this disposal site more than 400,000 tons of CKD have been accumulated over a period of 12 years. The results of the characterization tests are compared to an extensive database collated from the literature and are used to discuss potential applications being considered for both fresh and landfilled CKD.

INTRODUCTION

CKD "is particulate matter that is collected from cement kiln exhaust gases and consists of entrained particles of clinker, unreacted and partially calcined raw materials, and fuel ash enriched with alkali sulfates, halides, and other volatiles" (Abeln et al. 1993). The generation of CKD in cement plants arises from both product quality and plant operation constraints associated respectively with the need to produce low alkali clinker from high alkali raw materials, and avoid plug formation in the kiln system and frequent unscheduled kiln shutdowns (Kessler 1995).

Generation of CKD is estimated at approximately 30 million tones worldwide per year (Dyer et al. 1999). While modern dust-collecting equipment is designed to capture virtually all CKD, and much of this material can today be returned to the kiln, for various reasons, a significant portion, in some cases as much as 30%-50% of the captured dust, must be removed as industrial waste (Kesser 1995, USEPA 1998). As a result in the United States more than four million tons of CKD, unsuitable for recycling in the cement manufacturing process require disposal annually (Todres et al. 1992). In 1993 the United States Environmental Pollution Agency (USEPA 1993) estimated that of this material, 52% was disposed of in landfills, 43% percent in piles, and less than 1% in ponds.

Due to the large amounts of CKD produced, the costs associated with its disposal, and the continuous interest in seeking more cost effective construction materials, there has been great interest in finding applications for this industrial by-product. Researchers have investigated the re-use of CKD in various fields (e.g. as a soil fertilizer, as a stabilizer of waste water

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streams, as a partial replacement of soda in glass production, as an anti-stripping agent in asphalts, as a component of blended cements and masonry products etc., e.g. see Klemm 1980, Bhatty 1995). However, as with other industrial waste materials, due to the large volumes of materials involved in construction, there has and continues to be great interest in exploring the viability of using CKD in partial substitution of traditional construction materials, for example, as a pozzolanic initiator, for subgrade soil stabilization/modification (e.g. Baghdadi et al. 1995 , Bhatty et al. 1996, Miller and Azad 2000, Miller et al. 2003), for the construction of highway bases and subbases (e.g. Collins and Emery 1983), etc.

So far most of the work performed has been limited to freshly generated CKD, while the issue of reusing already landfilled material has been mostly unexplored. Landfilled CKD is available in significantly greater quantities than the fresh CKD, with accumulations of these stockpiles estimated to be well in excess of 100 million tons in the US as of 1983 (Collins and Emery 1983). While the recycling of landfilled material poses additional challenges associated with the variability in age, the exposure during storage to varying environmental conditions, and potential contamination, the environmental impact of this material, the growing costs of disposal and storage, and in some cases the need to re-landfill this material as a result of new, more stringent disposal regulations, suggest that investigation of prospects of its industrial as well as non-industrial use is of great practical significance.

The paper presents preliminary results of work undertaken to investigate re-use applications in the area of highway construction of fresh CKD and landfilled CKD produced in a US plant. Specifically, the paper focuses on the experimental work performed to characterize the chemical and physical properties of these two materials.

VARIABILITY IN PROPERTIES OF CKD

Though the chemical composition of ordinary Portland cement from most parts of the world is found to be remarkably consistent, and despite the fact that CKD is derived from the same raw materials as Portland clinker, significant variation in chemical composition and physical characteristics has been observed for CKDs obtained from different plants. This variability can be ascribed to differences in the type of kiln operations, in the dust collection facility (e.g. dusts collected from the alkali bypass of precalciner kilns have been observed to be typically coarser, more calcined, and concentrated with alkali volatiles - Klemm1980); in the location within the system where the dust is collected, in the fuel used (e.g. dusts from gas-or oil-fired kilns have been reported to contain higher proportions of soluble alkalis as compared to those from coal fired kilns - Klemm 1980), etc. Collins and Emery (1983) have also reported that the there are often significant differences between total and separated dust collected, with the finer dust particles usually having a higher concentration of sulfates and alkalis, and a lower free lime content.

The variability in the chemical composition of fresh CKD is well illustrated in Table 1a which summarizes statistics on the oxide composition of CKD based on the analysis of 63 published datasets (58 of which from plants located in the United States). The table presents the average percentages of the main oxides present in the CKD, as well as of the loss on ignition LOI, and of the free lime content (not available for all datasets). Also reported are the values of the hydration modulus (Kamon and Nontananandh 1991, Miller et al. 2003) and the total reactive oxide content (Collins and Emery 1983) which have been related to the self-cementing characteristics of the dust (increasing reactivity with increasing TRO, and greater self cementing characteristics for HM between 1.7 and 2.4). Note that the samples represent CKDs from different kiln type and operation, fuel type(s), dust collection system etc. While CaO and SiO_2 are the major constituents for all CKDs, the data indicates a large range in variation for all the oxides, as well as in the LOI, and in the free lime. All the data of free lime and LOI are summarized in the histograms presented in Figures 1a-b. It is shown that

the majority of the CKDs have low free lime content (<5% for 27 out of 63, with 13 of these having less than 1%), and a LOI in the 20-35% range. A preliminary analysis of the data shows a good correlation of the TRO with both the LOI (increasing TRO for decreasing LOI) and the free lime content (increasing TRO with increasing free lime).

Table 1b presents the oxide composition of two stockpiled CKDs (Collins and Emery (1983). These CKDs are characterized by a LOI at the high end of the range for the fresh material and by the absence of free lime.

In terms of mineralogical composition, the most extensive database is provided by Haynes and Kramer (1982) who analyzed 113 CKD samples from 102 plants located in the US, observing that the major constituents of CKD are calcite, and, to a lesser degree, lime, anhydrite, quartz and dolomite.

Table 1 –CKD composition data from published data

a) statistics on composition of fresh CKD (63 different CKDs)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	LOI	Free CaO	Total Alkali	TRO	HM
Mean	43.99	15.05	4.43	2.23	1.64	6.02	0.69	4.00	21.57	6.75	3.32	21.49	2.33
SD	8.01	4.74	1.82	1.04	0.68	3.93	1.02	3.01	8.50	7.83	2.44	12.97	1.61
COV (%)	18	31	41	47	41	65	147	75	39	116	74	60	69
Max	61.28	34.30	10.50	6.00	3.50	17.40	6.25	15.30	42.39	27.18	11.42	56.08	13.91
Min	19.40	2.16	1.09	0.24	0.54	0.02	0.00	0.11	4.20	0.00	0.14	1.86	0.53

Sources: Al-Jabri et al. 2002 [1 CKD]; Baghadi et al. 1995 [1]; Collins & Emery 1983 [28]; Dyer et al. 1999 [2]; El-Awady & Sami 1997 [1]; Konsta-Gdoutos & Shah 2003 [4]; Kumar et al. 2002 [1]; McCoy & Kriner 1971 [8]; Miller et al. 2003 [5]; Miller & Azad 2000 [1]; Nisbet 1997 [2]; Salem & Ragai 2001 [1]; Sayah 1993 [1]; Shoaib et al. 1999[1]; Todres et al. 1992 [3]; Udoeyo & Hyee 2002 [1]; Wang et al. 2002 [1]; Zaman et al. 1992 [1].

Notes: Oxide values expressed in % by mass of cement; HM = hydration modulus = $CaO/[SiO_2+Al_2O_3+Fe_2O_3]$ TRO = total reactive oxide content = $[CaO+MgO-LOI]-[K_2O+Na_2O]$; Total alkali = $Na_2O+0.658\ K_2O$.

b) data for two stockpiled CKDs (Collins and Emery 1983)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	LOI	Free CaO	Total Alkali	TRO	HM
31.40	11.00	3.18	2.16	0.97	8.24	0.13	1.65	40.40	0.00	1.22	-	2.07
44.20	11.90	3.24	1.45	1.73	2.40	0.27	2.92	30.20	0.00	2.19	12.54	2.62

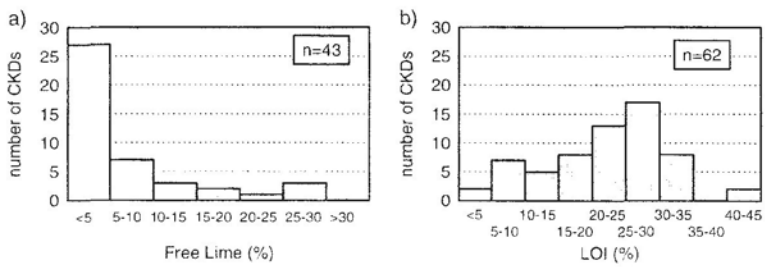

Figure 1. Free lime and LOI statistics from published data (sources as in Table 1).

Particularly as a result of the method of dust collection and on the method of separation, different CKDs may also vary significantly in particle size distribution. Figure 2 shows some results collected from the literature that illustrate the range in particle size of this material (all data derived from sedimentation analysis in water). Typical curves for ordinary Portland cement and two microcements (Santagata and Collepardi 1998) are also plotted for comparison purposes.

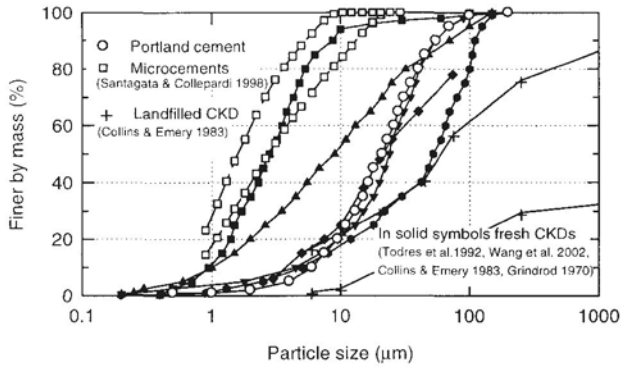

Figure 2. Examples of CKD particle size distributions from the literature

As seen in the figure the various fresh CKDs show significant variation in the mean particle size (D_{50} = 2.8 μm to 55 μm), as well as in the gradation (C_u =5-25). For the most part these values straddle the data for ordinary Portland cement, and are greater than those reported for microcements. The particle size of two landfilled CKDs (Collins and Emery 1983) for which the authors could find data in the literature (note that one of these was first ground) indicates that this material is somewhat coarser and better "graded" than the fresh CKDs. Blaine fineness values of CKD reported in the literature vary between 4500 and 14000 cm^2/g (e.g. Collins and Emery 1983 and Konsta-Gdoutos and Shah 2003), and are consistently above typical values for ordinary Portland cement (~3000-5000 cm^2/g), suggesting that in the case of CKD particle texture and morphology may play a significant role. Values of the specific gravity of CKD reported in the literature show some variation and typically fall in the range of 2.6 to 2.8. The pH of CKD is typically between 11.8 and 12.1 (Collins and Emery 1983). Overall the data examined above indicate that there exists no "average" cement kiln dust, and that each CKD source should be considered as having its own unique properties.

CKD SOURCES AND SAMPLING OF LANDFILLED CKD

For the present investigation, two CKDs, from the same US plant were used. The plant has three long dry kilns with single stage preheater system, and collection of the CKD occurs through electrostatic precipitators. The first CKD, hereafter referred to as *"fresh CKD"* was obtained directly from the manufacturer's outlet at two separate instances. These different samples are referred in the following as *fresh I* (November 2000) and *fresh II* (March 2003). Note that changes in the processing technology were implemented in the period between these two sampling operations. According to the manufacturer these changes have impacted the quantity but should have affected to a lesser degree the nature of the CKD generated.

The second CKD, termed *"landfilled CKD"*, was obtained in March 2003 from the landfill in proximity to the plant, which had been used for a duration of about 12 years for disposal of all CKD produced. Figure 3 shows a plan of this disposal facility, which is a monofill with only dry CKD filling it at the time of disposal. While no moisture conditioning of the CKD was performed during placement of the CKD, exposure to the environment (drying/wetting, freeze/thaw cycles, etc.) has created non uniform conditions in the CKD "deposit".

Mining of the CKD (primarily for use as agricultural lime) has been in process at the landfill for a few years. These operations have been conducted in proximity to the road of access to the landfill (see map) where the material is excavated with a backhoe and then fed into a screener. A significant amount of material has been removed through this process from the front of the landfill, creating a vertical cut 15-20 feet (5-6.5 m) high, and a two-level terrain.

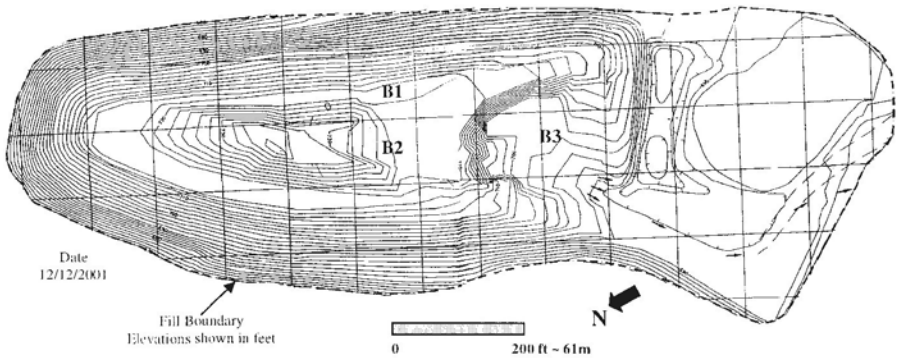

Figure 3. Layout of CKD landfill and location of borings.

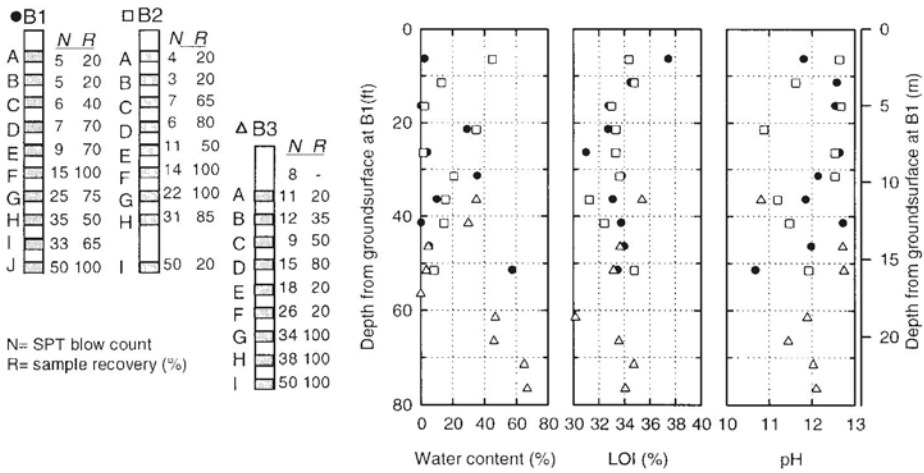

Figure 4. Location of borehole samples and results of water content, LOI and pH tests

Given that the main objective of this phase of the work was to evaluate the variability in the characteristics of the landfilled CKD, it was decided to obtain samples that would reflect different ages as well as different "storage" conditions of the material. For this purpose, samples of the CKD were obtained at depth using soil tube sampling equipment. The number of samples and the sampling locations were ultimately limited by the accessibility of the boring equipment to the landfill, the maximum boring depth available with the equipment (50 feet~15 m), and the cost of the operation. Three borings were conducted. Two borehole (B1 & B2) were located on the upper terrain of the landfill and the third borehole (B3) was located in the lower terrain (see Figure 3) in proximity to the bottom of the vertical cut described above. Unfortunately given that no precise records of the disposal had been kept, the CKD at any given location could not be in any way "dated". The boring was done by using simple auger boring-spiral type auger. Samples were obtained every 5 feet (~1.5 m) using a split-barrel sampler equipped with a plastic sleeve (2 ft [~60 cm] long and 2 inches [~5 cm]) in diameter), which was advanced inside a hollow auger. The standard penetration test (SPT) was carried out at regular intervals, to gain additional insight into the uniformity of the deposit. Figure 4 summarizes the "*tube samples*" (dark gray boxes indicated by a capital letter) collected and provides the sample recovery (R) as well as the blow count (N). Overall

throughout most of the "deposit" the CKD was powdery in nature, making the recovery quite poor. Only in the case B3, the borehole reached the natural soil below the landfill.
Samples of CKD were also collected from the landfill, near the vertical cut where mining operations were in progress. This material is herein referred to as "*screened CKD*".

EXPERIMENTAL PROGRAM AND TEST RESULTS

The portion of the experimental program discussed in this paper was performed with the primary goal of evaluating the variation in chemical and physical properties of the fresh and landfilled CKD for which applications in construction were sought. Table 2 summarizes the tests conducted and the samples used.

Table 2. Summary of experiments conducted

TEST	Fresh	Screened	B-1	B-2	B-3
Chemical composition	I II	-	F	C,F,I	B,D
Free lime	II	-	Composite sample for each boring		
XRD	I, II	√	-	-	-
Water content, LOI, pH	I, II	√	All	All	All
Specific gravity	√	√	F	D	
Particle size	√	√	E	D,I	I
SEM	II	√	-	-	-

Table 3. Oxide composition of fresh and landfilled CKD

Sample	Fresh I	Fresh II	B1-F	B2-C	B2-F	B2-I	B3-B	B3-D	Mean	SD
CaO	50.4	45.93	42.96	53.19	46.3	44.59	42.14	44.54	46.15	3.98
SiO_2	N.A.	9.30	7.62	8.7	7.82	7.99	7.1	12.37	8.80	1.91
Al_2O_3	2.66	3.20	2.5	2.87	2.66	2.56	2.43	2.82	2.67	0.18
Fe_2O_3	1.09	1.06	0.96	1.11	1.05	1.11	1.00	1.57	1.17	0.22
MgO	0.7	1.11	0.83	1.02	0.88	0.91	0.99	1.93	1.14	0.41
SO_3	3.5	2.30	4.62	4.92	3.76	4.12	4.17	2.59	3.91	0.81
Na_2O	0.18	0.13	0.3	0.23	0.12	0.08	0.23	0.11	0.15	0.086
K_2O	2.16	1.22	2.14	2.39	1.43	1.39	2.32	1.19	1.74	0.53
LOI	33.62	33.30	33.86	33.00	33.64	34.80	34.10	33.16	33.74	0.65
Tot.Alkali	1.60	0.93	1.71	1.80	1.06	0.99	1.76	0.89	1.34	0.41
TRO	15.14	12.36	7.49	18.59	11.99	9.24	6.49	12.00	11.66	4.36
HM	-	3.39	3.87	4.19	4.01	3.82	4.00	2.66	3.74	0.55

Notes: oxide values expressed in % by mass; mean and standard deviation refer to tube samples alone

Chemical and Mineralogical Composition

The chemical composition data of the fresh and landfilled CKD are summarized in Table 3. In general the results appear quite consistent, with no major difference between the fresh and the landfilled material. In particular, the values of the LOI are very consistent, and at the higher end of the data reported in the literature. Comparison to the data in Table 1, also indicates a SiO_2 percentage and an alkali content at the low end of the range reported in the literature, a very high LOI, and a low. As a result, in particular of the high LOI, the values of the TRO fall below the average from the literature. Measurements of the free lime conducted on composite samples obtained combining CKD from select samples form each of the borings, indicate values less than 1%, at the very low end of the values reported in the literature. Preliminary data for the second batch of the fresh CKD (fresh II) are consistent with these low values. Despite this, some difference in the compressive strength of cubes formed employing the two CKDs at the same water/CKD ratio was observed (Sreekrishnavilasam 2004). While measurements of the free lime were not conducted on the fresh I CKD, "historic" data obtained from the manufacturer indicate that the free lime of this material may have been higher (3-6%). Additional testing is currently being performed. X-ray diffraction analysis of the fresh and screened CKD was performed in the Materials

Laboratory of Purdue's School of Civil Engineering. Representative XRD patterns are shown in Figure 5. The results indicate that calcite and SiO_2 are the major component in both the fresh and the landfilled CKD. Free lime was detected only in the fresh I CKD, while the peaks of ettringite, resulting from the hydration reactions having occurred in the field, were identified in the landfilled material. No other major minerals could be identified.

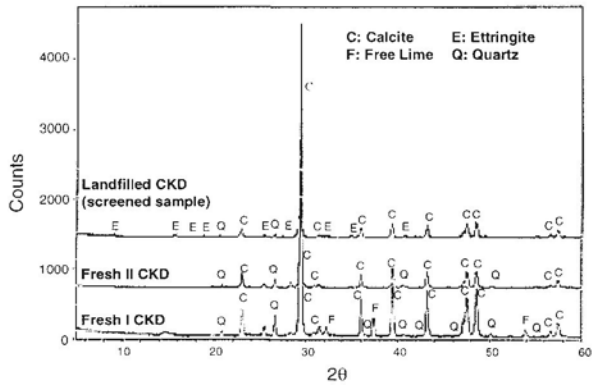

Figure 5. XRD patterns for fresh and landfilled CKD

Variation in Water Content, pH and LOI in Landfilled CKD

While chemical and mineralogical analyses were limited to a small number of the field samples, measurements of the "natural water content", the pH and the LOI were performed on all tube samples immediately after the tubes were received in the geotechnical laboratory. The results of these measurements are plotted in Figure 4. The water content data show significant variation, from almost 0% to around 65% for the deeper samples obtained from B3. The values of the LOI determined by igniting the powder in a muffle furnace at 950°C for 2-3 hours after overnight drying at 105°C, are quite consistent for all the tube samples (33.57 ± 1.44), with no correlation with water content, and as discussed above, at the high end of those reported in the literature. Despite the long exposure to the atmosphere of the landfilled material, there is no significant difference between the tube samples and the fresh CKD (LOI=33.62 and 33.30 for fresh I and II, respectively). The pH of the tube samples, determined using a Corning pH meter 44, a pH glass electrode and a calomel (reference) electrode, has an average value of 12.

Particle Size and Morphology

Particle size distribution of select samples of the fresh and landfilled CKD were obtained employing the hydrometer test in water with sodium hexametaphosphate as a dispersing agent. The results of these tests are summarized in Figure 6a. The fresh material is characterized by a mean particle size of about 2μm and by 95% finer than 7 μm, making this CKD finer than any of those shown in Figure 2. The results for the landfilled CKD show some sample to sample variability. While this material is somewhat coarser (D_{50}~3-5 μm) than the fresh CKD (this is an expected result which may derive from changes in microstructure occurring as a result of chemical reactions [e.g. hydration], or contamination from other materials, and has been reported for both stockpiled fly ash [McLaren and DiGioia 1987] and another landfilled CKD [Collins and Emery 1983]), overall all the data for the landfilled CKD fall at the low end of the range obtained from the literature.

Insight into further differences between the fresh and the landfilled CKD is provided by examination of the two micrographs obtained for the fresh and the landfilled (screened

sample) using the scanning electron microscope (Figures 6b and 6c). The micrographs indicate that there exist significant morphological differences between the two CKDs. While, the fresh CKD particles are irregularly shaped and have a fairly smooth surface, the landfilled material shows clear evidence of reaction products in form of fibers. Recent work shows that these differences significantly impact the engineering properties, in particular the compaction behavior of these two CKDs, including a reduction of more than 30% in γ_{dmax} for the landfilled material (Sreeskrishnavilasam 2004).

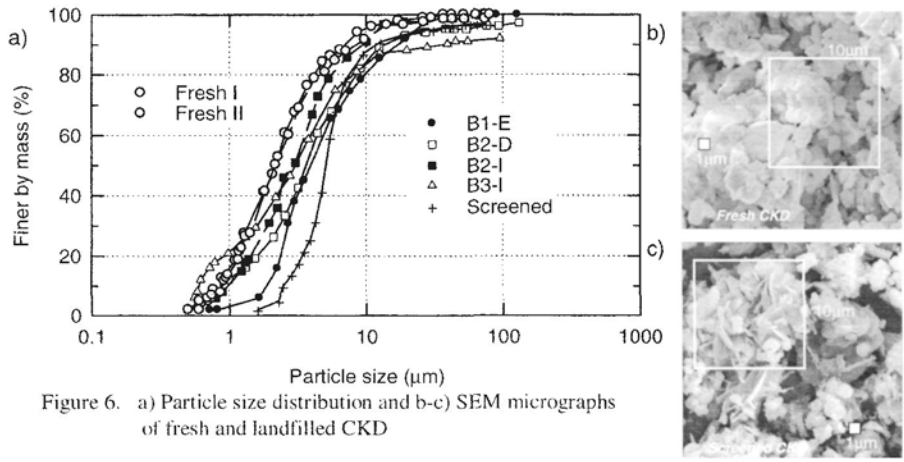

Figure 6. a) Particle size distribution and b-c) SEM micrographs of fresh and landfilled CKD

POTENTIAL APPLICATIONS FOR THE CKDs

Based on the physical and chemical characterization performed, several potential applications are being considered for the two (fresh and landfilled) CKDs under investigation.

The primary application currently under investigation is soil modification/stabilization. While the low free lime raises questions on the reactivity of the CKDs for soil treatment, preliminary tests performed with the fresh CKD (Santagata and Bobet 2001) show some promising results. Work is currently being conducted (Sreeskrishnavilasam 2004) to investigate the use of the CKDs in combination with Portland cement for enhanced performance in this application

The fineness of the material suggests that, despite the possibly limited reactivity of the CKD, this material may be effectively used in grouting mixtures either as a "filler" for bleed reduction, or, where limited strength is required from the grout, as a binder (alone or, again, in combination with another material). Along the same lines, it appears that in particular the fresh CKD may be an attractive candidate for use in low strength flowable fill mixtures. Finally, the high water absorption capacity (which has not been discussed in this paper) and the limited cementing properties of landfilled CKD potentially make this an ideal daily cover material for sanitary landfills.

SUMMARY AND CONCLUSIONS

The paper has presented an investigation of the chemical and physical characteristics of a fresh and landfilled CKD obtained from the same US cement plant. The work which involved tube sampling at the landfill material and extensive laboratory testing was aimed at: a) performing a preliminary evaluation of the variability in characteristics of the landfilled CKD; b) comparing the fresh and the landfilled material; and c) evaluating the two materials with respect to other CKDs, based on published data.

The main conclusions from the work performed can be summarized as follows:

- Overall the landfilled material exhibits very consistent characteristics both in terms of chemical composition and particle size.
- The chemical composition of both materials falls within the range of data reported in the literature for other CKDs. In particular both materials show small (fresh CKD) to zero (landfilled CKD) free lime and a fairly high (~30%) LOI. These data suggest that the reactivity of the two CKDs and in particular that of the landfilled material may be limited.
- A distinct characteristic of both CKDs is the very small particle size (80-95% finer than 10μm) at the very low end of data available for other CKDs. Despite the similarity in size, the particle morphology of the two CKDs differs greatly due to the presence of hydration reaction products in the case of the landfilled CKD.

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The Interpretation of CPT Data from Hydraulically Placed PFA.

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ABSTRACT
This paper reports a site investigation on an old hydraulically placed pulverised fuel ash (PFA) deposit. The results of cone penetration tests (CPTs) at the site are reported, along with the results of oedometer compression tests on undisturbed specimens recovered during the site investigation. Review of the in-situ test data indicated that no undisturbed specimens were recovered from the softest region of the PFA. This highlights the potential danger of biased sampling in very loose non-cohesive materials unless depth profiling is undertaken by in-situ measurement.

Oedometer test results on resedimented PFA are also reported. These tests showed that PFA can undergo significant secondary compression with time, which must be accounted for when estimating the engineering properties of aged PFA. The correlation between volume compressibility and cone resistance, $m_v=1/(\alpha.q_c)$ is fitted to compressibility data from undisturbed samples to determine α. The resulting CPT compressibility profile is then compared with compressibility trends estimated for aged PFA using properties measured in the oedometer tests on resedimented ash. The estimated compressibility trends show good agreement with CPT profiles. It is therefore recommended that a value of $\alpha=11$ should be used for normally consolidated PFA that has aged (i.e. been in place) for 20 years.

INTRODUCTION

Pulverised fuel ash (PFA) is a fine particulate solid usually collected by electrostatic precipitation from the combustion flue gases of coal fired electricity generation. Fly ash particles are typically spherical, ranging in diameter from <1μm to 150μm and, owing to the rapid cooling of the flue gases, consist primarily of non-crystalline particles or glasses (about 80%), and only a small amount of crystalline material (Cabrera et al., 1986).

PFA is commonly disposed of by producing a water based slurry which is pumped to fill voids. Where the void is water filled, pluviation of the fine particles can result in a very loose material, especially for particles such as PFA where the specific gravity can be relatively low (typically in the range 1.9 to 2.6; Cabrera et al., 1986; Joshi and Lohtia, 1997). The behaviour of such unusual very soft sediments is of interest both academically and generally because the PFA filled lagoons have development potential.

To develop PFA disposal sites, it is necessary to determine the geotechnical properties of the hydraulically placed PFA. However, it is very difficult to take undisturbed samples of hydraulically placed PFA as any disturbance can lead to strength loss in loose non-cohesive deposits and severe changes of structure. Where the PFA is very loose it is impossible to recover even notionally undisturbed samples. Thus, unless an in-situ method has been used to

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

measure the material properties, there is a danger that the results of the laboratory test programme will be biased towards the zones within the PFA that could be sampled (i.e. predominantly from firmer layers). As other in-situ testing methods have their draw-backs and difficulties the relatively low costs and ease of use make the cone penetration test (CPT) a very attractive method for testing very loose hydraulically placed PFA.

A major site investigation has been carried out on a 50m deep PFA disposal lagoon in West Yorkshire to determine its suitability for redevelopment. During this investigation the CPT was extensively used, partly as it was an economical way of determining the depth of the PFA (the boundary between the hydraulically placed PFA and the underlying coal measures produced a sharp contrast in the CPT output), and also because in-situ tests were the only way to estimate the geotechnical properties of the PFA where it was very loose.

This paper is about the interpretation of CPT results from this investigation. A total of thirteen CPT probes were conducted on the PFA deposit, and samples of disturbed PFA were recovered from the site. Empirical correlations with cone resistance have been developed that yield approximate values of volume compressibility (Robertson and Campanella, 1983a &1983b; Meigh, 1987; Lunne et al., 1997). However, the CPT is not ideally suited to the reliable estimation of the compressibility, so it is essential that empirical correlations are calibrated to the particular soil type. Therefore PFA recovered from the site was re-sedimented and then consolidated in the laboratory, replicating the stress history of the very loose zone of PFA found on the site. The compressibility measured for this very loose resedimented PFA and that measured on notionally undisturbed PFA samples recovered from firmer zones on site is compared with compressibility values estimated from correlations with the CPT data. Values are recommended for the constant in that correlation. The work may also be of interest for researchers and engineers working with other very loose particulate systems, both natural deposits and man-made, for example mine tailings.

THE SITE

Details of the site have been reported by Cousens and Stewart (2003). Briefly, the area of interest is a 50m deep PFA disposal lagoon (lagoon 19) adjacent to a river. A large void was created during the 1950s and 1960s by opencast coal mining and the extraction of sand and gravel. This was partially backfilled with colliery spoil and embankments of the same material were constructed to form a series of lagoons for PFA disposal. PFA was pumped into lagoon 19 as a water-based slurry, allowed to sediment, and excess water was allowed to overflow a series of weirs into the nearby river. PFA disposal at the site took place from 1970 to 1994, with most occurring during the early to mid 1970s, none in the early 1980s, and a final 2-3m added before 1994.

GROUND INVESTIGATION

In July 1999 a ground investigation was carried out on the site described above to determine the depth, variability, strength and compression characteristics of the PFA. The main investigation was performed by Norwest Holst Soil Engineering Limited, and consisted of five boreholes advanced by cable percussive techniques, with the collection of both disturbed and undisturbed samples for laboratory testing. As part of the investigation thirteen CPT probes were undertaken by Fugro Limited using a 7.5 tonne capacity electric cone, with a rate of penetration of approximately 2cm per second measuring the cone end resistance and local side friction. In addition, further bulk disturbed samples were taken in 2003 by the University of Leeds so that laboratory testing of resedimented samples could be undertaken.

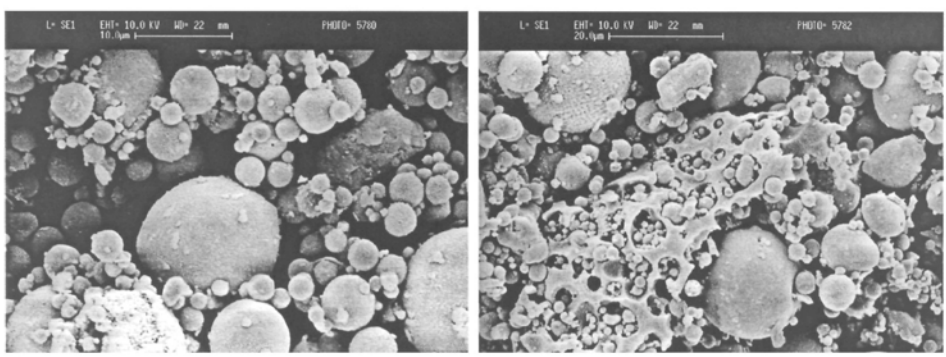
The particle size distributions of most of the samples taken from the site were very similar, which suggests that the PFA is relatively uniform over the site with 5-10% clay sized particles and 60-80% silt size (Cousens and Stewart, 2003). Occasional thin coarse layers were detected in the PFA, but their extent is unknown although they appear to be limited. Scanning electron microscopy on the silt and clay sized fraction of a near surface sample of PFA shows that it consists primarily of very rounded, almost spherical particles with sizes predominantly in the range 1-20μm (see Figure 1). Some micrographs also showed a weak open matrix (Figure 1b) which probably represents unburned carbon in the ash. The measured specific gravity of the PFA is 2.3, which is in the middle of the range of 2.23 to 2.40 reported by Cabrera et al. (1986) for ashes produced by burning local bituminous coals in Yorkshire power stations and the PFA is non-hardening, Class F.

The PFA had an average liquid limit of 46% (range 38-56%), an average plastic limit of 42% (range 32-54%), giving an average plasticity index of 4% with some samples showing no plasticity. The PFA classifies as an inorganic silt with slight plasticity. The in-situ moisture content of the PFA showed a general pattern of a central band with a very high moisture content (55% to 78%) with lower values above and below (38% to 44%). These values suggest loose material, especially in the central band. The in-situ bulk density is estimated as between 1.54 and 1.66 Mg/m^3 (a void ratio, e, of 1.28 to 0.88 assuming full saturation), the former values corresponding with the soft zone. An e of 1.28 corresponds to a moisture content of 55% at saturation, thus either the very high moisture content samples contained additional water from the borehole, or it was not possible to obtain a sample sufficiently intact to obtain a bulk density from the very loose material.

METHODOLOGY

A series of one-dimensional compression tests were conducted on PFA recovered from lagoon 19 and re-sedimented in the laboratory. A 70mm diameter fixed ring oedometer was used with top and bottom drainage. To avoid the need to move the specimen, with the inherent risk of sample disturbance, sample preparation was undertaken with the oedometer within the lever-arm loading apparatus.

To replicate the very high void ratios determined for the PFA deposit, and to reproduce the primary feature of the deposition process on site, the specimens were prepared by water pluviation. During sample preparation thin-walled extension tubes were fitted to the water bath and oedometer collar. Equal water levels were established in both the inner and outer



(a) (b)

Figure 1: SEM images of the PFA.

tubes, about 120 mm above the oedometer cell, and approximately 80g of PFA was sprinkled slowly into the inner tube. The PFA had been air-dried, passed through a 2mm sieve, and then disaggregated with light pressure from the flat surface of a palette knife. The suspension was left to settle for at least 1hr, the inner tube was carefully removed, the water level was lowered to the top of the water bath and the outer extension tube was removed. This technique resulted in a specimen of very loose PFA about 20 mm in height.

The top-cap assembly was placed on the sample and loaded in increments to a maximum of about 3.5 MPa. Each loading step was monitored for a period 30 minutes, which was found experimentally to exceed the time for 90% consolidation. After some loading increments the specimen was monitored for up to 3 days to observe any secondary (or creep) compression. Small stress increments were used initially on reloading after a creep period. After unloading the specimen was extruded and its height measured. After weighing, the whole sample was oven dried so that its moisture content could be determined. Disturbance during extrusion meant that the sample height could not be determined accurately, and the final void ratio of the specimen was determined from the final moisture content (assuming that the specimen was fully saturated).

RESULTS

Cone Penetration Testing

Typical CPT data from the deeper part of the lagoon are shown in figure 2 (CPT6C was approximately in the centre of the lagoon). All the tests clearly indicated the bottom of the PFA deposit, and characterize the PFA as either "granular" or "cohesive" with much described as very loose to loose or soft to firm, although there are dense/firm zones and inter-layering is common. As the particle size distribution data shows little variation in the PFA over the site, the variations in classification must reflect variation in density rather than composition. Thus there are considerable depths of loose/soft material but it is very difficult to discern a pattern, either vertically or laterally, except for an increasing depth of loose material towards the south of the site.

Figure 3 shows a plot of the relative density of the PFA against depth which has been produced using the relationship for high compressibility quartz sands described by Meigh (1987). In this relationship between relative density and $q_c/(\sigma_v')^{½}$, the in-situ vertical stress has been calculated assuming a total unit weight of 15.5 kNm^{-3} and that the water table is at a height of 19m AOD (6m below average ground level). The absolute values of relative density are questionable (the relationship between q_c, σ_v' and relative density is significantly influenced by soil compressibility, Campanella et al., 1984), but the variation of relative density reveals an interesting pattern. The data suggest an upper relatively dense layer above a height of 15m AOD over a far looser zone. In the middle of the lagoon the PFA is loosest at a height of about 10m AOD and the relative density increases gradually with depth. This pattern is broadly in agreement with the moisture content distribution.

Given the levels of the lagoon (present ground level about 25m AOD) and river (about 15m AOD) and the filling procedure used to deposit the PFA the density pattern might have been created in the following way. Initially the void, whose deepest point is about -30m AOD, would either have been water-filled, or would have rapidly become so as the PFA slurry was pumped in, resulting in the PFA sedimenting through water. This would have continued with the excess water overflowing through settling ponds into the river once the water level reached about 17m AOD. As the inlet point was at the northern edge of the lagoon, the PFA

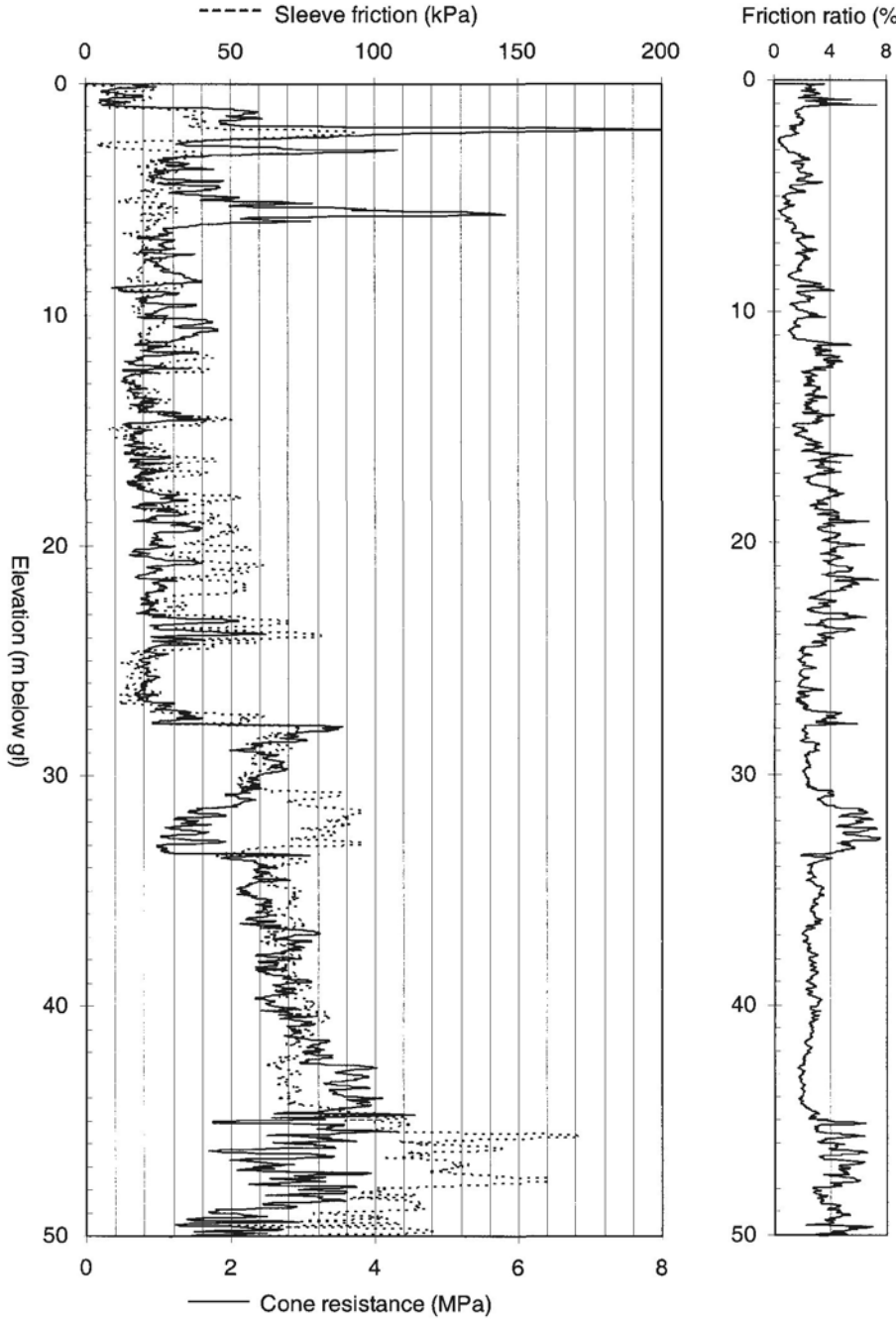


Figure 2: Data obtained from CPT6C

would tend to sediment from the north, possibly resulting in slumping failure of the PFA underwater, which would give a very loose packing. As the depth of sedimented solids reached 17m (i.e. the water level in the lagoon) the pattern of deposition would have changed to one where the slurry would have dewatered while flowing over the ground surface (i.e. the water would have drained downwards out of the PFA), rather than particle sedimentation through water, which would have given a denser structure, an effect possibly increased by surface drying.

Therefore it would appear that the PFA below 15m AOD is close to a normally consolidated state, as it has been deposited through water to achieve a very loose state, and then subsequently compressed by the material deposited above. It is also likely to have undergone secondary compression over the time since deposition (approximately 20 years). The stress history of the material above 15m AOD appears to have been more complicated, with surface deposition and subsequent pore suction variations resulting in a denser state than that resulting from sedimentation through water, and thus it can be generally described as "over-consolidated"

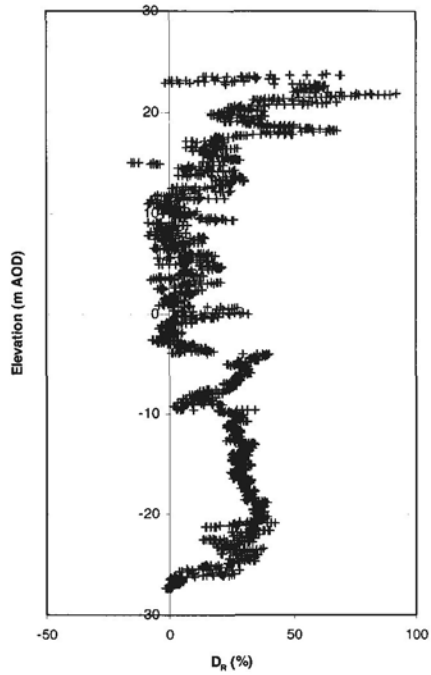


Figure 3: Relative density profiles determined from CPT6C.

Oedometer Testing of Re-sedimented PFA

Figure 4 shows e vs σ'_v for three tests. The tests presented were all very loose on first loading and exhibit normally consolidated behaviour almost from the start of testing. The relationship between e vs $\log\sigma'_v$ is highly linear between 100 kPa to about 3 MPa. Upon unloading the relationship between e and the $\log\sigma_v'$ was also linear but the response is far stiffer than on loading. All the tests conducted gave very similar values of both C_c and C_r (the average values are 0.27 and 0.036, respectively), and the only significant difference between the tests was the value of the initial void ratio. The method of sample preparation and test meant that the initial and final heights are not known exactly and e is determined from the final water contents, assuming complete saturation, and the measured change in specimen height. This introduces a small uncertainty into the absolute values of void ratio presented in Figure 4. Thus it is believed that all the test specimens were exhibiting essentially the same behaviour with most of the differences in void ratio being due to slight inaccuracies in measurement and saturation at the end of the test.

At selected loading increments during tests 4 and 6 the loading was held constant after the consolidation response had been observed (i.e. after t_{90} had been reached) so that the secondary compression (or creep) response could be observed. The data have been fitted with straight-lines of the form:

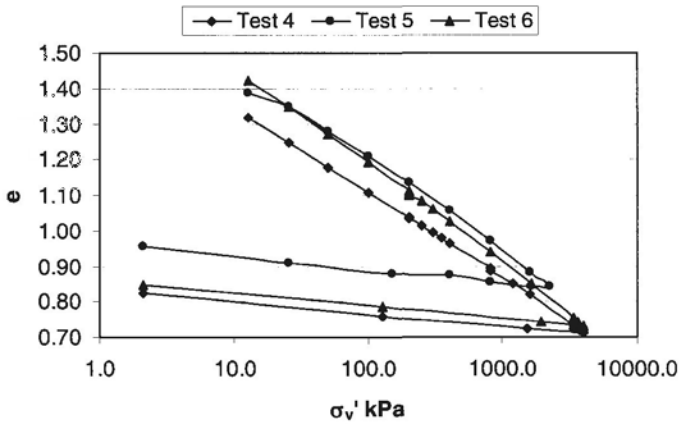


Figure 4: Oedometer tests on loose PFA prepared by water pluviation.

$$\Delta e_{creep} = C_\alpha \log_{10}(t_{creep}/t_{90}) \quad (1)$$

where Δe_{creep} is the change in void ratio during secondary compression and t_{creep} is the time elapsed since a change in the loading. The average value of C_α measured over 5 creep stages was 0.0036 (which is only slightly less than would be anticipated for normally consolidated clay; Lambe and Whitman, 1979).

DISCUSSION

The oedometer data can be used to estimate the volumetric compressibility, m_v, of the PFA (see Bjerrum, 1967). For normally consolidated PFA, after a period of creep, e_o can be estimated by combining equation 1 with the equation of the normal consolidation line to give:

$$e_o = e_{1kPa} - C_c \log_{10}(\sigma_v'_o) - C_\alpha \log_{10}(t_{creep}/t_{90}) \quad (2)$$

where e_{1kPa} is the void ratio on the normal consolidation line when σ_v'=1kPa (see Figure 5). If a stress increment that is sufficient to bring it back onto the normal consolidation line is applied, m_v on reloading can be estimated from;

$$m_v = \frac{1}{1+e_o}\frac{\Delta e}{\Delta \sigma_v'} = \frac{1}{1+e_o}\frac{C_c \log_{10}(\sigma_v'_1/\sigma_v'_{ncl})}{\sigma_v'_1 - \sigma_v'_o} \quad (3)$$

where $\sigma_v'_{nlc}$ is the effective stress at the point on the normal consolidation line where $e=e_o$: the value of $\sigma_v'_{nlc}$ can be estimated from e_o and the equation of the normal consolidation line. If the stress increment is insufficient to bring the PFA back onto the normal consolidation line, m_v can be estimated from the void ratio after creep, e_o, and the slope of the rebound line from;

$$m_v = \frac{1}{1+e_o}\frac{C_r \log_{10}(\sigma_v'_1/\sigma_v'_o)}{\sigma_v'_1 - \sigma_v'_o} \quad (4)$$

The m_v profiles shown Figure 6 have been calculated using equations 3 and 4 by assuming γ=15.5 kN/m^3, ground surface at 25m AOD and a water table at 19m AOD. The NCC (normal consolidation, creep) trend is given by equation 3 using average e_{1kPa}, C_c and C_α values from the oedometer data and a stress increase of 100kPa. All the oedometer tests gave similar C_c values, and m_v is not particularly sensitive to small errors in e_{1kPa}, so void ratio errors in the consolidation data have a small effect on m_v, but the amount of creep consolidation controls how far the initial condition of the specimen is from the normal consolidation line and

potentially can have a big effect on m_v. The PFA level was close to its current level by the late 1970's and filling ceased after adding a further 2-3m in the mid to late 1980's. Thus the upper m_v profile for sedimented PFA shown in Figure 6 has been estimated by assuming a creep duration of 20 years. However the C_α value has been evaluated over a time period more than 3 orders of magnitude smaller and thus must be treated with caution.

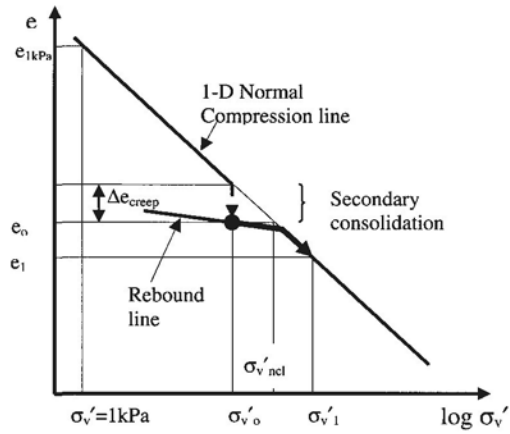


Figure 5: Schematic diagram showing the stress path of PFA that has undergone primary consolidation and creep upon subsequent stress increase.

The OC (over-consolidation) trend on Figure 6 is based on equation 4 and approximates to the situation where there has been sufficient creep for the reloading stress-path to remain on a rebound line. It has been calculated for a stress increment of 100 kPa using the average C_r value from the oedometer tests. It can be seen from equation 4 that variations in the initial void ratio have only a fairly small effect on m_v for stress-paths following a rebound line (for the entire range of e_o exhibited by the PFA of $0.7 \leq e_o \leq 1.4$ the $1/(1+e_o)$ term only varies between 0.59 and 0.42), and so the e_o value used to calculate m_v for specimens that undergo sufficient creep to remain on a rebound line on renewed loading was that calculated for 20 years of creep.

The m_v values measured on specimens from U100 samples are also shown in Figure 6. These m_v values were for a stress increase of 100 kPa. When reviewing this data it should be remembered that it was very difficult to get samples from the very soft region between 15 and -10 m AOD and therefore the m_v values for the two specimens recovered from this depth range may be unrepresentative. The m_v values measured on the U100 samples from the zone on site that was sedimented through water fall between the two estimated m_v profiles.

Two further m_v profiles are shown in Figure 6 as dashed lines. These profiles are for comparison with the data for the PFA that was surface deposited above the water level during the first filling stage and may be considered overconsolidated. The initial void ratio and subsequent response of the PFA in this region cannot easily be estimated by using consolidation data, so the profile has been estimated using an initial void ratio of 0.9 (a representative value for this region) and the rebound index C_r for a 100kPa stress increment assuming that the PFA has become over-consolidated as described above. The u=0 trend assumes that there is no pore water pressure above the water table, whereas the SAWT trend assumes the PFA is fully saturated above the water table with the pore water in suction.

The oedometer specimens from the U100 samples from shallow depths were inundated with water once a seating load had been applied, thus m_v values will not be representative of the PFA on site, which will have been stiffer due to the effect of pore suction. These m_v values are comparable with the u=0 trend shown in Figure 6. Here, despite the uncertainty about the

initial void ratio, the data fit is reasonably good. This gives some credibility to using equation 4 and an estimated initial void ratio to estimate m_v in this region of the PFA.

The coefficient of volume compressibility can also be estimated from CPT data using the equation:

$$m_v = 1/(\alpha.q_c) \qquad (5)$$

where α is a constant of proportionality that depends on the soil type (Robertson and Campanella, 1983a &1983b; Meigh, 1987; Lunne et al., 1997). Suggested values of α for cone resistance measured with a reference tip are 3 to 11 for normally consolidated sands, 5 to 15 (or even 30) for over-consolidated sands, 3.5 to 7.5 for low to medium plasticity silts, and 2.5 to 10 for organic silt.

The CPT data from CPT6C has been visually fitted to the m_v values measured in oedometer tests on specimens from U100 samples recovered from the site by varying the α-value until there is good agreement. As cone resistance is primarily a measure of strength, which in an undrained material will be a function of the void ratio, it should be anticipated that α may vary with OCR as normally and over-consolidated soils at the same void ratio have very different compressibility (indeed, different α-values are recommended for normally and over-consolidated sands; Robertson and Campanella, 1983a; Meigh, 1987). Therefore only the compressibility of specimens recovered from below 15 AOD, where the PFA is thought to be normally consolidated, were intentionally fitted by the CPT correlation. Also, as borehole BH2 is close to CPT6C, particular emphasis was placed on the relationship between the CPT estimate and the compressibility of specimens from the nearest borehole when selecting a suitable α-value for the m_v correlation. The best visual fit of the CPT estimates to the compressibility of the undisturbed specimens was obtained with an α-value of 11.

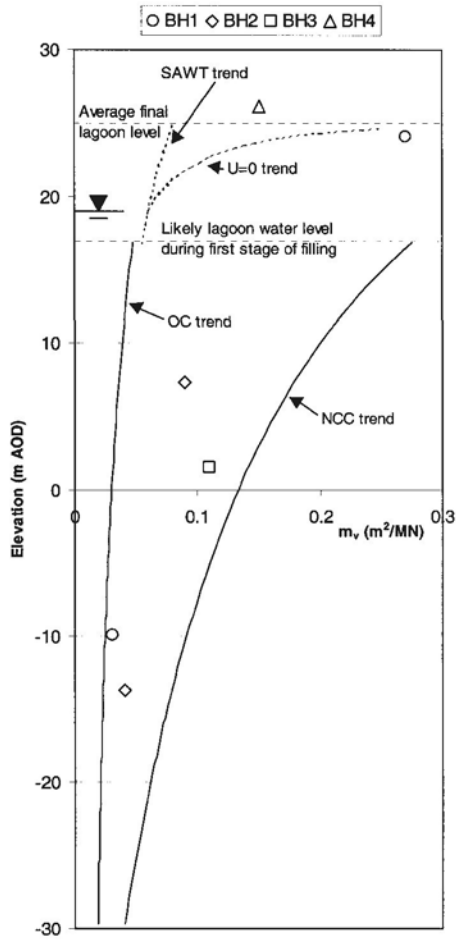
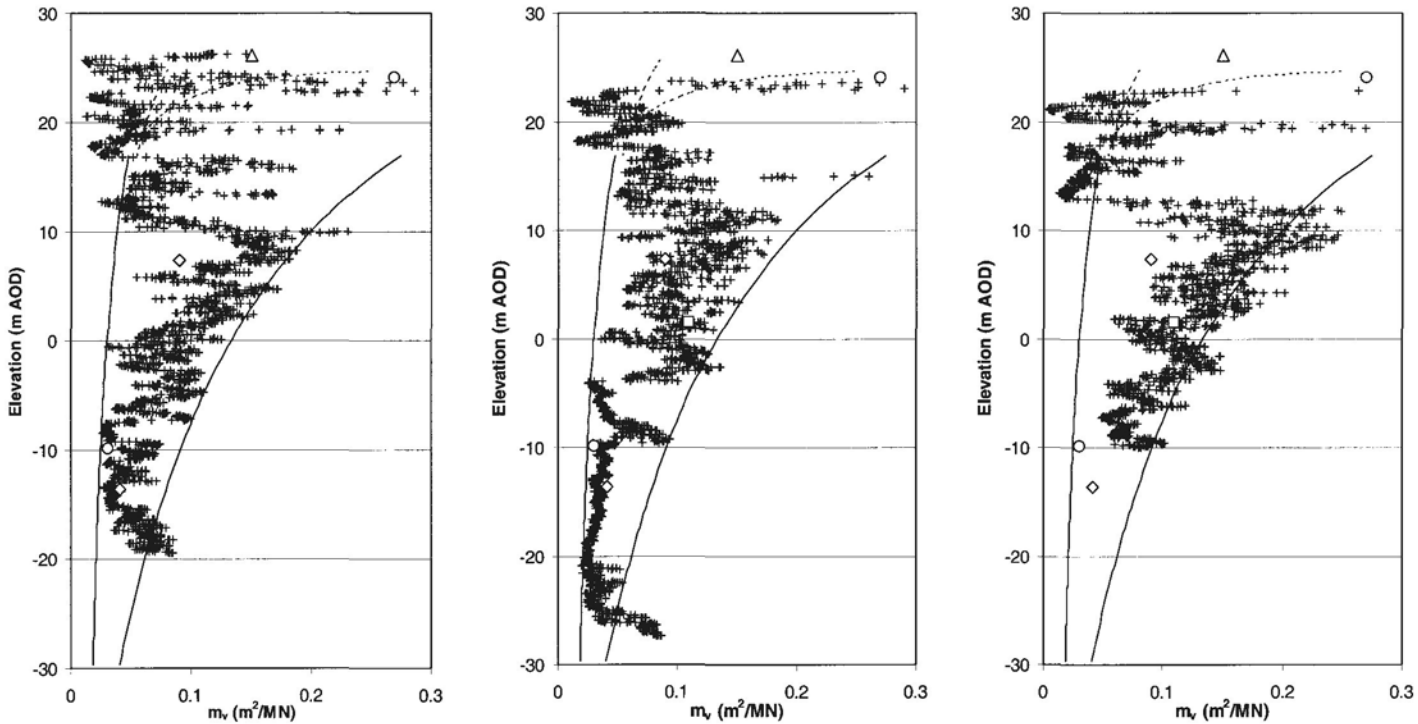


Figure 6: Idealised m_v profiles and m_v values from the U100 samples.

The compressibility profiles estimated from the CPT data with α equal to 11 are shown in Figure 7, together with the compressibility of the undisturbed samples and the compressibility profiles estimated from the oedometer tests on the resedimented PFA. Figure 7 contains data for 3 CPT tests. Below 15m AOD, where the PFA is thought to be largely normally consolidated, the volume compressibilities estimated from CPT data fall largely between the NCC and OC trends calculated from the resedimented PFA data with a trend towards the OC



(a) CPT4C (b) CPT6C (c) CPT7C

Figure 10: Volume compressibility, m_v, determined from (a) CPT4C, (b) CPT6C, and (c) CPT7C using α=11 (trend lines are defined in Figure 9).

prediction with increasing depth. Given the uncertain history of the PFA sedimented through water (arising from the tendency to form underwater mounds near the inlet, which then slump to fill the lagoon) it is quite remarkable that the compressibility of aged, water-sedimented PFA falls so overwhelmingly between the NCC and OC trends, which represent a best estimate and a lower limit on the compressibility of an originally normally consolidated deposit that has become slightly denser through creep.

As already stated, it is inappropriate to assume that the α-value for PFA surface deposited and hence overconsolidated is the same as that for PFA that has sedimented through water. Also, m_v has not been correctly measured on the U100 samples from the surface deposition zone, as the samples were saturated, and so the PFA is in a different state from that tested in-situ. Thus it is difficult to make definitive statements about a suitable α-value for PFA that has undergone surface deposition. However, it can be observed from the CPT estimate of m_v that surface deposition and subsequent pore suction variation appears to result in a material with a far more variable compressibility than sedimentation through water. It is also interesting to note that in the surface deposition zone the CPT estimates of compressibility based on an α-value of 11 generally fall around the SAWT trend line except very near the ground surface where it falls near the u=0 trend line. As the methodology used to estimate the PFA compressibility in this zone is given some validity by the fit of the u=0 trend to the m_v values from the inundated oedometer tests, it is reasonable to treat the SAWT trend as a guide to the compressibility in this region (and particularly just above the water table). Thus it is tentatively suggested that an α-value of 11 is of the correct magnitude for over-consolidated PFA.

CONCLUSIONS

In very loose hydraulically placed PFA it is not possible to establish the variation of engineering properties within a deposit simply by the laboratory testing of undisturbed specimens recovered during a site investigation. This is because it is very difficult to recover undisturbed samples, especially of the loosest material. Thus it is essential that an in-situ method is used to depth profile the material.

In the current work the CPT has been successfully used to establish the variation in the volume compressibility of aged hydraulically placed PFA deposits by employing the widely used correlation with cone resistance, $m_v=1/(\alpha.q_c)$. As the CPT is not ideally suited to determining the compressibility of low permeability soils, it was necessary to determine the constant in this correlation for the material being investigated. Two approaches have been used to determine a suitable value of α. Firstly the m_v profile from the CPT correlation was compared with m_v measured in oedometer tests on undisturbed PFA samples taken from depth. However, as the volume compressibility estimated from the CPT was at some locations more than twice that measured, further corroboration was considered necessary. Therefore PFA was resedimented in an oedometer cell and its consolidation response was measured. It was found to undergo significant secondary compression, which must be accounted for when estimating m_v for aged PFA deposits. Thus, m_v profiles for aged PFA deposits that were in good agreement with the measured compressibility values, and bounded the CPT correlations, were derived. In this way it was established that a value of α=11 should be used for constant of correlation for normally consolidated PFA that has aged for 20 years.

Calibration chamber testing has been widely used to determine the correlation between CPT data and various soil properties. An implication of this work is that it is inappropriate to rely

on a correlation derived from chamber tests, where ageing cannot be replicated, to determine the compressibility of a material that undergoes significant secondary compression.

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Assessing the potential for attenuation of organic substances within mineral landfill liners

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ABSTRACT

Organic contaminants (e.g. toluene and Mecoprop) are ubiquitous in leachates from biodegradable waste landfills in the UK. The recently introduced Landfill Regulations and the Groundwater Regulations prohibit the entry of these List I substances into groundwater. In landfills, low permeability liners are used as a barrier to reduce the flow of leachate into groundwater, and may also reduce the concentration of such contaminants by attenuation processes such as sorption or biodegradation. However, little is known about the attenuation of organic compounds in landfill liners, and it is necessary to gain an improved understanding of these processes in order to be able to predict their effectiveness over time. The paper briefly describes a programme of research which will extend our understanding of attenuation of organic compounds in landfill liners, and experimental tests which will be used to quantify biodegradation rates and sorption coefficients for common List I organic substances in UK leachates in environmental conditions typical of UK liner materials.

INTRODUCTION

Leachates from UK biodegradable waste landfills contain a wide range of xenobiotics including a number of List I substances such as toluene, naphthalene and Mecoprop (Knox et al, 2000). The EC Groundwater Directive 80/68 (as implemented by the Groundwater Regulations 1998) requires member states to prevent List I substances entering groundwater which creates potential difficulties with regard to the design and operation of such landfill sites. Modern landfills typically rely on low permeability liner systems to reduce (but not prevent) the flow rate of leachate into groundwater. A liner may also reduce the concentration of organic contaminants in the leachate flowing through it as a result of sorption and/or biodegradation processes (Christensen *et al*, 2001). However, the attenuating capabilities of liner materials is rarely considered when the source materials are being chosen. Furthermore, evidence suggests that organic compounds can diffuse through liners even if they are well engineered, although it may take many years (or decades) for the contaminant to reach groundwater in this way (Edil, 2003).

The processes of sorption and biodegradation that determine the fate and transport of organic pollutants within landfill liners are poorly understood. Existing data on biodegradation and sorption of organic substances for use in risk assessments are rarely derived from site-specific observations, and are often taken from studies on surface water or soil environments, which may not be appropriate for the predominantly anaerobic conditions which are found within and beneath landfill liners. Consequently, there is limited confidence in the values being used

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

in regulatory risk assessments. A quantitative understanding of the polluting potential of leachate and the attenuating capacity of artificial geological barriers has, therefore, assumed a high priority, particularly where groundwater is sensitive.

Although a limited number of research projects have demonstrated that organic contaminants diffuse through clay soils, further research is needed to encompass the wide range of List I substances present in UK landfills and the numerous types of clay mineral used in liner systems. This paper describes a programme of research commissioned by the Environment Agency in 2003. The research programme includes a literature review of: (1) the occurrence of List I organic substances in landfill leachates, (2) the range of liner materials used in the UK, and, (3) where the data is available, the attenuation of a number of List I organics in landfill barrier environments. The paper also discusses the laboratory experiments which will be carried out to verify and extend the information collected during the literature review.

LITERATURE REVIEW OF ATTENUATION OF LIST I CONTAMINANTS IN LANDFILL LEACHATES

More than 30 trace organic substances were identified in leachates in the UK Pollution Inventory studies (Knox et al, 2000). This project focuses on the List I substances widely found in UK leachates including BTEX, PAHs, naphthalene, Mecoprop, and organotin substances. Atrazine, trichloroethylene and trichlorobenzenes are found only occasionally in UK leachates, but have been reported in EU landfills (Christensen et al, 2001). Diazinon has been considered because of its use in sheep dip and consequent presence in landfills that received carcasses during the recent UK Foot and Mouth Disease epidemic.

Some of these contaminants are known to biodegrade anaerobically, but the available degradation rates are primarily derived from sub-surface soils or groundwater studies (Table 1). Investigations beneath landfills have demonstrated that anaerobic redox conditions are created due to the passage of landfill gas and leachate (Robinson & Lucas, 1985). Low permeability liner materials will therefore dominated by anaerobic redox conditions (methanogenic or sulphate-reducing) where degradation rates will be different from aerobic environments. Most of these contaminants readily partition onto organic materials and are therefore likely to be retarded by organic-rich clay materials such as those used in mineral liners. Mecoprop however, is only weakly sorbed to clay minerals or organic material at neutral pH, although at lower pH, sorption to mineral surfaces has been demonstrated (Haberhauer et al, 2000).

Table 1: Biodegradation half-lives for a range of List I organic substances.

	Half life (days)			
Contaminant	Methanogenic		Sulphate reducing	
Toluene	33 [1]	Anaerobic groundwater studies	16.5 [1]	Anaerobic groundwater studies
Phenanthrene	NA	—	49 [2]	Unconsolidated sand aquifer
Naphthalene	NA	—	82.5 [3]	Triassic sandstone aquifer
Mecoprop	NA	—	NA	—
1,2,4 trichlorobenzene	2.1 to 34.6 [4,5,6]		NA	—
Trichloroethylene	69[a] [7]		69[a] [7]	
Atrazine	165-315 [8]	Clay-rich soils	NA	—
Diazinon	34[a] [9]	Sandy loam	34[a] [9]	Sandy loam

a – redox conditions not specified NA – no evidence of degradation under these redox conditions

References: [1] Aronson and Howard (1997), [2] King et al (1999), [3] Thornton et al (2000), [4] Middeldorp et al (1997), [5] Adrian et al (1998), [6] Bosma et al (1988), [7] Haston et al (1994), [8] Gu et al (2003), [9] EPA (1999).

EXPERIMENTAL PROGRAMME

Experiments will be carried out to determine anaerobic biodegradation rates, sorption coefficients and retardation factors for a range of List I substances under conditions which reproduce those which might be found in UK landfills.

List I organic contaminants

The number of compounds that could be investigated in the experimental programme will be restricted to toluene, naphthalene, Mecoprop (the three most widely detected List 1 substances in UK leachates), trichloroethylene (widely reported in European and US leachates) and 1,2,4-trichlorobenzene (on-going research (Simoes et al., 2003)). The concentrations of the compounds used in this study will be chosen such that it is not be less than the median concentration found in UK leachates, so that the findings are as relevant as possible to UK conditions. However, to ensure that attenuation processes can be followed with normal analytical techniques, concentrations will be at least 10 times greater than the readily-achievable detection limit. The range of concentrations of List I organic substances used in the study is given in Table 2.

Table 2. Concentrations of the List I organic substances relevant to this study.

Substance	Frequency of occurrence (%) in UK leachates[1]	Median conc. (µg/l) found in UK leachates[1]	Typical detection limit (µg/l)	Proposed conc. (µg/l) for biodegradation tests[3]	Proposed conc. (µg/l) for sorption tests
Toluene (BTEX)	54	21	0.1	100	10-1000
Naphthalene	70	0.46	0.1	38	0.5-50
Mecoprop	98	11	0.1	11	1-100
Trichlorobenzenes	<5	1[1]	0.1	42	0.3-30
Trichloroethylene	<5	5.6[2]	1	33	1-100

Notes. 1. Knox et al (2000).
2. Mean report in study of US landfills, where compound was present in ~70% of samples (Ref).
3. Initial concentrations adjusted to allow for sorption of contaminant to liner material.

Synthetic leachates will be used in the experiments to ensure consistency. Four classes of landfill leachate have been identified: conventional MSW (municipal solid waste)/non-hazardous landfill; leachate from separated and composted MSW (mechanical biological pre-treatment (MBP) leachate); leachate from bottom ash after incineration of MSW; and leachate from treated hazardous wastes meeting European acceptance criteria (EA, 2003a & 2003b). The MSW leachate has been chosen as an example of a methanogenic leachate and the MSWI bottom ash leachate as an example of a sulphate-reducing environment.

Liner materials

There are a wide range of clays and mudrocks available across the UK for use in the construction of landfill mineral liners. The high cost of haulage means that locally derived materials are preferred. The materials used are engineered to meet certain performance criteria, which typically include a maximum hydraulic conductivity of $1x10^{-9}$ m/s. Most UK clays and many mudrocks (with a reasonable degree of plasticity) can be engineered to meet

these requirements. The ratio of smectite to total solids provides an approximate indication of the plasticity of a liner material. Smectite may contribute to sorption of trace organics but generally, the amount of organic material in a liner has the greatest effect on partitioning and sorption. Three liner materials have been selected for study to provide a wide variation in organic carbon content:

1. Mercia Mudstone (30-60% illite) or Etruria Marl (40% kaolinite) – low organic content (1%), .
2. London Clay – moderate organic content (~2-4%), approximately 50% illite, 30% smectite and 20% kaolinite (as a proportion of total clay).
3. Oxford Clay – high organic content (6 %) dominated by illite and kaolinite.

Samples of the three liner materials will be characterised with respect to: (i) organic carbon content, by high-temperature after carbonate removal by acid, (ii) CEC, by the BaCl2-triethanolamine method (EA, 2000), (iii) particle size distribution (by wet sieving and laser diffraction), (iv) mineralogical composition by X-ray diffraction, (vi) specific surface area, and (vi) reactive Fe-Mn oxides (Heron et al, 1994).

Biodegradation tests

Organic contaminants can be transformed into intermediate products and/or carbon dioxide by the action of naturally occurring microorganisms present in the environment. The intermediate products may be more or less persistent, and more or less hazardous, than the parent compound. For biodegradation to occur the contaminant must be in aqueous solution; sorption onto the matrix may render contaminants less available to microbial transformation. Anaerobic biodegradation may involve the direct utilisation of contaminants as sources of carbon and energy. Some organic compounds cannot be biodegraded in this way, but other processes, such as reductive dehalogenation, may also lead to the microbial degradation of such substances. This often requires the presence of other biodegradable materials, which can include other contaminants.

The biodegradability of organic contaminants in or below a landfill liner may be investigated by three different approaches: (i) microcosm studies, (ii) detailed monitoring of the organic contaminant distribution in a leachate plume, and (iii) field injection experiments (Christensen *et al.*, 2001). Microcosm studies typically involve isolating a volume of the liner material with leachate containing the organic contaminants in a reactor, and subsequent measurement of the contaminant fate over time. Detailed monitoring of the organic contaminant distribution in landfill plumes is usually associated with labour and cost-intensive sampling and analysis, and hence has been studied in great detail only at a few landfills. Field injection experiments involve the injection of a stock solution of the organic contaminants into the subsurface and monitoring of the cloud formed. Both injection or plume monitoring techniques provide useful information under field conditions, but microcosm studies allow better control of experimental conditions and are the chosen technique for this experimental programme.

The biodegradation of each List I substance will be studied by microcosm studies under two redox conditions (methanogenic and sulphate reducing). 1 L bottles containing synthetic leachate, bacterial seeds, the liner material and the mixture of List I substances will be sealed and stored in an anaerobic cabinet. The bacterial seeds will be obtained from leachate taken from selected sites, preferably already containing the List I substance to ensure that the microorganisms are acclimatised to the contaminants. The liner is expected to sorb some of the organic contaminant making it unavailable to biodegradation and the mass of liner added

to each bottle will take this into account. A gas headspace of 80/15/5 (%nitrogen/carbon dioxide/hydrogen) will be applied above the liquid level of the bottles. Approximately 10 samples of 20 ml of leachate will be collected from each bottle during the period of the test. Analysis of the List I organic substances will be carried out by GC/MS electron impact scan (EI) and GC/MS/MS to identify biodegradation products (EA, 2003c). For each redox condition studied, two control tests will be included:

1. Biodegradation in the absence of liner material,
2. Biodegradation inhibited to allow sorption to the liner material to be evaluated.

The limitations of the time available for this study only allow the biodegradation tests to be carried out under one incubation temperature (25°C) and one initial inoculum concentration of each List I substance. In addition to biodegradation tests containing a mixture of all five List I substances, a second test containing only Toluene, Naphthalene and Mecoprop will be run. As all these substances are widely found in UK leachates, a mixture containing them all is a realistic scenario to investigate. A third biodegradation test with one liner material and naphthalene will provide information on competitive biodegradation processes involving naphthalene in the presence of the other contaminants.

Sorption tests

A number of laboratory methods are commonly used in the literature to determine sorption coefficients: (i) laboratory batch method, (ii) miscible displacement, and (iii) equilibrium dialysis. The techniques used and the assumptions underlying each experimental method are different. Consequently, sorption coefficient values measured by different methods commonly have values ranging over an order of magnitude. In this study, batch sorption tests and miscible displacement tests will be carried out. Batch sorption tests, also known as batch isotherm tests (where the tests are carried out at a specific temperature), are standard methods used to determine the sorptive capacity of a soil for a dissolved substance. In batch testing, the uncontaminated solid (clay) is placed into a vial to which solutions of containing a range of contaminant concentrations are added. The vials are sealed, shaken until equilibrium is reached, and then centrifuged to allow the sorbed and aqueous concentrations to be determined (Figure 1). For each contaminant concentration, the sorbed mass is plotted on a graph and in the case of linear sorption, the slope of the graph will be a straight line with gradient K_d.

In this study, the sorption coefficients for List I substances on each liner material will be obtained from sorption isotherms determined over a concentration range of two orders of magnitude (Table 2). Sorption of each List I substance will be studied individually (single solute isotherms). Stock solutions of the List I substances will be prepared by adding the appropriate amount of each compound to a suitable solvent, such as methanol, prior to mixing with the synthetic leachate. To reduce experimental errors, the amount of the liner material used will be adjusted to achieve 20-80% sorption of the List I compound. The liner material will be air dried, lightly ground with a mortar and pestle, then weighed into glass bottles (internal volume 122 ml, Sigma Aldrich UK) which will be filled to the top, leaving no headspace, with the synthetic leachate containing the List I compound. Biological inhibitors such as sodium azide or mercuric chloride will be added to the bottles to repress biological activity (Nielsen *et al.*, 1996). The bottles will then be sealed with aluminium caps with Teflon®–coated septa (Supelco UK). All sorption tests will be carried out at 20°C in a constant temperature room. On completion of each batch test, duplicate samples of the supernatant liquid will be collected from each vial for analysis.

For each test, three sets of controls will be prepared:
Control 1. Synthetic leachate, List I compound and biological inhibitors but no liner material – sampled at the start of the sorption test to provide a reliable value for the initial concentration of the List I compound(s).
Control 2. Synthetic leachate, List I compound and biological inhibitors but no liner material – to identify any loss of the compounds by sorption to the bottles.
Control 3. Synthetic leachate, List I compound and liner materials but no biological inhibitors –to assess if the biological inhibitors are effective.

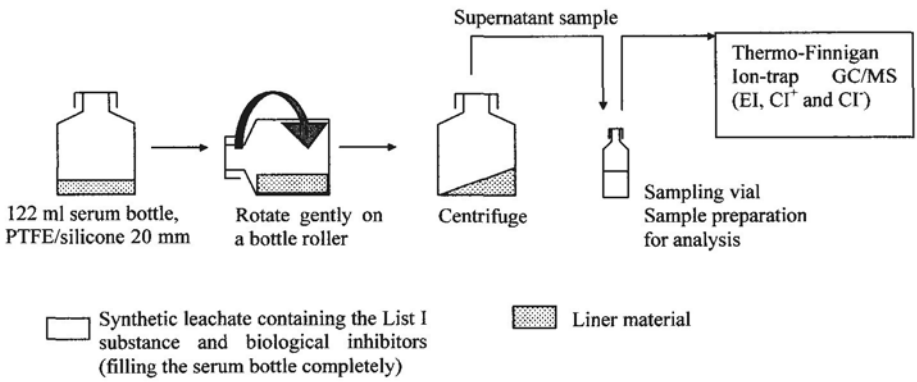

FIGURE 1: Experimental set-up of the batch sorption tests

Soil column tests

In the miscible displacement technique a solution containing the solute is injected under saturated, steady state flow conditions, through a column packed with the soil or sediment until sorption equilibrium is reached (equal inlet and outlet concentrations). Samples of the column effluent are collected over time and analysed. A known amount of non-adsorbing tracer may also be introduced into the column and its time-varying concentration used to provide information about the pore-water velocity. The sorption coefficient can then be calculated from the retardation factor (ratio of the pore-water velocity to the contaminant velocity) and soil properties. Methods involving soil columns are appealing in that they couple the effects of transport through the soil with chemical and/or biological reactions. One of the unique characteristics of this method is that non-equilibrium conditions can be imposed. This is especially true under conditions in which the solute has slow sorption kinetics or when groundwater flow is fast, where a measure of sorption at equilibrium may overestimate the extent to which sorption occurs under actual field conditions.

In this study, soil column tests will be carried out using inert (PTFE) triaxial cells (Figure 2). This is a novel method by which the *in-situ* void ratio and soil structure of a landfill liner can be maintained and the typical stress conditions found at the base of a landfill replicated. The triaxial cell also eliminates the possibility of preferential flow occurring between the sample and the side of the apparatus. Different horizontal and vertical stresses can be applied to the soil sample simultaneously to closely replicate the expected field conditions. The triaxial cells consist of a transparent acrylic cylinder enclosed by corrosion-proof metal top and base plates. A cylindrical sample of liner material is contained inside a thin latex membrane and

saturated with water. The soil sample is subjected to an all-round isotropic stress obtained by pressurising the cell fluid (confining pressure). In this study, suitable confining pressures and hydraulic gradients will be applied to the liner materials using constant pressure systems. The liner materials will be prepared to give a hydraulic conductivity of approximately $1x10^{-9}$ m/s, with a maximum applied hydraulic gradient of 20.

Diffusion tests on the PTFE layer surrounding the liner material in the triaxial cell will be carried out to determine whether the organic contaminants are diffusing through this layer. The liner materials will be initially saturated in distilled water to establish mechanical equilibrium. After this, the contaminant cocktail (synthetic leachate containing the List I substances selected for the study), will be introduced and at least five pore volumes will be allowed to pass through the sample. A known amount of conservative tracer (e.g. bromide or deuteriated water) will be included and its concentration measured over time to allow calculation of the pore-water velocity. Sampling of the column effluent will proceed for the duration of the test. Upon completion of the test, the triaxial cell will be dismantled and the liner material sliced to facilitate identification of the contaminant front throughout the length of the liner material. The data collected will allow the determination of retardation factors.

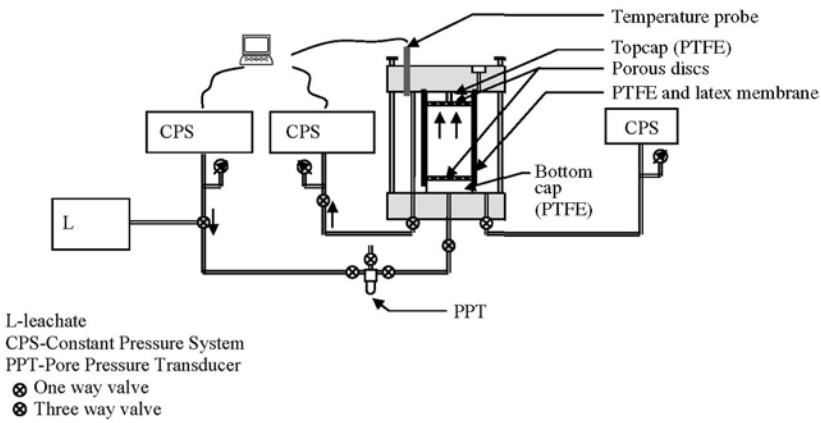

Figure 2: PTFE Triaxial cell

SUMMARY

Little is known about the attenuation of organic List I contaminants found in landfill leachate by mineral landfill liners. A research project commissioned by the Environment Agency has reviewed the literature on organic pollutants in leachate, the characteristics of common UK mineral liners, and the sorption and anaerobic biodegradation of List I substances in conditions typical of the liner environment. An experimental programme is being carried out to verify and extend the results of the literature review. The results from this work will provide improved data for the performance assessment of the attenuating capabilities of mineral landfill liners for organic pollutants, and therefore support implementation of the Landfill and Groundwater Directives.

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MINE WASTES AND WATERS

Comparative Plant Growth and Metal Removal in Two Adjoining, Cognate Wetlands (Shilbottle, UK), One Receiving Acid Mine Spoil Leachates, the Other Alkaline Surface Runoff from Revegetated Spoil.

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ABSTRACT
The generation of contaminated waters from abandoned mine sites is a widespread problem and continues to adversely affect many water courses in the UK and throughout the world. The abandoned mine of Shilbottle Colliery, Northumberland is an example of acidic spoil heap discharge that contains elevated levels of many metals including Fe, Mn and Al. Aerobic wetlands planted with the common reed, *Phragmites australis* were constructed at the site to treat surface runoff from the spoil heap. However the presence of a perched water table within the spoil heap resulted in one of the wetlands (lower) receiving acidic metal contaminated water from within the spoil heap. The other wetland (upper) received alkaline, uncontaminated surface runoff from the spoil heap which had been mulched with paper waste This unique situation enabled the comparison of metal uptake and growth of plants used in treatment schemes in two cognate wetlands.
Results from 18 months of monitoring indicated a significant difference in plant growth between the two wetlands in terms of shoot height and seed production. The inhibition of growth in the lower wetland was attributed to one or more of three possibilities which are discussed in detail:- i) the toxic effects of high levels of metals, particularly iron in shoot tissues, ii) the inhibition of Ca (an essential nutrient) uptake by the presence of metals and H^+ ions, and iii) low concentrations of bioavailable nitrogen sources in the lower wetland resulting in nitrogen deficiency in plants.

INTRODUCTION

Vegetation is an important component of constructed wetlands designed to treat metal-contaminated mine water (e.g. Batty 2003). However, in some cases the vegetation has either failed or has proved difficult to establish (D.Phillips, B.Hedin pers. comm). The reasons for this have not been thoroughly investigated. The presence of reed beds at the mine site of Shilbottle, Northumberland, UK has provided the opportunity to undertake investigations into the potential effects of highly contaminated waters on wetland vegetation.

Coal mining at the now-abandoned site of Shilbottle Colliery resulted in the production of a large spoil heap at the location. Water infiltrating into the spoil heap has resulted in the generation of highly acidic spoil drainage which runs into the Tyelaw Burn and has been causing pollution of this watercourse over many years. The initial remediation scheme, which was installed in 1996, involved revegetation of the spoil heap together with construction of a series of three aerobic reedbeds (planted with *Phragmites australis*) to treat the surface runoff from the spoil heap. However, this remediation proved unsuccessful as the

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

majority of the highly polluted water was present as groundwater and thus bypassed the two upper reed beds and flowed either into the lower reed bed or directly into the Burn. These groundwaters typically have a pH of 3, zero alkalinity and contain iron and manganese concentrations of 1000mg.L^{-1} and 500mg.L^{-1} respectively. These polluting discharges caused staining of a significant portion of the Burn and smothering of aquatic life by ochre precipitation.

A second stage of remediation requiring treatment of the groundwater was installed in the winter of 2002 and consists of a subsurface permeable reactive barrier (Younger *et al.* 2003). In the intervening period between the two stages of remediation, the revegetation of the spoil heap was successfully completed through the use of waste paper mulch and surface runoff from the heap enters the two upper reed beds.
This provided a unique opportunity to compare and contrast the growth of plants and metal uptake by plants in two adjoining and cognate wetlands, eliminating normal problems of site-specific environmental (climatic) conditions.

METHODS

Sampling at the Shilbottle site was carried out at 2-monthly intervals from December 2000 and continued until May 2002 with a 6 month hiatus due to the Foot and Mouth outbreak in the UK in 2001. The interval between sampling dates allowed a certain amount of recovery in the wetlands. Sampling was undertaken in one of the upper wetlands receiving surface runoff from the spoil heap and in the lower wetland receiving the groundwater leachate. For each wetland there were three sampling sites located at the inlet, centre and outlet of the wetland. Samples were collected at least 1 m from the edge of the wetland.

Six samples of surface water were taken on each date which allowed for three replicates of acidified, using concentrated nitric acid (for metal analysis) and non-acidified (for anion analysis) water. Samples were collected in clean polyethylene bottles and kept at 4°C until analysis which was carried out by Atomic Absorption Spectrometry (AAS) (Unicam 929) for metals, and Ion Chromatography (Dionex DX-100) for anions.

Random quadrat (1m x 1m) sampling was undertaken in each wetland. Within each quadrat shoot density, shoot height and number of seed heads were analysed as an assessment of plant growth. Due to the rhizomal nature of *P.australis* it was not feasible to assess the number of individuals in each quadrat and thus shoot density was substituted for this measure.

Bulk plant samples (3 individuals) were collected at each of the 6 sampling sites. Each plant sample was thoroughly washed in distilled water prior to being divided into roots, rhizomes and shoots. Each section was placed in a labelled envelope and dried at 40°C for 3 days. The resulting material was placed in a desiccator and cooled to room temperature before being ground in a knife mill. A subsample (0.5g) of dried plant material was then acid digested in 5 mL of 30% HNO_3 at 90°C for a minimum of 8hrs. Total metals were determined using AAS. A further subsample (0.5g) of plant material was subjected to a Total Kjeldahl Nitrogen digest in order to determine organic nitrogen content which was measured as ammonia using a Vadopest method. Adequate blanks and a standard reference material (BCR Hay powder) were used to check for contamination and extraction efficiency (calculated to be 95%). All surface waters and plant samples were analysed for Fe, Mn, Al, Ni, Ca, Mg, Na, K and nitrogen. Surface waters were also analysed for sulfate.

RESULTS AND DISCUSSION

Due to the large amount of data collected it is not possible to present all the results here, many of which did not show any discernable pattern or relationship. However there were some important patterns that were identified.

Concentrations of Fe, Mn, Al, Ni, Ca and sulfate (all results not shown) were all significantly higher in the contaminated wetland and this was particularly true for the input samples. In the case of Fe (figure 1) significant amounts of the metal were removed by the lower wetland decreasing from ≈ 450 mg. L^{-1} to between 0.5 and 10 mg.L^{-1} at the output. This is mostly the result of the formation iron hydroxide deposits in the wetland, evident as thick orange deposits. It is surprising in light of this, that there was not a corresponding fall in pH across the lower wetland as the formation of iron hydroxides generates acidity. This suggests that there is a certain amount of buffering capacity within the lower wetland.

The height of shoots in the uncontaminated wetland (Table 1) were consistently higher than those in the contaminated wetland, with a difference which varied from ≈ 30 to 100cm. This suggests that the high concentrations of metals and sulfate that are present in the contaminated wetland may have adversely affected growth of *P. australis*. Alternatively this

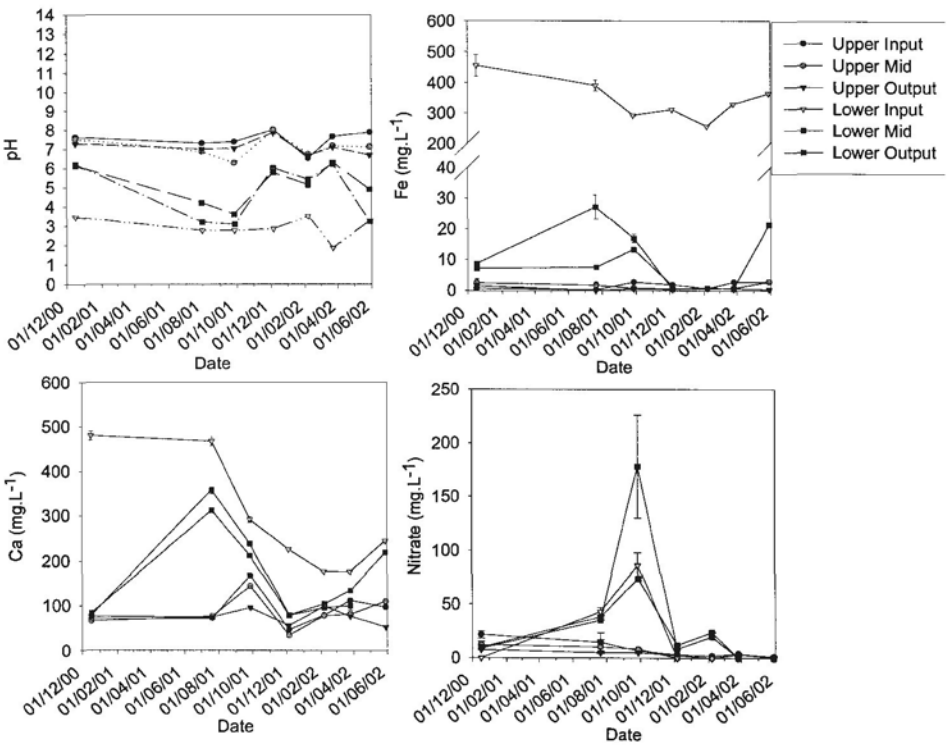

Figure 1 pH, Fe, Ca and nitrate concentrations of surface waters in upper (uncontaminated) and lower (contaminated) wetland. Error bars are mean ± SE (n=3)

inhibition of growth may have been caused by differences in nutrient concentrations although phosphate concentrations were below detection in both wetlands.

Shoot density was not significantly different between the two wetlands suggesting that production of shoots was not adversely affected by high metal concentration. In both wetlands visual observations identified the presence of large areas of open water where there is no plant growth. This may be due to variations in water depth across the wetlands, but this needs further investigation.

The production of seeds appeared to be inhibited by the presence of high metal concentrations with consistently lower numbers of seed heads being produced in the contaminated wetland. Investigations into the viability of the seeds produced indicate that both wetlands produce seeds with extremely low viability. This is not unexpected as northern populations of *P. australis* have been shown to flower too late to produce viable seeds (McKee & Richards 1996). Spread of the population therefore is most likely to be by vegetative propagation through rhizomal spread.

	Shoot Height (cm)						**Shoot Density (no/ m^2)**						**No of Seed Heads/ m^2**					
	Wetland 1 (Uncontaminated)			**Wetland 2 (Contaminated)**			**Wetland 1 (Uncontaminated)**			**Wetland 2 (Contaminated)**			**Wetland 1 (Uncontaminated)**			**Wetland 2 (Contaminated)**		
Date	In put	Mid	Out put	In put	Mid	Out put	In put	Mid	Out put	In put	Mid	Out put	In put	Mid	Out put	In put	Mid	Out put
12/00	194 ±7	187 ±9	186 ±13	153 ±17	161 ±15	112 ±9	153	140	124	99	220	162	14	13	2	8	1	1
07/01	202 ±14	243 ±10	206 ±13	179 ±10	179 ±10	163 ±4	167	137	103	117	170	117	–	–	–	–	–	–
09/01	200 ±8	251 ±12	250 ±12	175 ±10	176 ±11	120 ±7	165	140	108	100	180	120	8	1	7	3	0	6
11/01													16	16	9	5	7	7
01/02													-	-	-	-	-	-
03/02																		
05/02	135 ±3	124 ±6	134 ±10	102 ±3	94± 2	96± 5	170	145	156	87	135 0	123	-	-	-	-	-	-

Table 1. Ecological characteristics of vegetation at Shilbottle. Shoot height is given as mean ± SE (n=3)

Shoot height and density is not measured in winter when the plants are dormant.

Root concentration of iron (figure 2) was consistently higher in plants from the contaminated wetland than the uncontaminated reaching a maximum concentration of 124368 $mg.kg^{-1}$ dry wt. Fe. There was no consistent pattern across the wetland despite large differences in the surface water concentration of Fe across the wetland (Figure 1) This indicates that there is a limit to the root concentration that can occur which cannot be exceeded despite increased Fe availability. The majority of the iron measured as root concentration was present as a deposit upon the root which is referred to as iron plaque (e.g. St Cyr *et al.* 1993; Batty *et al.* 2000)). This was either visible upon roots as either a deep orange colour where Fe concentrations were low or as a visible solid deposit upon the root particularly on plants from the inlet of the lower wetland. In the upper uncontaminated wetland the plaque was present as a light orange/brown colouring on the roots which was not visible on all roots excavated from the site. This is reflected in the quantitative data.

