www.environment-agency.gov.uk

Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste and sludges

Science Report SC980003/SR2

CHEMOSPHERE

Chemosphere 56 (2004) 481–491

www.elsevier.com/locate/chemosphere

Low-grade MgO used to stabilize heavy metals in highly contaminated soils

M.A. García [a], J.M. Chimenos [a,*], A.I. Fernández [a],
L. Miralles [b], M. Segarra [a], F. Espiell [a]

[a] *Department of Chemical Engineering and Metallurgy, University of Barcelona,*
Martí i Franqués, 108028 Barcelona, Spain
[b] *Department of Geochemistry, Petrology and Geophysical Prospecting, University of Barcelona,*
Martí i Franquès s/n, 108028 Barcelona, Spain

Received 10 July 2003; received in revised form 24 March 2004; accepted 21 April 2004

Abstract

Low-grade MgO may be an economically feasible alternative in the stabilization of heavy metals from heavily contaminated soils. The use of MgO is described acting as a buffering agent within the pH 9–11 range, minimizing heavy metals solubility and avoiding the redissolution that occurs when lime is used. The effectiveness of LG-MgO has been studied as stabilizer agent of heavily polluted soils mainly contaminated by the flue-dust of the pyrite roasting. The use of LG-MgO as a reactive medium ensures that significant rates of metal fixation, greater than 80%, are achieved. The heavy metals leachate from the stabilized soil samples show a concentration lower than the limit set to classify the waste as non-special residue. Regardless of the quantity of stabilizer employed (greater than 10%), LG-MgO provides an alkali reservoir that allows guaranteeing long-term stabilization without varying the pH conditions.

Keywords: Heavy metals; Contaminated soils; Magnesium oxide; Stabilization; Landfill

1. Introduction

Heavily polluted soils contaminated with heavy metals may be harmful to living human and other organisms due both to the relatively high toxicity of these metals, even at low concentrations, and to their abundance in the hydrological cycle (Alpaslan and Ali Yukselen, 2002). Soils contaminated with heavy metals have increased markedly in the last 75 years owing not only to the increased consumer use of materials containing these metals but also to technological developments. The main sources of metallic and non-metallic contamination are disposal of industrial waste, mining and smelting operations, fertilizers, and fly ash from incineration and combustion processes (Majid and Argue, 2001).

Remediation of metal contaminated soils is currently an important worldwide issue, of concern to many communities and municipalities. Many technologies are employed to restore contaminated soils, including thermal, biological, and physical–chemical treatments (Holden et al., 1989). Removing or extracting pollutants from soil matrix is an energy-intensive and time-consuming process, while immobilization technologies are a much more cost-effective solution (Alpaslan and Ali Yukselen, 2002). The majority of these immobilization

---

[*] Corresponding author. Tel.: +34-9340-37244; fax: +34-9340-35438.
E-mail address: chimenos@material.qui.ub.es (J.M. Chimenos).

0045-6535/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2004.04.005

processes include sorption, ion exchange, precipitation, and encapsulation mechanisms. The stabilization/solidification treatment process by means of chemical additives that limit the solubility of contaminants is the most cost-effective and promising option for soils contaminated by heavy metals. Recently, the potential of phosphate and phosphate and carbonate mixtures as stabilizer has been tested for in situ immobilization of heavy metal contaminated soil, mainly lead and cadmium (Ma et al., 1993; Hettiarachchi et al., 2000; Wang et al., 2001; Hamon et al., 2002). However, most of the stabilizer materials used for the removal and attenuation of heavy metals are either very selective or only effective within a narrow pH range, i.e. hydroxyapatite has a high capacity to remove lead in situ when the solution's pH is low enough (5–6) (Ma et al., 1993), but the presence of other metals in the solution inhibits Pb immobilization (Ma, 1994). The attenuation of heavy metals availability will depend on factors such as solid–solution equilibrium, or the solubility product (K_{sp}) of the solid phase (Hamon et al., 2002). The leaching of metals is pH-dependent, and the solubility of heavy metal hydroxides such as lead, cadmium, zinc, and nickel, among others, is minimal within pH range 9–11 (Chimenos et al., 2000).