Shoot concentrations of iron were consistently higher in those plants from the contaminated wetland and in many cases the concentration exceeded that normally defined as being phytotoxic (1100 to 1600 $mg.kg^{-1}$ dry wt (Marschner 1995)). With the exception of two samples the toxicity level is exceeded only in the plants from the contaminated wetland

which may be one of the causes of the reduced growth in the lower wetland. Although tolerance to metals is often species-specific it is likely that the extremely high concentrations of Fe encountered in shoots from the lower wetland (up to 8445 $mg.kg^{-1}$ dry wt) has a negative effect on plant growth. Details of aluminium results have not been presented here, but the high concentrations of Al found in the waters entering the lower wetland ($\approx$ 200 $mg.L^{-1}$) may also impact upon the growth of *P.australis*. Aluminium can be toxic at low pH causing inhibition of root growth (Taylor 1988), however when there are extremely high concentrations of H^+ ions, this can actually have an ameliorative effect on Al toxicity due to high competitiveness with Al^{3+} of H^+ (Grauer 1993).

For the majority of the year the concentrations of calcium in shoots was higher in plants from the upper wetland than the lower contaminated wetland. This is particularly true for the two main growth activity periods of the year for *Phragmites australis*, May and September. Calcium concentrations in rhizomes were also higher during these periods in plants from the upper wetland. This pattern was not apparent for the root concentrations. Calcium plays a vital role in the structure of macromolecules such as cell walls and plasma-membrane and is also important in the cation-anion balance in vacuoles. Concentrations of Ca for adequate growth in plants is normally around 0.5% shoot dry matter. In the majority of cases both for the upper and lower wetlands this percentage was not reached although some plants in the upper wetland do contain more than 0.5% Ca shoot dry matter. Concentrations of Ca in new shoots is particularly important as Ca cannot be mobilised from older tissues thus forcing the developing tissues to rely on the immediate supply of Ca (White & Broadley 2003). However, calcium requirements in monocotyledons (e.g. *Phragmites australis*) is often lower than that for dicotyledons (Loneragan *et al.* 1968) and thus those plants in the upper wetland which overall contain higher concentrations of Ca in shoot tissues may be able to function normally, the lower concentrations in the contaminated wetland may be significant enough to reduce growth. The lower concentrations in the contaminated wetland plants occurred despite higher concentrations of Ca in the surface waters of the lower wetland. It is possible that the presence of elevated concentrations of metals in the lower wetland may inhibit uptake of Ca into plant tissues. Ca requirements have been shown to be higher with increasing external concentrations of heavy metals (Wallace *et al.* 1966). H^+ ions can also inhibit uptake of Ca by competing for binding sites on roots. The low pH in the lower wetland indicates the presence of high concentrations of hydrogen ions. Calcium deficiency although rare in nature has been shown to occur where there is high levels of acidic deposition (McLaughlin & Wimmer, 1999). It may be the case that the presence of iron plaques on the roots may also reduce Ca uptake. However there was no statistical correlation between iron in roots and Ca in shoots suggesting that there is not a causal relationship. This is most likely due to the fact that Ca uptake is much higher in apical than basal root zones (Ferguson & Clarkson 1976; Haussling *et al.* 1988). Iron plaques do not occur at the apical part of the root tip (Crowder & St Cyr 1991; Batty *et al.* 2000) and as such would not impede the uptake of Ca at this active part of the root.

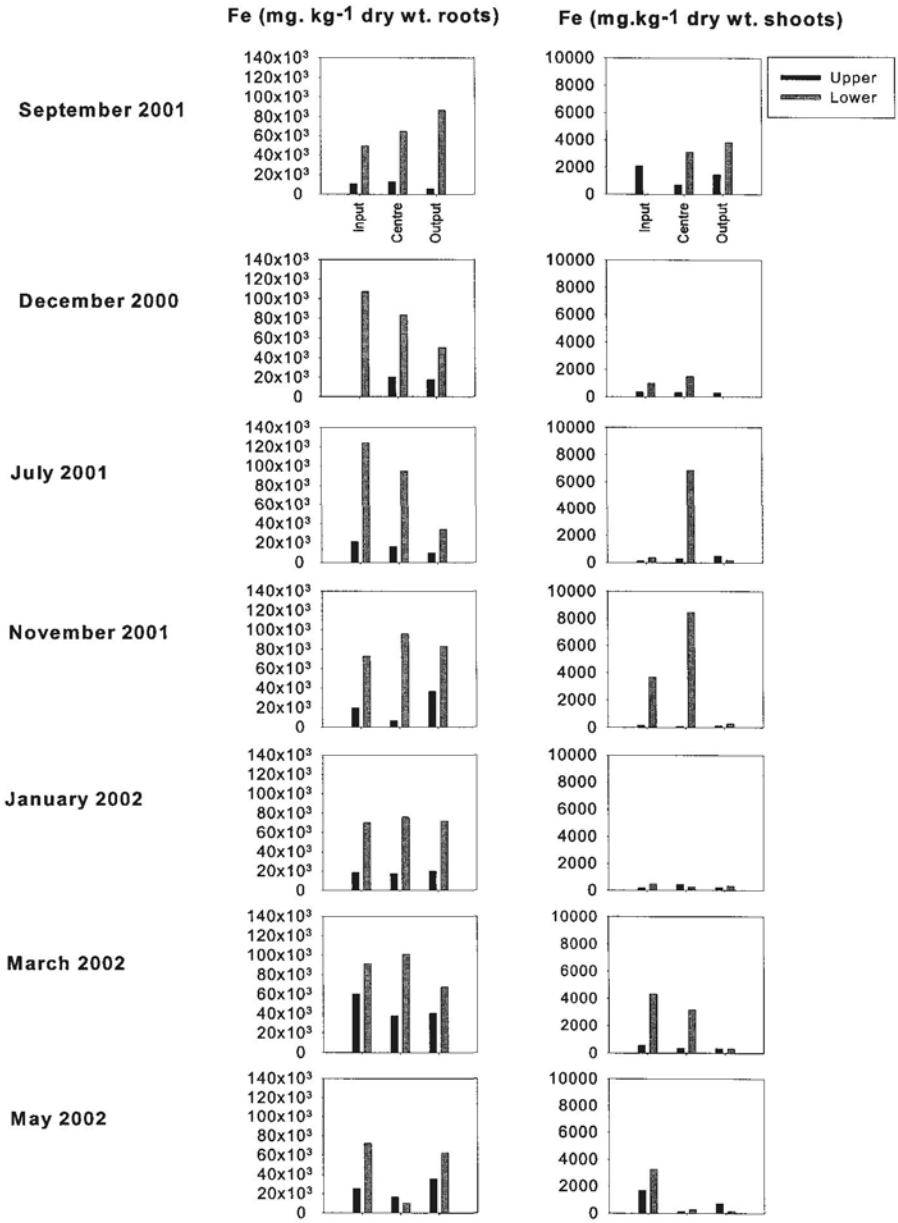

Figure 2. Fe concentrations (mg.kg^{-1} dry wt.) in plant tissues from the Shilbottle wetland (upper wetland is uncontaminated. lower contaminated).

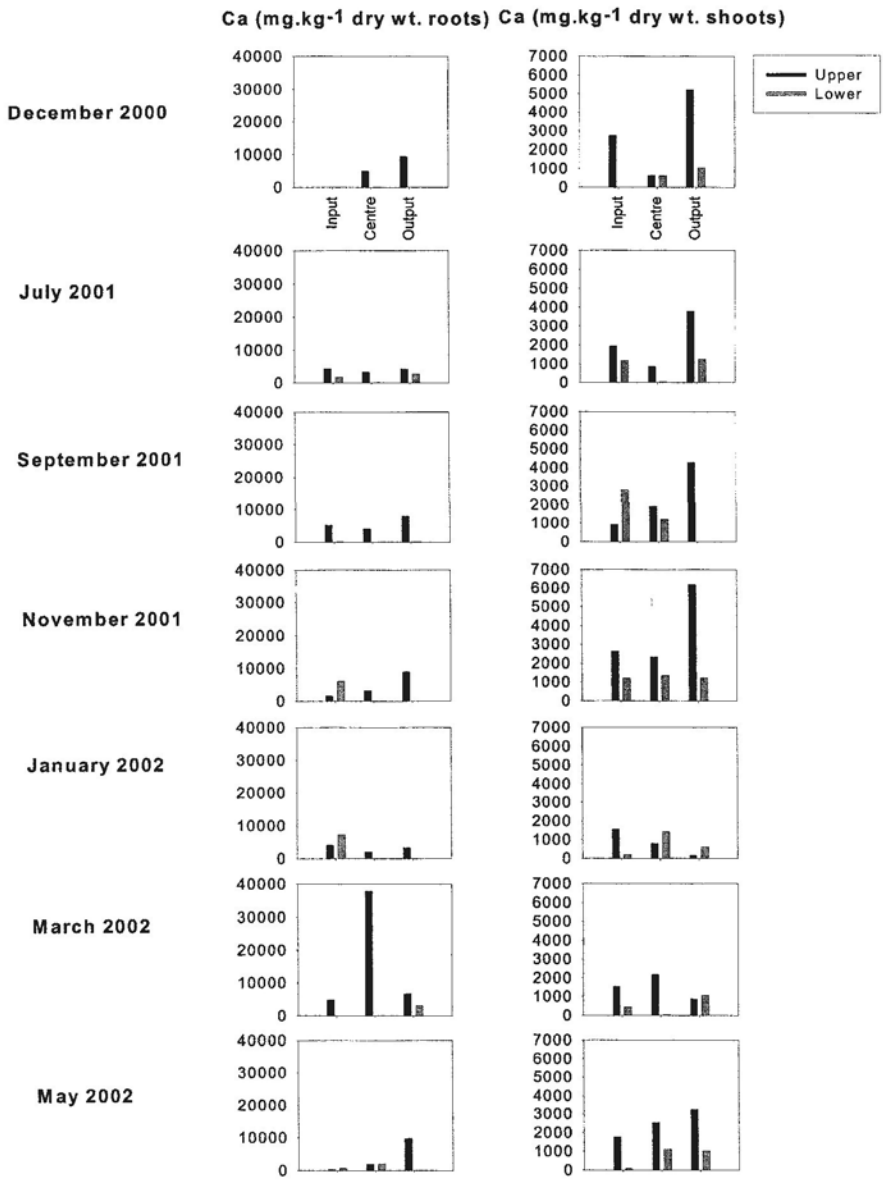

Figure 3. Ca concentrations (mg.kg^{-1} dry wt.) in plant tissues from the Shilbottle wetland (upper wetland is uncontaminated. lower contaminated)

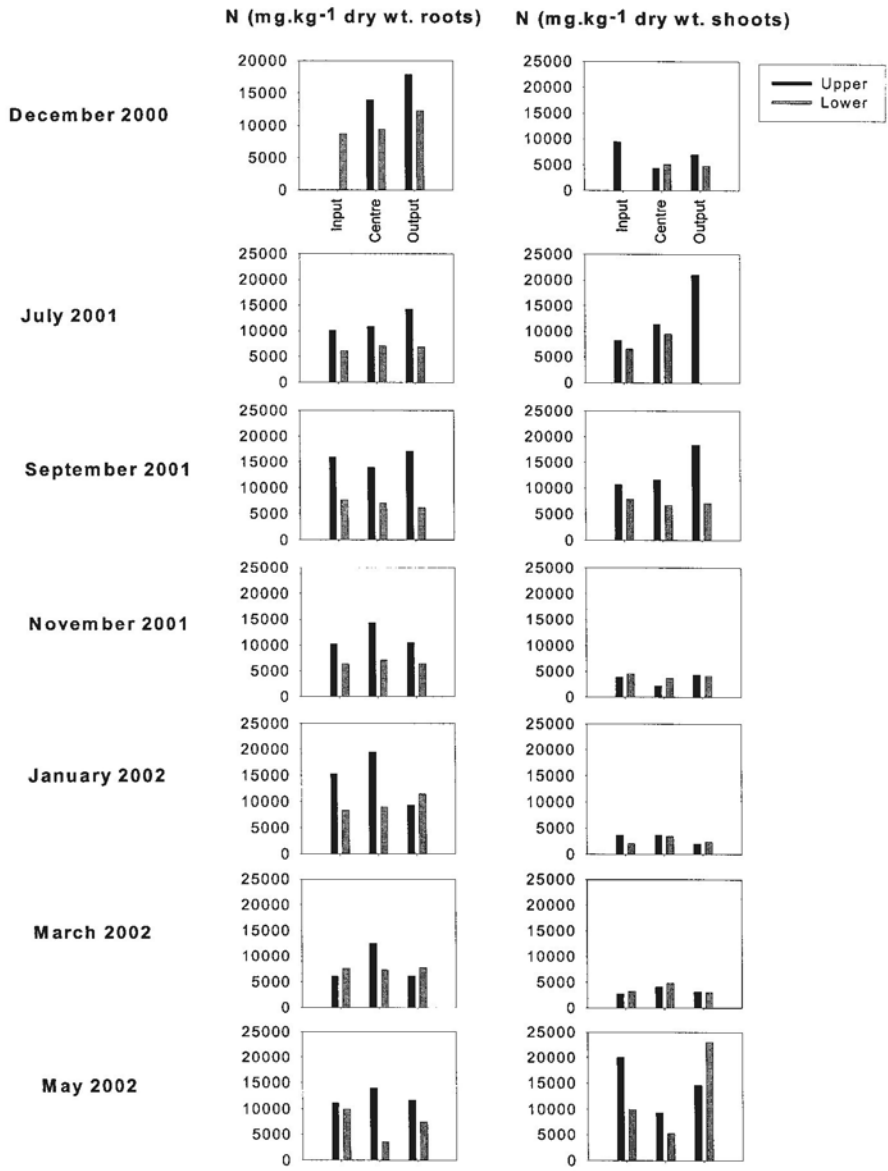

Figure 4. Nitrogen concentrations (mg.kg dry wt.) in plant tissues from the Shilbottle wetland (upper wetland is uncontaminated. lower contaminated)

Concentrations of nitrogen in shoot tissues was higher in the growth periods of *P. australis* which is to be expected. Concentrations in plant tissues were generally higher in plants from the upper wetland during growth periods, whereas there was little difference between plants from the two wetlands during the dormant period. In the majority of cases, particularly in the lower wetland nitrogen concentrations were typically lower than those considered to be adequate for normal plant growth, about 1 to 5% of plant dry weight (Marschner 1995). Concentrations of nitrate entering both wetlands fall between the classifications of moderate to very high in terms of normal stream water as classified by the UK Environment Agency and thus supply of nitrate should be sufficient for uptake by plants. However plants that are adapted to low soil redox potential such as wetland rice have a preference for ammonium as the source of nitrogen (Ismunadji and Dijkshoorn 1971). Thus it may be the case that although nitrate concentrations may be higher than normally found in stream waters, the plants are unable to use this and the ammonium concentration is much lower. Unfortunately ammonium concentrations are not available and so this hypothesis cannot be tested.
Root concentrations of nitrogen were higher in plants from the upper wetland in most of the samples. This is despite generally lower concentrations of nitrate in the surface waters. This again could be due to differences in the forms of nitrogen in the surface waters but concentrations of ammonium are not available. The differences in concentration could also be due to competition in the lower wetland from the elevated concentrations of metal ions and sulfate.

CONCLUSIONS

Vegetative analysis of the contaminated and uncontaminated wetlands identified significant differences in the growth of *Phragmites australis* which was evident as a reduction in shoot height and reduced seed development. No differences were found in shoot density which showed great variation and was more likely to be due to variation in water depth across the wetlands. Analysis of the plant tissues in the two wetlands showed large differences in many cases between the two wetlands. However, it appeared that there were a number of potential explanations for the differences in growth observed.

Although it seems plausible that there is some impact of nutrient deficiency in terms of nitrogen and calcium upon the growth of *Phragmites australis* in the lower wetland, the presence of potentially phytotoxic concentrations of Fe in the shoots of the plants is more likely to be the cause of the reduced growth. It has been found that the ability to tolerate excessive Al, Mn and Fe that largely determines the flora of acid soils (Lee 1999) rather than nutrient deficiency. Further investigation are necessary to determine whether this is the case for *Phragmites australis* growing in temperate wetland conditions.

These conclusions have important implications for the engineering of constructed wetlands. The presence of very high concentrations of metals both in the roots and shoots of the plants growing in the wetlands Seasonal die-back of shoots and natural turnover of roots may release significant quantities of metals back into the dissolved phase than has previously been thought. However as the majority of the Fe is associated with roots and rate turnover of roots varies with species it is unlikely to occur concurrently in all plants in a given wetland although further investigations are required.

It appears from the results that metal toxicity is the most likely cause of reduced growth of plants in wetlands suggesting that the use of plants may not be suitable for situations where waters to be treated contain extremely high levels of potentially phytotoxic metals. In addition the potential problems associated with reduced nutrient uptake possibly connected

with the presence of high concentrations of metals and H^+ ions has important implications for the suitability of planted wetlands for heavily contaminated waters. If the uptake of nutrients are impeded by the activity of metals and H^+ ions then simple additions of nutrients may not overcome any deficiency problems. Further investigations are required into these engineering considerations.

ACKNOWLEDGEMENTS

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The Co-treatment of Sewage and Mine Waters

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ABSTRACT
A groundbreaking trial aerobic wetland has been built by Newcastle University at Birtley, Gateshead, Tyne and Wear. The wetland is the first of its kind to treat both a mine water and a secondary sewage effluent together. Both of these discharges currently enter the River Team, a tributary of the River Tyne, and have a significant effect on its water quality. The total mine water and sewage water discharges to the river are ~300L/s and 100L/s respectively and therefore the waters are being treated in this ratio at pilot-scale (25m x 25m). The main drivers for remediation are Fe (~3mg/L in the mine water), BOD (~14mg/L in the sewage water), N-NH_3 (~2mg/L in the sewage water), suspended solids (~23mg/L in the sewage water) and PO_4 (~7mg/L in the sewage water).

The combined treatment has many advantages over separate treatment of the discharges. The synergistic relationship between the two waters results in greater removal rates for all the main contaminants. Suspended solids in the sewage water encourage iron floccs to form and precipitate and may also enhance manganese removal. Phosphate, which is generally difficult to remove using either active or passive treatment is removed via sorption onto iron oxyhydroxide precipitates. In addition, the ochreous deposits provide numerous ideal sites for the attachment of nitrifying and denitrifying bacteria.

Although the wetland is still immature, initial results suggest that co-treatment is highly successful. Effluent concentrations have consistently been lower than Environment Agency effluent design standards and removal rates for all parameters are likely to improve with time as both biological and microbiological communities become established.

BACKGROUND

The River Team is an urban river which flows generally northwards from Stanley in County Durham to join the River Tyne at Dunston Coal Staithes in Newcastle upon Tyne. Water quality in the River Team is poor and the Team is currently graded as a Class 4 watercourse on the Environment Agency's (EA) General Quality Assessment (GQA) scale. The two largest discharges into the stream (see arrow on Figure 1) are the secondary sewage effluent from Northumbrian Water's (NWL) Sewage Treatment Works (STW) (~100L/s Dry Weather Flow (DWF)) at Birtley and the Coal Authority's (CA) net-alkaline pumped mine water discharge (~300L/s) from Kibblesworth. The River Team Revival Project has been set up by the Environment Agency to improve the status of the river and the surrounding environment. As part of this aim, the encouragement of all industries operating in the catchment to invest in further environmental improvements is a key activity. The major drivers for NWL in line

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

with AMP4 requirements are BOD, N-NH_3 and SS (currently ~ 14mg/L, 2mg/L and 23mg/L respectively in STW water, averaged since the start of the pilot scheme). The CA are interested in reducing the impact of iron concentrations (currently ~3mg/L) on the River Team. The issue of consent to discharge for the wetland is not straightforward due to the joint venture nature of the project but the Environment Agency are working together with both parties in order to ensure that this issue is resolved satisfactorily.

INTRODUCTION

Wetlands are a common form of treatment for both sewage effluents and for mine waters (eg Weedon, 2001 and Younger, 2002). However there are grounds for supposing that the combined treatment of both sewage and mine water together is advantageous. Data provided by Surface *et al* (1993) show that constructed wetlands similar to those used for mine water treatment, were able to successfully remove BOD, organic carbon, P, NH_4^+, Fe, Mn and K from a landfill leachate. Although traditional thermodynamics suggests that iron (and manganese especially) will not be oxidised until ammoniacal nitrogen has been oxidised (via nitrite to nitrate) (Vandenabeele, 1995) several authors have found (Gouzinis, 1998, Mouchet, 1992) that when ammonium concentrations are low (<2mg/L) iron removal is seemingly unaffected. For this reason it was predicted that combined treatment would have many advantages over separate treatment of the discharges. Of course, a wetland which will treat both discharges is also an attractive option both from a logistical (in terms of land required) and most probably a financial point of view. From a hydrochemical point of view, the synergistic relationship between the two waters results in greater removal rates for all the main contaminants. Suspended solids in the sewage water encourage iron floccs to precipitate. Phosphate, which is generally difficult to remove using either active or passive treatment will be removed via sorption onto these iron oxyhydroxide precipitates (Cooke, 1994 and Drizo, 1999). In addition, the ochreous deposits also provide numerous ideal sites for the attachment of nitrifying/denitrifying bacteria (Surface *et al*, 1993, Demim *et al*, 2002).

At present there are no pollutant removal rate criteria data upon which to base design calculations for a combined sewage/mine water treatment system. The pilot-scale wetland system was constructed to to derive such criteria. The pilot-scale was sized using iron removal as the key design criterion, for the following reasons:

- this is the main contaminant of concern in the Kibblesworth discharge;
- the Kibblesworth discharge is larger than the Birtley STW discharge;
- the formation of iron oxyhydroxides within the wetland will control phosphate removal;
- the formation of iron oxyhydroxides will increase ammonia removal providing more potential sites for the attachment of nitrifying/denitrifying bacteria.

A trial wetland measuring 25m by 25m was constructed in June 2003 ('X' marks the site on Figure 1). The trial wetland was one hundredth of the size (by area) of the potential full-scale wetland based on iron removal criteria. It was planted up with a mixture of *typha latifolia*, *phragmites australis* and some yellow flag iris in July 2003. Both the mine water and the STW discharges were being treated together from the beginning of August 2003. The ratio of these waters in the trial wetland was originally the same as the ratio of full-scale discharges which is ~ 3:1 but has since varied due to problems with the mine water pumping set-up. However, this variation has proved useful as it has given an indication of the resulting hydrochemistry under alternative flow scenarios.

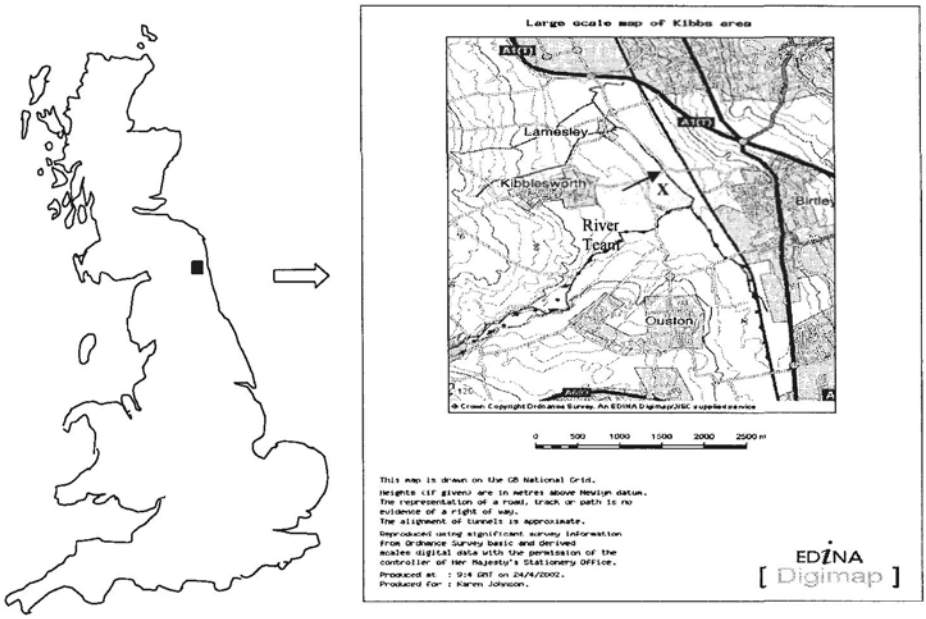

Figure 1: Map of trial wetland (marked by 'X') and discharges (marked by the arrow) into the River Team

HYDROCHEMICAL MONITORING

Daily samples of the Birtley STW final effluent, the Kibblesworth mine water and the Reedbed final effluent were taken. NH_3, NO_3, SS, BOD, Fe and P were all measured on a daily basis for the first ten weeks and from then onwards on a weekly basis. Cl, SO_4, HCO_3, Na, K, Mg, Ca, Cd, Cr, Cu, Pb, Mn, Ni and Zn have all been measured on a weekly basis from the beginning. Flow measurements were taken every week using the bucket and stopwatch method. Field parameters such as pH, temperature, Eh, conductivity and dissolved oxygen were measured *in-situ* on a weekly basis.

Percentage Removal Rates

The average effluent concentrations for all parameters of concern over the four months of monitoring have consistenly been below EA effluent design standards (Fe<2mg/L, N-NH_3<3mg/L, BOD<15mg/L). It is clear from Figure 2 that percentage removal for the six parameters of interest has been variable. However it is possible to point out some trends:

Fe – Iron removal has been relatively stable in the range of 40-80% mass removal. There has also been a steady improvement in percentage iron removal;

P – Phosphorus removal has mirrored iron removal although there has been a more significant reduction since the start of October, coinciding with the onset of colder weather. Percentage removal has been between 10 - 50%;

$N\text{-}NH_3$ – Ammonia removal was consistent for the first two months at ~35-50% but there has been a significant reduction since the beginning of October. Approximately 5-20% $N\text{-}NH_3$ has been removed since the beginning of October;

BOD – Biochemical Oxygen Demand removal has been variable ranging between 20 -75%. Interestingly there has been no significant decrease since October;

$N\text{-}NO_3$ – Nitrate removal was between 20 - 85% until the beginning of October when the wetland stopped removing nitrate and started to release a small amount;

SS – Suspended solids removal has been variable but this variation can be accounted for by fine-tuning of the manifold system during the start-up phase of the wetland. Ignoring this initial hiccup in SS removal, SS removal has varied between 30 - 70% with no reduction since the beginning of October.

It is clear that both ammonia and nitrate removal have been influenced by the colder weather whereas in comparison iron, BOD and SS removal seem less affected by the cold weather. Since nitrifying and denitrifying bacteria are very sensitive to cold temperatures (Wallace *et al*, 2001) this is not unexpected. In addition, BOD oxidising bacteria are more successful at winning oxygen than ammonia oxidisers and therefore BOD removal is generally less susceptible to seasonal effects. The wetland is also removing significant quantities of magnesium, calcium, sulphate and bicarbonate although the data is not presented in this paper.

Effluent manganese concentrations have steadily decreased despite steady influent concentrations (see Figure 3) indicating that percentage manganese removal is increasing. This is significant as manganese is rarely removed successfully in wetlands particularly when there is dissolved iron present in the water. It is particularly notable since manganese is present at concentrations of only ~1mg/L in the influent water and contaminant removal is more difficult at lower influent concentrations. Despite the limited data available due to the immaturity of the wetland, there is a trend (see Figure 4) between influent suspended solids concentration and effluent manganese concentration. It should be noted however that there is a lag time between the influent and effluent samples (which are taken at the same time) as the hydraulic residence time of the wetland is 14 hours.

Hydrochemical Modelling

The geochemical modelling package, Geochemist's Work Bench (GWB) was used to calculate the dissolved species present in the influent waters and effluent waters (both at 3:1 and 0.5:1 mine water: STW water ratios). Sulphate complexes are the dominant species for all metal ions in the effluent water, regardless of whether the mine water: STW water ratio is 3:1 or 0.5:1. Iron is the exception where the dominant complex is the aqueous $Fe(OH)_3$ complex in all waters (except the STW influent water where it is $FeHPO_4$).

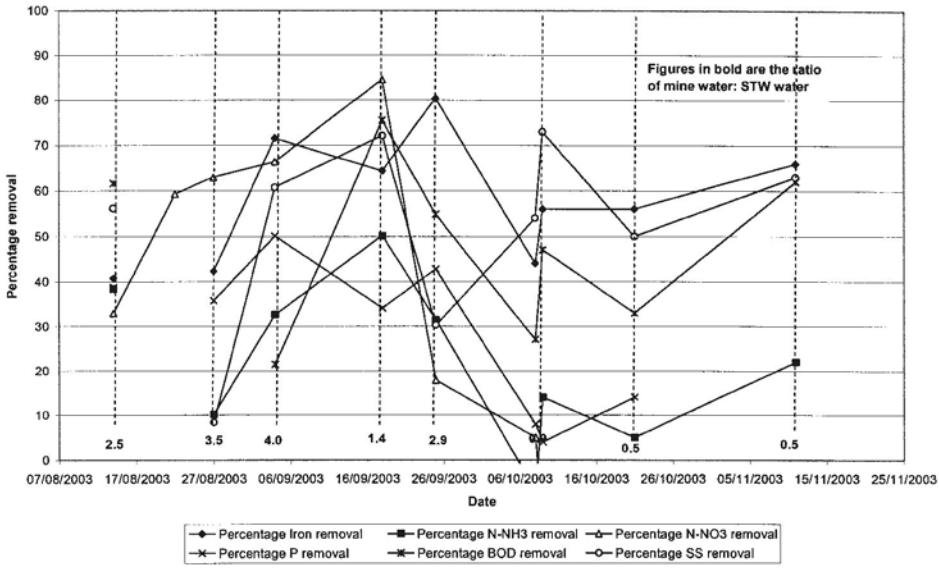

Figure 2: Percentage removal of contaminant in the Birtley/Kibblesworth wetland from August to November 2003

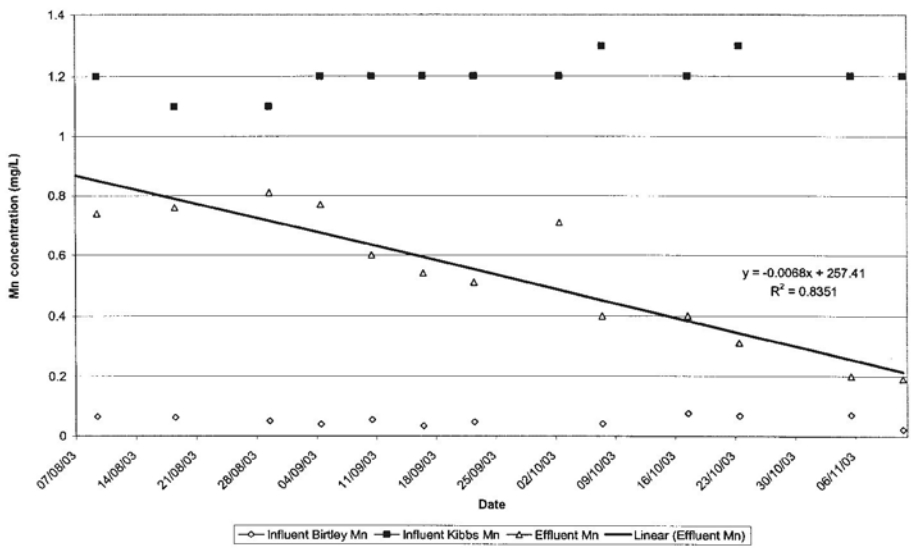

Figure 3: Manganese concentrations in the trial wetland from August to November 2003

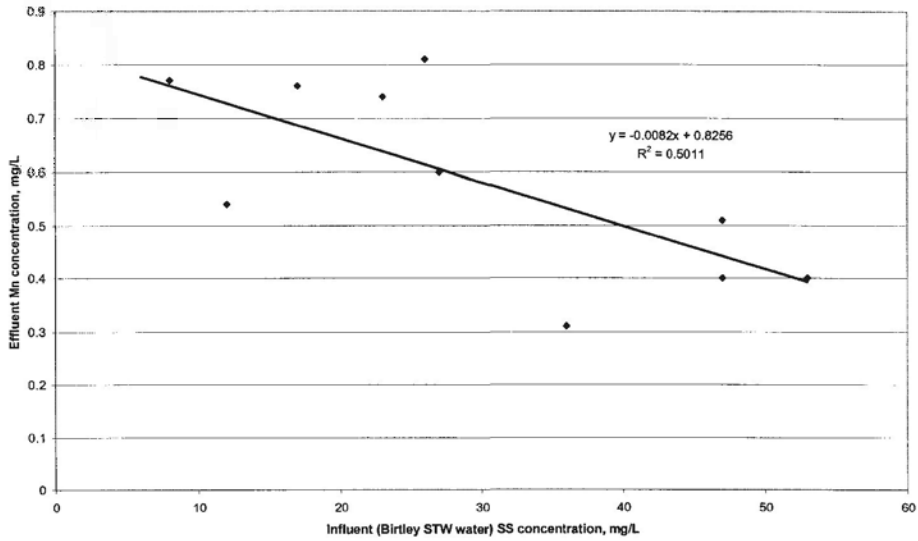

Figure 4: Effluent Mn concentrations vs. influent SS concentrations in the Birtley trial wetland (data from August to November 2003)

It is interesting to note that there are very few hydrochemical relationships between parameters in the influent waters but that there are many more in the effluent water. This suggests that hydrochemical reactions are occurring in the wetland and that certain minerals are controlling the hydrochemical composition of the effluent water. The precipitation and/or retention of minerals in a constructed wetland treatment system is a complex process with no single dominating control sequence. Rather, multiple reactions and interactions occur simultaneously at the surface and within the substrate, creating a mixed composition of soluble and insoluble species. Characterisations of the effluent water using the geochemical modelling package (GWB) suggests that certain minerals may be being precipitated in the wetland:

- The model predicts that amorphous iron minerals such as $Fe(OH)_3$ are being precipitated in the wetland. Although, low Fe^{3+} activity and low oxygen diffusion rates in the wetland will inhibit the kinetics of crystalline iron precipitation, some goethite may exist near the surface of wetland substrate due to increased oxygen levels from surface aeration and/or oxygen transport by plant roots. This precipitation of iron oxyhydroxide minerals would explain the iron removal in the wetland. Removal rates in terms of $g/m^2/day$ (just over $1 g/m^2/day$) are relatively low but this is not surprising as the wetland is immature and influent iron concentrations are low (removal rates are generally lower when influent concentrations are low). Although the model predicts that manganese oxide minerals are supersaturated, it is known that the kinetics for these reactions are very slow without some sort of catalyst and manganese removal in wetlands is usually poor (Nairn and Hedin, 1993);
- The model predicts that calcite is precipitating in the wetland. Both the significant removal of Ca and HCO_3 and the straight-line relationship between Ca and HCO_3

support this prediction. Bicarbonate alkalinity is also utilised by ammonia-oxidising bacteria. The decrease in percentage ammonia removal with the onset of colder weather correlates very well with a decrease in percentage bicarbonate removal;

- The significant trend between Ca and SO_4 concentrations in the effluent water suggests that gypsum dissolution is controlling the concentrations of these two parameters. The modelling suggests that gypsum is undersaturated which would mean that it is dissolving in the wetland. Since the land where the wetland has been built used to be agricultural land this could be a source of gypsum (which is added to agricultural land to increase soil aggregation, reduce surface crusting, increase water infiltration and permeability etc);
- It is less clear what may be responsible for the dramatic reduction in effluent sulphate concentrations. The model suggests that jarosite ($KFe_3(SO_4)_2OH_6$) may be precipitating but this is unlikely (although not unfeasible) as the mineral usually precipitates under more acidic conditions. However there are likely to be numerous hydroxysulphate minerals, not listed in the database for GWB and it is therefore entirely possible that some sort of hydroxysulphate mineral is being precipitated in the wetland.

DISCUSSION AND CONCLUSIONS

The average effluent concentrations for all parameters of concern over the four months of monitoring have consistently been below EA effluent design standards (Fe<2mg/L, N-NH_3<3mg/L, BOD<15mg/L). It is clear that percentage iron removal is improving. This increasing trend is to be expected as iron oxidation is an autocatalytic reaction and therefore iron removal will increase with time as more ochre is deposited. As phosphate is removed via sorption onto iron oxyhydroxides, phosphate removal mirrors iron removal. It is expected that P removal will also improve in line with Fe removal as more ochre is deposited in the wetland. In addition, once a greater depth of ochreous deposits has developed and more sorption sites are created it is likely that P removal will be less affected by seasonality. It is also expected that percentage ammonia and nitrate removal will increase with time as more ochre will provide more sites for the attachment of nitrifying/denitrifying bacteria.

Although manganese is not a contaminant of concern at this site, there is increasing interest in successful manganese removal schemes due to ever-tightening water quality legislation (Johnson, 2003). The successful removal of manganese observed in this wetland correlates with suspended solids removal. It is entirely plausible that manganese is being removed via sorption onto suspended solids (eg Morris, 1979) although clearly more data is required to confirm this theory. Passive manganese removal is notoriously difficult in wetlands (Nairn and Hedin, 1993) and the impressive manganese removal in this combined sewage and mine water wetland may have important implications for the future design of manganese removal treatment systems.

The initial results from this wetland are very encouraging and suggest that co-treatment of mine waters and sewage waters is an attractive option. However, it is expected that the mine water: STW water ratio will be subject to change. With high levels of rainfall the STW flow can increase to as much as three times the dry weather flow (DWF). During high rainfall it is likely that the mine water: STW water ratio will drop from 3:1 to approximately 1:1. Since the wetland has been designed with iron removal as the design criteria this change in ratio is not likely to affect iron removal. Hydrochemical modelling also suggests that whether this ratio is high or low the effluent water chemistry is still dominated by sulphate metal-complex chemistry. In addition the same minerals are predicted to be precipitating in the wetland

regardless of a high or low mine water: STW water ratio. It is therefore expected that contaminant removal rates will not be significantly affected by this potential variation in influent water ratios.

Finally it is important to point out that the wetland is still immature and that both the reeds and the microbial communities will not have become fully established yet. Wallace *et al* (2001) have noted dramatic improvements in removal rates after the conclusion of the first growing season. Planning for the full-scale wetland (6 hectares) is currently being undertaken and the Coal Authority and Nortumbrian Water Ltd will be jointly responsible for the combined discharge from the reed bed to the River Team.

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Performance of a Functionalised Polymer-Coated Silica at Treating Uranium Contaminated Groundwater from a Hungarian Mine Site

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ABSTRACT
The performance of a recently developed active material for treating uranium contaminated groundwater within a permeable reactive barrier (PRB) is reported. This material, PANSIL, is an example of a tailored ligand system that selectively removes the contaminant from solution. The active medium is a polyacryloamidoxime resin derived from polyacrylonitrile, which is deposited from solution onto the surface of quartz sand to form a thin film coating.

PANSIL is effective at sequestering cationic and neutral uranyl species when the solution pH is above 4, due to the stability of the polyacryloamidoxime-uranyl complex formed. However the rate of sequestration decreases rapidly when the pH exceeds about 8 where neutral uranyl species are present only at very low concentrations. PANSIL can preferentially sequester UO_2^{2+} in the presence of divalent groundwater cations. In mildly alkaline conditions performance is very sensitive to the concentration of uranyl complexing ligands, such as bi-carbonate, which affect the sequestration rate. Such behaviour has important consequences for PRB design as it will determine the barrier thickness required for a particular flow rate.

INTRODUCTION
Groundwater pollution caused by uranium mining activities is a widespread ecological problem in both Europe and North America. Some of these workings are now abandoned which exacerbates the pollution problems. The threat posed to the environment arises not only from the radioactive emissions from decaying uranium atoms but also from the toxicity of uranium species. Uranium exists in aqueous solution as the very stable UO_2^{2+} cation, which has a linear shape, but favours co-ordination from ligands in the plane orthogonal to the O=U=O axis. Thus the speciation of the uranyl ion is very pH dependent, partly due to hydrolysis, but also due to the formation of carbonate species in systems open to atmospheric CO_2 or where carbonate minerals are present. The resulting groundwater chemistry is quite complex, making the treatment of contaminated groundwater difficult.

Permeable reactive barriers (PRB) have recently become established as an economical technology for the in-situ treatment of groundwater for many contaminants (see for example

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

Gavaskar, 1999; Puls et al., 1999; Blowes et al., 2000; Boyd and Hirsch, 2002). A PRB consists of a permeable treatment zone that is formed underground in a natural aquifer and intercepts the pollution plume carried along by the natural head differences in the aquifer. The reactive component may immobilize the contaminant by one of a number of different attenuation mechanisms (for example, adsorption, chemical reduction, bioremediation, etc.) and a wide range of materials has been used to form barriers.

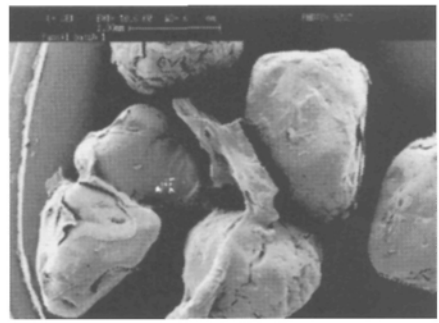


Figure 1: Electron micrograph of PANSIL.

This paper reports on the performance of a recently developed active material called PANSIL for the treatment of uranium contaminated groundwater within a PRB. This material has been extensively investigated in the laboratory (Bryant et al., 2003; Stewart et al., 2003; Barton et al., forthcoming), and so this paper focuses on its performance with uranium contaminated groundwater extracted from near a mine tailings disposal site in Hungary.

MATERIALS

PANSIL is polyacryloamidoxime resin coated quartz sand (≈2% resin by wt., Bryant et al., 2003). PANSIL functionality is thought to be derived from the amidoxime groups that act as bidentate ligand systems for uranyl cations. The lone pairs of electrons on the amino nitrogen and the oxime oxygen are donated to the positive metal centre to form a five-membered ring including the metal (such rings are noted for their stability due to the minimum bond strain). The oxime oxygen can undergo metal-assisted deprotonation (Rivas et al., 2000) further increasing the stability of the ring at intermediate pH. Figure 1 shows an electron micrograph of PANSIL, which consists of sub-rounded particles, with some variation in size and shape, but with an average particle size of about 1mm.

The typical chemical composition of groundwater extracted from near a mine tailings disposal site in Hungary is given in table 1. The pH of this groundwater is about 7. The uranium concentration is not given in Table 1 because it varies spatially, and is generally increasing with time, but generally varies from several hundred μg of UO_2^{2+}/l to just over 1 mg of UO_2^{2+}/l. The important ions in the groundwater used as the test column influent are shown in table 2 (Na^+, K^+ and Cl^- concentrations were not measured in the column influent). The uranium concentration in the column influent was 1.4 mg of UO_2^{2+}/l , and the concentration of the other ions are similar to those in table 1.

Table 1: Typical groundwater composition at the Hungarian mine site (the uranyl concentration tends to vary spatially and temporally but is about 1mg/l).

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Concentration mg/l	70	17	168	53	45	337	484

Note: The error in charge balance is less that 0.5% of the total charge.

Table 2: Average measured composition of the groundwater used as the column influent (Na^+, K^+ and Cl^- concentrations were not measured during the column experiment).

	Ca^{2+}	Mg^{2+}	SO_4^{2-}	HCO_3^-	UO_2^{2+}
Concentration mg/l	163	67	385	595	1.4

Table 3: Measured composition of the synthetic groundwater prior to addition of $UO_2.(NO_3)_2$.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
Concentration mg/l	64.9	38.4	31.4	43.0	35.5	253	182

Note: The error in charge balance is less that 2% of the total charge.

"Synthetic groundwater" representative of a natural groundwater contaminated with uranium was also used in the laboratory programme. It was made up from laboratory grade reagents (200 mg/l $CaCO_3$, 272 mg/l $CaSO_4$, 194mg/l $4MgCO_3.Mg(OH_2).5H_2O$, 252 mg/l $NaHCO_3$, 75 mg/l KCl), and the pH was adjusted to 7 using H_2SO_4 (0.6ml per l of 0.1 mol/l). After pH adjustment an undissolved residue remained, so the synthetic groundwater was filtered and its composition was measured (see table 3), before the addition of either 18.6 or 55.8 mg/l $UO_2.(NO_3)_2.6H_2O$ (equivalent to 10 and 30 mg/l UO_2^{2+}) which dissolved completely (samples were analysed for UO_2^{2+} concentration). After standing the pH of the synthetic groundwater was between 6.8 and 7.8, at which pH the aqueous carbonate specie is HCO_3^-.

METHODS

With the exception of the column test with site groundwater, which was conducted separately (and described below), all the tests reported below were conducted in the same laboratory, and all solution samples treated using the same protocol. The tests were conducted at room temperature (typically 22-25°C) and no attempts were made to exclude atmospheric $CO_2(g)$. Solution samples taken for analysis were filtered at 0.45 μm (using Whatman Puradisc 25PP disposable filters), had their pH measured, and then were acidified by adding a few drops of concentrated nitric acid and stored at 4°C. Their uranium concentration was measured using a spectrophotometric method based upon the complexing reagent 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (known as Bromo-PADAP) developed by Johnson and Florence (1971). This technique has a detection limit of ~0.2 mg/l.

A preliminary series of increasing duration batch exposure tests were conducted on PANSIL with a uranyl nitrate solution at a liquid to solid (L:S) ratio of 30:1 (see Stewart et al., 2003). These tests indicated that an exposure time of less than 4 hrs was sufficient for PANSIL to reach equilibrium with a uranyl nitrate solution containing 10 mg of UO_2^{2+}/l at a pH of ~6.

Column Test with Site Groundwater – A large column test (length 840mm, cross-sectional area $100mm^2$) was conducted using PANSIL to treat the groundwater from the Hungarian mine site. It was conducted at room temperature (20-25°C) and the flow-direction was from bottom to top. The test duration was 256 days, and the total volume of water passed through the column was 4288 ml at a flow-rate of about 17 ml/day. The porosity of the PANSIL was 40.7%, so the flow-volume was equivalent to 126 pore volumes, with a residence time of 2 days. Thus, the superficial seepage velocity was about 0.4m/day, which is at least an order of magnitude higher than the groundwater flow velocity at the Hungarian mine tailings site. Effluent volume was monitored daily, and collected weekly. Uranium concentrations were determined using a fluorimetric method, the measurement being carried out on a fusion of the sample residue after evaporation with sodium fluoride and sodium carbonate. The detection limit is of the order of a few μg/l.

Small Column tests - In the small column tests 10g of PANSIL was mixed with 20g of acid washed quartz sand to reduce the amount of PANSIL used for a particular column length (which reduced column capacity, and thus test duration, without reducing exposure time). The PANSIL/sand mixture was placed in a 25ml glass column, which resulted in a pore volume of approximately 10ml. The columns were then saturated by the upward flow of

distilled water. Once saturation was achieved the water was displaced with the upward flow of the desired contaminant solution at a constant flow rate of 1.6ml/hr. This gave a residence time of ~6hrs. Effluent solutions were diverted through a spur at the top of the columns into covered collection vessels and were collected daily. Their volume and pH were measured prior to acidification for UO_2^{2+} analysis. Two column tests were conducted as follows;

(i) PANSIL was exposed to uranyl nitrate solution containing 30mg/l UO_2^{2+} buffered to pH6 until the uranium concentration in the effluent equalled that in the influent and then the column was leached with uncontaminated synthetic groundwater.

(ii) PANSIL was exposed to contaminated synthetic groundwater containing 30mg/l UO_2^{2+} until the UO_2^{2+} concentration in the effluent equalled that in the influent and then the column was leached with uncontaminated synthetic groundwater.

In addition a control test on acid washed sand using a 30mg/l uranyl nitrate solution at ~pH5 was also run. In this test, initial breakthrough occurred immediately, and influent and effluent UO_2 concentration were equal when the average column loading was only 0.008g/kg. Thus it is assumed that the amount of uranium sorbed by the sand in the column tests can be ignored.

pH controlled batch exposure tests - The effectiveness of PANSIL at extracting uranium from water over a range of pH was investigated by batch exposure tests. PANSIL was added to stoppered glass bottles containing a uranyl nitrate solution (10mg of UO_2^{2+}/l) whose pH was adjusted to values between 1.5 and 11 using either HNO_3 or NaOH. The L:S ratio was 30:1. The bottles were shaken for 24 hours, and the supernatant liquor was sampled.

The leachability of uranium sequestered by PANSIL was also investigated. Exposed PANSIL from two batch exposure tests (with a final pH during the exposure step of between 5 and 6) was subjected to two further leaching steps. Once the initial solution had been decanted off, the PANSIL was twice shaken end-over-end in distilled water at a liquid to solid ratio of 30:1 for 24 hours. The water from both these steps was sampled.

Four more batch exposure tests were conducted over the pH range of 8 to 11. In these tests small samples of the test solution were taken for analysis after 24, 48 and 96hrs. After 96hrs the contaminant solution was decanted off, and the exposed PANSIL was subjected to three further leaching steps. In these leaching steps PANSIL was shaken in distilled water at a liquid to solid ratio of 30:1 for 24 hours. The water from each step was sampled for analysis.

Further batch exposure tests were conducted using synthetic groundwater containing 10mg/l of UO_2^{2+}. The L:S ratio was 30:1 and the test duration was 24 hrs.

RESULTS

Column Test with Site Groundwater – During the large column test using the Hungarian groundwater the influent uranyl concentration was approximately 1.4 mg of UO_2^{2+}/l. For the first 192 days of testing the effluent uranyl concentration was typically less than 0.05 mg of UO_2^{2+}/l, and no individual measurement was greater than 0.13 mg of UO_2^{2+}/l (Figure 2a). At some point between 193 and 198 days breakthrough occurred[1]. By the end of testing the UO_2^{2+} concentration in the effluent reached about a third of the concentration in the influent. The column loading at breakthrough was about 35 mg of UO_2^{2+} per kg of PANSIL. The pH of the column effluent was about 8.1 throughout the test (Figure 2b). Both the bicarbonate concentration and possibly the calcium concentration were lower in the column effluent than in the site groundwater (Figure 2c &d).

[1] In this study initial breakthrough is defined as the point beyond which there is a detectable and thereafter increasing UO_2^{2+} concentration in the column effluent.

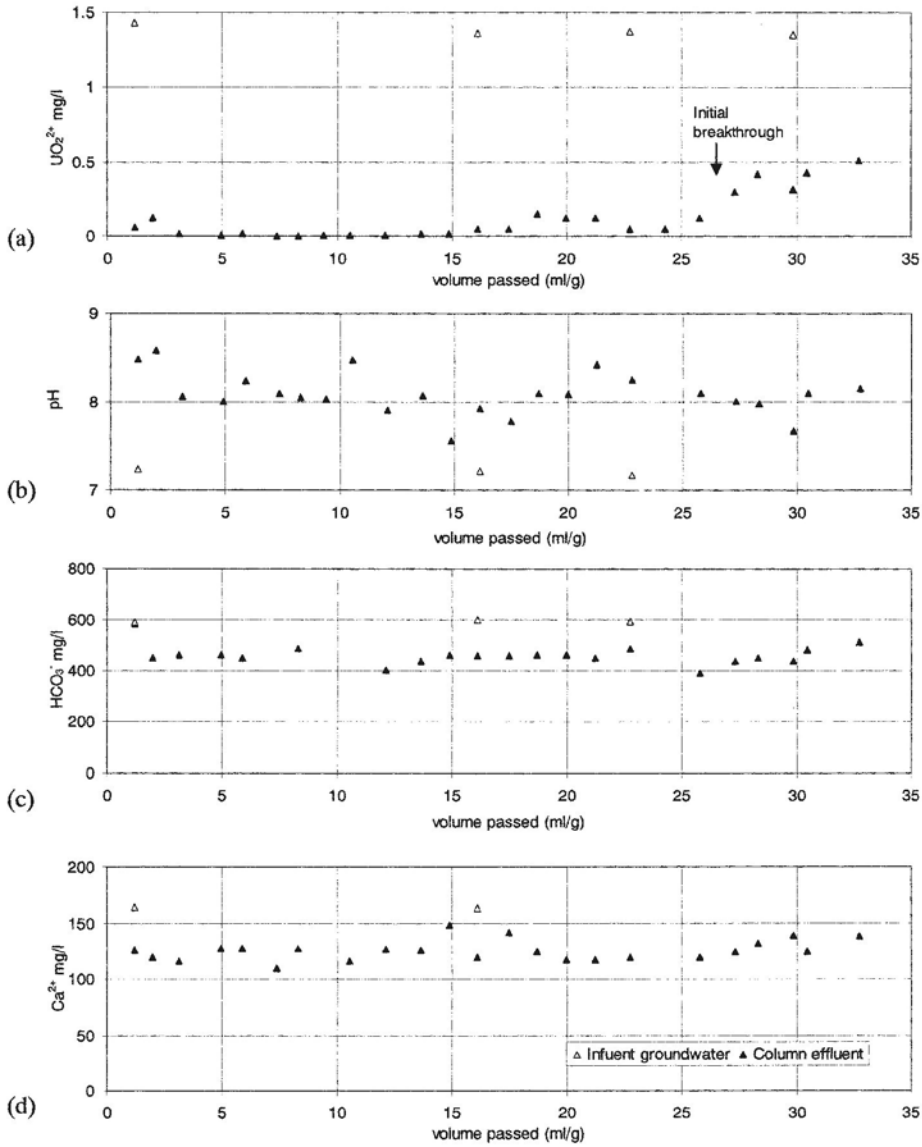
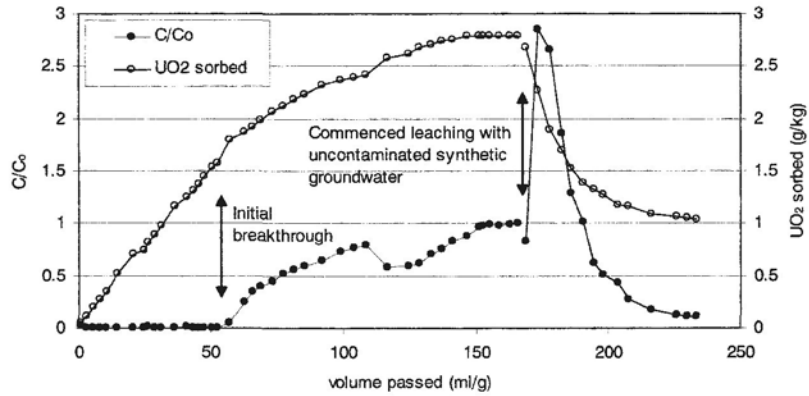
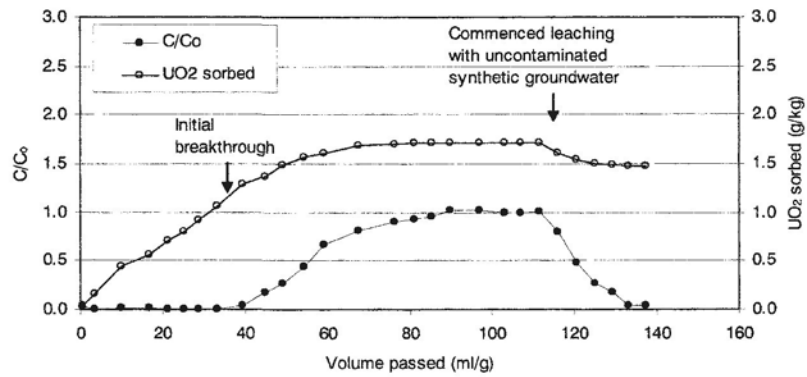


Figure 2: Column tests on PANSIL using the groundwater from a Hungarian mine site containing ~1.4 mg/l UO_2^{2+}.

Laboratory Column tests – In the smaller laboratory column tests on PANSIL exposed to uranyl nitrate at pH6, initial breakthrough occurred at column loading of ~1.5g UO_2^{2+} per kg, and influent and effluent UO_2^{2+} concentrations were equal when the average column loading was 2.8 g/kg (Figure 3a). Subsequent leaching with uncontaminated synthetic groundwater (at ~pH7.5) initially liberated UO_2^{2+} from the column so that the effluent concentration spiked at nearly three times the influent concentration, but in the long- term the PANSIL retained



(a)



(b)

Figure 3: Column tests on PANSIL using (a) uranyl nitrate solution at pH6 and (b) synthetic groundwater at ~pH7.5 (both solutions contained 30mg/l UO_2^{2+}).

~1g UO_2^{2+} per kg. When exposed to synthetic groundwater (30mg of UO_2^{2+}/l at ~pH7.5), initial breakthrough occurred at an average loading of ~1.1 g/kg, and influent and effluent UO_2^{2+} concentrations were equal when the average column loading was ~1.7 g/kg (Figure 3b). During subsequent leaching the effluent UO_2^{2+} concentration showed no spike, instead it gradually declined, until in the long-term the PANSIL retained about 1.5 g of UO_2^{2+} per kg.

Batch exposure tests - The 24hr batch exposure tests conducted with uranyl nitrate solutions buffered to a range of pH values show that PANSIL was effective over a pH range 4.5 to 8, with optimum performance in the pH range 5 to 7.5 (Figure 4). PANSIL was also very effective at treating the synthetic groundwater (also shown in Figure 4).

In the two-stage, distilled water batch leaching tests on PANSIL that was loaded with UO_2^{2+} at pH 6, the UO_2^{2+} concentration in the leachate from the first stage was below the detection limit, and was undetectable in the second stage of these tests. This indicates that, at the loading used in the batch tests (300mg of UO_2^{2+} per kg of PANSIL), PANSIL strongly binds UO_2^{2+}, and once bound that UO_2^{2+} remains unleached in mildly acidic uncontaminated water.

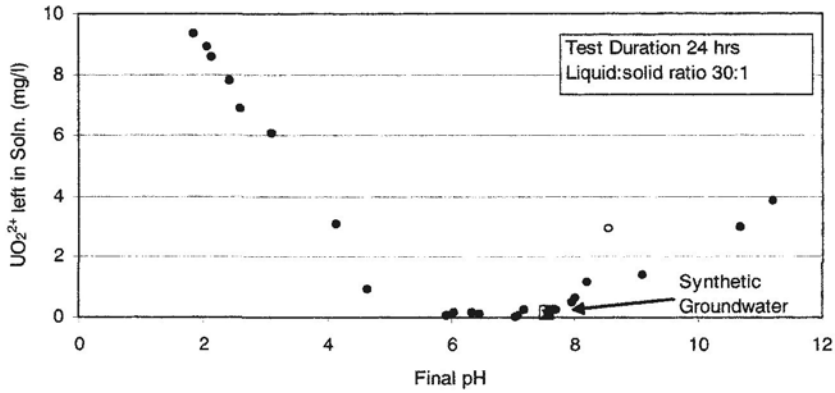


Figure 4: Variation of uranium sorption with pH by PANSIL in uranyl nitrate solutions containing 10mg/l of UO_2^{2+}. The mean (±1 standard deviation) of 7 tests with synthetic groundwater (□) are also shown.

The results of the additional longer duration batch exposure tests are reported in Figure 5. When the pH>8 the time taken for PANSIL to reach equilibrium is greater than 48hrs (and may exceed 96hrs), which is far longer than at pH6 where equilibrium was reached in less than 4 hrs. The leachate from the first distilled water leaching step on the PANSIL exposed for 96hrs contained 1mg of UO_2^{2+}/l when the pH was 8 during exposure, with the leachate concentration increasing slightly with pH to 1.3 mg of UO_2^{2+}/l for pH 11. The leachate from the second leaching step contained 0.6mg of UO_2^{2+}/l when the pH was 8, increasing with pH to 1mg of UO_2^{2+}/l for pH 11. The UO_2^{2+} concentration in leachate from the third leaching step was below the detection limit for all the specimens. Thus, for exposure at pH8 82% of the UO_2^{2+} in the original solution was still attached to the PANSIL, reducing to 48% at pH11.

DISCUSSION

To understand the variation in performance of PANSIL with pH and solution composition numerical modelling has been undertaken using PHREEQE (version phrq96) equilibrium geochemical modelling software. Two solutions were modelled, uranyl nitrate conditioned with 100mg/l carbonate (as sodium carbonate) to replicate the effect of atmospheric CO_2, and the synthetic groundwater. Both of these solutions were modelled under oxic conditions with a uranyl concentration of 10mg/l of UO_2^{2+}. The speciation of these solutions is shown in Figure 6 as a percent of the total UO_2^{2+} in particular species as a function of pH. In general the uranyl speciation in the two solutions follows similar trends, with the UO_2^{2+} cation important below pH5, neutralUO_2CO_3 and $UO_2(OH)_2$ species important 5<pH<7, and anionic uranyl carbonate species dominant above pH7.

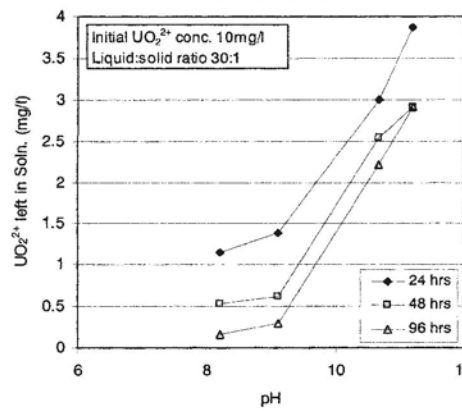
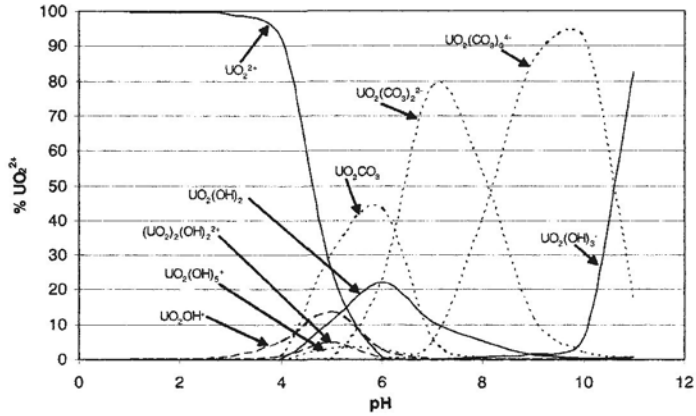
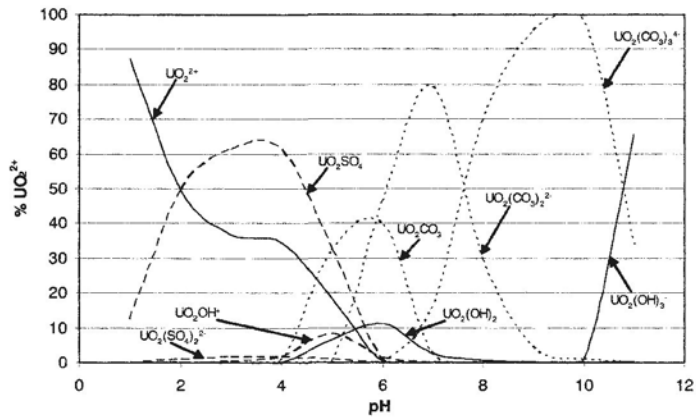


Figure 5: Effect of test duration on UO_2^{2+} by PANSIL at high pH



(a)



(b)

Figure 6: Geochemical modelling results; (a) uranyl nitrate containing 100 mg/l of carbonate, and (b) the synthetic groundwater.

However two differences are that a neutral specie, UO_2SO_4, is important between pH 2 and 5 in synthetic groundwater, and that the neutral $UO_2(OH)_2$ specie persists at a significant percentage level to a higher pH in the carbonated uranyl nitrate than in the synthetic groundwater.

As stated earlier, PANSIL functionality is derived from the amidoxime groups that act as bidentate ligands for UO_2^{2+}. Thus two factors are thought to explain the pH dependence of UO_2^{2+} sequestration by PANSIL in the batch exposure tests. At low pH, protonation of the lone pair electrons on the nitrogens and oxygens effectively blocks the active sites on PANSIL. Otherwise it is the speciation of the uranyl ion that controls the effectiveness.

In the 24hr batch tests using uranyl nitrate that was in equilibrium with atmospheric CO_2 PANSIL was effective up to ~pH 8. At such a pH the geochemical modelling indicates that the dominant uranyl species are either neutral or anionic. Likewise PANSIL was effective with the bicarbonate buffered synthetic groundwater system at ~pH7.5 where, again, the dominant uranyl species are either neutral or anionic. As the amino and oxime ligands on

PANSIL are unlikely to interact effectively with anionic uranyl carbonate species, it is suggested that PANSIL can sequester neutral uranyl species.

In the extended duration batch tests using uranyl nitrate PANSIL was still reasonably effective in the alkaline range, although the rate of reaction was significantly slower. There seem to be two possible mechanisms by which PANSIL could operate in this range. Either PANSIL can sorb anionic specie (probably electrostatically to locally slightly positive sites on the PANSIL), or the amino and oxime ligands sequester neutral species present at very low concentrations at high pH and thus, as equilibrium between the various uranyl species in solution is continually re-established, PANSIL can slowly sequester significant amounts of uranium. The performance of PANSIL in alkaline conditions is compatible with a combination of these mechanisms operating. The extended time periods required to reach equilibrium is compatible with sequestration of a minor specie, and the retention of significant amounts of uranium after three leaching steps suggests that most of the uranium is strongly sequestered, presumably by bidentate amidoxime ligands. However, a proportion of the UO_2 sorbed in alkaline conditions was subsequently leached, indicating that there is some weakly sorbed uranyl, which may be due to weak physisorption of anionic uranyl carbonate species.

In column tests PANSIL was very successful at treating both uranyl nitrate exposed to atmospheric CO_2 at pH~6 and the synthetic groundwater at pH~7.5, with a capacity in the range 1-1.5 g of UO_2^{2+} per kg of PANSIL. However the capacity of PANSIL in the groundwater from a Hungarian mine site was significantly lower, at about 35 mg UO_2^{2+} per kg of PANSIL. Given the relatively small differences between the synthetic groundwater and the Hungarian groundwater (the former contained 30 mg of UO_2^{2+}/l and 180 mg/l of carbonate at ~pH 7.5, the latter contained 1.4 mg of UO_2^{2+}/l, ~600 mg/l of carbonate at pH 8.1), the large difference in column capacities is initially surprising. However the geochemical modelling has shown that the carbonate concentration has a significant effect on the concentration of the neutral $UO_2(OH)_2$ specie in mildly alkaline conditions. In mildly alkaline conditions PANSIL operates by sequestering neutral species, and thus it is suggested that performance difference was caused by differences in the concentrations of such species. Thus a residence time of 6hrs was more than sufficient to remove most of the uranium from the synthetic groundwater, but a residence time of 2 days was only just sufficient to successfully treat the Hungarian groundwater. Breakthrough probably occurred in the Hungarian groundwater column because the sequestration capacity of the PANSIL near the inlet end of the column became exhausted, reducing the effective residence time.

The extended residence time required to treat the Hungarian groundwater does not necessarily mean that PANSIL cannot be used to treat that solution because, within reason, a PRB can be designed to achieve the required residence time. The groundwater flow velocity at the Hungarian mine site is more than an order of magnitude lower than used in the column test, but as PANSIL is likely to be used within a "funnel and gate" type barrier (where the groundwater is channelled through a reactive zone), the flow velocity used in the column test is of the right magnitude. However the residence time within the barrier can be extended by increasing the barrier thickness, which can be achieved without using more active material by adding an inert filler, such are clean sand, to increase the volume of the reactive zone.

CONCLUSION

PANSIL is effective at sequestering cationic and neutral uranyl species when the solution pH is above 4, due to the stability of the polyacryloamidoxime-uranyl complex formed. However the rate of sequestration decreases rapidly when the pH exceeds about 8 where neutral uranyl

species are present only at very low concentrations. Under such conditions PANSIL is thought to sequester those neutral species, and can slowly accumulate significant amounts of uranyl as equilibrium is continually re-established between the various uranyl species in solution. Thus optimum performance is obtained in the pH range 4.5 to 7.5. Once sequestered the uranium is not readily leached from PANSIL.

PANSIL can preferentially sequester UO_2^{2+} from solutions that are typical of the groundwater from a mine tailings site. However it has been shown that its performance is sensitive to the exact groundwater water chemistry. Small changes in the pH and the concentration of uranyl complexing ligands such as bi-carbonate can dramatically affect the sequestration rate, which is an important design parameter for a PRB as it controls the barrier thickness required to treat a particular groundwater flow rate.

This work has shown the value of geochemical modelling in understanding the behaviour of PRB materials in groundwater of different composition, and in particular the importance of bi-carbonate complexation of UO_2^{2+} on the performance of PANSIL. It is recommended that geochemical modelling of the groundwater be a standard part of PRB design.

ACKNOWLEDGEMENT

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Effect Of Wastewaters On The Geo-Technical Properties Of Laterite

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ABSTRACT

Soil contamination arises from variety of sources, which include acid rain, hazardous liquid and solid waste from industries, animal waste, salt-water intrusion, etc. Literature relevant to the soil-pollutant interaction reveals that soil properties and behaviour is influenced and altered due to contamination by pollutant. The soil pollutant interaction depends on various factors such as nature and chemical composition of soil, dielectric constant of pore fluid, organic matter etc.

Sulphur dioxide and oxides of nitrogen are the two most important parameters responsible for acid rain. Atmospheric pollution has resulted in the precipitation having pH less than 5.6 disturbing the nature's delicate balance and also contamination of soil. The soil and ground water contamination will result in Socio-economic and environmental impact. Several studies by various researchers have highlighted the influence of physico-chemical factors on the engineering properties of soil. The alteration of characteristic properties of the soil in the vicinity of industrial plants occurs mainly as a result of their pollution. Literature review on the effect of acid rain on soils indicated that the pH value of soils generally decreased with continuous infiltration. The major soil chemical parameters affecting the contaminant partitioning are hydrogen ion concentration in the soil, which influences all chemical reactions and biological activities.

Laterites and lateritic soil have a very important place in Civil Engineering activities in India, especially in the South and Central parts. They form a good foundation material and are composed essentially of hydrated aluminium and iron oxides. In this paper, the results of an investigation on the effect of pH on the characteristic properties of laterite soil procured from the quarry near Mangalore, located on the western coast of south India, has been discussed. The effect of pH on the characteristic properties of laterite was studied under different pH conditions (i.e. pH =5.0, pH=7.0, pH=8.0). The pH of water in which the laterite blocks were soaked (up to ninety days) was maintained using buffers. The important properties considered for the study are: compressive strength of laterite blocks, Atterberg limits, shear strength properties and chemical characteristics of laterite soil (pH, conductivity, alkalinity, hardness, chloride, sulphate and ammonia nitrogen).

From the investigation it is observed that the engineering properties and chemical characteristics of laterite soil are altered in all the three pH conditions (pH=5.0, pH=7.0, pH=8.0). The compressive strength of laterite blocks reduced under all the pH conditions and considerable reduction in strength was observed when the pH of water was maintained as 5.0. The pH of adjoining water body has remarkable influence on the pH of soil. Accordingly when the pH of water was low (pH=5.0), the corresponding pH of soil decreased from its initial value. Similarly soil pH increased when the pH of water was maintained as 8.0 for soaking up to ninety days. The various other effects on the engineering behaviour and chemical characteristics of laterite are noted and discussed in the present work.

Key words: Soil contamination, Lateritic soil, Effect of pH.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

1. INTRODUCTION:

Environmental Geo-technology is an interdisciplinary science, aimed at forecasting, analyzing and solving the geo-technical problems involving the influence of environmental factors (Manassero & Deangeli, 2002). Literature relevant to the soil – pollutant interaction reveals that the soil properties and behavior is influenced and altered due to contamination by pollutants. Soil – pollutant interaction depends on various factors such as nature and chemical composition of soil, nature and chemical composition of pore fluid, electrolyte concentration of pore fluid, type of anion and cation, ion valency and size of hydrated radii of ion, dielectric constant of pore fluid (Wagh, 2002).

Hydrocarbon contaminations are most obvious concerns of the industrial age. The leakage and spills of oil occurred at one of the petroleum industrial complex around Vododara city (Gujarat) resulted in the earth slope failure due to loss of in-situ shear strength and change in other properties of the ground (Shroff et.al, 1998). In another study by Masashi Kamon et.al (1996), infiltration and soak tests were conducted at different pH levels of artificial acid rain to experimentally simulate the erosion process on stabilized soils, which were used for sub grade and base course materials. Three types of lime and cement stabilized soils were used to study the physico-chemical behaviors of the eroded soils. Results obtained show that the pH values of the lime and cement stabilized soils generally decreased with continuous infiltration or soaking and the decrease was greater under higher acidic condition. A large reduction of the unconfined compressive strength was observed by the higher acid rain.

In the present investigation an attempt has been made to study the effect of pH on the characteristic properties of laterite when soaked in water for ninety days. The effect of pH on the characteristics properties of laterite soil was studied under different pH (pH=5.0, pH=7.0, pH=8.0) conditions in the laboratory.

2. METHODOLOGY

In order to simulate the field condition in the laboratory, laterite blocks were initially dipped in tap water and pH was monitored daily and was maintained using buffers. The laterite blocks from the field were initially tested for compressive strength. Six laterite blocks at a time were dressed properly and a thin coat of cement mortar was applied on both the surfaces. This is to make the surface level. After curing the blocks were tested in a compression-testing machine. The crushed material from the compression-testing machine was hand sorted carefully so as to remove the cement mortar coating. This soil was air dried, pulverized and sieved, to collect the material passing through 20mm and down size. Apart from this, soil from the field was tested for its index and engineering properties as per the relevant Indian Standards. The soil was also subjected to chemical analysis. Chemical analysis of water in which the laterite blocks were soaked was done daily up to ninety days as per the Standard Methods (APHA,1985).

3. RESULTS AND DISCUSSION

The possibility of laterite getting contaminated due to industrial discharges and other activities is possible in the west coast lateritic belt of India. Laterite is the topsoil in the region and forms the foundation for most of the structures. The contaminants may be many such as: leachate from land fills, sanitary wastes from underground constructions etc. This study is aimed at assessing the behavior of laterite when it comes in contact with contaminants.

3.1 Chemical characteristics of laterite soil

Fig. 3.1(a & b) shows the variation of different chemical parameters of laterite soil with time, when the pH of water is maintained as 5.0. It is observed form the fig 3.1(a) that the alkalinity of soil decreases with time from 0.0124 % w/w (unsoaked condition) to 0.0030 % w/w (after soaking for ninety days). The relationship is linear. Fig. 3.1(a) also indicates that the sulphate content and hardness of soil decreases with time. The decrease in soil alkalinity is probably due to the low pH value of water in which the laterite soil was soaked. Chloride ion can replace the carbonate (CO_3) ions to form Calcium Chloride. As a result Carbonic acid will be formed and hence alkalinity may decrease. This can be expressed in the form of Eq.1.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \qquad .....(1)$$

The decrease in sulphate concentration may be due to the leaching of sulphate ions into the adjoining water body. Fig. 3.1(b) illustrates the relationship between chloride, conductivity and nitrogen content of soil with time. It is observed from fig. 3.1(b) that the chloride content and conductivity of soil increases with time. However nitrogen (as NH_4-N) decreases, probably due to conversion of Nitrogen into nitrate (NO_3) at the end of the soaking period. Increase in chloride concentration and decrease in hardness indicate probable leaching out of metallic cation. Similar observations were made on lateritic soil when the pH of water (in which the laterite blocks were soaked) was maintained as 7.0 and 8.0. Thus it was observed that at lower pH values (pH= 5.0) alkalinity, hardness, sulphate and nitrogen content of soil decreases whereas chloride and conductivity of the soil increases. The increase in chloride concentration of soil along with low pH conditions will be detrimental to the foundations, which are constructed using R.C.C. The increase in chloride content of soil may enhance the corrosion rate. At higher pH levels (pH=8.0) alkalinity, nitrogen and conductivity of soil increase with time. The chloride content remains almost constant. Sulphate and hardness of soil shows variation. At intermediate pH condition (pH=7.0) alkalinity decreases. The chloride and sulphate content of the soil remain constant.

Thus the chemical characteristics of laterite indicate that low pH conditions are unfavorable for construction activities and slightly higher pH values are better.

3.2 Variation of Maximum dry density (Υ_d max) and Optimum moisture content (OMC)

Fig. 3.2 illustrates the relationship between maximum dry density and OMC with time. The laterite blocks were soaked in water for a period ranging from fifteen days to ninety days whose pH was maintained at 5.0 using acid buffer. It is observed that the OMC increases and maximum dry density decreases from an initial value of 1.72 g/cc (unsoaked condition) to 1.40 g/cc (after soaking for ninety days). Similarly the experimental results of maximum dry density and Optimum moisture content when the pH of water was maintained as 7.0 and 8.0 indicated that in all the three pH conditions, a decrease in maximum dry density was observed when compared to the initial value (unsoaked condition). The decrease in maximum dry density was higher when the pH of water was maintained as 5.0.

3.3 Variation of soil pH with time

Fig. 3.3 illustrates the variation of soil pH with time of soaking of laterite blocks under different pH conditions of water. It is observed from fig. 3.3 that the pH of soil decreases from 5.34 (unsoaked condition) to 4.0 (for soaking up to ninety days) when the pH of water was maintained as 5.0. However the pH of soil increases from 5.34 (unsoaked condition) to 8.5 (for soaking up to ninety days) with time when the pH of water was maintained as 8.0. As

observed from fig. 3.3, the pH of soil remained almost constant when the pH of water was maintained as 7.0.

3.4 Variation of liquid limit and plastic limit with time

Fig. 3.4 illustrates the relationship between liquid limit and time. It is observed from fig.3.4 that the liquid limit of soil increase from 42 % (unsoaked condition) to 52 % (for soaking up to ninety days) when the pH was maintained as 5.0. The trend in variation of the liquid limit is linear. Similarly again from fig.3.4 it is observed that the liquid limit increases and the trend in variation (when pH was maintained as 7.0) is linear. However it is observed from fig.3.4 that liquid limit decreases with time when the pH was maintained as 8.0. A similar trend in variation (as that of liquid limit) of plastic limit was observed from fig. 3.5.

3.5 Effect of pH on Specific Gravity

Figure 3.6 illustrates the variation of specific gravity with time, for soaking up to ninety days. It is observed from fig. 3.6 that the trend in variation of specific gravity of soil is not regular for all the three conditions of pH (pH=5.0, pH= 7.0, pH =8.0). The specific gravity varies from 2.55 (unsoaked condition) to 2.26 (soaking up to ninety days).

3.6 Variation of compressive strength of laterite blocks

Six laterite blocks at a time were dressed properly and a thin coat of cement mortar was applied on both the surfaces. This was to make the surface level. The blocks were then tested in compression testing machine. The compressive strength is reported as an average of six values.

Fig. 3.7 illustrates the effect of pH on compressive strength of laterite blocks with time for soaking up to ninety days. It is observed from fig.3.7 that the compressive of the laterite blocks decreases with time of soaking in all the three conditions of pH, (i.e. pH=5.0, pH=7.0, pH=8.0). The trend in variation is linear in all the three cases. Table-1 gives the percentage reduction in compressive strength of laterite blocks with time. The decrease in compressive strength is probably due to loss of cementation properties or aggregate bonds. Probably the acidic conditions destroy the iron oxide coatings on the soil particle releasing the same which was held by cementation. This was also manifested by the decrease in hardness of the soil.

Table-1 Wet Strength of Laterite Blocks and Percentage Reduction with Time

Sl. No.	No. of days	pH= 5.0 Compressive Strength (kg/cm^2)	% Reduction	pH=7.0 Compressive Strength (kg/cm^2)	% Reduction	pH=8.0 Compressive Strength (kg/cm^2)	% Reduction
1.	**	15.65	-	15.55	-	15.65	-
2.	15	15.62	1.90	15.34	1.90	15.46	1.20
3.	30	15.24	2.60	15.12	3.38	15.24	2.60
4.	45	14.26	8.89	15.10	3.35	11.55	26.20
5.	60	12.47	20.32	14.10	10.00	10.67	31.82
6.	75	11.90	23.94	13.56	13.35	10.20	34.82
7.	90	08. 00	48.89	12.00	23.32	09.00	42.50

** Initial unsoaked

3.7 Chemical characteristics of water under different pH conditions

Fig. 3.8 shows the variation of alkalinity and sulphate in water with time. It is observed from fig.3.8 that the alkalinity of water increases up to thirty days and then decreased with time at

the end of ninety days. It was observed from fig. 3.1(a) that the alkalinity of soil also decreased with time. This is probably due to low pH value of water in which the laterite soil blocks were soaked. The sulphate concentration in water increases with time as observed from fig. 3.8. This may be due to leaching of sulphate from soil. Narayan & Suresh (1989) had reported that the addition of sulphate (SO_4) to the ground waters takes place from the breakdown of organic substances in the soil leachable sulphate. Hence increase in sulphate concentration of water is probably due to breakdown of organic substances in the lateritic soils. Fig.3.9 illustrates the variation of hardness with time. It is observed that the hardness of water increases with time from 50 mg/l to 4500 mg/l at the end of ninety days. From fig. 3.1(b) it was observed that the hardness of soil decreases with time. Therefore it can be inferred that when hardness of soil decreases the corresponding hardness in water increases. This may be due to leaching action under low pH condition. Fig. 3.10 illustrates the variation of chloride and conductivity of water with time when the pH was maintained as 5.0. It is observed from fig. 3.10 that when the chloride concentration increases, the conductivity of water also increases. It was seen in fig. 3.1(b) that when chloride concentration increases in water, the corresponding chloride content in soil also increases.

When the pH of water was maintained as 7.0 the parameters such as alkalinity, hardness, sulphate, chloride and conductivity remained almost constant.

From the chemical analysis of water (when pH was maintained as 8.0) it was observed that alkalinity increases up to 40 days period. After 40 days alkalinity of water decreases suddenly and remains constant after 60 days. When alkalinity of water decreases the corresponding alkalinity in soil increases. Sulphate concentration remains almost constant. Hardness shows varying trend. Chloride increases up to 40 days and decreases after 60 days. A similar variation was observed in conductivity of water.

4. Summary and conclusions

The engineering properties and chemical characteristics of the natural laterite soil are susceptible to change due to addition of inorganic chemicals in the adjoining water body. The maximum dry density of natural laterite soil decreased with time (for soaking up to ninety days) under all the three pH conditions (i.e. pH=5.0, pH=7.0, pH=8.0). The decrease in maximum dry density was more pronounced under low pH condition (i.e. pH=5.0). The results of consistency limits indicate that the liquid limit of the lateritic soil increases under low pH values (i.e. pH=5.0, pH=7.0) and the liquid limit decreased when the pH was maintained as 8.0. The similar trend was observed in plastic limit of lateritic soil. A reduction in compressive strength of laterite blocks was observed during soaking under different pH conditions. Maximum decrease in strength was observed when the pH of water was maintained as 5.0. The effect of pH was also observed on the shear strength properties of laterite soil such as cohesion (c) and angle of internal friction (ϕ). The cohesion of lateritic soil decreased during soaking up to ninety days under all the pH conditions. The decrease in value of cohesion was more when pH was maintained as 5.0. The angle of internal friction of lateritic soil increased when cohesion decreased. The chemical characteristics of lateritic soil indicated that the hardness, alkalinity, sulphate and nitrogen content of soil decreased with time when pH of water was maintained as 5.0. However chloride content and conductivity of lateritic soil increased with time of soaking. The increase in chloride concentration and decrease in hardness of soil indicated probable leaching of metallic cation. Leaching of metallic cation from laterite could be one of the reasons for the decrease in compressive strength with time of soaking. When the pH of water was maintained as 7.0 it was observed that the trend in variation of hardness was not very regular. However alkalinity of soil

decreased linearly. Not much variation of sulphate content in laterite soil was observed. The chloride content remained almost constant. The conductivity of the soil increased in a polynomial fashion when compared with the initial value of natural lateritic soil. When the pH of water was maintained as 8.0, alkalinity of lateritic soil increased with time for soaking up to ninety days. The variation of hardness and sulphate content in lateritic soil was not regular. However nitrogen concentration and conductivity of the lateritic soil increased with time. The chloride content remained constant. The chemical characteristics of lateritic soil indicate that the low pH conditions are unfavorable for construction activities, and a slightly higher pH values is better. The slightly acidic nature of the natural lateritic soil is may be due to the decay of the organic matter present in the soil. The chemical characteristics of the water have influence on the engineering behavior and chemical characteristics of the natural lateritic soil from which some important conclusions can be drawn.

The following are some of the important conclusions drawn from the above investigation after studying the effect of pH on the Engineering properties and chemical characteristics of laterite.

1. The Engineering properties and chemical characteristics of the natural lateritic soil is susceptible to change when comes in contact with the wastewater. The impact on the Geo-technical properties and chemical characteristics of the lateritic soils is a function of time.

2. It observed from the present investigation that the important properties like maximum dry density, shear strength parameters (c and ϕ) compressive strength of laterite blocks etc., decreased with time of soaking and the effect was more under low pH conditions (i.e. pH=5.0).

3. The chemical characteristics of the adjoining water body has influence on the behavior of lateritic soil and some important conclusions, like leaching of metallic cation etc., can be drawn from the analysis results.

4. The pH of lateritic soil decreased to very low (pH=4.0) when the pH of adjoining water was maintained as 5.0. Similarly the pH of laterite soil increased to 8.5 when the pH of water was maintained as 8.0. However the pH of soil did not vary much when the pH of water was maintained as 7.0.

5. A complete detailed investigation is required further so as to know how the laterite behaves when it comes in contact with the more aggressive chemical environment.

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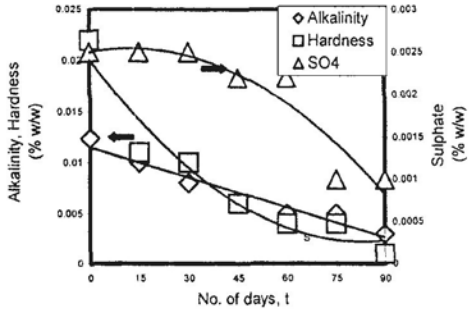

Fig. 3.1. Variation of the chemical properties of soil with with time for soaking of laterite soil blocks (pH=5.0)

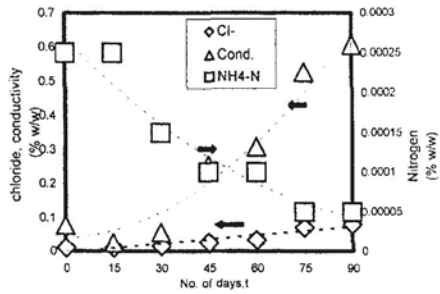

Fig. 3.1(b). Variation of chemical properties of soil with time for soaking of laterite soil blocks (pH=5.0)

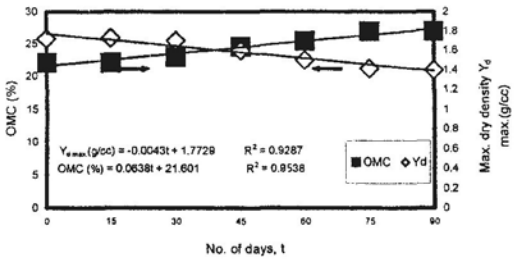

Fig. 3.2. Variation of Maximum dry density and Optimum moisture content with time (pH =5.0)

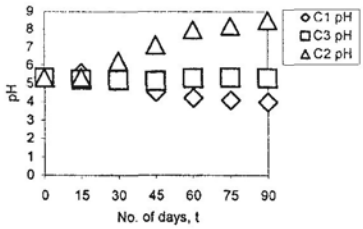

Fig. 3.3. Variation of soil pH with time for soaking of laterite soil blocks

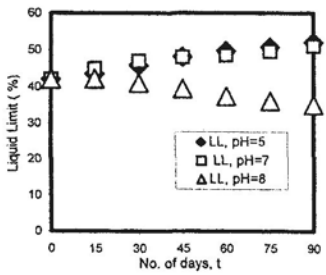

Fig. 3.4. Variation of Liquid limit with time under three pH conditions for soaking of laterite soil blocks

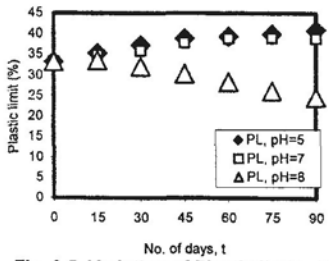

Fig. 3.5. Variation of Plastic limit with time under three pH conditions for soaking of laterite soil blocks

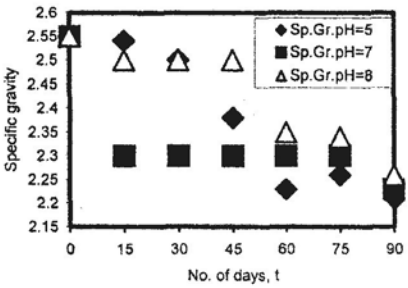

Fig. 3.6. Variation of specific gravity with time under different pH conditions

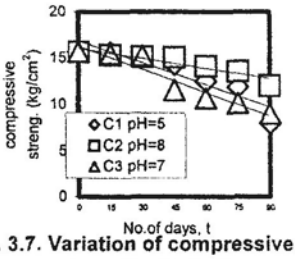

Fig. 3.7. Variation of compressive strength of laterite blocks with time for soakimg upto ninety days

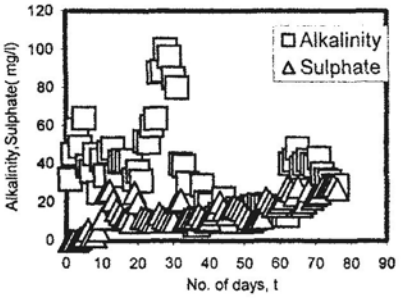

Fig. 3.8. Variation of Alkalinity and sulphate of water with time (pH maintained as 5.0)



Fig. 3.9 Variation of Hardness in water with time (pH maintained as 5.0)

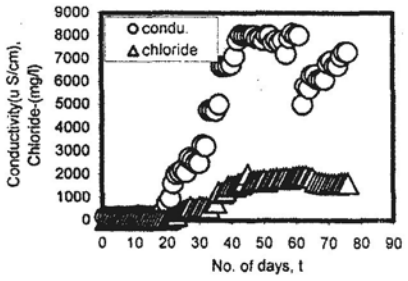

Fig. 3.10. Variation of Conductivity and Chloride in water with time (pH 5.0)

APPENDIX

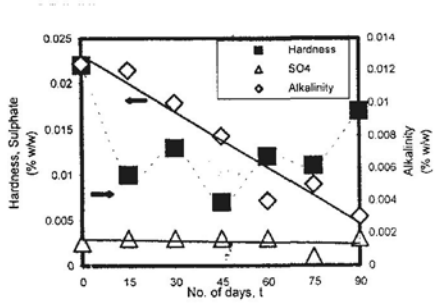

Fig. 3.1(c). Variation of chemical properties of soil with time for soaking of laterite soil blocks (pH = 7.0)

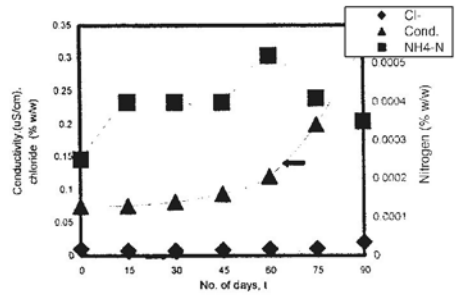

Fig 3.1(d).Variation of Chemical properties of soil with Time for soaking of laterite soil blocks (pH=7)

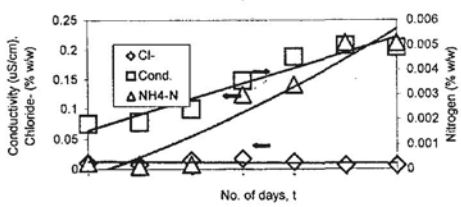

Fig. 3.1(e). Variation of Chemical properties of soil with time for soaking of laterite soil blocks (pH=8.0)

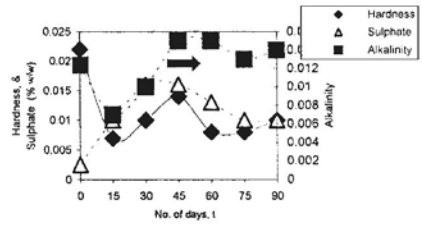

Fig. 3.1(f) Variation of chemical properties of soil with time for soaking of laterite soil blocks (pH=8.0)

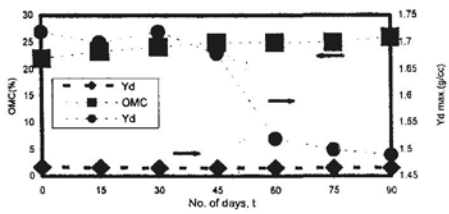

Fig 3.2(a). Variation max. dry density and optimum moisture content with time (pH = 7.0 and 8.0)

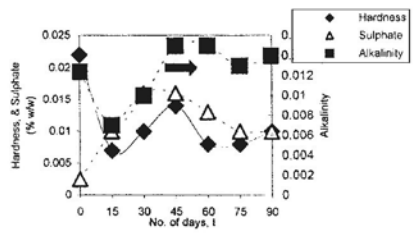

Fig. 3.1(f) Variation of chemical properties of soil with time for soaking of laterite soil blocks (pH=8.0)

Acidic leachate, limestone goaf: hydrogeochemical observations and predictions for remediation planning at Blenkinsopp Colliery, Northumberland (UK).

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ABSTRACT

Hydrogeochemical investigations of the water encountered underground during the working of Blenkinsopp Colliery, Northumberland (UK), revealed the presence of highly heterogeneous water quality. It emerged that specific qualities of water were logically related to details of the flowpaths the waters were known to have taken to reach the accessible sampling points. Working from this information, and taking into account observations of mineralogical and mining engineering aspects of the workings, a conceptual model was developed which assisted in predicting the likely geoenvironmental response of the colliery to abandonment and flooding. On the basis of this conceptual model, estimates were made of the time required for the workings to flood to surface, and of the water quality likely to be encountered after decant of water to the surface environment, providing the basis for planning remedial interventions. This case study illustrates the importance of taking mining practices into account when developing hydrogeochemical conceptual models for such deep mine systems.

COLLIERY CLOSURE AND THE QUEST FOR PREDICTIVE POWER

It has been appreciated since at least the mid-1970s, when the first documented cases were published (e.g. Cairney and Frost 1975; Frost 1979; Henton 1979, 1981), that the flooding of coal mine workings after closure tends to lead to a marked deterioration in water quality. More recent research (reviewed in detail by Younger *et al.* 2002) has further developed our understanding of the array of geochemical processes responsible for both water quality deterioration (primarily the dissolution of pyrite oxidation products) and for natural attenuation of the resulting pollutants (involving neutralisation of mine waters by dissolution of carbonate and silicate minerals). The process of flooding is an inevitable result of the withdrawal of dewatering facilities despite the persistence of ground water inflows to the mined system. The terms "ground water rebound" or "mine water rebound" are often used to denote the process of water level rise during flooding. Completion of rebound is marked by a cessation of further water table rise within the mined system, which denotes the attainment of a condition in which outflows from the flooded mine system match residual inflows. The outflows which terminate rebound most often take the form of point discharges of polluted mine water to surface water catchments via old mine entrances or seam outcrops, though in some cases outflow may also occur to an overlying aquifer. Depending on the scale of the mine system in question and on the rate of ground water inflow which it receives, completion of rebound may take a number of years, or even a few decades.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

In order to lay adequate plans to prevent any deterioration in the water quality status of rivers and / or aquifers following completion of rebound, which would be contrary to the requirements of the EU Water Framework Directive, water managers need to be able to estimate the timing of, and degree of water quality deterioration associated with, specific instances of rebound. A recent review of the evolution of predictive methodologies for such problems has been provided by Younger and Robins (2002). Depending on the scale of the system in question, the amount of data available, and (critically) the resources dedicated to the predictive work, forecasting of rebound timing can be achieved using a range of methods, including empirical extrapolation of observed rebound curves, semi-distributed mass balance modelling and rigorous physically-based 3-D numerical modelling (e.g. Adams and Younger 2001). Forecasting of changes in water quality during and after rebound is even more difficult than predicting rebound rates. The earliest published methodology (Glover 1983) established an empirical approach which has subsequently been refined (Younger 2000) and applied to number of real cases. Rigorous, predictive geochemical modelling of water quality changes during rebound using established thermodynamic software such as PHREEQC has been attempted in a number of cases (e.g. Younger *et al.* 1995; Chen *et al.* 1999). Such predictive exercises have tended to reveal limitations in our process understanding and / or in our knowledge of the abundances of key mineral phases in mined systems. Reconstruction of observed changes in water quality by means of 'inverse modelling' (using the NETPATH code and, more recently, the inverse modelling package of PHREEQC) has gone some way to indicating the relative importance of various buffering minerals. Calcite is an obvious postulate as a buffering mineral. However, in most UK coalfields the Coal Measures sequence (Westphalian: Stephanian) is devoid of discrete limestone beds, and also lacks disseminated calcite within the clastic strata themselves. In these cases, the main buffering phases appears to be the Ca-Mg-Fe carbonate mineral ankerite, which is often present as cleat surface linings in many coal seams (Younger 2004). In the Lower Carboniferous coalfields of northern and western Northumberland, however, discrete limestone beds are often present in close association with the coal seams, and where mining has been undertaken by longwall techniques, limestone can be the dominant lithology in the 'goaf' (i.e. mining-induced breccias) which form in collapsed panels from which coal has previously been removed. This apparently benign circumstance is tempered by the fact that the marine depositional environment of these strata also resulted in abundant diagenetic development of fine-grained pyrite within the coal seams and seat-earth mudstones. There is thus a close juxtaposition of acid-generating and buffering phases in this setting, and the details of hydrological pathways can be crucial in determining the overall balance of acidity in a given mine water. This paper explores the implications of these observations for a practical case of current concern: the August 2002 closure of Blenkinsopp Colliery, the last working coal mine in the Lower Carboniferous of Northumberland.

BLENKINSOPP COLLIERY: OUTLINE OF GEOLOGY, HYDROGEOLOGY AND MINING HISTORY

Blenkinsopp Colliery is located approximately four kilometres to the west of the town of Haltwhistle, in the far west of Northumberland (Figure 2). The Colliery worked a single seam of coal, known as the Little Limestone Coal, which immediately underlies the 15m-thick limestone bed of the same name. These strata, and all the super-incumbent beds below rockhead, are of Namurian (Lower Carboniferous) age. The floor of the worked coal seam is a pyritic mudstone. The sedimentary sequence overlying the Little Limestone mainly comprises cyclothemic alternations of thinly-bedded (generally < 0.5m) mudstones,



Figure 1 - Location of study site

siltstones, sandstones and occasional limestones. Three of the thicker sandstone units in this sequence (the 12.5m-thick Firestone Sill, base 65m above the roof of the worked coal seam; the 10m-thick White Sill, base 40m above seam roof; and the 11m-thick Pattinson's Sill, base 24m above seam roof) are minor aquifers, which feed significant quantities of water into the workings. The Little Limestone itself is massive, sparsely jointed and of low transmissivity. While it did yield some significant feeders when first broken by caving of the No 1 Shearer Face (see Figure 2) in 1994, the limestone has very low specific yield and all available evidence suggests that it quickly drained down to the level of active mining, with most residual feeders originating from the still-saturated sandstone aquifers above. The colliery has been worked for several centuries, with the earliest recorded workings dating from the early 19th Century (by which time they were already at a depth of several hundred metres, and more than 2km from the portal of the mine). The colliery was originally worked until the 1940s, after which time it was abandoned for some thirty years, before being re-opened in the 1970s as a private licensed mine, until the most recent (and probably final) closure in August 2002.

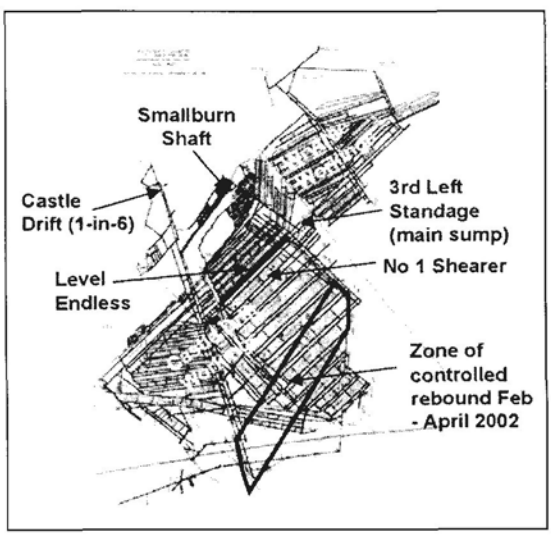

Figure 2 - Annotated mine plan for Blenkinsopp Colliery. All workings in a single seam. Note that geological dip is to SSE parallel to Castle Drift.

Figure 2 shows the layout of the workings, with labels indicating some of the more important features of the mine which are mentioned in the following text. Blenkinsopp Colliery comprised two distinct bodies of working (which were originally separate mines), i.e. the Wrytree workings and the Castle Drift workings. Access to both of these bodies of workings was primarily by means of inclined drifts, of which the 1-in-6 Castle Drift was the main production and man-access drift during the later years of working. The Smallburn Shaft is a 4m diameter cylindrical structure 100.22m in total depth. A run of tubbing from surface to 37m depth holds back loose sands and gravels of Quaternary age, and also serves to partially hold back the

waters of the Firestone Sill aquifer. This shaft was never used for regular man-access, but rather as the downcast ventilation shaft and the route to surface for the dewatering pipe ranges. Blenkinsopp was one of the last collieries in England to use traditional hand-filling methods for loading coal from working faces, and modern mechanised longwall working (using drum shearers and self-advancing hydraulic supports) was only introduced in 1994. Conventional longwall was actually difficult to apply in this colliery, because the great strength of the Little Limestone meant that it caved to form goaf only irregularly, and often in very large blocks. A 'hanging roof' often developed during shearing, leading to problems with face "weightings". Furthermore, sudden caving of very large blocks of limestone directly onto face supports (which occurred on a few occasions) was capable of flattening these completely. The strength of the limestone roof also gave rise to some impressive features in the mine, such as a number of uncaved hand-filler panels which had stood unsupported for more than ten years by the time of closure. The very good roof conditions also meant that old bord-and-pillar workings dating from the 1830s and 1840s, which in most collieries would by now have degraded beyond repair, were for the most part standing intact after 170 years. In these old workings, in accordance with antique regional practice, the top two feet of coal were always left in place as "top coal". The effective worked thickness of coal in this district of the mine was thus around 1.27m (compared with about 1.52m elsewhere in the mine).

Some lateral variations in the geology of the Little Limestone Coal and its roof strata were behind the losing battle with economic viability faced by the mine within the artificially hostile market for indigenous coal created by successive UK governments. A mid-seam parting of pyritic mudstone was found to become ever thicker as the mine workings proceeded towards the southeast, eventually exceeding 0.5m in the most south-easterly workings. This resulted in an increase in the ash and sulphur contents of the run-of-mine coal, significantly reducing its market value. At the southwestern edge of the workings shown on Figure 2, the seam was pierced by a sub-vertical dolerite dyke (dipping to the southwest at around 60°). Contact metamorphism by this dyke reduced the volatile content of the coal over an area of several hundred square metres, effectively turning the coal into a semi-anthracite. While elevated rank coals such as this once attracted high premiums, the low volatile content rendered this coal unsuitable for its sole remaining market (i.e. blending for use in coal-burning power stations). Finally, as the seam is followed up-dip towards outcrop, for instance by ascending the Castle Drift, a thin parting of pyritic mudstone begins to appear between the coal and the overlying limestone, an observation with importance for predictions of post-rebound evolution of water quality.

Detailed monitoring of quantities of pumped water were undertaken in various parts of the mine between 1994 and 2002. The results of this period of regular monitoring can be summarised as follows. The total water make of the Blenkinsopp workings varied between extremes of 3615 m^3/d and 6583 m^3/d, with a median value of around 4500 m^3/d. The variations were seasonal, with minima occurring between July and mid-November, and maxima between mid November and late June. Peak annual flows of around 5100 m^3/d normally occurred in February. The distribution of this total water make within the workings was such that around 18% originated in the Wrytree workings, 18% originated from old bord-and-pillar workings in the Castle Drift workings, around 25% corresponded to the residual water make from the first shearer panel to cave in the mine (No 1 Shearer panel; Figure 2), 30% originated from all the other shearer panels combined, and finally around 9% was sourced from inflows local to the main pumping sump in the 3rd Left Standage.

HYDROCHEMISTRY OF BLENKINSOPP COLLIERY

Regular samples of the water pumped from the mine (via the Smallburn Shaft), as well as of individual inflows of water within the workings, were gathered during 2001 - 2002. Table 1 summarises the findings of these investigations.

Table 1 - Summary of typical chemical characteristics of mine waters encountered in Blenkinsopp Colliery during 2001 - 2002[1]. Fig 2 identifies locations.

Water source	pH	T (°C)	Cond. (µS/cm)	Alk. (mg/l[2])	Fe (mg/l)	Mn (mg/l)	SO_4 (mg/l)
1. Wrytree water (entire make) pumped to sump in Castle Drift workings	6.72	13.0	1265	68	30	0.9	539
2. Local drainage to Smallburn Shaft from old bord-and-pillar workings up-dip	6.84	11.7	672	176	2	0.1	160
3. Water pumped from main sump (3rd Left) up to Smallburn Shaft (= all water in workings except for local drainage to shaft)	7.41	13.4	1749	168	20	0.5	701
4. Residual water make from No 1 Shearer Panel, sampled at Main Gate tank	7.1	12.8	750	230	2.6	0.08	129
5. Drainage from old hand-filler faces flowing into Castle Drift	6.9	16.5	1220	15	5.6	0.1	621
6. Roof drippers associated with fault cut by the Level Endless	6.7	13.8	3220	n.d.	134	5.3	2088
7. Extremely acidic water in floor pools of old bord-and-pillar workings between Smallburn Shaft and Castle Drift	2.0	13.0	7695	0	1293	9.9	6054
8. Water draining into 2 SW development heading from old bord-and-pillar workings up-dip	6.9	12.9	958	285	5.8	0.5	212
9. Water pumped from recently-flooded workings in the 3rd South district	4.7	15.1	2360	0	48.5	1.8	1496
10. Roof drippers from base of Little Limestone in the deepest part of the workings (12W development heading)	6.6	19.5	1533	n.d.	13.6	0.4	163
11. Drainage from a previously-flooded shearer face (No 21) which was drained down after the water had been static within the goaf for more than one year	6.5	17.8	1764	136	4.2	1.4	838
12. Final mix of water pumped to surface at Smallburn Shaft	6.7	12.5	1536	62	35	1.1	826

[1] Note that not all sample points were synchronously visited, hence mis-matches between 2, 3 and 12, which one would expect to be similar in quality. [2] as $CaCO_3$ equivalent.

Water quality in this mine system is clearly heterogeneous. Nevertheless, a few generalisations can be made. It is clear that the overall mixture of water pumped from the shaft, and thus, unsurprisingly, most individual sources of water in the workings was net-alkaline (i.e. alkalinity > acidity) ranging up to around 45 mg/l. Acidic waters were regularly found in only two settings within the mine:

(i) water running across the pyritic seat-earth floor in old bord-and-pillar workings (e.g. sample 7), which had extremes of pH (2.0) and iron (1293 mg/l)
(ii) water in the recently-flooded No 7 to No 5 Shearer panels (e.g. sample 9).

The evolution of the latter waters has considerable importance in terms of understanding the likely evolution of the Blenkinsopp waters during rebound. Before flooding of these panels commenced early in 2002, water pumped from them had a pH of 6.8, with 23 mg/l Fe, 905 mg/l SO_4 and an alkalinity of 141 mg/l as $CaCO_3$ equivalent. After the period of rebound, samples collected in May 2002 showed a much lower pH (4.7 - 5.1), around 50 - 60 mg/l Fe, 1242 - 1496 mg/l SO_4 and zero alkalinity. Continued monitoring of waters pumped from this area showed a relatively rapid recovery in quality, so that by 20th June 2002 the following parameters were recorded: pH 6.2, 39 mg/l Fe, 800 mg/l SO_4 and alkalinity 35 mg/l as $CaCO_3$ equivalent. The inference is that:

- generation of acidic leachates occurred rapidly as water levels rose, due to dissolution of secondary minerals (which were conspicuously present as efflorescent crusts on floor shales and in the prominent inter-seam parting in this part of the mine)
- neutralisation of these acidic leachates occurred rather more slowly, by means of open-system dissolution of calcite present in limestone clasts in the goaf.

Further bolstering confidence in the capacity of the limestone goaf to neutralise acidic leachates and thus limit the mobility of Fe is sample 11, which is water draining from a completed shearer panel which had been flooded for more than a year, before a borehole was drilled into its goaf from a down-dip position (to remove the potentially dangerous accumulation of water before some (ultimately abortive) development work) The high alkalinity (136 mg/l as $CaCO_3$) and low Fe concentration (4.2 mg/l) of this water are very encouraging in terms of the kind of water the deepest workings of Blenkinsopp are likely to yield in the long-term.

One possible use of the type of data presented in Table 1 is the identification of types of water which can be expected to be head-dependent. These will by and large be deep-seated groundwaters, typically characterised by elevated mineralisation, and probably also by elevated temperature. Inspection of the data presented in Table 1 suggests that the most deep-seated groundwaters are characterised by temperatures in excess of 13°C, and typically also by conductivities in excess of 1500µS/cm. If this threshold is applied to the waters encountered in the pit, simple calculations lead to the conclusion that around 60% of the total water make can be interpreted as being head-dependent in nature.

CONCEPTUAL MODEL FOR POST-ABANDONMENT FLOODING AND CHANGES IN WATER QUALITY

A conceptual model has been developed for the likely system response to abandonment and flooding, based on the observed water flows and qualities during the working of the mine and on the distribution of pollutant source / sink minerals within the workings (which is related both to geology and the type of mining voids present in different parts of the mine). This conceptual model may be summarised in the following suite of assumptions:

(i) The rate of ground water inflow to the workings will gradually decrease as the workings slowly fill with water, as the head differences between the interior of the mine and the source aquifers gradually decline.
(ii) The final, residual water make of the mined system following completion of rebound will be around 40% of that measured during mining.

(iii) Water quality evolution will occur rather differently in the deep modern workings and in the shallower more ancient workings, according to the following principles:
- In the deeper workings, ready availability of calcite in the form of limestone clasts in longwall goafs will result in neutralisation of the acidity derived from dissolution of pyrite oxidation salts (which are abundantly present in the seam, inter-seam parting and floor strata). The evolution of water quality is likely to closely resemble that observed during the flooding of the No 7 to No 5 Shearer panels in April to June 2002, as described above.
- In the shallower workings, which are up-standing 19th Century bord-and-pillar workings, with either 30 to 60cm of 'top coal' still in place or else pyritic shale as the immediate roof bed, acidic leachates will form in abundance. However, the isolation of the overlying limestone from the voids means that there will be far less scope for neutralisation reactions. While some neutralisation may be afforded by disseminated ankerite (albeit none was observed in the seam during mining), calcitic stone dust (spread in line with explosion prevention precautions, and which will only dissolve once hydrophobic coatings on particles are breached), and some aluminosilicate minerals, overall it is expected that mine waters rising through this zone will undergo net acidification.

(iv) Following completion of flooding and the onset of mine water outflow to the surface environment, a flushing process will ensue, resulting in an improvement in mine water quality over time, in accordance with the generic model proposed by Younger (2000). Long-term mine water quality is likely to closely resemble that observed in a number of other abandoned collieries which worked the same coal seam in this area.

PREDICTIONS OF REBOUND TIMING AND WATER QUALITY EVOLUTION

This conceptual model has been converted into an equivalent quantitative model using the array of modelling approaches described by Younger and Adams (1999) and Younger (2000). The key findings of this predictive work may be summarised as follows:

A. The only likely point of emergence for the Blenkinsopp mine waters after the completion of rebound is the Smallburn shaft, and the earliest date at which overflow might occur is May 2004. However if the assumption of a 60% reduction in inflows is vindicated, numerical modelling suggests that overflow may not commence until April 2005.

B. Post-rebound flow rates to be expected from the shaft are anticipated to average about 1800 m^3/d (varying between 1560 m^3/d in the summer, and 2040 m^3/d in winter).

C. Post-rebound water quality is likely to vary over time. The very first waters to emerge from the shaft may well be acidic, reflecting the dissolution of pyrite oxidation products (iron hydroxysulphates) in the bord-and-pillar workings closest to surface. pH is likely to be less than 4 (possibly around 3.5) and total iron may approach 300 mg/l. These conditions are unlikely to persist very long, before more buffered waters originating from the deeper flooded workings mix with the more acidic waters at the top of the water column and give rise to an improvement in mine water quality. Iron concentrations closer to 100 mg/l, and a pH around 6, are likely to characterise this second stage of overflow, a few weeks after the commencement of decant. Water quality will slowly improve thereafter, eventually settling down to neutral pH and total iron around 14 mg/l in the long-term (as observed at other abandoned collieries in this area), albeit these stable conditions may not be established until 7 or more years after overflow commences.

ACKNOWLEDGEMENTS

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RISK ASSESSMENT AND MODELLING

Application of Tidal Dispersion Effects in Groundwater Risk Assessment

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ABSTRACT
A former chemical works in Dorset is currently being redeveloped for residential and other purposes. This follows successful completion of two years of remedial works, comprising soil excavation, air sparge/soil vapour extraction and groundwater pump and treat, to address ground contamination (comprising mainly chlorinated solvents and benzene) that resulted from former industrial activities. The principal environmental receptor of concern was the adjacent, high quality, Back Water Channel feeding Poole Harbour.

A conceptual hydrogeological model was developed for the site and sophisticated numerical fate and transport modelling was used to determine potential risk to the Channel and remedial groundwater target concentrations. The numerical models MODFLOW and MT3D were used to simulate the groundwater flow and transport of five contaminants of concern (COCs). The models were rigorously tested by a process of calibration and sensitivity analysis to ensure that model simulations represented the site conceptual model, particularly the on-site aquifer conditions, as accurately as possible. Remedial targets for the five principal COCs were back-calculated using a semi-probabilistic technique and appropriate saltwater Environmental Quality Standards as target concentrations, without incorporating dilution from the Back Water Channel.

Further clarification of the complex conceptual hydrogeological model was provided through monitoring of key physicochemical parameters in groundwater and the Channel to evaluate the tidally influenced area adjacent to the Channel. Statistical assessment of the parameters resulted in estimation of a tidal dispersion zone and tidal dispersion factor. This was then applied to the results of the numerical modelling to refine the COC groundwater remedial targets for the site.

After two years of intensive remediation, a substantial improvement in the environmental quality of the site groundmass and shallow groundwater and a marked reduction in source contamination, environmental and development risk were achieved. More importantly risk to the Back Water Channel, which was low initially, was further reduced. Cost-benefit analysis of the continued operation of the remedial system, using the Environment Agency's own 'cost-benefit' methodology (developed by Atkins in 1999), was able to support the case for the cessation of active groundwater remediation. Application of tidal dispersion to the simulated remedial targets confirmed that risk from the five principal COCs to the Back Water Channel was insignificant.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

INTRODUCTION

Background and History of Site Activities

The 1.9-hectare site is located in Dorset, adjacent to the Back Water Channel on the north west boundary which drains into Poole Harbour, and is bounded on the east, west and south west sides by commercial properties. Since the 1800's the site has comprised by mud flats (later reclaimed), a saw mill, joinery works and other buildings, including terraced houses on the southern part of site. The site began its 50-year history as a chemical manufacturing, storage and research facility in 1946. Operational use ceased in 1998 in readiness for site sale and redevelopment.

A road, oriented north east /south west, divides the site into two principal areas. Area 1 is located adjacent to the Channel and Area 2 is located south east of the road (Figure 1). Area 2 was used primarily for storage and packaging, including acid filling, electrical engineering workshops and stores, a general chemicals store, a petroleum store, mill room and stains manufacturing until the mid 1960s. Following demolition of the original buildings in the late 1960s, new research, storage and manufacturing facilities were constructed with commissioning during 1970. Manufacturing in Area 2 was scaled down from 1995, as the result of more modern facilities being constructed on Area 1, and finally all operations ceased in 1998.

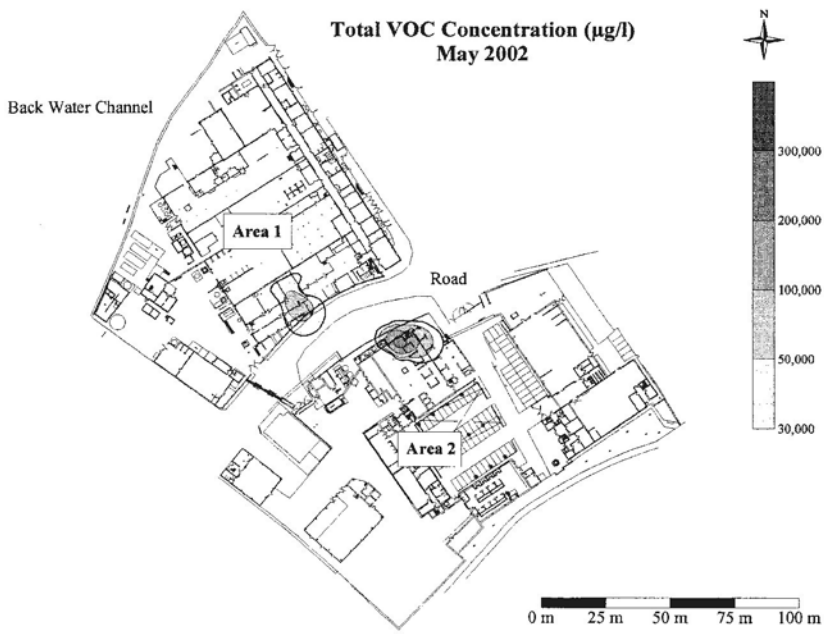

Figure 1. Site map showing residual total VOCs hot spots in groundwater, following two years of remediation.

Soil and groundwater investigations of the site occurred between 1997 and 1999 resulting in the detection of metals and volatile organic compounds (VOCs), predominantly consisting of chlorinated VOCs and benzene, in soils and groundwater. A phased remediation programme was initiated in early 2000 focussing on the south eastern portion of Area 1 and northern portion Area 2, and comprised the following elements:

- excavation and off-site disposal of 3,200 m^3 of contaminated soil between February and June 2000;
- air sparging coupled with soil vapour extraction from July 2000 to April 2002, including the installation of 62 air sparging wells; and
- groundwater pump and treat from May 2001 to July 2002 using eight extraction wells.

A Tier 4 quantitative controlled water risk assessment was undertaken to determine appropriate groundwater remedial targets for the site and a formal cost-benefit analysis was conducted to support the decision to cease operation of the groundwater pump and treat system, thus avoiding unnecessary remediation costs.

CONCEPTUAL HYDROGEOLOGICAL MODEL

The site is underlain by 0.5 to 3.5 m of made ground and a silty sand alluvial aquifer (Poole Formation), which is designated as a minor aquifer by the Environment Agency. The silty sand aquifer consists of discontinuous clay and silt lenses located between 3 and 4m depth; a deep clay horizon lies at approximately 6m to 10m depth, forming the base of the aquifer. A cross-section through the site from the northwest to the southeast, and roughly parallel to the groundwater flow direction, is presented in Figure 2 to include the main features of the conceptual model.

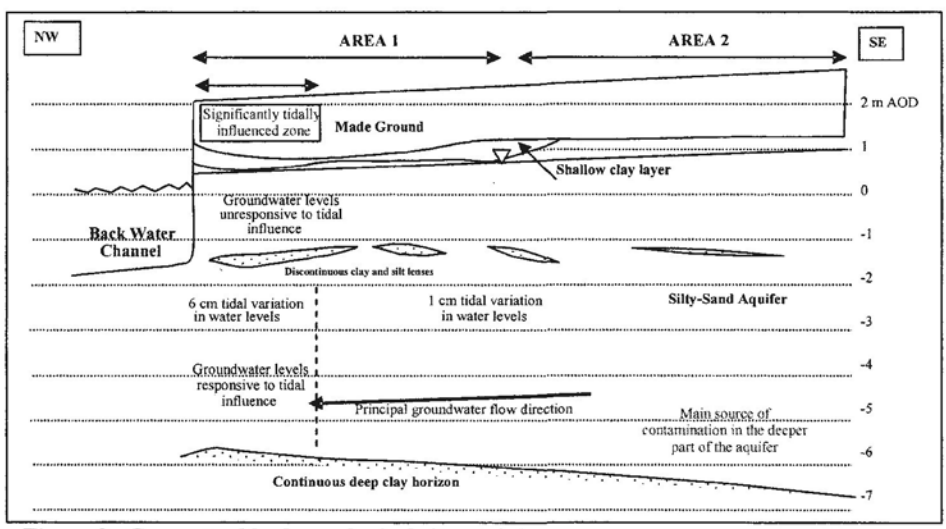

Figure 2. Conceptual hydrogeological site model.

In summary the source of the COCs is in the deeper part of the silty sand aquifer, below the discontinuous clay/sit lenses. The deeper part of the aquifer is tidally influenced, which proves a hydraulic link between the Back Water Channel and the COC source zones. Monitoring data show that groundwater levels in the deeper part of the aquifer change by approximately 6 to 2 cm located 50 to 100 m distance from the Back Water Channel. The tidal cycle within Poole Harbour is known to be complex due to its proximity to an amphidromic point with more than two high and low tides within one day, demonstrating an unevenly spaced daily tidal cycle.

Groundwater flow directions are generally towards the Back Water Channel in a north-westerly direction. However, groundwater flow directions are more complex in the centre of the site between Areas 1 and 2 where an alternating groundwater mound and sink has been observed at different monitoring events. Though the cause of this feature is not clear, the groundwater flow is possibly influenced by the drainage systems beneath the intersecting road. Hydraulic conductivity values were estimated from pumping tests conducted in Areas 1 and 2 and ranged from 10 to 45 m/day.

Locations of the on-site source zones are dependent upon the varying site uses (e.g. manufacturing, storage areas), and therefore usually vary for each COC. However, the hot spots are generally located in the centre of the site towards the southern boundary of Area 1 and towards the northern boundary of Area 2. Figure 1 displays the two primary groundwater hotspots for total VOCs outlined as the upper 10% concentrations from the May 2002 sampling event.

GROUNDWATER CHEMISTRY

Contaminants of Concern

Groundwater investigations at the site identified several VOCs present in groundwater beneath the site at levels above saltwater Environmental Quality Standards (EQSs), resulting in the installation of the remediation system briefly described above. The primary COCs were identified as benzene, chloroform (trichloromethane), dichloromethane (DCM), 1,2 dichloroethane (1,2 DCA) and total VOCs. During the remediation monitoring, the groundwater pH was noted to have decreased, potentially increasing the mobility of metals in the saturated zone. Therefore, several metals were also identified as COCs (i.e. arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, silver, vanadium and zinc).

Physicochemical Parameters

Physicochemical monitoring was conducted at eight locations, progressing linearly from the Back Water Channel towards the centre of the site at approximately 150 m inland. Seven key parameters were monitored on two occasions, one during a neap tide event (the tidal event of least amplitude) and one during an intermediate stage in the tidal cycle. During both tidal monitoring events, key parameters were monitored seven times during an 11-hour period, which included two high tides and one low tide. The key parameters included chloride, bromide, electrical conductivity, dissolved oxygen, pH, temperature and water levels, and were used to assess the influence of the Channel tidal nature on groundwater chemistry.

GROUNDWATER FATE AND TRANSPORT MODELLING

The numerical models MODFLOW and MT3D have been used to simulate the groundwater flow and transport of COCs at the site, applied as the Tier 4 risk assessment to the Back Water Channel. The aim of the modelling was to simulate the important conceptual model features, except that of the tidally influenced groundwater flow conditions of deeper portion of the silty sand aquifer. Because the tidal cycles are (i.e. do not follow regular 12-hour and 36-minute cycles), it was impractical to discretise the stress periods within the groundwater.

The location of the metal and VOC source zones and initial concentrations used in model runs were defined based on the most recent groundwater chemistry data compiled from the January through May 2002 monitoring events following two years of remediation. Pre-remediation soil investigation data were also considered to ensure that the model runs were based on the most conservative starting point, particularly with regard to metal hotspot areas, their proximity to the Back Water Channel, and maximum detected starting concentrations.

The flow and transport models were rigorously tested by a process of calibration and sensitivity analysis to ensure that model simulations represented the site conceptual model and aquifer conditions on site as accurately as possible. The sensitivity analysis tested the range of each of the input parameters that gave a good model calibration. These ranges for the most sensitive parameters were then used in the semi-stochastic analysis to back-calculate the groundwater remedial targets. The semi-stochastic input parameters comprised made ground and aquifer hydraulic conductivities, boundary condition parameters, recharge, longitudinal and transverse dispersivities and degradation half lives.

The model was initially used to simulate conservative migration times to the Back Water Channel to assess whether the contamination could potentially reach this receptor. Migration times were simulated using deterministic particle tracking, the results of which were then used to calculate revised migration times to include contaminant retardation. These simulations did not include the effects of contaminant degradation.

The model was then used to calculate the remedial targets for each of the COCs by applying the EQS values at a hypothetical point in the aquifer adjacent to the Back Water channel; this did not take into account tidal dispersion effects. The groundwater remedial targets were back-calculated by a process of manual iteration since the MODFLOW/MT3D model works in a forward mode. In other words, it will only simulate concentrations at a down gradient point of interest migrating forward from a given source concentration.

The model was also used in a semi-stochastic manner in order that all physically feasible ranges of parameters were applied to obtain a confidence level for each of the final remedial targets. Five values for each input parameter were applied to obtain a set of remedial target values for each COC. Crystal Ball®, a statistical software package, was then used to obtain the 95% confidence level final remedial target from more than 100 remedial target values for each COC. The outcome of this series of modelling stages was that conservative remedial targets were estimated without inclusion of tidal dispersion effects that may be present at the site.

TIDAL DISPERSION

Tidal dispersion factors (TDFs) were calculated to quantify the relationship of the tidal dispersion effect on the VOC groundwater concentrations adjacent to the Channel, applying the physicochemical parameters monitored during neap and intermediate tidal conditions. It was confirmed that a tidal mixing zone exists adjacent to the Back Water Channel during neap tides, as well as intermediate tides, which extends up to 50 m from the Channel.

Minimum and average TDFs of 3.2 and 7.4 were calculated to occur in the aquifer at a distance of 10 m from the Channel, values which are likely to increase closer to the Channel. The TDFs were determined from the seawater to groundwater ratios for chloride concentrations and conductivity measurements at the nearest well location to the Channel (MW1), located 10 m from the Channel. The seawater to groundwater ratios for MW1 ranged from 2.2:1 to 9:1. Figure 3 displays the seawater to groundwater ratios calculated at each monitoring location compared with the distance from the Channel for both neap and intermediate tidal conditions.

The minimum seawater to groundwater ratio of 2.2:1 occurred during neap tidal conditions, with an average ratio of 6.4:1 applying both tidal data sets. Therefore, the data demonstrate that at 10 m from the Channel, seawater disperses the groundwater concentration by a minimum TDF of 3.2 or an average TDF of 7.4 (where total parts of water equals 7.4 split between 1 part groundwater and 6.4 parts seawater). At a closer distance to the Channel the TDF could be larger than 7.4.

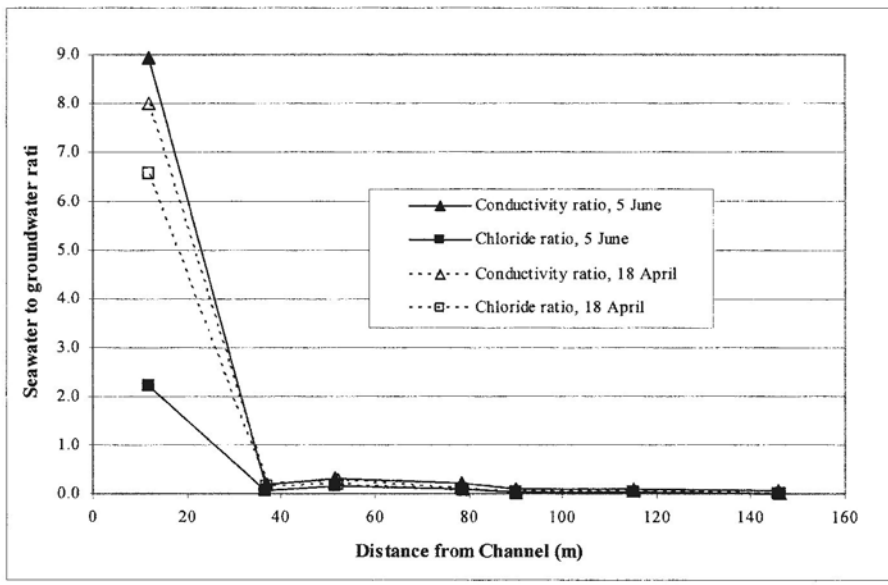

Figure 3. Tidal influence of Back Water Channel on groundwater chemistry.

GROUNDWATER REMEDIAL TARGETS

Remedial targets, back-calculated using the semi-stochastic model and compiled at a 95% confidence level, were developed for Areas 1 and 2 individually. Tidal dispersion effects observed adjacent to the Channel were incorporated by multiplying the simulated remedial targets by the minimum and average TDFs of 3.2 and 7.4. For demonstration of the remedial target derivation process, semi-stochastic remedial targets and revised targets incorporating tidal dispersion for VOCs (not metals) are presented below in Table 1, compared with maximum groundwater concentrations detected in May 2002 for both Areas 1 and 2.

Table 1. Groundwater remedial targets compared with May 2002 concentrations

VOC	EQS (µg/l)	Simulated remedial target (µg/l)	Revised remedial target (µg/l)		Maximum measured concentration (µg/l)
			TDF = 3.2	TDF = 7.4	
Area 1					
Benzene	30	12,210	39,072	90,354	3,252
Chloroform	12	44,583	142,666	329,914	5,802
DCM	2,000[a]	>solubility	>solubility	>solubility	28,840
1,2 DCA	10	26,106	83,539	193,184	67,007
Total VOCs	13[b]	44,869	143,581	332,031	104,901
Area 2					
Benzene	30	58,756	188,019	434,794	4,286
Chloroform	12	52,670	168,544	389,758	15,222
DCM	2,000[a]	>solubility	>solubility	>solubility	37,480
1,2 DCA	10	84,663	270,922	626,506	258,080
Total VOCs	13[b]	181,190	579,808	1,340,806	315,068

[a] a project-specific PNEC value for DCM was derived by the Environment Agency.

[b] Calculated as the weighted average of EQS values for benzene, chloroform and 1,2 DCA.

From comparison of maximum measured concentrations to groundwater remedial targets, the 1,2 DCA and total VOCs concentrations exceeded the simulated remedial targets for both Areas 1 and 2. DCM remedial target was simulated to be above its solubility limit due to application of the high EQS value. Therefore, the DCM EQS was not used within the calculation of the weighted EQS for total VOCs. When both the minimum and average TDFs have been applied to the remedial targets calculated previously for 1,2 DCA and total VOCs using the semi-stochastic model, the maximum observed concentrations for May 2002 at Areas 1 and 2 fall below the revised remedial targets.

SUMMARY

Shallow soil and groundwater contamination beneath the former chemical works site was significantly reduced as a result of an intensive two-year remediation programme. Metals and five VOCs (benzene, chloroform, DCM, 1,2 DCA and total VOCs) were identified as COCs in groundwater, located primarily within the centre of the site. Tier 4 risk assessment, tidal influence monitoring and a remedial cost-benefit analysis were applied to support the decision that substantial environmental quality improvement and source contamination reduction were achieved, thus further reducing environmental risk to the adjacent Back Water Channel.

Evidence of a tidal groundwater mixing zone was observed adjacent to the Channel within which tidal processes are dispersing the COC concentrations. This was first suspected as elevated concentrations were not detected in the aquifer near the Channel, and subsequently demonstrated through a carefully designed programme of monitoring. The results of the tidal influence monitoring of key groundwater parameters indicated that:

1. a tidally influenced zone exists near the Back Water Channel during both neap and intermediate tidal conditions where seawater is mixing with groundwater;
2. the most significantly influenced area of the groundwater mixing zone extends up to 50 metres from the Channel;
3. at approximately 10 m from the Channel in MW1 the seawater to groundwater ratio ranges from 2.2:1 to 9:1, depending on the tidal amplitude; and
4. chloride concentrations and electrical conductivity measurements provide the clearest evidence for the presence of the mixing zone.

A Tier 4 risk assessment, comprising numerical groundwater flow and transport modelling using a semi-stochastic methodology, was applied for back-calculating groundwater remedial targets for comparison to measured on-site concentrations. Tidal dispersion processes were not directly included within the numerical model since the Back Water Channel in the vicinity of the site is characterised by irregular spacing of the daily high/low tides. Instead, the simulated remedial targets were multiplied by the minimal and average TDFs of 3.2 and 7.4 to yield revised targets. Maximum groundwater concentrations for total VOCs and 1,2 DCA were found to exceed the semi-stochastic remedial targets. However, upon comparison to the revised targets incorporating tidal dispersion, both total VOCs and 1,2 DCA concentrations for Areas 1 and 2 of the site were below theses values. Application of risk-based remedial targets incorporating observed tidal dispersion, along with a remediation cost-benefit analysis, supported the decision that no further reduction in environmental risk to the Back Water Channel was required through continuation of the groundwater pump and treat system.

Acknowledgements
Liaison with the Environment Agency was maintained throughout the site investigation, remedial works, tidal influence monitoring and risk assessment process. Their review and recommendations provided valued input to the project. IT Corporation implemented the remediation works and Plejades, environmental consultants in Germany, provided additional review on behalf of the client.

An Investigation into the Role of Secondary Leachate Collection System in Landfills by Laboratory Modeling

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ABSTRACT
The role of secondary leachate collection system in solid waste landfills was investigated in a laboratory model. The model was designed to incorporate three-layer soil system, a top source reservoir, and a bottom receptor reservoir. From top to bottom, the source reservoir simulated the primary leachate collection system (PLCS), the first clayey silt layer simulated the primary compacted liner, the fine gravel layer simulated the secondary leachate collection system (SLCS), the second clayey silt layer simulated the secondary liner, and the bottom receptor reservoir simulated the underlying aquifer. During the test source and receptor solutions were taken and analyzed for chloride concentrations. Also samples were taken from the fine gravel layer to observe the chloride concentration change in the SLCS with time. At test termination, the soil samples were extruded from the model, sliced, and chloride concentration was measured in soils depth. The computer code POLLUTE was used to predict the observations. The results showed that the unsaturated SLCS could play a role in concentration decrease in the underlying soils. The model is shown to perform well and provide a useful laboratory methodology for small scale experimental modeling of engineered landfills. The observations were in good agreement with the theoretical predictions made by POLLUTE.

INTRODUCTION
Some modern landfills are built using multi-layered barrier systems consisting of primary and secondary clayey liners with a secondary leachate collection and removal system (SLCS) in between. This layer is expected to remain unsaturated. The contaminants migrating through the overlying liner would pass through this unsaturated coarse-grained layer.

The migration of chloride and sodium in an unsaturated stone secondary leachate collection system has been investigated using a laboratory model (Rowe and Badv, 1996; Badv, 1995). In this investigation a two-layer large scale model was used. An unsaturated 38 cm thick clear stone layer, consisting of a relatively uniformly graded clear stone having a diameter from 20 to 50 mm, was located underneath a 12 cm thick clayey silt layer. There was a 10-cm layer of sodium chloride solution as a source reservoir over the clayey silt layer and an initially uncontaminated receptor reservoir below the stone layer. During the tests there was flow from the source through the clayey liner and unsaturated stone into the receptor. Figure 1 shows a picture view of the laboratory model used in this investigation and Figure 2 shows the observed and predicted chloride concentration profiles through the clayey silt layer and underlying unsaturated stone layer. As shown in Figure 2 relatively high and uniform concentrations were observed in the unsaturated stone layer and the experimental observations were accurately predicted using one-dimensional advective-diffusive theory. The groundwater velocity played a significant role in contaminant transport through unsaturated stone even at a Darcy velocity of 5.5×10^{-10} m/s (see Badv, 1995 and Badv and Rowe, 1996 for more details and discussions).

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.



Figure 1. A view of the large-scale two-layer laboratory model used to study the chloride migration through an unsaturated clear stone layer simulating a secondary leachate collection system (after Badv, 1995)

In modeling multi-layered systems, all conventional techniques (e.g., finite element, finite layer, etc.; see Rowe et al., 1995) assume that the migration can be simulated by adopting appropriate layer properties and invoking continuity conditions at the layer boundaries. This has been verified by laboratory modeling on two layer saturated/unsaturated soils (Rowe and Badv, 1996a, 1996b; Badv and Rowe, 1996, 1998). The theoretical model (POLLUTE) used to analyze the results (Rowe and Booker, 1994) was selected because of its ability to easily simulate the conditions of the conducted test.

The present study focused on three-layer soil system simulating the primary and secondary clayey liners with a granular drainage layer in between, as a secondary leachate collection system.

THE LABORATORY MODEL

Figure 3 shows the picture view of the laboratory model used in this investigation. The model consists of the following segments: (1) Two Teflon tubes, with 14-cm and 10.4-cm height and 8.9-cm inside diameter, containing the upper and lower compacted clayey silt layers (simulating primary and secondary clayey liners). A space above the upper clayey silt layer contained a sodium chloride solution as a source reservoir (simulating a contaminant source in the primary leachate collection system). (2) A Plexiglas ring with 8.9-cm inside diameter and 3.8-cm height was used to create a space for the coarse sand drainage layer (to simulate the secondary leachate collection system). Two ports in opposite directions were installed in the tube; the left port was to maintain the atmospheric pressure inside the upper unsaturated portion of the coarse sand drainage layer. The right port was used as a septum port for sampling from the lower saturated portion of the coarse sand drainage layer. (3) A Teflon receptor reservoir with inside diameter of 8.9-cm and height of 5-cm, with inlet and outlet valves and a septum sampling port was located underneath the lower Teflon tube. (4) The bottom and top aluminum plates with four steel rods were used to hold the tubes.

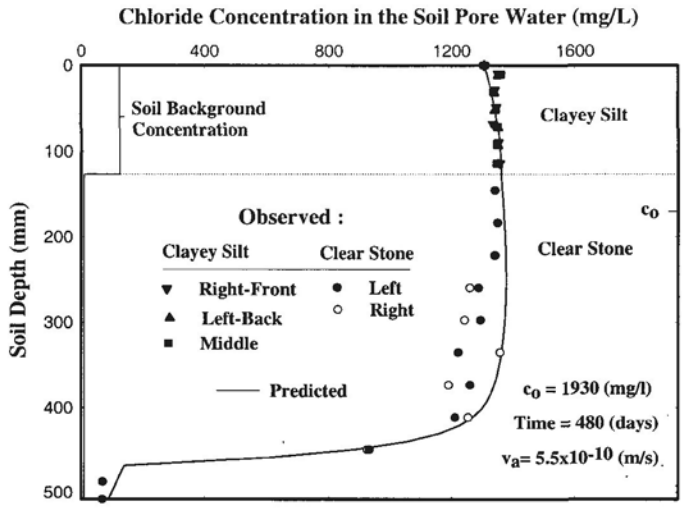

Figure 2. Observed and predicted chloride concentration profiles through the clayey silt and underlying unsaturated clear stone layer in the large-scale laboratory model used to simulate the secondary leachate collection system (after Badv, 1995)

(5) A pipette was attached to the receptor reservoir to facilitate sampling from the receptor reservoir. (6) The model was located on top of a magnetic stirrer to stir the receptor reservoir solution during the test by means of a magnetic bar inside the reservoir. The upper source reservoir solution was stirred manually during the test.

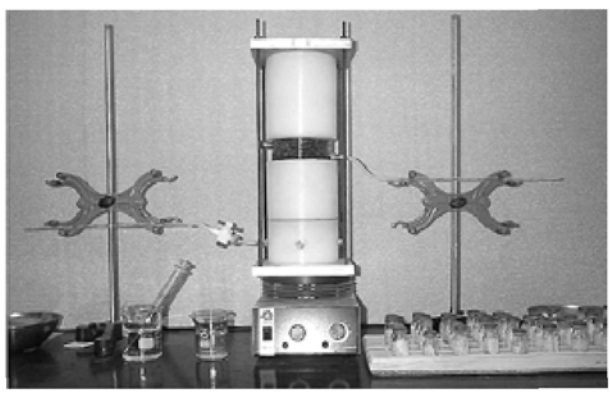

Figure 3. A view of the three-layer laboratory model used to study the chloride migration through saturated/unsaturated coarse-sand drainage layer simulating a secondary leachate collection system

MATERIALS

The low plasticity clayey silt sample was obtained from the Urmia City landfill site (Iran). The sample was air dried, pulverized, and passed through a No. 4 sieve (<4.7 mm).

Uniformly graded coarse sand was used as a drainage layer, in between the compacted clayey silt layers. The sand sample was washed with distilled water and air dried before use. Table 1 shows the physical characteristics of the soil samples. The sodium chloride solution of known concentration for chloride was used as a contaminant source. The chloride ion was used as a tracer in the experiments.

Table 1. Physical characteristics of soils used in the experiments

Properties	Clayey silt	Coarse sand
Liquid limit (%)	22	-
Plastic limit (%)	14	-
Specific gravity	2.73	2.72
Maximum dry density (g/cm^3)	1.81	1.61
Range of particle size (mm)	0.002-4.6	2.4-4.75

TEST METHOD

The air dried clayey silt sample was mixed with tap water to a 2-4 weight percent wet of optimum water content to obtain a minimum hydraulic conductivity after standard compaction (Mitchell, 1993). The wet sample was then compacted inside the upper and lower Teflon tubes using the standard proctor method to a height of about 7-cm.

The Teflon receptor reservoir was placed on top of the magnetic stirrer and the lower Teflon tube containing the compacted lower clayey silt layer was placed on top of the reservoir. A porous disk separated the reservoir and the soil. The coarse sand layer was placed and compacted inside the ring. The upper Teflon tube containing the upper compacted clayey silt layer was placed on top of the Plexiglas ring. The upper aluminum plate and the rods were installed and the test cell was tightened. The source sodium chloride solution was poured on top of the upper clayey silt layer and the test was started. The infiltrated solution through the upper clayey silt layer, passed the upper unsaturated coarse sand layer and was collected, drained, and analyzed for chloride concentration, regularly. The concentrations were plotted against elapsed time as shown in Figure 4. The source reservoir was sampled during the test and analyzed for chloride concentration as shown in Figure 5a. The infiltrated solution into the receptor reservoir, ex-filtrated through the pipette as shown in Figure 3. The chloride concentration change in the receptor reservoir was monitored with time and plotted in Figure 5c. The Darcy velocity through the upper and lower clayey silt layers was calculated based on the volume of solutions infiltrated through these layers.

At the test termination, the source solution was drained from the upper reservoir, the upper Teflon tube was detached and the clayey silt sample was extruded and sliced into equal thickness. The upper unsaturated portion of the coarse sand layer was collected by a spoon, and its chloride concentration was measured using the wash method (Barone et al., 1990). For the lower saturated portion of the layer, enough pore water was extracted by a syringe and analyzed for chloride concentration. The clayey silt samples were squeezed by a soil pore water squeeze apparatus and the extracted solutions were analyzed for chloride concentration. The observed chloride concentrations in the upper clayey silt layer, upper unsaturated portion and lower saturated portion of the coarse sand layer, and lower clayey silt layer, were plotted against soils depth as shown in Figure 5b. As shown, the unsaturated coarse sand caused drop in chloride concentration in the underlying soils, giving rise to the effect of increased tortuosity and reduced chloride diffusion. The test geometrical, physical, and chemical data are listed in Table 2. The test was performed at 23 ± 2 °C.

Table 2. Three-layer soil test geometrical, physical, and chemical properties

Properties	Soil layers		
	Upper and lower clayey silt	Unsaturated coarse sand	Saturated coarse sand
Soil depth (cm)	7	1.5	2.3
Average volumetric water content (cm^3/cm^3)	0.34	0.084	0.42
Dry density (gr/cm^3)	1.81	1.61	1.61
Chloride background concentration (mg/l)	90	20	20
Chloride effective diffusion coefficient (x 10^{10} m^2/s)	6.38	2.3	11.6
Source solution height (cm)	5		
Source solution concentration (mg/l)	1950		
Upper clayey silt Darcy velocity (x 10^9 m/s)	7.4		
Lower clayey silt Darcy velocity (x 10^9 m/s)	3.0		
Test duration (days)	30		

THEORETICAL MODELING

The transport of contaminants through saturated or unsaturated soils can be described by the advection-diffusion equation (Goodall and Quigley, 1977, King et al., 1993; Rowe, 2001) which can be written as:

$$(\theta + \rho K_d)\frac{\partial c}{\partial t} = \theta D \frac{\partial^2 c}{\partial z^2} - \theta v \frac{\partial c}{\partial z} \qquad (1)$$

where c is the contaminant concentration at a depth z at time t; θ is the soil volumetric water content (θ=n, the soil porosity for saturated soil); v is the average linearized ground water velocity (seepage velocity); ρ is the dry bulk density of the soil, K_d is the distribution coefficient, nv=v_a is the Darcy velocity, and D is referred to as the coefficient of hydrodynamic dispersion. The coefficient of hydrodynamic dispersion D is commonly defined as the sum of the coefficient of mechanical dispersion, D_{md}, and effective diffusion coefficient in the porous medium, D_e.

The analysis of the tests involves solving these equations subject to appropriate boundary conditions. The boundary condition imposed by the source reservoir whose concentration $c_s(t)$ reduces with time due to the movement of chloride into the soil and also sampling, can be modeled (Rowe and Booker, 1987; Rowe et al., 1995) by:

$$c_s(t) = c_o - \frac{1}{H_f}\int_0^t f_s d\tau - \frac{q_c}{H_f}\int_0^t c_s(\tau)d\tau \qquad (2)$$

where c_o is the initial concentration in the reservoir, H_f is the height of fluid in the source reservoir, q_c is the volume of fluid per unit area per unit time removed from the reservoir for chemical analysis during the test and replaced by distilled water, and f_s is the contaminant flux into the soil.

For the advection-diffusion tests with a fluid receptor, the concentration in the receptor at time t can be described by:

$$c_R(t) = \int_o^t \left[\frac{f_R(\tau)}{h}\right] d\tau - \frac{q_b}{h} \int_o^t c_R(\tau) d\tau \qquad (3)$$

where $f_R(\tau)$ is the flux entering the receptor at time τ, h is the thickness of the receptor, and q_b is the volume of fluid per unit cross sectional area of the soil per unit time removed from the receptor for chemical analysis during the test.

A solution to equation 1 has been given by Rowe and Booker (1987, 1994) and has been implemented in a computer program POLLUTE (Rowe and Booker, 1994). This program is used in this study to predict the observed data from the laboratory models discussed earlier. The predicted profiles are shown as solid lines in Figures 4 and 5. As shown in the figures there is a good agreement between the observed data and predictions made by the theoretical model (see Badv and Mahooti, 2003, for more details and discussions).

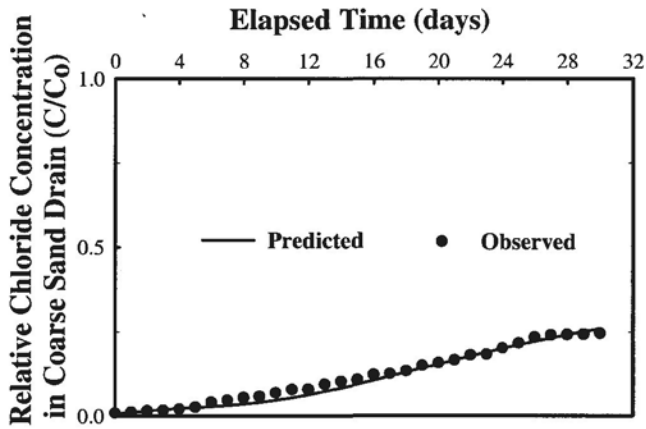

Figure 4. Observed and predicted relative chloride concentration profiles in coarse-sand drainage layer in three-layer soil laboratory model (the coarse-sand layer simulated a secondary leachate collection system)

SUMMARY AND CONCLUSIONS

The chloride migration through a secondary leachate collection system was simulated by laboratory models. In large scale two-layer laboratory model a coarse clear stone layer played a role as a secondary leachate collection system. Relatively uniform chloride concentrations were observed and seepage velocity played a significant role in chloride movement through the unsaturated stone collection layer. The theoretical model accurately predicted the observed data in the model. In another three-layer laboratory model a coarse sand saturated/unsaturated drainage layer played a role as a secondary leachate collection system in between the upper and lower clayey silt layers. A drop in chloride concentration was observed in the unsaturated portion of the coarse-sand layer showing the effect of increased tortuosity in slow movement of chloride in this portion of the layer. The theoretical model accurately predicted the observed data in this test.

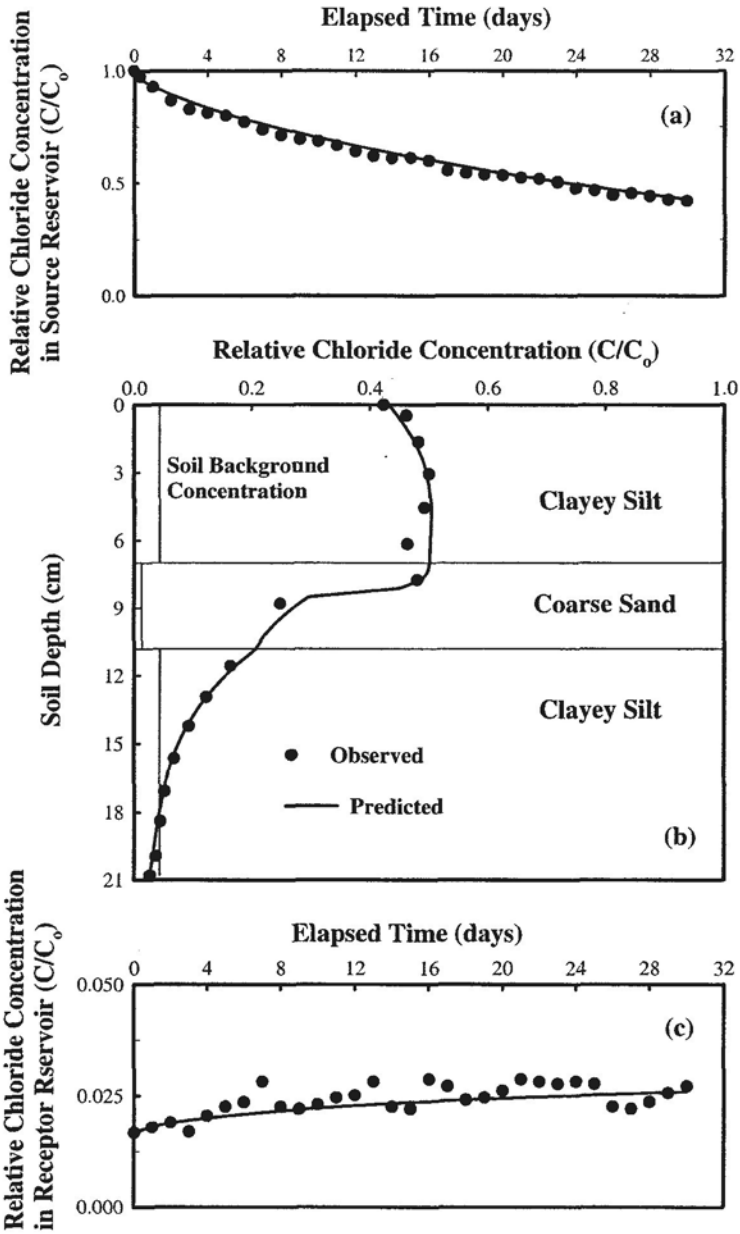

Figure 5. Observed and predicted relative chloride concentration profiles in (a) source reservoir (b) soils depth, and (c) in receptor reservoir, in three-layer soil laboratory model simulating the secondary leachate collection system

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Characterization of maximum infiltration areas using GIS tools

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KEYWORDS: Maximum infiltration areas, aquifer vulnerability, GIS, Portugal.

ABSTRACT

The main goal of this study is the spatial identification of maximum infiltration areas and aquifer vulnerability in order to delineate a protection strategy for municipal water supplies. A two-step Geographic Information System (GIS) model is presented: (i) in the first step, hydrological parameters are classified by grades of infiltration and combined, in order to delimit the most important areas; (ii) in the second step, maximum infiltration areas are merged with hydrostatic water level layer and a final map of the favourable aquifer recharge areas is obtained as an indicator of aquifer vulnerability to potential contamination. This methodology was implemented using ArcGis 8.2 software, and applied to Seixal Municipality, an urban/industrial area near the capital of Portugal, Lisbon, where negative impact on groundwater resources is a major concern.

INTRODUCTION

The objective of the study is the identification of maximum infiltration areas, taken as groundwater infiltration zones, in order to delineate a protection strategy for municipal water supplies. In this work a methodology for the delimitation of maximum infiltration areas and

aquifer vulnerability is presented based on hydrogeological criteria that describe the infiltration potential of present ground conditions in the municipality of Seixal (Portugal).

The areas of maximum infiltration will be those presenting the most favourable conditions for recharge of the aquifer systems. Considering that these areas are the most sensitive to contamination risk they should be classified using criteria that reflect the vulnerability of the aquifer system to possible contamination. Thus, the evaluation of maximum infiltration areas must consider, directly or indirectly, the hydrogeological characteristics of the terrain, such as its permeability and the hydrodynamics of the aquifer system.

METHODOLOGY

Conceptual modelling

The objective of any infiltration model is the identification and spatial characterization of land parcels that present a high potential for infiltration of surface waters. Infiltration occurs preferentially in areas where the permeability of the terrain, associated with other factors, allows the rapid vertical penetration of surface waters (Schneider *et al*, 2001). Part of this water percolates through the non-saturated zone of the ground and, on reaching the water table, recharges the aquifer. In figure 1 a diagram of the general conceptual model of infiltration is presented, illustrating the possible paths of surface water that contribute to recharging underground aquifers.

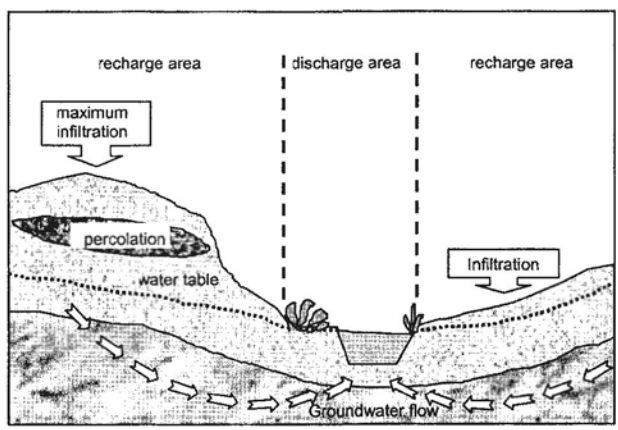


Figure 1 - Conceptual infiltration model (adapted from Schneider *et al*, 2001)

Additionally, aquifer vulnerability could be reflected by a parameter that results from the intersection of maximum infiltration areas with the depth of the hydrostatic water level. This parameter works as an indicator of aquifer vulnerability since it represents the vertical distance that a contaminant has to travel to arrive at the underground aquifer. The greater the depth of the water level, the more slowly a contaminant reaches the aquifer, and the lower its vulnerability.

GIS modelling

An infiltration model is proposed based on the selection and integration of information in GIS software (ArcGis 8.2), that combines several key hydrological parameters, categorized on a scale representing the suitability of the terrain to water infiltration. Other authors have used similar methods to assess aquifer vulnerability (e.g. Aller *et al*, 1987; Francés *et al*, 2001). In this study, a GIS methodology is applied in two steps, in order to separately assess (i) maximum infiltration areas, taking into account the relative importance of each hydrogeological parameter, and (ii) indicators of aquifer vulnerability. The methodology consists of two main steps: 1) identification of groundwater infiltration areas throughout the county; 2) modelling and mapping groundwater vulnerability to contamination. Final priority protection areas result from the combination of maximum infiltration mapping and the aquifer vulnerability indicator map. This final result provides strategically important information on the location of priority protection areas regarding the vulnerability of the aquifer.

Maximum infiltration GIS modelling

In the first step, hydrological parameters transformed to digital layers are combined and the output classified by grades of high to low capacity of infiltration. Four parameters were selected to represent terrain infiltration capacity: (i) geology, to characterize substratum permeability; (ii) soil type, to assess the permeability of non-consolidated sediments; (iii) slope, for the identification of surface drainage areas; and (iv) water streams, to identify flooding zones. As all water streams can be considered areas of maximum accumulation of superficial flow, when not taking into account the remaining parameters (geology, soils and slope), the infiltration potential within their respective areas of influence must be considered high.

Different weights are given to each parameter, representing their relative importance in the conceptual infiltration model. In this step, assuming that the infiltration potential is an independent measure from run-off amount, all built areas (union of all infrastructures polygons) were considered as non-infiltration areas and were withdrawn from the entire municipality area.

The infiltration potential (IP) model proposed can be mathematically expressed by equation 1.

$$IP = \sum_{i=1}^{N} (W_i . C_i) \qquad \textit{(equation 1)}$$

IP – infiltration potential

i – parameter index (i =1 to N)

N – number of infiltration parameters

W_i - weight of parameter i

C_i - class of parameter I

The *infiltration potential* is a weighted measure of the capability of each cell to contribute to aquifer recharge: high values define maximum infiltration areas and zero values define no-infiltration areas. The weights applied to each criterion depend on its relative importance within the parameters considered; the sum of all weighting factors is one (or 100%).

Aquifer vulnerability modelling

After delineation of maximum infiltration areas, the second step of the GIS model concerns the selection of areas where the aquifer is most sensitive, taking into account the depth of the hydrogeological water supply strata. To improve hydrostatic water level mapping and evaluate estimation uncertainty, geostatistical techniques were used, in particular the ordinary kriging method. Geostatistical modelling involves modelling of experimental variograms for assessment of variable spatial structure and estimation of variable behaviour by kriging, using variogram parameters (Goovaerts, 1997).

CASE STUDY

The impact of industry on groundwater resources is one of the major concerns of Seixal municipality (Portugal). Its strategic location near the capital of Portugal, Lisbon, combined with intensive industrial activity, mainly metallurgical, chemical, shipyards and open pit mining, has led to high population growth and has spread negative environmental effects all over the municipality. As a consequence, the implementation of appropriate strategies in

order to minimize environmental risk is extremely important. This municipality, with an area of about 95 km^2, is dependent on its own groundwater in order to supply drinking water, industrial needs, and commercial and institutional activity. Therefore, a more thorough understanding of groundwater infiltration areas and a protection strategy are required to ensure unpolluted water resources.

Assessment of maximum infiltration areas

To assess maximum infiltration areas, the four parameters that influence land infiltration potential (geology, soils, slopes and flooding areas) were digitized and categorized into classes that represent the grade of infiltration capacity of the ground. Infiltration mapping is obtained by the application of equation 1 to the information classified and weighted as in table 1.

Table 1 – Classification of infiltration parameters and respective weights

Parameter	Weight	Description	Infiltration capacity	Class code
Geology[1]	0.4	Quaternary - Alluvium and coarse sands	High	2
		Pliocene and Pleistocene - Sandy units, sandstones and clayey sandstones	Medium	1
Soils[2]	0.1	Al, Ap, Rg, Rgc, Sbl	High	3
		Cal, Par, Ppr, Ppt, Pz, Vt	Medium	2
		Assa, A, Et, Pzh	Low	1
Slope	0.4	[0-2%] – no runoff	High	3
		[2-5%] – low runoff	Medium	2
		> 5% - medium to high runoff	Low	1
Flooding areas	0.1	Inside water streams' area of influence	High	2
		Outside water streams' area of influence	Low	1

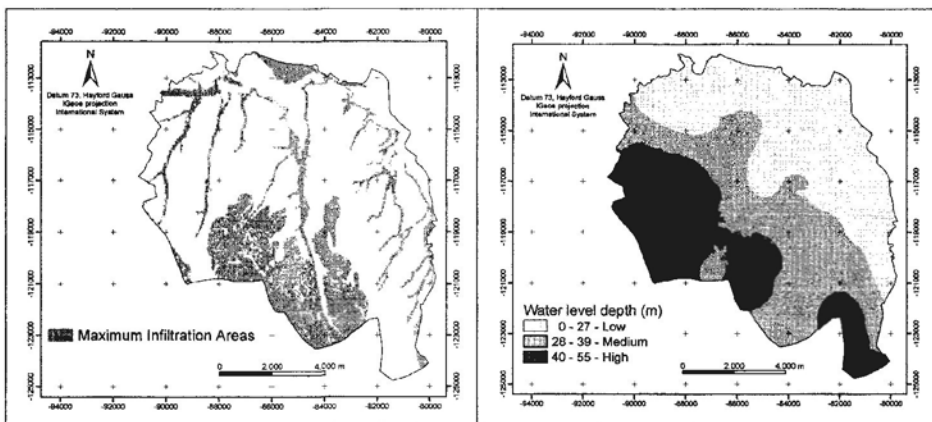
It is worth noting that, in respect to the classification of the geology parameter, the lowest class of infiltration capacity is not considered because, in general, the geological units present suitable characteristics for the occurrence of surface water infiltration in the whole Seixal area (Costa & Brito, 2001).

[1]Geological units adapted from Manuppella *et al* (1999), Zbyszewski (1963).
[2]Soil terminology according to Vasconcelos & Bessa (1970).

The final map is a matrix in which each value represents the potential infiltration grade of the terrain, classified as low, medium and maximum infiltration capacity. The class of highest potential infiltration will define the maximum infiltration areas. The final *maximum infiltration areas* map is obtained after omitting non-permeable areas (constructions, roads, etc.). Figure 2 shows the municipality of Seixal classified into maximum infiltration areas and classes of depth to water table.

Assessment of aquifer vulnerability

Overlaying maximum infiltration areas with the depth of the hydrostatic water level results in a map that represents an indicator of aquifer vulnerability to contamination. Water level mapping is performed by estimation of the hydrostatic water level, measured in a set of 273 water supply boreholes, in different years, from 1995 until actual. Geostatistical modelling was performed using ArcGis 8.2 software. Water level mapping was estimated by ordinary kriging and classified in classes of equal frequency. Figure 2 illustrates the maximum infiltration areas (above a threshold) within municipality of Seixal and depth of the water table classified in classes.



a) Maximum infiltration areas | b) Depth of water table

Figure 2 –Maximum infiltration areas and depth of water table

From figure 2 it can be observed that *maximum infiltration areas* are mainly found in the southern part of the municipality, along main water streams, and in the northern part, around Seixal bay. On the other hand, shallow water table depths occur in the NE part of the municipality, reaching greater depths in the SW and SE. Figure 3 illustrates aquifer

vulnerability mapping resulting from the interception of *maximum infiltration areas* with water level depth classes.

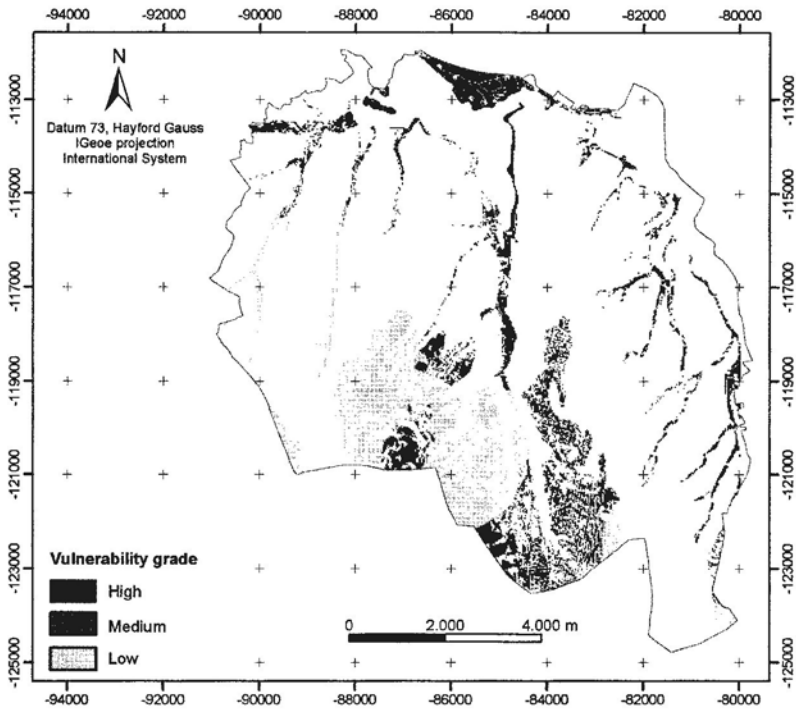


Figure 3 – Aquifer vulnerability in maximum infiltration areas

It can be seen that the areas of higher grade of vulnerability are mainly located in the northern part of the municipality where, simultaneously, ground conditions are prone to water infiltration.

CONCLUSIONS

This approach has enabled assessment of aquifer vulnerability areas taking into account ground potential for water infiltration. With this GIS methodology it has been possible to separately assess (i) maximum infiltration areas and (ii) groundwater vulnerability mapping. The combination of maximum infiltration mapping and the aquifer vulnerability indicator map results in a final map that summarizes the most favourable conditions for recharging aquifer systems and provides important strategic information on the location of priority protection areas regarding the susceptibility of the aquifer to potential contamination.

For Seixal it can be concluded that, although maximum infiltration areas are located in both the southern and northern parts of the municipality, the areas of higher vulnerability are located in the northern part of Seixal due to the shallow water table depth, which allows easy access of potential contaminants to the aquifer media.

The final vulnerability map can be seen as a guide for a municipal water protection strategy, as it locates aquifer area that is prone to contamination.

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Modelling the three-dimensional behaviour of a prototype nuclear waste repository

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ABSTRACT
This paper presents a study of the full three-dimensional thermo/hydro/mechanical behaviour of SKB's Prototype Repository experiment. In particular, the three-dimensional interaction of the multiple barrier system consisting of MX-80 bentonite buffer with the host rock is investigated. These materials are subjected to a steep thermal gradient representing the heat produced by high-level nuclear waste. A hydraulic gradient is also present due to the host rock acting as a source of water. The simulation is achieved via the application of the numerical code, COMPASS, which implements a coupled thermo/hydro/mechanical approach to model the behaviour of saturated/unsaturated media. These patterns of behaviour require a large three-dimensional model in order to represent the non-symmetrical, complex geometry of the proposed repository. A range of simulation results are presented detailing the hydraulic, thermal-hydraulic and thermal-hydraulic-mechanical behaviour of the Prototype Repository. Attention has been given to the micro-macro interaction occurring within the MX-80 bentonite buffer as the material begins to saturate and swell. This approach represents the effect of adsorbed water in the micropores reducing the hydraulic conductivity and "choking" the flow of water in the macropores. Attention is also given to the mechanical behaviour of the pelletised bentonite slot filling material. The simulation results have been compared with the experimentally measured results. It is found that the model is able to capture both the trends and patterns in the thermal field and hydraulic field.

INTRODUCTION
The Prototype Repository is an international, EC-supported project with the objective to investigate, on a full-scale, the integrated performance of engineered barriers and near-field rock of a deep repository intended for the disposal of high-level nuclear waste. It has been constructed at the Äspö Hard Rock Laboratory, in Sweden (Dahlström, 1998). The experimental configuration, as the name suggests, is a full-scale prototype repository representing the proposed final SKB concept for disposal. The work program is extremely comprehensive, with system design, characterisation of the rock mass, preparation of emplaced materials, through to handling and deposition of canisters being considered.

The Prototype Repository has been constructed in a 65m long TBM drift at approximately 450m below the ground surface in crystalline rock. Section I of the experiment consists of four 1.75m diameter, 8m deep full-scale deposition holes. Heater canisters have been emplaced in these holes with a combination of bentonite blocks, bentonite pellets and backfill material used to form a series of engineered barriers in accordance with the KBS-3 concept (Dahlström, 1998). This was installed during 2001 with the activation of the heaters taking

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

place from September 2001. A large range of experimental data pertaining to Section I has been collected and is readily available (Goudarzi and Börgesson, 2003). Section II, consisting of two identical deposition holes, has recently been installed with the heaters being switched on in May 2003. Figure 1 shows a schematic view of the layout of the Prototype Repository and deposition holes.

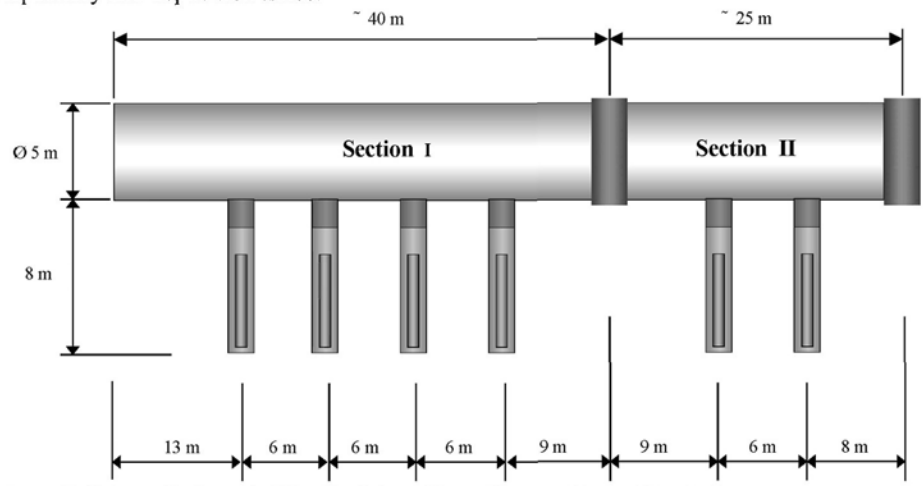

Figure 1: Schematic layout of the Prototype Repository and deposition holes

MODELLING APPROACH

The simulation work has been performed using COMPASS (**CO**de for **M**odelling **PA**rtly **S**aturated **S**oil), a mechanistic model where the various aspects of soil behaviour under consideration, are included in an additive manner. In this way the approach adopted describes heat transfer, moisture migration, solute transport and air transfer in the material, coupled with stress/strain behaviour. Detailed presentation of the formulation employed within COMPASS can be found in Thomas and He (1995 and 1998), Thomas et al. (1998) and Thomas and Cleall (1999). In order to undertake large-scale analyses the modelling infrastructure of COMPASS has been developed via the use of data visualisation techniques, parallel computing and iterative solution techniques. The strategy adopted in the work presented here is to balance the requirement to correctly capture detailed behaviour with the need to simulate the effect of the three-dimensional geometry of the Prototype Repository.

MATERIAL PARAMETERS

The mechanistic model employed in this work requires a number of material parameters to define the behaviour of each individual material present. Due to limitations of space full details of the parameters used and their determination can not be presented here. A summary of the parameters is given in Table 1. Five separate materials have been considered. Each of these requires a series of material constants and constitutive relationships to describe their thermal-hydraulic-mechanical behaviour. This information has been obtained from experimental work performed by a number of groups (Patel et al., 1997; Dahlström, 1998; Johannesson et al., 1999; Börgesson and Hernelind, 1999; Börgesson et al., 2001, 2002). In some cases mathematical equations have been fitted to experimental data to cast the material relationships in a form suitable for computer modelling.

Table 1: THM material parameters used in the analyses

Parameter	MX-80 (Cylinder)	MX-80 (Ring)	MX-80 (Pellets)	Backfill (30/70 mix)	Rock (Äspö diorite)
ρ_d (kg/m^3)	1660	1780	1200	1750	2770
e	0.67	0.56	1.55	0.57	0.005
Initial Sr	0.81	0.87	0.23	0.57	1.0
C_{ps} (J/kg.K)	800	800	800	850	750
Retention Curve	$S_r = \left[\frac{\theta_{res} + (\theta_{sat} - \theta_{res})}{\left(1 + \left(\frac{1000 \cdot \alpha \cdot S}{\rho g}\right)^{b}\right)^{(1-1/b)}} \right] / n$				See equation (1)
α	4.5×10^{-7}	4.5×10^{-7}	4.5×10^{-7}	0.00014	-
b	1.75	1.75	1.75	1.19	-
θ_{res}	0.0001	0.0001	0.0001	0.000001	-
θ_{sat}	0.4	0.36	0.61	0.363	-
β	-	-	-	-	0.33
Hydraulic Conductivity	$k_{unsat} = k_{sat.}(S_r)^3$				See equation (2)
k_{sat} (m/s)	1×10^{-13}	1×10^{-13}	1×10^{-13}	1.5×10^{-10}	10^{-9} - 10^{-12}
κ	0.17	0.17	2.0	0.17	-
κ_s	0.094	0.094	1×10^{-7}	0.094	-
G (Pa)	1×10^{7}	1×10^{7}	1×10^{7}	1×10^{7}	27.6×10^{9}
ν	0.499	0.499	0.499	0.499	0.25

$$S_r = \left[\left(1 + \left(\frac{s}{P_0} \right)^{1/(1-\beta)} \right) \right]^{-\beta} \quad (1)$$

$$k_{unsat} = k_{sat}(S_r^{1/2}(1-(S_r^{1/\beta})^{\beta})^2 \quad (2)$$

GEOMETRIC MODEL

A full three-dimensional model of SKB's Prototype Repository incorporating all of the primary features of the tunnel has been developed. The model domain measures 200 m by 100 m by 200 m and is shown in Figure 2(a). This model has been discretised using 8 noded hexahedral elements and consists of 158,175 elements and 146,380 nodes and is shown in Figure 2(b). The mesh has been refined in and around the buffer with a coarser mesh discretisation used in the far-field rock. The size of the model has been reduced by 50% via the introduction of a vertical symmetry plane along the centre of the tunnel and hence the computational requirements of the model are considerably reduced. This geometrical model has been used for the majority of the numerical modelling work with smaller three-dimensional and two-dimensional models being implemented to investigate the mechanical response of the buffer and pellets under thermal and hydraulic gradients.

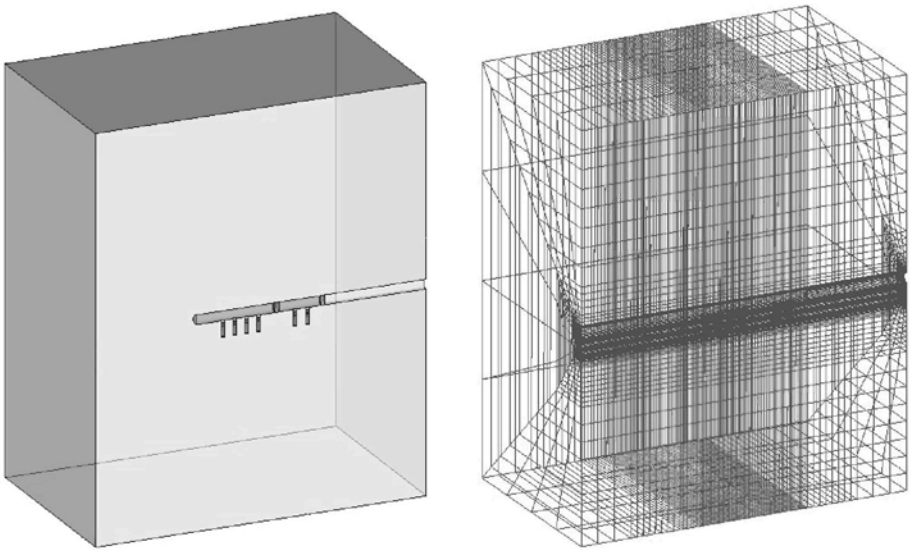

Figure 2(a): 3D tunnel domain **(b): 3D tunnel mesh**

RESULTS

Results from a series of analyses are presented here and are compared with reported experimental results presented by Goudarzi, R. and Börgesson, L. (2003).

Hydraulic Analysis of the Rock Mass prior to emplacement

A number of analyses of the rock mass prior to emplacement have been performed with the hydraulic conductivity of the rock being varied from 10^{-11} to 10^{-12} m/s. A set of analyses incorporating a "representative" fracture have also been undertaken. All analyses have been performed using the full 3D tunnel domain. Figures 3(a) and 3(b) show the steady-state pore water pressure contour plots for the full 3D tunnel mesh. Figure 3(a) is taken for a homogeneous rock mass with hydraulic conductivity of 10^{-11} m/s and it was found to reach steady-state pore water pressures after 2 years. Figure 3(b) incorporates a fracture with a hydraulic conductivity of 10^{-9} m/s and it was found that this analysis reached steady-state conditions after 180 days.

Thermal-Hydraulic Analysis of Section I

A large number of coupled thermal-hydraulic analyses have been performed to investigate the complex flow patterns that occur in the Prototype Repository following heater activation. In order to establish an understanding of these processes a comprehensive step-wise approach to the modelling has been adopted. A full range of 3D tunnel section and 2D axisymmetric analyses have been undertaken with the results being presented previously (Thomas et al., 2002). However, more recently a full three-dimensional, thermal-hydraulic analysis of Section I has been performed. This analysis captures the thermal and hydraulic behaviour for the first 600 days before Section II was installed. The performance of the full repository, after Section II has been installed, with the heaters in boreholes 5 and 6 being activated has also been performed. Recent research has shown that the micro and macro structure of a bentonite buffer material may have a pronounced effect on the saturation rates of the material

(Thomas et al., 2003). It was proposed that as water enters the buffer the majority of it becomes adsorbed within the micropores and hence is unavailable for further flow. Depending on the degree of mechanical restraint swelling of the micropore will lead to some reduction in the size of the macropores (Pusch, 1998). As the only water available for flow is contained in the macropores, the swelling of the micropore in a restrained material would thus tend to 'choke' moisture flow and further reduce the effective hydraulic conductivity of the material. Following the approach presented in Thomas et al., (2003) the hydraulic conductivity relationship used here has been modified accordingly. In the case of the Prototype Repository, compared to the buffer investigated in Thomas et al., (2003), the buffer is relatively free to deform, due to the presence of a loose pellet region, therefore the effect of microstructural swelling choking of the macro structure has been reduced. This has led to the following relationship being assumed as a first approximation:

$$k = k_{unsat} k_l \cdot [S_a + 0.06 S_r (\exp(0.01(1-0.06)S_r))] \quad (3)$$

Figure 4 shows both the simulated and experimentally measured temperature plots after 624 days for 3 different radii positions in Borehole 3. At a radius of 0.585m the temperature has been simulated to be 76.1 °C after 624 days, at a radius of 0.785m the temperature is simulated as 68.6 °C. The corresponding experimentally measured results are 77.1 °C and 67.2 °C respectively.

Figure 5 shows simulated and experimentally measured relative humidity plots in Borehole 3. It can be seen that initially there is a slight increase in relative humidity for both the simulated and measured results closer to the heater as the temperature in this region rises rapidly. This is followed by a general reduction in the relative humidity as drying begins to take place via the movement of vapour away from the hotter regions closest to the heater. At a radius of 0.585m the relative humidity is simulated to reach a minimum of 58.7 % after 190 days. The simulation follows the experimentally measured trends where there is a corresponding minimum relative humidity of 60.3% after 230 days. In both cases resaturation take place slowly up to 624 days. The initial overprediction of moisture movement at a radius of 0.785m is possibly due to an over estimation of suction in the nearby pellet region.

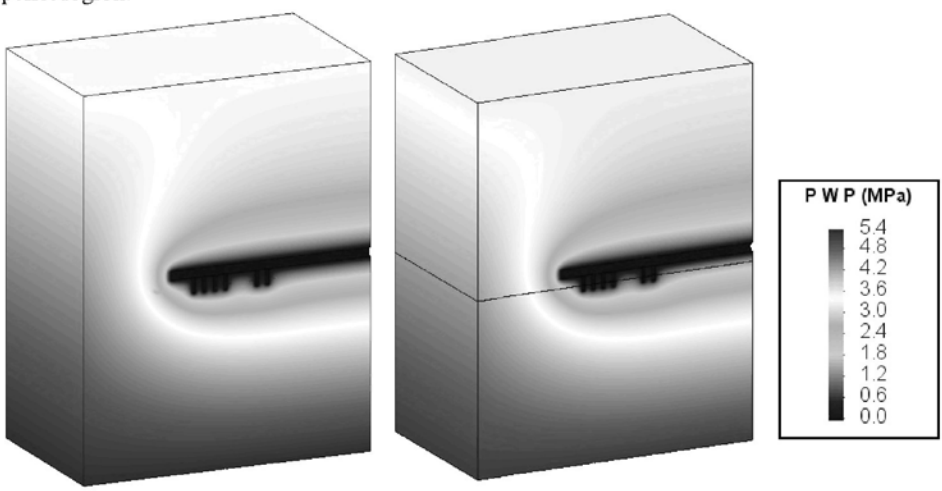

Figure 3(a): $k_{rock} = 10^{-11}$ m/s **(b): $k_{rock} = 10^{-11}$ m/s and $k_{fracture} = 10^{-9}$ m/s**

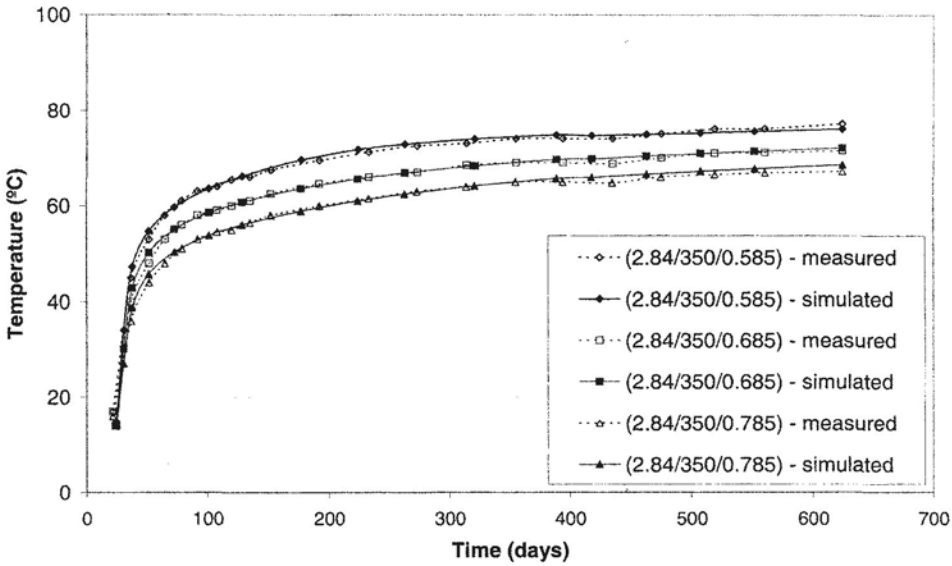

Figure 4: Measured and simulated temperature plots for Borehole 3

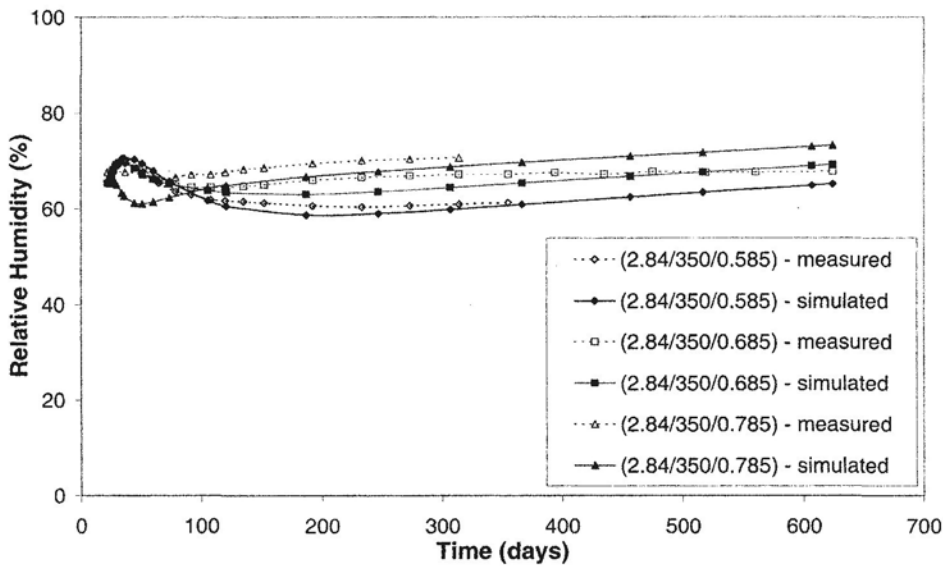

Figure 5: Measured and simulated relative humidity plots for Borehole 3

Thermal-Hydraulic-Mechanical Analysis

The coupled mechanical response of the system due to changes in the hydraulic and temperature fields is of importance particularly in the swelling materials present within the system. These materials although effectively restrained by the rock mass are able to deform locally. As discussed earlier the magnitude of such deformations and development of swelling pressures may have an influence on the flow fields. Results showing the variation of void ratio and stresses in the MX-80 buffer have been presented in previous work (Thomas et al., 2002) with recent work has focusing on the mechanical properties of the pelletised bentonite slot filling material. It is anticipated that under saturated conditions the buffer and pellets will swell and combine to form a homogenous material with the same void ratio throughout (Dahlström, 1998; Börgesson et al., 2002). In order to capture this behaviour a sensitivity analyses has been undertaken to ascertain approximate values for the mechanical material parameters for the slot filling material. Figure 6 shows the development of void ratio within the buffer, slot filling and near field granite region. It can be seen that over a period of time the buffer swells and the slot filling is compressed leading to a reduction of void ratio. By the end of the analysis the buffer and pellets have formed a more homogenous material with a void ratio in the range of 0.65 and 0.68.

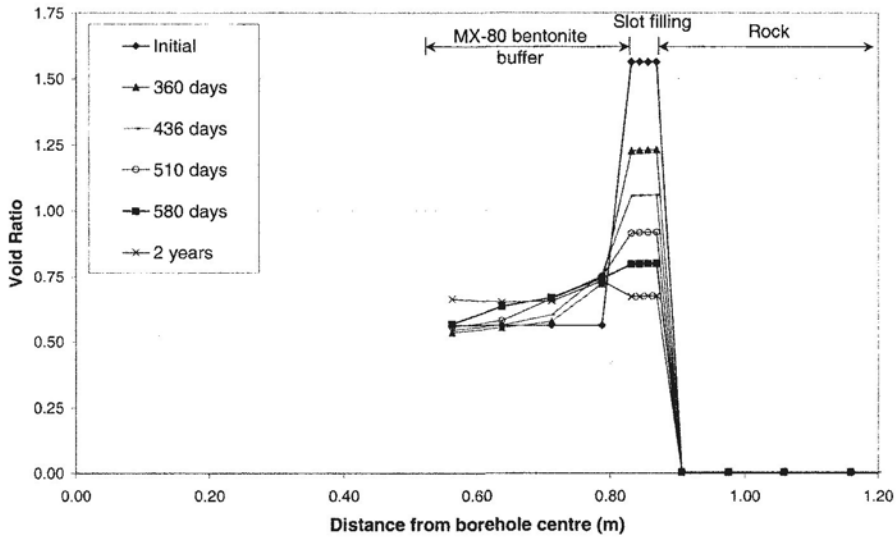

Figure 6: Variation of void ratio through the centre of the buffer and pellets over time

CONCLUSIONS

In conclusion a series of coupled mechanistic thermal-hydraulic-mechanical analyses of the behaviour of the Prototype Repository have been presented. In particular, full three-dimensional analyses of the system have been performed. A range of simulation results have been presented detailing the hydraulic, thermal-hydraulic and thermal-hydraulic-mechanical behaviour of the Prototype Repository. Particular attention has been given to the micro-macro interaction occurring within the MX-80 bentonite buffer as the material begins to saturate and swell. It was assumed that as the material saturated water was adsorbed in the micropores hence swelling and reducing the hydraulic conductivity and "choking" the flow of

water in the macropores. The simulation results have been compared with the experimentally measured results and it was shown that a good correlation was found in the thermal field and a reasonable correlation in the hydraulic regime. Attention was also given towards the accurate modelling of the mechanical behaviour of the slot filling material. Following a sensitivity analysis if was found that the void ratio in both the buffer and slot filling materials approached similar values and hence formed a more homogenous material as a result of saturation. Hence, the thermal-hydraulic-mechanical analysis was able to simulate the expected mechanical behaviour of the barrier materials.