Heavily contaminated soils are considered as hazardous wastes that are highly harmful to the environmental system. In these cases, the ex situ treatment of waste prior to its landfill disposal is recommended and, according to remediation technologies described above, the stabilization/solidification process is the most frequently employed procedure for heavy metals immobilization. On the other hand, the use of lime, Portland cement, or a mixture of both is the most cost-effective waste treatment, e.g. electric arc furnace dust (Smith, 1993). The use of different types of dolomitic limes with varying amounts of MgO equivalents is described as acting as a buffering agent within the pH 9–11 range, minimizing heavy metals solubility and avoiding the redissolution that occurs by using only lime or limestone (Smith, 1996).

There are many advantages in using MgO as raw material: magnesium oxide has minimal environmental impact, low solubility, and high alkalinity, reaching a maximum pH of 10, which helps to neutralize acids and precipitate metals (Teringo, 1987). However, due to the high cost of pure MgO, which is 8–10 times more expensive than the same grade of lime, it could only be a feasible alternative if low-grade MgO (LG-MgO) is used.

The present study aims to assess the effectiveness of LG-MgO as a stabilizer used to remove heavy metals from heavily contaminated soils. The data shown could be of significance in both in situ and ex situ treatment of contaminated soils with heavy metals; currently, there is no known publication describing the use of MgO as a stabilizer material for heavy metal stabilization. In agreement with the definition given by Conner (1990) the term stabilization is used to refer to a treatment with a stabilizer that has a buffering capacity and forces the system pH towards values in which the solubility of some heavy metals is minimized. Waste stabilization by pH control involves the solubility and precipitation of heavy metals.

2. Method and materials

2.1. Experimental procedure

The bulk chemical characterization of the polluted soil was determined after performing total acid digestion ($HClO_4/HNO_3$, HNO_3/HF) of the samples, carried out in a microwave. The leachates were further analyzed with inductive coupled argon plasma atomic emission spectrometry (ICP-AES) to determine the heavy metals and non-metallic species metals (Pb, Zn, Cu, Cr, Ni, V, As and Cd). The pH values were determined from a solid to liquid ratio 1:10 water leaching test.

Some representative samples were measured by means of X-ray diffraction (XRD) in order to determine the different mineralogical phases and by scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS) to identify the presence of the trace metals in particular solid phases.

The effectiveness of the stabilizer reactants was evaluated by means of DIN 38414-S4 (1984) leaching test procedure, used in Catalonian Regulations (Spain) to classify solid waste. The limit parameters stated by the Catàleg de Residus de Catalunya (1995) are shown in Table 1. Three waste quality standards are established: inert solids where all analyzed parameters are lower than the values described in column A, non-special waste where some values exceeded those in column A, and special waste where some parameter exceeded the values in column B. The leaching test procedure is based on the leaching of water-soluble substances released under continued exposure to nominally clean water percolation, predicting the short-term behavior. The DIN 38414-S4 leaching test experiments consisted of batch water leaching at liquid/solid ratio of 10 (i.e. amount of sample equivalent to 100 g of dry polluted soil per liter of deionised water). The experiments were performed in 2 l closed polyethylene reaction vessels with continuous stirring (3–5 rpm) at room temperature. After 24 h of equilibration, the final pH was recorded and the resulting suspensions were filtered through 0.45 μm membrane filters. Clear filtrates were divided into two samples. One sample was acidified with concentrated HNO_3 for the analysis of heavy and other metals in the leachate (Pb, Zn, Cu, Mn, Sn, Cr, Ni, V, Al, Fe, As, Se, Sb, Ca and Cd) by ICP-AES. By ion chromato-

Table 1
Catalonia Regulatory limits according to DIN 38414-S4 leaching test procedure and results obtained from the leachate of low-grade MgO