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The Use of Risk Analysis in Landfills Remediation: a Case Study

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1 INTRODUCTION

Nowadays, contaminated sites remediation is one of the main problems connected to the environment safeguard. The concern about effects on human health deriving from inappropriate environmental practices, and the limited amount of "clean land" in industrialised areas have led to the growing need to evaluate the extent of contamination and to carry out site remediation when necessary. Some European networks, such as NICOLE (Network for industrially contaminated land in Europe) and CLARINET (Contaminated land rehabilitation network) lead to the conclusion that the most appropriate approach would be the "risk-based land and soil management".

Risk analysis is a set of mathematical algorithms establishing the risk that a contaminating event causes to people in consequence of the exposure deriving from natural migration of polluting agents in different environmental matrixes (Riganti et al., 2001).

In Italy contaminated sites remediation is regulated by the Ministerial Decrees 471/99. In particular, this Decree states that remediation actions have to reduce pollutants to values lower than the admissible concentrations indicated in the Decree itself. The use of risk analysis is only allowed when *"the admissible concentrations can not be reached even if the best available technologies not entailing excessive costs (the so-called BATNEECs) are adopted"*. It is clear that risk analysis is not considered as a crucial decisional tool, and this fact moves Italy away from the other European Countries.

In the specific case of landfills, the extreme heterogeneity of waste and the variability of constructive characteristics and operation criteria make the choice of the optimal remediation technology more difficult; hence, this choice should be taken only after a risk assessment phase following a deep site characterisation. As a general rule, it is possible to state that (Bertanza et al., 2002):

- isolation techniques and solutions involving waste removal can be theoretically applied to any kind of landfill;
- if a large amount of wastes is recoverable or recyclable (combustible fraction, metals, etc.), *landfill mining* can become favourable;
- *in situ aeration* is effectively applicable to landfills containing organic waste; this technique can also be used in order to reduce harmful and odorous gaseous emissions before the waste excavation;
- *in situ stabilization/solidification* can be applied to landfills containing inorganic waste, while *in situ vetrification* can be applied to landfill containing waste characterized by a low content of moisture and coarse metallic pieces.

Furthermore, it must be underlined that some of these techniques can be used together.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

The aim of this paper is to present the monitoring data and the risk assessment phase carried out on an industrial landfill placed in the North of Italy, that, because of the laceration of the bottom impermeable liner and the consequent release of leachate, has caused the contamination of the underlying groundwater.

2 THE CASE STUDY

2.1 Construction characteristics and buried wastes

The landfill, placed in the North of Italy, was realised in an old gravel quarry, which was about 13,000 m^2 wide and 20 m deep. The nearest urban centres are about 1 km far from the plant but there is a rural settlement only 150 m far from it.

The underlying groundwater table varies between 2 and 5 m under the landfill bottom impermeable liner. The hydraulic conductivity varies between $0.80 \cdot 10^{-3}$ and $1.04 \cdot 10^{-3}$ m/s and the hydraulic gradient is equal to 0.12 %; the pore velocity is about 0.54 m/d.

The landfill (Figure 1) consists of two cells, divided by a small embankment set on the bottom. 280,000 t of wastes are buried in the landfill:

- 9,000 t of MSW;
- 20,000 t of dry wastes deriving from MSW separation processes;
- 100,000 t of wastes deriving from the paper recycling process (buried mainly in cell 1);
- 150,000 t of industrial municipal-like solid wastes (i.e. foundry sands, incineration fly ashes and scoriae, contaminated soils, painting filters, containers or rags contaminated by solvents, inks, paints, glues, pesticides, etc.).

The bottom and slopes impermeable liners and the capping were made up of a composite lining, constituted by natural and artificial materials.

2.2 Leachate monitoring

Both cells are provided with a leachate collection well (Figure 1: "A" and "B" stand for cell 1 and cell 2 wells, respectively).

Leachate production reached the maximum value (around 3,600 m^3/month) during the waste disposal phase in the first cell, while during the operation of the second cell it decreased down to 500-600 m^3/month. The realization of the capping system caused a further reduction of the leachate production to 150-300 m^3/month.

Leachate-annual rainwater ratio reached values between 30% and 60% during the waste disposal phase and sensitively decreased down to 10-12% after the realization of the capping system (similar values for other landfills are reported in Collivignarelli at al., 2000).

Qualitative characteristics of leachate can be resumed as follows: pH has increased from values of 6-7 up to values of 8-9; during the waste disposal phase COD concentration showed the typical bell-course (the pick reached 20,000 mg/L), later it has decreased to 3,000-5,000 mg/L; metals concentrations have decreased, as expected, in accordance with the pH and the redox potential variation; ammonium concentration increased until autumn 1999 (reaching 8,000 mg/L), afterwards it has suddenly decreased to about 2,500 mg/L.

2.3 Groundwater monitoring and comparison with the admissible concentrations

The groundwater control system includes seven piezometers (Figure 1): one upstream (P3) and the others downstream the landfill (P1, P2, P4, P5, P6, P7), according to the groundwater flow direction.

Groundwater monitoring showed high iron and manganese concentrations downstream the landfill (greater than the admissible ones established by the Italian law: 200 μg/L and 50 μg/L, respectively). In particular, the highest iron and manganese concentrations were,

respectively, 3,650 μg/L in P6 and 320 μg/L in P5.
Furthermore, all the downstream wells presented high concentrations of ammonium, up to 200 mg/L in piezometer P6. The Italian law does not impose an admissible concentration for ammonium, therefore 0.5 mgNH_4^+/L was taken as reference concentration to evaluate the groundwater contamination state; in fact, this value is indicated in both the Decrees 31/01 (that brought into force the Directive 98/83/CE on the quality of water intended for human consumption) and 152/99 (that brought into force the Directives 91/271/CEE concerning urban waste water treatment and 91/676/CEE concerning the protection of waters against pollution caused by nitrates from agricultural sources).

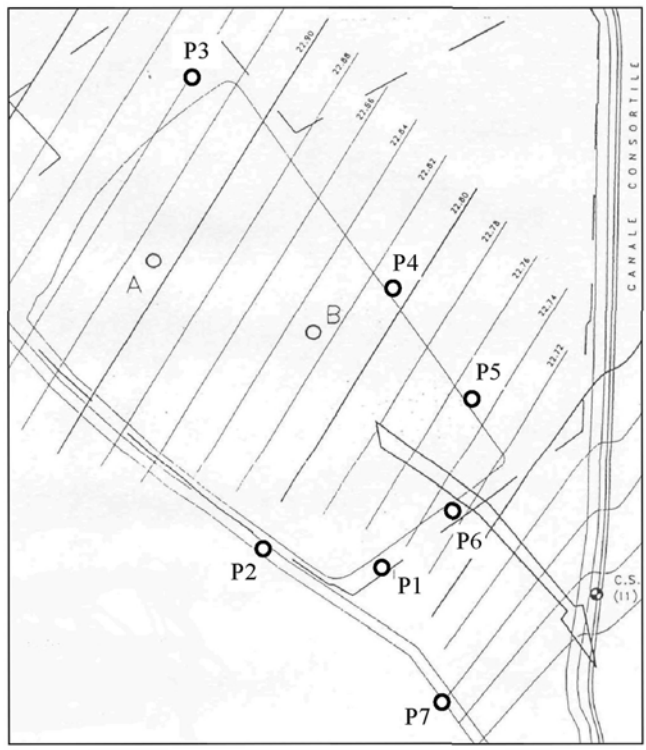

***Figure 1** - Wells and piezometers displacement and groundwater direction*

In the downstream piezometers also 3-sec-butyl-6-methyluracil was found (in particular, in P6 it reached 39 μg/L); this compound, probably deriving from the anaerobic degradation of bromacil (an herbicide used for brush control on non-cropland areas) (USEPA, 1996), was measured in high quantity (5,500 μg/L) in the landfill leachate collected in well B. Furthermore, an investigation conducted by the Regional Environmental Protection Agency confirmed the presence of 3-sec-butyl-6-methyluracil in some downstream private wells (placed more than 1 km far from the landfill), but it was not quantified.
Chemico-physical and toxicological data about 3-sec-butyl-6-methyluracil are not available, so it has to be associated with bromacil. Bromacil is considered by the US EPA to be a possible human carcinogen, but its slope factor is not known, yet; USEPA (1996) suggests a

reference dose of 0.1 mg/kg·d. Moreover, USEPA (1988) has established a Lifetime Health Advisory (LHA) level of 90 μg/L for bromacil in drinking water.
In order to find out the possible causes of this contamination, several geophysical investigations were carried out; they located a 10 m length break in the bottom impermeable liner of cell 2, probably caused by a local sinking of the underground.

3. ESTIMATION OF THE LEACHATE FLOW RATE RELEASE

The groundwater contaminating phenomenon is illustrated in Figure 2, where:
S_w = width of the contamination front in the mixing zone,
S_d = thickness of the mixing zone,
W = source length along the flow direction,
I_{eff} = leachate infiltration,
k_s = hydraulic conductivity,
i = hydraulic gradient,
C_L = contaminant concentration in the leachate,
C_0 = contaminant concentration in the mixing zone, calculated as follows:

$$C_0 = \frac{C_L}{LDF} \qquad \text{(eq. 1)}$$

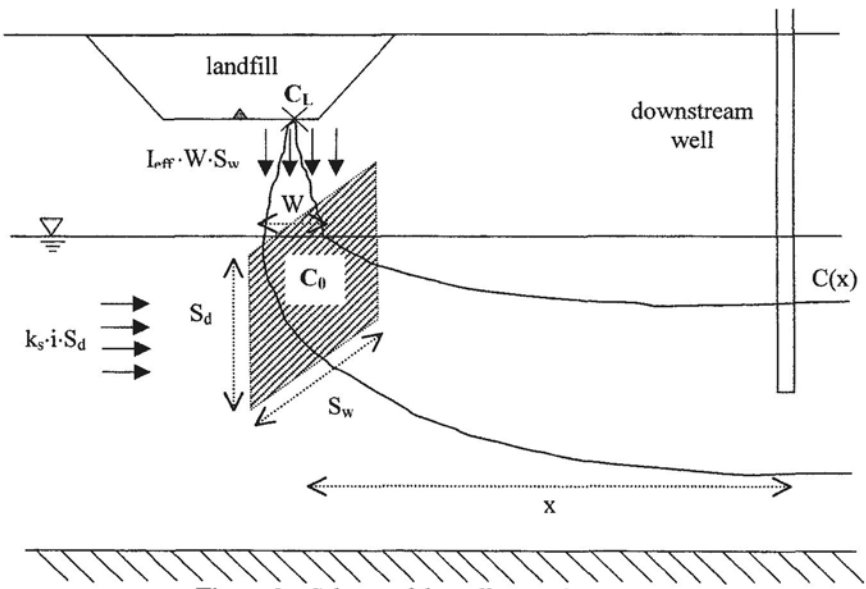

***Figure 2** – Scheme of the polluting phenomenon*

The Leachate Diluition Factor (LDF) can be calculated as follows (USEPA,1994):

$$LDF = \frac{I_{eff} \cdot W \cdot S_W + k_s \cdot i \cdot S_d \cdot S_W}{I_{eff} \cdot W \cdot S_W} = 1 + \frac{k_s \cdot i \cdot S_d}{I_{eff} \cdot W} \qquad \text{(eq. 2)}$$

and S_d can be estimated by means of:

$$S_d = \sqrt{2 \cdot \alpha_Z \cdot W} + b \cdot \left[1 - \exp\left(-\frac{W \cdot I_{eff}}{k_s \cdot i \cdot b}\right)\right] \qquad \text{(eq. 3)}$$

where α_z = vertical dispersivity ($\alpha_z = 0{,}05 \cdot \alpha_x$; API, 1987),
b = aquifer thickness.

C(x, y, z, t) can be calculated by means of the following equation (Domenico, 1987):

$$C(x,y,z,t) = \frac{1}{8} \cdot C_0 \cdot \exp\left\{\frac{x}{2\alpha_x}\left[1-\sqrt{1+\frac{4\lambda\alpha_x R}{u}}\right]\right\} \cdot erfc\left\{\frac{Rx - ut\sqrt{1+\frac{4\lambda\alpha_x R}{u}}}{2\sqrt{\alpha_x uRt}}\right\} \cdot$$

$$\cdot\left\{erf\left[\frac{y+0.5S_W}{2\sqrt{\alpha_y \cdot x}}\right] - erf\left[\frac{y-0.5S_W}{2\sqrt{\alpha_y \cdot x}}\right]\right\} \cdot \left\{erf\left[\frac{z+S_d}{2\sqrt{\alpha_z \cdot x}}\right] - erf\left[\frac{z-S_d}{2\sqrt{\alpha_z \cdot x}}\right]\right\} \quad \text{(eq. 4)}$$

where α_x = longitudinal dispersivity ($\alpha_x = 0{,}1 \cdot x$, Pickens et Grisak, 1981),
α_y = transverse dispersivity ($\alpha_y = 0{,}33 \cdot \alpha_x$, API, 1987),
λ = first order degradation rate constant,
R = time delay coefficient,
u = pore velocity.

Since piezometer P6 is 65 m far from the landfill bottom break, it is possible to assume that leachate takes about 120 days to reach piezometer P6. The comparison between variation of ammonium concentration in both landfill leachate and P6 (Figure 3) confirmed this assumption and enabled to associate five leachate ammonium concentrations (C_L) with five correspondent groundwater ammonium concentrations measured in piezometer P6 (C_{P6}).

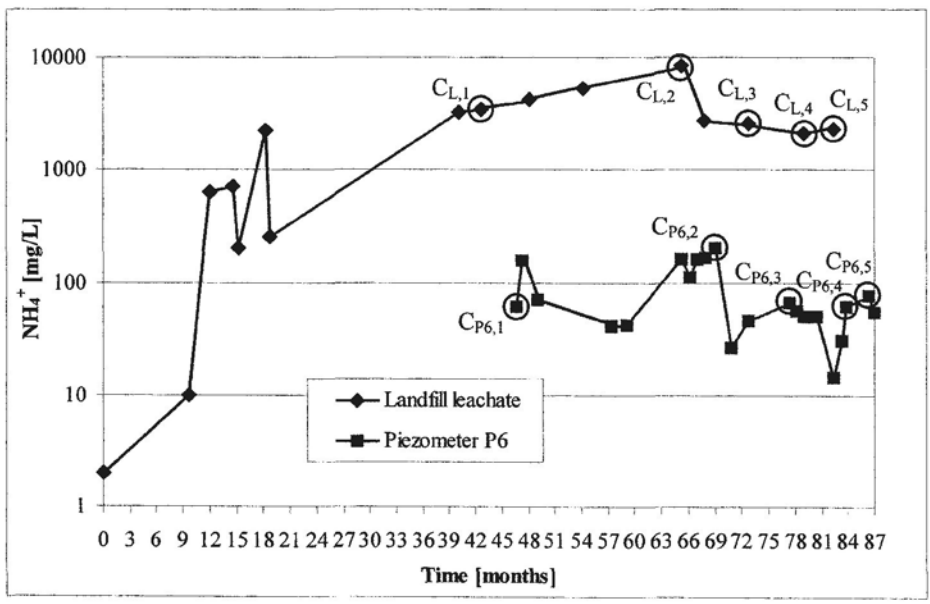

***Figure 2** –Ammonium concentration in landfill leachate and piezometer P6*

Under the hypotheses that:
- the polluting phenomenon is in a steady-state condition (leachate release time t > 500 d brings to erfc ≈ 2),
- ammonium (R = 1.15) is the reference contaminant and its first order degradation rate constant is equal to 0,

and setting W = 10 m and S_w = 0.1 m, it was possible to calculate the leachate flow rate released in the groundwater ($Q_L = I_{eff} \cdot W \cdot S_w$) and the Q_L/Q_{tot} ratio, where Q_{tot} is the amount of landfill leachate produced monthly. The results, reported in Table 1, show that Q_L reached 25.1 % Q_{tot}.
A sensitivity analysis, performed varying W (in the range 0.1-10 m) and S_w (in the range 10-30 m), allowed to state that W and S_w influence slightly the Q_L value.

	C_L [mg/L]	C_{P6} [mg/L]	Time lag [d]	Q_L [m^3/month]	Q_{tot} [m^3/month]	Q_L/Q_{tot} [%]
1	3,500	60	118	29.7-38.7	132-171	18.3-22.6
2	8,300	200	115	42.3-54.9	280-292	15.1-18.7
3	2,600	66	126	40.4-57.9	240-258	16.8-22.5
4	2,100	60	113	50.4-65.5	250-265	20.1-24.7
5	2,350	77	118	56.1-73.8	276-293	20.3-25.1

***Table 1** – Results of the landfill leachate leakage estimation*

3 THE RISK ASSESSMENT PHASE

Risk assessment was performed in steady-state condition, with the following hypotheses:
- Q_{tot} is 260 m^3/month (equal to 15% of precipitation, whose average has been 866 mm/y for the last 6 years),
- Q_L is 65 m^3/month (equal to 25% of Q_{tot}),
- ammonium, manganese and iron concentrations in the landfill leachate are 3000 mg/L, 1000 µg/L and 100 µg/L, respectively (it means that they are slightly greater than the highest values measured during the last two years).

Both groundwater quality state and risks for population were assessed by means of the Hazard Index (ASTM, 1995; 1997):

$$HI_{groundwater} = \sum_i \frac{C_{EP_i}}{AC_i} \qquad \text{(eq. 6)}$$

$$HI_{man} = \sum_i \frac{E_i}{TDI_i} \qquad \text{(eq. 7)}$$

where: i = ammonium, iron, manganese,
$C_{EP\,i}$ = contaminant concentration at the exposure point,
AC_i = contaminant admissible concentration in groundwater (0.5 mg NH_4^+/L, 200 µgFe/L, 50 µgMn/L),
TDI_i = contaminant tolerable daily intake (0.4 mgNH_4^+/kg·d, TERA, 2003; 0.8 mgFe/kg·d, 0.14 mgMn/kg·d, ANPA, 2002),

$E_i = \frac{C_{EP_i} \cdot IR \cdot EF \cdot ED}{AT \cdot BW}$ = contaminant daily intake,

IR = ingestion rate (1 L/d for children, 2 L/d for adults),
EF = exposure frequency (350 d/y),
ED = exposure duration (6 y for children, 30 y for adults),
AT = averaging time (equal to ED for not carcinogenic compounds),
BW = body weight (15 kg for children, 70 kg for adults).

These values, chosen accordingly to the values used in *ROME*, a software developed by the Italian Environment Protection Agency (ANPA, 2002), lead to $HI_{child} = 2.33 \cdot HI_{adult}$.
The contaminants concentrations at the exposure point were calculated by means of:

$$C_{EP_i}(x,y,0) = \frac{1}{2} \cdot C_{L_i} \cdot \left\{ \operatorname{erf}\left[\frac{y + 0{,}5S_W}{2\sqrt{\alpha_y \cdot x}} \right] - \operatorname{erf}\left[\frac{y - 0{,}5S_W}{2\sqrt{\alpha_y \cdot x}} \right] \right\} \cdot \left\{ \operatorname{erf}\left[\frac{S_d}{2\sqrt{\alpha_z \cdot x}} \right] \right\} \quad \text{(eq. 8)}$$

The estimated leachate plumes (areas with HI ≥ 1) are shown in the following Figure 4. Even if the first rural settlement is interested by the groundwater contamination, there are not risks for population because no wells are placed inside the contaminated plume.

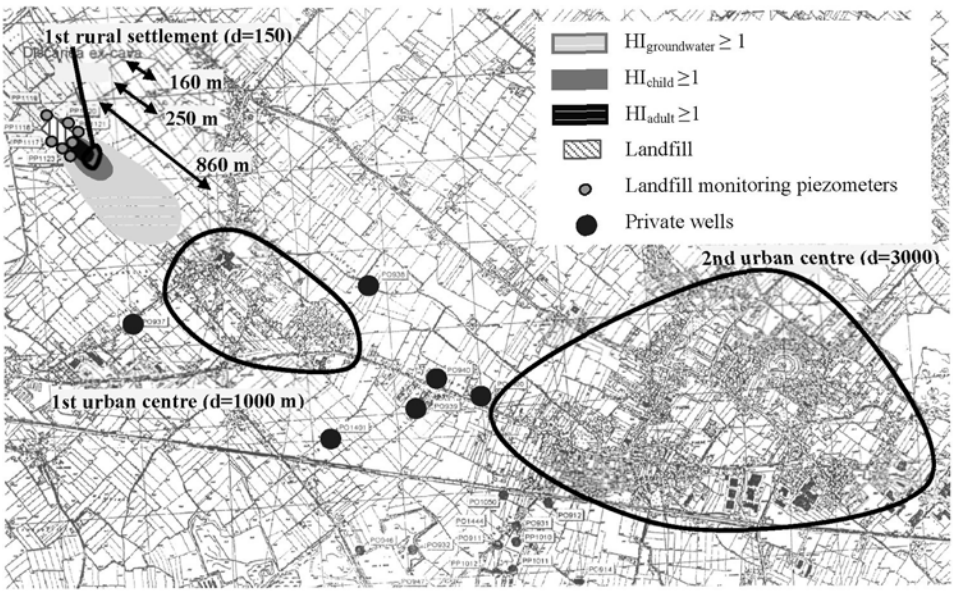

***Figure 4** – Location of the landfill and its estimated leachate plumes.*

4 CONCLUSIONS

The analysis of the landfill monitoring data and the following risk assessment phase enable to state that, referring to ammonium, iron and manganese, the aquifer quality is probably compromised until about 850 m downstream the landfill, but the absence of wells near the landfill excludes the possibility that the contamination could cause hazard to population.
Referring to 3-sec-butyl-6-methyluracil, at the moment no data about its characteristics are available; this compound, present in high concentration in the landfill leachate and discovered in some private downstream wells, is a possible human carcinogen, even if its slope factor is not available yet.
These remarks lead to the conclusion that, in the meantime, monitored natural attenuation can be adopted but further studies have to be performed (as soon as possible) in order to define the chemico-physical and toxicological characteristics of 3-sec-butyl-6-methyluracil. If these studies would lead to the need of adopting more invasive remediation actions, *in situ aeration* technique could be performed in order to reduce considerably ammonium and 3-sec-butyl-6-methyluracil concentrations in the leachate landfill.

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Evaluation of Waste Thickness Effects on Landfills

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ABSTRACT
A one-dimensional multiphase mathematical model is developed to simulate the landfill settlement. It is assumed that the refuse decomposition generates a mixture of gas. As a result of gas generation, gas and liquid pressures change, which causes changes in various parameters such as porosity, total stress, etc. Finally, these changes result in a settlement of the landfill. After the governing equations are discretized using the Galerkin finite element method, the Gaussian elimination technique is employed for a solution.

In this study, the effect of refuse depth on landfill settlement is investigated using the model developed. Simulation results are obtained in various times for landfills having different initial heights, i.e. 10, 15, 20, and 25 meters. The results show that the effect of refuse depth on settlement in landfills is significant.

INTRODUCTION

One of the most pressing problems facing modern society today is the efficient and long-term disposal of municipal solid waste (refuse). Landfills are considered to be the predominant refuse management strategy since it is the simplest and the most cost-effective method of waste disposal. In 1999, 61 % of the refuse was deposited in landfills in the USA (Glenn, 1999). Landfills are very complex systems in which numerous interactive processes proceed simultaneously (Senior and Balba, 1987). For example, gas generation, as a result of microbial decomposition of the waste within a landfill, may increase the internal pressure and cause the top cover to crack and leak. This may lead water, from precipitation and irrigation, to pass through the cracked cover, and thus to form more leachate. Since the gas generation rate depends on moisture content of the waste, the generation rate may increase, causing still more cracking. The waste decomposition may also increase the waste porosity due to the mass loss and lead to a reduction of the strength of the landfill structure. Finally, the whole process may result in a settlement of the landfill.

Organic fraction is approximately 80 % of refuse, and almost all of the organic components (food wastes, garden waste, paper products, textiles, wood, plastics, etc.) can be converted biologically to gases and relatively inert organic and inorganic solids. In landfills, decomposition of organics is the largest source of gas, mainly comprised of CH_4 and CO_2. The landfill gas production increases with increasing moisture content of the waste (Farquhar and Rovers, 1973).

Settlement in landfills is governed by the result of several mechanisms defined as mechanical, raveling, physicochemical change, biochemical decay, and interaction among these mechanisms (Sowers, 1973). Following waste placement, distortion, bending, crushing,

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and reorientation of the materials takes place, hence causing a mechanical deformation. Furthermore, movement of small size particles into the larger voids causes an additional settlement. However, it is usually difficult to distinguish raveling from other mechanisms. Physicochemical changes mainly by corrosion, oxidation, and combustion and biochemical decay due to the anaerobic and aerobic decomposition processes cause a mass loss, leading to additional vertical settlement. Moreover, interactions among these mechanisms may cause even further settlements. For example, organic acids and heat released from decay may produce corrosion and support combustion. According to Sowers (1973), landfill settlement occurs in three stages. The first stage is immediate compression that occurs directly when an external load is applied to the solid waste. This stage is associated with the immediate compaction of void space and particles due to applied load at the time of waste placement. The second stage, primary compression, is compaction due to the dissipation of pore water and gas from the void spaces and it may be completed shortly after the waste placement, i.e., within a few months. The last stage, secondary compression, is generally caused by long-term slippages, reorientation of particles, and delayed compression of some waste constituents. This stage can account for a major portion of the total landfill settlement and takes place over many years. The total settlement is determined as the sum of settlements caused by these three stages. These three stages require careful determination of waste parameters. Uncertainty associated with material properties in landfills makes these conventional soil mechanics approaches less attractive for wastes when compared to soils.

Closed landfills are considered viable sites of land for numerous purposes such as golf courses, sport fields, wildlife and conservation areas, parking lots, industrial parks, recreational facilities, etc., (Magnuson, 1999; Conrad, 2000). Since landfills are not open dumps, but an engineered method of waste disposal, their design, construction, operation, and maintenance must be performed properly and adequately. In other words, landfills must be constructed so that future use will not be restricted. In the literature, many incidents are reported as case studies related to improperly designed and constructed landfills (e.g., Roche, 1996; Eid et al., 2000). It is also reported that the most common problem related with landfills is an assessment of the settlement. A non-predicted settlement may have negative effects on the integrity of any post-closure structure on landfills. Moreover, accurate prediction of the settlement is essential for better estimates of the remaining life of the existing landfills and for ultimate use of the landfill surface. Hence, it is essential to know the extent of the settlement through the landfill at some time in the future. However, it is not always practical to perform field or laboratory experiments to estimate the landfill settlement. Therefore, mathematical modeling becomes a useful tool in understanding and predicting the long-term landfill settlements.

MODELING APPROACH

The author developed a one-dimensional multiphase mathematical model to simulate the settlement involving liquid and gas flows in a compressible landfill. The refuse was represented by a chemical composition, and a global stoichiometric reaction was used for estimation of maximum yield of gas generation. The refuse was represented by three categories based on their biodegradability, i.e., readily, moderately, and slowly decomposable, each with a corresponding gas production rate constant. It was assumed that refuse consists of food waste (12% of the wet weight), garden waste (18%), paper products (41%), textiles and leather (1.5%), wood (2.5%), plastics and rubber (5%), metals (8%), glass (7%), and ashes, dirt, and fines (5%). It was also assumed that the waste decomposition generates a gas mixture comprised of methane (CH_4) and carbon dioxide (CO_2), and the generation rate followed an exponentially decaying function of time. The average density of

solid waste was assumed to be 775 kg/m^3, which gave a total capacity of gas production of 502 kg-gas per m^3-MSW. This gas production corresponded to 55% of CH_4 and 45% of CO_2 by volume. As a result of gas generation, gas and liquid pressures changed, which caused changes in various parameters such as waste porosity, total stress, liquid and gas saturations, permeability, effective stress, etc. Finally, these changes resulted in a settlement of the landfill.

The gas generation model was developed based on a first-order kinetic single-bioreactor approach. Although simple, it is the most widely used approach available in the literature, and provides a reasonable description of the gas productions in landfills (Emcon Associates, 1980).

Following the gas generation model, a two-phase model, i.e., liquid and gas phases, was developed. Then, the solid phase was incorporated into the model (Figure 1). The gas generation rate was employed as a source and sink for solid and gas phases. After governing equations were developed, the Galerkin finite element technique was employed to discretize the partial differential equations. The Gaussian elimination method was employed to solve the resulting equations with a computer program written in standard Fortran.

Throughout the landfill, the pressure distribution was initially assumed to be hydrostatic due to the complete liquid saturation. Although the landfill surface was assumed to be pervious, the landfill bottom was assumed to be impervious against all fluids and solid particles. In addition, it was assumed that the rate of strain was initially zero in the whole domain. The reader is referred to Durmusoglu (2002) for a detailed presentation of the model development and the numerical solution.

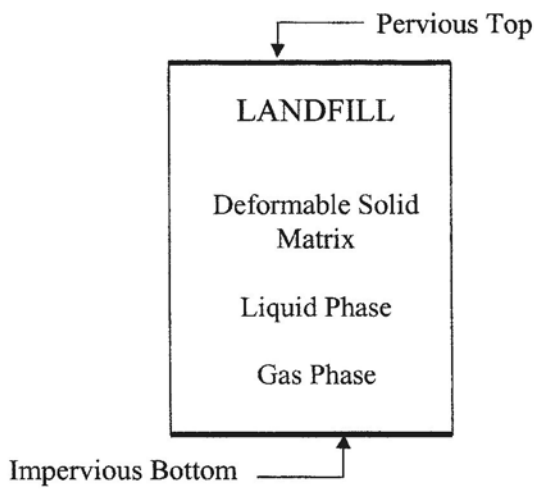

Figure 1. Schematic diagram of landfill idealization for the model development

RESULTS AND DISCUSSION

Tchobanoglous et al. (1993) has reported that typical landfill heights are between 15 and 25 meters. Therefore, the initial heights considered are 10, 15, 20 and 25 meters in this study. The impact of various landfill initial heights on the landfill characteristics is also presented. The landfill is divided into elements of equal size and the simulation results are obtained.

Figure 2a shows the porosity spatial profiles for landfills having different initial heights at 10 years. At this time period, the porosity is increased for all the landfills. However, the porosity in a particular depth is lowest for the 25m-long landfill. For example, the increase in porosity at 5 meters for the 25m-long landfill is almost 5% higher than that for the 10m-long landfill. Since the overburden pressure is much higher at 5 meters for the longest landfill, the void space as well as porosity is lower. Similar profiles are obtained at 100 years, as presented in Figure 2b. Although, the porosity at the bottom is higher than the initial value, i.e. 0.4, for the 10m-long landfill, the lower porosity values are obtained for the longer landfills in 100 years. This is also due to the overburden pressure and the mass loss.

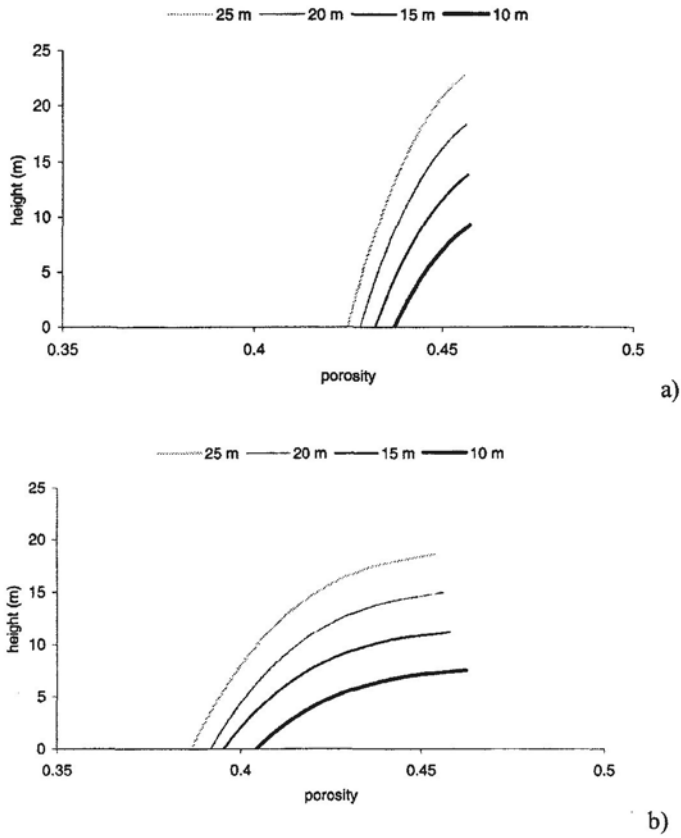

Figure 2. Porosity spatial profiles for deformable landfills with various initial heights a) at 10 years b) at 100 years

The gas saturation profiles with depth and different landfill initial heights are shown in Figures 3a and 3b at 10 and 100 years, respectively. More waste is deposited in the longer landfills. Since the more waste the more potential for gas production, higher gas saturation values are obtained in the longer landfills.

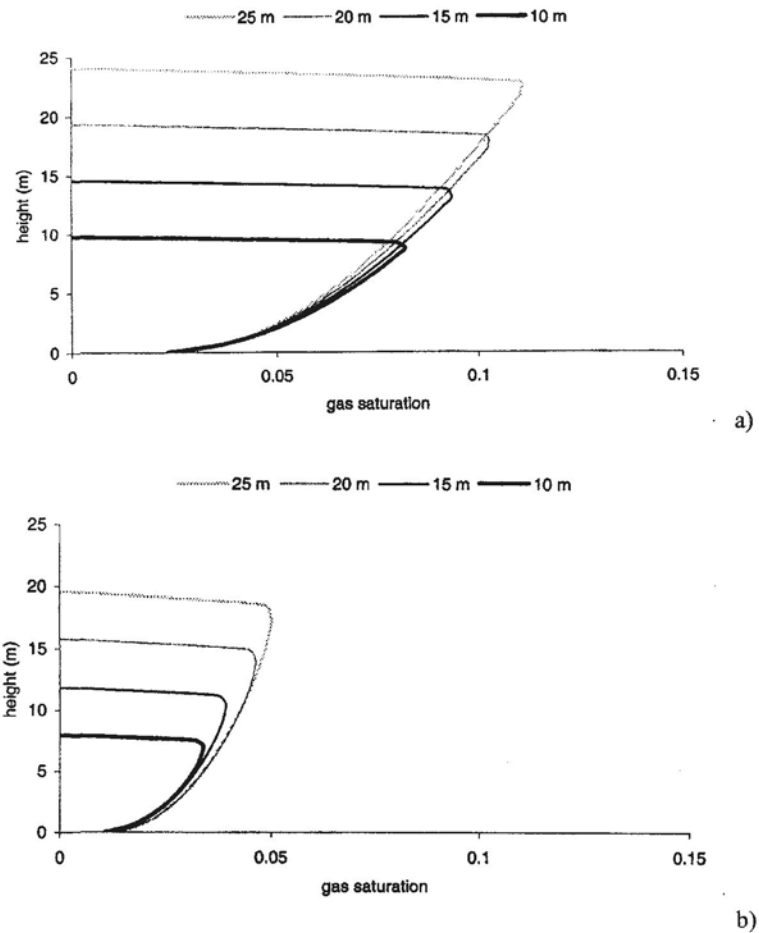

Figure 3. Gas saturation spatial profiles for deformable landfills with various initial heights a) at 10 years b) at 100 years

Figure 4 shows the porosity temporal profiles at the landfill bottom in 100 years. In the early years, e.g., in 5 years, the same increasing pattern is followed by all four landfills having different initial heights. The highest increase in porosity is obtained for the shortest landfill, i.e., 10m-long, and is continued to increase up to approximately 10 years. After then, the porosity starts to decrease due to a reduction in gas generation potential. The increasing pattern is stopped first in the longest landfill, i.e., 25m-long, because it has higher overburden

pressure. Eventually, although the initial porosity is re-established for the 10m-long landfill, an approximate 5% reduction is obtained for the 25m-long landfill in 100 years.

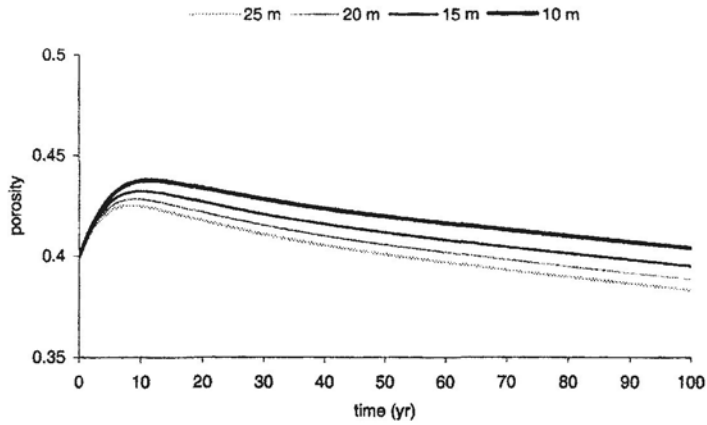

Figure 4. Porosity temporal profiles at the bottom for deformable landfills with various initial heights

The settlement profile for this particular case in 100 years is shown in Figure 5. The settlement is almost identical in the early years, i.e., in 10 years. Among the others, the amount of settlement in the longest landfill is highest. This is due to the fact that the longest landfill has much more overburdened pressure than the others have. Furthermore, the settlement rate follows the gas production rate. The high gas production rate in the early years slows the settlement rate. Following this initial gas production rate and the gas buildup, pressure decreases exponentially and approximately half of the total settlement occurs in the first 30 years. Eventually, the total settlement in the longest landfill, i.e., 25m-long, reaches to approximately 24% in 100 years.

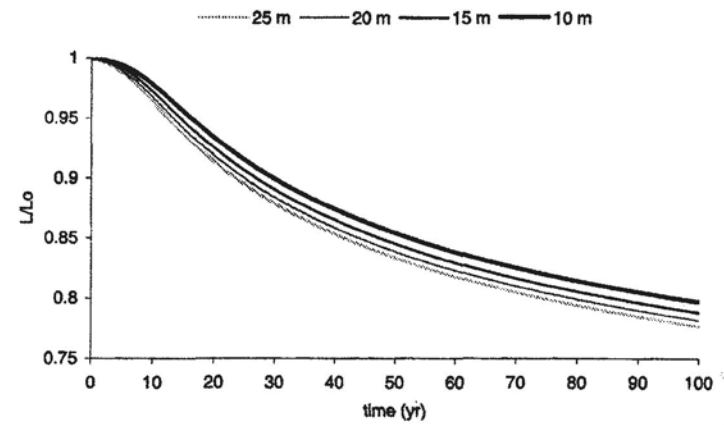

Figure 5. Settlement profiles for deformable landfills with various initial heights

CONCLUSION

Very interesting vertical porosity profiles were obtained. Due to the decomposition, the porosity was increased in the early years. However, it started to decrease in the following years because of the exponential nature of the gas production. It is concluded that the amount of settlement in the longest landfill is highest. The reason is believed to be the overburden pressure that increases downward with refuse depth in the landfills.

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Evaluating the Real Risk of Development on Former Land Fills.

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INTRODUCTION

Increased pressure to build housing on Brownfield Sites became government policy when John Prescott announced that local authorities should seek to build 60% of all new homes on previously used land. A very high proportion of such land has been subject to land filling to some degree or other. Increasingly attention is turning to sites where greater depths of fill exist and where significant landfill gas concentrations are apparent.

Industry Guidelines

ICRCL guidance lays down a strong presumption against the construction of houses with gardens that would require precautions including high rates of sub floor and cavity ventilation due to the uncertainty surrounding their continued operation during the life of the development. Other forms of development such as blocks of flats and supermarkets are considered to be acceptable as the gas protection measures and its performance during the life of the development are more readily available.

Waste Management Paper 27 was first issued in 1988 and updated in reinforces this philosophy with a general preclusion against development to uses other than agriculture or similar uses on actively gassing sites. It goes on to state that uses such as warehousing or large retail units such as supermarkets are possible where adequate investigation has been carried out and measures to control the risk are included within the building design. WMP 27 recommends that no houses be constructed on a gassing landfill or within 50m of any landfill with gas concentrations in excess of 1% by volume methane and 1.5% by volume carbon dioxide. The Building Regulations reinforce this guidance.

The Environment Agency have in collaboration with others been involved with provision of guidance documents aimed at the regulators, designers, developers and other interested parties on the safe development of gassing sites. In the 2001 manual the EA and the BRE provided guidance on the detailing and construction of passive gas protection measures. The EA have recently closed a public consultation on the need for and emphasis on a risk based approach compared to previous advice in Waste Management Paper 27.

PLANNING GUIDANCE

Planning policy Guidance Note (PPG) 23 underlines the sustainability principal and encourages the reuse of brown field land in accordance with the suitable for use principal. Developers have a responsibility to provide information of the contamination and the planning authority need to take into account if the proposal takes adequate account of it.

The East Herts decision of March 1998 determined that as there was no reliable method of control over the actions of the future residents and site users the fact that part of the remediation plan for the site was to incorporate gas protection measures within the houses to be constructed forced the inspector to conclude that the construction of houses should not be permitted. This was in spite of the acceptance that a managed gas venting system located in public open space would protect a proposed development with the gas protection measures constructed within the dwellings being a secondary and largely redundant measure. As part of this decision the inspector confirms that managed apartments would be acceptable as there is less chance of uncontrolled development that may effect the gas

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protection measures. Interestingly it should be noted that the inspector disregarded comparisons with data within documents published after PPG23 as they had not been incorporated into planning policy in the same way that Waste Management papers and ICRL notes had.

NORMAL CONCERNS

The normal concerns relating to construction on or near to a landfill site relate to the accumulation of asphyxiant or potentially explosive gasses within the building. The gasses can migrate and accumulate in voids due to pressure driven flow and or by active generation forcing the gas to move to other areas. Gas is most likely to migrate during periods of falling barometric pressure particularly during sudden and unusual pressure drops such as that experienced during the gas explosion at Loscoe in 1986 or when there is prolonged period of sustained barometric pressure.

REQUIREMENTS FOR PRIVATE HOUSING

Based on the above for private housing to be constructed on or in the vicinity of gassing landfill site based on the above will be that it will be necessary to demonstrate that the gas regime within the foundation zone is less than the trigger concentrations for methane, carbon dioxide and other gasses and therefore there is no reliance on building design, such as low permeability gas membranes and sub floor ventilation. It will also be necessary to demonstrate that there is no maintenance liability to residents and that the gas protection measures at the site will be effective from the first day of inhabitation until the dwellings are demolition to make way for the next development of the site. This could be in the region of 100 years.

KEY FACTORS

There are four key factors affecting the feasibility of building houses on sites on which ground gas is present.

1. The rate at which the gas is being generated will affect both concentration and emission rates. For sites that contain large proportions of putrescible materials, gas generation rates may be high. Where such materials form only a minor constituent gas conditions are typically variable, with little or no measurable emission flows or differential gas pressures present.

2. Changes in barometric pressure induce pressure gradients, which, if severe may dwarf pressures due to active gas generation. The explosion at Loscoe occurred only during an unusually severe barometric low.

3. Permeability of the ground to the passage of gas will dictate the rate at which it will outflow. Flows will be greater along pathways of higher permeability and, where pathways are constrained elsewhere, a higher proportion of the total volume being expelled may be concentrated into relatively small areas.

The permeability of the ground also affects the way in which barometric pressure changes affect the movement of gas and air within the site. Highly permeable soils will enable rapid inflow of air and dilution of gases during high-pressure periods and rapid outflow when pressure falls.

4. The presence of ground water has a marked effect on gas movement. As degree of saturation of the soil increases, permeability to gas falls rapidly. Ground water rise is unlikely to be at a sufficient rate to induce anything more than marginal rates of flux

RISK ASSESSMENT THROUGH MODELLING.

Residential development requires a high level of confidence about the conditions that will be experienced in the foundation and surface zones of the site. A method of modelling the behaviour of landfill gas is being prepared jointly between Waterman Environmental and Cardiff University's Geoenvironmental Research Centre in connection with a proposed housing development.

The site is a former clay pit that has been backfilled, predominantly with clays and construction waste, but also contains a proportion of more degradable matter. The filled pit covers an area of about 6 hectares, is up to 30 metres deep and has a volume of about 2 million cubic metres. Investigations have shown areas and layers with compositions varying from predominantly granular / high permeability to predominantly fine grain / low permeability.

Gas conditions vary significantly, with some locations having negligible gas and others with concentrations of methane up to 99% within the body of the fill. Surface flux box testing generally indicated normal atmospheric gas mixtures at the surface, although at one location methane was collected at a concentration of up to 5%. No significant gas flows have been detected and where small flows have been recorded, these have been found to reverse direction between monitoring visits.

The variable nature of the materials and the large volumes involved means that it is virtually impossible to obtain data that is representative of all parts of the site. This problem has been addressed by modelling a variety of conditions, including extremes (e.g. all sand and all clay).

The applicability of the model to represent the site has been assessed by comparison of the results for the un-remediated site with actual measurements. The model has also been applied to the proposed remediation solution. This is illustrated in Figure 1. Essentially it comprises a densely compacted layer, 3 to 5 metres thick, providing a foundation medium for the development. This is separated from the waste below by a granular layer that is vented to the atmosphere through vertical stacks. A low permeability saturated clay layer provides a pathway barrier between the granular layer and the upper part of the site. A monitoring layer is provided above the protection measures as a means of verification that the system is performing to the designed specification.

Modelling method

A number of models have been developed by researchers (Moore, Rai and Alzaydi, 1979; Findikakis and Leckie, 1979; Metcalfe and Farquhar, 1987; Thomas and Ferguson, 1999) to simulate simple gas transfer problems. A general theory for multiple gas species migration in unsaturated soil based upon a mechanistic approach is utilised in this work. Implementation of this model this has been presented previously in Zhou et al, (2001). In this model diffusion of each gas species is described via Fick's law. The bulk flow of the gas mixture is described via Darcy's law approach. In order to include the effects of temperature and pore water of the soil heat and moisture transfer are also included. This allows the couplings between the multiple gas species, hydraulic and temperature fields to be fully incorporated. A numerical solution of the resulting governing differential equations is achieved via the finite element and finite difference methods. A computer program has been developed to implement the numerical solution.

Representation of the existing site

Due to the complexity of both the modelling method and the site, initial development of the model has been one-dimensional. Gas flows have been analysed for individual columns to explore the effects of pressure fluctuations on vertical flows only. A variety of conditions have been examined in order to establish results, which are reasonably consistent with measurements taken at the site. Further development of the model is currently ongoing. Once this is complete modelling in three dimensions will be attempted. This will allow the lateral flow of gas between adjacent columns to be explored.

As mentioned above evidence of existing gas conditions was available as the results of monitoring of gas wells. A logical interpretation of the evidence provided by the gas monitoring was that, although landfill gas persists in much of the filled area, the rate of generation is insufficient to generate a measurable pressure and that the main driver of flow will be externally imposed gas pressures and to a lesser extent diffusion. Fluctuations in barometric pressure occur constantly and will cause differential pressures between the ground surface and the gas within the soil pores. The pressure gradient will result in inward flow after barometric pressure rise and outward during barometric pressure fall.

The model of gas conditions is based on the concept of a constant methane concentration being maintained below approx. 5 m depth, but subject to the effects of advective and diffusive flows in the upper layers. In order to establish a representation of existing "normal" conditions in the landfill the model has been run, starting with methane throughout the filled clay pit and extending to the surface at a concentration representative of that measured in the wells. This has then been subjected to a series of simulated fluctuations in surface pressure. These reflect the typical pressure variations reported by the local Meteorological Office. Finally a severe pressure drop of 40 mbar in 3 hours has been imposed and then sustained for 48 hours. This pressure drop event has been selected from information about historic events. Figure 2 shows the barometric pressure applied at the surface of each of the columns. Simulations have been carried out for two separate types of soil column; namely a clay type soil and a sandy type soil. The total soil gas pressure was maintained 100 kPa with a gas concentration of 70% at the base of the 4.7 m column

The methane concentration simulated at 0.5m below the surface of each of the columns is shown in Figure 3. Within the clay column diffusive flow is dominant with the methane concentration reaching a constant value of approx 8% and being unaffected by the variation in barometric pressure. In the sandy column advective flow dominates. Any pressure variation between the top and bottom of the column leads to large variations of concentration at the surface. A rise in barometric pressure leads to clean air being driven into the column and a reduction in concentration to less than 1 %. A severe pressure drop results in the contaminant gas flowing upwards leading to a concentration of 70 % being established and maintained until the barometric pressure rises again. These results suggests that where the soils are permeable, gas movement is dominated by advective flow driven by fluctuations in barometric pressure. The system is relatively unstable and highly sensitive to large pressure differentials. Under severe conditions, gas concentrations that are similar to those at depth in the body of the filled ground can occur near to the surface.

Comparison with monitoring

It is difficult to compare the results of the simplified model with the variability of the gas monitoring results, especially as gas wells had intakes covering a large depth range. However the mechanisms modelled are credible as representative of those operating at the site. The model does provide an explanation of the presence of relatively high gas concentrations at depth in the ground measured in the wells, but very low or negligible concentrations at the near surface as indicated by the flux box results. The modelling results for the clay column show a higher gas concentration near to the surface than is indicated by the flux box testing. An explanation for this may be attributable to the very low flux that results from diffusion. Even slight ventilation of the flux boxes would be sufficient to deplete the gas collecting within them. The sandy column results suggest that significant near surface gas concentrations are unlikely to occur except under severe conditions. This would also result in negligible gas in the flux boxes, since it is unlikely that the severe case occurred during the monitoring period.

Representation of the remediated site and development

Modelling of the remediation proposal is performed in two parts. Firstly the column of soil below the venting layer and the venting layer are simulated. This is best visualised as an inverted "L" shaped column with the soil (lower) part of the column being vertical and the venting layer (upper) part being horizontal. The base of the soil column is 5 m below the venting layer and the gas concentrations and partial pressures maintained at the base are the same as in the existing site model. The length of the venting layer part of the column (5m) is taken as 1/2 the spacing of the proposed pipe network within the venting layer and which will be connected to vertical stacks to above the surface. As with the existing site model, a clay and a sandy soil have been considered. The model has been subject to the same sequence of pressure variations as the existing model.

Secondly a soil column through the engineered cap, above the venting layer, to the ground surface is simulated. This column is considered to be aligned vertically above the soil column below the venting layer analysed in the first model. This has been simplified to a single material of relatively low

permeability. For this, the base of the column is the top of the venting layer and the gas conditions here are defined by the values calculated for the venting layer in the first model.

The methane concentration simulated at 0.5m below the surface of the engineered layer each of the columns is shown in Figure 4. For both the clay and sand column flows in the engineered cap were dominated by diffusion resulting in linear distribution between the venting layer and the ground surface. The critical factor being the concentration at the base of the engineered layer. For the clay column the gas concentration at 0.5 m depth tended towards 4% and was not significantly affected by the severe pressure drop. For the sandy column during normal barometric conditions the gas concentration was about 0.1%, but increased to 7% after the severe pressure drop. This was due to the increased methane concentration which occurred in the venting layer at that time.

It is recognised that a number of limitations and uncertainties should be noted in relation to the modelling work performed. In particular in relation to the source of the contaminant gas, its concentration and the pressures reached within the landfill the variability of the soil / waste types and the length of time during which they have been in place make gas generation rates unpredictable and have therefore led to the simplifying assumptions used. The depth to the base of the column clearly affects all pressure and concentration gradients and investigation of different column depth is required, also lateral gas movement should be considered. In relation to the parameters used; typical values for porosity, permeability and diffusivity have been adopted. Also effects of moisture content on permeability and tortuosity on diffusion have not been considered again these assumption require investigation.

CONCLUSIONS

The method of modelling described above has the potential to provide a valuable means of testing the behaviour of gas movements in landfill sites under a range conditions. The method requires further development and also verification against actual measurements in order to refine its use and to provide confidence in its ability to accurately predict real conditions.

Ultimately it is hoped that this will result in more realistic development solutions to be designed and enable more previously filled land to be brought into beneficial use.

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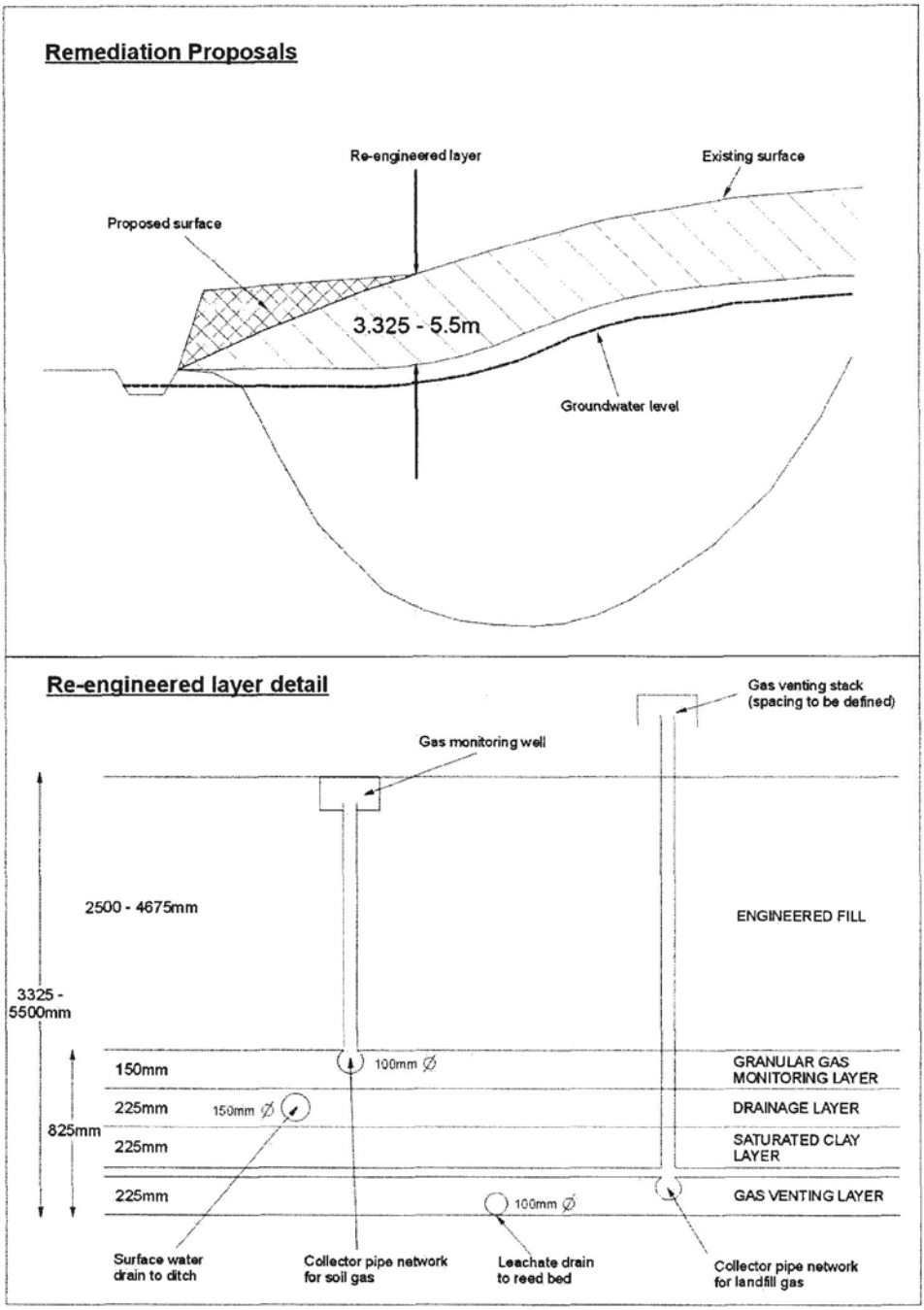

Figure 1 : Proposed remediation scheme

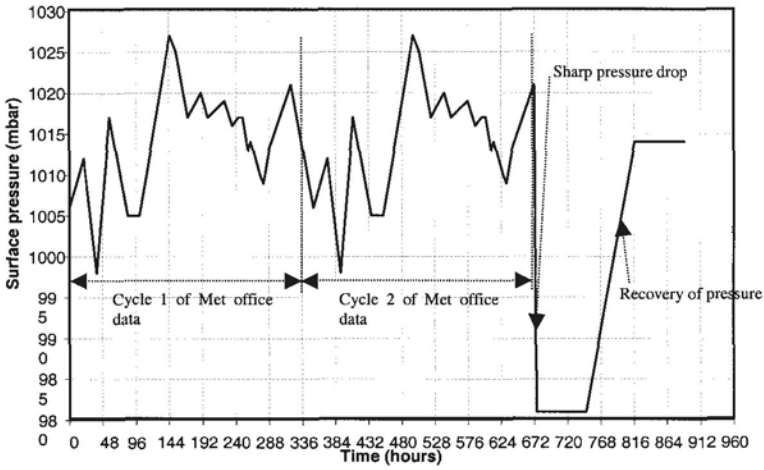

Figure 2 Variation of air pressure prescribed at the surface vs. time

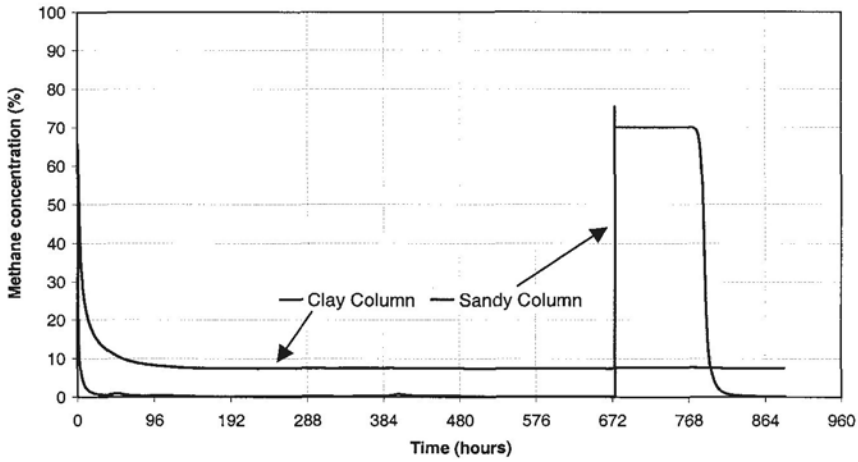

Figure 3 Methane concentration at surface of columns, existing conditions

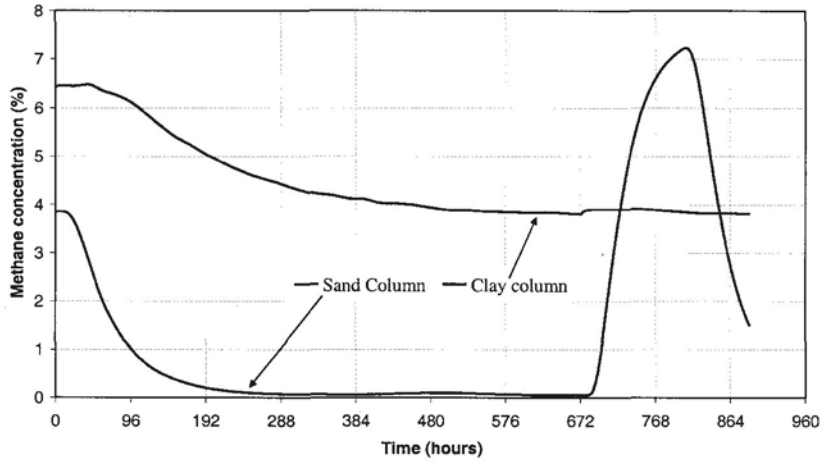

Figure 4 Methane concentration at surface of columns, remediated conditions

Assessment of Groundwater Contamination Hazard Potential of Underground Petroleum Storage Tank (PST) Facilities Using GIS technology

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Abstract: The objective of this work was to integrate a variety of analysis procedures for identifying and mapping groundwater contamination hazard potential of underground petroleum storage tank (PST) facilities in Tarrant County, Texas, US, through the use of GIS technology. Collected information on PST facilities was converted into GIS shape files based on PST physical addresses. Shape files were enriched with related attribute tables containing hydro-geologic settings at each specific PST site. A numerical evaluation system, the Petroleum Storage Tank Index, was introduced in order to assess the PSTs groundwater contamination hazard potential. GIS maps were generated to display PST facilities with moderate, high, and very-high groundwater contamination risk potential based on PSTI classification, identifying PST facilities that require immediate inspection actions.

Introduction

According to the US Environmental Protection Agency, over 705,000 underground storage tank systems (USTs) are used nationwide to store EPA-regulated petroleum products and other hazardous substances. Many of these tanks have been found to have leaked or are currently leaking, causing considerable soil and groundwater contamination. In the state of Texas alone, the number of EPA's registered facilities with active USTs exceeds 60,000, and the number of confirmed product releases is over 23,000 (EPA, 2003). Table 1 summarizes the basic physical properties of the most common UST petroleum products (Rittman and McCarthy, 2001).

The Texas Commission on Environmental Quality (TCEQ) keeps track of all registered USTs in the state. However, the increasing number of PSTs, along with ever more demanding EPA requirements, has raised the need for more powerful computer-based, database management tools to interactively locate, monitor, analyze, and keep an up-to-date record of all USTs. Geographic Information Systems (GIS) provide a technology ideally suited for this purpose. However, little progress has been reported in this area in Tarrant County, Texas, where local city and state officials and private consultants have manifested a great interest in such powerful tool for assessments of this type.

Objective

The overall objective of this work is to integrate a variety of GIS-based spatial analysis procedures to locate, map, classify, and assess the current status and associated groundwater

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contamination risk potential of existing PST facilities in a heavily populated study area of the Dallas/Fort Worth metroplex, Texas.

The work consisted of seven major tasks: (1) Collection of PST/LPST data from reports and web sites of federal and state agencies, (2) Collection of GIS compatible data/maps with hydro-geologic information, (3) Building of PST/LPST databases into GIS compatible databases, (4) Location of PSTs/LPSTs as point features into GIS maps, (5) Spatial analyses on PST shape files to update attribute tables with hydro-geologic settings, (6) Development of a numerical evaluation system to classify PSTs based on groundwater contamination risk potential, and (7) Mapping and displaying of PSTs with moderate, high, and very-high groundwater contamination risk potential. Fig. 1 shows the data-flow diagram.

GIS Data Collection and Processing

The study area lies within the limits of the City of Fort Worth on the central part of Tarrant County, in north central Texas. It had an estimated population of 556,700 in year 2002, with an estimated area of 298.7 square miles (Fig. 2). Databases of existing PSTs and LPSTs were collected from TCEQ online data and reports from environmental firms. Fig. 3 shows the TCEQ online data format for a selected PST facility. ArcView 3.3 and ArcInfo 8.0 softwares were used for data management, spatial analyses, and mapping (ESRI, 1998). In order to locate PSTs and LPSTs as point features on ArcView maps, the ArcInfo **Address-Geocoding** technique was applied (Razzaq, 2003). Fig. 4 shows the ArcView map with locations of PSTs on TCEQ online data.

GIS shape files for Texas counties and aquifers were downloaded from the Texas Water Development Board website. Shape files for Tarrant County's city boundaries, streams, lakes, landfills, wells, and landmarks were downloaded from the North Central Texas Council of Government website. A shape file for main streets was obtained from the City of Fort Worth GIS Department. Hard-copy maps for predominant soils in Tarrant County were obtained from soil surveys by the US Department of Agriculture and the Natural Resources Conservation Service. GIS shape files for major and minor aquifers, surface soil, subsurface soil, depth to groundwater, streams, water wells, landfills, and other sensitive receptors had to be generated and preprocessed within ArcInfo (Razzaq, 2003).

Petroleum Storage Tank Index (PSTI)

DRASTIC is a standardized numerical system to evaluate the groundwater contamination potential of any hydrologic or geologic setting at any given site (EPA, 1987). The system is based on three main criteria: weights, ranges (or types), and ratings. The most significant hydro-geologic factors are assigned a weight of "5" and the least significant factors are assigned a weight of "1". Each hydro-geologic factor is in turn divided into different ranges or distinctive types. Each range or type of a particular factor is assigned a rating between "1" and "10", depending on its expected groundwater contamination potential.

All seven DRASTIC factors, i.e., **D**epth to Groundwater, Net **R**echarge, **A**quifer Media, **S**oil Media, **T**opography, **I**mpact of Vadoze Zone, and Hydraulic **C**onductivity, are ultimately assigned one final groundwater contamination potential score by multiplying the weight of the factor by its corresponding rating. The sum of the final scores from all hydro-geologic factors at the site is called the site's DRASTIC Index.

The DRASTIC index, as briefly presented above, cannot be directly applied to existing PST records in the study area being considered in the present work for two main reasons: (1) its ranges does not perfectly suit the hydro-geologic settings of the area, and (2) it ignores two other critical factors identified herein for the study area, namely, the subsurface soil (5 – 15 ft) and the proximity to sensitive receptors. Hence, a more suitable system, the Petroleum Storage Tank Index (PSTI), was developed for existing and planned PSTs in the study area.

Tables 2-9 summarize the ranges (or types) and the proposed weight and rating criteria for each hydro-geologic factor considered in the calculation of the final PSTI value for each identified PST site at the study area.

Assessment of PST Contamination Hazard

The attribute tables of the themes of all the hydro-geologic settings of each PST site were spatially joined to the previously created PSTs shape file by taking the **Address** field as the common field. The joined PSTs table was then exported and saved as a database file and uploaded in Microsoft Excel (Razzaq, 2003). One Excel spreadsheet contains the PST's name, address, surface soil, aquifer media, subsurface soil (5 – 15 feet), vadoze zone media (15 – 20 feet), depth to water, slope, net recharge, and sensitive receptors located within 500 feet of the PST. A second Excel spreadsheet contains the PST's name and address, the corresponding score for all hydro-geologic factors, and the final PSTI value. Both spreadsheets were again imported into GIS-ArcView and joined to the original PSTs attribute table using **Name** as the common field. The joined attribute table now contains the PST facilities name and address, the description of all settings existing at each facility, their relative scores, and the proposed PSTI value for each facility.

Existing PST facilities were classified into four distinctive categories based on their final PSTI values, as show in Table 10. This classification is based exclusively on PSTI standard deviation values automatically calculated using the **Statistics** function of GIS-ArcView. A GIS-ArcView query was finally conducted in order to create the shape files and the associated attribute tables for the four proposed PST classes in Table 10, and ultimately to display them on ArcView maps. Fig. 5 shows an ArcView map with all PST facilities classified as having Very-High groundwater contamination potential.

Concluding Remarks

The developed PC-supported, user-friendly, GIS-based framework, along with the proposed PSTI classification system, serves as an expedite risk assessment tool to assist officials in the study area in prioritizing the protection, monitoring, and corrective action plans for PST sites with very high groundwater contamination potential associated with them (Class IV), as well as the planning and location of new PST sites in the area. The developed GIS-based framework can be updated and refined as additional data concerning PST sites in the area, and associated hydro-geologic settings, become available. The tool may be readily applied at any other major city with slight modifications of the PSTI system to adapt it to the predominant site-specific conditions. Additional TCEQ data regarding specific characteristics of each PST facility can be used to further refine the classification of PSTs, including material of construction of the tanks, owner and insurance information, regulated substance stored, and leak detection and control systems installed at the site.

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Table 1. Physical Properties of Common UST Petroleum Products

Compound	Density at 20^0C (g/cm^3)	Henry's constant, H ($atm\text{-}m^3/mol$) at 20^0C	Water Solubility (mg/l) at 20^0C	Octanol/Water Partition Coefficient ($\log K_{ow}$)
Benzene	0.880	0.0055	1,780	2.13
Ethylbenzene	0.880	0.0088	152	3.34
Naphthalene	1.140	0.00046	31	3.29
Pyrene	1.270	8.9×10^{-6}	0.15	5.13
Toluene	0.870	0.0066	535	2.69
Dichloromethane	1.330	0.002	20,000	1.26

Table 2. PSTI Weight and Rating Criteria for Aquifer Media

Formation	Aquifer Media	Weight	Rating	Score
Antlers	Sand and gravel	3	8	24
Paluxy	Sand inter-bedded with clay and shale	3	6	18
Twin Mountain	Sands, silty clays	3	7	21
Travis Peak	Sands, silts, limestone	3	6	18
Glen Rose	Limestone	3	6	18
Woodbine	Minor aquifer	3	1	1

Table 3. PSTI Weight and Rating Criteria for Surface Soil

Surface Soil	Permeability (in/hr)	Weight	Rating	Score
Loamy fine sand or absent	> 20	2	10	20
Sandy loam	2.0 – 6.0	2	6	12
Sandy clay loam, sandstone, loam, limestone, fine sandy loam, gravelly clay loam	0.6 – 2.0	2	5	10
Silty clay	0.2 – 0.6	2	2	4
Clay	< 0.06	2	1	2

Table 4. PSTI Weight and Rating Criteria for Depth to Water

Depth (ft)	Weight	Rating	Score
0 – 5	5	10	50
5 – 6	5	9	45
> 6	5	8	40

Table 5. PSTI Weight and Rating Criteria for Net Recharge

Net Recharge	Weight	Rating	Score
High	4	9	36
Moderate	4	8	32
Slow	4	6	24
Very Slow	4	1	4

Table 6. PSTI Weight and Rating Criteria for Topography

Slope (%)	Weight	Rating	Score
0	1	10	10
0 – 3	1	9	9
3 – 5	1	8	8
5 – 20	1	6	6

Table 7. PSTI Weight and Rating Criteria for Impact of Vadoze Zone (15 – 20 ft)

Soil Media	Weight	Rating	Score
Saturated (Water)	5	10	50
Gravel and Sand	5	8	40
Lime	5	6	30
Clay	5	3	15
Rock	5	1	5

Table 8. PSTI Weight and Rating Criteria for Subsurface Soil (5 – 15 ft)

Soil Media	Weight	Rating	Score
Gravel	3	10	30
Sand	3	8	24
Lime	3	5	15
Clay	3	1	3

Table 9. PSTI Weight and Rating Criteria for Proximity to Sensitive Receptors

Proximity to wells, streams, landfills, LPSTs, and other sensitive receptors (ft)	Weight	Rating	Score
0 – 500	2	10	20
> 500	2	0	0

Table 10. Classification of PST Facilities in Study Area Based on Proposed PSTI System

PST Class	PSTI Value	PST Groundwater Contamination Potential
I	0 – 124	Low
II	125 – 146	Moderate
III	147 – 165	High
IV	> 166	Very High

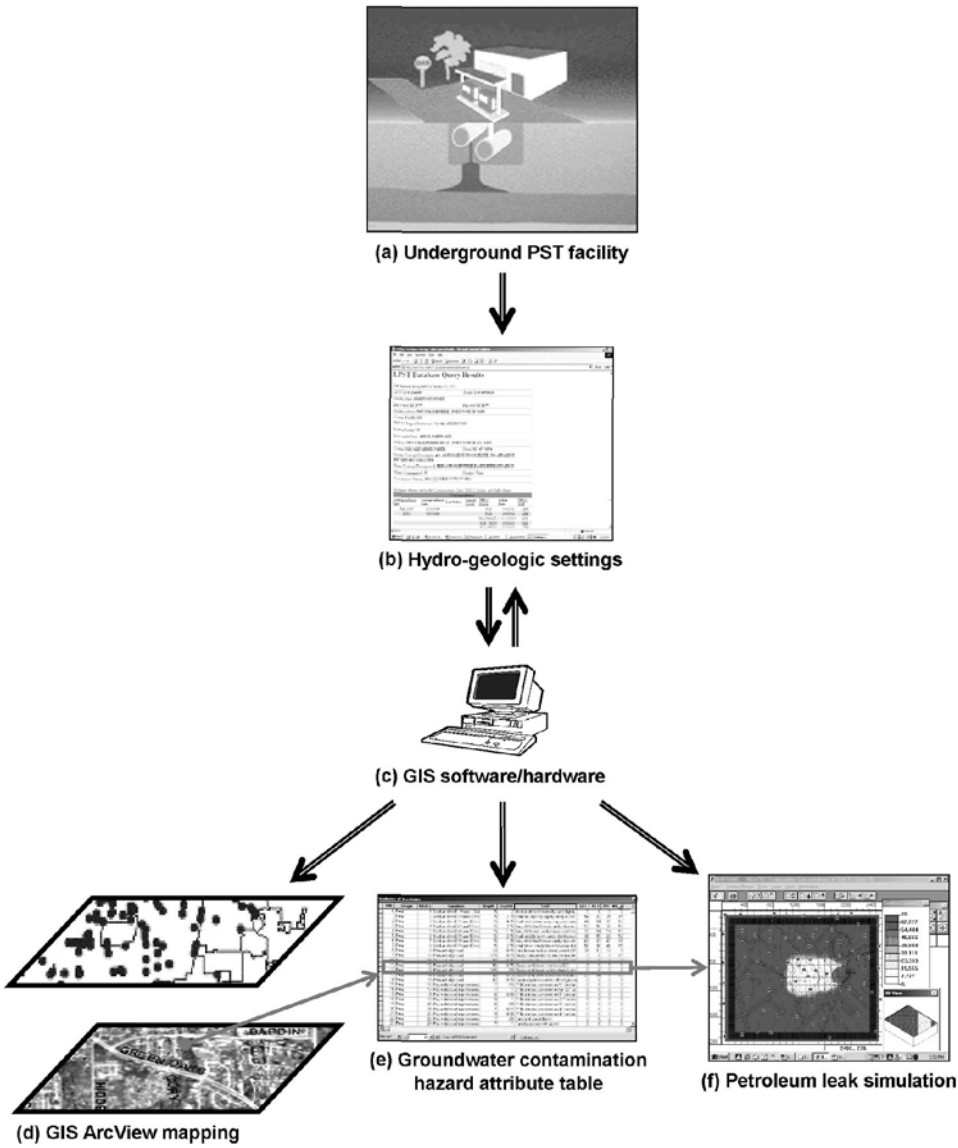

Fig. 1. Integrated system and data-flow diagram.

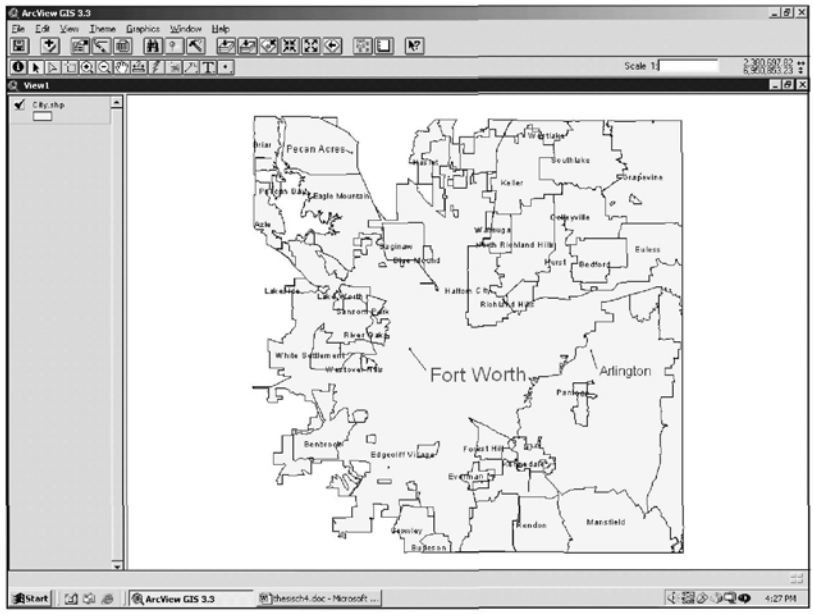

Fig. 2. ArcView map of study area (Fort Worth city limits) and neighboring cities.

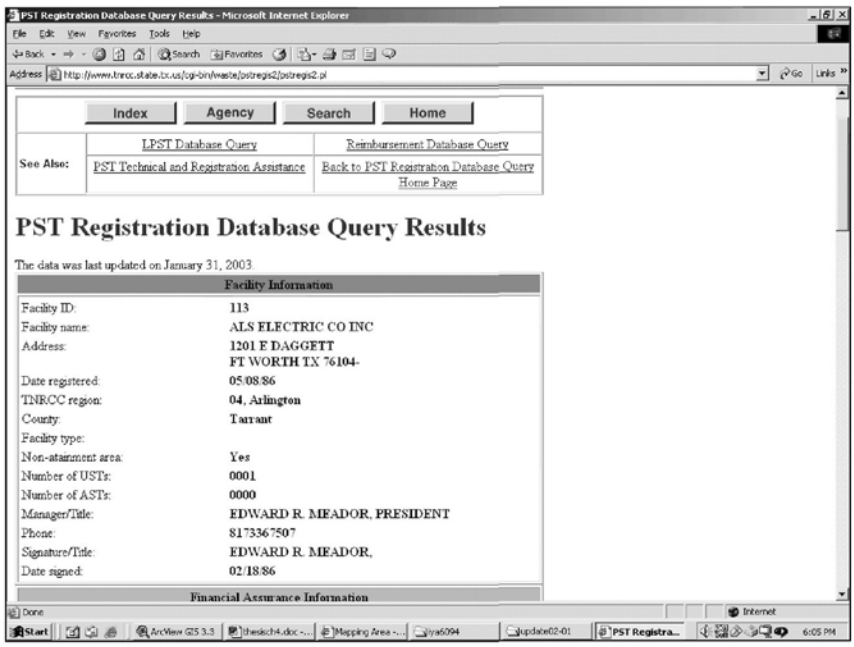

Fig. 3. TCEQ online data format for PST facilities in the study area.

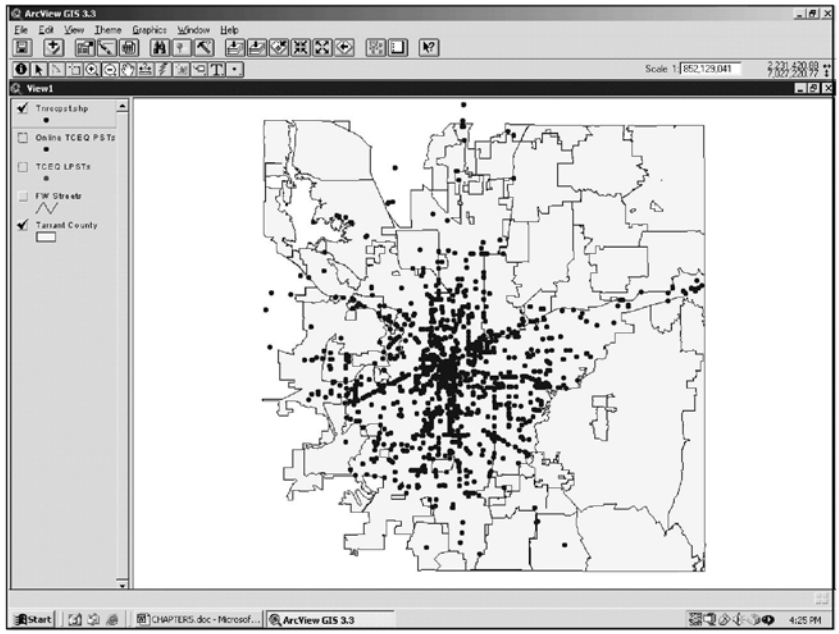

Fig. 4. PST locations based on TCEQ online data.

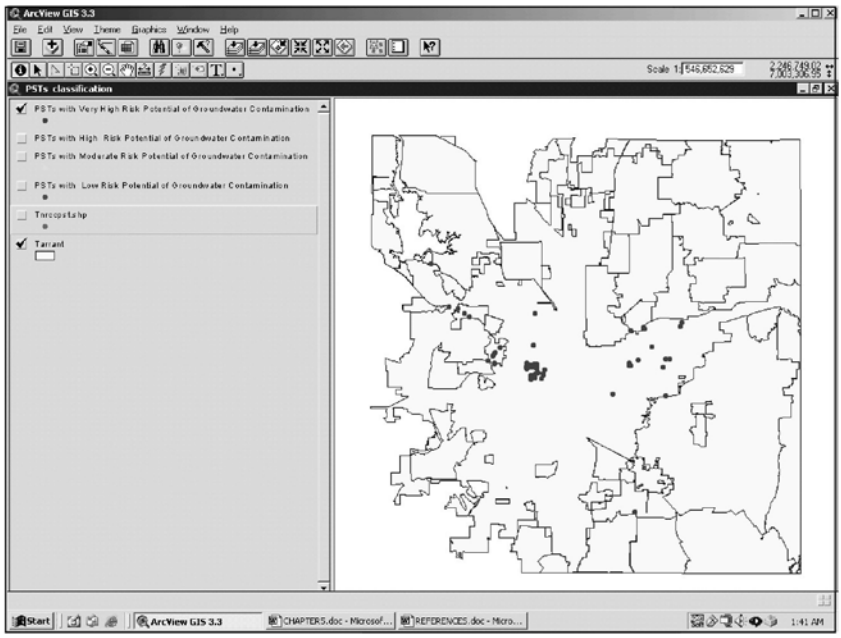

Fig. 5. PSTs with very high groundwater contamination potential.

Groundwater and Solute Transport Modelling for Advanced Raccuremedial Technologies

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Abstract

Advanced Remedial Technologies are growing applications for the in situ treatment of contaminated groundwater. Field scale implementation of such technologies requires detailed design involving complex and versatile inputs. This can be achieved by using numerical groundwater flow and transport modelling, based on site-specific hydrogeology and contaminant plume characteristics. Pump and Treat and Hydraulic Containment are common features in numerical groundwater modelling studies. But it is less widely known that other more advanced remedial techniques can also be designed using finite element or finite difference groundwater and solute transport models. In general, remediation models have many advantages. Based on model simulations decision makers can select, in a quantitative way, the most appropriate cost-effective remediation design and the most sustainable remedial solution according to site-specific conditions. The remediation model can incorporate further variations of parameters over time, resulting in precise optimised models that are representative of real phenomenon. This way they can provide adequate quantified solutions to future problems. In this paper, combinations of groundwater flow modelling, particle tracking and solute transport modelling are used to illustrate the modelling approach for the design of different advanced remedial technologies like groundwater circulation wells (GCWs) and permeable reactive barriers (PRBs).

INTRODUCTION

Advanced Remedial Technologies (ART), such as permeable reactive barriers and groundwater circulation wells are increasing being used for the *in situ* treatment of contaminated water [1] [2]. Numerical modelling can be used at different stages of the implementation of such innovative technologies, including the initial feasibility assessment, the well location selection, the design itself, the future evolution and the comparison with pilot-scale testing. The use of numerical modelling allows several complex and versatile inputs to be incorporated simultaneously, which results in precise optimised simulations that are representative of real phenomenon, and that can provide adequate solutions to future problems.

This paper reviews the use of hydrogeological and solute modelling in the design and implementation of permeable reactive barriers and groundwater circulation wells. It includes the general modelling approach, the detailed design regarding key parameters and a presentation of two case studies carried out in Belgium.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

PERMEABLE REACTIVE BARRIERS

Modelling Approach

Laboratory tests are usually carried out before developing permeable reactive barriers (PRBs) models in order to estimate the reactions half-lives, the most efficient reactive media and the feasibility of the degradation of the contaminants of concern [3].

The preliminary design of PRBs is dependent of many different physical and chemical aquifer parameters, as well as the plume dimensions and characteristics. Stratigraphy, groundwater depth, groundwater flow direction, groundwater velocity, porosity, hydraulic conductivity, and the depth to the confining layer are involved in the design [4]. These parameters are reflecting the site-specific conditions and are typically obtained through a combination of preliminary studies at the subject site and literature studies. The groundwater flow model can be developed and calibrated by means of particle-tracking and budget zones. Particle-tracking allows the determination of captures zones, while budget zones allow the calculations of volumetric flow budgets for the reactive cells. The model should be built with a processor that allows transient runs. Transient runs can take in account the influence of pumping wells or other activities at the vicinity of the site that are involving flow variations with time. Temporal variations in the groundwater velocity or flow direction can be critical aspects for the design of the barriers. This is especially of concern when resulting in increase of travel times through the gate and in the creation of new pathway around the funnels and gates.

Key factors

Overflow/underflow

A three-dimensional approach is recommended but not strictly required to model permeable reactive barriers. 3D modelling offers the advantage of taking into account the overflow and underflow problems that are considered as key factors for the design of permeable reactive barriers [5]. One of the major hydraulic concerns is related to the vertical dimension of the barrier gate in relation to the aquifer properties. A narrow gate will have to support accelerated flow, which could theoretically overflow the gate itself. To prevent the flow of contaminated water under the barrier, the distance between the bottom of the gate and the top of the impermeable layer is a critical point regarding underflow.

Heterogeneities

The selected modelling software should also be able to support large contrasts of permeability within a short distance, in particular at the gate and funnel interfaces where variations of hydraulic parameters are very important. Numerical instabilities can result from these large contrasts of permeability [4], a problem that less sophisticated software typically cannot solve. To reduce these instabilities, one solution can be to simulate the gate and funnel walls by using very small cell sizes. But this results in a large number of cells in the model and corresponding time-efficiency problems. These small cell dimensions also result in very low head convergence criteria during the numerical calculations [6]. Some processors are offering alternative solutions, like MODFLOW [7] with their horizontal flow barrier boundary conditions [8], and should be considered for complex applications, such as these described above.

PRB key factors

There are two key parameters to be considered in the modelling of PRBs. These are residence time and the hydraulic capture zone width. Residence time refers to the time the contaminated water is in contact with the reactive medium. It has been reported that the permeability of the aquifer is the key controlling parameter for residence time. Indeed, the increase of flow through the gate is limited by the transmissivity of the aquifer up and downgradient of the gate [9]. Capture zone is related to the width of the groundwater that will be captured and funnelled through the gate of the permeable reactive barriers. It should be noted that the capture zone is more sensitive to the length of the funnel than to the permeability of the aquifer in homogenous systems [4].

Objectives and attributes

The first objective of the groundwater model is to determine a suitable location for the PRB with respect to the site-specific conditions, as well as the plume distribution. Once the location is found, the suitable configuration of the PRB is designed. The width and number of reactive cells, and the width of the funnel are therefore simulated to optimise the design of the PRB. Evaluation of the potential underflow and overflow as well as simulations of flow effects on the design can therefore be undertaken by the model.

Different remedial scenarios and future evolution of the plume can be simulated. In addition, future potential flow bypass due to reduced porosity can be incorporated in the model. System operation can be monitored and adequate actions undertaken. The effect of future remedial activities carried out on site, like excavation works, pump and treat or dewatering systems can be added to the simulation and their interaction on the PRB calculated and evaluated.

Case Study

A PRB modelling study was performed for an industrial site situated in Flanders. The site geology consists of a sandy aquifer of 15 meters thickness. The contamination consists of chlorinated hydrocarbons with a plume width of 300 meters. The groundwater table is located 2.0 meters below ground level and groundwater flow is northwards. A detailed site description is given by Vermeiren et al. [10].

The model was constructed in order to determine the appropriate configuration of the PRB in relation to the site-specific conditions. To simulate the PRB, the commonly used codes MODFLOW [7] combined with MODPATH (particle-tracking code [11]), ZONE BUGET [12] and RT3D [13] were used. The aquifer was divided in 10 layers for which the permeability was calibrated, using head measurements, core drilling and undisturbed sampling, conventional pumptests, and transport modelling data. The transport modelling was calibrated based on identified sources locations, contamination, and historical inputs.
The appropriate reactive medium and associated reactions were determined in column tests (labs tests zero valent iron) and the results incorporated in the model to simulate the gate characteristics. The geochemical interactions near the gates were simulated using the multi species transport model RT3D.

The first simulation consisted of a wall ($k < 10^{-9}$ m/s) covering the whole width (350m) of the contamination front such that the contaminant plume would be captured at 99%. For this scenario, two gates ($k = 1.5*10^{-4}$ m/s) are provided with a calculated flowrate of 5m³/day. As the length of the wall and the number of gates is a critical factor regarding PRB costs, an alternative design has been simulated to decrease the length of the wall and the number of

gates. This alternative design consists of installing a drainage trench up-gradient of the reactive wall to guide the water to the reactive gate. However it is shown on figure 2 that the groundwater escaping the drain is not entirely captured by the PRB.

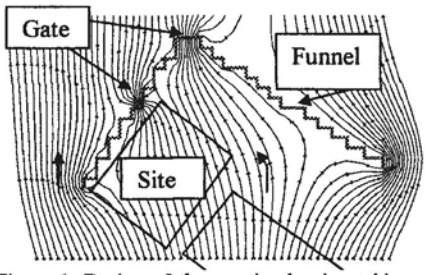

Figure 1: Design of the reactive barrier, taking a catchment of 99% of the contamination into account

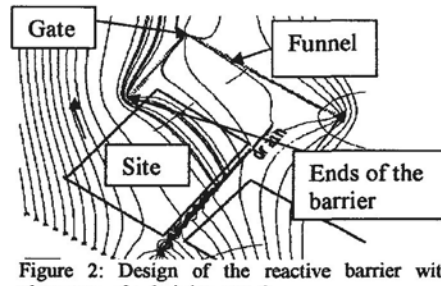

Figure 2: Design of the reactive barrier with placement of a draining trench

The application of modelling to the case study project was a very effective tool in understanding the groundwater dynamics, as well as the chemical interactions at the PRB system. The model allowed for the influences of diverse parameters to be identified and simulated with the ultimate aim of identifying and optimising the most cost-effective PRB design. Important parameters involved in the final design like the length of the wall, the depth of the PRB, the dimension and number of gates, the residential time in the reactive media, and the flush time, have been all identified, and taken in account the site-specific conditions.

GROUNDWATER CIRCULATION WELLS

Introduction

The groundwater circulation well (GCW) is a new remedial technology and is considered as a remedial alternative for conventional pump and treat systems [14]. Standard GCW consist of conventional pumping wells with two screens, which are separated by inflatable packers. Water is extracted from the lower screen and injected in the upper screen, this way creating a circulation cell in the well and in the aquifer. This scheme can be changed in a so-called reverse mode where water pumped in the upper screen and injected at the lower screen. Contaminated groundwater is generally treated in the well (in well stripping, bioreactor [15]). GCWs are commonly used as an alternative for hydraulic barriers to prevent further downgradient migration of contaminant plumes.

Modelling approach

Introduction

The preliminary design of GCW systems is dependent of many different groundwater flow-governing parameters, as well as contaminant plume characteristics. Contaminant distribution, core drilling and undisturbed sampling, conventional pumptests, specific analytical calculations and numerical models are used to develop an initial design of the GCW system. This design comprises the number and position of GCWs, their dimensions and flow rates. To effectively prove that a groundwater circulation cell can be created in the aquifer a hydraulic dipole pumptest is undertaken. The pumptest results will be used to determine the design parameters for the full scale GCW design. Numerical groundwater modelling is generally used to evaluate the pumptest results.

Pumptest modelling

In general there are two ways to calibrate a pumptest using a numerical groundwater model. Either the flowrate is fixed, or the groundwater head is fixed. In the first case, the drawdown induced by this flowrate is calculated and compared to observed head results. Conductivity and storage coefficients are modified by trial and error method to determine the best realistic fit. The grid employed has to be very fine in order to limit the error due to mean of values for a whole cell. If the groundwater level is fixed in the inactive well cell at a lower value than the steady-state value, a flow coming out this cell is created. This flow can be measured and compared to the flowrate used during the pumptest. The problem of mean value can be limited by taking a refined grid only near the pumping well. But, the wellbore effects are often neglected and therefore, hydraulic parameters calibrated this way can be over or underestimated. GCW pumptests cannot be calibrated using the second method because of an important wellbore effect and numerical errors due to the pumping and injection at the same horizontal location. To simulate pumptests, a processor that allows transient runs is needed.

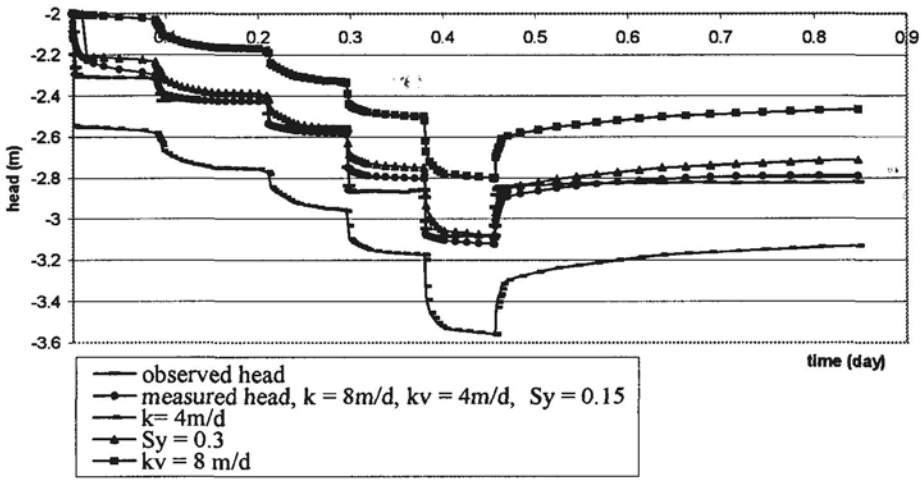

Figure 3: Influence of diverse parameters in a piezometer situated at 9 meters from the pumping well, depth of 44 meters.

A good understanding of the GCW behaviour within the aquifer is necessary to refine the design of the whole GCW barrier and to determine more precisely the interactions between different parameters of concern. GCW pumptests have been carried out and modelled. This modelling needs a refined grid, especially around the well to avoid convergence troubles. Different parameters have been tested in order to see their effect on the groundwater circulation wells. This is important in the vertical dimension to best reproduce the exact interaction between the injection and the pumping zone. The GCW modelling also allows the determination of the horizontal and vertical anisotropy. These are considered as the most critical factors in the design of groundwater circulation wells [16]. Figure 3 shows the main influence of the aquifer parameters on the drawdown created during pumping. Reduction of hydraulic conductivities (horizontal and vertical) and of the specific yield/storage causes an increase of the simulated drawdown. Whereas an increase of the specific storage/specific yield causes to smooth the curves since the equilibrium of the aquifer in reaction to the pumping is not reached. At short distance, the injection and pumping are introducing some

changes in the aquifer itself, by forcing water to penetrate or be pumped. Special pathways are therefore created, influencing largely the hydrogeological parameters.

Site Modelling

Results from the pumptest modelling are incorporated in the general site model, and the influence of the groundwater circulation wells on the groundwater contamination is simulated. The groundwater flow model is developed and calibrated by means of groundwater head, inverse modelling, short-term and long-term conventional pumptests and transport modelling.

Key factors

Modelling robustness

A three-dimensional approach is required to model GCWs. The three-dimensional modelling allows different input-outputs at different depths, which is obligatory to GCWs. The software chosen should also be able to support high variations of flowrate, due to injection and pumping at the same horizontal location. To diminish resulting numerical instabilities, one solution consists of increasing the number of layers, especially between the two screens. But, as well as for PRBs, this technique results in time-efficiency problems.

Heterogeneities

As well as for PRBs, heterogeneities are critical parameters with regard to GCW modelling. Local variations of permeability and porosity will introduce numerical problems resulting in increasing convergence time. The extent and limit of such variations are usually difficult to determine with precision but are creating important changes in groundwater circulation well cells and therefore in the whole design of the GCW barrier.

Well bore effect

The boundary condition at the pumped screen is composed of one term representing the flow rate from the aquifer into the well, and of a second term representing the rate at which water is removed from the wellbore itself. Together, these two rates should sum the real well discharge. The second term is function of the square of the casing radius, which is usually relatively important in groundwater circulation wells. In pumptest interpretation method, this results in a horizontal shift of data curve, along the time axis. It can be eliminated using derivate-based curve method [17] But, using standard modelling techniques, this effect can not be reproduced unless the permeability and specific yield/storage are set up to the pumping well cell and vicinity.

Groundwater circulation wells parameters

The radius of influence, the stagnation point (radius of influence in the groundwater flow direction), and the flushing time are the parameters involved in the design of GCW [16]. These parameters are function of hydraulic data, such as hydraulic conductivity and porosity, and of well construction data, such as the screen dimensions. The construction parameters are usually fixed during the first part of the work with spreadsheet and existing modelling. The smaller the screen is, the larger the cells are.

Case Study

The GCW pilot well was installed on an industrial site situated in Flanders. The geology consists of a sandy aquifer of 160 meters thick. The contamination plume length is over 700m, 400m width and 160m deep. The groundwater flow has a southward direction. The scheduled GCWs are situated at the southern site border to create a hydraulic barrier to prevent further downgradient contaminant migration.

To simulate the cells created with these groundwater circulation wells, the processor PATHWAY [12] is used. As seen on figure 4, the radius of influence and stagnation point of the groundwater circulation wells installed on site can be reproduced by means of groundwater modelling. The hydraulic barrier can therefore been designed.

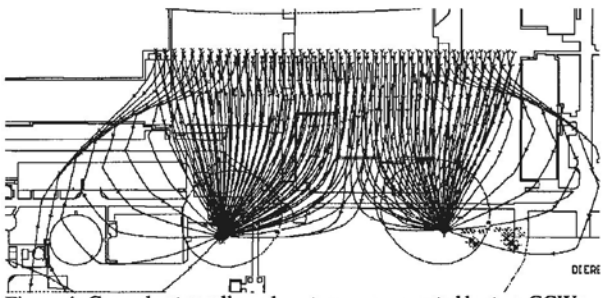

Figure 4: Groundwater cells and capture zones created by two GCWs

The flush time (considering only advection) can be calculated by means of the developed model, calculating the time needed for particles to be captured by the well at a distance corresponding to the radius of the cell. The higher the porosity is, the lower the velocity is. While, the lower the permeability of the aquifer is, the higher the flush time is (figures 5)

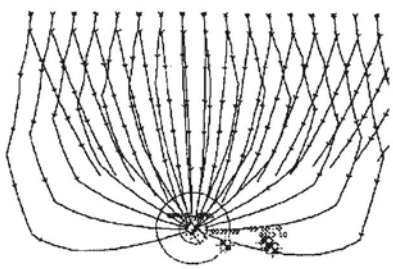

Figure 5a: Particles tracking with k = 8m/d, flushing time = 4000 days

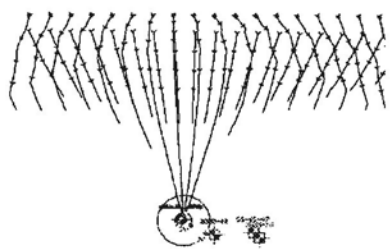

Figure 5b: Particles tracking with k = 4m/d, flushing time = 4000 days

During this project, the model was as well a useful tool to optimise the design of the hydraulic barrier. Several configurations have been tested. As a result, a combination of three GCWs operating in reverse mode (injection at the lowest screen) from 0-50m deep and two GCWs operating in standard mode from 50-100m deep have been determined as being the most cost effective solution. Flowrates, varying from 7.5 to 12.5 m^3/day were also determined. It allowed the prediction of the pore volume flushing time, the evolution of the contamination and the evaluation of the impact of the GCW on several other remediation techniques and works carried out on site (pump and treat, excavations).

CONCLUSIONS

Hydrogeological modelling provides an efficient tool for feasibility studies, design and evaluation of advanced remedial technologies, such as permeable reactive barriers and groundwater circulation wells. They can take in account site-specific conditions and hydrogeology heterogeneities, together with the optimisation of the key parameters of the ART modelled. Modelling allows diverse simulations on hydrogeological/transport parameters and helps the engineer to point out the critical factors in the design and full-scale assessment. It can also easily reproduce the interactions of diverse remedial techniques undertaken at the same time on site.

Modelling is therefore an useful tool to select the cost effective design and to determine and quantify physical and chemical parameters intervening in the design of Advanced Remedial Technologies. The number of gates, the length of the walls, the depth of the barrier, the addition of drains for the PRB, the number and the dimensions of the wells (depth, screen), their operating mode, the optimised flowrate for GCW can be determined. The interactions between the hydraulic parameters of concern can be modelled and different scenarios simulated and compared in terms of contamination effects. Concerning future evolutions, modelling allows the identification of possible problems related to the full-scale remedial technique and is then an easy and fast tool to provide adequate solutions.

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Human Health Risk Assessment for Dioxins and Related Compounds

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SUMMARY
The aim of this paper is oriented to critically analyze the current scientific literature related to health effects of dioxins and related compounds in order to identify issues concerning the risks that may be occurring in the population exposed to these dangerous substances.
Hence, the paper describes the process to develop Risk Assessment step by step considering the definition of dioxin like compounds, the estimation of their exposure/dose relationship, the characterization of sources and exposure, environmental fate and transport modelling, human exposure modelling and finally risk characterization.
Lastly a risk evaluation at the concentration of "screening value" of TEQ for residential soil (ATSDR, 1998a) has been performed and critically considered.

DEFINITION OF "DIOXIN LIKE COMPOUNDS"
"Dioxin like compounds" contain the following chemical classes: polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzonfurans (PBDFs), and polychlorinated biphenyls (PCBs). "Dioxin like" refers to the fact that these compounds have similar physical-chemical properties, chemical structure, and toxic effects: they also persist and bioaccumulate in fatty tissues because of their resistance towards metabolism and their hydrophobic nature.
Among these different classes it is possible to identify "dioxin like toxicity" in 12 of the 209 PCBs congeners, 7 of the 75 CDDs, 10 of the 135 CDFs or BDFs. The physical chemical properties of each congener vary according to the degree and position of chlorine and/or bromine substitution, and very little is know about occurrence and toxicity of the mixed chlorinated/brominated dioxin, furan, and biphenyl congeners.
The most widely studied of this general class of compounds is 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) and it represents the "reference compound". The available epidemiology data on this compounds suggest it is a "human carcinogen and there is a relationship with soft-tissue sarcoma, non Hogkins lymphoma or respiratory cancer.
CDDs, CDFs and PCBs are commonly found as complex mixtures when detected in environmental media and biological tissues: humans are exposed to variable distributions of CDDs, CDFs, and dioxin-like PCBs congeners that vary by source and pathway of exposures. For this reason it is difficult to estimate the human health risk assessment associated to these chemical mixtures: in order to address this problem, scientific community has introduced the concept of toxicity equivalency factor TEF. This factor compares the potential toxicity of each "dioxin like compound" comparing the mixture to the well studied toxicity of 2,3,7,8 TCDD which is assigned a TEF of 1.0 as indicated in the following **Table 1**.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

Table 1: TEQ_{DPF}-WHO_{98} (Van der Berg et al., 1998)

Dioxin (D) congener	TEF	Furan (F)Congener	TEF	Dioxin like PCB (P)	TEF
2,3,7,8 TCDD	1.0	2,3,7,8 TCDF	0.1	PCB-77	0.0001
1,2,3,7,8 PeCDD	1.0	1,2,3,7,8 PeCDF	0.05	PCB-81	0.0001
1,2,3,4,7,8 HxCDD	0.1	2,3,4,7,8 PeCDF	0.5	PCB-126	0.1
1,2,3,6,7,8 HxCDD	0.1	1,2,3,4,7,8 HxCDF	0.1	PCB-169	0.01
1,2,3,7,8,9 HxCDD	0.1	1,2,3,6,7,8 HxCDF	0.1	PCB-105	0.0001
1,2,3,4,6,7,8 HpCDD	0.01	1,2,3,7,8,9 HxCDF	0.1	PCB-118	0.0001
1,2,3,4,6,7,8,9 OCDD	0.0001	2,3,4,6,7,8 HxCDF	0.1	PCB-123	0.0001
		1,2,3,4,6,7,8 HpCDF	0.01	PCB-156	0.0005
		1,2,3,4,7,8,9 HpCDF	0.01	PCB-157	0.0005
		1,2,3,4,6,7,8,9 OCDF	0.0001	PCB-167	0.00001
				PCB-114	0.0005
				PCB-189	0.0001

To apply the TEF concept, the TEF of each congener present in a mixture is multiplied by the respective mass concentration and the products are added to represent the 2,3,7,8-TCDD toxic equivalence (TEQ) of the mixture, as described in the following ***equation 1***:

$$TEQ = \sum_i Congener_i \cdot TEF_i \qquad (1)$$

ESTIMATION OF EXPOSURE/DOSE RELATIONSHIP FOR DIOXIN-LIKE COMPOUNDS

TCDD, CDDs, CDFs, and dioxin like PCBs are a class of well-studied compounds whose human cancer potential is supported by a large database based on epidemiological studies.

The EPA Guidance for Risk Assessment (US EPA, 1996b) accepts a causal relationship between 2,3,7,8 TCDD exposure and cancer hazard and all complex mixtures of 2,3,7,8 TCDD and dioxin-like compounds are characterized as "likely" carcinogens according to the concept of TEQ previously explained. Humans can adsorb these compounds via inhalation, oral, and dermal routes of exposure. In general, absorption is vehicle-dependent and congener-specific and, for most mammalian species, the liver and adipose tissue are the major storage sites. 2,3,7,8 substituted CDDs are the predominant congeners retained in tissues and body fluids and there is some evidence that they are partially excreted in the feces in the form of metabolites. It is also important to remember that CDDs are lipophilic compounds which can concentrate in maternal milk (Abraham et al., 1994, 1996).

CHARACTERIZATION OF SOURCES AND EXPOSURE

CDDs and CDFs are highly persistent compounds and they have been detected in air, water, soil, sediments, animals, and foods. They are released to the environment during combustion processes (e.g. municipal solid waste, medical waste, and industrial hazardous waste incineration; fossil fuel and wood combustion) as well as in cigarette smoke.

The production, use, and disposal of certain chemicals (e.g. PCBs, chlorinated benzenes, chlorinated pesticides) and the production of bleached pulp and of several metals represent a sources of CDDs too.

CDDs and CDFs are ubiquitous in the environment and are found at low background level (parts per trillion, parts per quadrillion) in the air, water, and soil. Over the past decade,

typical concentrations of CDDs in urban air in the United States have averaged in 2.3pg/m^3: 2,3,7,8 TCDD has been detected in some urban areas but rarely in rural ones (Reed et al., 1990).
Thanks to different studies on chemical residues in fish (EPA 1992), the most frequently detected CDD compound (1,2,3,4,6,7,8, HpCDD) was found in fish tissues at 89% of the sites in USA. 2,3,7,8 TCDD was found at a mean concentration of 6.9ppt and a maximum of 204ppt. The detection of CDDs in blood, adipose tissues, breast milk, and other tissue samples from the general population indicates universal exposure to CDDs from environmental sources: the general population is exposed to CDDs released from industrial and municipal inicineration processes; exhausts from vehicles using leaded gasoline; cigarette smoke; and foods, including human milk (Pohl and Hibbs 1996; Schecter et al. 1994e).
The major human intake (more than 90%) is however associated with meat, dairy products, and fish (Beck at al, 1989 a; Schaum et al., 1994).
Workers involved with incineration operations, recreational and subsistence fishers, and farmers living in CDD contaminated areas, are at a greater risk from exposure to "dioxin like compounds" (EPA 1996a).

ENVIRONMENTAL FATE AND TRANSPORT MODELLING

The environmental fate and transport of CDDs involve volatilization, long-range transport, wet and dry deposition, photolysis, bioaccumulation, and biodegradation (Kieatiwong et al. 1990). Due to their low vapour pressure and low aqueous solubility, they are general immobile in soils and sediments and photolysis is probably the most important transformation process in environmental systems: estimates of the half-life of 2,3,7,8 TCDD on the soil surface can range from 9 to 15 years, whereas the half-life in subsurface soil may range from 25 to 100 years (Paustenbach et al.,1992). Emissions to the atmosphere from incineration and combustion sources result in a wide spread distribution of these compounds. Considering the stationary source category in the USA (EPA 1998), the percentage contribution of the five highest source categories are: 68% from municipal waste incineration, 12.3% medical waste incineration, 8.9% from Portland cement manufacture using hazardous waste in the kiln, 3.5% from secondary aluminium smelting, and 3.0% from other biological incineration.
Considering the water matrix, "dioxin like compounds" can enter water by different mechanisms: urban runoff, direct discharge by industrial facilities, deposition of particulates from combustion sources, runoff and drift from the use of chlorophenol based pesticides, and leaching from chlorophenol-containing waste sites.
In the soil, these compounds have been deposited onto soil through pesticide applications and disposal of contaminated industrial wastes but also atmospheric fall out of CDD particulates.
CDDs deposited on soils will strongly adsorb organic matter and may enter the atmosphere on soil dust particles or surface waters. Because of low water solubility and high lipophilicity these compounds bioconcentrate in aquatic organisms and in plants. The bioconcentration factor BCF is defined as the ratio of the concentration of "dioxin like compounds" in an organism living in water over the concentration of these compounds in water. Many experiments show bioconcentration tends to increase with the degree of chlorination up to TCDDs, and then to decrease as chlorination continues to increase up to OCDD congener (Loonen et al., 1993). For terrestrial mammals, the BCF value marks the quotient of the concentration in the tissues divided by the concentration in food. The primary way by which these compounds enter the food chain are by atmospheric wet and dry deposition. The contamination of plant foliage via atmospheric deposition seems to be at greater rate than root uptake.

HUMAN EXPOSURE MODELLING

Consumption of food (including human milk) is by far the most important pathway for exposure for the general population representing over 90% of the total daily intake. Other pathways include inhalation from municipal, medical, and industrial waste incinerators, ingestion of drinking water. Food is the major source of human exposure to CDDs. As shown in **Table 2**, the average daily intake of 2,3,7,8 TCDD by adults of US population is 47pg/day: meat contributes for 50% of the total.

Table 2: estimated average daily intake for US Population (Travis and Hettemer-Frey, 1989)

pathway	Daily intake (pg/day)	Percentage of total daily intake
Ambient source	**1.01**	**2**
Air/inhalation	1	2
Water/ingestion	6.5E-03	<0.1
Soil/ingestion	-	-
Food sources	**46**	**98**
Fruits and vegetables	5	11
Milk	13	27
Meat	23	50
Fish	5	10
Total intake	**47**	**100**

However, for certain subpopulations (recreational and subsistence fishers), fish consumption may be a more important source of dioxin like compounds: maximum daily intake for residents who regularly consume fish from the Great Lakes region in USA has been estimated to range from 390 to 8400 pg/day (EPA 1995).

Occupational exposure to these compounds occurs primarily through inhalation and dermal contact in fire fighters, cleanup workers involved with transformers containing PCBs, in incineration operations and in handling and production of pesticides.

When analyzing childhood exposure to these compounds, it is important to remember child's exposure can differ from an adult's exposure in many ways: children drink more fluids, eat more food, and breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. The human's source of nutrition changes with age and child's behaviour and lifestyle also influence exposure: they play and spend more time outdoor, they put things in their mouths and they are closer to the ground.

Among child subpopulation there are children classified as "at additional risk of exposure": infant who are breast-fed, children of recreational and subsistence fishers, farmers and hunters living in contaminated areas.

In addition to children and to individuals who are occupationally exposed to CDDs there are several groups within the population with potentially high exposures: individuals exposed as result of industrial accidents, through environmental contamination and living in proximity of incinerators and hazardous waste sites.

RISK CHARACTERIZATION.

As previously described, characterizing risks from dioxin and related compounds requires the integration of complex data sets and the use of science based inferences regarding hazard, mode of action, dose response, and exposure.

The Agency for Toxic Substances and Disease registry (ATSDR, 1998a) has adopted policy guidelines to assess health implications of dioxin and dioxin like compounds in residential

soil near or on hazardous waste site considering direct ingestion of contaminated soils as pathway of exposure; the recommendation of ATSDR is that the guidelines apply only for this route of exposure and may not be appropriate for other exposure scenario.
ATSDR indicates the following "health guidance values":

- ***Screening level***: concentration ≤ 0,05 ppb TEQs
- ***Evaluation level***: 0,05 ppb TEQs ≤ concentration <1 ppb TEQs
- ***Action level***: concentration ≥ 1 ppb TEQs

where TEQ (Toxicity Equivalent Quotient) of TCDD is calculated by multiplying the exposure level of a particular dioxin like compound by its Toxicity equivalency factor (TEF) as shown in **Table 1.**
Screening levels are concentrations used to select contaminants of concern of a site. Based on the value of minimal risk level MRL 1pg/kg/day for 2,3,7,8 TCDD, ATSDR has stated 0.05 ppb as screening value for dioxins in soil. If one or more soil samples contain a concentration value exceeding 0,05 ppb of toxicity equivalent, additional site investigation are necessary.
Evaluation levels are concentrations used to assess the nature, the extent of contamination, and the impact, considering bioavailability, ingestion rates, pathway analysis, soil cover, climate, demographics, and background exposure. This evaluation process is followed, if necessary, by the action level. Evaluation level means that a carefully evaluation of contamination extension need to be assessed as well as spatial and temporal distribution in order to ascertain if daily, weekly or monthly exposures be likely to occur. Particularly attention need to be posed to accessibility to the contaminated soil by adults or children and if vegetation is present or not.
Action levels are concentrations at which it is necessary to interdict exposure and to evaluate potential public health actions such as surveillance, research, health studies, community education and information, physician education and eventually population investigation; lastly, if necessary, such remediation action will be operated.

RISK EVALUATION

In order to evaluate the risk connected to the presence of a "screening level concentration" of TEQ in the soil (0,05 ppb as indicated above), the software package **RISC 4.0 (BP Oil)** has been used to assess the risk related to different exposure pathways.
As indicated in the RAIS [Risk Assessment Information System] database 2,3,7,8 TCDD is classified as a "carcinogenic compound" with the *slope factor* for ingestion and dermal exposition routes, as reported in **Table 3**.

Table 3: slope factors for 2,3,7,8 TCDD

slope factor		slope factor
INGESTION	(mg/kgday)-1	1,50E+05
DERMAL	(mg/kgday)-1	3,00E+05

The risk evaluation has been performed for two types of receptors: adult resident and child resident, both divided in "typical " and "RME" (Reasonable Maximum Exposure), using a deterministic approach.
Taking in mind that the "dioxin like" compounds may accumulate in vegetables via root intake as well as particulate deposition on vegetable leafs, the following exposure pathways have been considered: soil ingestion, dermal contact, root vegetables ingestion, above ground vegetables ingestion.

The exposure parameters for Adult and Child resident used in the calculation are reported in **Table 4**.

Table 4: Intake parameters for Adult and Child

Parameters	units	Adult Typical	Adult RME	Child typical	Child RME
Body weight	kg	70	70	15	15
Life time	years	70	70	70	70
Exposure duration	years	9	30	6	6
Dermal contact					
Exposure frequency	Days/year	40	350	130	350
Skin surface	cm^2	18400	23000	6800	7280
% of exposed skin	cm^2/cm^2	0.11	0.56	0.13	0.55
Soil ingestion					
Exposure frequency	days/year	350	40	130	350
Ingestion rate	mg/day	40	100	90	200
Bioavailability	Fraction	1	1	1	1
Vegetable ingestion					
Above vegetables ingestion rate	g/day	127	127	55.8	55.8
Root vegetables ingestion rate	g/day	87.5	87.5	48.5	48.5
Fraction of organic carbon in garden soil	g/gsoil	0.05	0.05	0.05	0.05

The obtained results of risk evaluation are reported in **Table 5**.

The results shows that, in the case of "RME receptor", for adult as well as for child, the estimated risk exceeds the accepted value of 10^{-6}, at least in risk evaluator community. Thus, it suggests more carefully investigations and the necessity of refining the concept of Minimum Risk Level in order to prevent, as possible, any debate not only in the risk evaluator community but at stakeholder levels too. In some cases, risk values of 10^{-5} are accepted but several difficulties area daily encountered in risk assessment communication with stakeholders and local communities.

Nowadays a universal criteria of acceptability isn't still available. Different countries have different reference values (Swartjes, 2002) and in some cases within them such similar situations give different "accepted" value. In this context it is more and more important to define a shared "screening value" as tool to mitigate risk acceptance debate.

Table 5: Risk evaluation for residential soil at "screening level"

	CARCINOGENIC RISK			
	RESIDENTS			
Exposure routes	Adult RME	Child RME	Adult TYPICAL	Child TYPICAL
Soil ingestion	**2,20E-06**	**4,10E-06**	3,00E-08	6,90E-07
Dermal contact	**3,00E-06**	**2,00E-06**	3,70E-08	1,60E-07
Root vegetables ingestion	6,20E-07	3,20E-07	7,50E-08	1,30E-07
Above ground vegetables ingestion	9,00E-07	3,70E-07	1,10E-07	1,50E-07
TOTAL	**6,72E-06**	**6,79E-06**	**2,52E-07**	**1,13E-06**

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The assessment of pollution risk from hydrogeological data and the management of solid waste landfills

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ABSTRACT

During the last years, the occurrence of degradational processes of the underground waters are continuously more frequent especially as concerns the quality of this resource. Polluting processes produced by landfills consisting of urban and industrial refuses are particularly critical for the type of contamination and for the intrinsic difficulty in applying any remedy. In the present research, we estimate the environmental compatibility of the controlled landfills by applying an integrated method based on i) the hydrogeological behaviour of the area surrounding the landfill according to the map of the intrinsic vulnerability of the aquifer(s), ii) the setup, the management and the control of the landfill defined by its risk index. The application of this approach to several landfills located in different geological conditions allowed us to evaluate the efficiency of the control system of the existing landfills and the priority list of the intervention to be performed to improve the future management and to protect the surrounding environment.

INTRODUCTION

The worldwide socio-economic development of several countries has the direct outcome to produce large quantities of wastes from urban, municipal and industrial sectors. Due to the commonly low-quality building characteristics of the landfills and the sometimes critical hydrogeological conditions, these artefacts can pollute the surrounding environment. Italy is one of the European countries with the largest number of municipal waste equivalent to 1.3 kg/person/day (Koufodimos and Samaras, 2002). Among these, only the 70% of the waste weight is deposited in landfills and just the 15% is burned in the incinerators.

A recent census by the Italian Corps of Foresters (October 2002) has documented as many as 4866 unauthorised landfills for a total surface of more than 20 millions of square meters. They also found more than 700 cases of dangerous refuse, therefore emphasising the need of an organic action of precautionary measures. The 46% of the documented landfills are in areas undergoing hydrogeological bond.

Even in case of authorised landfills underlain by waterproof systems, the dispersion of polluting materials towards the underground aquifers is highly possible due to the lost of

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

functionality and the break of the artificial confining system. The effects on the environment are strongly influenced by the lithostratigraphic characteristics and by the geotechnical and hydrogeological properties of the underground.

It is therefore obvious that the location of the landfills cannot be random or influenced exclusively by morphological, economical and logistic factors but the site selection should be the result of a rigorous study based on the joint evaluation of the impact hazard and of the degree of vulnerability of the aquifers.

Recently, a large number of studies have been performed relative to, firstly, treatment methods (prevention/minimisation, materials recovery, incineration, landfill) and integrated management of the produced refuses (Tchobanoglou *et al.*, 1993) and, secondly, the impact of the landfill leachates on the surface and underground resourses (Abu-Rukal and Al-Kofahi, 2001; MacFarlane *et al.*, 1983).

In this article, we present the preliminary results obtained by applying an integrated methodology that considers the way the refuses are treated, the management procedure of the landfill and the impact of the leachate in the underground water resources. We also verify the whole method for some landfills located in different geological conditions (Fig. 1) like i) the coarse-grained fluvial sediments and dolomite bedrock (landfill of Imer, Trento Province), ii) the fine-grained alluvial deposits (landfills of Sant'Agostino anf Jolanda di Savoia, Ferrara Province) and iii) the carbonate complex bedrock of the Lauria Mountains in the Southern Apennines (Basilicata Region). The first site is located along an glacial valley of the Southern Alps, the second in the eastern Po Plain, while the third in a intra-mountain basin of the Southern Apennines.

All the results are represented in different thematic maps and discussed.

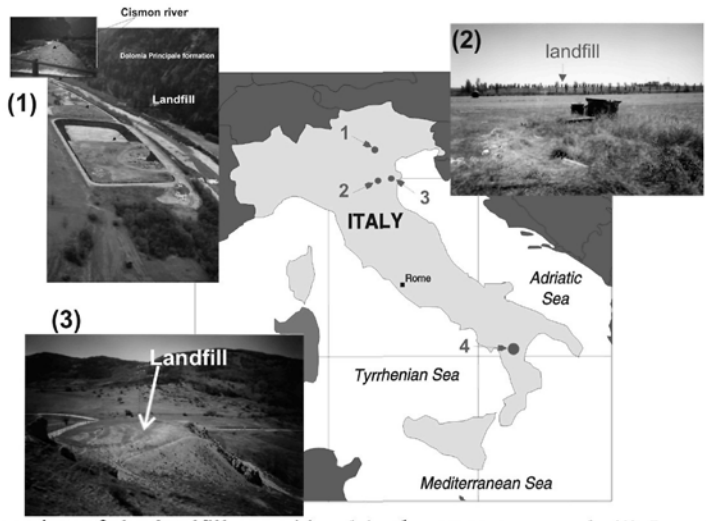

Figure 1: Location of the landfills considered in the present research (1) Imer landfill; (2) Sant'Agostino landfill; (3) Jolanda di Savoia landfill; (4) Basilicata landfills.

METHODOLOGY

The investigating methodology proposed by Mancini *et al.* (1999), based on the determination of the intrinsic vulnerability to pollution of the aquifers and the hazard induced by the landfill quantified as a specific parameter allows i) to identify the suitable sites to host

new implantations for the refuse digestion and ii) to define the priorities in the monitoring and reclamation operations to be fulfilled in case of potentially dangerous landfills or sites that have been already compromised.

The whole procedure is simplified in the sequence of research phases. Firstly, geological, geomorphologic, hydrological and hydrogeological data are collected and elaborated in order to define the conceptual hydrogeological model of the area, the underground water circulation and the piezometric level during the hydrological year.

Secondly, the created database is implemented in a GIS to estimate the intrinsic vulnerability of the aquifer systems. This second step is achieved by using the method most suitable method for the local hydrogeological conditions, among those available from the literature (Albinet and Margat, 1970; Civita and Di Maio, 1997; Aller *et al.*, 1987).

Thirdly, based on the construction techniques, the more hazardous elements for the landfill are identified as well as the intrinsic potential dangerousness of the landfill and the quantitative evaluation of the risks according to the different technical solutions chosen both during the planning phase and the management phase. A weight "W" related to the impact potentiality is attribute to each of the above risk elements, whereas for the single elements is defined a reduction factor "R" of the magnitude of the potential damage in relation to the specific used technical measures (table I). Consequently the evaluation of the dangerousness index "I_d"is obtained as follows: $I_d = \Sigma\ Wi*Ri$

Table I: Reduction factor, R, of the weight, W, of the single risk elements.

Risk elements	W		R		R		R		R
Potentiality of the plant	5	< 10 ton/d	0.1	10-50 ton/d	0.2	50-500 ton/d	0.4	>500 ton/d	1
Leachate collection system	5	Free drainage and external collection	0.1	Internal drainage and extraction with pump	0.3	Storage and seasonal recycle	0.5	Not present	1
Type of refuse	3	Inert	0.1	Urban	0.5	Industrial – not dangerous	0.8	Dangerous	1
Physical state of refuse	3	Solidified with inert matrix	0.1	Solid	0.2	Sludgy W<70%	0.5	Sludgy W>70%	1
Typology of stabilisation	2	Non biodegradable	0.1	Aerobic	0.3	Both (anaerobic and aerobic)	0.5	Anaerobic	1
Monitoring system	2	Monitoring well + under geomembrane net	0.1	Under geomembrane net	0.3	Monitoring well	0.5	Not present	1
Disposal criteria	1	Compacted with hydraulic press	0.1	Compacted with steel wheel compacto	0.2	Compacted with crawler	0.5	No compaction	1
Final cover	1	Compacted clay + soil	0.1	Only compacted clay	0.2	Only soil	0.5	Not present	1

Fourthly, the relationship between the intrinsic vulnerability of the site and the potential danger of the landfill we permitted the subdivision of the territory into zones best suited for the location of new waste disposal plants and the definition of the priorities for reclamation interventions (tables II, III)

According to this methodological approach for ever level of priority classes we propose the required actions (table IV) allowing the efficient management of the landfill in order to improve its functionality as a whole and consequently to protect the natural environment.

Table II: Index of dangerousness "I_P" allowable for areas of different vulnerability.

I_P	Allocation area
< 3	Any area
3 – 6	Medium vulnerability area
6- 10	Low vulnerability area
>10	Is necessary to take measures to reduce intrinsic dangerousness

Table III: Individuation of priority classes

Site Vulnerability	Landfill danger. index	Priority classes	Site Vulnerability	Landfill danger. index	Priority classes	Site Vulnerability	Landfill danger. index	Priority classes
High	<3	**	Medium	<3	*	Low	<6	*
	3-6	***		3-6	**		6-9	**
	>6	****		6-9	***		9-15	***
				>9	****		>15	****

Table IV: Measures to be taken according to the level of priority

Priority		Actions
Low	*	– Site delimitation and supervision system to avoid further discharges of material – Actions of total material removal and site restoration are required only for area re-use projects.
Medium	**	– Site delimitation and supervision system to avoid further discharges of material – To proceed, urgently, with a program of environmental contamination assessment according to the most important parameters – Realisation of a monitoring system for evaluating the site contamination evolution
High	***	– Application of all previous measures – Measures for leachate reduction (surface impermeabilisations) or the control of its dispersion (low permeability barriers, drainage and extractions)
Very high	*** *	– Application of all previous measures – Evaluation of a possible technique for material removal.

APPLICATIONS

In the present paper, we calculated the intrinsic vulnerability of the aquifer(s) following the 'SINTACS' point count system model (Civita and Di Maio, 1997). The parameters here considered are i) the depth to water table, ii) the effective infiltration, iii) the soil and the unsaturated zone attenuation capacity, iv) the hydrological characteristics and the hydraulic conductivity of the aquifer and finally v) the topographic surface average slope.
The index of the intrinsic vulnerability in the barycentre of each cell is obtained according to the equation:

$$I_{SINTACS} = \sum_{j=1}^{7} P_j \times W_j$$

where P, is the rating of the SINTACS parameters that the method considers and W, the correlated weigh inside the chosen string.

Landfills in carbonate bedrock of the Lauria Mountains in the Southern Apennines (Basilicata Region)

The analysed territory has an extension of about 290 km^2 (Fig.1). Within the area are Mount Zaccana (1580 m) and Mount Rossino (1238 m) among several other peaks and two of the most important rivers flowing in the Basilicata Region, the Sinni and the Noce, representing the northern and the western border of the investigated area, respectively.

In the territory there are also two small lakes the Rotonda lake, a natural sheet of water placed in the area between Serra Rotonta (1285 m) and Serra Destra di Tornesiello (1145 m), and the Cogliandrino lake, an artificial reservoir obtained by damming the Sinni river.
The geological setting is characterised by different lithologies belonging to the Carbonate platform Unit and the Liguride Unit, representing two structural-stratigraphic units of the Southern Apennines. Quaternary alluvial and scree deposits also occur.
The principal aquifer is represented by the dolomite and calcareous-dolomite complexes. The modality of the underground circulation into the aquifer system is basically conditioned by the density, degree of opening and orientation of the fracture system and by the presence of karstic phenomena.
Following the SINTACS method, the intrinsic vulnerability of the aquifer system generally shows a medium to high vulnerability (Fig. 2). As expected in basins of mainly karst origin this represent high vulnerability areas.

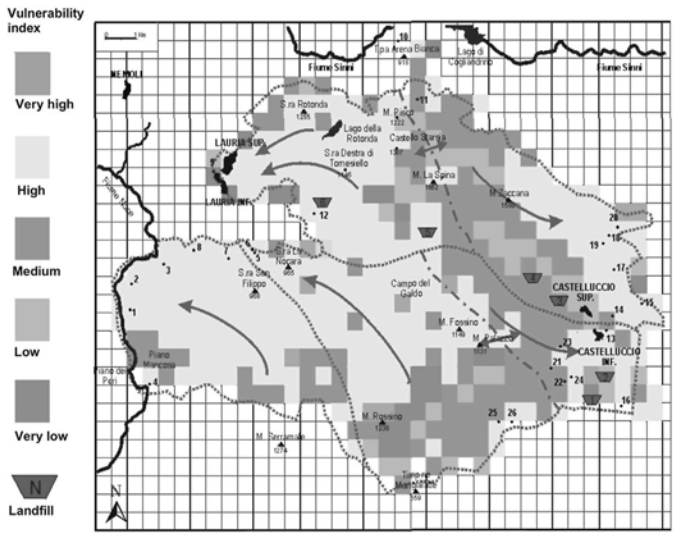

Figure 2: Vulnerability map of the investigated area. The number represents the main springs of the Lauria Mounts carbonate aquifer system.

Seven Municipal Solid Waste (MSW) landfills have been located in the study area (Fig. 1; Fig. 2). Some of these landfills are unauthorised, the others are realised in sanitary emergency condition, without any safety measure, particularly as concerns the leachate control.
The application of the integrated method allowed us to obtain in most cases relatively high values of the dangerousness indexes of the landfills (tabl. V). In particular, these values depend on the total absence of a system of leachate collection and control, of any kind of landfill operation and of a correct final cover.

Seven sites are included in the Regional Restoration Plan. In these sites, the priority class is reduced (table V) performed the following operations i) delimitation of the dangerous areas and the collection of the dispersed material; ii) consolidation of the material and of the areas of instability; iii) cover of the landfills with natural or artificial materials characterised by low permeability; and iv) collection of external waters.
However, since these actions have been planned for about 1000 similar sites, it is likely that all these operations will not occur in due time with the required priority.

Table V: Evaluation of dangerousness index, vulnerability index and priority class of the landfills located in the Lauria Mounts carbonatic aquifer system.

Elements of danger		landfills					
Landfills number	W	1	2	3	4	5	6
Potentiality of the plant	5	0.1	0.05	0.1	0.05	0.1	0.1
System of leachcate control	5	1	1	1	1	1	1
Typology of refuse	3	0.5	0.5	0.5	0.5	0.5	0.5
Physical state of refuse	3	0.2	0.2	0.2	0.2	0.2	0.2
Typology of stabilisation	2	0.5	0.3	0.5	0.3	1	1
Monitoring system	2	1	1	1	1	1	1
Criteria of landfill operation	1	1	1	1	1	1	1
Final capping	1	1	1	1	1	1	1
Dangerousness index		12.6	11.95	12.6	11.95	13.6	13.6
Site vulnerability		low	low	Medium	Medium	High	High
Priority class		***	***	****	****	****	****
After the realisation of the actions of risk reduction							
Dangerousness index		7.3	6.65	7.3	6.65	8.3	8.3
Priority class		**	**	***	***	****	****

Landfills in the alluvial deposits of the Po plain (Ferrara Province)

The eastern sector of the Po plain, Northern Italy (for location see figure1) is draped by fine-grained Holocene sediments of alluvial origin overlying Pliocene and Pleistocene deposits accumulated in marine, deltaic, marshy and fluviatile conditions (Pieri and Groppi, 1981). From a palaeogeographic point of view, the fluvial dynamics of the Po and Reno rivers deeply influenced the evolution of the whole territory. Accordingly, nearly two thirds of the surface of the Ferrara Province are nowadays below the sea level including the landfills investigated in the present research. During the last decades, man activities increased, mainly farming (fruit trees, corn, wheat and soya) and secondarily the industrial ones, therefore favouring the emission of large quantities of polluting substances in the environment and particularly in the aquifers (Rapti Caputo, 2000). As a consequence, the territory surrounding Ferrara, the unconfined aquifer suffered a severe qualitative degradation due to the low depth to water table. In this geological and geomorphologic framework have been settled the solid waste urban deposits of Sant'Agostino and Jolanda di Savoia considered in the present work.

Sant'Agostino landfill

The area where is located the Sant'Agostino landfill (Fig. 1) is characterised by a very flat relief with altitudes between 10 and 11 m crossed by an dense artificial drainage system. The geological setting is characterized by the presence of the alluvial deposits of the Reno river consisting of alternating sandy and silty-sandy layers.

In the underground, we can distinguish two principal aquifer bodies (Fig. 3a). The first is unconfined or locally semi-confined at few metres depth, while the second is a confined aquifer at a depth of about 17 m. The unconfined aquifer consists of sandy or silty-sandy material with several alternating peat lenses. The depth to water table varies between 2 and 3 m. The unsatured zone consists of silty-clay materials with several alternating lenses of peat and silty-sands. The intrinsic vulnerability of the unconfined aquifer in the area around a landfill present variations between low and medium (Fig. 3b), while the index of dangerousness I_P, associated to the constructing characteristics and the monitoring modality is equal to 8,7 (table VI). Accordingly, the intervention priority if of second class (**), mainly due to the lack of an efficient monitoring system for evaluating the site contamination evolution.

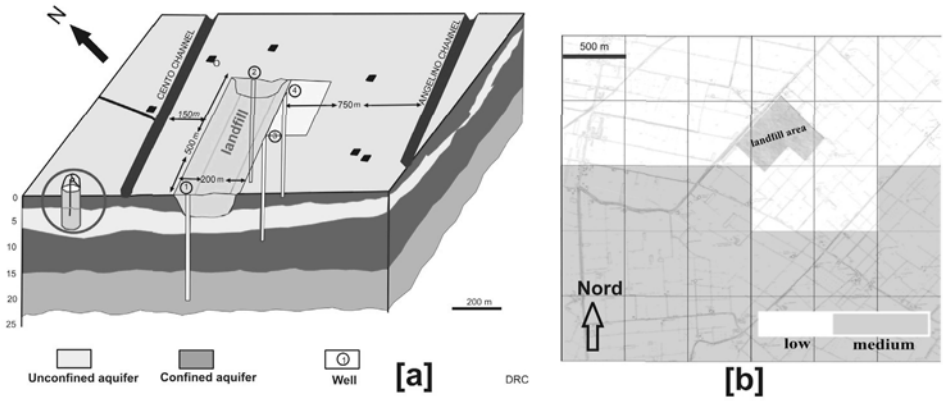

Figure 3: Sant'Agostino landfill. [a] conceptual hydrogeological model; [b] Vulnerability map.

Jolanda di Savoia landfill

In the eastern sector of the Ferrara plain alluvial deposits of the Po river occur, characterized by alternating sands and silty-sands. The Jolanda di Savoia landfill (Fig. 1) is here located at an altitude between 0.5 and –0.9 m. According to the hydrogeological conceptual model, two separate aquifer bodies exist. The first one is unconfined at few metres depth, while the second is confined at a depth of about 15 m. The unconfined aquifer consists of sandy or silty-sandy material with several alternating peat lenses. The depth to water table varies between 1.5 and 2.5 m. The unsatured zone is represented by silty-clay materials with several alternating peat lenses. The Intrinsic vulnerability of the unconfined aquifer system varies from low to medium (table VI) with an Index of dangerousness equal to 6.82 and an associated third priority class (***).

Table VI: Evaluation of dangerousness index, vulnerability degree and priority class of the landfills located in the alluvial deposits aquifer system.

	Sant'Agostino landfill	**Jolanda di Savoia landfill**
potenzial of the plant	41,6 ton/d	300,0 ton/d
leachate collection system	free drainage and external collection	storage and seasional recycle
type of refuse	urban	urban
physical state of refuse	solid	solid
typology of stabilisation	anaerobic	anaerobic
monitoring system	not present	monitoring well + under geomembrane net
disposal criteria	no compaction	compacted with crawler
final cover	compacted clay+soil	compacted clay+soil
dangerousness index	**8,7**	**6,82**
vulnerability	**low**	**medium**
priority class	**	***

Landfill in the fluvial sediments of the Cismon river (Trento Province)

The solid waste urban landfill of Imer is located along the Cismon river, in the province of Trento (Fig. 1), within a Quaternary glacial plain at an altitude of about 600 m. The alluvial deposits infilling the Cismon valley mainly consists of heterogeneous gravels and secondarily of sands and locally silt materials. In the underground the occurrence of an unconfined or locally semi-confined aquifer developed in the alluvial deposits shows high permeability values. The depth to water table varies between 1.1 and 6.5 m, while the prevailing flow direction is from North to South. The potentiality of the plant is about 16.47 ton/d consisting

of an anaerobic system associated to a free drainage and external collection of the leachate. The landfill is isolated from the surrounding environment by a geomembrane net, while the final cover is realized with compacted clay and soil.
The intrinsic vulnerability of the unconfined aquifer varies from high to very high, the index of dangerousness "I_P" is about 5.9 and consequently the priority classes is the third (***), mainly due to the high vulnerability of the aquifer and to the lack of a monitoring system.

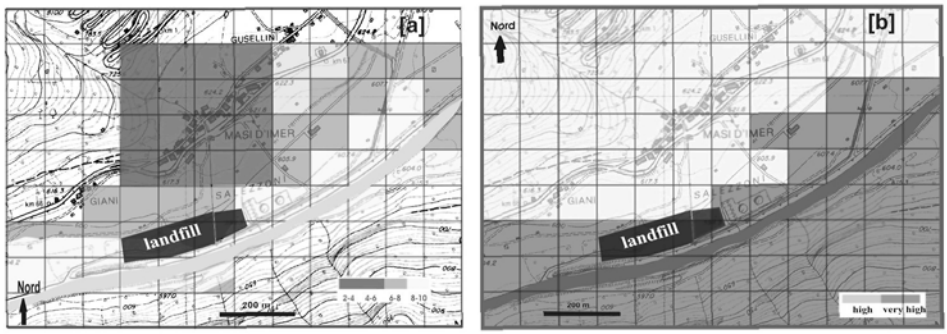

Figure 4: Imer landfill. [a] SINTACS point relative to the 'topographic surface average slope'; [b] Vulnerability map.

CONCLUDING REMARKS

Notwithstanding the environmental policies of the European Union (European Commission, 1999) and the severe national legislation, groundwater contamination due to the Municipal Solid Waste (MSW) landfill leachates is recognized as a serious socio-economic and environmental problem in many countries.
The integrated analysis of the intrinsic vulnerability of the aquifer system and the estimate of the intrinsic potential danger of the landfill expressed by the dangerousness index allowed us the evaluate the suitability of the sites to host a landfill and to define the reclamation priority for the existing landfills. Moreover, for the new landfills, the proposed methodology permits us to suggest the better constructing strategy and the protection of the surrounding environment. The application of this procedure to some existing landfills standing in different geological conditions gives satisfactory results.

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Modelling the behaviour of soluble salts in a highly compacted bentonitic clay

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ABSTRACT

This paper presents a study of the behaviour of soluble salts (major ions) in a highly compacted bentonite subjected to a thermo-hydraulic gradient. This is achieved via the application of a numerical model, COMPASS, which implements a coupled thermo/hydro/chemical/mechanical approach to model the behaviour of saturated/unsaturated soils. In this study, thermal transfer is considered to take place via conduction, convection and latent heat transfer; moisture transfer in both the liquid and vapour phases due to liquid and vapour gradients, and chemical transfer due to both advection and hydrodynamic dispersion are also considered. Chemical reactions considered include ion exchange reactions involving major cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) and precipiation-dissolution of trace minerals (calcite, dolomite, anhydrite and halite). As a first approximation an elastic constitutive deformation model is implemented in this study. Comparisons between experimental and numerical results have been presented for various variables. For the simulation of the thermal field moisture it is claimed that the models can represent the important mechanisms occurring in the soil. Considering the behaviour of major ions, the model is able to qualitatively simulate the experimental behaviour. This suggests that the influence of moisture and heat flow, in this advection dominated problem, on chemical transport has been captured. Therefore, confidence in the coupling of the heat, moisture and chemical variables has been gained. Moreover, since the ions are also undergoing simultaneous geochemical reactions, with the main processes being ion exchange and precipitation/dissolution reactions, confidence in the coupling between the geochemical and the chemical transport model has also been gained. As regards the mechanical behaviour, where an elastic model was assumed as a first step, in the absence of experimental results, the model showed acceptable trends.

INTRODUCTION

Numerous experimental investigations have been carried out to date on bentonitic clay to study the physical-chemical-mechanical behaviour when used as an engineered barrier for nuclear waste repositories (Graham et al. 1997; Dahlstrom, 1998; Huertas et al., 2000). Such studies are of paramount importance as engineered barriers are expected to play a key role in the long term isolation of waste under the conditions that exist in a typical repository. In a typical repository, a thermo-hydraulic gradient exists due to the heat generated by the waste canisters and progressive wetting of the initially unsaturated bentonitic clay by the water table in the host formation. Since bentonitic clays are highly expansive, a thermo-hydraulic gradient can cause swelling/shrinkage (Thomas and He, 1995). Furthermore, the presence of various ions in bentonite pore water and its interactions with the bentonite can modify the chemical properties of the bentonite and weaken its barrier capacity. For instance, the composition of the bentonite pore water and their oxidation potential govern the solubility of

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

radionuclides, affect their sorption on mineral surfaces and influence the corrosion rate of the vitrified waste matrix (Cuevas et al., 2002). Therefore, in order to assess the performance of bentonitic clays as engineered barriers, the complex couplings that exist between the thermal, hydraulic, chemical and mechanical behaviour should be considered.

This paper presents an application of the numerical model, COMPASS, to simulate the coupled thermo/hydro/chemical/mechanical behaviour of unsaturated bentonitic clay. The numerical model incorporates a coupled thermo/hydro/chemical/mechanical formulation. Heat transfer formulation includes flow due to conduction, convection, and latent heat of vaporisation (Thomas, 1985). Moisture movement in both liquid and vapour form, caused by pressure gradients is governed by Darcy's law, and vapour transfer due to diffusion is represented by a modified Philip and de Vries approach, (Ewen and Thomas, 1989). Chemical transport is governed by advection and hydrodynamic dispersion. Geochemical interaction is incorporated using an equilibrium-based approach. MINTEQA2, a geochemical model is utilised to solve the chemical equilibrium equations (Allison et al., 1991). Finally, the stress/strain behaviour of the soil is represented with an elasto-plastic constitutive relationship and is governed by a stress equilibrium equation (Thomas and He, 1995).

This paper deals with the modelling of a small cell heating and hydration experiment carried out by CIEMAT, Spain, on a bentonite clay as part of a major research study entitled FEBEX (Cuevas et al., 2002). In the following sections, the experimental work and experimental observations are introduced first. The assumptions in the modelling work, material parameters and initial/boundary conditions are then presented. Finally, a comparison of simulated and experimental results is presented for moisture and two major anions (chloride and sulphate). Results for sodium ions and the exchange complex have been presented elsewhere (Seetharam, 2003). Deformation behaviour in terms of changes in void ratio has also been presented.

SMALL CELL BENTONITE EXPERIMENT

The experiments carried out by University of Madrid and CIEMAT (Cuevas et al., 2002) have been performed in hermetic cells in which a compacted block of bentonite is hydrated on the top while a thermal gradient is applied from the bottom. A schematic diagram of a typical hermetic cell was shown in figure 1 (Cuevas et al., 2002). The specimen is 2.5cm long and 5.0cm diameter. A temperature gradient of 12°C/cm is applied across the bentonite cell. The temperature at the hydration end was kept constant at 30°C by the circulation water, whilst a constant temperature of 65°C was applied by a heater at the opposite end. Granitic water was supplied at a pressure of 1MPa. The influence of the chemistry of the hydration water on the processes achieved by verified by using granitic water, which simulate the conditions of the outer part of the barrier (Cuevas et al., 2002). A series of tests were performed for different durations related to the saturation time - $t_{1/4}$, $t_{1/2}$, t_1, t_2, and t_5, which corresponds to a duration of 4days, 8days, 16days, 32days and 80days respectively. At the end of each experiment the bentonite cells have been sliced horizontally into 5 sections of 0.5cm each. In these samples, the concentration of major ions and pH in the pore water were determined for a 1:4 bentonite-water aqueous extract.

Cuevas et al. (2002) reported that the bentonite cell reached saturation in 16 days. As regards, the behaviour of ions under a thermo-hydraulic gradient the following major processes were observed (Cuevas et al. 2002); (i) advective movement of ions from the cold end towards the hot end during initial stages, (ii) consequent build up ion concentrations at

the hot end, (iii) backward diffusion of ions from hot end towards cold end as the bentonite cell reaches saturation, and (iv) equilibrium distribution of ions after saturation. Although these are the typical processes that all ions undergo, ions such as sulphate, sodium, calcium and potassium are also affected by dissolution-precipitation and ion exchange reactions. As stated earlier, the simulated behaviour of only chloride and sulphate are discussed in this paper.

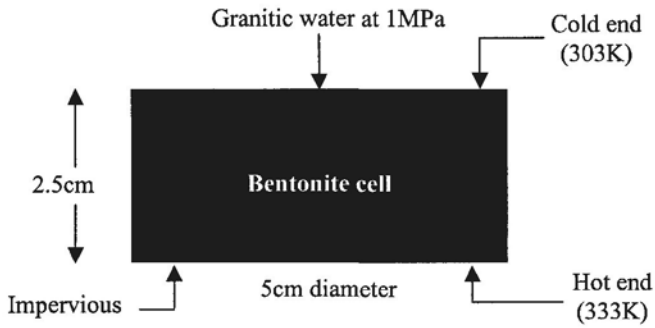

Figure 1: Conceptual diagram of the thermo-hydraulic experiment (Cuevas et al. 2002)

SIMULATION OF A SMALL CELL HEATING AND HYDRATION EXPERIMENT

The experimentally observed behaviour suggests that there are four main fields of behaviour that interact in a complex manner; these are moisture, heat, chemical and displacement. Therefore, a simulation of the coupled thermo/hydro/chemical/mechanical (THCM) behaviour of the bentonite clay has been undertaken. Several assumptions have been made in the analysis and these are discussed below. As regards the numerical strategy for coupling the transport with the geochemical reactions, a sequential non-iterative approach has been adopted. Although this method is found to yield less accurate results when heterogeneous reactions are involved, the efficiency of the computational time has been the motivating factor in choosing this method. Specific attention is drawn to the initial conditions for the chemicals in the bentonite water, and the initial conditions for ion exchange complexes in the bentonite solid. The initial conditions of the chemicals in the pore water and the exchange complex were determined using MINTEQA2 (Allison et al., 1991). This was necessary, as it is extremely difficult to determine experimentally the pore water composition at very low water contents (Fernandez et al., 2000). Due to limitations of space, the geochemical modelling using MINTEQA2 is not presented in this paper, but is reported in full in Seetharam, (2003).

Assumptions

A number of assumptions have been made as regards the chemical processes and deformation behaviour. These are: (i) dissolution-precipitation of only halite, calcite, dolomite and anhydrite is considered, (ii) ion exchange reactions involve only calcium, magnesium, potassium and sodium ions, (iii) ion exchange of hydrogen ions and protonation/deprotonation reactions are ignored, (iv) thermodynamic stability of the clay fraction (at $7 < pH < 11$) is considered, (v) the geochemical reactions are modelled on the basis of an instantaneous equilibrium assumption, (vi) carbon dioxide transport in the gaseous phase has been ignored, and (vii) an elastic model for the deformation behaviour has been assumed, since this is a first attempt at modelling coupled deformation and reactive multicomponent chemical transport.

Material parameters

There are a series of sets of material parameters required for the purpose of simulation, covering flow, geochemical and deformation analysis. Five of these concern flow analysis and are; i) moisture retention relationship, ii) hydraulic conductivity relationship, iii) thermal conductivity relationship, iv) diffusion coefficient, and (v) material constants. The sixth set concerns geochemical parameters, whilst the seventh concerns deformation parameters. The information pertaining to the first four sets of material data are based on Huertas et al. (2000) and Martin et al. (2000). The material constants have been extracted from Mayhew and Rogers (1976) and Huertas et al. (2000). The information regarding the geochemical parameters and the deformation parameters have been taken from Fernandez et al. (2000) and Mitchell (2002) respectively.

Initial and boundary conditions

The bentonite cell is initially set to be in equilibrium with the laboratory conditions (14% gravimetric water content) (Cuevas et al., 2002). It is assumed that the temperature is in equilibrium with the laboratory conditions and is equal to 298K. The initial conditions for the chemical components are presented in table 1. These are based on the geochemical modelling performed using MINTEQA2. For the deformation analysis, an initial uniform isotropic pressure of 200kPa has been assumed. As regards boundary conditions, the pore water pressure is fixed at the top face (Dirichlet), whilst for temperature both the top and bottom face are fixed (Dirichlet). For the ions, a Cauchy's boundary condition is applied at the top face, as the influx of chemicals into the bentonite cell depends on the influx of hydration water. A zero flux condition is applied to the remaining faces. Displacements are restrained in the z direction on the top and bottom edges of the domain (figure 1). Whilst, on the left and the right edges, displacement in the x direction is restrained.

Table 1: Initial composition of dissolved and precipitated ions in the initial pore water and the exchange complex in the bentonite solid

Ions/ exchange complex (mmol/100g)	Cl^-	SO_4^{2-}	CO_3^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	CaX_2	MgX_2	NaX	KX
dissolved	2.23	0.63	0.008	2.66	0.036	0.18	0.21	18.86	15.97	30.76	1.89
precipitated	0.00	0.403	6.00	0.00	0.00	0.85	5.56	-	-	-	-

Simulation results

The simulation results for the temperature, moisture, chloride and sulphate ions, and the deformation behaviour are discussed in this section. As stated earlier, (section 2), once the experiment has been completed, the bentonite plug is sliced into 5 sections of 5 mm each and the sample is subjected to an 1:4 aqueous extract analysis in order to determine the concentration of ions. However, due to this method, the final bentonite sample will come into contact with an additional quantity of water, which may affect the equilibrium composition of ions due to further dissolution of trace minerals. This could also trigger ion exchange reactions. Therefore, in order to compare the model results with the experimental ones (1:4 aqueous extract method), it is necessary to re-equilibrate the model results with the additional amount of water and then compare the re-equilibrated results with the experimental results. Hence in this paper re-equilibrated results are presented for comparison purposes.

Temperature and moisture distribution

The simulation results predicted the temperature distribution to nearly reach an equilibrium distribution during the first 1-hour and a final equilibrium distribution after 4 days. This is due to the fact that at the hot end the thermal conductivity drops due to drying. However, as resaturation occurs, the temperature distribution tends towards equilibrium. As regards the moisture field, the model predicted 85% saturation in 8 days and 100% saturation in 16 days. This is in agreement with the experimental observation (Cuevas et al., 2002).

Chloride (Cl^-)

Figure 2 presents a comparison of re-equilibrated model results against the experimental results for the dissolved chloride ion concentration at three different time intervals – $t_{1/4}$, t_1 and t_5. The results presented are the average concentration for each slice (5mm). From figure 2, it can be seen that there is a good correlation between the experimental and model results at $t_{1/4}$. However, the model slightly over predicts the dissolved concentration both at the hot end and the cold end compared to experimental results. Mass balance calculations suggest that the average experimental chloride concentration is less than the initial experimental chloride concentration. This suggests that some chloride ions are lost from the system. Cuevas et al. (2002) suggested that such a decrease in the mass of the chloride ions in the bentonite cell may be attributed to ion exclusion. Therefore, this leads to an over prediction by the model. At t_1 the model results show an over prediction at the hot end. However, the experimental results show that the chloride concentration has nearly achieved a steady state value. Once again the key feature of the comparison is the discrepancy in the mass balance between the model and the experimental results. At t_5 it is obvious that the chloride concentration has halved in the experiment. This means half of the mass of chloride ions has been lost from the system due to anion exclusion. This feature has not been captured by the model as the effect of anion exclusion has been ignored. Nevertheless, the model is able to capture the effect of advection during the initial hydration phase and backward diffusion during later phase, i.e. near saturation.

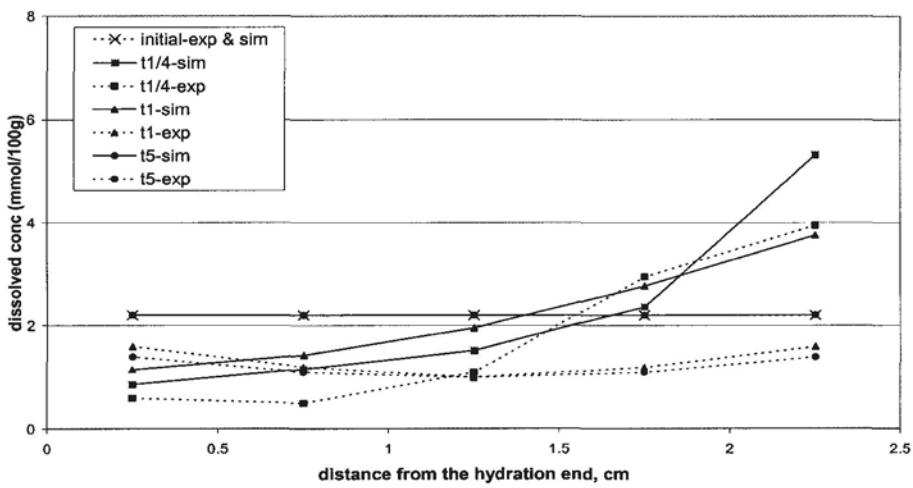

Figure 2: Comparison of simulated and experimental results for Cl^- ions at 4 days ($t_{1/4}$), 16 days (t_1) and 80 days (t_5) - 1:4 aqueous extract

Sulphate (SO_4^{2-})

Figure 3 presents a comparison of re-equilibrated model results against the experimental results for the dissolved sulphate ion concentration at three different time intervals – $t_{1/4}$, t_1 and t_5. From this figure it can be seen that there is a reasonable qualitative agreement between the two results for all time intervals. The model shows an under prediction at the cold end and an over prediction at the hot end compared to the experimental results at both $t_{1/4}$ and t_1. This suggests that the mobility of sulphate ions have been over predicted by the model. It is believed that the under prediction at the cold end is due to the instantaneous equilibrium approach implemented, which will result in an instantaneous dissolution of anhydrite mineral rather than a slow rate of dissolution. This will then lead to an overestimation of the sulphate ions in the dissolved phase. As a result these over predicted sulphate ions are carried towards the hot end by the fast rate of hydration. Another possibility for the over prediction at the hot end may be attributed to the fact that when modelling the re-equilibrated condition, it is assumed that the soil slice has stabilised at room temperature (25°C). Therefore, under ambient temperature, which is much lower than the temperature in the in-place condition (60°C), the dissolution process is favoured (Langmuir, 1997). At t_5, there is a good qualitative and quantitative agreement between the re-equilibrated model and the experimental results up to 2cm distance from the hydration end. Once again the exception is the hot end where over prediction is still seen. The reason for this behaviour remains same as explained above.

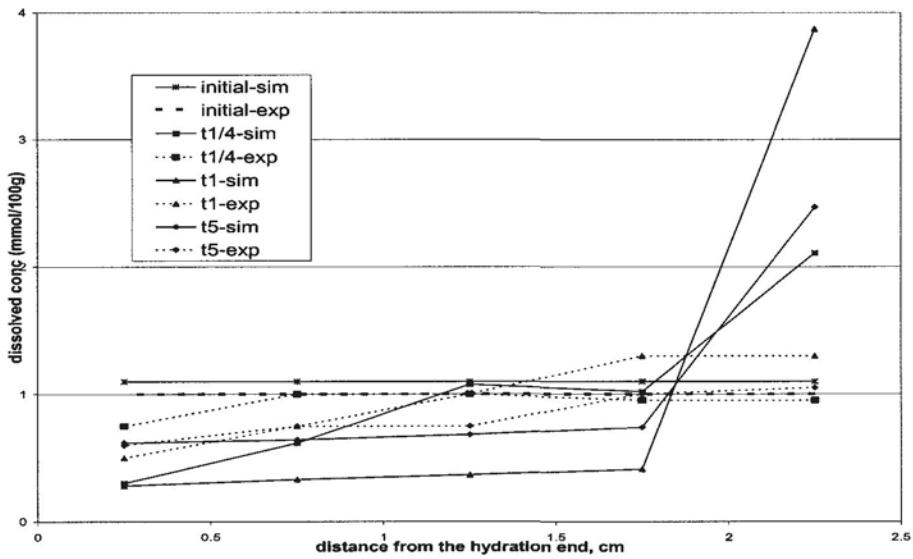

Figure 3: Comparison of simulated and experimental results for SO42- ions at 4 days (t1/4) - 1:4 aqueous extracts results

Deformation

The stress-strain response of the sample has been presented in terms of change in void ratio. Figure 4 shows the transient results of void ratio changes in the bentonite clay at four different time intervals – $t_{1/4}$, $t_{1/2}$, t_1 and t_5. It can be seen from the figure that during the initial stages, i.e., at $t_{1/4}$ and $t_{1/2}$ the model predicts an increase in the void ratio near the hydration end and a corresponding decrease in the void ratio towards the hot end. This behaviour is caused by swelling of the bentonite clay near the hydration end as the hydration

water enters the bentonite cell and shrinkage due to drying at the hot end. Since the bentonite clay is in a confined cell, the overall volume of the sample remains constant and therefore some compression at the hot end due to swelling at the hydration end will occur. As hydration continues, the bentonite clay continues to swell, until full saturation is reached. At t_1, the model predicts swelling in up to 2cm of the domain. However, the last 0.5cm still shows a decrease in the void ratio. It is suggested that this may be due to the fact that at t_1, the model predicts the hot end to be still slightly unsaturated. Nevertheless after t_1 the model predicts complete saturation with the void ratio returning to its original value as seen in figure 13. The reason that the model shows the regaining of initial state in terms of void ratio is because of the elastic model adopted for this simulation study. Unfortunately there is no published experimental data in order to compare the void ratio results. However, the void ratio behaviour is consistent with the expected physical behaviour.

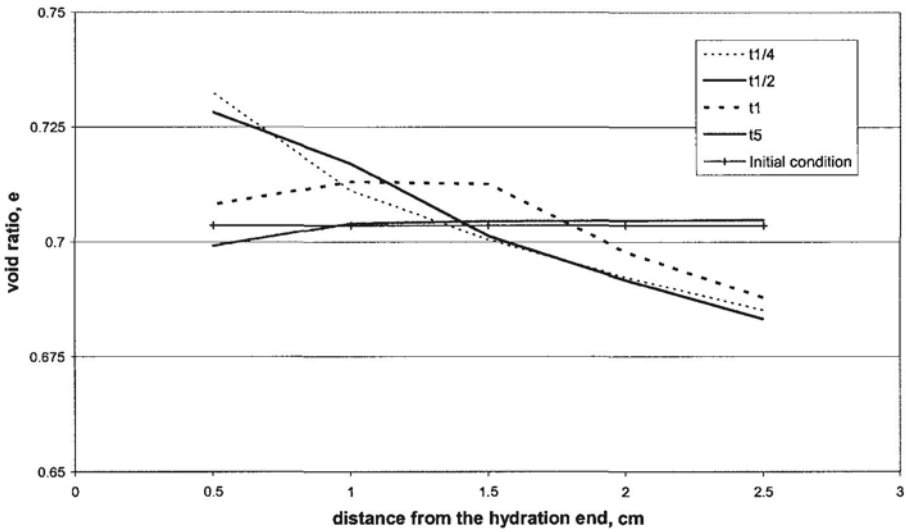

Figure 4: Simulated void ratio changes in the bentonite cell during various time intervals

CONCLUSIONS

This paper has demonstrated the capability of the numerical model, COMPASS, via the simulation the small cell heating and hydration experiment carried out as part of the FEBEX project. The nature of the experiment demanded that a thermo/hydro/chemical/mechanical analysis be carried out in order to successfully predict the behaviour of various components in the bentonite experiment. Specifically, the behaviour of four important primary fields have been presented, namely; temperature, moisture, chemicals (Cl^- and SO_4^{2-}) and deformation.

The response of both temperature and moisture fields is captured well in the simulation. As regards to chemical transport, the behaviour of two anions was presented. The Cl- and SO_4^{2-} ions showed a good qualitative and a reasonable quantitative trend with respect to experimental results. However, one of the key observations was an over prediction of ion concentration at the hot end and an under prediction at the hydration end for all the ions.

This was mainly attributed to the initial fast rate of hydration and also due to the instantaneous equilibrium approach implemented in the numerical model, which might have influenced dissolution/precipitation to a large extent. Nevertheless even with this implementation of instantaneous equilibrium approach, the model still showed good qualitative trends in all the cases. As regards the mechanical behaviour, where an elastic model was assumed as a first step, in the absence of experimental results, the model showed acceptable trends. Finally, it is acknowledged that a number of simplifications have been made in the simulation work, and hence it is expected that improved solutions can be achieved by including more complexities into the model. Nevertheless, the model results have been satisfactory and thus have provided improved confidence in the model's ability to simulate the thermo/hydro/chemical/mechanical behaviour of bentonite type soils.

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RISK MANAGEMENT AND REMEDIATION OF CONTAMINATED LAND AND GROUNDWATER

Enhancement of pH of Stabilized Soil with Ash and Cement

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ABSTRACT
Timber Industry Ash (TIA) and ordinary Portland cement (OPC) were evaluated for its ability to increase the pH of an acidic meta-sedimentary residual soil. The residual soil samples were obtained from within the campus of *Universiti Kebangsaan Malaysia* (UKM), Bangi. The average initial soil pH is 4.75. The results showed (1) a trend of increasing pH over time, (2) a trend of increasing pH with increasing water content (decreasing pH over weight to volume dilution ratio), and (3) a general trend of increasing pH with the increase of the amount of ash, cement and mixture of ash and cement. The data also showed that the best results in increasing soil pH values to between 9.5 and 11.0 were a mixture of 20% to 75% TIA in a soil-TIA mix or 1% to 2% cement in a soil-cement mix. The results also illustrated the importance of specifying the duration of pH measurements, and the weight to volume ratio of samples to facilitate comparisons with other researchers' data.

INTRODUCTION

The management of contaminated soil is a major problem in many countries. In order to reduce the harmful effects and environmental risks, treatment and clean-up processes are required. Solidification/stabilization (S/S) is one of the major treatment methods in dealing with hazardous and contaminated soil. In fact, S/S is referred to as the Best Demonstrated Available Technology (BDAT) in the USA for treating a wide range of characteristic and nonwastewater wastes listed by Resource Conservation and Recovery Act RCRA. (Barth et. al., 1990; U.S. Environmental Protection Agency, 1993)

Measurement of pH is one of the most important and frequently used identification tests. As an example, pHs of stabilized/solidified products are monitored during leaching/extraction tests such as Toxic Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), or Acid Neutralization Capacity (ANC) tests. Analysis of various literature showed that different analysts have adopted different soil-water dilution ratios from 1:1 to 1:10 to measure soil pH. Only US EPA specifically stated that Method 9045C can be used to measure both soil and waste pH i.e. with soil-water and waste-water dilutions. Table 1 summarized some of the various methods used to estimate soil pH. These

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

methods are basically electrometric (potentiometric) method, which uses pH meter with glass electrode and a reference electrode or a combination electrode. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is then determined by extrapolation (APHA 1998).

Table 1: Comparison of a few method of pH analysis

Method	*BS 1377: Part 3:1990: 9*	*Method 9045C US EPA SW846, (1995)*	*Method 8156 Hach, (1996)*	*Hesse, P. R. (1971)*	*Rowell, D. L. (1994)*	*Tan. K. H. (1996)*	*Soil and Plant Analysis Council, Inc. (1999)*
Mecha-nism	Electro-metric	Electro-metric	Electro-metric	Electro-metric	Electro-metric	Electro-metric	Electro-metric
Weight of soil (g)	30	20	20	10	10 ± 0.1	25	5
Container	Glass beakers with cover glasses	50 mL beaker & cover	Plastic container	Small beaker	Bottle and screw cap	Beaker	Any cup (glass, plastic, or waxed paper)
Type of solution	Distilled water	Reagent water	Deionized water	KCl or Distilled water	Distilled water	KCl or Distilled water	Pure water
Vol. Of water (mL)	75	20	20 or 40	25	25	25	5 or 10
W/V ratio	1:2.5	1:1 or more	1:1 or 1:2	1:2.5	1: 2.5	1:1	1:1 or 1:2
Shake/ swirl time (min)	A few minutes	5 minutes	1 min at 10 min intervals for 30 min	N.D.	15	15	5 sec
Time to record pH	24 hr	1 hr	30 min (Max. 6 hr)	1 hr	30 sec (1)	30 min	10 min

(1) after stirring the suspension and swirling the suspension over the electrode.
(2) N.D. - No detail description or information provided.

The purpose of this study is to assess the use of TIA and cement in increasing the pH of soil. Soil pH is of paramount importance in S/S treatment of contaminated soil. Higher pH is advantageous for S/S since at this pH the contaminants are immobile.

Two alkaline materials would be used namely TIA and cement to produce stabilized products. Van der Sloot, et. al. (1989) stated that the alkalinity of a stabilized product was a significant factor in controlling leachability. This was due to the high pH in the pore solution of the product which would form insoluble hydroxides or due to adsorption phenomena.

TIA is a type of ash derived from incinerated rubberwood (*Hevea Brasiliensis*) which is a form of waste products of the fiberboard industries in Malaysia. In the manufacturing process of fiberboard, rubberwood logs were initially debarked before converted to chips, and later into fibers. The waste barks were incinerated, the ash stored and later sent to a landfill. Malaysia presently has 7 medium density fiberboard (MDF) factories producing more than 750,000 m^3/yr MDF. In addition, a cement-bonded particleboard (CBP) factory (Cemboard

Sdn Bhd.) in Chembong, Negeri Sembilan consumed approximately 20,000 ton/year of rubberwood logs to produce approximately 35,000 m^3 of CBP per year. The increase production of fiberboard and particleboard would also result in the increase of waste ash. For economic reasons, it is always preferable to utilize a waste rather than dispose of it, provided that this can be done in a way that does not pose an unacceptable risk to the environment.

MATERIALS AND METHODS

Samples of residual soil and timber industry ash were air-dried and ground to pass through a 2-mm sieve before use. Local ordinary Portland cement samples (*Seladang*) were taken directly from its 50 kg bag.

The oxide compositions of the soil, TIA and OPC were determined using X-ray fluorescence (XRF) spectrometry technique. The major elements that can be examined by XRF technique included Si_2O, TiO_2, Fe_2O_3, MgO, K_2O, CaO, Na_2O, MnO and P_2O_5.

For the pH experiment, mixtures of Soil-TIA, Soil-Cement and Soil-TIA-Cement were prepared at different proportions on a dry weight basis (w/w). Approximately 80 grams of each mixture (consisting of soil, cement and TIA) were manually mixed and placed in a universal grinder which rotated at 20,000 rpm. The samples were ground for 30 seconds to ensure homogeneity of the sample. The samples were then divided into approximately 20g mixtures or four replicates for statistical analysis.

In the second part of the experiment, a 1:2 dilution (w/v) was used and left overnight for 24 hours. This was done to ensure chemical bonding of mixtures with cement to occur. In each 120 mL snap-top plastic container, accurately weighed 20 g samples were added. Forty mL of deionized water with a pH of 6.993 $\pm$ 0.73 and conductivity of 2.21 $\pm$ 0.51 µS/cm at 27 $\pm$ 1 °C was used in this experiment. The deionized water was obtained through an ultra-pure distilled-demineralized system. The pH was measured using a pH meter equipped with a glass electrode and temperature sensor for automatic compensation. Sample temperature was controlled at room temperature i.e. 27 $\pm$ 1 °C before measurement of pH.

RESULTS AND DISCUSSION

The oxide compositions of the residual meta-sedimentary soil, TIA and OPC samples are shown in Table 2. The mean pH of the residual soil is 4.75. Acidic soil is usually deficient in calcium and magnesium but it may contain high amounts of aluminum. Silica and aluminum formed the main composition (approximately 90%) of the residual meta-sedimentary soil. The main composition of TIA consisted of silica, calcium, aluminum and potassium while ordinary Portland cement consisted of calcium, silica, aluminum and iron.

Table 2 Main oxides of meta-sedimentary residual soil samples, TIA and OPC

Oxides:	*SiO_2*	*TiO_2*	*Al_2O_3*	*Fe_2O_3*	*MnO*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*P_2O_5*	*LOI*
Soil	79.48	0.33	10.39	1.99	0.002	0.12	0.03	N.D	0.06	0.02	5.77
TIA	54.48	0.67	8.00	2.63	0.14	1.12	13.96	0.07	5.36	1.15	11.92
OPC	20.41	0.22	4.88	3.21	0.07	1.29	62.34	0.18	0.50	0.11	3.21

LOI is Loss on Ignition at 1000°C N.D. – Not detected

The results of the initial part of this study is illustrated in Figure 1 which showed a general trend of increasing pH over time, peaked, followed by decreasing and stabilizing pH phase for all samples i.e. soil, TIA, and cement with different w/v ratios. The initial increasing trend

could be explained by the release of bases through the dissolution of the samples with deionized water (Hesse, 1971). However, after a short stationary phase (peak phase), the pH of the soil samples started to decline progressively. After 48 hours the decrease in pH of the soil samples seemed to level off. The declining trend of the pH could be partly explained by the influence of CO_2 in the atmosphere which introduces carbonic acid, H_2CO_3 into the solution (Rowell, 1994). The TIA samples however showed a much longer stationary phase of less than 20 hours before declining and stabilizing the pH. The OPC increasing pH phase was very short i.e. the first 1 hour with a short peak, and continuously decreasing and finally stabilized pH phase. There were no liquid in the OPC samples with a 1:1 w/v dilution ratio after 24 hour which has completely hardened while the samples with a 1:2 w/v dilution ratio hardened after 48 hours.

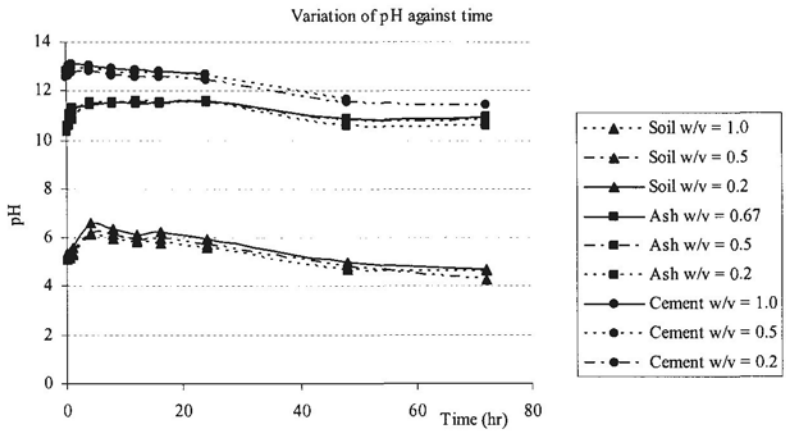

Figure 1 Variation of pH (i.e. pH equilibrium) against time (hours)

The difference between the initial pH of the samples (first 10 minutes pH values) and the 24 hour pH; and the 1 hour pH (USEPA) against the 24 hour pH (BS1377) are shown in Table 3. These differences in pH values caused by adding different volumes of water are known as suspension effects (Rowell, 1994).

Table 3 Difference of initial pH with 24 hour pH and 1 hour pH with 24 hour pH

Sample	*w/v dilution*	*(Initial pH) – (24 hr pH)*	*(1 hr pH) – (24 hr pH)*
Soil	1:1	- 0.51	-0.32
	1:2	- 0.47	-0.36
	1:5	-0.60	-0.38
TIA	1:1.5	-1.05	-0.32
	1:2	-1.21	-0.40
	1:5	-1.09	-0.72
OPC	1:1	0.21	0.44
	1:2	0.23	0.35
	1:5	0.15	0.33

Initial pH – Soil and Plant Analysis Council (1999) Method
1 hour pH – USEPA Method 9045C (1995) and 24 hour pH – BS1377 Part 3 (1990)

The mean pH and standard deviations of the results of the second part of the experiment are illustrated in Tables 4, 5, and 6. Figure 2 showed the trend of increasing pH value with increasing water content for the acidic meta-sedimentary soil at three different durations i.e. 0.5 hr, 1.0hr and 4 hours. In other words, the pH values decreases over weight to volume dilution ratio for the acidic soil. This is in agreement with the findings reported by Hesse (1971). However, Figures 3 and 4 showed an opposite trend of decreasing pH values with increasing water content for alkaline samples of cement and TIA or a trend of increasing pH over weight to volume ratio for the three durations. This trend is expected from alkaline samples.

Table 4 pH variation of soil mixed with TIA

Mix components	*Mean pH*	*S.D. (n)*	*(100% TIA pH) – (Mean pH mixtures)*
S – Soil (Control)	4.75	0.01 (4)	6.4
ST1 – S 99 + TIA 1	6.93	0.13 (4)	4.22
ST3 – S 97 + TIA 3	7.03	0.06 (4)	4.12
ST6 – S 94 + TIA 6	8.21	0.06 (4)	2.94
ST13 – S 87 + TIA 13	8.71	0.05 (4)	2.44
ST25 – S 75 + TIA 25	9.18	0.04 (4)	1.97
ST 38 – S 62 + TIA 38	9.71	0.09 (4)	1.44
ST 50 – S 50 + TIA 50	10.11	0.15 (4)	1.04
ST 62 – S 38 + TIA 62	10.93	0.07 (4)	0.22
ST 75 – S 25 + TIA 75	10.95	0.02 (4)	0.20
ST 87 – S 13 + TIA 87	11.03	0.12 (4)	0.12
T – TIA (Control)	11.15	0.21 (4)	0.00

Table 5 pH variation of soil mixed with cement (OPC)

Mix components	*Mean pH*	*S.D. (n)*	*(100% OPC pH) – (Mean pH mixtures)*
S – Soil (Control)	4.75	0.01 (4)	8.19
SC1 – S 99 + C 1	10.08	0.22 (4)	2.86
SC3 – S97 + C 3	11.57	0.06 (4)	1.37
SC6 – S 94 + C 6	11.68	0.07 (4)	1.26
SC13 – S 87 + C 13	11.77	0.04 (4)	1.17
SC25 – S 75 + C 25	11.81	0.04 (4)	1.13
SC38 – S 62 + C 38	11.84	0.37 (4)	1.10
SC50 – S 50 + C 50	11.90	0.11 (4)	1.04
SC63 – S 37 + C 63	12.55	0.55 (4)	0.39
SC75 – S 25 + C 75	12.58	0.06 (4)	0.36
SC88 – S 12 + C 88	12.60	0.02 (4)	0.34
C – OPC (Control)	12.94	0.05 (4)	0.00

Table 6 pH variation of mix components (soil, cement, and ash)

Mix components (in percent)	*Mean pH*	*S.D. (n)*
SCT (A) – S 50 + C 38 + TIA 12	12.44	0.02 (4)
SCT (B) – S 50 + C 25 + TIA 25	12.37	0.05 (4)
SCT (C) – S 50 + C 13 + TIA 38	12.26	0.06 (4)
SCT (D) – S 85 + C 12 + TIA 3	12.21	0.02 (4)
SCT (E) – S 85 + C 10 + TIA 5	11.58	0.03 (4)
SCT (F) – S 85 + C 8 + TIA 7	11.53	0.02 (4)
SCT (G) – S 90 + C 7 + TIA 3	11.47	0.04 (4)
SCT (H) – S 90 + C 5 + TIA 5	11.46	0.02 (4)
SCT (I) – S 90 + C 3 + TIA 7	11.28	0.06 (4)
SCT (J) – S 95 + C 4 + TIA 1	11.24	0.05 (4)
SCT (K) – S 95 + C 3 + TIA 2	11.23	0.08 (4)
SCT (L) – S 95 + C 2 + TIA 3	11.2	0.05 (4)

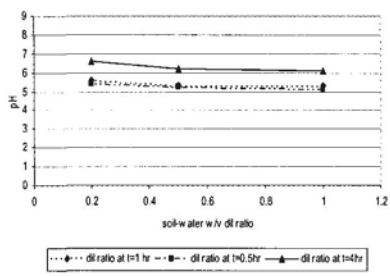

Figure 2 Variation of pH for different Soil-water dilution ratio (T=0.5, 1.0 & 4 hr)

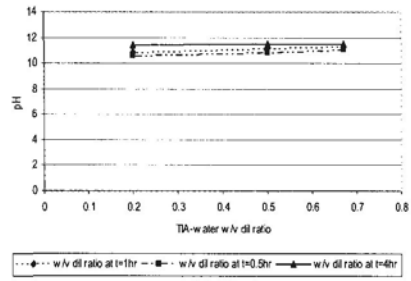

Figure 3 Variation of pH for different TIA-water dil. ratio (T=0.5, 1.0 & 4 hr)

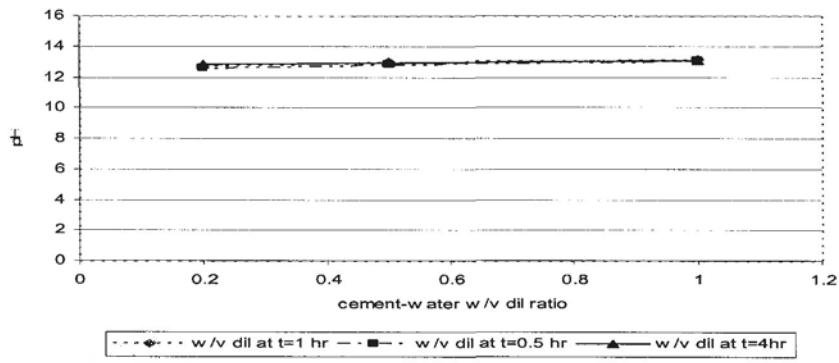

Figure 4 Variation of pH for different cement-water dilution ratio (T=0.5, 1.0 & 4 hours)

The second part of the investigation also involved the determination of pH for different mixes of soil-TIA, soil-cement and soil-cement-TIAs (SCTs). The results of this study are illustrated in Figures 5 and 6. The data showed a trend of decreasing pH with the increase of soil-TIA and soil-cement mixtures. The initial pH of cement was 12.94 and TIA was 11.15 while the initial pH of soil was 4.75. The difference of the pH values for soil-TIA was 6.4 units and soil-cement was 8.19 units. The overall change in pH was significantly higher in soil-cement compared to soil-TIA.

Many toxic metals are amphoteric (i.e. show increased solubility at both high and low pH's). Depending upon the metals present, the optimum pH is usually between 9.5 and 11.0 (Barth et. al. 1990; Knox, et. al., 2001). de Groot, et. al. (1989) discovered that lead, copper, cadmium, and zinc showed minimum solubility at high pH (>11.0) while aluminum and silicon had two minima in the pH range of 7 to 9 and at pH values higher than 11.0. As shown in Figure 5, a mixture of 40% to 75 % TIA in a soil-TIA mix would be required to maintain pH values of 9.5 and 11.0. Figure 5 also showed that a mixture of 1% to 2% cement is sufficient to maintain pH values of 9.5 and 11.0. Figure 6 showed that all the SCT mixes i.e. consisting of soil, cement and TIA have pHs above 9.5. This suggests that engineers may safely increase the proportion of waste TIA and reduce the proportion of cement to stabilize the acidic residual soil as a means to reduce the cost of cement.

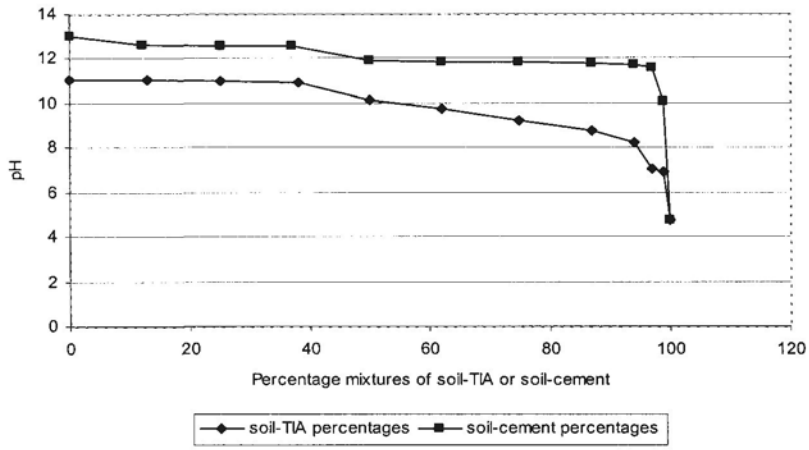

Figure 5 Variation of pH with different percentages of soil-TIA and soil-cement mixtures

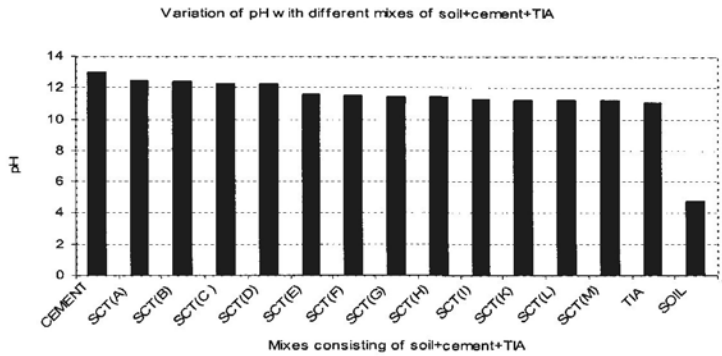

Figure 6 Variation of pH with different mixtures of soil, cement and TIA

CONCLUSION

Analysis of the treatments conducted on acidic meta-sedimentary residual soil using timber industry ash and cement showed that cement has a greater influence in increasing the alkalinity of the soil when compared to TIA alone. A mixture of 40 % to 75 % TIA in a soil-TIA mix would be required to maintain pH values of 9.5 and 11.0 while only 1 % to 2 % cement is sufficient to maintain pH values of 9.5 and 11.0. However insufficient data is available to predict accurately a mixture of cement and TIA that would increase the pH of the soil to 9.5 and 11.0. The results of this experiment also showed that acidic soil would gradually increase its pH with increasing water content while the pH of alkaline materials would decrease gradually. The results also showed that the duration of pH measurements and the weight to volume ratio should be stated when reporting pH.

ACKNOWLEDGEMENT

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Application of Time Release Electron Acceptors and Electron Donors for Accelerated Bioremediation

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ABSTRACT

Natural attenuation of groundwater contaminated with fuels or solvents provides a pragmatic and low-cost means of remediation. However, the appropriateness of the approach is often limited by rate or by unacceptable migration of plumes toward identified receptors. The microbially-mediated component of natural attenuation can be accelerated by overcoming the factors limiting microbial biodegradation processes. This presentation describes the use of slow release electron acceptor and donor compounds to overcome respiratory rate limitations of biodegradation of fuels and chlorinated solvents and the consequent acceleration of natural attenuation.

Oxygen Release Compound (ORC®) is proprietary formulation of intercalated magnesium peroxide that releases oxygen slowly, for up to one year, and facilitates the aerobic degradation of a range of environmental contaminants including petroleum hydrocarbons, ether oxygenates like methyl *tert*-butyl ether (MTBE), certain chlorinated hydrocarbons and aromatics, and pesticides such as atrazine.

Hydrogen Release Compound (HRC®) is a proprietary polylactate ester that is food grade and, upon being deposited into the aquifer, is slowly hydrolysed to release lactic acid and other organic acid derivatives for up to 18 months. The organic acids are fermented to hydrogen, which in turn donates electrons that drive reductive biotransformation processes. This process is primarily directed at a wide range of chlorinated hydrocarbons, but can be used to biodegrade contaminants such as nitrate/nitrite, perchlorate, nitroaromatics, and chlorinated pesticides.

The chemistry and characteristics of ORC and HRC will be presented, as will lessons learned after 10,000 applications of these products. Case histories of their use will also be presented, including cost information.

INTRODUCTION TO THE TECHNOLOGY: THE CHEMISTRY

Bioremediation has become a widely accepted protocol for the management of contaminated sites. One of the critical variables in the bioremedial process, whether natural or engineered, is the "electron status" of the system. The presence of electron acceptors is required for aerobic biodegradation and conversely, the presence of electron donors is required for anaerobic biodegradation.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

In engineered systems the rate of supply of these electron acceptors or electron donors can be an important variable in achieving cost effective bioremediation. A commercially available time-release electron acceptor is Oxygen Release Compound (ORC®), and a commercially available time-release electron donor is Hydrogen Release Compound (HRC®). The following is a review of the chemical technology and engineering applications. Field performance is summarized herein and individual case details can be found in the extensive bibliography that is provided at www.regenesis.com.

AEROBIC BIOREMEDIATION WITH ORC

ORC is a source of oxygen, and oxygen is an electron acceptor - meaning that oxygen sits at the bottom of the mitochondrial electron transport chain and catches or accepts the "spent" electrons from contaminant molecules that are being degraded by microbes for energy and raw materials. ORC is a proprietary formulation of magnesium peroxide that releases oxygen very slowly when hydrated. ORC is insoluble and releases its oxygen while being converted to ordinary magnesium hydroxide, which is also insoluble, in accordance with the following reaction:

$$MgO_2 + H_2O \rightarrow \frac{1}{2} O_2 + Mg(OH)_2$$

Magnesium peroxide and magnesium hydroxide are environmentally benign and are safe enough to ingest. In fact, they are both recognized as medicinal antacids - the more common one being magnesium hydroxide, also known as Milk of Magnesia.