Catalonia Regulatory limits			
Parameter	Inert (A)	Non-special (B)	LG-MgO
pH	$5.5 < X < 12$	$4 < X < 13$	10.80
Cond. (mS cm^{-1})	6.0	50.0	2.10
Pb (mg l^{-1})	0.5	1.0	<0.10
Zn (mg l^{-1})	2.0	5.0	0.07
Cu (mg l^{-1})	2.0	5.0	<0.02
Cr (mg l^{-1})	0.5	2.0	<0.04
Cd (mg l^{-1})	0.1	0.2	<0.02
As (mg l^{-1})	0.1	0.5	<0.10
Ni (mg l^{-1})	0.5	1.0	<0.05
Al (mg l^{-1})	–	–	<0.10
Si (mg l^{-1})	–	–	<0.20
Ca (mg l^{-1})	–	–	565.50
Fe (mg l^{-1})	–	–	<0.02
Ba (mg l^{-1})	–	–	0.03
Mn (mg l^{-1})	–	–	<0.01
Sn (mg l^{-1})	–	–	<0.20
SO_4^{2-} (mg l^{-1})	500	1500	1323.76

graphy, sulphate concentration was analyzed on second sample, leaving it untreated.

Two different batches of experiments were performed at the same time. Different LG-MgO and lime ratios (5%, 10%, 15% and 20% in dry basis) are used to stabilize the contaminated soil in order to determine the best percentages of the stabilizer agent. This allows the determination of the optimal conditions to establish a stabilizer reservoir, which assures long-term stabilization. The results obtained in the stabilization using LG-MgO were compared with those obtained using the same amount of lime as stabilizer agent.

2.2. Characterization of the contaminated soil and sampling

The contaminated soil is an industrial site of about 125 000 m^2 located in the coastal of a city close to Barcelona (Spain). Early in the 20th century, a factory was located there and copper sulphate and phosphorous-based fertilizers were produced, mainly superphosphate.

Normal superphosphates are prepared by reacting ground phosphate rock with 65–75% of sulphuric acid. The sulphuric acid used in this type of manufacture is mainly extracted from pyrite minerals. In this case, most of these pyrites came from the south of Spain which contained enough copper (3% or 4%). The process starts with the roasting of pyrites as a source of sulphur dioxide, which is later oxidized to sulphur trioxide by means of a catalytic contact process with vanadium peroxide. The gas produced in the burning of sulphur ores holds a considerable quantity of flue-dust in mechanical suspension, which was removed before this gas was subjected to further treatment. The principal content of such dust is ferric oxide, zinc oxide, copper oxide, arsenious, sulphuric acids, and small quantities of different metals occurring in the raw ore. Moreover, this burning process also generates other minor contaminant streams: the ash collected in the precipitation chambers on leaving the kilns and sludge. The former contains a significant amount of arsenic, antimony, and selenium, all of which are trioxides, while the sludge are composed mainly of lead sulphate and small quantities of sulphates of barium and of tin.

During the production of fertilizers, the wastes were disposed in the area of interest for this work. Because of the long-term deposition of these wastes in the system, they were exposed to atmospheric conditionings and mixed with water, i.e., rainwater. Therefore, the pH dropped to low values since large amounts of dissolved metals and acid were released. As a consequence of that, both the soil and the groundwater were heavily contaminated with heavy metals which were finally poured into the sea.

The soil on which the wastes were deposited is formed by heterometric clean sands and gravels, mainly constituted by silica matrix, i.e., feldspars and quartz, with scant presence of slimes. Most of the polluted soil area is fully covered by a variable thickness of the deposited roasting pyrite and other wastes.

Samples were taken from the site at two separate times. In the first series (88 samples), soil samples were taken at different depths by means of prospecting pits and drilling-mills in order to assess the affected areas and contaminant distribution. Table 2 describes the analytical results obtained for most contaminant elements, divided into three different layers according to depth: upper layer (0–100 cm), middle layer (100–300 cm) and bottom layer (300–600 cm). The values in Table 2 corroborate the high heavy metal content in the polluted soil. These metals are heterogeneously distributed according to the wide range of concentration analyzed in the same layer. These results show that there are heavily polluted delimited sites located close to old fertilizer production facilities. Another effect is the decrease of metals and non-metals content with depth, in those places where the top layer is the most polluted layer while this bottom layer still presents a high species concentration. These results confirm two things: (a) the main focus of contamination is the uncontrolled deposition of pyrite roasting wastes on the soil, and (b) the pollutant mobilization mechanism is water percolation.

The different mineralogical phases present in the representative sample of the highest degree of soil pollution were identified by means of X-ray analysis (Fig. 1). In this diffractogram, different ferric oxides are identified such as

Table 2
Chemical composition of polluted soil as a function of depth

	Upper layer (0–100 cm)	Middle layer (100–300 cm)	Bottom layer (300–600 cm)
pH	1.6–7.9	1.6–8.8	5.7–12.3
V (mg kgl^{-1})	<5–1944	<5–684	<5–340
Cu (mg kg^{-1})	10–152 505	<10–4766	<10–687
Zn (mg kg^{-1})	21–8642	<10–3092	<10–2123
Pb (mg kg^{-1})	12–44 259	<10–4587	<10–340
Ni (mg kg^{-1})	<10–2087	<10–1304	<10–119
As (mg kg^{-1})	5–3630	<5–1145	<5–377
Cd (mg kg^{-1})	<10–391	<10–737	<10–134
Cr total (mg kg^{-1})	<10–112	<10–19	<10–16

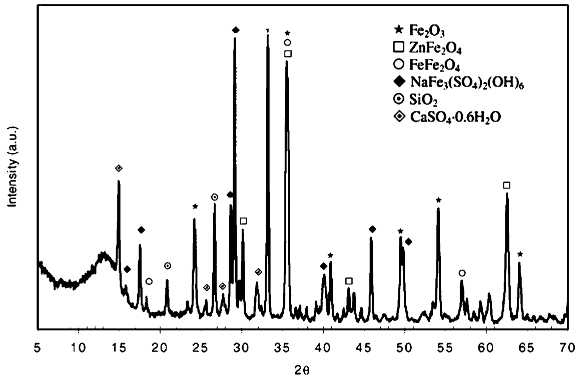


Fig. 1. XRD pattern of a representative sample from the polluted soil top layer (0–5 cm).

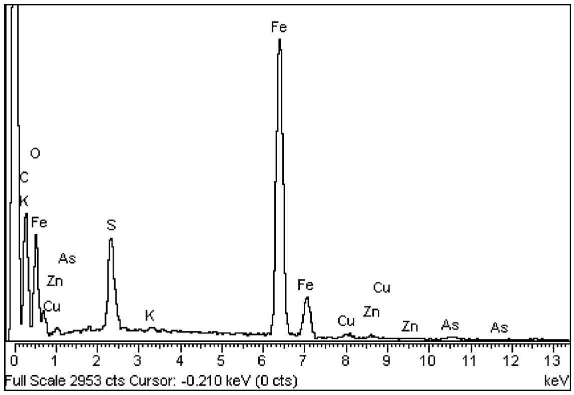


Fig. 2. Energy dispersive spectrum (EDS–SEM) of a representative sample from the polluted soil top layer (0–5 cm).

hematite (Fe_2O_3; PDI 33-0664), magnetite (Fe_3O_4; PDI 19-0629) or zinc iron oxide ($ZnFe_2O_4$; PDI 1-1109), and natrojarosite ($NaFe_3(SO_4)_2(OH)_6$; PDI 11-0302) and calcium sulphates ($CaSO_4 \cdot 0.6H_2O$; PDI 43-0605). These substances/oxides are typically generated in the pyrite roasting. The presence of heavy metals and metalloids traces is also determined in representative samples of the upper layer by means of EDS coupled to SEM. Fig. 2 shows the presence of some heavy metals and metalloids such as arsenic, zinc and copper, as well as iron, oxygen and sulphur, which are widely distributed in the sample. Likewise, the presence of other metals as lead, chromium, cadmium, and selenium are also detected by SEM–EDS analysis of different sites of the sample.

According to the results obtained above, a second series of samples were taken from the upper layer, which was characterized as the most polluted layer, to carry out the stabilization experiments. Two different stabilizer reactants LG-MgO and lime were used in order to stabilize the heavy metals.