ORC is not simply magnesium peroxide, but rather a patented formulation of the compound intercalated with food-grade phosphate ions (Figure 1). This gives ORC the time-release properties that are critical in a passive, low-cost oxygen application system. The term intercalation defines the fact that the phosphate ions permeate the magnesium peroxide crystal, partially inhibiting the transmission of water into the structure. Controlling the rate of hydration of the crystal affects a "timed" oxygen release. The concentration of phosphate, and the manner in which it is reacted with and permeates the magnesium peroxide crystal, creates a product that is well matched to the needs of

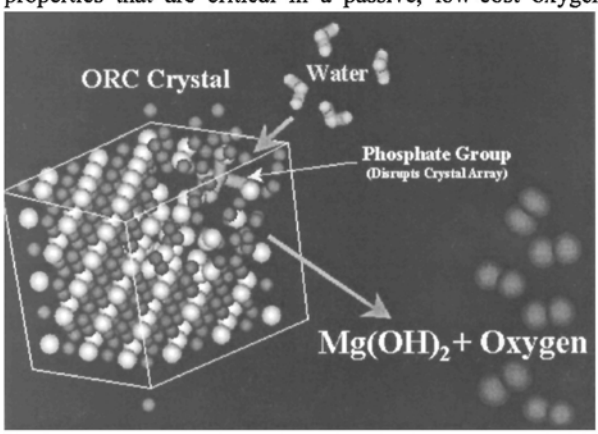


Figure 1: ORC – An Phosphate-Intercalated Magnesium Peroxide

subsurface remediation. Finally, intercalation allows the release of 100% of ORC's oxygen content by preventing a "hydroxide rind" from sealing up individual particles during the hydration reaction. Intercalation also increases shelf life stability; ORC can be stored for several years without risking significant product degradation.

Remediation experts, looking for a long-lasting oxygen source without incurring the cost of having to install continuous oxygen injection systems, or having to return to the field for

multiple re-injections of other oxygen releasing chemicals that do not have slow-release capabilities, have employed ORC. ORC has been actively used for 10 years and to date has been applied at nearly 10,000 sites in 50 states and 20 countries. The ORC technology is a useful strategy insofar as the aquifer microorganisms involved in bioremediation are not present in very high numbers, in comparison to other environments, and they are often challenged with only a very small mass of contaminant fluxing through the system. Consequently, only a small amount of electron acceptor is necessary to drive bioremediation – but it must be present on a constant basis. ORC's controlled release of oxygen provides constant levels of oxygen in response to microbial demand.

The first applications of ORC were for the treatment of benzene, toluene, ethylbenzene, and xylenes (BTEX) and other light petroleum hydrocarbon fractions. Use has now expanded to the treatment of heavier fractions such as heating oil and some of the polyaromatic hydrocarbons (PAHs). More recently, ORC has been used to bioremediate the highly mobile and problematic gasoline oxygenate methyl *tert*-butyl-ether (MTBE) and has been applied to sites impacted with chloroaromatics, nitroaromatics and some of the lower-order chlorinated hydrocarbons that can be treated aerobically—most notably dichloroethene (DCE) and vinyl chloride (VC).

With regard to the lessons that have emerged from nearly 10,000 applications of ORC, a high level of success has been achieved at most sites when the site conditions are adequately understood and a proper design can be implemented. At one point, earlier in the technology development and roll-out process, the first thousand or so sites were implemented directly with Regenesis' oversight and 600 of those projects were subsequently tracked. In this population there were reports of 20 full technical failures – a rate of 3%. In a full technical failure we are referencing the complete inability for an ORC application to decrease contamination at a site.

Technical failures, when they arise, can be classified as "intrinsic" and "non-intrinsic". Intrinsic problems are related to conditions on the site that are independent of proper characterization of contaminant concentrations and locations. These are rare events and are essentially traced to very high levels of dissolved iron or natural organic matter in the system, i.e., unmanageable chemical and biological oxygen demand. Non-intrinsic problems are related to any one of a number of issues involving poor site characterization, such as unidentified and unremoved sources and poor understanding of groundwater flow dynamics. Free-product LNAPL conditions are essentially beyond the scope of ORC to control from stiochoimetric standpoint; not enough oxygen can be input to meet the demand of LNAPL.

ORC APPLICATION FOR BTEX AND MTBE

Site Description and Application Details

A prime downtown real estate construction project in San Francisco, CA was in jeopardy due to persistent residual groundwater contamination. During excavation, BTEX and MTBE plumes were discovered at this former service station site. Although one year of soil vapor extraction (SVE) removed a majority of soil contamination, unacceptable BTEX and MTBE groundwater contamination remained. In the source area, BTEX concentrations were as high as 15,140 ug/L. The SVE system reached low asymptotic levels and could no longer reduce the contamination. The office tower construction project was held up indefinitely due to this problem and generated a risk of major financial loss. ORC was deemed to be the best

remediation technology to achieve the consultant's objective of safe and cost-effective remediation. In addition, the use of ORC would avoid disruptive remediation equipment operation, which was important in this setting.

The aquifer material consists of interbedded silt and sandy silt overlying a cemented fine to medium-grained sand interval. The depth to groundwater is approximately 7.6 meters below ground surface and groundwater flow direction is predominantly to the south at a velocity ranging up to 0.15 meters per day. Approximately 1,136 kilograms of ORC slurry were injected into 50 injection points for treatment using a cone penetrometer rig due to extremely tight upper soils (Figure 2). About 23 kilograms of ORC were injected in each injection point extending from 3 meters to 9 meters below groundwater.

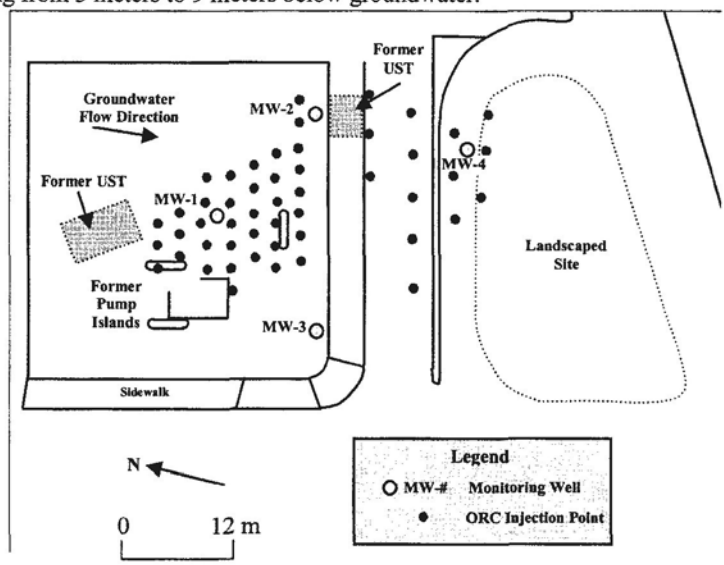


Figure 2. San Francisco, CA Site Map and Injection Layout.

Results and Conclusion

Outside the source area, in MW-2 (3 meters downgradient of the source area) BTEX concentrations decreased from 98.1 ug/L at baseline to 2.36 ug/L at 175 days post-ORC application, a reduction of 97% (Figure 3). In MW-4 (21 meters downgradient of the source area) BTEX concentration decreased from 1,570 ug/L at baseline to 533 ug/L at 175 days post ORC application, a reduction of 66% (Figure 4). A slight rebound was recorded but there was adequate recovery without ORC reapplication, indicating the source was light to moderate and manageable.

A first order rate analysis (rate = rate constant*concentration) on data from wells MW-2 and MW-4 before and after ORC injection was performed to quantitatively asses the impact of ORC on contaminant removal rates. The results are given in Tables 1 and 2. Clearly, ORC increased the BTEX removal rate over historical rates.

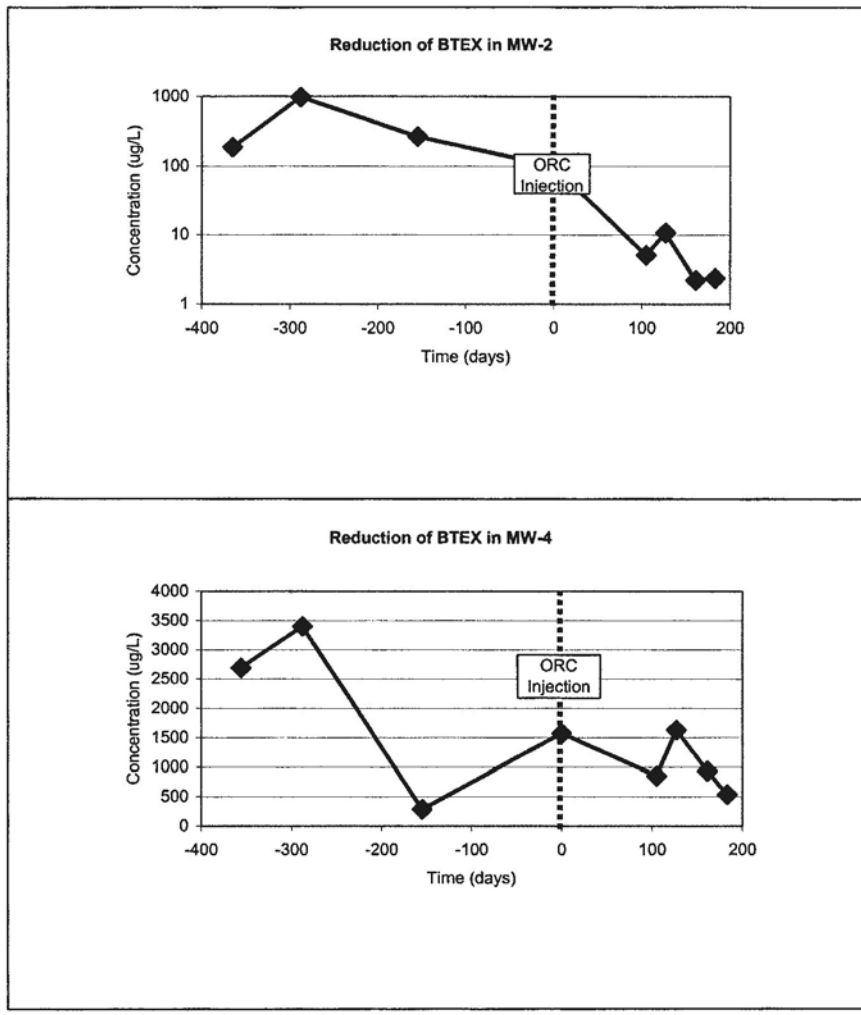


Table 1: First order rate constants
(rate constant = $\ln(C_0/C)/t$, C_0=initial concentration, C=concentration at time, t)

Monitoring Well	Historical (day -356 to day 0)	Post-Injection (day 0 to day 183)
MW-2	0.0018 1/day	0.20 1/day
MW-4	0.0015 1/day	0.0059 1/day

Table 2: BTEX half-lives
(half life = ln(2)/rate constant)

Monitoring Well	Historical (day -356 to day 0)	Post-Injection (day 0 to day 183)
MW-2	381 days	34 days
MW-4	458 days	117 days

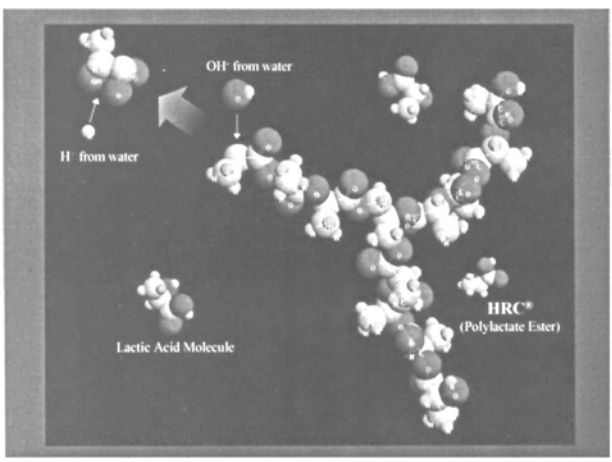
The cost of equipment, installation and monitoring of combining soil vapor extraction (SVE) with ground water extraction (GWE) systems was estimated to be $200,000 to $250,000, with 2 years of monitoring. Installing, operating and maintaining an air sparging combine SVE system for about a year was estimated to cost between $100,000 to $150,000. The actual cost for ORC application was $13,470 and an additional $15,000 for the cost of drilling for a grand total of $28,470.

Based on the site results, regulators recognized that ORC significantly reduced the contaminant source mass, and ORC would continue to accelerate the natural attenuation of the contaminant long after the construction project was underway. The regulators granted "no further action" required and this site has been submitted for closure. The building construction project got back on track and was finished on time.

ANAEROBIC BIOREMEDIATION WITH HRC

HRC is a source of hydrogen, and hydrogen is an electron donor – meaning it can provide required electrons that facilitate the degradation or "reduction" of certain contaminants like chlorinated hydrocarbons. The term reduction means that electrons, carrying a negative charge, are being added, the contaminant is reduced, and the electron donor is oxidized. In aerobic reactions, such as with ORC, the contaminant is actually the electron donor (e.g., benzene, which gets oxidized) and oxygen is the electron acceptor (becomes reduced). With HRC, the electron acceptor is the contaminant itself—most commonly a higher-order chlorinated hydrocarbon such as perchloroethylene (PCE) or trichloroethylene (TCE).

By example, we can look more closely at the microbially mediated, sequential destruction of chlorinated hydrocarbons such as PCE and TCE. This essentially translates to the removal, under anaerobic conditions, of various numbers of chlorine atoms from the molecule until it is rendered either benign or aerobically degradable, whichever comes first. With an electron donor like hydrogen that HRC produces, PCE, which has four chlorine atoms, is reduced to TCE (three chlorines), then to dichloroethene (DCE) (two chlorines), then to vinyl chloride (VC) (one chlorine), and then to ethene (chlorine-free skeleton). The process just described is termed reductive dechlorination. In reductive dechlorination, indigenous anaerobic microbes use electrons in the hydrogen produced by HRC to dechlorinate the contaminants.



HRC's active ingredient is a proprietary, environmentally safe, food-quality, polylactate ester, specially formulated for the slow release of lactic acid upon hydration. The lactic acid is important because, when fermented by soil microorganisms, it produces hydrogen. Esters are compounds that are formed in a reaction between an organic acid and an alcohol. In this reaction a molecule of water drops out (condensation reaction), forming the ester

Figure 5: Glycerol Polylactate

linkage. When the water re-enters the molecule at the ester linkage (hydration), the alcohol and acid can separate once again. Glycerol polylactate, or GPL, is a polylactate ester in which the lactic acid, or in this special case a proprietary lactic acid complex, is esterified to an alcohol. In GPL, glycerol is used as the "alcohol backbone". One of the unique features of the polylactic acid complex is that lactic acid is esterified to itself. This is possible because lactic acid has both an OH and a COOH group. As a result tetramers of lactic acid create a "polylactic acid complex" or "polylactate complex", which is in turn esterified to the foundation OH donor as described.

A variety of organic substrates can serve as electron donors, what is necessary is that they be "fermentable" to hydrogen. However, not all fermentable substrates are created equal. Many issues such as longevity, efficiency and solubility need to be taken into account. HRC is a unique formulation of glycerol polylactate and has many of the desirable features just mentioned. HRC has been applied at more than 500 sites around the world.

HRC TREATMENT OF TCE IN A FRACTURED BEDROCK SETTING

Site Characteristics and Application Details

At a site in Crozet,VA, TCE contamination was detected in the aquifer at levels ranging from 22 to 220 ug/L, with cis-1,2-DCE at levels ranging from 59 to 120 ug/L. The aquifer at this site is composed of crystalline fractured bedrock. Groundwater flow is to the southwest at a velocity of 0.012 to 0.12 m/day, and depth to groundwater is 3 meters. An HRC pilot study was conducted to determine its effectiveness in a fractured bedrock setting. An application of 304.5 kg of HRC was made into a 3-well pilot barrier (3 meters upgradient of monitoring well MW-8), with wells spaced 2.4 meters-on-center. Injection into the bedrock was accomplished using a packer system, in order to isolate the application into certain identified fractures within the aquifer. HRC was applied across a vertical thickness of 6 m.

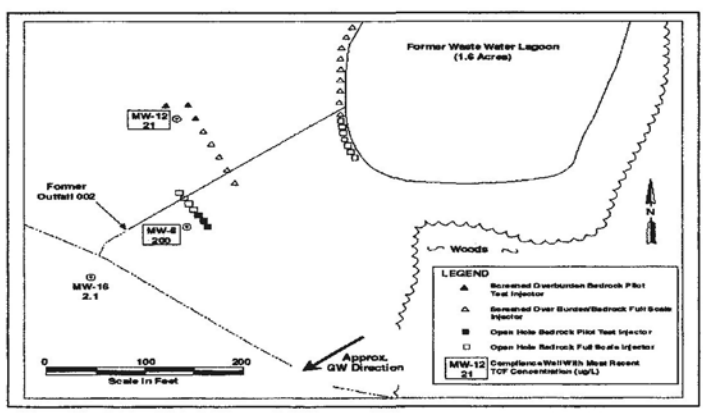


Figure 6. Crozet, VA Site Map.

Results and Conclusions

Results through 15 months show TCE concentrations dropping in the bedrock application area from 220 ug/L to 10 ug/L, a decrease of 95%. Daughter products have increased and decreased in concentration, a positive indicator of reductive dechlorination taking place. Cis-

1,2-DCE increased initially from 120 ug/L to 300 ug/L, but has decreased since and is currently at 39 ug/L. Likewise, VC increases initially from 7 ug/L to 59 ug/L, but has decreased since and is currently at 24 ug/L. Ethene, the end-product of the reductive dechlorination pathway, has continued to increase throughout the monitoring program, going from 1.4 ug/L at baseline to the current level of 42 ug/L (Figure 7).

Although complete mass balance (from parent product to daughter product) is rarely exhibited at most sites, this site showed exceptional mass balance when compared to other sites where HRC was applied. This may be due to the fact that the reactions are occurring in discrete fractures, which resemble subsurface "test tubes". Starting with 1.67 umol/L TCE and 0.05 umol/L ethane at baseline, at day 463 there was 0.08 umol/L TCE and 1.50 umol/L ethane. Elevated metabolic acids from HRC and total organic carbon (TOC) concentrations indicate that HRC is still affecting the aquifer through 15 months. Through this monitoring period, HRC has been able to significantly decrease contaminant concentrations in a bedrock setting. As a result of this successful HRC pilot test, a full-scale application is scheduled to take place this summer.

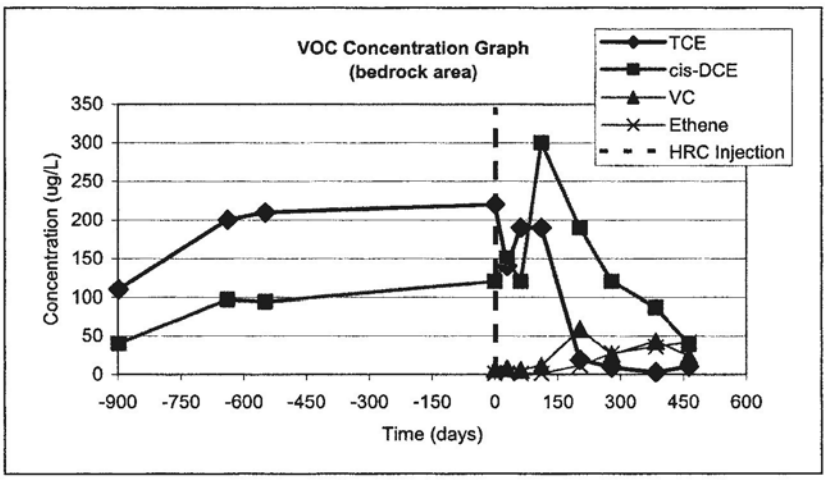


Figure 7. MW-8 VOC Concentration Graph.

CONCLUSION

Among the limited options available for cost-effective groundwater and soil remediation, accelerated bioremediation with time-release electron acceptors and electron donors has been demonstrated as economically feasible and has lead to site closure or no further action status with great savings at many sites. Aerobic bioremediation with the slow-release electron acceptor ORC and anaerobic bioremediation with the slow-release electron donor HRC are sensible strategies for groundwater and soil remediation because they consistently deliver results while 1) minimizing design, capital, and management costs and 2) allowing for the engineering of a low-impact, invisible remediation process.

REFERENCES

Please see www.regenesis.com, call 1-949-366-8000, or email Jeremy@regenesis.com for a complete bibliography of published papers and case studies.

Groundwater Circulation Wells: A Flexible Advanced Remediation Technology

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Abstract
One of the key factors for successful groundwater remediation is the adaptability of the selected remedial technique to keep operating efficiently under changing boundary conditions.
Groundwater Circulation Wells are based on the principle of creating a three dimensional circulation cell in the aquifer. This circulation cell is established by installing a multiple screened pumping well. Groundwater is extracted from one screen and after treatment in the well casing or a subsurface vault, it is circulated back into the aquifer through the second screen. This flow creates a three dimensional flow of water in the aquifer which is defined as a circulation cell.
By changing the circulation rates and modes GCWs can easily adapt to changing boundary conditions such as changing groundwater elevations, groundwater velocity changes and groundwater gradient changes. Since groundwater is circulated, it is possible to add nutrients or other additives to the circulated groundwater.
In this paper two case studies are presented where GCWs were installed to operate under varying boundary conditions. The case studies include key design elements, detailed groundwater modelling and long-term pilot testing.

INTRODUCTION

Emergence of advanced remediation technologies has recently resolved significant drawbacks inherent in classical Pump & Treat (P&T) methods [1]. High pumping rates and cumbersome treatment units usually required by these techniques can noticeably be reduced, providing then a cost-effective solution to extensive contaminated land issues.

Among these innovative techniques, Groundwater Circulation Well (GCW) can be used to contain and treat plumes of various chemical compounds in groundwater.
In the early 1990's the first Groundwater Circulation Wells (GCWs) were designed and installed to remediate groundwater contaminated with volatile contaminants in sandy aquifers [2]. Ten years later this technique has overcome the problems that were associated with its early use and its application fields have broadened to nearly all type of contaminants under different hydrogeological settings.

Groundwater Circulation Wells are based on the principle of creating a three dimensional circulation cell in the aquifer [3]. This circulation cell is established by installing a multiple screened pumping well. Groundwater is extracted from one screen and after treatment in the well casing or a subsurface vault; it is circulated back into the aquifer through the second screen. This flow creates a three dimensional flow of water in the aquifer which is defined as

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a circulation cell. Both downward and upward circulation modes, respectively known as standard and reverse flow, can be created according to the desired remedial objectives.

GCW technologies are applicable in a wide range of remediation objectives, extending from source removal operations to off-site migration prevention, focusing respectively here on the circulation time and there on the layout of the circulation cells.
Successful associations of basic units can offer possibilities of treatment wall execution for various geological and contamination boundary conditions, allowing efficacious performances up to more than 100 meter of saturated thickness.

A GCW is considered as an active remediation technique because it induces higher groundwater velocities around the well to expedite remediation. By changing the circulation rates and modes GCWs can easily adapt to changing boundary conditions such as changing groundwater elevations, groundwater velocity changes and groundwater gradient changes. Since groundwater is circulated, it is possible to add nutrients or other additives to the circulated groundwater. This way GCWs can react to changing physico-chemical conditions in the contaminant plume or can enhance natural attenuation processes in the contaminated aquifer.

Due to its configuration, long-term GCW maintenance, re-development and re-dimensioning according to groundwater level changes are easily practicable. Recent modeling performances about global climate change predict modifications in terms of groundwater recharge conditions [4].

TYPES OF GCW

According to the required remedial strategies, simple to complex versions of groundwater circulation can be implemented: The Single Well (Figure 1) is the basic unit and requires two screened sections isolated from each other by an inflatable packer.
Both downward and upward circulation modes, respectively known as standard and reverse flow, can be envisaged. The Stacked Well (Figure 2) involves three screened sections and creates two circulation cells so that they share the middle screen.

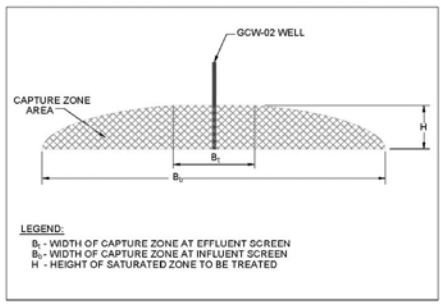


Figure 1: Single Well

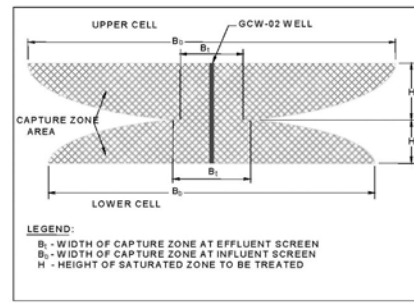


Figure 2: Stacked Well

CASE STUDIES

The Campine area

URS has recently conducted remediation feasibility assessments at two major industrial sites both located in the Campine area (Northern Belgium). The geology of the Campine area results in a succession of various layers of sand and clay [5]. All the layers have a mild dip to

the Northeast. The Campine area is almost entirely underlain by a 100m thick layer of impermeable clay: the Boom Clay, to be considered as the bottom of most Quaternary and Tertiary aquifers.

The aquifers in the Campine area, have a saturated thickness that ranges between 100 and 300 meters. It is therefore particularly suited to remediation using GCW technologies. This is in contrast to more traditional methodologies such as Permeable Reactive Barriers (PRBs) which would in all likelihood be technically unfeasible in such a thick aquifer and which, if technically feasible, would require substantial initial investment in comparison to a GCW system. [6].

First study case

Geology and Hydrogeology

The first site is underlain by 160 meter of sandy deposits (Table 1), fully saturated till approximately 2 to 3 mbgl. The general groundwater flow pattern in the aquifer at the site is to the South. Based on a conventional pumping test, the average hydraulic conductivity is about 7 m/day ($8{,}1.10^{-5}$ m.s^{-1}). The vertical gradient at the site is downward.

Table 1. Site Lithology

Depth m bgs	Depth m (See level)	Formation	Lithology
0	25	*Quaternary deposits*	Slightly fine sand with clay lenses. Locally peaty.
15	10	*Lillo Formation*	Greenish fine sand, well rounded and well sorted with shelly beds and shelly lenses
40	-15	*Kattendijk Formation*	Glauconitic fine sand with shell fragments. Lots of lateral variation in the grain size
50	-25	*Diest Formation,*	Glauconitic medium to coarse sand. Coarsening-upward.
130	-105	*Berchem Formation*	Fine sandy deposits, locally clayey.
160	-135	*Boom Formation, Putte Member*	Continuous impremeable layer consisting of dense clay.

Source of Contamination

The identified soil and groundwater contamination was mainly caused by historical spills and leakages at aformer chemical plant, a former underground NRS tank and the former underground sewer system in the vicinity of the former chemical plant.

Contamination

The main contaminants of interest (COI) in soil and groundwater (Table 2) are aromatics (mainly benzene and toluene), volatile oil, chlorinated hydrocarbons

Table 2. Contaminants of interest (COI)

	Maximum site concentration mg/l	Expected COI load µg/l
Benzene	16 000	9.9
Toluene	306 000e	13.6
Diethylether	2.5	18.9
Volatile Oil	1 500	63.0
Tetrahydrofurane	1 211	4.4

(mainly trichloromethane and dichloromethane), alcohols (mainly methanol, ethanol and propanol) and organic solvents (mainly acetone, tetrahydrofurane, methylethylketon and methylisobutylketon).

The contamination consists of a huge plume of approximately 400 meter wide and 700 meter long, reaching a depth of about 160 meter. The geometry of the contamination results not only in the influence of the natural groundwater flow patterns. Numerous dewatering works

have taken place during the last decades and have considerably modified the shape of the plume.

Remedial Concept

The remedial concept is a combination of containment of the source area, with the prevention of hydraulic downgradient migration of the contaminant plume. The containmentwill be achieved with combination of several remedial techniques, including excavation of source areas, installation of airsparging / SVE system, and a P&T system [7]. For the migration prevention, a hydraulic barrier consisting of groundwater circulation wells (GCW) was selected, in combination with monitored natural attenuation (MNA). The hydraulic barrier will be installed on site and will be active till a depth of 100 meters. MNA [8] was selected for the contamination below 100 meters, and for the part of the plume that has already migrated beyond the downgradient zone of influence of the GCWs.

No particular cleanup targets were defined in the remediation proposal. Primary objective of the remedial measures is to contain the source area, and prevent further downgradient migration as described above.

Design of the GCW barrier

The barrier consists of a hydraulic treatment wall composed of Single Cell GCWs positioned in rows perpendicular to the groundwater flow direction (Figure 4). A row of shallow Single Cell GCWs will operate between 0 and 50 mbgl using an upward circulation mode while a row of deep Single Cell GCWs will operate between 50 and 100 mbgl through a downward circulation mode (Figure 3).

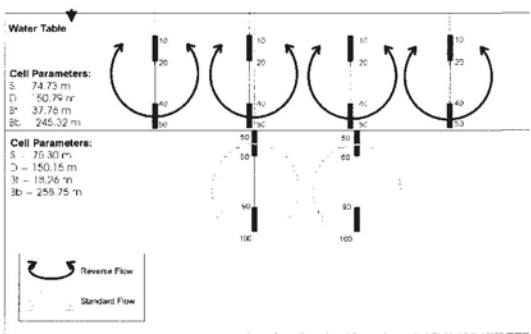


Figure 3: GCW Barrier

Key element of the design consists of maximizing the GCW capture zone extents while keeping the circulation rates as low as possible. Several scenarios were considered in order to assess the most appropriate combination of circulation cells.

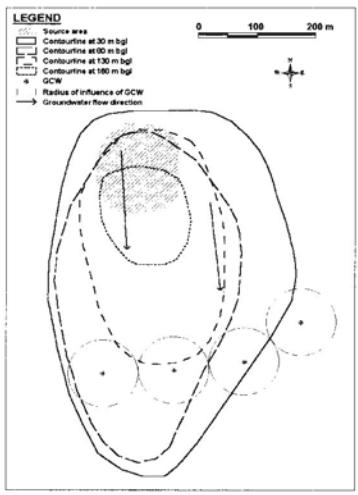


Figure 4: Plume Layout

The site-specific dimensions of the GCW system were modeled using equations developed by Herrling and Stamm [9]. The aquifer parameters and system designed values are summarised in Table 3 and Table 4.

Preliminary numerical modeling of site conditions was performed at a recirculation flow rate of 7.5 m³/h for the shallow GCWs, and of 15 m³/h for the deep GCWs. The following parameters were taken into account (Table 5):

- The upstream and downstream stagnation points (S);
- Width of capture zone at influent screen at a distance of 5H from the GCW system (Bb);
- Width of capture zone at effluent screen at a distance of 5H from the GCW system (Bt);
- The distance D (maximum spacing between GCW systems. This spacing provides for approximately 10% overlap of the conservatively estimated radius of influence.

Table 3. Aquifer parameters

Hydraulic gradient	I	0.0015 m/m	
Horizontal hydaulic conductivitiy	Kh shallow	7 m/day	
	Kh deep	15 m/day	
Porosity		15 %	
Anisotrophy	Kh/Kv	10	
Depth to groundwater		2 m bgs	
Groundwater flow direction		South	
Saturated thickness	H	shallow	40 m 10 – 50 mgl
	H	deep	50 m 50 – 100 mbgl

Table 4. System design values

Shallow GCWs		
Length of upper screen	At	10 m (10 to 20 m bgl)
Length of lower screen	Ab	10 m (40 to 50 m bgl)
Treatment thickness for each cell		40 m
Circulation rate for each cell	Q	7.5 m³/hr
Deep GCWs		
Length of upper screen	At	10 m (50 to 60 m bgl)
Length of lower screen	Ab	10 m (90 to 100 m bgl)
Treatment thickness for each cell		50 m
Circulation rate for each cell	Q	15 m³/hr

Pump tests have reinforced the preliminary design values and the aquifer parameters. They proved the effectiveness of GCW technology under the site conditions. It was demonstrated that downward flow operation could lead to excessive mounding of groundwater in the upper-screened section under the range of flow rates investigated. It is why the upward mode was chosen for the shallow GCWs row.

In addition, experience has shown that the use of stacked GCWs can become problematical for deep aquifers. Both superimosed circulation cells can compete with each other because of the vertical variability of the hydraulic conductivity.

Regarding the site of concern, a zone with a higher permeability was indentified below 50 mbgl, corresponding to the Diest formation. In the case of a stacked system, the groundwater would have flown preferentially in the coarser sand area as compared to the formation above, which is less permeable. This way, a circulation cell would never have been achieved in the upper part.

Table 5. Circulation cell parameters

		Shallow GCWs	Deep GCWs	
Stagnation Point	S	75	75	m
Width Capture Zone	Bt	38	18	m
	Bb	245	260	m
Maximum Spacing	D	150	150	m

The GCW spacing was chosen to allow a better adaptability in case of changing boundary conditions. An increase of groundwater gradient would reduce the capture zone extent. Increasing the circulation rate slightly could then eliminate gaps generated in the barrier.

A regular maintenance has been foreseen every three months. It mainly consists of standard well redevelopment and does not require cumbersome operations.
Continuous measurement of head changes can be recorded by means of a data acquisition system, allowing a better step-by-step supervision of the capture zone changes. Monitoring wells are sampled on a regular basis to follow up the evolution of COI.

Second study case

Geology and Hydrogeology
This site is underlain by 100 meter of sandy deposits (Table 6), fully saturated till approximately 2 to 3 mbgl. The general groundwater flow patterns in this aquifer is to the South. Based on a conventional pumping test, the average hydraulic conductivity is about 5 m/day ($5{,}8.10^{-5}$ m.s^{-1}). The vertical gradient at the site is downward.

Table 6. Site Lithology

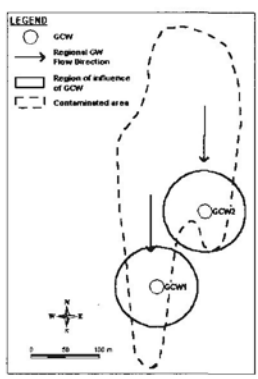
Depth m bgs	Depth m (See level)	Formation	Lithology
0	22	*Quaternary deposits*	fine sand to clayey deposits and horizons
9	13	*Kasterlee Formation*	green grey to green glauconitic and clayey fine sand
16	6	*Diest Formation*	grey green glauconitic homogeneous coarse sand with clay lenses and layers of iron sandstone
57	-35	*Diest Formation, Dessel Member*	homogeneous, glauconitic, little clayey fine sands
97	-75	*Boom Formation, Putte Member*	dark gray massive clay with black beds characterized by a high organic matter content

Contamination
The groundwater contamination mainly consists of toluene, chlorinated methanes and organic solvents (acetone, methylethylketon, methylisobutylketon, THF) (Table 7). In the soils, there are several hot spots related to historical spills and failures of the underground chemical sewer system. NAPL are present at several places.

Table 7. Contaminants of interest (COI)

	Maximum site concentration µg/l	Expected COI load µg/l
Acetone	1,900,000	41,000
Toluene	78,000	10,000
Dichloromethane	250,000	
Volatile Oil	370,000	23,000
Tetrahydrofurane	190,000	2,300

Figure 5: Site Layout



The geometry of the contamination (Figure 5) consists of a two-fingered plume: the central part of the plume dives like a typical DNAPL-tongue to a depth of 100 m while the eastern part of the plume alike reaches a depth of 65 m.

Remedial Concept
The remedial concept is pretty similar to the first site. It consists of a containment of the source area including a Dual Phase Extraction system [10] combined with a limited P&T system.
For the migration prevention, a hydraulic barrier consisting of groundwater circulation wells (GCW) was selected, in combination with monitored natural attenuation (MNA). The hydraulic barrier will be installed on site and will be active till

a depth of 85 meters. MNA [8] was selected for the contamination below 85 meters, and for the part of the plume that has already migrated beyond the downgradient zone of influence of the GCWs. In this case, the COI load is higher which requires a lower circulation time.
Similarly to the first site, no particular cleanup targets were defined in the remediation proposal.

Design of the GCW Barrier
The barrier consists of two stacked GCWs, operating respectively between 10 and 65 mbgl (GCW2), and between 20 and 85 mbgl (GCW1).

Table 8. Aquifer parameters

Hydraulic gradient	I	0.002 m/m
Horizontal hydaulic conductivitiy	Kh	5 m/day
Porosity		20 %
Vertical hydaulic conductivitiy	Kv	0.5 m/day
Anisotrophy	Kh/Kv	10
Depth to groundwater		3 m bgl
Groundwater flow direction		South
Saturated thickness GCW2	H-1	30 m upper cell 25 m lower cell 55 m (10 to 65 m bgs)
Saturated thickness GCW1	H-2	35 m upper cell 30 m lower cell 65 m (20 to 85 m bgs)

Table 9. System design values

GCW2		
Length of upper screen	At	15 m (10 to 25 m bgl)
Length of middle screen	Am	10 m (35 to 45 m bgl)
Length of lower screen	Ab	10 m (55 to 65 m bgl)
Circulation rate for each cell	Q	10 m³/hr
GCW1		
Length of upper screen	At	10 m (20 to 30 m bgl)
Length of middle screen	Am	10 m (47.5 to 45 m bgl)
Length of lower screen	Ab	10 m (75 to 85 m bgl)
Circulation rate for each cell	Q	10 m³/hr

The site-specific dimensions of the GCW system were modeled using the aquifer parameters and system designed values summarised in Table 8 and Table 9.
Preliminary numerical modeling of site conditions was performed at a recirculation flow rate (Q) of 10 m³/h generated the values summarized in Table 10.

Pump tests demonstrated the effectiveness of GCW technology under the site conditions [11]. Interpretation of pilot tests showed that the anisotropy ratio (K_h/K_v) was lower in the upper part of the aquifer (ranging around 1 to 2) as compared to the lower part (ranging around 10).
The circulation flow rates were consequently adapted in order to achieve the designed capture zone extent. The upper cell circulation rates were increased to 18 m³/hr and 20 m³/hr respectively for GCW2 and GCW1 while the lower cell circulation rate of GCW2 was increased to 12 m³/hr.
This discrepancy in terms of circulation rate helped to better match the aquifer heterogeneity and to avoid the drawbacks inherent in stacked systems as described above. This way, it was

Table 10. Circulation cell parameters

		GCW1	GCW2	
Stagnation Point	S	795	66	m
Width Capture Zone	Bt	58	59	m
	Bb	244	203	m
Maximum Spacing	D	163	139	m

possible to sustain the appropriate circulation rates without creating a damaging competition between the upper and the lower circulation cells.

The pump tests illustrated the adaptability of the GCW technology. On the other hand, the stacked system maintenance generates more efforts since the in-well equipment makes the system slightly less flexible, which should create higher O&M costs.
A similar monitoring system to the first site has been foreseen. Due to the relatively high COI load and if the treatment unit performance decreases, it could be envisaged to add nutrients or other additives to the circulated groundwater in order to enhance natural attenuation processes in the contaminated aquifer.

CONCLUSION

This paper has sought to demonstrate the flexibility and adaptability inherent in GCW technologies. Such attributes are a fundamental requirement for systems which must have design lives that extend potentially into several decades. The ability of a remediation system to adapt to the physical and physiochemical changes that will inevitably occur within the aquifer during such period is crucial to its overall success. Our planet and its environment are in a constant state of flux - [12] the best remediation systems will be those that will foresee and respond to these changes.

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Full Scale Stimulation of Reductive Dechlorination Using the LINER® Technique

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ABSTRACT
Following the results of an earlier pilot study, a full-scale remediation project was undertaken at an operational factory in the Dutch town of Zwolle. Contamination from chlorinated aliphatic hydrocarbons (CAHs) in the source zone was treated using a novel gas injection and nebuliser system called LINER. Ethyl lactate was selected as a carbon substrate to stimulate in-situ bioremediation. It was atomised and injected at a rate of 500ml/day over a 3 minute duration from 6 no injection wells with a total of 12 no injection filters at 24-25 m and 44-45 m depth. The performance of the remediation technique was observed using an array of groundwater monitoring wells. The results are variable with biodegradation to ethene proceeding well at depths of 14-15 m and 44-45 m depth. Limitations in biodegradation were attributed to the variations in stratigraphy and limited zone of influence near the injection points.

KEYWORDS: In-situ bioremediation, chlorinated solvents, sparging, nebuliser, ethyl lactate, LINER®.

INTRODUCTION

One of the biggest technical obstacles facing the in-situ bioremediation of chlorinated solvents is the reliable and efficient distribution of carbon substrates for the treatment of deep groundwater pollution. The substrates are needed to stimulate the biological process by donating electrons for the reductive dechlorination of these pollutants. Without a reasonable distribution of substrates, the bioremediation process is patchy, leading to localised biodegradation. This is well illustrated by the pilot test results published by Dyer et al (2003) for degradation of 1,2-dichloroethane at a chemical works in Rotterdam Botlek area using an array of extraction and injection wells.

To overcome some of the difficulties with groundwater re-circulation, there has been a growing interest with the use of gases to supply electron donors. These developments have drawn on existing air sparging techniques, originally intended for aerobic degradation of hydrocarbon fuels (typically BTEX compounds). The sparging gases are typically injected into the sub-surface at a rate of 60-80 Nm^3/hr within a radius of influence of approximately 6 m. The sparging techniques have been extended to include injection of hydrogen as a highly reactive electron donor to reductively dehalogenate chlorinated solvents (Newell et al 2000) as illustrated in Table 1.

Mode of gas release	Type of gas	Role	Reference
Direct injection down well	H_2 and He_2	H_2 acts as electron donor for reduction of chlorinated solvent	Newell et al 2000
Direct injection of atomised substrate	N_2	Delivery of atomised carbon substrate for reduction of chlorinated solvent	Marnette et al 2001
Direct injection down well	Propane/air mixture	Co metabolic degradation of TCE and cis-DCE	Trovanabootr et al 2001

Table 1 Examples of remediation technologies using gas injection to stimulate in-situ soil bio-remediation of chlorinated aliphatic hydrocarbons (CAHs)

One of the gas injection methods is the so-called LINER® method. The technique involves atomising a carbon substrate such as methanol, ethyl lactate or acetone into micron size droplets that can be transported into the ground at depth using a carrier gas. Nitrogen is used as the carrier gas in order to maintain anaerobic conditions in the groundwater, which are conducive to reductive dechlorination of the chlorinated solvent (Marnette et al 2001). Recently the viability of the technique has been tested using a full-scale remediation project at a former Philips factory in the Dutch town of Zwolle. The results from the study are reported as follows.

SITE DESCRIPTION AND HISTORY

The site is located in the Dutch city of Zwolle in the province of Overijssel. It is occupied by a metal processing factory for manufacturing car components. During the 1970's and 1980's perchloroethylene was at the factory for the degreasing of metal components. The solvent was stored in a bath in the northeast corner of the factory, which leads to accidental spillages of the chemical. Soil and groundwater surveys since 1989 have detected high levels of the chlorinated solvent and reduced by-products (PCE, TCE, cis-DCE, VC and ethene) with a source zone in the vicinity of the old solvent bath as well as a plume of contaminant migration in a southwest direction underneath the factory. The maximum aqueous concentrations of chlorinated compounds detected in the source zone are given in Table 2.

Chlorinated Hydrocarbons	PCE	TCE	cis-DCE	VC	Ethene
Aqueous concentration (µg/l)	68,000	17,000	32,000	6,825	3,451

Table 2 Maximum aqueous concentrations of chlorinated aliphatic hydrocarbons detected in soil survey for borehole 900 in vicinity of source zone in northeast corner of factory

There have been three phases of soil surveys carried out at the site since 1989 using a combination of cone penetration tests, hand and mechanically augured boreholes. The visual logging of boreholes and interpretation of CPT results identified three main strata underlying the site as described in Table 3.

Depth (m)	Stratigraphy	Hydrogeology
0 - 4	Medium to coarse sand with lenses of clay and peat	Surface layer
4 - 74	Medium to coarse sand with occasional layers of loamy silt and gravel	Unconfined regional aquifer with typical groundwater velocity of 3-5 m/year
> 74	Very stiff clay	Aquiclude

Table 3 Summary of ground conditions (after Marnette et al 2003)

REMEDIATION SYSTEM

Following the results of a pilot study in 2002 (Marnette et al 2001), full-scale remediation was started in August 2002. The remediation system consisted of 6 no injection wells each with 2 no injection filters at depths of 25m and 44m bgl. The layout of individual wells is shown schematically in Figure 1 along with a summary of the monitoring results. The wells were located in the source zone in the northeast corner of the factory. In addition 8 no groundwater-monitoring wells were installed between the injection wells. The monitoring wells contained groundwater sampling filters at depths of 4-5 m, 9-10 m, 14-15 m, 24-25 m, 34-35 m and 43-44 m. Both the injection and monitoring wells were constructed using HDPE tubing with a 50 mm inner diameter. Likewise the injection and sampling filters were surrounded with a granular backfill and isolated using a bentonite plug. The configuration of injection and monitoring wells/filters is listed in Table 4. Groundwater samples were tested using gas chromatograph headspace analysis at the laboratories of TAUW.

Well No	900	901	902	903	904	905	906	907	908	909	910	911	912	913
Injection Filter														
24-25 m				x	x			x	x			x		x
44-45 m				x	x			x	x			x		x
Sampling Filter														
4-5 m						x	x			x	x		x	
9-10 m	x													
14-15 m		x	x	x		x	x			x	x		x	
24-25 m	x	x	x			x	x			x	x		x	
34-35 m		x	x	x		x	x			x	x		x	
39-40 m	x													
44-45 m		x	x			x	x			x	x		x	

Table 4 Depths of monitoring and injection filters for individual wells

Ethyl lactate was selected as the carbon substrate based on the results of the pilot study. The liquid substrate was atomized into a fine spray using a jet nebuliser at the top of the well. The jet nebuliser was operated at a gas pressure of 9 bars. Nitrogen gas was supplied using a 2000 kg liquid nitrogen tank and vaporizer. The gas was stored at a temperature of minus196 deg C and vaporized to a temperature of approximately 10 deg C before injection. The substrate was stored in a 220L drum. The injection system comprised a substrate pump, nebuliser and a gas manifold, which was installed in a site office. The gas/substrate injections were processed online.

In addition to the jet nebuliser, nitrogen gas was used as a carrier gas to sparge the ground with the atomised substrate. The injection pressures were limited to prevent liquefaction of the ground at the two different injection depths of 25 and 45 m depth (after Boelsma et al 2000). The operating procedure involved injecting 500 g of ethyl lactate during a 3 minute injection period using the pressures and flow rates given in Table 5. Furthermore, injections were restricted to 3 minutes per filter per day in order to minimize the risk of stripping chlorinated compounds from the contaminated groundwater into the atmosphere.

Volume of injected substrate (ml/day)	500
Duration of injection (min)	3
Frequency of injection (day^{-1})	1
Injection gas flow rate (Nm^3/hr)	50-65
Injection gas pressure at 25m depth (bar)	3.5-3.7
Injection gas pressure at 45m depth (bar)	6.2-6.5

Table 5 Operational flow rates and pressures for LINER injection system

The amount of ethyl lactate required was calculated by estimating the volume of chlorinated hydrocarbons (PCE, TCE, cis-DCE, VC and ethane) that required treatment within the source zone (400 m^2 by 40 m depth) along with the consequential reduction of sulphate by the sulphate reducing bacteria. The analysis makes several assumptions such as the porosity of the soil (porosity = 0.3) and efficiency 2% (factor 50) in order to estimate the total mass of ethyl lactate required based on stochiometric calculations.

RESULTS and DISCUSSION

The substrate was injected into the source zone over a 59 week period from August 2002 to September 2003. In total 1,500 kg of ethyl lactate was injected into the ground. The corresponding results for groundwater monitoring show that substrate injection lead to biostimulation but not uniformly across the site. A visual and statistical analysis of variations in the aqueous concentrations of PCE, TCE, cis-DCE, vinyl chloride, ethene and ethane show that substrate injection lead to strong biostimulation being observed at two sampling depths (14-15 m and 44-45 m) whilst only marginal biostimulation was witnessed between 24-25 m sampling depth with negligible biostimulation between 34-35 m depth. A summary of the interpretation is given in Figure 1.

A good example of strong biostimulation is the results for monitoring well 906 at 14-15 m in Figure 2. The results clearly show a reduction in the relative aqueous concentration of cis-DCE and VC with a pronounced increase in the concentration of ethene and ethane. This was repeated for the whole of the monitoring well no 906 but elsewhere was restricted principally to the readings for 14-15 m and 44-45 m depth sampling filters. Here the results have been plotted in relative molar concentrations rather than mass/volume (μg/l) in order to better illustrate the changes in relative proportions of compounds, which could otherwise be masked. It is also worth noting that strong biostimulation tended to coincide with low aqueous concentration of sulphate, which would otherwise act in competition as an electron acceptor for sulphate reducing bacteria. So, in general biodegradation proceeded well at depths of 14-15 m and 44-45 m.

In comparison, the results for groundwater sampled at 24-25 m depth only show marginal biostimulation such as in monitoring well 909 (Figure 3). Although vinyl chloride, ethene or ethanes were detected there was still a pronounced increase in the degradative by-products cis-DCE. This pattern of behaviour was repeated in other monitoring wells at depths of 4-5m and 24-25m. A number of reasons could be put forward to explain the poor performance at these depths. At 4-5m depth for example, the biodegradation of PCE and decay by-products would be masked by the ongoing leaching of PCE from the overlying layer of organic soils. In contrast the injection of gas and substrate at 24-25 m depth would have resulted in a very

limited radius of influence at the point of injection; whilst having the adverse effect of potentially mobilising more contaminants into the groundwater.

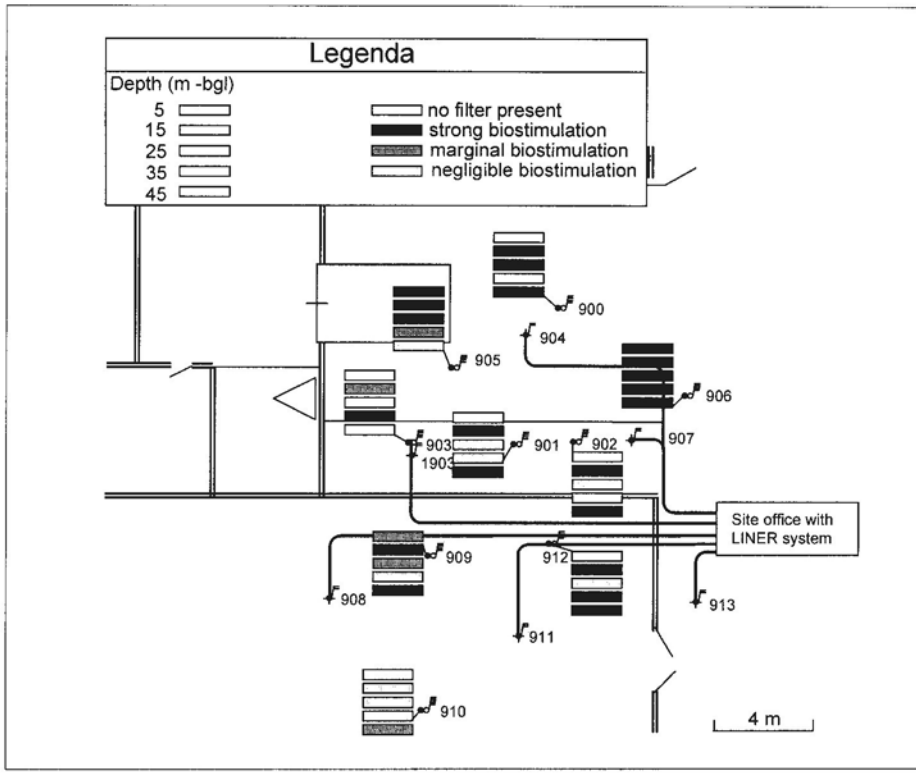

Figure 1 Summary of the relative bioremediation observed in monitoring wells over the 59 week period of substrate injection.

Lastly, at some locations negligible biostimulation took place. This was particularly the case at a depth of 34-35 m as shown in Figure 4 for well 901. The poor performance could be attributed to a layer of fine sand at 35m depth that would have restricted the upwards migration of injected gas/substrate.

The observations for individual monitoring wells can be shown to represent a more general pattern of behaviour by using some simple statistical analysis along with a comparison of the combined aqueous concentration for all chlorinated hydrocarbons at the beginning and end of the 59 week injection period. For example the results for the statistical "T-test" are shown in Table 6. The results provide a comparison of the aqueous concentrations measured at the

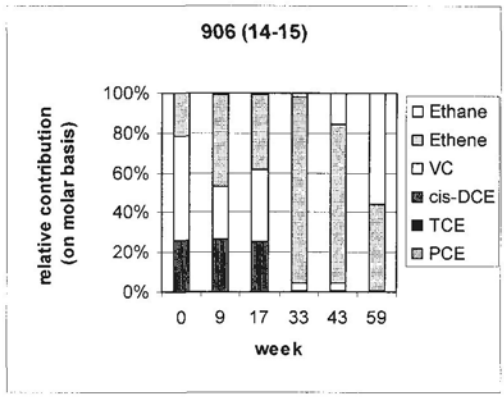

Figure 2 Strong biostimulation in monitoring well 906 (14-15 m depth)

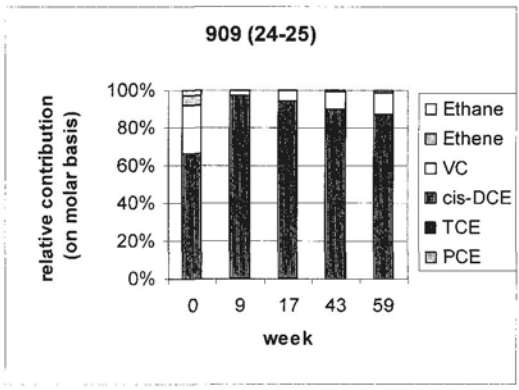

Figure 3 Marginal biostimulation in monitoring well 909 (24-25 m depth)

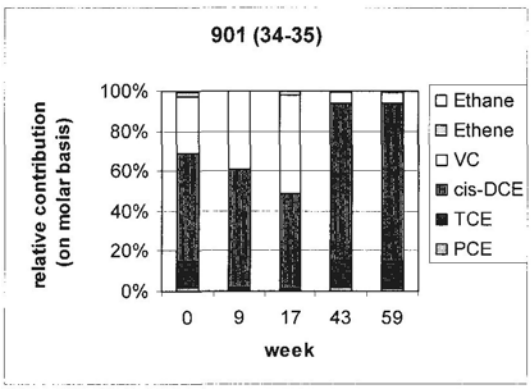

Figure 4 Negligible biostimulation in monitoring well 901 (34-35 m depth)

start and end of the injection period of 59 weeks. The results show very low values for reductive dechlorination at depths of 14-15 m and 44-45 m, which are indicative of a significant change in aqueous concentration. Whereas the higher "t- test" values at other depths indicate a lower likehood of reductive dechlorination taking place.

Depth (m)	PCE week 0 > PCE week 59	TCE week 0 > TCE week 59	cis-DCE week 0 > cis-DCE week 59	VEE week 0 < VEE week 59
4	0,41	0,78	0,07	0,22
14	0,03	0,004	0,21	0,09
24	0,94	0,50	0,26	0,10
34	0,39	0,26	0,87	0,09
44	0,30	0,02	0,08	0,001

VEE = sum of vinyl chloride, ethene, ethane
Shaded areas represent 95% probability of biostimulation taking place

Table 6 Statistical "t- test" for differences in aqueous concentrations

In comparison, a plot of mean aqueous concentrations for chlorinated hydrocarbons can also be used to indicate the overall trend in reductive dechlorination at the site. The mean aqueous concentrations are shown in Figure 5. Although the plot does not indicate the statistical significance of the results, the results nevertheless show a general increase in biodegradative by-products during injection of the substrate. In particular there is a pronounced increase in mean combined aqueous concentration for vinyl chloride, ethene and ethane that confirm a general trend towards complete mineralization of the higher chlorinated ethenes. However there is also a relatively high aqueous concentration of cis-DCE, which indicates negligible biostimulation in some parts of the site as mentioned earlier.

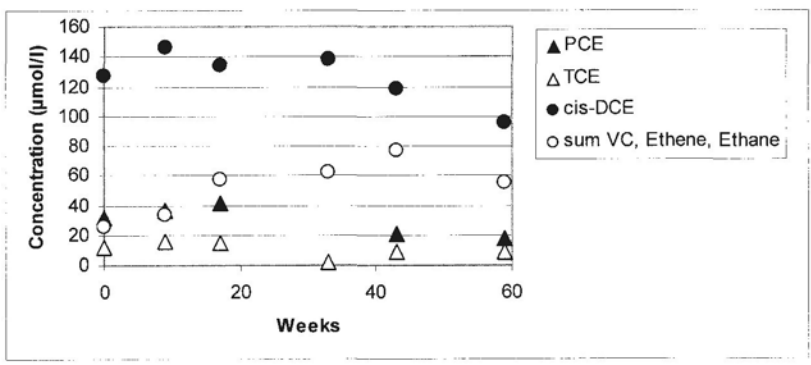

Figure 5 Mean aqueous concentration of chlorinated hydrocarbons

One further indication of the general trend towards reductive dechlorination in the treatment zone is a comparison of the mean aqueous concentrations for the sum of chlorinated hydrocarbons (PCE, TCE, cis-DCE, VC) excluding ethene and ethane. The mean aqueous concentrations given in Table 7 show and initial increase in combined chlorinated hydrocarbons up to week 17 followed by a reduction in mean aqueous concentrations. The initial increase could be attributed to mobilisation of the contaminants due to sparging followed by a mean reduction due to biostimulation. The marked reduction in mean aqueous

concentrations for week 33 was due to a limited sampling of only those wells reporting strong biostimulation and as such was not generally representative of the site.

Week No	Mean aqueous concentration (µg/l)
0	191
9	219
17	227
(33)	(170)
43	192
59	157

[(33) refers to sampling limited to wells reporting strong biostimulation]

Table 7 Variations in sum of mean aqueous concentrations of chlorinated hydrocarbons

CONCLUSIONS

The LINER® technique provided a novel and innovative technique for the distribution of carbon substrates for reductive dechlorination of chlorinated ethenes. In particular the full-scale remediation project demonstrated that significant biostimulation could be achieved during the 59 week treatment period by the injection of nebulised ethyl lactate. Extensive ground water monitoring however showed that the effectiveness of the technique was limited by a layer of fine sand at 34-35m depth. The lower permeability of the fine sand appeared to restrict the gas sparging pathways and hence the distribution of the nebulised substrate to higher levels, especially 24-25 m depth where biostimulation was only marginally observed. Nevertheless, visual and statistical analysis of the ground water monitoring data showed a clear pattern of biostimulation that was more significant at certain depth but overall resulted in noticeable decrease in chlorinated hydrocarbons.

ACKNOWLEDGEMENTS

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Seawater Purification with Vessel installed Filter Units

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ABSTRACT
In order to purify seawater, filter units consisting of beach sand and steel slag were developed. The filter units were installed on a barge which was being used for land reclamation from sea. Thirty eight filter units (1.5 m x 3.6 m) were used to purify seawater in a small bay as demonstration. The case study showed that the purification capacity is about 30 m/day. The quality of purified seawater can be satisfied in terms of SS, COD, pH, DO, etc. This technique can be used in various kinds of marine works, including measure of dredging, anti-red tide and anti-blue tide.

INTRODUCTION
In nature, seawater is being purified with natural depuration which consists of the filtration by sand beach, food chain, biomass actions in marine forest, etc.

As a result of development, the excess discharge of substances through human activities and the decrease in natural coastal environment such as sand beach have decreased the natural depuration. Consequently, the seawater and sediments in some sea areas are seriously polluted.

In order to clean up polluted sea area, both the sediments and seawater should be treated. As a sediment treatment, the dredging of polluted sediments or the sand capping on polluted sediments has been used. To conserve the rehabilitated environment, the natural depuration is inevitably required. Therefore, the total rehabilitation of coastal environment can be achieved by the recovery of natural depuration which consists of physical, chemical, biological and/or combined actions. To achieve the recovery, good quality of seawater is always required. For example, sea grass which provides for marine biomass grows only in clean water, because seaweeds need photosynthesis. Dredging of sediments often causes suspension. Since the pollutants are adhered to the particles, the diffusion of suspension results in the diffusion of pollutants. In this case, the suspended solids should be collected. Thus, a key point for the rehabilitation of coastal environment is water purification.

The primary objective of seawater purification is to remove the suspended solids. The suspended solids consist of inorganic and organic matter. The removal of phytoplankton may prevent the occurrence of red tide. The organic matters contained in sediments will be decomposed by microorganism, when nutrients, i.e., phosphorus and nitrogen, will be regenerated from the sediments. The dissolution of nutrients into seawater causes eutrophication. Therefore, the removal of organic matter from seawater will provide the reduction of nutrients in seawater and the decrease in the organic matter of settling particles.

The removal of suspended solids results in the removal of hazardous substances from seawater. Thus, the removal technique of suspended solids from seawater is primarily

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

necessary for the preservation of sea environment.

BARGE WITH FILTER UNITS

The filter units developed have a dimension of 1.5 m x 3.6 m in area and 50 cm in height. The filter consists of steel slag layer with a thickness of 40 cm and overlying sea sand. The initial coefficient of permeability of the steel slag is an order of 10^{-1} cm/s. On the other hand, the coefficient of permeability of the surface sand is usually an order of 10^{-2} cm/s. Therefore, the percolation of seawater becomes unsaturated flow in the slag, as shown in Figure 1. In fact, the steel slag was installed in the bottom basket made from textile mesh. Therefore, the steel slag layer has ventilation. This condition may keep the filter units aerobic during filtration.

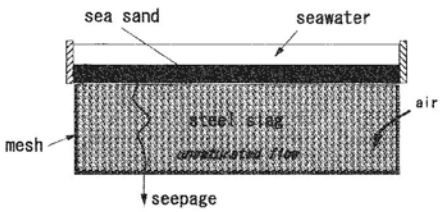

Fig.1 Filter unit.

Thirty eight filter units were installed in an old barge (2350 t) which was being used for transporting sand materials for the reclamation of the Kansai International Airport. Feature of the barge is shown in Figures 2 and 3.

PURIFICATION SYSTEM

The purification system developed consists of the following parts and steps;

a) pumping of seawater, 10000 m^3 /day,
b) water tank to allow settling of larger particles,
c) carbon fiber tank to catch organic matter,
d) two waterways to connect to the watering pipes,
e) watering on the filter units through the pipes,
f) filtration,
g) discharge of filtered seawater.



Fig.2 Barge in the experimental site.

EXPERIMENTAL SITES

The barge was towed by a tugboat into Kasaoka bay which is like a narrow waterway, as shown in Figure 4. The present geographical feature of the bay was formed by the reclamation started from 1972. The length is approximately 3 km and the width ranges from 20 meters to several hundred meters. As the Kasaoka port locates at the northern part of the bay, many boats and ships navigate in the narrow route.



Fig. 3 Filter units and other facilities.

It may be important to note that a specified part of Kasaoka Bay is designated for the natural monument for breeding place of Japanese horseshoe crab which is now on the red list published by the Ministry of Environment of Japan. This is because the place is the northern limit of the habitat. However, at present horseshoe crab can hardly be found in this region (Fukue *et al*, 2001).

The area of the bay is approximately 2500000 m^2 and water volume is 3200000 m^3. The tide is quite high, say 4 m in maximum. The average water depth is only 1.3 m, whilst the sea route is kept more than 3 m.

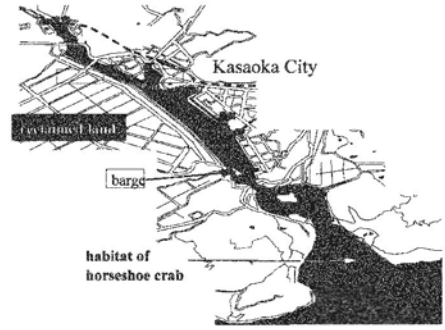

Fig. 4 Experimental site in Kasaoka Bay.

RESULTS AND DISCUSSION

The purification experiment was performed substantively for 80 days, from Aug. 1 to Oct. 25, 2002. The observation and measurement were made on suspended solid, *SS*, dissolved oxygen, *DO* chemical oxygen demand, *COD*, pH, etc. for pumped and filtered water.

Water quality

The quality of Seawater in Kasaoka bay may be described as a *SS* of 30 mg/L. This value may not satisfy any standards for water quality. For example, Japanese standards of SS for fish are less than 1mg/L, 2 mg/L and 3mg/L for 1st, 2nd and 3rd grades, respectively.

It is well known that filtration will remove SS. Figure 5 showed pumped and filtered seawater, i.e., before and after filtration. The detail will be discussed later.

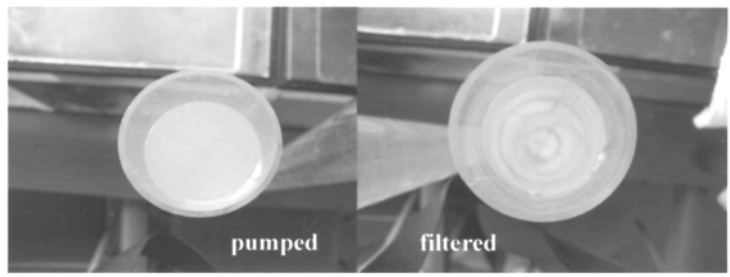

Fig. 5 Pumped and filtered seawater.

Dissolved oxygen

Basically, sprinkled water on the filter units and dropping water on sea surface cause aeration and result in the increase in dissolved oxygen. As the slag layer in the filter units is kept aerobic, it acts against to be anaerobic condition.

On the other hand, the decomposition of organic matter due to microorganism consumes oxygen in the seawater. The results obtained are shown in Figure 6. The figure shows that the dissolved oxygen is relatively high for the filtered seawater. The calculation of saturated DO with water temperature showed that the filtered seawater contains enough oxygen.

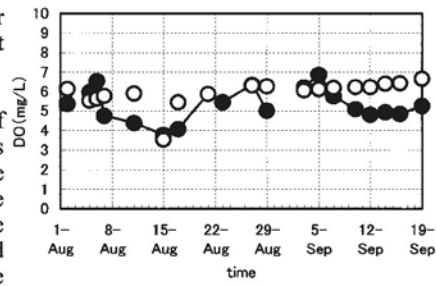

Fig. 6 DO for pumped and filtered seawater. (●:pumped, ○: filtered)

Chemical oxygen demand, COD

Chemical oxygen demand is one of the important indices for the water quality. The Japanese standards for seawater quality indicates less than 2 mg/L, 2-3 mg/L, and 3-8 mg/L for 1st, 2nd class sea area and requirement for the conservation of environment, respectively.

The measured COD is shown in Figure 7. The values of COD vary with time and lower for

filtered seawater. This means that the seawater is cleaned by the filtering. The mean reduction of COD was 16 percent.

pH

Since the steel slag used has high pH value, its influence is feared. Figure 8 shows the change in pH value for the pumped and filtered seawater. The results show that there is no significant change in pH values between pumped and filtered seawater.

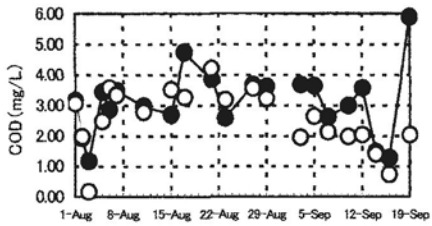

Fig.7 COD for pumped and filtered seawater. (●:pumped, ○: filtered)

Phosphorus

One of the reasons why steel slag was used for the filtration is to remove phosphorus from seawater. Steel slag contains iron which forms iron phosphate. Therefore, it is expected to prevent eutrophication by the removal of phosphorus from seawater.

The results show that phosphorus can be removed if the concentration is relatively high. However, when the concentration of phosphorus is relatively low, the phosphorus will be leached from the slag. Figure 9 shows experimental results obtained for Kasaoka bay and Shimizu port. The seawater of Kasaoka Bay contains less phosphorus and causes the leaching of phosphorus from the slag.

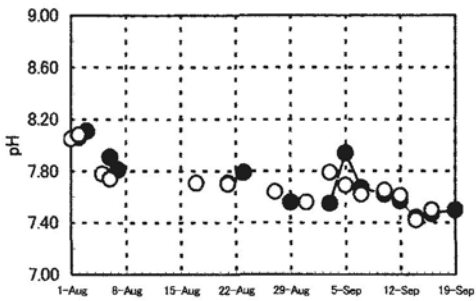

Fig. 8 pH values for pumped and filtered seawater. (●:pumped, ○: filtered)

Permeability change of filter

The SS remains on the surface of the sand filter. Since the size of SS is smaller than sand, the permeability of the filter decreases with filtration time. This causes reduction of the amount of filtration volume of seawater. The volume of filtration, Q, is given by the following Darcy's law,

$$Q = k A i \qquad (1)$$

where k is the coefficient of permeability, A is the total area of the filter and i is the hydraulic gradient.

The measured apparent k using one filter unit is shown in Figure 10. The measurement was obtained under a constant water head. The k of the filter unit was 1×10^{-1} cm/s initially, but it decreased with time. The decrease in k is due to the clogging of SS. It became 1×10^{-3} cm/s, after 700 hours.

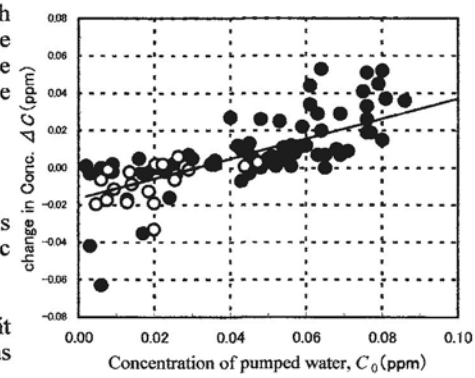

Fig.9 Change in phosphorus from pumped to filtered seawater.
(●:Shimizu port, ○: Kasaoka Bay)

When the k is very high, hydraulic gradient is small under a constant water supply. When the k becomes very small value, the filtration will be almost stopped. Under a limit hydraulic gradient, the decrease in k reduces the purification volume. In the experiment, the maximum hydraulic gradient was set to about 6 for a thickness of filter sand of 4 cm.

The average volume of the purified water is given by the accumulated volume of purified water divided by the operating time. During the experiment, it was tried to keep 6000 m^3/day.

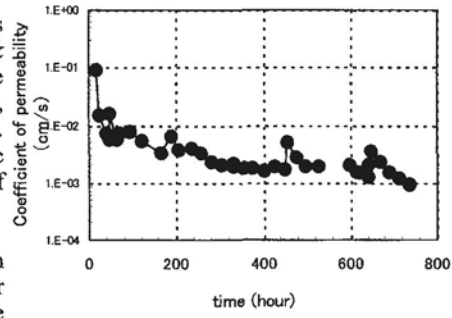

Fig.10 Change in permeability of sand filter.

Effects of Carbon fibers

Before the filtration of seawater, organic matter was tried to remove with carbon fibers, as shown in Figure 11. Three hundred bunches of carbon fibers were hung in the carbon fiber tank which is installed just before the waterways. The basic idea was to allow the breeding of microorganism on them, because the organic matter will be adsorbed on them and be consumed by microorganism. The amount of suspended solids was decreased at most 30 percent in the carbon fiber tank. However, it is noted that the excess breeding of microorganism increases the amount of SS because of the droppings. Therefore, the organic matter and microorganism were sometimes removed from the carbon fibers by washing.

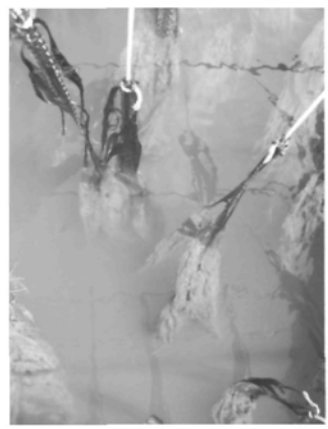

Fig.11 Carbon fiber bunches used.

Suspended solids

Thick drifting mud exists at the bottom of Kasaoka Bay and it is rolled up by the waves and currents induced by ferries and fishery boats. Therefore, the suspended solids in the seawater consist of the particles suspended from the bottom, phytoplankton generated and particles just discharged from the existing rivers. The microphotograph of suspended solids is shown in Figure 12. They are mostly silt-clay sized inorganic particles, organic matter, and diatom. The ignition loss of the suspended solids ranges from approximately 4 to 12 percent. These particles are filtered with the filter units. It is estimated that the particles suspended from the bottom occupy more than 50 percent of the total suspended solids. This may be one of the reasons why the inorganic content of the suspended solids is as much as 90 percent.

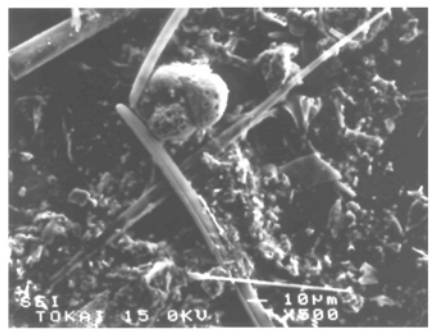

Fig.12 Microphotograph of SS.

Figure 13 shows the changes in SS for the pumped and filtered water. As seen in the figure, the SS changes with time and date, because particles are mostly suspended by waves and current in low tide. The SS of pumped seawater often exceeds 25 mg/L, while that of filtered seawater is

mostly less than 2 mg/L, as shown in Figure 13. Thus, the removal of SS is as much as 80 percent. This contributes to the transparency of seawater.

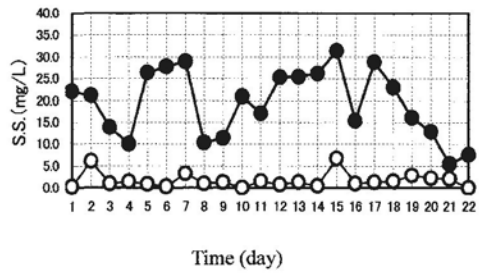

Fig.13 Changes in SS for pumped water, and filtered water. (●:pumped, ○: filtered)

Applications

Rehabilitation works in coastal regions may often require dredging of sediments. However, dredging causes turbidity of seawater. If the sediments are contaminated, the turbidity causes the diffusion of pollutants. Japanese government is trying to oblige the turbidity prevention. Therefore, the filter units can be used to purify the water during dredging works.

An excess generation of phytoplankton may cause red-tide. Therefore, it is possible to prevent red-tide, with removal of the plankton. On the other hand, the excess generation of phytoplankton is attributed to rich food, i.e., rich phosphorus and nitrogen in seawater. The nutrients are taken by phytoplankton. Then, the removal of phytoplankton will contribute the decrease in phosphorus and nitrogen. Thus, the generation of phytoplankton can be controlled by the removal of phytoplankton. This is a way of "removal of nutrients by phytoplankton".

Future study

An automatic mechanical system is needed to be developed for the removal of suspended solids deposited on the filter units. It is possible to use the suspended solids collected with the system as fertilizer.

CONCLUDING REMARKS

The barge with filter units can be useful to purify seawater in closed sea. The case study showed that the purification capacity is about 30 m/day. The quality of purified seawater can be satisfied in terms of SS, COD, pH, DO, etc.

This technique can be used in various kinds of engineering works in coastal regions, including anti-red tide.

ACKNOWLEDGEMENTS

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Evaluation of low temperature thermal desorption as a treatment option for hydrocarbon contaminated soils

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ABSTRACT

A low temperature thermal desorption (LTTD) system is to be used to treat hydrocarbon impacted soils at a 2.5ha site in southwest London. Concentrations of PAH and TPH of up to 17,400mg/kg and 38,570mg/kg respectively are present within the predominantly clay Made Ground. Japanese Knotweed is also present across the site.

It is proposed to develop the site for mixed residential and commercial use. The scheme comprises multi-storey apartment units set in open landscaping and commercial, amenity and leisure units.

The remediation will be carried out under a Mobile Plant Licence. Subject to required site levels, the soils will be either excavated or treated in-situ. The soils will be mixed with hot air at a temperature of up to 450°C to desorb hydrocarbon compounds from the soil. Fragments of Japanese Knotweed within the soil will also be destroyed in this process. Volatilised compounds will be passed through a gas treatment system prior to discharge to atmosphere. Following treatment, the moisture content of the soils will be adjusted, where appropriate, prior to placement and/or re-compaction.

The technique is relatively rapid and it is anticipated that up to 5,000m^3 of soil can be treated within a 2 to 3 month period. The costs relative to other commonly used treatment techniques are discussed. The system should be capable of achieving final soil concentrations of less than 500mg/kg (PAH) and less than 800mg/kg (TPH). As the system is able to destroy all parts of the Japanese Knotweed plant, in this context, it represents a quick and efficient method of controlling its spread.

INTRODUCTION

A 2.5ha former recreational and commercial site in southwest London is being redeveloped for mixed residential and commercial use. The development scheme comprises multi-storey apartment units set in open landscaping, basement car parking and commercial, amenity and leisure units.

The ground conditions consist of up to 3.4m of predominantly clay Made Ground underlain by a relatively thin local layer of Alluvium (<1.2m) over the London Clay Formation. The London Clay forms an aquiclude separating shallow limited perched water from the deep Chalk aquifer. A small river runs along one of the site boundaries.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

Hotspots of hydrocarbon contamination have been encountered at the site, with concentrations of polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPH) of up to 17,400mg/kg and 38,570mg/kg respectively being recorded. Japanese Knotweed is also well established and widespread.

Remediation of the site using 'dig and dump' was rejected at an early stage in the design process as being an unsustainable option. It was also recognised that due to the implementation of new legislation (i.e. the EU Landfill Directive), after July 2004 the number of facilities licensed to accept hazardous waste will be significantly reduced and pre-treatment will be required prior to disposal.

Various treatment options were considered, including ex-situ bioremediation and cement stabilisation. However, following consideration of applicability, versatility, costs and remediation time scales, and faced with very large disposal costs to deal with Japanese Knotweed[1,2], it was decided that a solution which addressed both issued was preferred, i.e. low temperature thermal desorption (LTTD). It is intended that the treated soil will be retained on site as general fill.

DESCRIPTION OF METHODOLOGY AND APPARATUS

Low temperature thermal desorption is regularly used to treat contaminated soils and sediments in the USA, however, to date, although recognised in the UK[3] it has rarely been used, although there has been a well publicised field trial at the BAe System's Facility in Chorley[4]. LTTD is a physical separation process that involves heating the soil to a sufficient temperature to cause contaminants to volatilise and desorb from the soil particles. Low temperature thermal desorption is effective for use in a wide range of soil types and is therefore suitable for the treatment of variable Made Ground.

At the site in London, LTTD will be carried out in conjunction with a patented Mobile Injection Treatment Unit (MITU). The MITU equipment and procedures are based on those developed under the scrutiny of the US EPA and patented in the USA and operated in the UK by Wrenwood Associates under a mobile plant licence issued by the Environment Agency.

The MITU can treat the soil either in-situ or ex-situ and the technology can be adapted to different sizes of mechanical plant to meet various treatment objectives and site constraints (see Table 1). A MITU 12 will be utilised at the site in London.

Designation	Description	Treatment depths
MITU 12	Modified trenching head mounted on tracked excavator	In-situ: 3-4m below ground level Ex-situ: 3m high windrows
MITU-LVR	Tracked trencher with specialised rotating drum attachment	1-2m below ground level (trench width 4.8m)
MITU 30	Large tracked trench excavator	10m below ground level

Table 1: Machine specifications[5]

The MITU 12 comprises a converted tracked excavator equipped with a modified trenching head and a vacuum/containment hood (see Figures 1 and 2). The hood is attached to the boom of the excavator and can be operated separately from the trenching head. Heat from the engine exhaust gases is re-cycled and ducted to the hood. With a standard hood, an operating temperature of 100°C can be achieved. A separate heat generation unit (powered by a generator) attached to the MITU provides forced hot air through the hood to the soil.

Hot air flow rates of up to 8.5m^3/min and air temperatures of up to 450°C can be achieved. The shearing action of the trencher breaks the soil into fine particles, increasing the surface area to volume ratio and increasing the contact between the soil and the hot air. A vacuum is applied beneath the hood to capture volatilised contaminants, which are then passed through a gas treatment system prior to discharge to atmosphere. The gas treatment system comprises either a thermal oxidiser using an after burner unit and/or an activated carbon filter. The temperatures reached will not destroy the pieces of Japanese Knotweed but will in effect 'cook' the plant material so that it can no longer grow or regenerate and becomes inert organic matter. The MITU 12 is capable of treating between 15-25m^3 of soil per hour, although a number of passes may be needed before target concentrations are achieved.

The ultimate soil temperature achieved depends on the soil characteristics, the retention time and heat losses from the system. The optimum retention time is determined in the field through frequent monitoring of the air and soil temperatures. The containment hood can be insulated to reduce heat losses.

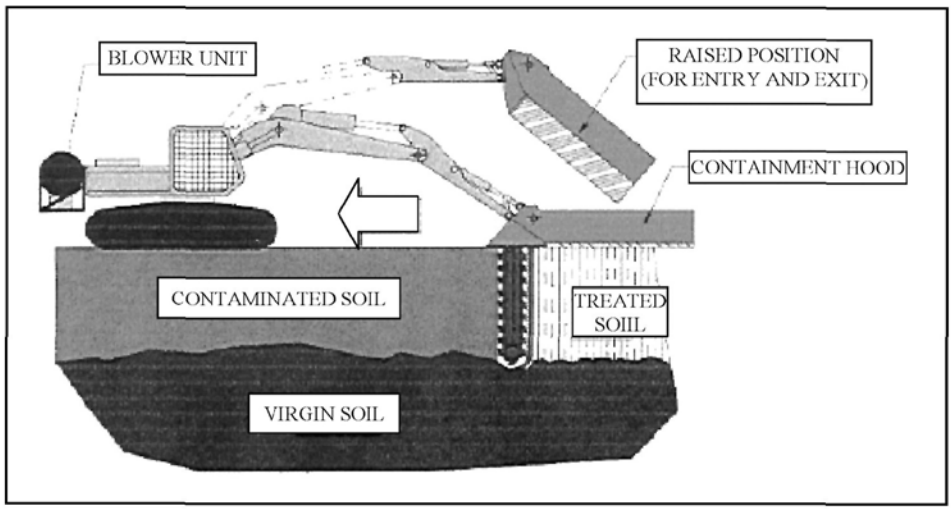

Figure 1: MITU 12 (in-situ operation)[5]



Figure 2: Ex-situ treatment using the MITU 12[5]

APPLICATIONS AND LIMITATIONS

Low temperature thermal desorption is suitable for the treatment of soils contaminated with low and middle distillate organic compounds as sufficiently high temperatures can be achieved at which the boiling point will be exceeded and effective desorption can take place. Treatment efficiencies of up to 95% removal of low to middle distillate compounds can be achieved with the MITU/LTTD. The system is also capable of destroying all parts of the Japanese Knotweed plant (including the seeds, rhizomes and stem segments). Higher chain organics with boiling points above 450°C are not suitable for treatment with the combined MITU/LTTD system. The MITU/LTTD is also not designed to treat free phase liquid contaminants. The temperature treatment requirements for various organics are presented in Table 2.

Contaminant	Boiling range (°C)	Viability of LTTD treatment using MITU
BTEX	80 – 144	Can be treated using exhaust and/or enhanced heaters
Solvents	100 – 150	
Gasoline	25 – 215	
Kerosene	150 – 250	
Jet Fuel	100 – 250	
Diesel	160 – 400	Majority capable of treatment but may struggle with top end depending on heat losses
Fuel Oils	160 – 400	
PAHs	218 – 536	Will only treat some
PCBs	335 (mean)	
Lubricating Oils	425 – 600	Unlikely to be treatable

Table 2: General treatment details[5]

With the MITU system, treatment via LTTD can be readily coupled with other treatment technologies such as in-situ chemical oxidation (via the injection of controlled amounts of

permanganate or peroxide) or enhanced in-situ bioremediation (via the injection of oxygen release and nutrient enriched compounds). The mixing processes provided by the MITU ensure efficient mixing and therefore rapid reactions between compounds. If further to treatment with LTTD, the target concentrations are exceeded due to recalcitrant higher chain organics, chemical oxidation can be effected with the MITU system through the injection of suitable reagents.

Pre-treatment is generally not required with the MITU system. However, where material is treated ex-situ, pre-screening of the material prior to treatment may be beneficial.

COST AND TIME COMPARISON

It is estimated that approximately 5,000m^3 of hydrocarbon impacted soil needs to be treated at the site in London. Approximate costs and time scales for the treatment options that were initially considered are summarised in Table 3. The prices do not include mobilisation costs.

Treatment	Cost exc. VAT (£/m^3)	Time required
LTTD (MITU 12)	30	2 – 3 months
Ex-situ bioremediation	25	4 – 6 months
Cement stabilisation	50	2 - 3 months
'Dig and dump' (prior to July 2004)	100	5 weeks

Table 3: Comparison of remediation options (treatment of 5,000m^3 of hydrocarbon contaminated soil)

Although ex-situ bioremediation was the 'least cost' option, it was rejected due to the time requirements. Low temperature thermal desorption was the next lowest cost option and had a shorter treatment time that bioremediation. It also had the added benefit that it was able to treat fragments of Japanese Knotweed within the soil. Cement stabilisation had a similar treatment time to thermal desorption but was more expensive. Finally, remediation via 'dig and dump' could be achieved in about half the time of the other treatment options, but the cost was prohibitive and it was deemed environmentally unsustainable. The need for pre-treatment prior to disposal and reduced hazardous waste landfill capacity after July 2004 was also of concern, as the site works were likely to extend beyond the July threshold.

In the final analysis, thermal desorption using the MITU 12 system was chosen as the preferred option based on its versatility and its relatively low cost and time requirements.

RE-USE OF TREATED MATERIAL

Treated material intended for re-use will be tested to demonstrate that the hydrocarbon concentrations do not exceed the target concentrations detailed in Table 4. These concentrations have been agreed with the Environment Agency and the Local Authority and reflect the nature of the site and the intended development. Where material exceeds the target concentrations, subject to the volume, it will either be re-treated or disposed to landfill.

Contaminant	Measured range (mg/kg)
TPH	800
PAH	500

Table 4: Site specific target concentrations

Geotechnical testing will also be carried out to demonstrate that the treated material has suitable engineering characteristics for its intended use. Most of the development is likely to be supported on piled foundations, however, the use of desiccated soils in areas of

conventional shallow foundations and beneath areas of soft and hard landscaping may cause problems due to shrinkage and heave. Therefore, where appropriate, the moisture content of the treated soils will be adjusted to the equilibrium moisture content prior to placement and re-compaction. All re-used material will be retained beneath an engineered capping layer.

LICENSING ISSUES

The generic methodology has been submitted as a Remediation Method Statement to the Regulators with positive response but the planning application for the site is still being processed and therefore site works, including remediation, cannot yet commence.

The remediation will be carried out under a mobile plant licence[6] issued in accordance with The Waste Management Licensing Regulations 1994. A generic working plan was prepared as part of the Mobile Plant Licence application. However, once the development layout and final site levels have been frozen, a site specific working plan and risk assessment will be submitted to the waste management regulator for approval. The site specific working plan will include details of the validation and monitoring procedures that will be carried out.

Air quality monitoring will be carried out at the boundary of the treatment area (using a portable monitor) and at the site boundary (using stationary diffusion tubes). The exhaust will also be monitored to check the effectiveness of the gas treatment system.

It is intended that treated material containing low levels of contamination will be retained and re-used on site. The site should be exempt from requiring a Waste Management Licence under Schedule 3, clause 19 (use of waste for 'relevant works') of The Waste Management Licensing Regulations 1994 and subsequent amendments. An application for an exemption will be made once all of the necessary details are available.

CONCLUSIONS

There is currently a heavy reliance on the remediation of contaminated sites via disposal of contaminated soils to landfill. Developers generally consider landfilling of wastes to be a quick and relatively cheap process and because it is perceived as a zero risk option. However, a dramatic loss of landfill capacity is expected after July 2004 and disposal to landfill will become significantly more expensive as gate fees and haulage distances increase.

The MITU system is an innovative remediation technology that can be applied to a range of soils and contaminants. Relatively short treatment times are achievable and the cost is generally not prohibitive. The ability to treat Japanese Knotweed and Knotweed impacted soils is a key attribute of the system, as few other remediation techniques are capable of this. It is anticipated that as developers become more aware of the benefits of adopting on-site treatment processes there will be an increased reliance on technologies such as low temperature thermal desorption.

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Development of a novel in situ aquifer assessment tool: The dipole flow and reactive tracer test

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INTRODUCTION

Monitored natural attenuation

During the last decade, the popularity of Monitored Natural Attenuation (MNA) as an alternative to traditional pump and treat methods for the restoration of contaminated land and groundwater has risen. This data-intensive approach exploits the physical, reactive and biodegradation characteristics of aquifer systems to reduce the concentration of contaminants in groundwater. Where MNA is proposed as a viable remediation strategy, it is essential that it is supported by detailed and reliable predictions outlining its future performance at the sites concerned. Unfortunately, such predictions are often subject to high levels of uncertainty, arising from the spatial and temporal variability in aquifer hydraulic, geochemical and microbiological properties. Additionally, results obtained by studies of aquifer hydraulic and transport properties are known to be strongly scale-dependent (Gelhar et al, 1992). Therefore, contaminated sites must be sampled at a resolution sufficient to produce an accurate site conceptual model and enable the fate of contaminants to be predicted with confidence. At large or complex sites, a prolonged characterisation exercise would prove costly in terms of time and money. Time constraints and practical difficulties associated with existing site investigation methodologies often lead to inefficient characterisation of aquifer physical and reactive parameters (Thornton et al, 2001), thereby introducing uncertainty at the second and third risk assessment tiers. Research undertaken in this project has the potential to be developed as a major site investigation tool to support MNA, offering increased certainty when compared to existing site investigation methods.

Dipole flow tests

The Dipole Flow Test (DFT) circulates groundwater between isolated injection (source) and extraction (sink) chambers within a single borehole until steady state has been reached (Figure 1). Steady state with respect to flow is achieved when pressure transducers located within the chambers record no further change in hydraulic head over time. A mathematical model incorporating the measured drawdown, pumping rate and dipole dimensions is then used to provide estimates of the horizontal and vertical hydraulic conductivities (Kabala, 1993).

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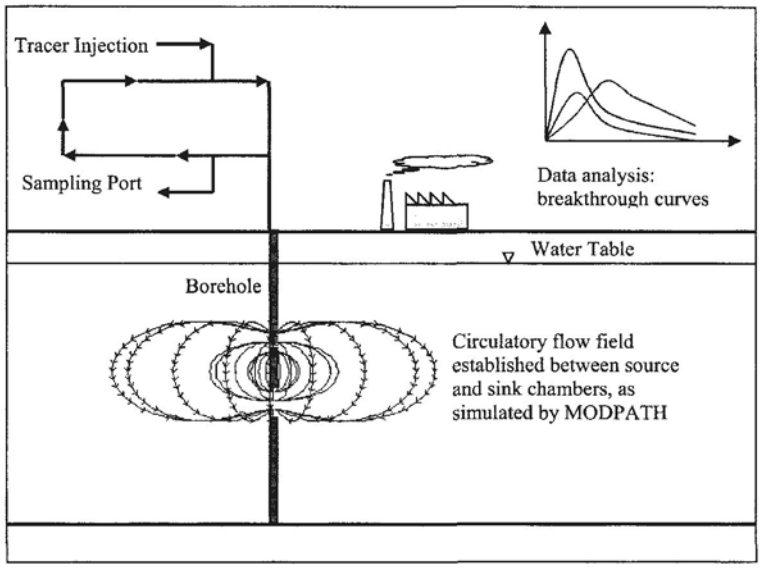

Figure 1 Schematic diagram of the Dipole Flow and Reactive Tracer Test. Pumping between hydraulically isolated chambers establishes a circulatory flow pattern in the aquifer. A suite of chemical tracers is added to the injection chamber and their extraction chamber concentration is plotted as a series of breakthrough curves.

A modification of the basic DFT in which an inert chemical tracer is introduced to the circulating flow is known as the Dipole Flow Tracer Test (DFTT). The arrival of this tracer in the sink chamber over a period of time can be plotted as a breakthrough curve (BTC) (Sutton et al, 2000). Interpretation of BTCs yields more detailed information about the hydraulic properties of the aquifer, in addition to providing estimates of longitudinal dispersivity. High quality estimates of horizontal conductivity, its spatial variability and anisotropy ratio are required for most remediation strategies. However, there are some situations where knowledge of vertical conductivity is also necessary. An example of this is the determination of optimal separation distance for vertical circulation wells; a remedial strategy often employed at sites contaminated by volatile organic compounds (Sutton et al, 2000). In general, vertical and horizontal hydraulic conductivities, which may differ from one another within the same locality by a factor of 20 or greater, can be estimated more precisely by the DFTT than by earlier single-borehole methods (Kabala, 1993; Domenico and Schwartz, 1990).

Introduction of sorbing or biodegradable tracers simulates the aquifer's potential to naturally attenuate pollutants. Sorbing tracer BTCs will show a quantifiable retardation, whereas biodegrading tracers will lose mass during transport from source to sink chambers. The Dipole Flow with Reactive Tracer Test (DFRTT), currently under development, shows the potential to deliver a range of high quality site investigation data from a single, cost-efficient test.

Principal project components

The primary project components are summarised in Figure 2. Research at The University of Sheffield comprises the following project components:

1. Laboratory-scale DFRTT trials in an aquifer physical model (sandbox)
2. Field-scale DFRTT evaluation at the Site for Innovative Research on Natural Attenuation (SIReN) (Swannell et al, 2001).
3. Development of a mathematical model to interpret DFRTT data

A Risk-Benefit Analysis calculator for the selection of site investigation strategies is currently under development at the University of Nottingham, and will include the DFRTT. Queen's University Belfast will provide assistance with the use of innovative tracers and tracer cocktails.