2.3. Characterization by sequential extraction procedure

The buffer function of soil for toxicants can be characterized by the relation of the soluble fraction to elements that is immobile either because of sorption on soil colloids or the precipitation process (Welp and Brümmer, 1999). On the other hand, it is known that the availability of these heavy metals depends greatly on the characteristics of the medium, on the kind and strength of the bond, and on the properties of the solution in contact with the soil sample (Petit and Rucandio, 1999). Thus, the use of the sequential extraction procedure for speciation of trace metals described by Tessier et al. (1979) will allow us to determine the availability, mobilization, and transport of trace of metals and metalloids. According to this extraction procedure, five fractions were considered: species associated with the exchangeable phase which is likely to affect sorption–desorption processes, species associated with the acid soluble phase (e.g. carbonates), species adsorbed into solid particles (e.g. iron and manganese oxides), species associated to oxidizable organic matter and, finally, a residual fraction with mineral matter remaining unattacked. Since the first and the second fractions are considered as feasible to be leached leachate in natural conditions, they were evaluated by the leaching test procedure established by the regulatory environmental agencies to assess the solid waste potential toxicity.

Table 3 shows the trace metals and metalloids leachate concentration according to sequential extraction. These results correspond to a representative sample of the top layer (0–5 cm) of the most polluted site area. In the same way, Fig. 3 represents the percentage of trace metals and metalloids associated with each aforementioned fraction. It can be observed that the trace metals and metalloids are mainly distributed into the iron oxide particles and final residual unattackable fraction. This means that most of the species are difficult to leach and therefore and not available in natural conditions. However, in the case of pyrite roasting wastes, the unattackable fraction corresponds to the hard burned or sinterized compounds, mainly iron oxides. On the other hand, the content of trace metals in the organic fraction, i.e., vanadium and nickel, is mainly due to the presence of unburned fuel adsorbed onto the polluted soil.

According to the results, and taking into account that the DIN 38414-S4 leaching test procedure uses water as leaching media, only a small fraction of metals and metalloids will be released, corresponding to the first exchangeable water fraction.

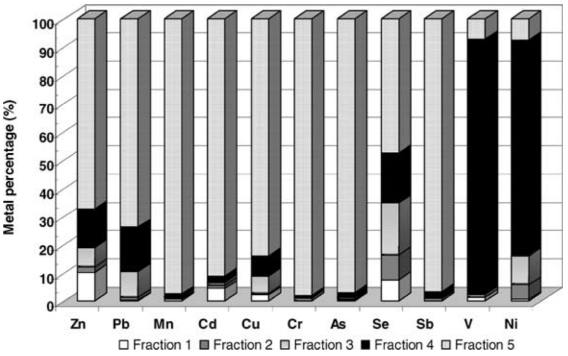


Fig. 3. Metal percentage associated to different soil fraction according to sequential extraction procedure. Fraction 1: exchangeable water phase; fraction 2: acid soluble phase; fraction 3: metals adsorbed into solid particles; fraction 4: oxidizable organic matter phase; fraction 5: residual unattacked fraction.

Table 4
Chemical composition of LG-MgO and used as stabilizer

	LG-MgO
MgO (%)	42.9
CaO (%)	4.5
Fe_2O_3 (%)	1.6
SO_3 (%)	2.0
SiO_2 (%)	2.0
Al_2O_3 (%)	0.8
d_{100} (μm)	100
d_{50} (μm)	10
d_{10} (μm)	3
LOI (1100 °C)	47.0

LOI: loss of ignition; d_x: accumulated fraction lower than particle size.

2.4. Characterization of stabilizer reactants

The LG-MgO used in this study, *Inertimag®*, is produced and sold by Magnesitas Navarras, S.A. It is a by-product of the calcination of natural magnesite in a rotary kiln at 1100 °C. In these operating conditions, the MgO obtained is termed “hard-burned” and shows a narrow range of reactivity. The flue-dust collected in the cyclones and fabric filters is stockpiled, tempered with water, and then weathered for a long period, resulting in the carbonation of the lime content. The product has an equilibrium pH of 10.5, controlled by the solubility of magnesium hydroxide. Table 4 shows the chemical composition of the LG-MgO used in this study. The MgO content ranges from 45% to 60% depending on the magnesite grade used as a raw material. The loss of ignition at 1100 °C depends on the moisture, the thermal

Table 3
Trace metals (mg kg^{-1}) associated to different soil fraction according to sequential extraction procedure

	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Zn	192.5	38.2	132.0	260.7	1288.0
Pb	6.0	39.9	283.5	488.0	2300.0
Mn	6.0	5.3	5.1	13.3	1159.5
Cd	0.7	0.2	0.2	0.4	15.3
Cu	82.2	16.4	226.7	258.6	3060.0
Cr	<0.01	0.05	2.4	2.2	228.4
As	2.3	1.5	2.0	8.2	462.2
Se	0.3	0.4	0.8	0.7	2.0
Sb	<0.01	0.7	0.1	1.6	69.6
V	0.5	<0.01	0.3	31.8	2.6
Ni	1.0	10.2	19.6	147.0	14.6

Fraction 1: exchangeable water phase; fraction 2: acid soluble phase; fraction 3: metals adsorbed into solid particles; fraction 4: oxidizable organic matter phase; fraction 5: residual unattacked fraction.

decomposition of carbonated lime and the presence of unburned dolomite and/or magnesite. Iron, aluminum, and silica do not interfere in the stabilization treatment and remain inert in the precipitated compound. Brucite ($Mg(OH)_2$; PDI 7-0239), magnesite ($MgCO_3$; PDI 8-0479), dolomite ($CaMg(CO_3)_2$; PDI 36-0426), calcite ($CaCO_3$; PDI 5-0586) and quartz (SiO_2; PDI 33-1161) were identified by means of XRD as major mineralogical phases present in LG-MgO used in this study. Finally, the cost of this stabilizer agent, *Inertimag*®, supplied by Magnesitas Navarras, S.A., is around to $40 per ton, which is cheaper than the cost of lime commonly used as alkali stabilizer agent ($48–57 per ton).

On the other hand, lime with calcium oxide purity greater than 99% (analytical grade reagent) was utilized as stabilizer agent to compare the results obtained in the soil stabilization process.

3. Results and discussion

The results obtained from the leaching test of the LG-MgO used as stabilizer reactant are also shown in Table 1. The concentrations of heavy metals and metalloids analyzed are very low and are clearly under the limits established for inert solids. As a consequence, the concentration of the heavy metals and metalloids analyzed in the stabilization experiments do not come from the reactant LG-MgO; therefore, they are released from the polluted soil.

First of all, a leaching test procedure for the non-stabilized polluted soil samples is performed in order to classify the waste and establish the initial values for a later remediation. According to the results obtained, 75% of polluted soil samples are classified as special waste (Fig. 4), since some of the analyzed values exceed the limits established in column B (Table 1). Zinc, lead and copper are the main contaminant metals released from polluted soil. So, in all the polluted soil samples classified as special residue, the zinc concentration exceeds the limit of column B, whereas 33% and 25% of the samples show, respectively, a lead and copper concentration greater than the limits established in column B.

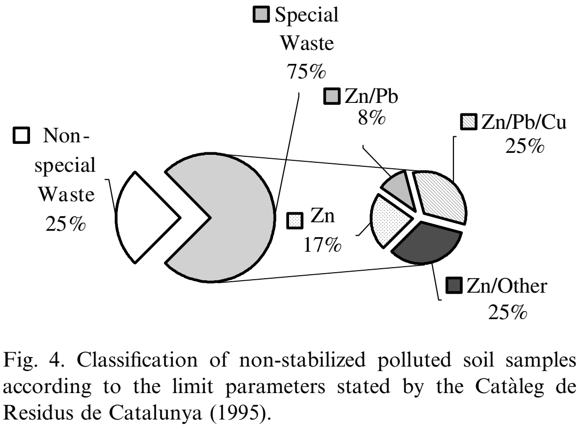


Fig. 4. Classification of non-stabilized polluted soil samples according to the limit parameters stated by the Catàleg de Residus de Catalunya (1995).