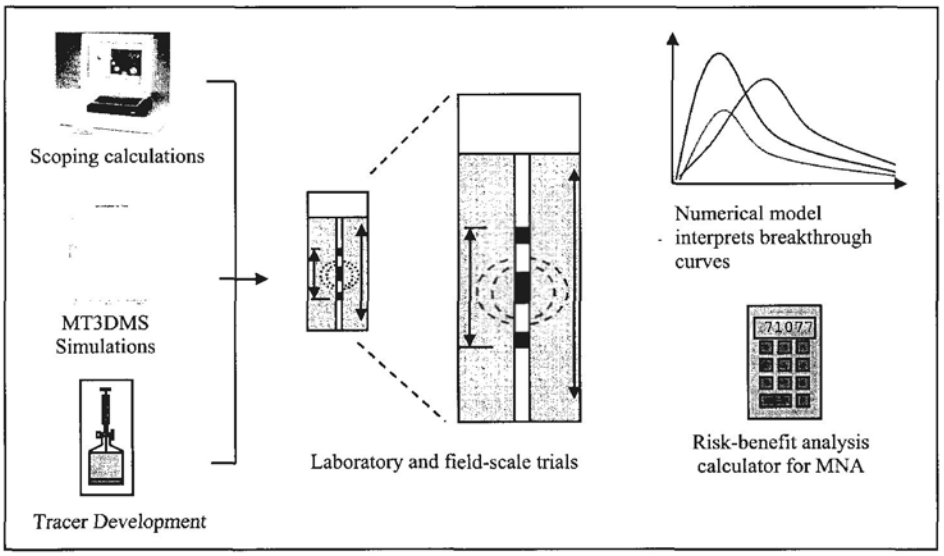

Figure 2 Outline of principal project components. The development of the dipole probe kit is conducted at the University of Sheffield, whilst the risk-benefit analysis calculator is developed simultaneously at the University of Nottingham. Queen's University Belfast provide expertise on the use of chemical tracers

DFRTT DESIGN PROCESS

A review of existing literature was conducted in order to identify the relationships between dipole probe dimensions, pumping rate and flow field dimensions. These formed the basis of a series of scoping calculations intended to guide the design of the laboratory and field scale experiments.

Subsequently, MODFLOW/MT3DMS were employed to refine the initial values and provide data for eventual comparison with laboratory and field data

Laboratory-scale experiments

A review of the available literature revealed that the sandbox physical dimensions could be determined by the radial extent of the flow generated by the dipole probe. Adopting the approach taken by Hantush (1964), Zlotnik and Ledder (1996) numerically modelled the dipole flow patterns within a vertical circulation well at steady-state in an unconfined,

infinite aquifer and provided the following approximations for the physical extent of a dipole flow field containing 90% of the circulatory flow

Minimum horizontal extent of flow = $10aL$ ($20aL$ diametrically) (1)
Minimum vertical extent of flow = $4L$ ($8L$ diametrically)

Where L is the half-chamber separation (or shoulder length; exactly half the distance between chamber centres), and a is the anisotropy ratio ($a^2 = K_r / K_z$, the ratio between the horizontal and vertical hydraulic conductivities). Therefore, a model dipole probe with a shoulder length of 10 cm in an isotropic medium would generate a flow field with a radius of 1m and would require a sandbox 2 m in diameter in order to minimise boundary interference. According to this theory, the same flow field would extend to ±40 cm from the centre of the dipole probe. Preliminary scoping calculations were conducted assuming a sandbox of dimensions 2 m x 2 m x 1 m, with the dipole probe (shoulder length not greater than 10 cm) located in a central well. A buffer zone of 5 cm was added to the horizontal dimensions.
It is intended that laboratory-scale trials will support the development of the test in the field. However, the sandbox and model dipole probe will provide useful datasets for calibration of the numerical model

Field-scale experiments
Field trials of the DFRTT will take place at SIReN, a large petro-chemical complex in Greater Manchester. Design of the field experiments was governed largely by the need to recover a suitable amount of tracer in a relatively uncharacterised porous media and also the need to choose a suitable test venue within this large, contaminated site.
A set of MODFLOW/MT3DMS simulations was conducted in order to predict the effects of anisotropy ratio and ambient hydraulic gradients on tracer recovery and breakthrough curve characteristics. Results of these simulations suggest that the DFRTT is extremely sensitive to increases in anisotropy ratio (beyond $Kr/Kz = 6$, breakthrough curves lose resolution rapidly as less tracer is recovered) but robust in ambient hydraulic gradients < 0.05
These findings have important implications for the laboratory-scale tests in addition to the field experiments. In the field, the DFRTT must be tested in a medium with a minimum amount of fracturing and layering. At SIReN, the shallow sand and gravel layer and more importantly, the clay layer must be avoided during testing. The same applies to the aquifer physical model, which must be packed in such a way as to minimise layering.
By contrast, MT3DMS simulations predict that the DFRTT will continue to produce high resolution BTCs in ambient hydraulic gradients far in excess of that at likely to be encountered in the sandstone layer at SIReN (≈ 0.005, estimated from contours in Figure A6, Jones et al, 2001).
Predictive studies of this nature confirm that the field-scale DFRTT will produce breakthrough data of usable quality provided that significant fractures and layers can be avoided.

Numerical model
In order for the DFRTT to fulfil its potential as an aquifer assessment tool, it must be accompanied by a numerical model with the capacity to interpret the complex and very specific data it produces. Commercially available simulation packages have difficulty resolving systems with rapidly converging and diverging flow within a relatively small spatial domain. Also, the use of a package such as MODFLOW requires significant time input from the user in order to refine the grid, choose the correct solvers, particle-tracking methods and so forth. With this in mind, it is likely that a readily available DFRTT

interpretation package will further increase the popularity of the technique with those involved in site investigation and remediation.

The model comprises a steady-state flow component, on to which the advection-dispersion and chemical reaction characteristics are imposed. A grid based upon the circulatory flow field induced by the DFRTT will improve the reliability of model results when compared to the regular grid arrangements offered by MT3DMS. Latter stages of this project component will see the model adapted to take into account fracture networks and layering.

Development of the model is currently being undertaken at the University of Sheffield and Waterloo University in Canada. Early test results from this model will be compared to those simulated by MT3DMS. Data from laboratory and field-scale trials will be used to calibrate the program.

Risk-benefit analysis calculator

Research at the University of Nottingham will result in a spreadsheet of available site investigation technologies and an associated risk-benefit analysis calculator.

The first phase of this project component will produce a spreadsheet of site remediation techniques, containing information such as parameters investigated, data quality requirements, and cost. On completion of laboratory tests, field trials and the numerical model, the DFRTT will be added to the spreadsheet; experience gained during technique development will provide information on the conditions under which it should be used and the costs required for conducting a suitably detailed study.

The risk-benefit analysis calculator will use the information contained in the spreadsheet to assist in the selection of suitable site investigation strategies and subsequent remediation options.

ACKNOWLEDGEMENTS

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Risk Based Approach of a Gasworks Site

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ABSTRACT

In the centre of the city The Hague, a site of a former gasworks is present. The production of gas started at about 1907 and the production finished in 1967. Due to the production of gas, waste is buried in the surroundings. By now, the buildings of the former plant are removed and the location attains its full development.

Contamination of soil and groundwater is observed in the past. The subsoil is contaminated with cyanides and (polycyclic) aromatics. Currently, there are no direct risks for humans or for the ecology due to use of the site, due to the depth at which the contamination is present and due to the fact that the groundwater at the site is not seeping towards the soil surface but infiltrating. Therefore, only the risk of migration of contaminants dissolved in the groundwater might remain. Several aspects related with the site and the contaminants are investigated in order to assess the risks of migration. These aspects are addressed in this paper.

DESCRIPTION OF THE PROBLEM

The soil is contaminated up to a depth of about 8 metre and the groundwater up to a depth of about 10 metre. Two contaminated areas can be distinguished: the area with a high concentration of contaminated soil (the so-called inner area) and the outer area where a plume of contaminated groundwater and several scattered locations with contaminated soil is present. The risk-based approach of the two areas differs.

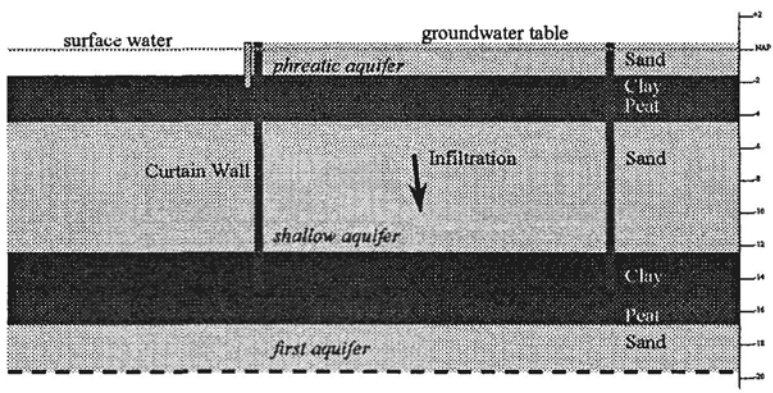

Figure 1 - Cross-section of the location with the various soil layers.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

At the end of the year 2002, an isolation of sheet piles (curtain wall) is realised around the inner area. The depth of the isolation reaches to about 14 metre below soil surface within a continuous low permeable layer of peat and clay (Figure 1). As a result of the isolation, horizontal flow of contaminated groundwater in the shallow aquifer is prevented. In the inner area the focus is upon the vertical migration of the contaminants. Interpretation of geotechnical soil data shows that the clay layer has a thickness of about four metres and the peat layer of about one metre. Therefore, vertical migration of contaminants is expected to be retarded due to sorption with lutum and organic material. Special attention needs to be paid to the area where production and storage facilities were concentrated in the past and where also the essence of the contamination seems to be located.

In the outer area, the focus is on the plume of dissolved contaminants. However, besides a plume of contaminated groundwater, also scattered spots of contaminated soil are present. Although their exact locations are unknown, these spots act as resources of contamination for the plume of contaminated groundwater. It will take several years, or even decades, before the spots are exhausted.

To analyse the risk of migration, attention is paid towards the phreatic and the shallow aquifer. For both areas, the inner and the outer one, special attention is focussed upon migration towards the first aquifer because this aquifer has regional significance.

OBJECTIVE

The objective of our approach is to maintain safe conditions for the current and coming vulnerable objects at the site e.g. surface water and the first (regional) aquifer. Furthermore, the current position of the plume of contaminants dissolved in the groundwater needs to remain stationary for the short term and to shrink on the long term. Following Dutch legislation, 'a stable situation' for the plume of contaminated groundwater should be realised within a time frame of thirty years after the start of remediation.

CONCEPTUAL MODEL

At the site the groundwater is infiltrating from the shallow aquifer to the deeper aquifer. Before installation of the curtain wall, horizontal displacement took place during infiltration. After installation of the curtain wall, in the inner area horizontal displacement during infiltration can be neglected. Only in the outer area horizontal displacement takes place during infiltration.

The driving force of migration of dissolved contaminants is the flow of groundwater. During migration of the contaminants, immobilisation as well as attenuation can be expected. Immobilisation is due to the interaction of dissolved species with the solid phase and due to (co) precipitation. Attenuation is due to degradation or conversion of dissolved contaminants [De Vries et al. 2003]. Therefore, research is carried out for the fate and behaviour of the relevant contamination.

STRATEGIC APPROACH

An integral approach is chosen as conceptual framework [Van Meurs et al. 2001]. This choice means that point information is translated into effects on a local scale. The translation is carried out with the aid of numerical modelling of the relevant phenomena affecting fate and behaviour of contaminants. Uncertainty in source strength, concentration levels and fate and behaviour are judged in their respective spatial and temporal domain.

Hypotheses about the actual fate and behaviour are formulated. Also additional questions are addressed. Hypotheses and questions are used to guide the monitoring program. Therefore, besides checking whether the migration is controlled, monitoring is used to verify the hypotheses about fate and behaviour. Subsequently, the effects of fate and behaviour in the short term as well as on the long term are predicted and analysed. Eventual measures are tuned to the outcome of this analysis.

The available point information consists of borings reflecting soil stratification and soil composition, and chemical analyses of soil and groundwater samples reflecting the degree of contamination. In the year 1990 an elaborate site investigation was carried out. Analyses of these results raised several questions. Among them were a reliable representation of the contour of the plume of contaminated groundwater in the shallow aquifer and whether or not the soil contamination in the outer area covers a continuous area or is made up of several discontinuous smaller spots. The fieldwork of 2003 is focussed upon these questions.

Furthermore, soil samples were taken and brought to laboratory to carry out degradation / conversion tests [Van der Veen & van der Werf 2002]. Especially the fate and behaviour of thiocyanates drew special attention. Also at a few locations groundwater samples as well as soil samples were taken. The analytical results are used to gain information about the distribution of contamination between the fluid phase and the solid phase.

As already addressed, a numerical model is made of the relevant phenomena affecting fate and behaviour of the contaminants of interest. The basis of the model is the representation of the groundwater flow. Further on, the mechanisms of advection, dispersion, sorption and degradation / conversion are taken into account for the fate and behaviour. As computer programs are applied ModFlow [McDonald & Harbaugh 1988] for the flow of groundwater and RT3D [Clement 1997] for the fate and behaviour of contaminants. Subsequently, the following aspects are dealt with in the numerical modelling:

- Determination of the relevant source area's;
- The distribution of contaminants between the water phase and the solid phase;
- Results of laboratory tests for degradation / conversion of contaminants.

DETERMINATION OF SOURCE AREAS

To determine the relevant locations that can be identified as source area, two different manners are followed. Firstly, use is made of historical information about the process of producing gas at this location. Secondly, use is made of analytical results of groundwater samples in combination with back tracing with the groundwater model.

Source areas based upon historical information

In the past gas is produced out of pit coal and from (carbureted) water gas. For both methods the raw gas needs purification due the presence of other compounds beside carbon in the original coal. Purification includes condensation, wet purification and dry purification. Figure 2 contains the locations (yellow areas) where purification took place in the past.

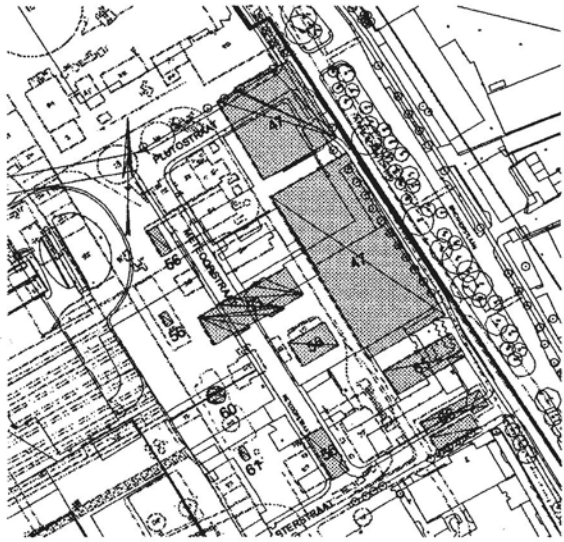

Figure 2 – Combination of a historical map (grey areas with grey lines and numbers relating to activities in the past) and the current topography (black lines). The thick line represents the location of the curtain wall.

From the historical map it can be concluded that purification activities were concentrated in a restricted area. This area can be seen as the essence of the original contamination.

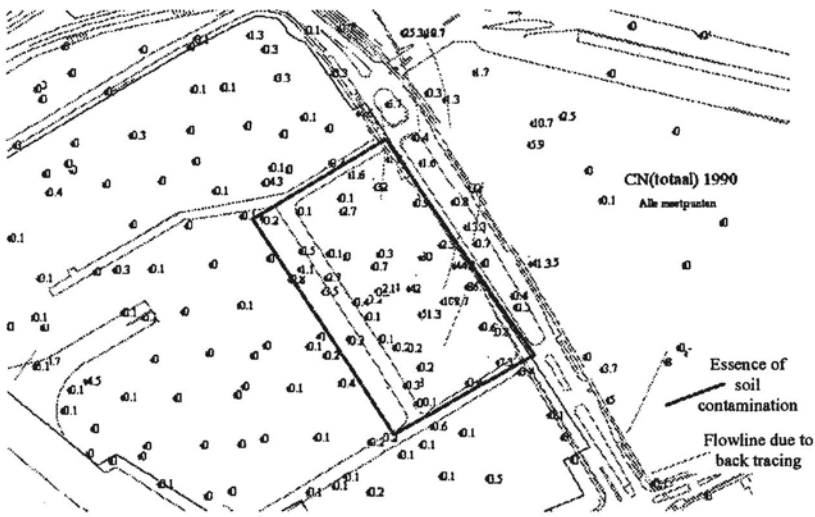

Figure 3 – Information about analytical results of cyanide within the groundwater samples.

Source areas based upon measurements

This approach consisted of visualisation of the results of chemical analyses of groundwater samples in a GIS. The results are presented as a factor by which the analytical result exceeds the Dutch intervention level. For locations at which this factor is larger then five, the groundwater model is used to determine the infiltration point that is correlated with the point of sampling (back tracing).

In Figure 3 all locations where Cyanide is measured in 1990 are represented. Each number represents the factor by which the analytical result exceeds the intervention level. Only when this factor is larger then five, back tracing is carried out. The light blue lines in Figure 3 represent the result of back tracing. Again, it can be concluded that the essence of contamination is comparable with the one based upon historical information. Exceptions can be found in the southeast and the southwest of the area.

DISTRIBUTION BETWEEN WATER AND SOLID PHASE

One of the objectives of the fieldwork was to investigate whether or not the dissolved contaminants interact with the solid phase. When there is interaction, also contamination of soil samples can be found. A consequence of this interaction is that the migration is retarded compared with the flow of groundwater.

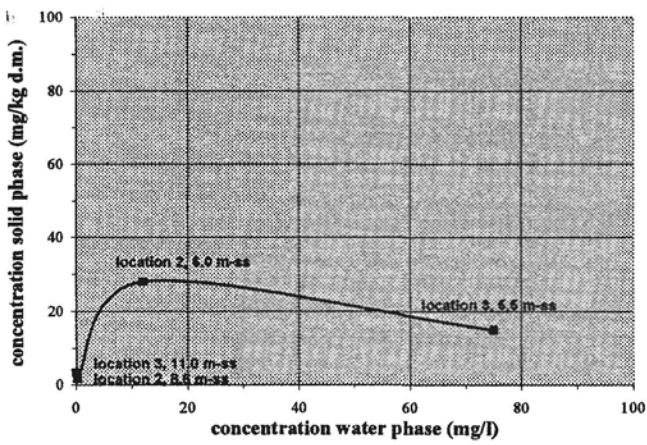

Figure 4 – The relation between the concentrations of hiocyanates sorped at the solid phase and dissolved in the water phase.

At two locations soil samples as well as groundwater samples are taken. At each location samples are taken from two depths. Chemical analyses are carried out for a set of relevant contaminants: cyanide, benzene and thiocyanates. The analytical results for thiocyanates are given in Figure 4. The main conclusion is that in the soil samples also contamination is found. This means that there occurs interaction between the water phase and the solid phase. Obviously, this relation is not linear. This means that the distribution coefficient, the proportion between the concentration at the solid phase and the concentration in the water phase, is not a constant and the process of sorption is not a simple one.

DEGRADATION / CONVERSION

During the site investigation, soil and groundwater samples were taken. These samples are used in laboratory to gain information about degradation or conversion of relevant contaminants. Degradation or conversion results in attenuation of the contaminants during migration. The effect is a reduction in concentration level.

At two locations soil samples are taken. With sample LOC5 a biotic degradation test is carried out, whereas with sample LOC4 a biotic as well as an abiotic degradation test is carried out. The abiotic test serves as a reference. To carry out these tests, each sample is mixed under anaerobic circumstances and five homogeneous samples were made each of 100 mg. The samples are used together with 100 ml of corresponding groundwater. At several times, one of the mixed samples is destructed for analytical purposes. The testing period amounted 24 weeks (Figure 5).

The results for thiocyanates (Figure 5) show that for the abiotic test, the concentration of thiocyanates hardly changes. This means that no abiotic conversion of thiocyanates takes place. Looking to the biotic tests, reduction in concentration takes place. After 24 weeks, there are hardly any thiocyanates left in the sample.

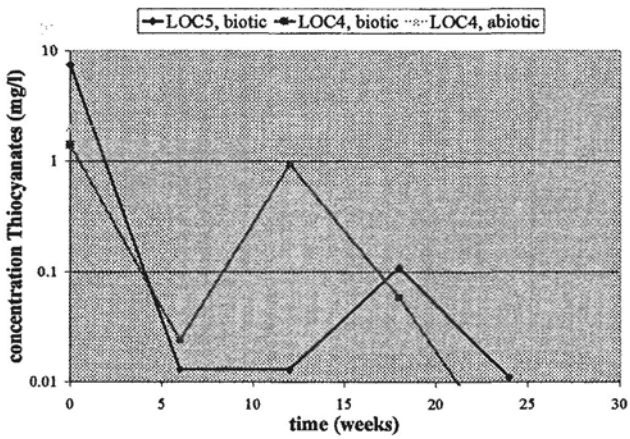

Figure 5 – Results of the degradation tests carried out in laboratory.

The main conclusion is that degradation / conversion of thiocyanates takes place in samples taken from the location. Based upon these results, the rate of degradation can be calculated. The rate of degradation ranges from 0.025 to 0.14 day^{-1}.

MODELING

Currently, a model for the flow of groundwater is created both without (before the year 2003) and with (after the year 2002) the curtain wall. The model for fate and behaviour is under construction. In this model, use will be made of the results of the fieldwork and of the results of the experiments carried out in laboratory for the rate of degradation. The behaviour of thiocyanates is rather complex. Unknown is the relation between complex cyanides and thiocyanates. For example, are complex cyanides converted into thiocyanates? However a few preliminary remarks can be made.

Calculations will be carried out for Cyanide, Thiocyanates and Benzene. First of all the numerical results will be compared with the data of 1990 and 2003. When agreement is obtained, the prediction about the development in the near future as well as on the long term will be carried out.

Preliminary results show that in the modelling of the fate and behaviour of cyanides, there is a clear relation between the source strength and the migration towards the deeper aquifer. Also, there seems to be a significant attenuation in the shallow aquifer.

Numerical modelling (calibration) is carried out for thiocyanates. The numerical results are compared with the measurements. Calibration shows that the actual degradation is significant. A rate of degradation of 0.004 day^{-1} seems to be appropriate. This agrees with the results of the degradation tests in the laboratory.

The hypotheses about the behaviour will be incorporated within the forthcoming monitoring. Therefore, monitoring has two functions: checking whether the migration remains controlled and verifying the formulated hypotheses. In this way a better understanding of the phenomena takes place and more reliable decisions can be made about the urgency of remedial measures [Van Meurs et al. 2001].

CONCLUSION

In this contribution a sketch is given of the strategic approach to deal with the contaminated subsoil of a former gas work site. The central theme in the approach is to investigate the effects of relevant phenomena governing fate and behaviour of the contaminants. The eventual measures will be carried out in order to obtain a stationary plume of dissolved contaminants at the site. The measures need to be flexible so that sustainable development is possible of the area towards a location with a high degree of urban quality.

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An Evaluation of Lead Leachability from Monolithic Solids under Modified Semi-Dynamic Leaching Conditions

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ABSTRACT
Modified semi-dynamic leaching tests (ANS 16.1) were conducted for artificial soils contaminated with lead oxide (PbO) in order to assess the long-term leaching behavior of lead (Pb). In order to simulate "worst case" leaching conditions, the ANS 16.1 test was modified by using 0.014 N acetic acid (pH = 3.25) instead of distilled water. Artificial soils were prepared by mixing amounts of kaolinite or montmorillonite with fine quartz sand. Stabilization/solidification (S/S) treatment using quicklime was then performed. Fly ash was also added, in some cases, to the artificial soils as a stabilizing agent. The effectiveness of quicklime treatment was evaluated by determining diffusion coefficients (D_e) and leachability indices (LX). A model developed by de Groot and van der Sloot (1992) was used in order to elucidate the controlling leaching mechanisms. Slurry tests were also performed by mixing PbO with quicklime and fly ash, in order to study the immobilization mechanisms of Pb. The resulting reaction products were identified using x-ray diffraction (XRD) analyses. Overall, the test results indicate that quicklime treatment was effective in immobilizing Pb and that the treated soils were acceptable for "controlled utilization" based on LX values. The controlling leaching mechanism was found to be diffusion, in most quicklime treated samples. Precipitation was identified as the most likely Pb immobilization mechanism in quicklime-fly ash treated slurries. Lead silicate, Pb_2SiO_4 (which is highly insoluble) is the most probable precipitate that can be associated with the decrease in Pb leachability. No evidence of pozzolanic reaction products such as calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH) was identified.

1. INTRODUCTION
Lead (Pb) has been identified as one of the most toxic elements to human health and is a widespread contaminant in many hazardous wastes sites (Lin et al., 1996). It has been reported that Pb can cause damage to the brain, red blood cells, blood vessels, kidneys and the nervous system (Long and Zhang, 1998; Lin et al., 1996). Human exposure to Pb is intensified due to industrialization. The transportation industry which contributes leaded gasoline and Pb storage batteries, the paint industry with leaded paints, the defense industry using Pb in various ammunitions, the plumbing and electronics with leaded solder and the food industry with Pb-contaminated cans are all adding Pb to the environment. Due to the widespread use of Pb over a period of many years, the Pb loading rate in soil is approximately 20 times (or more) its natural removal rate (Nriagu, 1990). Therefore, the risk to groundwater due to leaching of Pb from landfill areas and industrially contaminated land has received increasing attention (Gee et. al., 1997).

In this study, a stabilization/solidification (S/S) process was used in order to remediate Pb contamination, because S/S techniques have been widely applied in order to treat soils with heavy metal contamination (Yukselen and Alpaslan, 2001; Conner, 1990). During S/S treatment, the hazardous waste potential of waste materials can be minimized by converting the contaminant into forms which are less-soluble, less mobile or less toxic and encapsulating the waste within a

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

monolithic solid of high structural integrity (Conner, 1990). Various combinations of stabilizing agents have been used by numerous researchers in the treatment of soils contaminated with Pb. Li et al. (2001) studied Pb immobilization by using Portland cement (OPC) and pulverized fly ash (PFA). Wang and Vipulanandan (1996) used Type 1 Potland cement and class C fly ash as a stabilizing agent to evaluate Pb leachability. Long and Zhang (1998) used cement in combination with various additives such as lime, ash, clay, apatite, and silicate for treating Pb contaminated soils.

In this study, quicklime was used as the main stabilizing agent rather than cement and hydrated lime because: a) of its economic advantage over cement and hydrated lime b) its heat of hydration results in an accelerated rate of reaction c) of the limited information available to date regarding quicklime-based S/S.

Upon quicklime treatment of Pb contaminated soils, there are three possible Pb immobilization mechanisms: precipitation, inclusion and sorption.

Leaching is known to be a complex phenomenon because many factors may influence the release of specific constituents from a waste over a period of time (van der Sloot et al., 1996). These factors include: major element chemistry, pH, redox potential, complexation, liquid-to-solid ratio, contact time, etc (van der Sloot et al., 1996). Moreover, since very little is known about the chemical species present in waste forms and their behavior with respect to time, the long-term performance of S/S waste forms has been difficult to predict.

In order to predict the long-term leaching behavior, a diffusion model is frequently used to evaluate the leaching kinetics. In this study, a diffusion theory oriented test, an American Nuclear Society semi-dynamic leaching test (ANS, 1986), was utilized in order to examine the mechanisms governing Pb leachability in quicklime-based solids.

The objectives of this study are: 1) to assess the effect of clay surface area and mineralogy on Pb leachability 2) to evaluate the effectiveness of quicklime treatment 3) to evaluate the importance of fly ash addition in increasing Pb immobilization 4) to determine the controlling leaching mechanisms (diffusion vs. dissolution) of Pb in treated soils 5) to investigate the immobilization mechanisms for Pb by using x-ray diffraction (XRD) analyses.

2. REVIEW OF DIFFUSION MODEL

2.1. ANS model, diffusion coefficient (D_e) and leachability index (LX)

The long-term leachability of Pb from quicklime treated soils was evaluated using the ANS 16.1 model (ANS, 1986). This model was established based on Fick's diffusion theory and standardized by ANS (ANS, 1986). This model can be used to determine the cumulative fraction of Pb leached against time. It has been widely reported that the leaching of the contaminant from cement-based waste forms is mostly a diffusion-controlled process (Dutré and Vandecasteele, 1996; Godbee and Joy, 1974). Due to the slow diffusion rate of contaminants, it can be assumed that a quicklime-based waste form is a semi-infinite medium, much like the cement–based waste forms examined in previous studies (Côté et al., 1987; Godbee and Joy, 1974; Andrés et al., 1995). This implies that the release of the contaminant from the waste form is negligible when compared to its total mass. As a result of this implication, diffusion is expected to be the controlling leaching mechanism in soils treated with quicklime.

In order to assess the long-term leaching behavior of Pb in quicklime treated soils, the effective diffusivity (D_e) of the leached samples was determined based on the following ANS 16.1 model:

$$D_e = \pi \bullet \left[\frac{\left(\frac{a_n}{A_0} \right)}{(\Delta t)_n} \right]^2 \bullet \left[\frac{V}{S} \right]^2 \bullet T_n \qquad (1)$$

where a_n= activity of a metal ion released from the specimen during the leaching interval n, A_o= total activity of a given metal ion in the specimen at the beginning of the first leaching interval, $(\Delta t)_n = t_n - t_{n-}$

$_1$, V = volume of specimen in cm^3, S = geometric surface area of the specimen as calculated from measured dimensions in cm^2 and T_n is the elapsed time to the middle of the leaching period n in seconds. D_e is the effective diffusion coefficients (cm^2/sec). D_e values from equation (1) are termed "effective" because diffusion occurs in the liquid filling the interstitial spaces of a porous body.

The effectiveness of quicklime, fly ash and quicklime-fly ash-based S/S was assessed by determining the leachability index (LX). According to Environment Canada (1991), LX can be used as a performance criterion for the utilization and disposal of S/S waste. When LX values are higher than 9, a treatment process can be considered effective and S/S wastes could be used in "controlled utilization". This information indicates that the S/S wastes are acceptable for specific utilization such as quarry rehabilitation, lagoon closure, road-based material, etc. When LX values are higher than 8, S/S wastes can be used in segregated or sanitary landfills. S/S waste with an LX value lower than 8 is not considered appropriate for disposal. The leachability index is defined using the following formula:

$$LX = \frac{1}{m} \bullet \sum_{1}^{m} \left[-\log(D_e) \right]_n \tag{2}$$

where n is the number of the particular leaching period, and m is the total number of individual leaching periods.

2.2. Determination of controlling leaching mechanisms

In order to determine the controlling leaching mechanisms of Pb release, a model developed by de Groot and van der Sloot (1992) was used. The controlling leaching mechanism was determined based on the slope of the plot of the logarithm of cumulative fraction release, log (B_t), versus the logarithm of time, log(t) (de Groot and van der Sloot, 1992). If diffusion is the dominant leaching mechanism, theory suggests the following relationship:

$$\log(B_t) = \frac{1}{2} \bullet \log(t) + \log\left[U_{\max} \bullet d \bullet \sqrt{\left(\frac{D_e}{\pi}\right)} \right] \tag{3}$$

where D_e = the effective diffusion coefficient in cm^2/s for component x (Pb in this study), B_t = the cumulative maximum release of the component in mg/m^2, t = the contact time in seconds, U_{max}= the maximum leachable quantity in mg/kg, d = the bulk density of the product in kg/m^3.

According to de Groot and van der Sloot (1992), if the slope from Equation 3 is equal to 0.5, Pb release will be slow and diffusion will be the controlling mechanism. At a slope of approximately 1, the controlling leaching mechanism of Pb release is dissolution. In this case, the dissolution of material from the surface proceeds faster than diffusion through the pore space of the soil matrix. Occasionally, a soluble layer exists on the surface of the material. Initially, most of the soluble material on the surface will dissolve. This process, known as surface wash-off, typically results in a slope close to 0.

In most cases, following surface wash-off, contaminant release is diffusion controlled. Both dissolution and surface wash-off processes will result in the release of highly soluble materials. However, the material is not expected to be depleted during the dissolution process.

3. EXPERIMENTAL METHODOLOGY

3.1. Preparation of artificial soils

In this study, clays and fine quartz sand were combined in order to prepare artificial soils. Mixtures of clay and sand were used rather than pure clay to provide samples with a gradation more comparable to those of natural soils. Moreover, these mixtures are easier to compact than pure clay. Two types of clay minerals, kaolinite and montmorillonite, were selected in order to represent the two extremes of physicochemical clay behavior based on their surface area and cation exchange capacity (CEC). Therefore, the effects of a relatively non-reactive clay (kaolinite) on Pb immobilization were compared to those of a highly reactive clay (montmorillonite). Additionally, the amount of clay present was varied in order to evaluate its relative contribution to Pb immobilization. During the

leaching test, twelve types of specimens were tested; K15L0, K15L10, K30L0, K30L10, K5C25L0, K5C25L10, M15L0, M15L10, M30L0, M30L10, M5C25L0 and M5C25L10. Letters in the specimen designation show mineralogy, i.e., K: kaolinite, M: montmorillonite, C: class C fly ash, and L: quicklime. Numbers following the letters indicate the percent weight of the given attributes. Since the same type of fine quartz sand was added in all mixes, sand was not included in the specimen designation. Sand content is always complimentary to the clay or fly ash content on a 100% weight basis. For example, the specimen designation K15L10 stands for 15% kaolinite and 85% fine quartz sand at a treatment level of 10% quicklime added on a weight basis (clay-sand). Similarly, K5C25L10 stands for 5% kaolinite, 25% class C fly ash and 70% sand at a treatment level of 10% quicklime. An analytical grade lead oxide (PbO) was used as the source of Pb^{2+} contamination. This was added to the clay-sand mixes at a concentration level of 7000mg lead (Pb^{2+}) per kg of solid untreated soils.

3.2. ANS 16.1 tests

In this experiment, the ANS 16.1 method was modified by using a 0.014N acetic acid solution (pH = 3.25) instead of distilled water. This modification was performed in order to simulate the possible "worst case" leaching conditions of S/S waste being disposed of in a landfill environment. In this study, specimens with a 4.0±0.4cm height and a 4.70±0.05cm diameter were prepared by compaction (in accordance with ASTM D1557-91) at optimum water content (ASTM, 1993). Following compaction, all specimens were cured for 28 days in sealed sample bags at 20°C. Prior to the initiation of the specimen leaching test, the solids were immersed in distilled water for 30 seconds to rinse out any loose particles from the specimen surface. A nylon mesh harness was used in order to suspend each specimen near the centroid of the acetic acid solution in a polyethylene container. As specified by the ANS 16.1 method, the ratio of leachant volume (V_L) to the specimen external surface area (S) was retained at 10 ± 0.2cm. This ratio is maintained in order to minimize leachant composition changes as well as provide an ample concentration of extracted species for analysis (ANS, 1986). The leachate was collected and entirely replaced at designated time intervals (2, 7, 24, 48, 72, 96, 120, 456, 1128, and 2160 hours). The sampled leachate was separated using a 0.4 μm pore-size membrane filter. The concentrations of soluble Pb were analyzed with a Zeeman Furnace Atomic Absorption Spectrometer (AAS) (Varian SpectraAA-400).

3.3. Slurry tests

Two PbO-fly ash-quicklime slurries were prepared in order to elucidate the Pb immobilization mechanisms. Fly ash-quicklime was used rather than just fly ash or quicklime to prepare the slurries since the results from the ANS 16.1 tests showed that treatment was most effective in the presence of both fly ash and quicklime. The ratio of fly ash to quicklime was 2.5:1 (the same ratio used previously in artificial soils). In order to evaluate both high and low levels of Pb contamination, the concentrations of PbO used were 0.25% and 8% by weight of fly ash and quicklime. A liquid to solid ratio of 20:1 was used. All slurries were tumbled for 24 hours and then aged for 7 days. During the aging period, the slurries were shaken periodically. The leachate was filtered through a 0.4 μm pore-size membrane filter to separate solids from the leachate solution. The residue retained on the filter was air-dried and characterized by XRD analyses. The filtrate was analyzed for soluble Pb concentration. This filtration process was performed at 24 hours and then at 7 days.

4. RESULTS AND DISCUSSION

4.1. Cumulative release of Pb before and after S/S treatment

The cumulative Pb leachability values from untreated, fly ash treated, quicklime treated and quicklime-fly ash treated specimens are plotted as a function of leaching time in Figures 1 and 2.

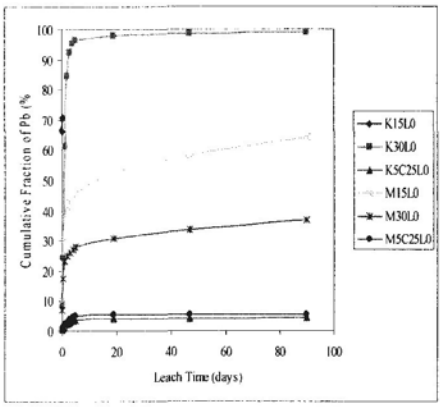

Figure 1. Cumulative fraction of Pb leached as a function of time for untreated and fly ash treated samples

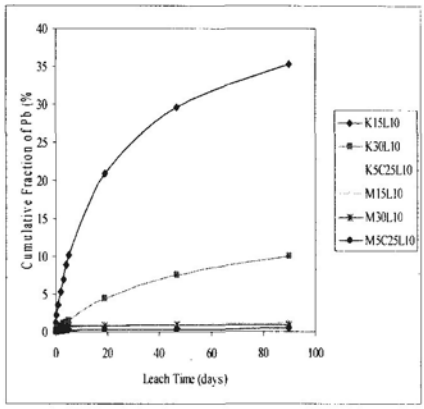

Figure 2. Cumulative fraction of Pb leached as a function of time for quicklime and quicklime-fly ash treated samples

The ultimate cumulative fractions of Pb leached from all samples upon test completion were summarized and presented in Table 1.

Table 1. Cumulative fraction of Pb leached (%) following test completion

Sample	Cumulative fraction of Pb leached (%)	Sample	Cumulative fraction of Pb leached (%)
K15L0	70.78	K15L10	35.3
K30L0	98.85	K30L10	9.99
K5C25L0	4.3	K5C25L10	1.00
M15L0	64.11	M15L10	1.15
M30L0	36.9	M30L10	0.87
M5C25L0	5.44	M5C25L10	0.39

In untreated samples, regardless of composition, an increased amount of clay (from 15% to 30%) led to decreased amounts of Pb leached (Figure 1 and Table 1). More specifically, in kaolinite-sand mixtures, even though the K15L0 sample disintegrated after 7 hours of testing, it was clear that a very high cumulative Pb fraction (71%) was leached out within this time period as compared to the K30L0 sample (24%) (Figure 1 and Table 1). Similarly, in montmorillonite-sand mixtures a significant (about 50%) reduction in Pb leachability was observed when clay content was increased from 15% to 30% (Figure 1 and Table 1). In untreated samples, montmorillonite was significantly more effective in reducing Pb leachability than kaolinite. This is probably due to the larger surface area and the greater cation exchange capacity (CEC) of montmorillonite.

Upon sole addition of fly ash (K5C25L0 and M5C25L0), Pb leachability was even further decreased (less than 6%) (Figure 1 and Table 1). This may be due to the formation of pozzolanic reaction products such as calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH). Ricou-Hoeffer et al. (2001) have shown that the formation of CSH, as a result of fly ash treatment, plays a role in the removal and stabilization of metallic cations. Therefore, it is possible that these pozzolanic reaction products may contribute to Pb immobilization by sorption and/or chemical inclusion.

Upon quicklime treatment, Pb leachability was significantly reduced in all samples. Even though the K15L0 sample disintegrated after 7 hours of testing, results from the K15L10 sample, within the same time period, showed significant Pb reduction (more than 60%) (Figures 1 and 2 and Table 1). Moreover, Pb leachability was reduced by approximately 90% in the K30L10 sample, as compared to the K30L0 sample (Figures 1 and 2 and Table 1). Lead leachability was also significantly reduced, by more than 60%, in the M15L10 sample versus the M15L0 sample. A reduction of approximately 36%

in Pb leachability was observed in the M30L10 sample versus the M30L0 sample. Samples containing montmorillonite (M15L10 and M30L10) showed very low Pb leachability (less than 1.2%) as compared to samples containing kaolinite (K15L10 and K30L10) (Figures 1 and 2 and Table 1).

Lead leachability was further decreased in quicklime-fly ash treated samples (K5C25L10 and M5C25L10). This indicated that Pb release can be more effectively reduced by using both quicklime and fly ash rather than quicklime alone.

Among all treated samples, Pb immobilization was most effective in the M5C25L10 sample (0.39% Pb release) and least effective in the K15L10 sample (35% Pb release)(Figure 2 and Table 1).

4.2. The controlling leaching mechanisms and effectiveness of quicklime, fly ash and quicklime-fly ash treatment

The controlling leaching mechanisms were evaluated by using a diffusion model (Equation 3) developed by de Groot and van der Sloot (1992). All slope and R^2 values obtained from the diffusion model are presented in Table 2.

For untreated samples (K15L0, K30L0, M15L0, and M30L0), slope values ranged from 0.05 to 0.31 (Table 2). This shows that surface wash-off appeared to be the main controlling leaching mechanism. However, the slope values increased to approximately 0.4 for fly ash treated samples (K5C25L0 and M5C25L0 samples) (Table 2). This indicates that diffusion was the controlling mechanism for Pb release in the fly ash treated samples. Upon quicklime treatment, slope values ranged between 0.51 and 0.64, except for the M15L10 sample where the slope was slightly higher at 0.71 (Table 2). These slope values suggest that Pb release was controlled by diffusion.

Table 2. Regression analyses results for Pb release.

Sample	Slope	R^2
K15L0	0.05	-
K30L0	0.31	0.68
K5C25L0	0.43	0.88
M15L0	0.21	0.77
M30L0	0.19	0.77
M5C25L0	0.4	0.86
K15L10	0.51	0.99
K30L10	0.6	0.98
K5C25L10	0.64	0.86
M15L10	0.71	0.92
M30L10	0.63	0.82
M5C25L10	0.6	0.95

Table 3. Mean effective diffusion coefficients (D_e) and Leachability indices (LX).

Sample	Mean De (cm^2/s)	Mean LX
K15L0	6.12E-06	6.55
K30L0	6.07E-07	7.73
K5C25L0	6.84E-10	9.74
M15L0	2.24E-07	7.76
M30L0	1.02E-07	8.07
M5C25L0	1.59E-09	10.04
K15L10	1.02E-08	8.07
K30L10	3.62E-10	9.57
K5C25L10	4.15E-11	11.02
M15L10	5.55E-11	10.33
M30L10	8.98E-13	12.64
M5C25L10	4.84E-12	11.98

Overall, the results obtained indicate that Pb release from quicklime and/or fly ash treated samples was mainly controlled by diffusion. Numerous researchers have previously reported this conclusion. Côté and Constable (1987) confirmed that diffusion was the main controlling leaching mechanism for Pb release in fly ash-lime treated waste. Andrés et al. (1995) have also demonstrated that diffusion was the dominant mechanism governing Pb release in stabilized steel foundry dusts.

Diffusion coefficients (D_e) and LX values (defined by Equations (1) and (2), respectively) were computed and are listed in Table 3. The diffusion coefficients (D_e) from treated samples were significantly lower than those from untreated samples.

Upon quicklime treatment, mean D_e values ranged from 1.02×10^{-8} (cm^2/sec) to 8.98×10^{-13} (cm^2/sec) (Table 3). Quicklime-fly ash treated samples (K5C25L10 and M5C25L10) had D_e values of 4.15×10^{-11} (cm^2/sec) and 4.84×10^{-12} (cm^2/sec), respectively (Table 3). According to Nathwani and Phillips

(1980), diffusion coefficients generally range from 10^{-5} cm^2/sec (very mobile) to 10^{-15} cm^2/sec (immobile). Therefore, it can be concluded that Pb mobility was significantly reduced upon treatment. More specifically, the K15L10 and K30L10 samples showed a D_e decrease of two and three orders of magnitude, compared to the K15L0 and K30L0 samples, respectively. A similar decrease was observed in the M15L10 and M30L10 samples compared to their respective untreated samples. The amount of clay also resulted in a reduction of D_e values for kaolinite- and montmorillonite-sand mixtures. The observed reduction was more pronounced upon quicklime treatment. Specifically, 30% kaolinite and montmorillonite samples showed D_e values two orders of magnitude less than their 15% counterparts.

In samples only treated with fly ash (K5C25L0 and M5C25L0), D_e values were also lowered by more than two orders of magnitude, compared to untreated samples (K15L0, K30L0, M15L0, and M30L0). This decrease was even more pronounced upon quicklime addition (K5C25L10 and M5C25L10), especially for M5C25L10 sample, where a decrease of three orders of magnitude in D_e was noted.

The type of clay was found to be an important factor which affected Pb leachability. A more pronounced reduction in Pb leachability was observed in montmorillonite samples than kaolinite samples. This is most likely due to the larger surface area and the greater CEC of montmorillonite.

Since LX values from most treated samples were higher than 9, most samples can be considered acceptable for "controlled utilization". The only exception was the K15L10 sample with an LX value of approximately 8.1. Therefore, the treatment of Pb contaminated soils with quicklime and/or fly ash mixtures was effective in immobilizing Pb.

4.3. Pb immobilization mechanisms

In the low contamination slurry (0.25% PbO), four major minerals were identified by XRD: portlandite - $Ca(OH)_2$, quartz - SiO_2, dolomite - $CaMg(CO_3)_2$, Periclase - MgO and calcium aluminum oxide sulfate hydrate - $Ca_4Al_2SO_{10}{\bullet}16H_2O$. The main difference identified after 7 days of aging was the formation of $Ca_4Al_2SO_{10}{\bullet}16H_2O$. The peak intensity of this mineral significantly increased after aging. Soluble Pb concentrations after 1 day and 7 days were 3.5 ppm and 2.9 ppm, respectively.

In the high contamination slurry (8% PbO), six major minerals were identified by XRD: portlandite, quartz, dolomite, periclase and glaucophane – $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$. The formation of lead silicate (Pb_2SiO_4) was identified, but could not be confirmed, using its two strongest peaks at d-space values 2.87 and 3.13. Confirmation of this formation was not possible because it shares these two peaks with portlandite and dolomite. The formation of litharge (PbO), the Pb source, was identified after 1 day of mixing. However, it was not observed after 7 days of aging. This was probably due to the limited solubility of PbO which results in a slow release of Pb. After aging, the intensity of dolomite and glaucophane peaks increased. Soluble Pb concentrations after 1 day and 7 days were 945 ppm and 360 ppm, respectively.

Overall, no evidence of pozzolanic reaction products such as CSH and CAH was observed by XRD in fly ash-quicklime slurries. Therefore, both the soluble Pb concentration and XRD results from the high contamination slurry indicate that lead silicate may be the reaction product most closely associated with a decrease in soluble Pb concentration. Palomo and Palacios (2003) found a different type of lead silicate (Pb_3SiO_5) when they studied fly ash contaminated with 3.125% Pb. Moulin et al (1999) also suggested that Pb can be retained through Si-O-Pb bonds.

5. CONCLUSIONS

Pb leachability in quicklime-based S/S of artificial soil samples was evaluated by performing semi-dynamic leaching tests. The specific conclusions pertaining to the results presented herein can be drawn as follows:

1. In all untreated samples, the amount of clay appears to be an important factor affecting Pb leachability. This indicated that sorption to the clay was most probably the prevailing mechanism for Pb immobilization.

2. The type of clay also had an important effect on Pb leachability. Montmorillonite samples showed a pronounced reduction in Pb leachability compared to kaolinite samples. This is most probably due to the larger surface area and the greater CEC of montmorillonite.

3. The sole addition of fly ash resulted in a significant decrease in the amount of Pb leached (reduced De and increased LX), compared to both untreated kaolinite and montmorillonite samples.

4. Quicklime treatment was successful in significantly reducing the mobility of Pb (reduced De and increased LX), thus allowing only trace levels to be released.

5. Upon quicklime and/or fly ash treatment, the controlling leaching mechanism of Pb appeared to be diffusion. In untreated samples, however, the controlling leaching mechanism was found to be wash-off.

6. Most treated samples were acceptable for "controlled utilization" based on their LX values.

7. No pozzolanic reaction products were identified using XRD analyses. Therefore, Pb immobilization was not controlled by inclusion/sorption to pozzolanic reaction products.

8. The controlling Pb immobilization appeared to be precipitation. The formation of Pb_2SiO_4 (a very insoluble compound) was observed, though not confirmed, by XRD analyses.

6. ACKNOWLEDGMENTS

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Remediation of a Heavy Metal Contaminated Soil by a Rhamnolipid Foam

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ABSTRACT

Studies were initiated with a rhamnolipid biosurfactant in columns to simulate in situ conditions. The biosurfactant was injected in the form of a foam and liquid solutions. The study was conducted in three steps: evaluation of the foam characteristics, investigation of pressure buildup by foam injection and removal of metals by the foam. Foam quality of the rhamnolipid was shown to vary between 90 and 99% with stabilities from 17 to 41 minutes. Pressure build up was then evaluated with different flow rates, foam quality and biosurfactant solutions. Metal removal was then evaluated from a sandy soil contaminated with 1,710 ppm of Cd and 2,010 ppm of Ni. Maximum removal was obtained by a foam produced by 0.5% rhamnolipid solution after 20 pore volumes. Removal efficiency for the biosurfactant foam was 73.2 % of Cd and 68.1% of Ni. For the biosurfactant liquid solution, 61.7% Cd and 51.0 % were removed. Distilled water removed only 18 % of both Cd and Ni. Liquid solutions with concentrations of 0.5, 1.0 and 1.5% rhamnolipid at pH values of 6.8, 8 and 10 were also evaluated for their ability to remove metals but they did not show any significant beneficial effects. Therefore, rhamnolipid foam may be an effective and non-toxic method of remediating heavy metal contaminated soils. Further efforts will be required to enable its use at field scale.

INTRODUCTION

Many common heavy metals are released into the environment due to a wide variety of domestic and industrial effluents. An example is cadmium which is rarely found in natural material but its presence is due to various sources including metal processing, batteries, plating, paints, fertilizers, waste disposal and fuel burning. Another heavy metal, nickel, is emitted by nickel mining, nickel processing, wastewater discharges, oil or coal burning and incineration. Cameron (1992) pointed out that the Environmental Protection Agency (EPA) placed heavy metals on the list of priority because they are extremely hazardous. Another problem is that the metals can reside in the environment for hundreds of years or more after they are emitted as they are not biodegradable.

Soil flushing can be used to remediate contaminated soils. However, efficient and cost effective methods for dealing with metal contaminants are still required (Mulligan et al., 1999). Biological removal of heavy metals has been the subject of several studies. Mulligan et al. (2001) presented the results of a study showing that heavy metals could be removed from sediments by biosurfactants. They reported that up to 65% of the copper could be removed from the sediments by rhamnolipids. Mulligan et al. (1999) also used biosurfactants to remove heavy metals from oil contaminated soil. In their study, they found that a combination of 2% rhamnolipid with 1% NaOH provided maximum removal of 25% of the copper from the soil. This combination was also effective for the removal of copper from a low-grade oxidized ore (Dahr Azma and Mulligan, 2003).

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

Biosurfactants are biologically-produced surfactants by bacteria, or yeasts from various substrates such as sugars, oils, alkanes and wastes. They are grouped as glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, polymeric and particulate compounds. Biosurfactants have potential due to their low toxicity and biodegradability. The biosurfactant that was used in this study, an anionic rhamnolipid, is from the glycolipid group and was produced by the bacteria *Pseudomonas aeruginosa* (Hitsatsuka, 1971; Tsujii, 1998). There are four types of rhamnolipids (Tsujii, 1998). Type 1 (R1) is L-rhamnosyl-β-hydroxydecanoyl-β-hydroxydecanoate of molecular mass 504 Da. Type II (R2) is L-rhamnosyl-β-L-rhamnosyl-β-hydroxydecanoyl-β-hydroxydecanoate of molecular mass 650 Da. The other two types of rhamnolipids contain either two rhamnoses attached to β-hydroxydecanoic acid or one rhamnose connected to the identical fatty acid. Rhamnolipid type I and type II are suitable for soil washing and heavy metal removal. (JENEIL, 2001). Surface tensions of 29 mN/m are characteristic of these compounds.

The properties of surfactant solutions are modified by simultaneous injection of surfactant and air to form foams (Chowdiah et al., 1998). Surfactant foam technology has been investigated to remove nonaqueous phase liquids (NAPLs) (Peters et al., 1994; Kilbane et al., 1997; Rothmel et al., 1998; Jeong et al., 2000) and pentachlorophenol (PCP) (Mulligan and Eftekhari, 2003) from contaminated soils. Foams enhance the flooding efficiency of surfactant flushing even in a heterogeneous porous medium, resulting in high removal efficiencies (Jeong et al., 2000).

In this study, experiments were performed to evaluate the foam quality and stability of rhamnolipid solutions. Next, the pressure gradient build-up in the soil column during foam passing through the column was investigated. Then, experiments were conducted to evaluate the feasibility of rhamnolipid foam enhanced remediation of cadmium and nickel contaminated soil. Comparisons of the metal removal abilities were made between the rhamnolipids in the liquid and foam forms.

MATERIALS AND METHODS

Materials

The biosurfactant, JBR425 (mixed rhamnolipids), was obtained from JENEIL Biosurfactant Co. (USA). The characteristics of the surfactants are described as follows. The rhamnolipids used in this study were biosurfactants type I and type II from the glycolipid group made by *Pseudomonas aeruginosa* with the trademark JBR425 from Jeneil Biosurfactant Co. JBR425 is an aqueous solution of rhamnolipid at 25% concentration. It is produced from a sterilized and centrifuged fermentation broth. Two major types of rhamnolipids, RLL (R1) and RRLL (R2), are present in the solution. Several tests (Organization for Economic Cooperation and Development, OECD) done by the manufacturer and independent laboratories (OECD 209ASRIT, OECD 301D and OECD 202) show the degree of biodegradability and toxicity of JBR425 meet the EPA requirements (JENEIL, 2001). The critical micelle concentration (CMC) was found to be 0.035 g/L through conductivity measurement at various dilutions (Dahr Azma and Mulligan, 2003). This value is equivalent to 0.003% rhamnolipid. Therefore, for all experiments, a concentration above the CMC was used to ensure the formation of micelles.

The soil sample, obtained from a site near Concordia University, was crushed with a mortar and pestle after drying at 105°C for 48 hours. It was then contaminated artificially in the lab. Metal salts ($NiCl_2.6H_2O$ and $Cd(NO_3)_2.6H_2O$) were dissolved with distilled water to give concentrations of 4000 mg/L of Cd and 4000 mg/L of Ni. The solutions

were then added together into the soil sample (without adjusting the pH value). The soil sample was left in the solution over two weeks, and then the suspension was shaken on a wrist action shaker at 60 oscillations/min for 24 hours at room temperature (25.0 ± 0.2 °C), and subsequently centrifuged. The supernatant was discarded and the contaminated soil was dried in an oven at 105 °C for 48 hours.

Experimental Setup

All experiments were conducted at room temperature (25.0 ± 0.2 °C). The experimental setup is shown schematically in Figure 1. A plastic column (L = 25 cm, D = 2.5 cm) with circular porous stone plates, was used for foam generation in the presence of the surfactant solution and air. A pump fed the surfactant solution and two flow meters (flow meter I and flow meter II) controlled the flow of the solution and the air before entering the foam generation column. Varying of the flow rates of the surfactant solution and air enabled control of the foam quality and generation rate. The foam exiting the column was sampled for quality and stability analyses after it reached a uniform and steady state in terms of bubble size and appearance. In each experiment, three 50 ml samples of the generated foam were taken and left until all of the bubbles collapsed. The time required for collapsing half of the foam was an indicator of the foam stability and the total gas volume per total volume of the foam sample at atmospheric pressure was calculated to indicate the foam quality.

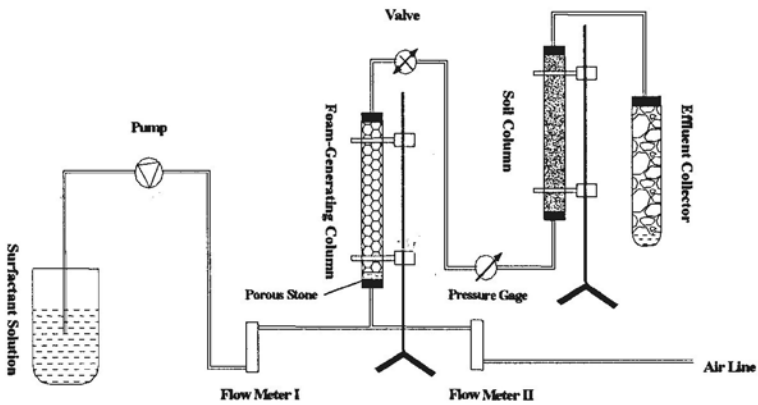

Figure 1. Schematic Setup of the Column Experiments

The soil column (L = 25 cm, D = 4 cm) was connected to the foam-generation column (Figure 1). The soil was packed uniformly in 5 layers. The total weight of the soil was 430 g (± 5 g). A pressure gauge was installed upstream of the soil column to measure the inlet pressure. The pore volume of the column was measured by saturating the soil column at a pressure gradient close to zero. A two-way valve was placed before the column to prevent injection of foam into soil before its uniformity and steady-state quality was reached. It also was used for taking foam samples before injection into the soil.

The pressure gradient build-up in the column was recorded while changing the foam quality and the foam flow rate as well as the concentration of the biosurfactant solution. Pressure was measured by a pressure gauge after the foam column and before the soil column as indicated in Figure 1. Pressure values were then divided by the column length to determine the pressure gradient.

Foam with controlled quality and flow rate was used to investigate the metal removal efficiencies. The foam exiting the soil column was collected for analyzing the metal concentration. Samples were collected according to the number of pore volumes passed through the contaminated soil and were left to collapse completely.

All studies were conducted at various initial pH values (6.8, 8.0, and 10.0) while maintaining a 0.5% rhamnolipid solution. The pH value of the solutions was adjusted by adding 1 N NaOH. To compare with results for the foam experiments, surfactant solutions without foam generation were also pumped through the column. Distilled water with adjusted pH values were used as the controls. Columns flushed by the rhamnolipid foam were chosen to evaluate the mass balance after the experiments. At the end of the experiments, samples of soil were taken from the flushed column for analysis for heavy metal concentrations. The results were compared with the results from effluent analyses to verify the metal material balances.

Analytical Methods

To measure the metal concentrations in the soil, samples were digested with 6 N HCl and then analysis was performed using an Atomic Absorption (AA) Spectrophotometer (PERKIN ELMER, AAnalyst 100). The characteristics of the contaminated soil were measured by US EPA or ASTM methods (APHA, 1995) and are listed in Table 1. Cationic exchange capacity (CEC) determination was according to the method of Gillman and Sumpter (1986).

Table 1. Characteristics of the Contaminated Soil

Parameter	Value
Organic matter content (%)	1.0
Cation Exchange Capacity (meq/100g)	7.9 (pH 7.0)
Hydraulic conductivity (cm/s)	0.02
Heavy metal content (mg/kg dry soil)	
Cd	1,706
Ni	2,010
Sieve analysis results	84.7% sand and 15.3% silt
Specific gravity	2.43

Heavy metal concentrations were measured in the column effluent by atomic adsorption spectrometry after acid (6 N and/or 12 N HCl) digestion to solubilize completely the metals and to hydrolyse the surfactants that can interfere with the analyses. The experiments were performed in triplicate and the results for the effluent metal concentrations did not vary more than 10%. The metal removal efficiency was determined by dividing the metal content in the effluent by the initial metal contents in the soil and multiplying by 100%. All results are presented as percent metal removal.

RESULTS AND DISCUSSION

Evaluation of Foam Quality and Stability

The effect of rhamnolipid concentration and pH on foam quality and foam stability was evaluated. Varying the pH from 6.8 to 10 by addition of concentrated NaOH had an insignificant effect on foam stability at all levels of foam quality (90, 95 and 99%). Therefore, only the values at pH 8 are shown in Figure 2. Increasing the rhamnolipid concentration however, from 0.5% to 1.5% increased the foam stability from 18 up to 32 minutes at a 90% foam quality and a pH of 8. At a high foam quality up to 99% foam stability increased from 17 minutes and 33 minutes at a pH of 8 while the concentration of the rhamnolipid solution varied from 0.5% to 1.5%.

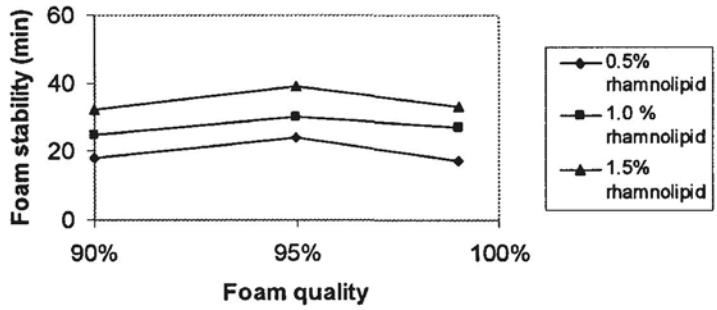

Figure 2. Effect of foam quality and rhamnolipid concentration on foam stability

Pressure Gradient

Experiments were performed on the foam injected into the soil column to determine the pressure build-up at various flow rates and concentrations of rhamnolipid solutions. The experimental results showed that the pressure gradient build-up in the soil column increased as quality decreased from 99% to 90%. Increasing the flow rates from 10 ml/min to 30 ml/min also increased the pressure gradient in an almost linear fashion at a 0.5% rhamnolipid concentration (Figure 3). The pressure gradient values obtained for the 99% quality foam were similar to those determined for the 1% rhamnolipid solution in the fine sand (Mulligan and Eftekhari, 2003) where it was recommended that flow rates do not exceed 10 to 15 ml/min. Flow rates were thus maintained at 5 ml/min for all experiments.

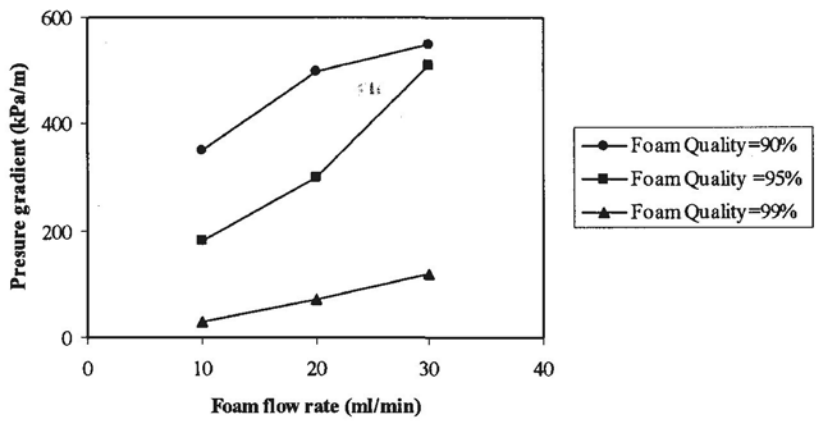

Figure 3. Pressure build up in the soil column as a function of foam quality and foam flow rate

The average hydraulic conductivity of the foams was calculated for each foam quality based on the Darcy's equation for the various pressure readings and flow rates in Figure 3:

Hydraulic conductivity (cm/s)

$$= \frac{Foam\ \ flow\ \ rate}{cross-sectional\ \ area} \Big/ \left[\frac{pressure\ \ /(water\ \ density\ \ x\ \ gravity\ )}{column\ \ height}\right]$$

The elevation head is much smaller than the pressure head and thus was not included in the equation. For a 90% foam quality, the average hydraulic conductivity was 4.1×10^{-4} cm/sec, for 95%, it was 1.5×10^{-4} cm/sec and for 99%, it was 2.9×10^{-3} cm/sec. Increasing foam quality decreases substantially the hydraulic conductivity. All these values are lower than the hydraulic conductivity of water which was 0.02 cm/sec (Table 1). This higher viscosity will allow better control of the surfactant mobility during in situ use.

Heavy Metal Removal

A series of experiments was performed using foam generated by 0.5% rhamnolipid solutions at different pH values (6.8, 8.0, and 10.0) to investigate the metal removal efficiencies. The best removal rate, 73.2% of the Cd and 68.1% of the Ni, was achieved by adjusting the initial solution pH value to 10.0, after 20-pore-volume flushing (Figure 4). Lower amounts of both metals were removed at the lower pH values.

The possible mechanisms for the extraction of heavy metals by surfactants include ion exchange, precipitation-dissolution and counterion association (Rosen, 1979; Doong et al., 1998). It was postulated that the metals were removed by forming complexes with the surfactants on the soil surface, being detached into the soil solution due to the lowering of the interfacial tension, and hence associating with surfactant micelles. As expected, the anionic surfactant gives good results because the cationic metals have an affinity for the negatively charged surfactants, and also the biosurfactant could enable more metal removal due to the more effective interfacial surface tension lowering. Solutions with high pH values seem to work better. Probably, this could be the result of a combination of the enhanced metal solubility and surfactant activity with the increase of the solution pH value.

As there is a significant organic matter content in the soil (1%), it is possible that the higher pH values enable the release of the metals from the organic matter. Both nickel and cadmium are known to complex with organic matter in addition to oxides (Cameron, 1992). Previously, it had been shown that copper that complexes with organic matter and zinc which was associated mainly with oxides can be removed from a contaminated sediments by the rhamnolipid (Mulligan et al., 2001). Nickel tends to behave in a manner similar to copper and cadmium similar to zinc.

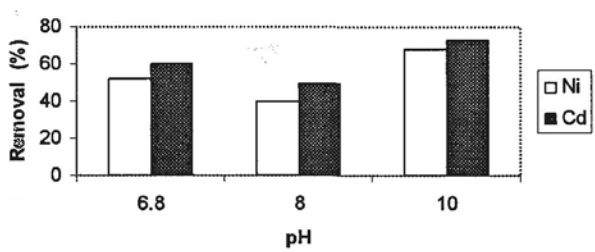

Figure 4. Effect of pH on metal removal by a 0.5% rhamnolipid foam.

Figure 5 illustrates the metal removal as the foam flushing through the column. It can be observed that the cumulative metal removal increased sharply within the first 5 pore volumes. Then it remained relatively constant when more foam passed through.

Metal removal by surfactant solutions and foams were compared (Figure 6). It was observed that over 11% more of the Cd and 15% more of the Ni were removed by rhamnolipid foam than the rhamnolipid solution with the same concentration of

rhamnolipid. Transfer from aqueous solution to foam greatly enhanced the metal removal efficiencies by the same concentration of surfactant. Because the transfer leads to a more uniformity and efficient contact of surfactant with the metals, and the injection of surfactant and air at the same time effectively restrained channeling in the column. The surfactants used to generate the foam can also improve soil wettability and desorption (Chowdiah et al., 1998).

The control was distilled water (pH adjusted to the same pH of the surfactant foam) to determine the metal removal without additives, which removed much lower levels of Cd and Ni than the liquid and foam solutions. It worked mainly by physical means and removed the metals that were loosely bound on the surface of the soil particles.

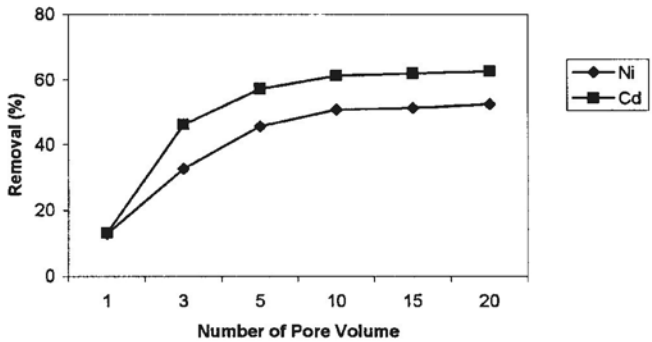

Figure 5. Metal removal by a 0.5% rhamnolipid foam at pH 6.8

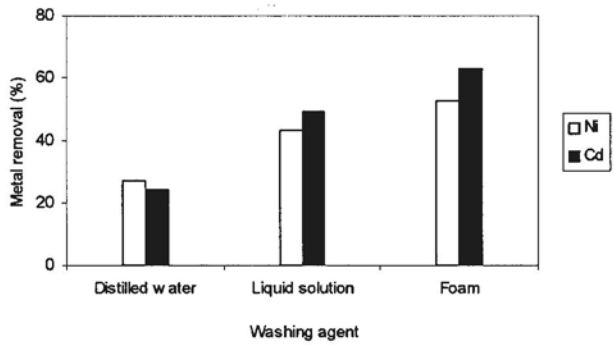

Figure 6. Comparison of liquid and foam 0.5% rhamnolipid solutions for metal removal (pH 6.8)

Soil samples were taken from each of the chosen columns flushed by rhamnolipid foam after the experiments. Heavy metal analysis was performed and showed that the mass balances were good during the experiments. Only 1.6% of the Cd and 0.4% of the Ni were not accounted for which is expected during the experiments.

CONCLUSIONS

This study demonstrates that rhamnolipid foam technology can be used successfully in the remediation of heavy metal contaminated sandy soil. The use of biosurfactant foam may be a better candidate for the remediation of contaminated sites because biosurfactants are of low toxicity and high biodegradability. Extensive future experiments in which both the soil and the foam are involved have to be done to investigate the influence on the removal

efficiencies of various factors such as soil matrix characteristics, the metal speciation as well as the surfactant type and concentration. The effect of co-contamination with organic contaminants such as solvents and hydrocarbons should also be investigated. Also further research is needed to evaluate the effectiveness of this technology in field applications.

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Assessment of the Stability of a Dispersive Soil Treated by Alum

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ABSTRACT:
Dispersive soils have been responsible for failures in several geotechnical and geo-environmental projects. Usually chemical treatments are used to overcome the dispersivity performance of these types of soils. Alum (alumina sulfate $\{Al_2(SO_4)_3.18H_2O\}$) is commonly used for the treatment of these types of soils. The interaction of soil-additives during the treatment process is a physico-chemical phenomenon. The main objective of this research is to study the fundamental mechanism of soil-alum interaction. A bentonite sample with different concentration of sodium sulfate (Na_2SO_4) is used for the study. The results obtained indicate that two different phenomena are responsible for soil improvement – ion exchange and pH effects. Replacement of sodium ions by alumina ions in the double layer of the clay particles results in a decrease in the thickness of the double layers associated with the particles. Physico-chemical evaluations indicate that reduction of pH due to the application of alum is a reversible process. Drying of the treated soil will result in an increase in the pH of the treated soil, creating a situation where part of the benefit from the alum treatment will be obviated. Increased quantities of alum are needed if wet-dry cycles are excessive. Mechanical experiments also indicate that the application of 1.5% alumina sulfate causes a noticeable decrease in dispersivity potential.

INTRODUCTION

Dispersivity is a physico-chemical process which is mainly affected by the type of soil minerals and chemical properties of the soil pore fluid (Yong and Warkentin 1966, Sherard et al. 1976,Yong and Sethi 1977, Penner and Lagaly 2001, Goodarzi 2003). Based on the effect of pore fluid on the dispersivity behaviour of soils, it can be said that once a dispersive soil is exposed to water, clay particles may disperse and remain as suspended particles. For this reason, the formation of dispersivity may cause the formation of piping phenomena in earth dams, deterioration and demolition of roads (Nevels 1993), and the erosions of compacted soils of landfill clay liners (Tallin 1984, Goodarzi 2003). Based on the importance of dispersivity phenomenon in the above-mentioned projects, it is necessary to study the dispersivity phenomenon from a physico-chemical point of view. In many geotechnical and geoenvironmental projects, a simple way to prevent the problems associated with dispersive soils is to replace them with another soil. However, in many cases, due to the limitation of the projects, it is necessary to improve the dispersive soil and re-use it after improvement. By and large, one of the common methods for dispersive soil improvement is by the use of lime, gypsum, and alumina sulfate (Ryker 1977). While more attention is given to the effect of lime and gypsum on the performance of dispersive soils, less attention is given to the interaction of alumina sulfate and soils. Alumina sulfate (alum) may improve dispersive soil performance due to the pH effect and ion exchange process. The main objective of this study is to assess

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the stability of a dispersive soil treated by alum as an additive. In this respect, attention is given to the variation of pH, ion exchange and hydraulic conductivity of improved dispersive soil. This latter point is important in terms of earth dams and landfill clay liners.

MATERIALS AND METHODS

Since bentonite soil is used in many geotechnical and geoenvironmental projects, it is used as the soil material in this research. It is reported that bentonite may be used as a material for earth dams (Koch 2002), in clay liners of landfills (Yong et al. 1992, Yong 2003), in radioactive waste disposal projects (Pusch and Schomburg, 1999), and as clay barriers in lagoons (Koch 2002). Tables 1 and 2 present some of the geo-environmental characteristics of bentonite used in this study. The range of sodium sulfate quantity was fixed within 1 to 100 meq/L. This is because dispersivity behaviour usually occurs with low electrolyte concentration (Yong et al. 1979, Guler and Balci 1998, Chen et al. 1990). Double hydrometer testing (ASTM 1992) in each soil-electrolyte mixture was performed to quantify the dispersivity of the artificial sample. Following this process, with the application of a hydrometer test for different samples having different electrolyte, the variation of particle size distribution was evaluated. Percent dispersion was defined as the ratio of clay size particles (0.005 mm); with no additive to the same clay size particles when mechanical and chemical agitation were used. The artificial dispersive sample was defined as a sample having at least 40% dispersion ratio (Deker & Dunnigan 1977). The artificial dispersive samples with the highest dispersivity percentage were used in the rest of the research.

Determination of Required Alumina Sulfate for Improvement of Dispersive Soil

To determine the amount of required alumina sulfate to improve and control the dispersivity of soil samples, several similar dispersive samples were prepared which had the maximum dispersivity, according to the required quantity of sodium sulfate to provide the maximum dispersivity. Using this maximum dispersivity condition, a series of soil-electrolyte mixtures with the soil water ratio of 1:50 were prepared. After equilibrium condition, as described before, different percentages of alum were added to these samples. Double hydrometer testing was performed on these samples to quantify the dispersivity condition.

To methods of drying were used in this study: air and oven drying. For the air-drying process, each sample was kept in 45° centigrade for 48 hours (called the "A.D." samples). After this period, samples were sieved through mesh #200 to provide a uniform sample. For the oven drying process, after the samples were prepared they were kept for 24 hours in 110°centigrade oven (called oven dried or "O.D." samples). Then these samples were sieved through #200 to provide uniform conditions.

Evaluating the Effect of Alum on Physical Properties of Dispersive Soil

For this purpose, the compressibility characteristics, plasticity characteristics, and hydraulic conductivity of dispersive samples with and without alum were evaluated. For this purpose, after preparing the dispersive soil, different percentages of alum were added to these samples. Samples were kept in the 1000 mL laboratory flask for 96 hours. During this period, samples were mixed for 15 minutes every day. Following the completion of equilibrium conditions, the samples were poured in specific long tubes with the length of 300 mm and 70 mm diameters (Mesri and Olsen, 1971, Ouhadi and Sedighi 2003). Samples were loaded with the application of 25 Kpa to provide undisturbed dispersive soil. This was performed by using an oedometer mold with a diameter of 50mm and height of 20mm. By performing consolidation testing on these prepared samples, the compressibility and hydraulic conductivity of samples could then be evaluated.

RESULTS AND DISCUSSIONS

Figure 1 shows the dispersivity variation of the bentonite sample artificially dispersed with different percentages of sodium sulfate. As can be seen, by increasing the concentration of sodium sulfate, the dispersivity potential of soil increased up to 5-meq/L sodium sulfate. However, following an increase of sodium sulfate above this point, the quantity of the percentage of dispersion decreases. The results confirmed the occurrence of dispersivity in low electrolyte concentration as presented by other authors (Yong et al. 1979, Abend and Lagaly 2000, Penner and Lagaly 2001). The formation of the dispersive structure after the addition of sodium ion can be attributed to the replacement of hydrogen ions by sodium ions in the double layer of clay particles (Chen et al. 1990). The maximum percentage of dispersion, presented in figure 1, is chosen for the rest of this research.

Variation of Dispersivity Percent Due to the Addition of Alum

Figures 2 presents the variation of dispersivity percent in the representative dispersive bentonite after the addition of different percentages of alum. As can be deduced from this figure, by adding 1.5 percent alum, the variation of dispersivity percent stabilizes. In fact, with the application of alum, the soil behaviour changes from dispersive structure to the more flocculated non-dispersive structure. Furthermore, the effects of alumina sulfate on the dispersivity of clay soils could be due to the pH effect, according to the following equation:

$Al_2SO_4 + Clay \longrightarrow Al[Clay] + H_2SO_4 \Longrightarrow$ A reduction in pH

Such a reduction in pH is an appropriate condition for enhancing the interaction of clay particles and electrolyte. A decrease in the double layer thickness happens and a change in soil fabric form is generally obtained (Yong and Sethi 1977, Yong et al. 1979).

Variation of Adsorption of Sodium by Clay Particles due to the Addition of Alum

Following addition of alumina sulfate, due to its solubility, the concentration of aluminum ions in the pore fluid increases. This increase accounts for the high tendency of these ions to replace sodium ions of the clay double layer. Since dispersivity is governed by the presence of adsorbed sodium ions, monitoring the variation of adsorption of sodium ions by clay particles can explain the fundamental mechanism of alum-soil interaction. Figure 3 shows the variation of sodium adsorption by clay particles for the representative dispersed bentonite at different concentrations of added alum. The results of this figure show that the artificially dispersed bentonite sample without alum as an additive has 46 percent adsorbed sodium. In these experiments, it can be observed that 46% of adsorbed sodium in the dispersive bentonite was decreased to almost zero percent of adsorbed sodium ions by the addition of 5 percent alum. By and large, this indicates the exchangeable phenomenon controls the dispersivity behaviour of the soil.

pH Variation of the Soil-Electrolyte in the Presence of Different Percentages of Alum

Figure 4 shows the results of pH monitoring of different artificial dispersed bentonite samples after equilibrium condition with added alum. It can be seen that with addition of alum, the pH concentration of soil-solution decreases from 10 to around 7.5. This reduction of pH decreases the extent of the oriented structure of clay particles to a relatively flocculated structure. This is due to the reduction in the repulsive force of clays. Such a reduction in pH can be attributed to the Gibse law, -- considering a possible evaporation of acids in different temperature and environmental conditions (Karger et al. 1973). In this aspect, artificial dispersed bentonites with different percentages of alum were monitored for pH variation with two different methods of drying. pH monitoring performed on three series of samples included: (1)-dispersive bentonite by sodium sulfate at different percentage of alum without any drying condition (simply called "As it is" samples), (2)-air-dried or "A.D." samples, (3)-

Table 1. Physical properties of bentonite.

Characteristic	Quantity measured
Liquid limit	314.5
Plasticity index	283
Soil classification	CH
Gs	2.79
Clay fraction%	72
Silt fraction%	23
Sand%	1
Optimum water content	23
Maximum Dry density (gr/cm^3)	1.56

Table2. Chemical Properties of Bentonite.

Characteristic	Quantity measured
pH (1:50, soil-water)	10
EC(dS/m) (1:50,soil-water)	0.64
Na^+ (cmol/Kg)	48.5
Ca^{2+}(cmol/Kg)	14.2
Mg^{2+} (cmol/Kg)	3.4
K^+(cmol/Kg)	2.1
CEC, (cmol/Kg)	68.2
SSA, (m^2/g)	418
Carbonate, %	8
Organic, %	<1%

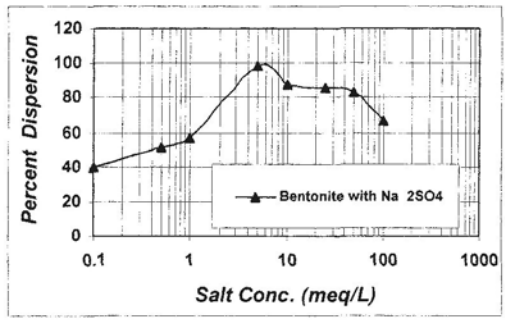

Figure1. Dispersivity variation of the bentonite sample artificially dispersed

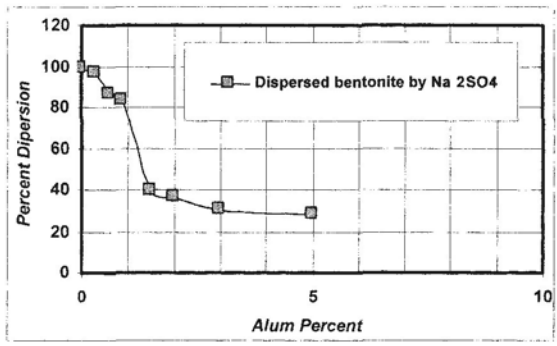

Figure 2. Dispersivity variation of the bentonite after the addition of Alum

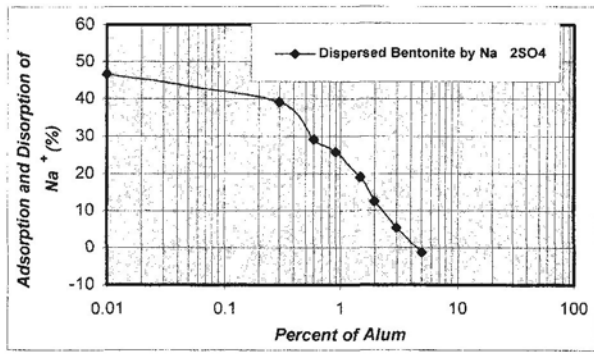

Figure 3. Sodium adsorption by clay particles, dispersed bentonite and alum

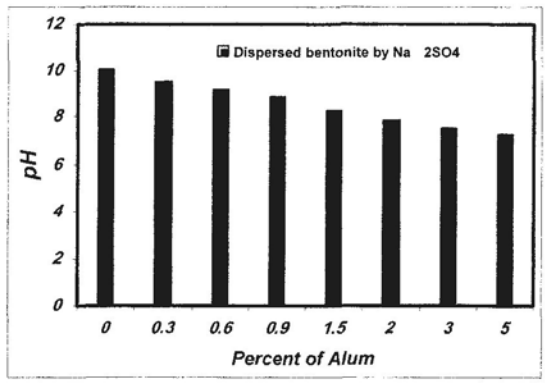

Figure 4. pH of artificial dispersed bentonite after the addition of Alum

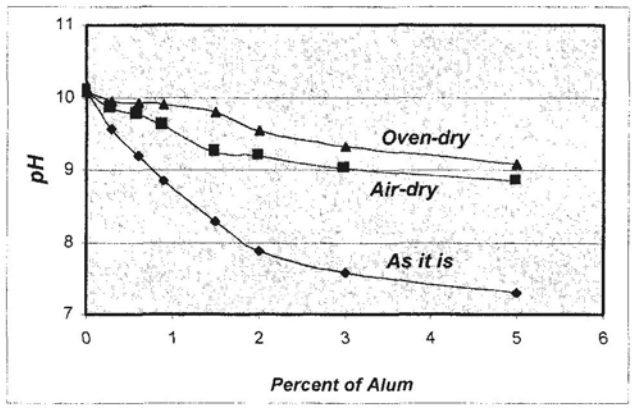

Figure 5. Effect of soil drying on pH variation

oven dried or "O.D." samples. Figure 5 shows the variation of pH for these three groups of samples. The results indicate that the drying process of dispersed bentonite causes a significant change in the pH variation of soil samples (almost 20 percent increase in pH). On the other hand, the oven drying process of dispersive samples causes about 25 % increase in pH. In fact, the drying process shows that one of the phenomena governing the controlling process of dispersivity behaviour is reversible. Due to this increase in soil pH, one may expect to face a change in the dispersivity potential of soil.

Further Evaluation of Dispersivity

Based on above mentioned pH effect on the dispersivity index of bentonite, another series of double hydrometer tests were performed on the "As it is", "A.D." and "O.D." samples. Figure 6 shows three dimension patterns of percentage of dispersivity, pH variation and the quantity of added alum for these three different series of samples. A drying process that causes an increase in pH, changes the un-dispersed sample to a dispersed sample. In other words, the drying of treated soil results in an increase in the pH of the treated soil, creating a situation where part of the benefit from the alum treatment will be obviated.

Physical Properties Variation Due to the Drying Process

Figure 7 shows the evaluation results of the liquid limit of different dispersed bentonite samples with different percentages of alum as an improving material. As can be seen in this figure, the addition of alum causes a decrease in the liquid limit of dispersive bentonite. Such a decrease is noticeable once the percentage of alum exceeds 2 percent. It is interesting to note that the addition of 5 percent alum decreases the liquid limit more than 50%. However, an increase in the liquid limit of samples following the drying process is obtained. These results correlate with the increase of pH of samples after the drying process as shown in Figure 5. Such behaviour can be attributed to the further increase in the thickness of the double layer after the drying process. A higher liquid limit of the sample after the drying process is a criterion for having higher water adsorption for this sample in comparison with the "As it is" sample. This is a point in which the dried sample may have a higher potential for water adsorption and consequently a higher potential for dispersivity.

Variation of Physico-Mechanical Characteristics of Soil After Application of Alum

For more investigation on this point, the permeability coefficients of improved dispersive samples are calculated based on the oedometer results (Figure 8). As can be seen from Fig. 8, in the dispersive bentonite sample and in improved samples the permeability coefficient decreases with the increase of the applied loading. This can be mainly attributed to the decrease of soil void ratio and an increasing density.

CONCLUDING REMARKS

Based on the presented results, it has been shown that the dispersivity potential of low electrolyte concentration increases due to repulsive forces overcoming attractive forces. With a further increase in sodium sulfate salt concentration, the dispersivity potential decreases.

The role of alum as an additive for controlling soil dispersivity can mainly be attributed to the pH and ion exchange effects. Such an application causes an improvement in soil dispersivity, and an increase in soil compressibility. However, the drying process causes a reversible pH effect in improved soil properties as a function of applied temperature for drying. As the quantity of applied alum increases, an increase in soil permeability is observed, due to the change of oriented structure to a more flocculated structure. Such an increase in soil permeability might cause differential settlement and cracking in compacted clay. From a

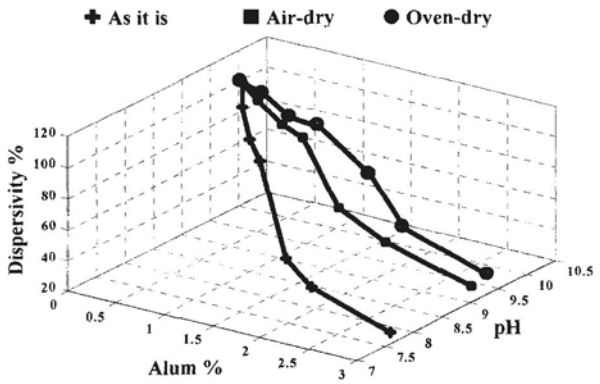

Figure 6. Three dimensions patterns of dispersivity, pH and quantity of alum

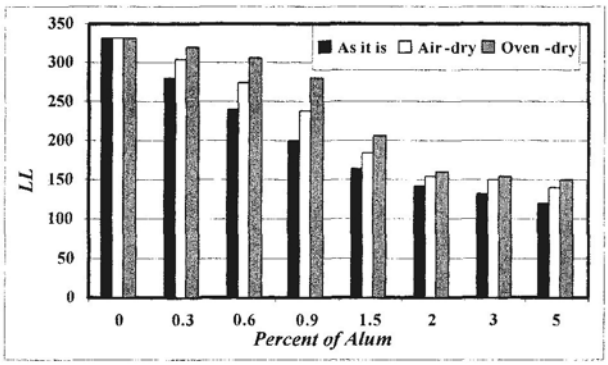

Figure 7. Effect of drying on the physical properties of samples

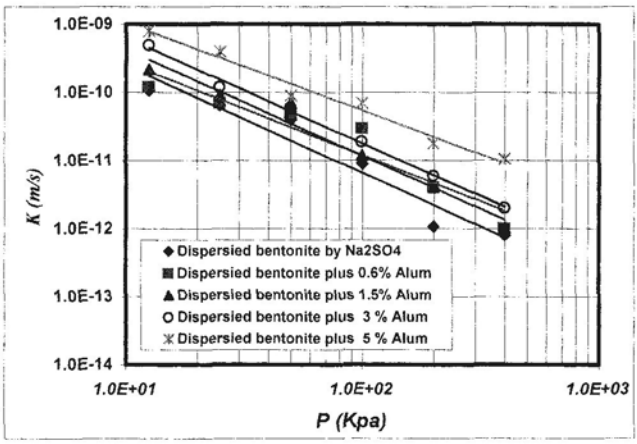

Figure 8. Permeability variations due to the increasing of density

geoenvironmental point of view, this might cause the possibility of contamination and an increase in contaminant movement in the clay liner.

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The Influence of Carbonation on the Behaviour of Cement-based Materials Used in Contaminated Land Treatment

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ABSTRACT
This paper details results of a preliminary investigation into the influence of initial heating followed by carbonation for accelerating the ageing of four cement-based grout mixtures used to treat contaminated soils. The four cement-based grouts differed in composition in relation to the binders in use. One of the grouts contained ash, the second ash and lime, and the third bentonite. The contaminants used comprised of compounds of five heavy metals (Pb, Cu, Cd, Ni and Zn) and paraffin oil. Samples were cured adopting an initial exposure period to elevated temperature followed by different durations of exposure to carbon dioxide (accelerated carbonation). Tests were conducted for strength, carbonated depth, leachate pH and leaching after 28 and 90 days of curing, with the control samples additionally tested after 180 days. The results suggested that the four grouts behaved differently under the exposure curing conditions. The initial exposure to elevated temperature generally had improved strength and leaching results and the exposure to different durations of carbon dioxide had an influence on the behaviour of the grouts with the longer durations of exposure generally yielding better results.

INTRODUCTION
The application of solidification/stabilisation (S/S) for the immobilisation of contaminated materials, by the addition of cement-based additives, has been widely practised for many years. However, most validation work has been restricted to testing at 28 days with very limited validation work carried out over longer curing periods (e.g. De Percin and Sawyer, 1991; Hockley and van der Sloot, 1991; Perry et al, 1992; Akhter et al, 1997; Board et al, 2000; Al-Tabbaa and Boes, 2002). This lack of long-term validation, which is essential for the success and sustainability of any remediation method, has raised serious concerns. Hence, in addition to obtaining real-time long-term work, there is also a need for the formulation of predictive methods by developing techniques for predicting the ageing of immobilised materials. Very limited work is available on these predictive methods at present (Kirk, 1996; Fuessle and Taylor, 1999).

Methods that have been considered for accelerated ageing of materials include curing under elevated temperature and carbon dioxide (accelerate carbonation). These two methods have been known for a long time but very little use has been made in studies involving contaminated material. Elevated temperatures have been used to accelerate the ageing of cement-based materials as it increases the rate of hydration and this increases the strength with increase of temperature and curing time (Clare and Pollard, 1954; Sherwood, 1993). The rate of hydration increases with the increase in temperature and based on this, the

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acceleration can be varied. However, it has been suggested that adopting temperatures over 80°C could have deleterious effects (Taylor, 1997).

Carbonation has been used in acceleration work by exposing the materials to an increased concentration of carbon dioxide (CO_2) while the material is still wet or after a prescribed curing period. In addition to increased concentration, the rate of carbonation is also dependent on other factors such as (i) CO_2 rate, (ii) permeability of the material, (iii) internal surface area, (iv) presence of certain ions, (v) temperature and humidity and (vi) binder system (Maries, 1992). The overall process relating to carbonation is quite complex and involves the principal phases in cement, i.e. tricalcium and dicalcium silicates (C_3S and C_2S) and the main hydration products, calcium silicate hydrate (CSH) and calcium hydroxide $Ca(OH)_2$. A simplified reaction scheme for the carbonation process of C_3S, CSH and $Ca(OH)_2$ is shown below:

$$C_3S + H_2O + CO_2 \rightarrow CSH + CaCO_3$$
$$CSH + CO_2 \rightarrow CaCO_3 + \text{silica} + H_2O$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

This process leads to a lowering of the pore fluid pH (Reardon and Dewaele, 1990), increase in weight, decrease in porosity and permeability, decrease in volume, reorganisation of the microstructure (Houst and Wittmann, 1994) and gain in strength (Lange et al, 1996). When accelerated carbonation of cement takes place in the presence of low-lime pulverised fuel ash (PFA) there will be competition between the PFA and the CO_2 over the $Ca(OH)_2$ formed and this could lead to retardation of the pozzolanic reactions of PFA.

This paper details results of a preliminary investigation into the influence of subjecting four cement-based grout mixtures, spiked with contaminants, to varying durations of exposure to CO_2 following an initial curing period at an elevated temperature. The initial exposure to elevated temperature was adopted in order to accelerate the initial hydration. This process would yield a higher amount of CSH and $Ca(OH)_2$ in the material than would result from normal curing, with which the CO_2 could react. In addition this may also allow the generally delayed PFA reactions to begin prior to carbonation. Varying the durations of exposure to CO_2 was adopted to observe the impacts on the samples.

MATERIALS

The four cement-based grout mixes, named grouts B, E, G and H, were made up using a combination of ordinary Portland cement (OPC), pulverised fuel ash (PFA), lime and bentonite as shown in Table 1. The four grouts were spiked with five heavy metal compounds and an organic compound. This was done to represent the S/S treated contaminated soil from a contaminated site used in a related study (Al-Tabbaa and Boes, 2002). The contaminant usage details are given in Table 2 and these are the same concentrations found in the contaminated site soils. Although only the grouts were tested in this study, it is assumed that all the contaminants will interact with the grout as a worse case scenario.