Heavy metals and metalloids analyzed from leachate obtained from three representative upper layer soil samples stabilized with LG-MgO are shown in Table 5. These samples were stabilized with different ratios of LG-MgO. The first column values are obtained from the leachate of the non-stabilized polluted soil, whereas the rest of the columns correspond to stabilized soil with different LG-MgO ratios. It can be observed that the pH of the non-stabilized polluted soil is extremely low. This fact may be attributed to the leaching of the products generated during the pyrite roasting process, e.g. jorosite and other iron sulphates, In accordance with this fact, the concentration of the sulphates is very high (values marked in bold in Table 5) and the measured values are clearly above the limit described in column B to classify the polluted soil as special waste. Likewise, the leachate also shows a high concentration of dissolved heavy metals, mainly zinc, copper, lead, arsenic and cadmium.

On the other hand, the contaminated soil stabilized with LG-MgO shows a pH close to 9.2 which is controlled by the solubility of the magnesium hydroxide. This fact is corroborated when using a greater amount of LG-MgO, e.g. 20%, the obtained pHs are again close to 9.2 and, therefore, independent of the quantity of stabilizer added. The measured pH values are always in the pH range where the metal and non-metal (hydr)-oxides show minimum solubility. Moreover, the leachate (Table 5) from the stabilized soil samples show a concentration lower than the detection limit of the analytical technique. In all cases, the metal and metalloids concentration are lower than the limit set in column A (Table 1) to classify the waste as inert. Only the leaching of sulphates from the stabilized soil samples shows a concentration greater than the non-stabilized soil. This fact is due to the high solubility of magnesium sulphate ($\approx 250\ g\,l^{-1}$) and the leaching of sulphates contained in the LG-MgO. The concentration of most of the measured heavy metals decreases as a function of percentage of the LG-MgO added to stabilize the contaminated soil. The profiles obtained are similar to the example shown in Fig. 5, concentration of lead in the leachate against percentage of LG-MgO and pH, for sample S2.

Fig. 6 summarizes the percentage decrease range of heavy metals and metalloids obtained from all upper layer polluted soil samples stabilized using different percentages of LG-MgO. In the figure, the minimum and maximum remediation percentage and the mean percentage for each metal and non-metal were represented. To calculate the percentage range, only the parameters whose analyzed concentrations from non-stabilized polluted soils were greater than the lowest standard solution used in the calibration of the analytical technique used

Table 5
Results obtained in the leachate (DIN 38414-S4) of the non-stabilized and stabilized polluted soil with LG-MgO

Parameters	S1				S2				S3			
LG-MgO (%)	0	5	10	15	0	10	15	20	0	10	15	20
pH	**2.7**[a]	9.3	9.4	9.4	**1.7**[a]	7.6	8.9	9.2	**3.6**[a]	9.1	9.6	9.6
Cond. (mS cm^{-1})	1.9	1.9	1.8	2.0	4.9	3.8	4.0	3.7	1.8	1.9	1.9	2.2
Zn (mg l^{-1})	**114.98**[a]	0.02	0.04	0.05	**292.19**[a]	0.33	0.25	0.12	**102.44**[a]	0.17	0.07	0.05
Pb (mg l^{-1})	0.08	0.10	0.08	0.08	**2.48**[a]	0.48	0.36	0.08	**2.94**[a]	0.10	0.03	0.01
Mn (mg l^{-1})	2.59	<0.01	<0.01	0.04	10.16	0.50	0.28	0.02	3.50	0.01	0.01	<0.01
Cd (mg l^{-1})	**0.36**[a]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**0.25**[a]	<0.01	<0.01	<0.01
Cu (mg l^{-1})	**163.66**[a]	0.02	0.02	0.03	**155.49**[a]	0.19	0.16	0.10	**41.98**	0.09	0.04	0.06
Cr (mg l^{-1})	0.04	<0.01	<0.01	<0.01	*0.53*[b]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
As (mg l^{-1})	*0.13*[b]	0.01	0.01	0.01	*0.26*[b]	0.09	0.07	0.02	0.07	0.16	0.08	0.05
Mo (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Se (mg l^{-1})	<0.01	0.02	0.01	0.01	0.06	0.06	0.06	0.07	0.01	0.01	0.01	0.01
Sb (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	0.18	0.03	0.02	0.03	0.03	0.06	0.05	0.06
V (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	0.08	0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01
Ni (mg l^{-1})	0.17	<0.01	0.01	0.01	*0.95*[b]	0.05	<0.01	<0.01	0.13	0.02	0.02	0.01
Hg (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cl$^-$ (mg l^{-1})	50.9	51.1	49.2	48.6	24.8	41.5	43.4	41.9	16.0	24.2	22.0	28.7
NO$_3^-$ (mg l^{-1})	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	2.1	2.0	<1.0	1.7	<1.0	<1.0
SO$_4^{2-}$ (mg l^{-1})	*697*[b]	*1151*[b]	*1230*[b]	**1682**[a]	**2158**[a]	**2708**[a]	**2852**[a]	**2656**[a]	*1052*[b]	*1175*[b]	*1162*[b]	*1349*[b]