Table 1. Details of the grout mixes (as weight ratios)

Grout	Cement : PFA : Lime : Bentonite	Water : Dry grout
B	3 : 8 : 0 : 0	0.42 : 1
E	2.5 : 8 : 0.4 : 0	0.42 : 1
G	8 : 0 : 0 : 0.8	0.80 : 1
H	11 : 0 : 0 : 0	0.42 : 1

Table 2. Contaminant concentrations used in the contaminated grouts

Contaminant	Compound	Quantity used (mg/kg soil)	Metal concentration (mg/kg soil)
Cadmium	Cadmium nitrate	24	8.7
Copper	Copper sulphate	3160	1264
Lead	Lead nitrate	4500	2801
Nickel	Nickel nitrate	525	105
Zinc	Zinc chloride	3310	1589
Paraffin	Paraffin oil	8.7 ml/kg of soil	-

PROCEDURE

All the grouts were prepared by mixing the relevant binder material for 10 minutes at the given water-to-grout ratio. The heavy metal compounds were added as a solution to ensure more homogeneous mixing. The mixes were then cast in cylindrical plastic moulds measuring 100mm height and 50mm diameter. These were demoulded after 3 days and then subjected to the curing environments described below.

The curing environments comprised of subjecting the contaminated grouts to an initial duration of 11 days at elevated temperature (using an oven) followed by various periods of exposure to carbon dioxide (in a carbonation tank) with subsequent curing in the humidity container, where necessary, until taken for testing. In addition, a control set kept in the humidity container for the duration was also tested. The elevated temperature adopted was 45°C throughout the experiment with the samples kept wrapped whilst in the oven. The humidity container was maintained at 21 ±2°C and 90 ±2% humidity and the carbonation tank was maintained at 22 ±2°C and 98 ±1% humidity. The samples were tested at 28 and 90 days with an additional test carried out for the control samples at 180 days. The following four different curing scenarios were used, where the numbers in brackets are for the 90 day tests:

Scenario 1: Control
28 (90) and 180 days at 21°C in humidity container.

Scenario 2: Heated and then carbonated 1 (5) days
3 days at 21°C, 11 days at 45°C, 1 (5) day carbonated, 13 (71) days at 21°C.

Scenario 3: Heated and then carbonated for 5 (25) days
3 days at 21°C, 11 days at 45°C, 5 (25) day carbonated, 9 (51) days at 21°C.

Scenario 4: Heated and then carbonated for duration
3 days at 21°C, 11 days at 45°C, 14 (76) day carbonated.

The samples were tested, at the stipulated periods of 28, 90 and 180 days, for their unconfined compressive strength (UCS) (ASTM D1633-00, 2002), carbonation depth (RILEM, 1988), leachate pH and leaching using the UK NRA leaching test (Lewin et al, 1994). The leachates were analysed for heavy metal concentrations adopting atomic absorption spectrophotometry (AAS). As carbonation is taking place by the diffusion of carbon dioxide through the sample, the outer part and the core of the original samples were tested separately when conducting the NRA leaching tests in order for a comparison to be made between the two regions.

RESULTS AND DISCUSSION

Unconfined Compressive Strength

The UCS results, with a margin of error of ±20%, are shown in Figure 1(a)-(d). Overall the strength range of the four grouts were in the order of grout B<grout E<grout G<grout H. Grouts B and E are lower in strength due to the presence of high levels of PFA. However, although similar in composition grout E has significantly higher strengths to grout B and this should be as the result of the presence of $Ca(OH)_2$ in the grout E mix design. Although grout G, like grout H, is comprised mainly of OPC it is lower in strength due to the presence of bentonite and the higher water-to-binder ratio.

The values of the four grouts over the 2 initial time periods generally illustrates that scenarios 2-4 have an increase in strength compared to the control scenario 1. This is as expected as the scenario 2-4 samples were exposed to elevated temperature with the aim of accelerating the hydration and as a result the strength. This increase in strength due to elevated temperature has also been observed in other studies conducted by the authors. Even though the changes in strength caused by carbonation is relatively small, the 28 and 90 day results, show that there could be an optimum level of carbonation but this need not be as a result of the same scenario for all the grouts. The least promising is from scenario 2, which exposed the samples to the shortest duration of CO_2. The dip in the UCS value observed for grout H scenario 1 samples were as a result of excess drying of these samples.

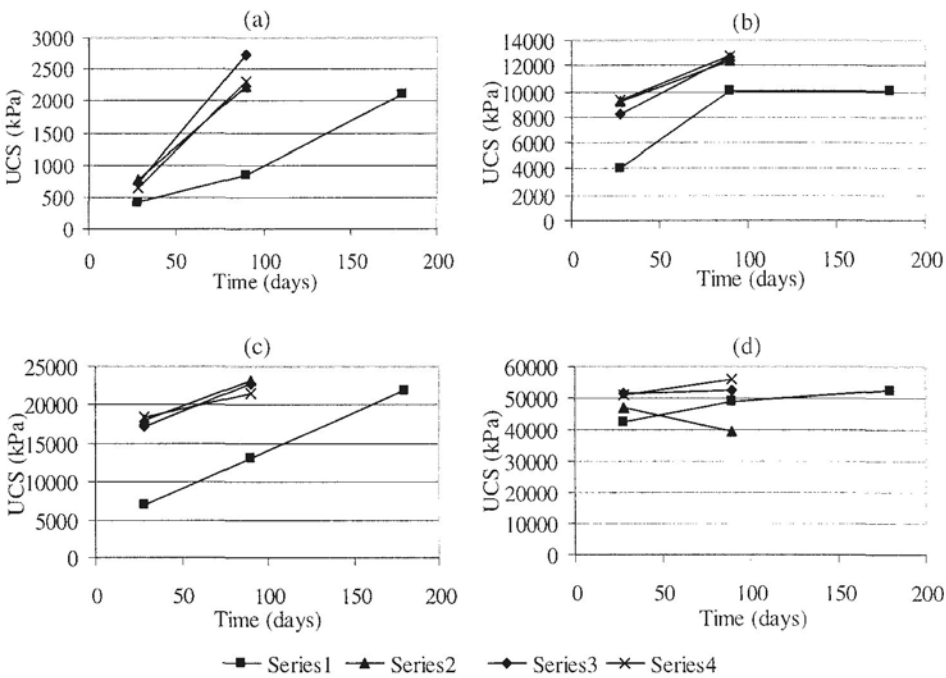

Figure 1. UCS results depicting (a) Grout B, (b) Grout E, (c) Grout G and (d) Grout H.

Carbonated Depth

The carbonated zones observed, as a result of the application of phenolphthalein, indicated that the diffusion of CO_2 into the samples were not necessarily uniform. The penetration values obtained for the samples are shown in Table 3. Overall grout B achieved a higher degree of CO_2 penetration in relation to the other 3 grouts, and this was due to their being more porous due to the high presence of PFA, and absence of the initial lime present in grout E. However, grout G was seen to have a higher carbonated depth in relation to grout E and H. The results also show that the penetration achieved increased with the increase in duration of exposure of samples to CO_2. However, even though penetration depths are reported for grout G and H some areas of the samples remained very slightly pink, instead of being completely colourless. Another phenomenon observed was that the outer skin of grouts G and H samples had a slight yellowish texture prior to application of phenolphthalein and it is unclear whether this had any influence on the measurements made.

It should be understood that carbonated depth only indicates the areas having a pore fluid pH of less than 8.3 (when using phenolphthalein as the indicator) and hence does not quantify the amount of carbonation. Other measurements are needed if quantification is required.

Table 3. Carbonated depths of uncontaminated and contaminated samples

	Carbonated depth (mm)		
	28 day	90 day	180 day
B scenario 1	0.0	<0.1	<0.1
B scenario 2	2.0	3.8	-
B scenario 3	3.7	6.1	-
B scenario 4	5.0	12.0	-
E scenario 1	0.0	0.0	<0.1
E scenario 2	0.2	0.2	-
E scenario 3	0.2	0.5	-
E scenario 4	0.3	3.0	-
G scenario 1	0.0	0.0	<0.1
G scenario 2	1.1	1.4	-
G scenario 3	1.1	1.5	-
G scenario 4	1.2	1.6	-
H scenario 1	0.0	0.0	<0.1
H scenario 2	0.0	0.0	-
H scenario 3	<0.1	0.2	-
H scenario 4	0.4	0.7	-

NRA leachate pH and leaching

The NRA leachate pH and leachate analysis results are shown in Table 4 and 5 respectively for the outer part and core of grout B and G samples only. The 90 day leachate pH results are given in brackets. The results in Table 4 show that grout B has lower leachate pH results in comparison to grout G. This is initially due to grout G comprising of more cement, whose hydrated products are responsible for increasing the pH of the pore fluid. Grout B is also more porous as a result of the presence of PFA and this enables the CO_2 to penetrate the samples more easily when compared with grout G, thus resulting in lower leachate pH results. The latter is clearly seen in the results. The results for grout B also show clearly that the NRA leachate pH decreases as the carbonation period is increased and that the pH has

reduced faster in the outer layer which was clearly subjected to more carbonation. However the results of the core clearly show that it is difficult for carbon dioxide to diffuse through to the centre of the sample. This is caused by the calcium carbonate formed, as the outer layer carbonates, reducing the porosity of the outer layer and hence increasing the difficulty of carbon dioxide further penetrating the outer layer. A drop in leachate pH is evident when comparing the grout G scenario 1 results with scenarios 2–4. This reduction is expected as elevated temperatures reduce the solubility of portlandite (St. John et al, 1998). This is not clearly evident in grout B as carbonation is more dominant.

Table 4. NRA leachate pH results at 28 and (90) days for grout B and G samples

	NRA leachate pH	
	Outer layer of sample	Core of sample
B Scenario 1	12.1 (11.9)	12.2 (12.1)
B Scenario 2	11.5 (10.8)	12.1 (12.1)
B Scenario 3	11.0 (10.6)	12.1 (11.9)
B Scenario 4	10.9 (9.1)	12.1 (11.2)
G Scenario 1	12.7 (12.6)	12.7 (12.7)
G Scenario 2	12.5 (12.3)	12.6 (12.6)
G Scenario 3	12.4 (12.3)	12.6 (12.5)
G Scenario 4	12.4 (12.3)	12.6 (12.5)

Table 5. NRA leaching results at 28, 90 and 180 days for grout B and G samples

	Cd (mg/l)		**Cu (mg/l)**		**Pb (mg/l)**		**Ni (mg/l)**		**Zn (mg/l)**	
	Outer	core	outer	core	outer	Core	outer	Core	outer	Core
B 28 Scen 1	0.00	0.00	0.00	0.00	10.51	10.53	0.00	0.00	0.56	0.56
B 28 Scen 2	0.00	0.00	0.00	0.08	0.95	21.31	0.00	0.00	0.03	0.79
B 28 Scen 3	0.00	0.00	0.00	0.09	0.19	15.75	0.00	0.00	0.00	0.58
B 28 Scen 4	0.00	0.00	0.00	0.09	0.22	10.29	0.00	0.00	0.01	0.53
B 90 Scen 1	0.00	0.00	0.09	0.02	16.09	16.12	0.00	0.00	0.77	0.71
B 90 Scen 2	0.00	0.00	0.00	0.03	0.13	4.83	0.00	0.00	0.00	0.32
B 90 Scen 3	0.00	0.00	0.00	0.00	0.06	1.90	0.00	0.00	0.00	0.07
B 90 Scen 4	0.00	0.00	0.00	0.00	0.06	1.22	0.02	0.00	0.00	0.07
B180 Scen 1	0.00	0.00	0.03	0.03	5.24	7.24	0.00	0.00	0.20	0.27
G 28 Scen 1	0.00	0.00	0.01	0.01	6.39	7.22	0.00	0.00	0.22	0.30
G 28 Scen 2	0.00	0.00	0.00	0.01	2.42	3.56	0.00	0.00	0.10	0.12
G 28 Scen 3	0.00	0.00	0.00	0.00	0.99	3.03	0.00	0.00	0.06	0.12
G 28 Scen 4	0.00	0.00	0.00	0.00	1.34	3.13	0.00	0.00	0.07	0.12
G 90 Scen 1	0.00	0.00	0.00	0.00	4.90	7.16	0.00	0.00	0.21	0.26
G 90 Scen 2	0.00	0.00	0.00	0.00	1.16	3.23	0.00	0.00	0.04	0.11
G 90 Scen 3	0.00	0.00	0.00	0.00	0.66	3.26	0.00	0.00	0.02	0.11
G 90 Scen 4	0.00	0.00	0.00	0.00	0.80	2.87	0.00	0.00	0.03	0.10
G180 Scen 1	0.00	0.00	0.20	0.10	4.02	3.94	0.00	0.00	0.19	0.16

Only the heavy metal concentration results, in Table 5, of lead and zinc show general trends due to the exposure conditions. The results indicate that overall grout G has the better capacity for immobilisation of these metals in relation to grout B and this is as a result of the higher cement content in grout G. However, it should be pointed out that the cause of the trend in the grout B core sample results at 28 days is not clear at this stage, except that the

core of the samples of scenarios 2–4 were observed to be moist and less firm than the outer portion, and this may have led to the presence of higher levels of contaminants in the leachate which were even higher than the scenario 1. This affect was not observed in the 90 day samples and the core results show an significant improvement which even goes lower than the grout G results which remain quite similar to that at 28 days. However, when considering the outer layers both grouts show improvement with time. The results, when compared between the outer part and core of the samples, show that the exposure to CO_2 has reduced the metal concentrations in the leachates and that the reduction is more with time. The exposure duration is seen to be important with scenarios 3–4 having the best results. However, although this improvement due to carbonation is seen even in grout G, the leachate pH results were not indicative of this.

Further, the benefit as a result of the initial accelerated hydration period is clearly seen, especially for grout G, with a substantial reduction in metal leaching concentration values when comparing scenario 1 with scenarios 2–4 results.

CONCLUSIONS

The results showed that the different grouts responded differently to the exposure conditions imposed in this study. Generally speaking the results were indicative of the accelerated hydration due to the initial exposure to elevated temperature and this acceleration, although at different rates, was observed for all grouts. The results also indicated that the exposure to CO_2 had an influence on the behaviour of the grouts with the duration of exposure under consideration also being important. In this study it was shown that the longer durations of exposure generally yielded the better results. The UCS results were the least representative of the influence of carbonation on the grouts and hence might not be a good parameter for conducting accelerated ageing studies involving accelerated carbonation. On the other hand carbonated depth, NRA leachate pH and NRA leaching were all good indicators of accelerated carbonation and would be the better parameters for conducting accelerated ageing studies. But these parameters needs to be considered carefully as the results might not always give similar trends which are in agreement with each other.

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Factors affecting Remediation Technology Costs in England & Europe

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INTRODUCTION

As part of a European 5th Framework project PURE (Protection of Underground REsources), a specific market-oriented research task was undertaken by the British service provider, VHE Technology Ltd (parent company – VHE Construction). The specific task was to obtain costings and market conditions/usage of remediation technologies across Europe, over the period 2000-2003; the full tabulated data is expected to be available on the Commission website (www.cordis.lu) as part of the approved, published research project during 2004.

DATA COMPILATION

Participation in data collection came from Regulators, Consultants and Contractors across Europe, primarily led by members of the NICOLE Network of Industrially-contaminated Land owners (www.nicole.org). Data for 34 technologies active in 11 participant countries has resulted in a database of nearly 300 cost items. This basic cost data was, in some cases, accompanied by background information on the number of operators in each market, and the share of the remediation 'workload' held by each technology. Information on these aspects is not reported in detail in this Paper, nor contained in the final PURE report; however, some inferences are made from that information herein.

Activities undertaken to gather information on the costs of remediation technologies across Europe chiefly involved personal discussions within member companies of the NICOLE network, and the evaluation of published material. Whilst the spread of companies in NICOLE might be deemed to be of a narrow range, they do comprise both Problem Owners and Solvers. The Service Providers group of NICOLE, of which the principal author was chairman for 2000/01, comprised both Consultants and Contractors; thus, in this respect, information could be gathered from 'both sides' of Industry.

From their own experience, principally in the UK but with live projects in Ireland & Belgium, the Authors were able to back up the data costs as tabulated with a 'reality check'. Similar checks were undertaken by third party NICOLE members in France, Italy and Sweden, particularly to update costs from their original accrual in 2001 to actuality in 2003. A final overview was taken by the four Industrial companies involved in the PURE project, as to the validity of the specific country information in their own contracted experience.

Regulatory views on remediation costings would be another source of Information. Indeed, the three lead country participants (France, Italy, Belgium) at the Paris NICOLE workshop in May 2001 were from regulatory backgrounds and they were invited to complete a template that soon became the 'standard' for information input to the PURE project throughout 2001/3.

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

In addition, the CLARINET project had been gathering information on technology costs from its regulatory participants, and published this information on its website in 2002 (www.clarinet.at). This data has been incorporated into the specific country cost databases, although the Authors have some concerns over the validity of the data (gathered in 1998/9) and its accuracy for some countries (data for Eire, for example, gave costs for all kinds of technologies, many of which have never yet been used in that Country).

Whilst every attempt has been made to 'standardise' the information, there may still be errors in compilation that could lead to statistical 'confusion'. For example, in calculating Cost per cum, reportees have been requested to use contaminated volumes of soil but more than one source (current or historical) may have used total site volumes including a 'clean' volume of overburden. Others, particularly for groundwater treatment, provided information on the volumetric throughput and/or the mass of contaminant removed in initial data. There is therefore bound to be some error in the Authors' interpretation of costs in some cases; a proposal to continue the data collation and clarification is being considered within NICOLE.

The final data was tabulated on a spreadsheet, which then allowed Maxima, Minima and Median data to be compiled from the input figures (in many cases, a spread of costs was provided by each source, but in some cases a specific figure was given). The UK data is shown below, with primary data sources, and the European summary Tabulation is overleaf.

UK	Source : CLARINET WG7			Source : Spon's Civil Engg Cost Database '02			Source : MSI Analysis of DTI Data (2001)			Source : BIPE Market Research (2001)			Source : RDTech RPT P5-056 (original calc 1.53			Overall		
	Cost : Euro / m3			Cost : Euro/ m3			Cost : Euro/ m3			Cost : Euro / m3			Cost Euro/ m3			Cost Euro/ m3		
Technique	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
On-site Biopiling	95	114	105	23	66	45							15	44	30	15	114	60
On-site Windrows													7	44	26	7	44	26
On-site Landfarming													15	30	22	15	30	22
On-site Thermal Treatment	95	399	247	584	935	759							585	585	585	95	935	530
On-site Soil Washing				31	66	49	22	59	41				30	89	59	22	89	50
On-site Immobilization							15	148	81				15	59	37	15	148	59
On-site Bioslurry Reactor													89	222	155	89	222	155
On-site Biological Treatment	95	124	110				15	222	119							15	222	128
Ex-situ Vitrification													44	74	59	44	74	59
On-site Phytoremediation													22	222	122	22	222	122
Pump and Treat	30	40	35													30	40	35
In-Situ Air Sparging	65	75	70													65	75	70
In-Situ Soil Venting	55	85	70	39	86	62							22	114	68	22	114	67
In-Situ Steam Injection																		
In-Situ Electro Reclamation													44	207	126	44	207	126
In-Situ Natural Attenuation																		
In-Situ Bioremediation													15	74	44	15	74	44
DVE (Dual Vapour Extraction)																		
In-Situ Biolsurping																		
In-well Vapour Stripping																		
In-situ Vitrification													518	814	666	518	814	666
Chemical Oxidation	55	110	83				59	126	93				30	30	30	30	126	68
Free Product Recovery	10	20	15													10	20	15
Hydrogeological Containment							22	52	37							22	52	37
Containment Walls																		
Reactive Walls																		
Bioreactive Barriers																		
In-situ Immobolization																		
Encapsulation (per m2)	55	170	113	30	118	74	59	178	118							30	178	102
Confinement (per m2)	20	40	30													20	40	30
Off-site Thermal Treatment																		
Off-Site Biological Treatment																		
Off-Site Soil Washing																		
Off-Site Immobilization																		
Off-Site Landfilling	20	140	80	74	222	148	44	111	78	25	37	31				20	222	84
Off-Site Incineration	2005	2679	2342				148	592	370	305	305	305	585	585	585	148	2679	900

Table 1 – UK-specific Technology Cost Data Tabulation

(All costs Euro/m3) Country:	BELGIUM			FINLAND			FRANCE			GERMANY			GREECE			IRELAND			ITALY			HOLLAND			SPAIN			SWEDEN			UK			ALL EURO DATA			
Technique	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	MIN	MAX	MEDIAN	# resp.	MIN	MAX	AVE. MIN MAX
On-site Biopiling	11	76	37	114	380	247	27	171	102	15	50	33							25	456	143	30	90	61	76	570	323	10	380	176	15	114	60	9	10	570	142
On-site Windrows																															7	44	26	1	7	44	26
On-site Landfarming																			95	114	105	30	90	60							15	30	22	3	15	114	62
On-site Thermal Treatment	26	114	67	76	390	233	90	415	236	80	120	100							100	500	261	45	100	74	200	250	225	76	390	224	95	935	530	9	26	935	238
On-site Soil Washing				57	171	114	27	270	131	50	200	108	67	295	181	20	152	65	50	456	177	38	114	57	15	25	20	57	200	118	22	89	50	10	15	456	116
On-site Immobilization	25	100	63	48	57	52	150	400	259	50	125	81	86	323	204				75	360	251							48	140	79	15	148	59	8	15	400	139
On-site Bioslurry Reactor																			114	133	124										89	222	155	2	89	222	122
On-site Biological Treatment	11	76	37																			38	86	55				80	80	80	15	222	128	4	11	222	76
Ex-situ Vitrification																			380	380	380										44	74	59	2	44	380	220
On-site Phytoremediation																															22	222	122	1	22	222	122
Pump and Treat	10	150	80	29	143	86										50	228	103	57	57	57	10	50	30							30	40	35	6	10	228	71
In-Situ Air Sparging	30	120	83	48	86	67													133	360	202	20	60	40				11	88	47	65	75	70	6	11	360	91
In-Situ Soil Venting	20	80	58	48	86	67	18	54	38										10	152	84	10	50	30				11	88	47	22	114	67	7	10	152	54
In-Situ Steam Injection																			50	300	175													1	50	300	175
In-Situ Electro Reclamation																															44	207	126	1	44	207	126
In-Situ Natural Attenuation																15	25	20																1	15	25	20
In-Situ Bioremediation	25	100	63	29	200	103	27	54	41	16	40	28				25	50	38	48	152	100	37	159	98				67	111	85	15	74	44	9	15	200	73
DVE (Dual Vapour Extraction)																						20	70	45										1	20	70	45
In-Situ Bidsurping	40	100	70																162	162	162	20	70	45										3	20	162	92
In-well Vapour Stripping																																		0			
In-situ Vitrification																															518	814	666	1	518	814	666
Chemical Oxidation																															30	126	68	1	30	126	68
Free Product Recovery																						20	70	45							10	20	15	2	10	70	30
Hydrogeological Containment																						40	80	60							22	52	37	2	22	80	49
Containment Walls																						40	60	50										1	40	60	50
Reactive Walls																						40	70	55										1	40	70	55
Bioreactive Barriers																																		0			
In-situ Immobilization	25	100	63				215	270	243	80	80	80																						3	25	270	128
Encapsulation (per sqm)																															30	178	102	1	30	178	102
Confinement (l-cum, UK-sqm)																			38	38	38										20	40	30	2	20	40	34
Off-site Thermal Treatment	50	350	143				60	450	261	90	120	105							15	456	175	57	152	102				105	600	329				6	15	600	229
Off-Site Biological Treatment	20	60	40				70	270	150	40	60	50																40	665	219				4	20	665	167
Off-Site Soil Washing	30	80	58				250	600	428	40	60	50							50	456	177							86	608	216				5	30	608	226
Off-Site Immobilization							215	270	243	65	130	98							114	114	114				50	50	50	70	140	93				5	50	270	112
Off-Site Landfilling	120	200	160	31	437	240	55	437	200	25	50	35	646	979	812	30	209	102	75	760	306	39	205	122	10	64	30	40	300	150	20	222	84	11	10	979	231
Off-Site Incineration				580	2024	1302	328	1000	588										456	2850	1231	740	740	740	184	590	387				148	2679	900	6	148	2850	885

Table 2 - Summary Remediation Technology Cost Data for 11 European countries.

DATA ANALYSIS

By the end of the PURE project, data had been gathered from 11 EU member states. The 4 countries not included, because nil or only one data set could be obtained, were *Austria, Denmark, Luxembourg and Portugal.* This was mainly due to a lack of contacts in Austria, a lack of a remediation market in Luxembourg & Portugal, and an unwillingness to divulge costs from contacts in Denmark. In addition, the data from *Finland, Greece, Eire & Spain* was sparse in extent, and may subsequently be challenged by further data coming from within that country.

Most confidence can be placed upon the data from *Belgium, France, Sweden* and *UK* because of a number of data sources providing the input. That from Germany, Italy and Netherlands remains subject to adjustment from additional data sources. In *Germany*, the information has been location-specific, because there are different markets in the Rhine area, the Ruhr and northern ports (also there is differing state legislation for environmental matters).

In *Italy*, as in Spain & Eire, the remediation market is in its infancy, and the costs are based on very few implementations of technologies; thus, when there is a more mature remediation market, these costs may swiftly change. In *Holland*, the market for insitu treatments is complex, there are many quasi-research trials, and there has been a reluctance from consultants to reveal market figures to the PURE project (probably due to a competitor's direct involvement). However, useful information was received from certain Contractors in the country, who also were able to provide confidence in adjacent market costings (Flanders).

Because of market changes in Germany, and to a lesser extent in the UK as the Landfill Directive was enacted into local legislation, a review was made of cost changes between 2001 and 2003 for those countries where information was first obtained. Thus, the data for Belgium, France and Italy has been brought up to date for 2003. The Swedish and British data is chiefly related to 2001/2, when 'national' surveys were carried out for their governments. It is apparent that the overall technology cost situation is fluid in several countries, is affected by regulatory changes, and subject to market forces, still being strongly affected by landfill prices in all but Holland & Belgium-Flanders (where legislation places landfill as the 'last resort' option).

However, some sense can be made of the database (Table 2) by producing a ranking based on 'median' cost across the most popular 15 technologies (by popular, this means that valid costs were found to be sourced, and verified, for this technology in 4 or more European countries). The data was abstracted for each technology and is tabulated in rising cost per Country, for the 15 technologies (Figure 1 overleaf). Two examples are also given for specific technologies deemed 'active' in several countries, Figures 2 & 3 following. The PURE project report, when released, will provide similar data plots on all those technologies.

In clarification of the plot, the vertical line represents the range from maximum to minimum, across all country cost ranges. The short cross-bar represents the European average of all the maxima & minima figures for each Country, combined in a simple calculation. For individual countries, the similar 'cross-bar' is a calculated median from all input data. Slightly different ranking of technologies resulted from a median of the medians calculation, rather than the average denoted.

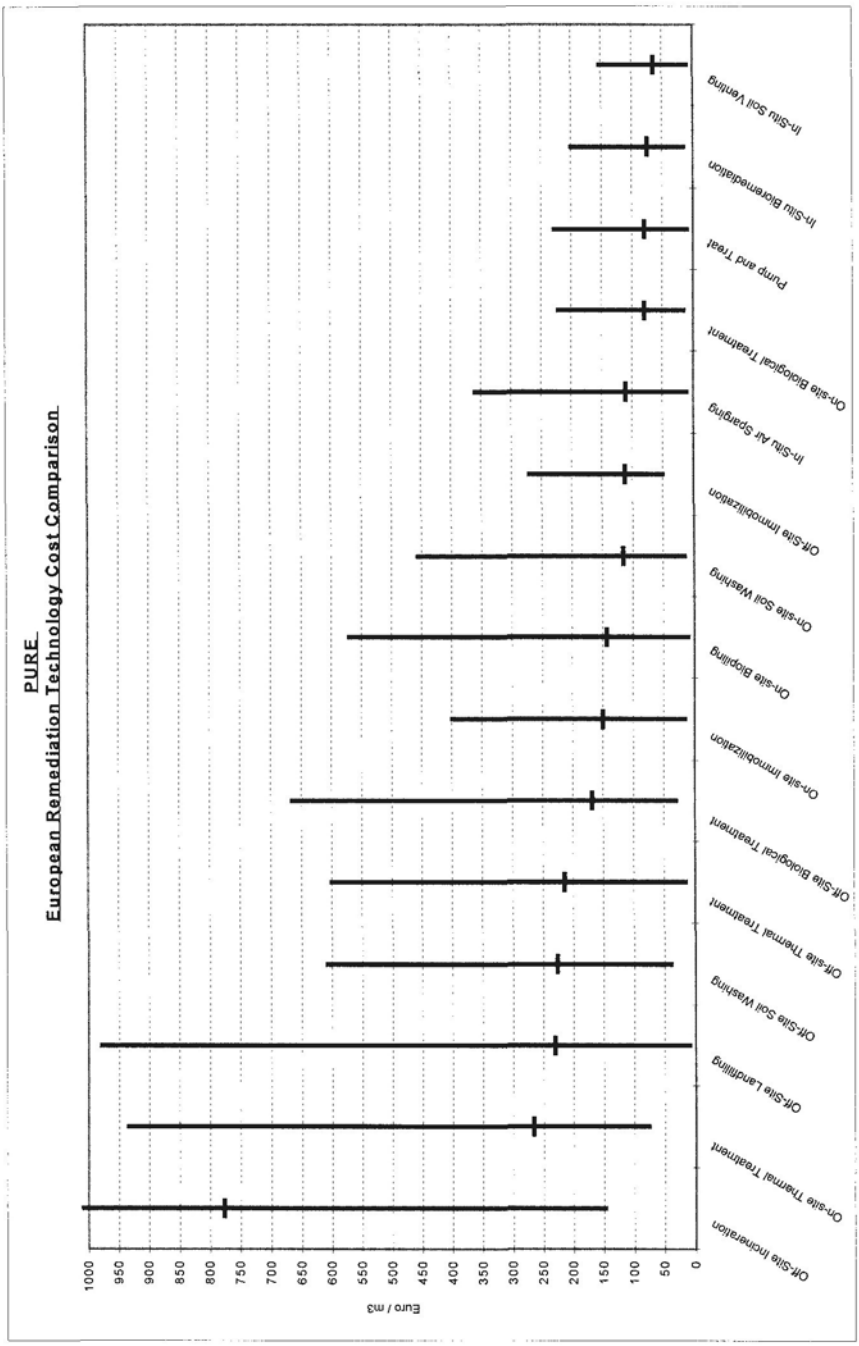

Figure 1 - Data sorted by Cost, all technologies.

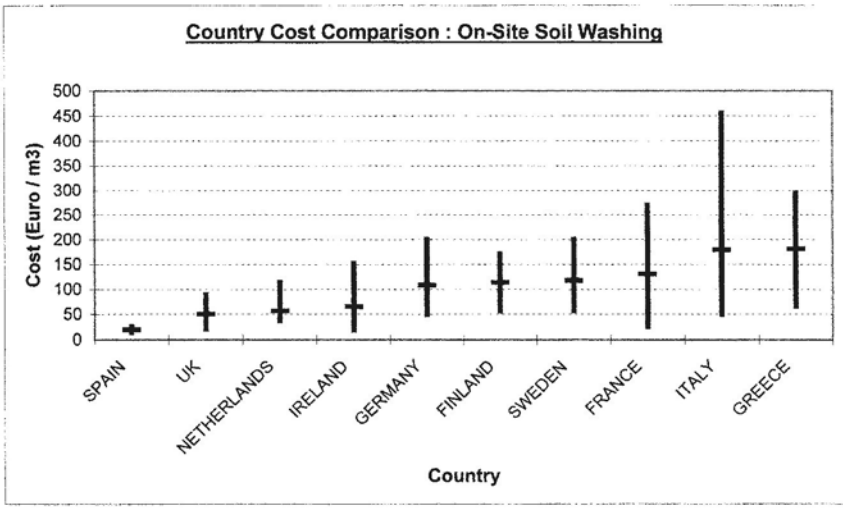

Figure 2 – Country variable Costs of on-Site Soil Washing

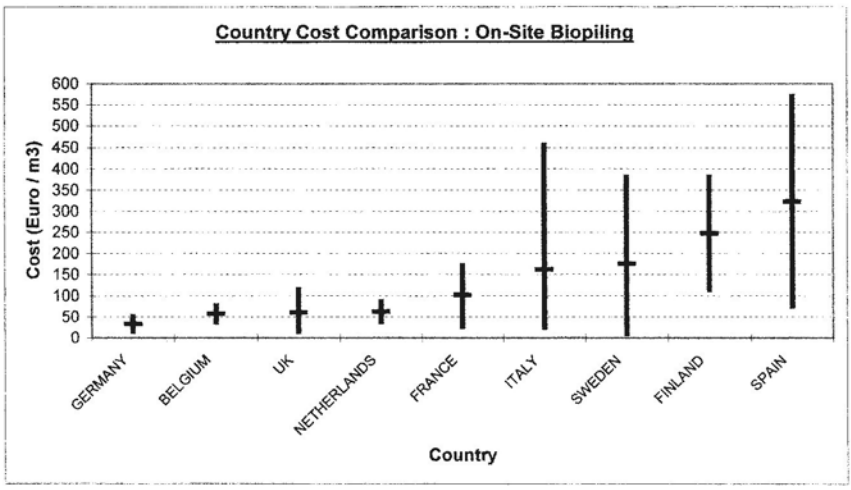

Figure 3 – Country variable Costs of exsitu Bioremediation (biopiling)

In the previous plots, note should be taken of the possibility of some mis-interpretations. For soil washing, the figure for Spain is probably related to 'simple' jet washing or tumbling on

site, not a specific washing plant. This equally applies to Ireland and Greece, whereas in Italy the data from two sources was widely different in cost (hence the large range). For biopiling, the larger range of costs in some countries is related to climate (heated aeration being used in Scandinavia to offset the colder winter), and to timescales (longer periods used in Mediterranean countries, with higher concentration starting points). Further research on these specific matters was beyond the scope of the PURE data-gathering exercise, but was the subject of discussion and certain Papers at CONSOIL 2003 in Gent (www.consoil.de).

CONCLUSIONS

The variability in the data obtained has not made interpretation very easy. It seems apparent that there are not only inter-national variations, but also intra-national cost variations particularly in the larger States. This should not be surprising as, for example, the cost of landfill will vary according to local availability (as well as the effects of commercial variations in the market). Also, a technique that is well-utilised in one area due to a preponderance of former industrial activity, or even of area-specific geology, may be competitively priced if there are several Contractors active in that region. This seems to be the case with biopiling, where in countries with only a few full-scale sites (Italy, Spain), the cost is much higher than in those with established 'industries' (UK/Belgium), even though their climate would suggest that this process could be performed in a shorter time period, all other aspects being common.

It may be significant that 4 of the 'cheapest' 5 technologies are insitu processes, and it is fairly inevitable that 8 of the cheapest 9 are deemed to be onsite processes. Only in the Netherlands, Germany, Denmark and Flanders has the concept of soil treatment ('hospitals') been translated into commercial reality, albeit with some governmental or legislative intervention. For example, the cost of off-site soil washing is cheaper than on-site in Germany, whilst the opposite applies in France; in the UK all such work is done in a site-specific manner.

The UK can be shown to be a low-cost operator in many technologies. Whilst the Authors would hope that this reflects the maturity of the marketplace here, that is evidently not the case when one visits Holland and adjacent countries in Europe. The economic fact that exsitu bioremediation costs halved in the UK from 1999 to 2002, as the number of licensed operators increased from 3 to 10, merely reflects the economics of the marketplace, and the inordinate reliance placed on landfill as the main option. The cost of landfill inevitably drives the viability of other options unless there is a specific technical reason dig'n'dump cannot compete.

ACKNOWLEDGEMENTS

The Authors would like to thank all the fellow members of the PURE consortium (thirteen companies and research bodies) for their assistance in obtaining the data used within this Paper, and for providing stimulating ideas at project meetings and site visits. Also the individual members of the NICOLE network, too many to mention, who contributed so much of their time and knowledge to the gathering of data for this purpose. Particular mention must be made of Wouter Gevaerts (Gedas Belgium), and Bertil Grundfelt (Kemakta Sweden), who worked assiduously on the NICOLE Paris workshop in 2001, after which the data gathering exercise gained momentum within the Network.

The data within this Paper is solely the responsibility of the two Authors, and in no way reflects the technology prices quoted by their former Employer for UK projects, now or in the future.

Insitu Assessment of a Cement-bentonite Containment System

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ABSTRACT
Slurry trench cut-off walls are widely used in the UK to contain contaminated groundwater. Specifications for these walls (ICE, 1999) call for a minimum unconfined compressive strength of 100kPa and a hydraulic conductivity lower than $1x10^{-9}$ m/s. Tests for these properties are carried out in a laboratory on samples cast from the poured slurry and allowed to set; currently there is no accepted method for testing the performance of the walls after construction. There are reasons to suspect that laboratory derived values do not reflect the properties *in situ*. For example there are no guidelines for the appropriate confining stress to apply to the laboratory samples when testing the hydraulic conductivity. An unrepresentative value will significantly skew the results. Material heterogeneity has a major influence on the measured hydraulic conductivity (the scale effect) and this is masked by the small size of the normal laboratory sample. To address these and other issues a series of field measurements of hydraulic conductivity were carried out in an 7 year-old cement-Bentonite containment wall, using a self-boring pressuremeter, a straddle packer system and piezocone. These cover the range of insertion procedures, from minimal to grossly invasive. The experimental programme examined the influence of insertion disturbance and different test procedures, and showed that consistent data can be obtained by a variety of means. In general the wall was found to be much more permeable than the initial laboratory tests had indicated, a difference that at this stage appears to be due to the scale effect.

INTRODUCTION
In order to improve the state of the art of design of containment systems there is a need for a better understanding of the in situ behaviour of these systems. Proper geotechnical characterization of the systems includes measurements of hydraulic conductivity, strength, and stiffness characteristics. At present these measurements are only obtained through testing of laboratory samples that are either created in the laboratory or cut from undisturbed samples taken in the field. Laboratory scale samples cannot represent field scale performance, and thus in situ tests are the preferred method. However, there currently exists no approved method for the determination of all the required parameters, particularly the hydraulic conductivity of cement-bentonite slurry walls (Tedd et al., 1995). Estimation of

Integrated management of groundwater and contaminated land, Thomas Telford, London, 2004.

these parameters from field sites is required in order to refine the design specifications (ICE, 1999) as well as to understand the long-term behaviour of such containment systems.

Several studies have been completed in the past (Manassero, 1994; Tedd et al., 1995; Tedd, 1997b; Ratnam, 2002) using different devices. They have met with varying degrees of success, possibly due to differences in technique but also because of the change in material behaviour that occurs in cement-bentonite walls after construction. Tests conducted in wall material near the end of construction, or even 90 days after construction can be successfully completed since the wall stiffness has not achieved its maximum value. This allows proper seals to be achieved for test methods that measure pore pressure response. At later stages in the design life, the wall stiffness can be very high, and so obtaining a proper seal is difficult unless an inflatable membrane can be used as part of the method (i.e. packer test, self-boring pressuremeter). Also, when block samples are excavated and investigated it is evident that the material is not necessarily homogeneous. The degree of homogeneity depends upon the method of wall construction as well as the type of host soil that the wall is constructed in. Soil inclusions and fissures are commonly identified in samples of wall material. These can render the proper interpretation of test results difficult. Thus, research is required in order to develop a method for assessing the homogeneity of existing walls and potentially to be used to quantify both the compliance with design specifications and the long term behaviour.

It is generally accepted that good quality field data give more representative material properties than those obtained from laboratory tests, and slurry trench walls are no exception. Localised heterogeneity exists in typical wall installations, partly due to the construction method and this cannot be replicated in a laboratory setting. Furthermore, excavation of samples from narrow walls (0.6m) can be difficult (Tedd et al., 1995) and the resulting data are likely to be affected due to the volume of material that is tested (i.e. due to a scale effect). A method that can test a varying volume of material would be the most appropriate since it would allow the investigation of any scale effect.

SITE DESCRIPTION

The site used in the current research project is that of a disused gasworks where approximately 120m of cement-bentonite cut-off wall were constructed. The walls are in the form of two boxes, square in plan, plus three isolated lengths of wall (Figure 1). Since 1996 the site has been used as part of a Building Research Establishment (BRE) test project in order to investigate the behaviour of slurry walls in chemically aggressive ground (Tedd et al., 1995, 1997a, 1997b). In the current research project, only the isolated walls are being tested using a variety of in situ techniques in order to determine the in situ strength, stiffness, and hydraulic conductivity. Typically the walls are 0.6m in width, 5m deep and were constructed using the single-phase method.

The site is contaminated, but to varying degrees. The test walls, Wall 1, and Wall 2 (Figure 1) are located in the generally less contaminated section of the site, while the boxes to the north are in the higher contamination zones (this is where the bulk of the former gasworks was located). The main contaminant consists of sulphates of varying concentration across the site, although there are other chemicals present in the fill material that makes up the first 3 metres of the soil. The chemicals present in the fill material consist of the following: Spent oxide, Coal residue, Carbon black, and Foul lime.

The 3 metres of made ground overlie a deposit of stiff Lower Lias Clay, with the groundwater typically 1.5 to 1.6 metres below the top of the wall (2.2 to 2.3 metres below ground surface). The tops of the walls were capped with compacted clay.

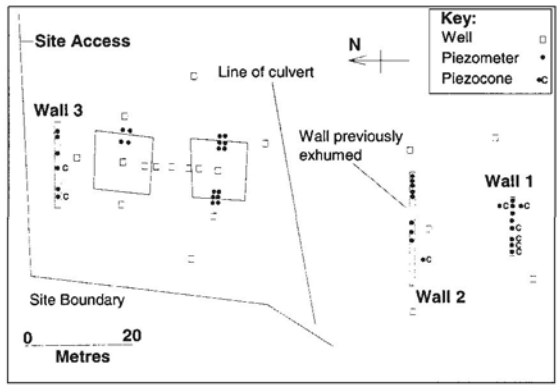

Figure 1 – Plan view of site

The wall was constructed using typical slurry trench construction methods, and used the following mix : (a) 40 kg of Sodium activated bentonite, (b) 30 kg of Ordinary Portland cement, (c) 120kg of Ground granulated blast furnace slag and (d) 1000kg of Water

The general geotechnical profile of a typical wall section is illustrated in Figure 2, with a self-boring pressuremeter hole (87mm) located in the centre of the cement-bentonite wall.

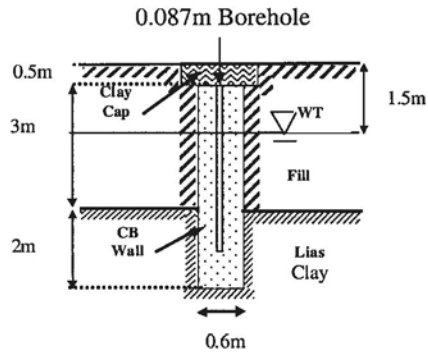

Figure 2 – Typical section

FIELD TEST RESULTS AND DISCUSSION

The testing in the field at the site consisted of interpretation from piezocone testing, a packer system and a self-boring pressuremeter. The results are shown in Figure 3. Although investigations took place to estimate the shear modulus (from self-boring pressuremeter), as well as the undrained shear strength (from self-boring pressuremeter or piezocone) only the results relating to hydraulic conductivity will be discussed. Each of the following sections discusses the test arrangement as well as the interpretation method used.

Piezocone Testing

Piezocone testing was carried out during a previous testing program (Tedd et al., 1997b) as well as the current program. The cone had three pore pressure measuring points (i.e. the face, shoulder, and behind the shoulder). The current testing program used a cone with only a face pore pressure transducer (i.e. the u1 position). The previous Piezocone work was conducted when the wall material was approximately 90 days old, whereas the current testing was conducted at an age of seven years. For each program, pore pressure dissipation tests were carried out in order to form an estimate of the hydraulic conductivity from the time at which 50% dissipation of pore pressure occurs (Burns and Mayne, 1999).

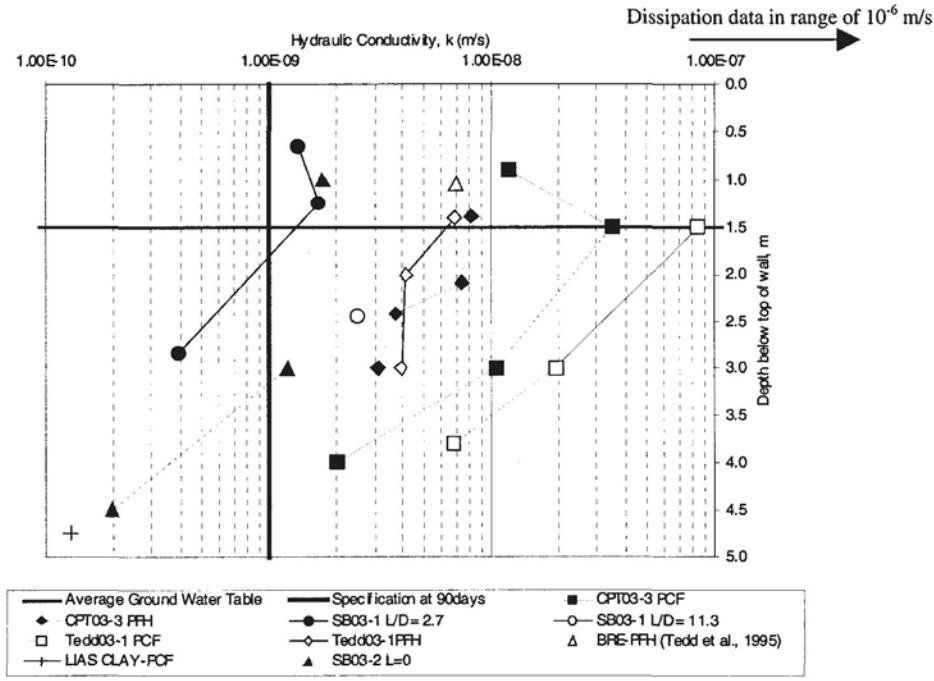

Figure 3 – In situ measurements of hydraulic conductivity

Dissipation data from the past cone testing (Tedd et al., 1997b) indicated values of hydraulic conductivity in the range of 10^{-6} m/s. This was contrary to falling head tests completed earlier at the same site (Tedd et al., 1995). The effect was then assumed to be due to hydraulic fracturing of the material during penetration, which would effectively increase the permeability of the material surrounding the test pocket. Instead, it is now suggested that during the initial dissipation tests, axial leakage had occurred along the side of the instrument, causing a higher computed permeability. To support this hypothesis, the same holes were re-tested using a packer system discussed in a later section. Axial leakage is due to the high stiffness of the cement-bentonite material, and the low effective stresses that exists in and around the walls. This fact may show that standard CPT testing in order to determine permeability of slurry-trench cut-off walls is not a desirable procedure and is very susceptible to the technique used. Also, standard CPT testing may only be applicable to walls at very early age (i.e. just after construction), while older walls will require methods that do not cause high shear strains around the device.

As part of the current research program, one hole was penetrated using a penetration rate approximately one tenth that of the standard rate in an attempt to reduce the generation of high excess pore pressures that could initiate hydraulic fractures in the material. However, the pore pressure response during penetration as well as during dissipation tests indicated that either fracturing or axial leakage had occurred since the dissipation was similar to a very porous material. Upon excavation of the clay capping on top of the wall, it was evident that vertical radial cracks had formed along the CPT hole (Figure 4).

For comparison purposes, data from both the past investigation program, as well as the current program were interpreted using the technique suggested by Manassero (1994). This resulted in more reasonable estimates of permeability of 10^{-9} m/s. However, it was found, similar to previous findings (Tedd et al., 1997b), that the method is very insensitive to the input parameters. Furthermore, computed values of permeability for the current testing were found to be much lower despite the fact that fracturing had taken place. Thus, use of this interpretation method should be treated with caution.

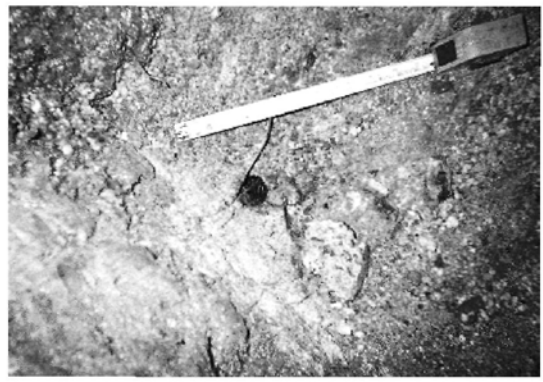

Figure 4 – Vertical radial cracks around CPT

Packer System Testing

A Packer device (Figure 5) was used in order to conduct measurements of horizontal permeability in Wall 1. The device consists of upper and lower membranes that are inflated using air pressure in order to seal off a water filled cavity between them. This water filled cavity is then subjected to either a constant flow permeability test, or falling head test procedures. The constants used as input for the various interpretation methods are the diameter of the hole (D=50mm) and the length of the test pocket (L=550mm).

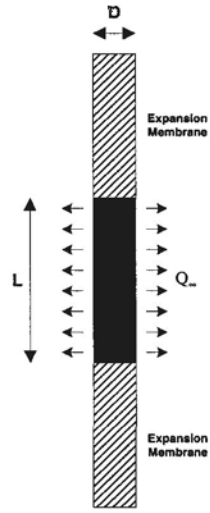

Figure 5 – Packer system

Hydraulic conductivity tests were conducted using the Packer system at the test site in two different types of boreholes. First, a hole of 50 mm in diameter was hand augured to a depth of 5 metres. Second, a hole previously created from a CPT test described previously (Tedd et al., 1997b) was uncovered and reamed out to a 50 mm diameter.

The geometry of the straddle packer cavity is known as the Mark I geometry and the tests are interpreted using the formulae by Ratnam et al. (2001). The formula assumes an infinite domain, which is not the case for such barrier systems, and an error in the range of 20-30% is expected (Ratnam, 2002). However, all the data were interpreted using this formula, so the use of an improved shape factor relationship would only shift all of the data. Future work includes generation of shape factors for systems of finite boundary conditions using 3D finite element analysis.

The packer tests conducted in the old Piezocone hole included falling head tests (CPT03-3 PFH in Figure 3) as well as constant flow tests (CPT03-3 PCF). The tests in the manually augured hole also included falling head tests (Tedd03-1 PFH) as well as constant flow tests (Tedd03-1 PCF). A constant flow test was also conducted in the Lias clay below the slurry wall (Lias Clay-PCF). Also shown in Figure 3 is the result (BRE-PFH) obtained from a previous falling head test (Tedd et al. 1995) using a BRE proprietary packer system.

The packer results to date appear to show a decrease with depth (Figure 3), and for this particular wall (Wall 1) have values above that of the specification (ICE, 1999). The reduction in permeability with depth is expected since results from lab tests (Manassero et al., 1995) indicate that increasing confining stress during setting decreases the hardened permeability of the material. However, the permeabilities are larger than those found from laboratory testing. It is proposed this is primarily the consequence of heterogeneity in the constructed wall (i.e. a scale effect exists).

Permeability values from constant flow tests were larger than those from falling head tests conducted in the same hole. The constant flow configuration requires a closed system and hence is affected by entrapped air. This tends to give a softer response during the test, and lower pressure values lead to higher permeability measurements. This effect will be investigated in future work with a modified constant flow apparatus for the Packer system.

In order to interpret the current results, which develop a matrix hydraulic conductivity, a permeability anisotropy ratio of unity was assumed. This value is preliminary until further testing can provide a more valid ratio. Thus, the permeability values shown in Figure 3 are inferred to be the same in horizontal and vertical directions.

Self-boring Pressuremeter Testing

The self-boring pressuremeter (SBP) followed a procedure developed by Ratnam (2002) to measure the hydraulic conductivity of the wall material using different pocket sizes. The test method uses a constant flow technique, and the results are interpreted using the formula developed for an infinite domain with such a test pocket, known as the Mark 2 geometry, (Ratnam et al., 2001).

It can be seen from Figure 3, that the permeability measured for larger pocket size (SB03-1 L/D = 11.3) is larger than that from smaller pocket sizes (SB03-1 L/D = 2.7 and SB03-2 L=0). This effect is attributed again to the scale effect. It is suggested that larger test pocket sizes provide a better estimate of the functional permeability of the wall system. Data from self-boring tests in Wall 1, with smaller test geometries, indicate lower values of permeability than data from the Packer system with its fixed and large test geometry (Figure 5). SBP test in a large pocket (L/D = 11) indicates a permeability much closer to that of the Packer system tests. This effect is again suggested to be the result of the more heterogeneous nature of the wall material. It is interesting that the values from the smaller pocket sizes compare well with those found from laboratory tests conducted on cast samples from the mixer as well as trimmed block samples tested at the Building Research Establishment ($k \sim 1 \times 10^{-9}$ m/s after 90days). Tests conducted on block samples at Cambridge University give results between 6×10^{-9} to 6×10^{-8} m/s (Ratnam, 2002).

Lack of homogeneity was evident in the laboratory when trimming block samples prior to permeation with dye. For some samples a preferential flow path was observed through inclusions or fissures, which depended entirely on the scale and location of the sample (Figure 6). Thus, the computed permeability from small-scale laboratory tests will be different depending upon whether these features are intersected or not.

CONCLUSIONS

The data gathered so far indicates several interesting trends and findings in need of further research. The measurements of hydraulic conductivity from the SBP tests as well as the

packer tests give values above that required by the specifications. This finding was not unexpected since the bulk of published laboratory data on hydraulic conductivity testing uses confining pressures much higher than that which exist in such shallow systems. However, until other walls that are known to be effective can be tested, the fact that this system showed values above the specification does not necessarily indicate it is a poor system. It is suggested that further in situ tests should be conducted in order to develop a proper database of the functional permeability of wall systems. This could then be compared with the effectiveness of each wall system in order to refine the technical specifications of slurry wall cut-off construction.

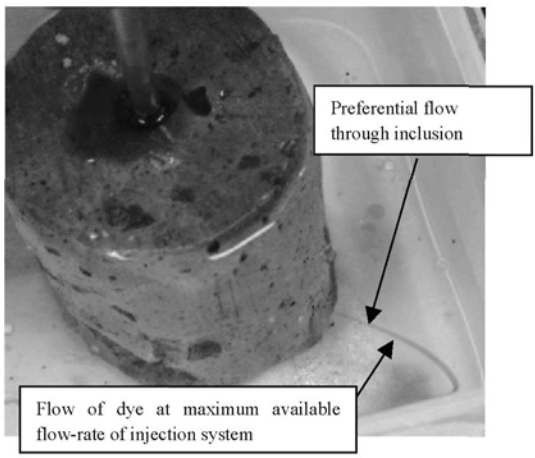

Figure 6 – Preferential flow through trimmed block

When the data are compared together an apparent scale effect seems to exist. This is proposed to be a result of localised heterogeneity in the wall occurring in the form of fissures or inclusions from the host soil during construction and hardening process. From the self-boring pressuremeter tests a change in pocket geometry by a factor of four resulted in an apparent increase in hydraulic conductivity by a factor of 2. Furthermore, the data from the packer tests (L/D =11) compare favourably with that of the larger pocket size self-boring tests. This aspect is to be further investigated through more testing with a variety of pocket sizes.

It is planned to excavate the wall material surrounding each test hole and to take large block samples away for testing in the laboratory. Further field studies will be completed in Wall 2, allowing the magnitude of scale effect that can occur in such systems to be better defined. Data will be presented as the change in measured permeability with respect to either the amount of material being tested, or the amount of fluid permeated in the test.

Finally, as part of ongoing EPSRC project, a guidance report will be developed in order to provide a reference for the proper in situ assessment of slurry trench systems. This will involve not only hydraulic conductivity measurements but also strength and deformation characteristics (from self-boring pressuremeter tests). It should be noted that the in situ mechanical properties may be just as significant as the hydraulic conductivity since it is the deformation characteristics which will be required in order to determine the possibility of cracking under various types of strain i.e. ground movement or volumetric strains due to chemical attack.

The measurements made to date at the test site have begun a process essential for understanding the behaviour of slurry trench systems better. Further work in this area is needed to verify trends identified at this site through testing of other walls, and ultimately a compilation of the various data from other systems, which will provide confidence in the specifications that are used in the design of such systems.

ACKNOWLEDGEMENTS

The authors would like to thank the EPSRC for funding of the current research project, as well as the Cambridge Commonwealth Trust. Also, gratitude must be paid to the assistance provided by BRE in conducting the Piezocone work, as well as project management of the site. Finally, the technical staff at the University of Cambridge Engineering Department, Steve Chandler and Chris Knight, are to be acknowledged for general assistance in the laboratory and field studies.

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Compressibility of an Electrokinetically Treated Residual Soil

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ABSTRACT
Laboratory experiments to study the impacts of electrokinetic processing on compressibility of a tropical residual soil were performed. Injections of selected chemicals ($CaCl_2$, $AlCl_3$ and H_3PO_4) at the anodes or cathodes depending upon the ion types into the soil samples were carried out in cylindrical electrokinetic cells via applications of 30 V DC electrical potential for 168 hours. Four different electrokinetic systems utilising different anolytes and catholytes (DW-DW, Al-DW, Ca-DW and DW-PA) were employed to treat the soil samples, which were compacted at 90% of the maximum dry density. Results of compressibility tests on the electrokinetically treated soil were compared to samples that were not electrokinetically treated. The DW-PA treated soil near the cathode showed a significant reduction in compressibility whereas other systems showed no significant changes.

1 INTRODUCTION
Several methods have been employed worldwide to improve engineering characteristics of soils. Such methods can be categorised into different classes of stabilisation, i.e., mechanical, chemical, thermal and electrical. With regard to electrochemical treatment to stabilise soils, chemicals are introduced at the anodes or/and cathodes, either in solution or by decomposition of the electrodes. As a result, the treated soil is strengthened due to the formation of cementing compounds that are highly resistant to shear and deformation.

Considering most electrokinetic processing are conducted on soils of temperate zones especially kaolinite, a laboratory study was initiated to investigate the effects of anolyte and catholyte types on the compressibility of an electrokinetically treated Malaysian granite residual soil. Enhancement of the engineering property was anticipated by homogeneous precipitation of the species.

2 BACKGROUND
2.1 Tropical residual soil
Most residual soils in Malaysia are high in iron and aluminium contents, which are very stable from further weathering (Taha *et al.*, 1997). A distinctive feature of the granitic residual soil is that it is a mixture of sand, silt, and clay in varying proportions (Ting and Ooi, 1976). One of the characteristics of such residual soils is the existence of bonds between

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particles. de Carvallo and Simmons (1997) attributed increased cohesional strength to the bridging or bracing between quartz grains by clay minerals and/or sesquioxides.

Barksdale and Blight (1997) found that all residual soils behave as if overconsolidated but their compressibility is relatively low at low stress. They also observed that once a threshold yield stress has been exceeded, the compressibility increases. According to Gidigasu (1976), Terzaghi's theory of consolidation has been found to be useful in predicting the settlement of structures on residual soils. Investigations by Sridharan (1988) on compressibility of tropical residual soil showed that shearing resistance near contact points between soil particles controls the compression behaviour.

2.2 Electrokinetics

Electrokinetic phenomena in porous medium are basically based on the relative motion between a charged surface and the bulk solution at its interface. The formation of an electric double layer at the charged surface of clay particles is responsible for electrokinetic phenomena of interest, namely electrophoresis, electromigration and electroosmosis. In addition, oxidation and reduction reactions took place at the electrodes as electrons are transferred in and out of the system, resulting in ion diffusion, ion exchange, development of osmotic and pH gradients, dessication by heat generation at the electrodes, mineral decomposition, precipitation of salts or secondary minerals, electrolysis, hydrolysis, physical and chemical adsorption, and fabric changes (Mitchell, 1993). At the same time, electrolysis of water at the anode and the cathode produces oxygen and hydrogen, respectively, which can be represented by the following equations;

$$2H_2O - 4e^- \rightarrow 4H^+ + O_2 \uparrow \quad \text{(anode)} \tag{1}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \uparrow \quad \text{(cathode)} \tag{2}$$

It is noteworthy that both H^+ and OH^- sweeps across the soil sample towards the cathode and the anode, respectively during the course of electrokinetic processing. Since H^+ travels approximately two times faster than OH^-, prolonged electrokinetic processing will result in acidification of the soil.

Electrokinetic processing has also been employed with the combination of chemical solutions to increase strength of cohesive soil. These chemical solutions can be fed at the anodes or the cathodes depending upon the ions to be transferred into the soil. The utilised chemical substances include amongst others calcium chloride (Harton *et al.*, 1967), aluminum chloride (Gray, 1970), and aluminum sulphate and phosphoric acid (Ozkan *et al.*, 1999).

3 EXPERIMENTAL PROCEDURES

3.1 Sample preparation

A residual soil obtained from a depth of 2 to 3 m below the ground surface was air-dried under laboratory condition, after which pebbles and plant roots were removed. Only soil passing 2.00 mm sieve was used in the electrokinetic experiments. Then the sieved soil was mixed thoroughly and kept in a securely tied large plastic bag to minimise the effects from the surrounding environment. The basic physical and chemical properties of the soil are tabulated in Table 1 and Table 2, respectively. Meanwhile, the fine fraction of the soil is classified as silt of very high plasticity, whilst the overall soil is classified as silt of high plasticity with sand and gravel (MVG) based on the British Soil Classification System (BSCS).

Table 1. Physical properties of soil

Specific gravity	2.71
Natural moisture content, %	36.5
Hydraulic conductivity, cm/s	3.60×10^{-6}
Liquid limit, %	74.5
Plastic limit, %	49
Plasticity index, %	25.5
Shrinkage limit, %	18.31
Maximum dry density, kg/m^3	1415
Optimum moisture content, %	33

Table 2. Chemical properties of soil

pH	5.30
Organic	2.0%
Chloride	0.012%
Sulfate	5.85%
Carbonate	0.20%

The inner diameter and length of soil compartment of each electrokinetic cell used in this study were 100 mm and 50 mm, respectively. Non-conductive silicon grease was thinly applied onto the inner surface of the soil compartment to avoid the formation of water film between the soil and the inner wall of the cylinder. This precaution was important to ensure that water would only flow through the soil during the experiments.

Soil sample with a dry density approximately 90% of the maximum dry density at its optimum moisture content were chosen as the basis of sample preparation for electrokinetic treatment. Every mixture of soil and distilled water weighing about 666 g prepared for electrokinetic treatment was then poured into the soil compartment. A triaxial test frame was utilised to press the mixture until a predetermined thickness of about 5.0 cm was achieved to obtain the required bulk density of 1695 kg/m^3. Then each sample was subjected to a water pressure of 40 kPa for 48 hours in order to saturate the sample.

3.2 Electrokinetic experiments

The electrokinetic experimental set-up is shown in Figure 1. Titanium meshes were utilised as the electrodes due to its high resistant to corrosion (Berkeley and Pathmanaban, 1990). For these electrokinetic experiments, the only electrical parameter held constant was the applied voltage, i.e. 30 V. No attempts were made to maintain the voltage gradients and the current densities. Four different open-anode and open-cathode electrokinetic systems were employed in this study, which consisted of:

a) Distilled water as both the anolyte and catholyte (DW-DW).
b) 1.0 M aluminium chloride as the anolyte and distilled water as the catholyte (Al-DW).
c) 1.0 M calcium chloride solution as the anolyte and distilled water as the catholyte (Ca-DW).
d) Distilled water as the anolyte and 1.0 M phosphoric acid as the catholyte (DW-PA).

Note that the left and right terms in each parenthesis represent the anolyte and catholyte, respectively. The selection of the chemical substances was based upon the types that have been utilised successfully on temperate soils, particularly kaolinite.

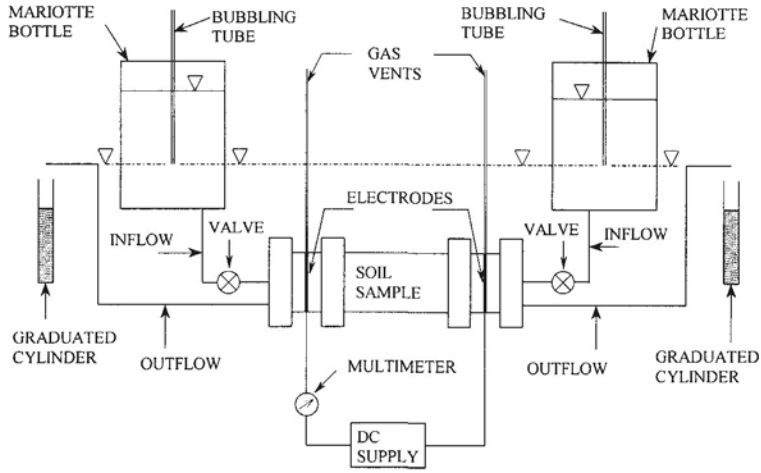

Fig. 1: Schematic diagram of the electrokinetic experimental set-up

3.3 Compressibility tests

After termination of electrokinetic processing, each treated sample was extruded and divided into two parts namely the cathode side and the anode side. Then each part of the treated sample was subjected to one-dimensional consolidation test using 50 mm diameter consolidation ring.

4 RESULTS AND DISCUSSION

Figures 2 and 3 show the normalised void ratios – log pressures curves representing the treated samples near the cathodes and anodes, respectively. Since disturbed samples were utilised for the consolidation tests, yield stresses σ_y will be referred to in the discussion instead of pre-consolidation pressures σ_c. In addition, the consolidation curve of the compacted and saturated sample (C&S) that was not electrokinetically treated will be utilised as a reference to any changes in compression index (C_c) and swelling index (C_s) resulting from the electrokinetic treatments. Table 3 summarises the values of indices and yield stresses obtained from the consolidation tests.

4.1 DW-DW system

It is observed from Figure 2 that the normalised consolidation curve of the DW-DW treated sample near the cathode resembles that of the C&S sample. As a result, the C_c and C_s as well as the σ_y of the DW-DW treated sample are similar to that of the C&S sample.

As for the DW-DW treated sample near the anode, it is observed from Figure 3 that the consolidation curve drops significantly at the early stage of the consolidation process and followed by a steady reduction in void ratios parallel to that of the C&S sample. As a consequence, the σ_y is reduced to about 25 kPa. Insignificant ionisation or desorption of cementing materials was the most probable reason for the insignificant compression during the final stage of the consolidation. Meanwhile, the resulting C_c and C_s are quite similar to that of the C&S sample.

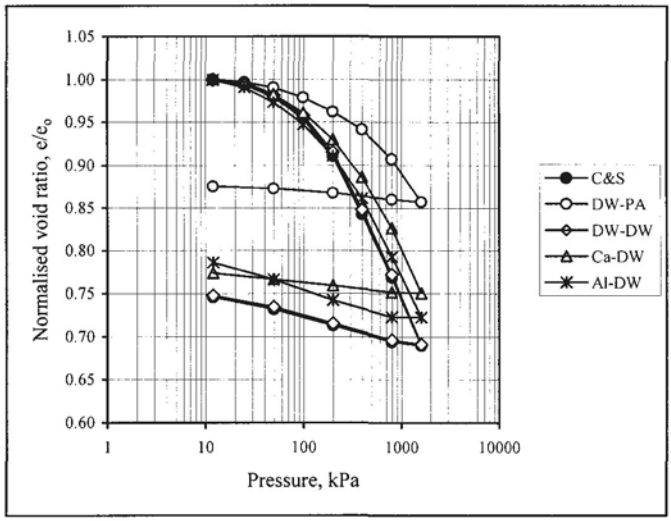

Fig. 2: Normalised consolidation curves of electrokinetically treated samples near cathodes

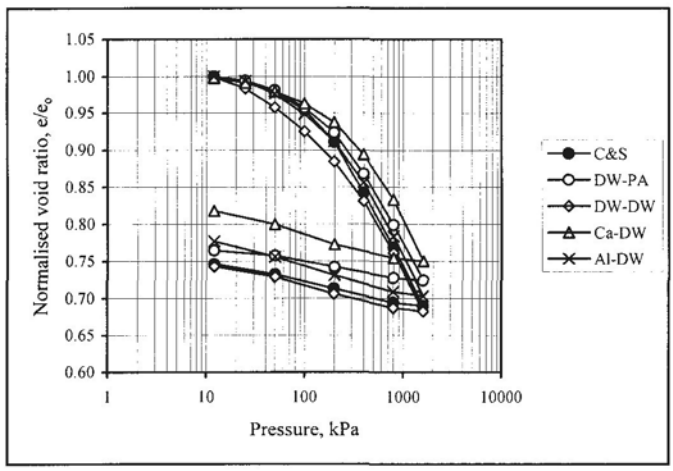

Fig. 3: Normalised consolidation curves of electrokinetically treated samples near anodes

Table 3: Values of Indices and Yield Stresses Obtained from Consolidation Tests

Treatment systems	**C&S**	**DW-DW**	**Ca-DW**	**Al-DW**	**DW-PA**
$C_{c(\text{anode})}$	0.25	0.24	0.23	0.25	0.24
$C_{c(\text{cath})}$	0.25	0.25	0.24	0.23	0.14
$C_{s(\text{anode})}$	0.03	0.03	0.03	0.04	0.02
$C_{s(\text{cath})}$	0.03	0.03	0.01	0.04	0.01
$\sigma_{y(\text{anode})}$ kPa	100	25	200	50	200
$\sigma_{y(\text{cath})}$ kPa	100	100	100	100	400

Note: anode – anode side cath – cathode side

4.2 Ca-DW system

The treated sample near the cathode was slightly less compressible than that of the C&S sample. The reduction in the C_c and C_s values might be due to the formation of calcium hydroxide adjacent to the cathode compartment as shown by the existence of a few thin whitish hard spots. These hard spots might be highly resistant to inter-particles sliding and deformation so that the treated sample was slightly less compressible. In the meantime, no change was observed in terms of σ_y value of the treated soil.

Similarly, the treated sample near the anode was less compressible than that of the C&S sample. The reduction in C_c could be due to changes in the pore water chemistry in addition to reduction in the hydraulic conductivity during consolidation process resulting in lower rates of pore pressure dissipation. On the other hand, the C_s was not affected by the treatment. In addition, the treated sample was apparently overconsolidated with σ_y of about 200 kPa.

4.3 Al-DW system

The C_c of the treated soil near the cathode decreased, whilst near the anode the value remained as 0.25. Meanwhile, the values of C_s near the anode and cathode increased slightly. It was found that the treated soil near the cathode was less compressible than the C&S at higher stresses. As part of the explanation, the formation of aluminium hydroxide gel (Murayama and Mise, 1953) might have reduced the voids between soil particles (Shin *et al.*, 2002) thus reducing the sizes of flow paths for dissipation of excess pore pressure during the consolidation process. It was also possible that the increased viscosity due to changes in pore fluid chemistry was responsible in reducing the pore pressure dissipation rate.

The σ_y values of the treated sample near the anode decreased to about 50 kPa whilst near the cathode it remained approximately 100 kPa. The acidic environment that dissolved certain compounds (Ozkan *et al.*, 1999) might increase the lubrication effects between soil particles (Ghazali, 1981), thus responsible for the reduction in σ_y near the anode. Swelling of the treated sample near the anode due to direct contact with the anolyte (Taha, 1996) as well as the released of stress during sampling were additional reasons for the reduction in σ_y value.

4.4 DW-PA system

The C_c and C_s values of the treated soil near the cathode decreased by about 44% and 67%, respectively with respect to the C&S sample. Near the anode, the DW-PA processing did not cause any significant change in terms of C_c, whilst the C_s was reduced by about 33%. Meanwhile, the values of σ_y of the treated soils near the cathode and anode increased to approximately 400 kPa and 200 kPa, respectively. Such changes were associated to the formation of phosphate compounds. These compounds encapsulated and bridged the soil particles together to form large soil grains and exerted internal effective stress under which the soil was consolidated due to the confinement of the sample in the electrokinetic cells. According to Lo *et al.* (1991), the samples were therefore virtually "overconsolidated" by the electrokinetic processing, and this is a reason why the effects of the treatment are permanent. It was also suspected that the cementing compounds and thus the cemented particles were highly resistant to sliding and deformation.

5 CONCLUSIONS

One-dimensional consolidation tests were performed on an electrokinetically treated tropical residual soil. It was observed that the DW-PA system resulting in a significant reduction in C_c of the treated soil near the cathode due to the formation of phosphate compounds and subsequent internal effective stress. The other systems did not significantly change the

compressibility of the treated soils both near the anode and the cathode. The formation of phosphate compounds and calcium hydroxides reduced the C_s values of the DW-PA and Ca-DW treated soils near the cathode, respectively. The significant reduction of C_c near the cathode and insignificant reduction of C_c near the anode of the DW-PA treated soil showed the non-homogeneity of chemical precipitation throughout the treated sample. In addition to compressibility, electrokinetic treatment also affected the yield stress values of the treated soil.

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From Risk Assessment to Risk Based Brownfield Engineering: An Integrated Approach

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ABSTRACT

Risk based assessment of contaminated land is traditionally carried out using a linear sequential approach, from "Phase 1" (non-intrusive studies), through "Phase 2" (intrusive investigation) to quantitative risk assessment. Remediation follows a similar sequential process, from strategy formulation, to remediation and finally verification and reporting.

This linear sequential approach is not congruent with the Brownfield development process. It fails to integrate with other aspects of development engineering and planning. If followed rigorously by a developer it has adverse timescale and cashflow implications and can result in considerable sums of money being spent at risk. Developers often therefore rely on low cost, poor quality assessment, with consequences for the robustness of the remedial measures implemented.

This paper argues that an effective risk-based approach to Brownfield development needs to be based on integration of the risk based contamination assessment process with development engineering and planning. A "Risk Based Brownfield Engineering" process is proposed, which aims to address the shortcomings of the traditional approach whilst delivering creatively designed and robustly implemented remediation and development solutions.

CRITICAL SUCCESS FACTORS FOR AN EFFECTIVE DEVELOPMENT FOCUSED BROWNFIELD ENGINEERING PROCESS

It is generally recognised that the technical complexity of assessment and remediation is regarded by many developers as an obstacle to brownfield development (Kirby and others, 2002). This paper argues that whilst technical complexity is unavoidable, developers' willingness to engage with this process can be improved if the process is made more effective. The following critical success factors can be defined for an effective brownfield development process (Westcott, 1998, Urban Task Force, 1999, CIRIA, 2000):

- **Solutions-driven**: the process needs to be targeted on providing solutions that enable development-related risks to be addressed and development to proceed. As such the key inputs to the process need primarily to be based on the post development use of the site, not the current use (or disuse) of the site;
- **Predictable process**: the nature of the engineering process, including inputs, deliverables and decisions required, and the time and cost required by the process, should be predictable;
- **Right first time**: avoidance of abortive work, for example, detailed assessments that are superseded by changes in end use or development layout;

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- **Matching of assessment and the planning process**: as contamination risks are end use specific it makes sense to limit pre-outline permission assessment to that required to demonstrate feasibility, and to carry out detailed assessment after the end use has been accepted in principle;
- **Delivered on time**: the process should not create delay and should be deliverable in a timescale comparable with the remainder of the development engineering process;
- **Cashflow**: avoid incurring expenditure on assessment earlier than necessary. This is particularly critical in the case of Brownfield development, where the cost of site assessment and remediation must be borne up front;
- **Integration with development engineering**: considerable synergies can be achieved if assessment and remediation is carried out as part of the development engineering process, together with design for roads, drainage and structures. The converse is also true, that if development and remediation engineering are not integrated, the results can include damage to remedial works or risk assessments being invalidated;
- **Robust and defensible assessment and remediation**: the assessment and remediation need to reflect the actual post-development end use and exposure scenario, rather than a generic or assumption-bound model developed and analysed before decisions on site engineering have been made. Implementation and verification needs to be integrated with similar processes for development engineering, including establishing a works specification (covering acceptance testing of materials as well as site specific contaminant target levels) and testing and verifying specification compliance;
- **Avoidance of stigma**: The process needs to be credibly presentable as a solutions-driven process that renders the site fit for re-use, rather than as an apparently never-ending series of phases and tiers. The latter can give the impression to non technical stakeholders that the assessors have a lack of confidence in the assessment.

HOW THE LINEAR SEQUENTIAL APPROACH MEASURES UP

Evolution of UK Approach

The early UK approach to dealing with contamination was to establish regulatory "trigger levels" for individual contaminants and for specific end use cases. The limitations of this approach are well understood, and following the legislative developments of the 1990's a more demonstrably risk-based approach was considered necessary.

The model for such an approach was available in the USA, having evolved for the specific case of assessing liabilities and clean-up requirements for contaminated sites under the "Superfund" legislation (USEPA, 1989). It is important to note that this approach did not evolve with the needs of development in mind. In most cases the assessment was carried out on an existing facility, with no redevelopment envisaged or intended. The risk assessment was a tool to be used to provide scientifically based support for, or defence against, legal and regulatory action. The process was therefore developed to be a sequential scientific enquiry-based process of investigation, evidence gathering and interpretation, rather than an engineering solutions-based redevelopment tool.

Outline of Process

The linear sequential approach consists of the activities outlined in Figure 1:

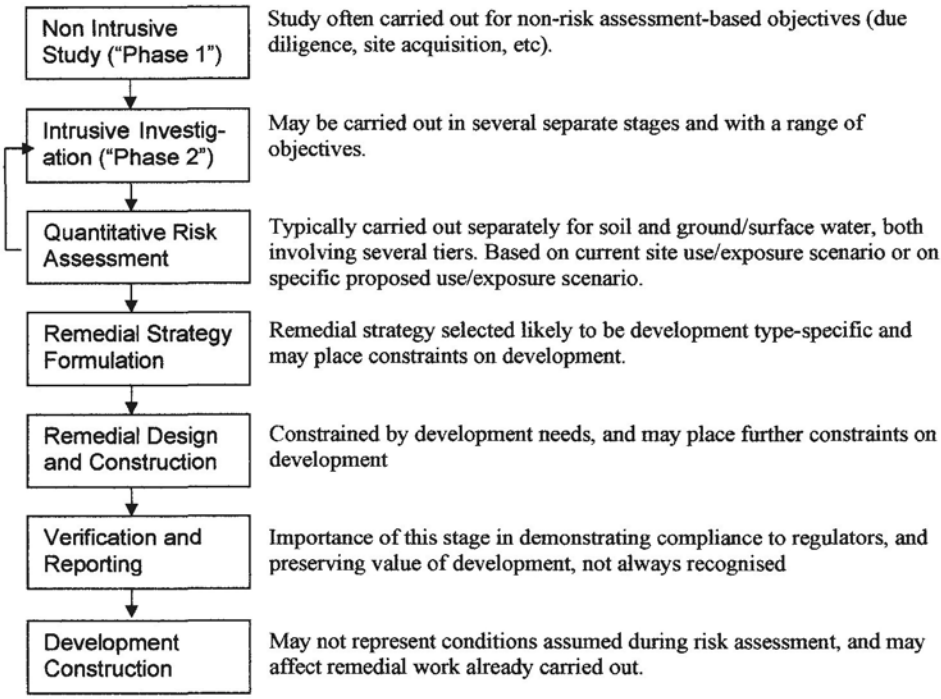

Figure 1 Outline of the Linear Sequential Risk Assessment and Remediation Process

Recent Developments

A number of recent developments affect the detailed application of the linear sequential contamination assessment process, and will need to be taken account of in proposing an alternative approach.

In August 2003 the Environment Agency issued a draft for consultation of Contaminated Land Report (CLR) 11, *Model Procedures for the Management of Land Contamination.* (Environment Agency, 2003). Although set out as a linear sequential process, the draft Model Procedures do allow an appropriate degree of flexibility to suit specific contexts such as redevelopment, and are intended to ensure that effort expended in risk assessment is proportionate to the circumstances of the activity. The Risk Based Brownfield Engineering approach outlined below uses aspects of the draft model procedures as tools within an engineering based process.

Proposals (Kirby, op. cit.) were presented in 2002 for a new "Remediation Permit" to cover all remediation activities on a site that could present a risk to the environment as a result of contamination, and which require regulatory controls. The advantage in the development context of such a permit is that it will provide a technical benchmark to demonstrate that appropriate standards have been followed in compliance with regulatory requirements, thus removing stigma. An additional would be the separation of decisions concerning technical adequacy of remediation proposals, from those related to town and country planning issues,

thus rendering a more straightforward planning process. The Risk Based Brownfield Engineering approach outlined would be consistent with the Remediation Permit proposals.

How the Linear Sequential Process Measures Up

As Table 1 shows, the linear sequential approach fails to integrate with other aspects of development engineering and planning, is difficult to control by clients due to the potential for proliferation of phases and tiers, and if followed rigorously by a developer it has adverse timescale and cashflow implications and can lead to abortive expenditure. The process was developed for assessment of liability and is not congruent with the Brownfield development process.

Critical Success Factor	Performance of Linear Sequential Approach
Solutions-driven	Approach is not structured to generate solutions in a development context.
Predictable process	Proliferation of phases and tiers renders time and cost for the process unpredictable and difficult for client to control.
Right first time	Carrying out detailed investigation at early stage in the process may result in abortive work. Changes in development type or form during the assessment process not readily managed.
Matching assessment and planning	The process is not structured to enable feasibility and design stages to be separately considered. As a result, a detailed level of end use-specific site investigation and assessment may be required before outline permission is granted for that end use. This expenditure has adverse cashflow implications and may be abortive.
Delivered on time	Additional phases and tiers can add considerable periods of time and cost to the assessment and create delay to the overall development. Whilst this may be acceptable to a party attempting to delay or minimise a potentially very large remedial liability at an existing facility, it is particularly undesirable in the development context.
Cashflow	Expenditure on site investigation, the major cost driver for the linear sequential process, is often incurred early in the process, resulting in adverse cashflow. Attempts to reduce unit investigation costs can affect quality of investigation.
Integration with development engineering	Process not structured in a similar fashion to the engineering design and project life cycle process. Tasks (such as site investigation) carried out at different times from similar engineering tasks make integration difficult or impossible.
Robust and defensible assessment and remediation	For assessment and remediation to be robust and defensible it must be based on the development form and design adopted, rather than a preliminary assumption made at the outset of the assessment. Remediation requirements established by the assessment process are not automatically incorporated into the engineering specification of the development engineering works.
Avoidance of Stigma	The assessment process is not targeted on providing a solution. Large numbers of phases and tiers can give the impression of uncertainty and lack of confidence in the outcome on the part of the assessors.

Table 1 How the Linear Sequential Process Measures Up

RISK BASED BROWNFIELD ENGINEERING: ESSENTIAL FEATURES

The Risk Based Brownfield Engineering process proposed is intended to embody the following features:

- The process must be **solutions-driven**, carried out as an engineering design process rather than a scientific enquiry process;
- The process should be **integrated** with development end use selection and other aspects of brownfield development engineering design, with an early feasibility/option selection stage being followed by detailed design and specification;
- **Phasing** of investigations, and tiers of risk assessment, should be employed specifically where necessary and expedient to address engineering design issues, rather than as an unfocused exercise in analytical refinement;
- The **robustness and defensibility** of the process should be no less than would be the case by following the linear sequential model, and should be improved by its integration with other aspects of brownfield development engineering;
- Above all, the process should be the **servant, not the master**, of the brownfield development and engineering process.

RISK BASED BROWNFIELD ENGINEERING: KEY TOOLS

Conceptual Development Model

Of fundamental importance in contamination assessment is the *Conceptual Exposure Model* (terminology, Environment Agency, 2003) which represents the possible relationships between contaminants, pathways and receptors. The purpose of the Conceptual Development Model proposed (the different terminology is deliberate) is to consider these relationships in the specific context of the proposed development.

As such, the model has to represent the impact of the post development physical conditions on these contaminant-pathway-receptor relationships. This necessitates taking full account of the development end use and layout and other aspects of the brownfield development engineering, such as new drainage and service runs, and structural foundations, including piling (Westcott, Smith and Lean, 2001).

To be effective, therefore, the development and updating of the model requires integration with other aspects of brownfield development engineering. Therefore the model will be a dynamic representation of the situation, subject to continuing review and updating as the development and engineering proposals take shape. At options/feasibility stage there may be a number of versions of this model for different end use/development layout cases, which will be reduced to a single model following option selection.

The conceptual development model serves as a key management tool for solutions-driven design as it identifies linkages that require to be addressed in the risk based brownfield engineering process, and consequently defines the scope of data acquisition and assessment necessary at the feasibility assessment, and later, the detailed design, construction and post construction stages.

Data Acquisition and Site Investigation

Data acquisition requirements (including the need for site investigation) will be defined by two criteria: the need to define the Conceptual Development Model, and the need to provide input data for feasibility study and detailed assessment. The traditional division of data acquisition into "Phase I" (desk study) and "Phase II" (intrusive site investigation) is of

relatively limited importance: what is important is to acquire the required data, whether derived from non intrusive or intrusive methods, as and when required for the Risk Based Brownfield Engineering process.

There are likely to be requirements for data derived from both non-intrusive and intrusive methods at both feasibility and detailed design stages. Intrusive investigation might take the form of an exploratory contamination investigation at feasibility stage, scoped to identify if potential linkages exist, followed by a comprehensive design data acquisition investigation, probably combined with geotechnical data acquisition, once the form and layout of the development is reasonably fixed, at detailed design stage. Carrying out the detailed investigation at this stage will maximise the development-specific utility of the investigation.

Further data acquisition will be required during the construction and post construction stages, notably for the purposes of verification of works carried out and for performance monitoring.

Quantitative Risk Assessment

In the Risk Based Brownfield Engineering model, quantitative risk assessment is regarded in the same context as any other numerically based engineering design tool, and requires the same disciplines as these other tools, such as conservatism, consideration of sensitivity and the use of experiential judgement, notably in the selection of input parameters and design cases analysed.

As with other engineering design tools, quantitative risk assessment can be used with the limited data available at feasibility stage to provide an early indication of issues to be faced in the development, to assist with early decisions on development form and layout, and to provide input to the EIA process. Clearly any quantitative risk assessment carried out at feasibility stage will require refining when more comprehensive design data is available: just as is the case with any engineering analysis.

Use of quantitative risk assessment as an integrated engineering design tool has the further advantages of allowing risks associated with different engineering options to be determined (for example, the impact on different hard surfacing types on infiltration, therefore leaching of contaminants), enables the contribution of the proposed development engineering to the remedial requirements for the site to be evaluated, and allows additional remedial measures required to be integrated into the development engineering design. Where the risk assessment results in a particular material performance requirement (for example, soil compaction, permeability or pH value) being identified as necessary, the integrated approach will enable the requirements to be incorporated into the engineering specification for the works.

Value Management/Engineering

A further advantage of adopting an engineering-based approach is the ability to use further tools developed for application in an engineering context. A particular example is the use of Value Management/Engineering approaches (ICE, 1996). These approaches focus on identifying the functional requirements of the constituent parts of the project through an integrated teamwork approach, and identifying the best value solution. They are particularly suited to application to the brownfield development situation, where adjustments to development end use, form and layout can create quite major benefits or adverse consequences in terms of remedial requirements.

RISK BASED BROWNFIELD ENGINEERING: THE PROCESS

Basis

To ensure the maximum potential for integration of contamination risk assessment, development end use and layout and other aspects of brownfield development engineering, the process is proposed to follow the same form as a traditional project life cycle process (Woodward, 1997; AGS, 1998). This can be considered under four headings[1]: **Feasibility, Detailed Design, Construction** and **Post Construction**.

Feasibility

The feasibility stage represents the initial stage of the project management cycle where the project scope is defined, options appraised, the environmental impact assessed and the viability of the project determined. For a brownfield development project, key determinants of the viability will include the cost of addressing contamination, the costs created by constraints on the development, and the cost implications of any restrictions on the development created by the planning process. Assessing, maintaining and if possible improving the viability will be the first task of the value management process

To provide answers to these questions it will be necessary to develop an understanding of the implications of the contamination present. The first stage in this process is to establish the Conceptual Development Model. There is also a potential role for quantitative risk assessment even at this early stage to address specific issues raised by the model, though it will be preliminary and require confirmation at the design stage. For example, a controlled waters quantitative risk assessment can be run "backwards" by taking compliance point limit concentrations and applying attenuation factors related to distance from the site and known or applicable generic soil properties, to establish a preliminary site specific target contaminant level, even in the absence of source delineation on the site.

In the geotechnical context, data acquisition at the feasibility stage is typically carried out on the basis of desk study alone but this is unlikely to be sufficient in the contamination context. However it is by no means essential to carry out a full contaminant source delineation at this stage provided that the presence and nature of contamination can be determined and acceptably bound estimates can be made of the extent of remediation required.

Much abortive work can be avoided at this stage by addressing contamination and development engineering in an integrated way: for example, if development requires that ground levels are reduced, detailed risk assessment of shallow contaminant impact is not necessary: what is required is an assessment of the cost for disposal of the excavated material.

The key point defining the boundary between feasibility and detailed design is the decision whether to proceed, or not, with the project. Once a positive decision is made, the expensive detailed design stage can be embarked upon. This decision is unlikely to be taken before the grant of "outline" planning permission.

Detailed Design

Detailed design is the stage at which the scheme is developed to a level of detail that allows the activities to be carried out during construction (of which remediation is a particular case) to be defined and documented. During this stage it is necessary to satisfy regulatory

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[1] Woodward defines these stages in a more general project management context as Scope Definition, Organisation, Implementation and Working Life.

requirements and address any concerns of the regulators: in the Risk Based Brownfield Development process, this is regarded as part of the design process, analogous to demonstrating that a structural design complies with a code of practice.

The Conceptual Development Model remains a primary management tool throughout the detailed design process. This will enable the requirements for data acquisition and risk assessment to be determined and implemented. Data acquisition may be by further desk based enquiry (for example, archive search to address particular issues such as past use and storage of chemicals) as well as by site investigation. Benefits of carrying out the main site investigation at this stage include the ability to relate the investigation with the adopted development layout and to combine it with simultaneous geotechnical investigation. Quantitative risk assessment carried out at this stage can also take account of the development form and layout, thus avoiding unnecessary conservatism.

A key aspect of successful integrated brownfield engineering design will be a requirement for each element of development form and layout and brownfield development engineering to have its impact on the Conceptual Development Model checked (if necessary by further quantitative risk assessment) and documented. Equally, any remedial requirements that can be addressed through other aspects of brownfield development engineering, for example, form of hard surfacing, can be established as design constraints on these activities. Value Engineering has a key role to play at this stage in achieving synergies between remedial requirements and brownfield development engineering.

Construction

The key tools - Conceptual Development Model, Data Acquisition, Quantitative Risk Assessment and Value Management/Engineering remain in use throughout the construction process. "Unforeseen" conditions are likely to be encountered during construction on Brownfield sites (though the process followed to this point should minimise these) and these will need to be addressed to preserve the robustness of the scheme overall. Equally, opportunities to achieve savings may be identified during the construction stage, particularly through Value Engineering. As in the design stage, any design related decisions made during construction will require to be checked against the Conceptual Development Model.

A key aspect of data acquisition during construction is the verification of the work. As with the preparation of "as constructed" records of structures, the verification provides details that provide reassurance both to regulators and to future site users that the work was carried out as designed, that assumptions made in the design process were proved correct, and that any residual hazards that require to be addressed in future works (for example, service trenches) are fully documented. The verification process should not be merely factual, but should enable a confirmatory check to be made against the updated Conceptual Development Model, and the re-running of elements of the quantitative risk assessment to provide confirmation that the risks have been addressed.

Post Construction

Confirmatory monitoring, commonly a regulatory requirement for the post-construction stage, should be established and carried out to address specific issues identified from the Conceptual Development Model, and should be monitored in the context of this model, with the same tools as used in the earlier stages used to address the implications of the results obtained from the monitoring.

Any further groundworks on the development site should be subject to the same disciplines as those to which the main design and construction was subject. The requirement of the CDM Regulations to establish a Health and Safety File enables the details of the Risk Based Brownfield Engineering process to be passed on to those responsible for future works, to enable a consistent approach to be taken (Westcott, 2002).

CONCLUSIONS

The Risk Based Brownfield Engineering process outlined enables the investigation, risk assessment and remediation of contaminated land on Brownfield developments to be integrated with other aspects of development planning and engineering. It uses similar tools to those defined within the Environment Agency's draft Model Procedures, and other applicable engineering tools, but applies them within the same project life cycle process that will be applied to other engineering aspects. It treats these tools primarily as design tools, and uses them to find solutions, rather than merely as an aid to scientific enquiry.

Effective use of these tools in the integrated manner required will require the integration of skills of project managers, engineers, geologists and environmental scientists. There is no doubt that this integration of skills will be challenging. Project managers and engineers understand the project life cycle and design processes but may not be familiar with the key drivers and requirements for environmental protection and risk assessment. Geologists and environmental scientists will understand the environmental issues at stake and the basis of risk assessment but are unlikely to be familiar with the project life cycle and design and construction "business process".

Two models of skills integration are likely to be effective. The first is a single organisation with an integrated team with all the required skills represented. The second is the formation of a project team from specialists in different organisations co-ordinated by a specialist project manager. The required integration is unlikely to be achieved in organisations where one single skill set dominates, or where the other skill sets are bought in by an arms length subcontract process.

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