[a] Values greater than limits established in column B (Table 1).

[b] Values greater than limits established in column A (Table 1).

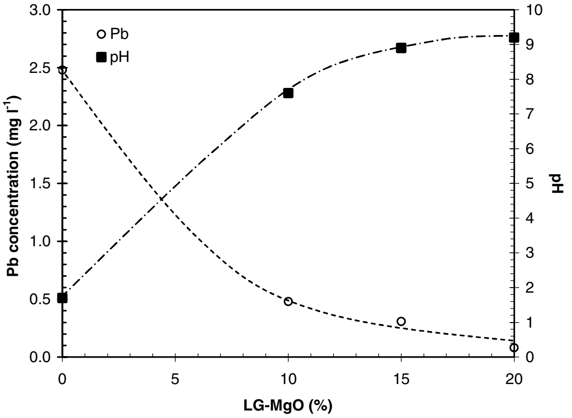


Fig. 5. Lead concentration in the DIN 38414-S4 leached as a function of pH and percentage of LG-MgO stabilizer agent added (sample S2).

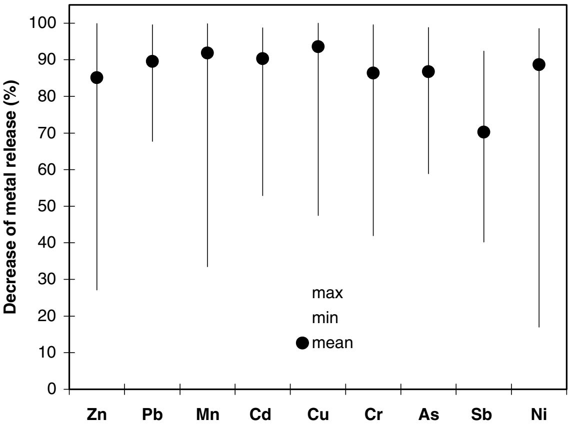


Fig. 6. Decrease of the metals release from the polluted soil samples stabilized with LG-MgO.

(ICP-AES) were considered. In the same way, percentages decreasing less than the quantizing error haves not been considered. It can be observed in Fig. 6 that the maximum release remediation for all metals analyzed is very close to 100%. On the other hand, the minimum remediation is a function of species concentration in the leachate obtained from the non-stabilized soil samples. So, the decrease of metals whose concentrations are very close to theoretical equilibrium solubility, such as metal hydroxide, is very small and of the same magnitude order as the quantizing error. In spite of that, the mean decreases of metals and metalloids release, as can be observed in Fig. 6, are in most cases close to 90%. Thus, according to the leaching of species, all polluted soil samples stabilized with a percentage of LG-MgO greater than 10% can be classified as inert (Table 1). However, for some heavy metals and metalloids, the pH-dependent species are those corresponding to lower oxidation states, i.e. As(III), Cr(III) or Sb(III), whereas the higher oxidation states, as As(V), Cr(VI) or Sb(V) are suitable to form anionic species which are non-pH-dependent. In these cases, its reduction becomes necessary previously to stabilization using alkali stabilizer agents.

Table 6 shows the results obtained in the stabilization with lime of the same contaminated soil samples studied above. The percentage of lime used in this experimental series is the same as that used in the stabilization with LG-MgO. In this case, the pH is controlled by the solubility of portlandite–$Ca(OH)_2$. However, the use of small percentages of lime shows an oversaturation of portlandite with pHs greater than 12.5. As a consequence, at these pH values, some metal hydroxides may redissolve from the polluted soil to form their corresponding soluble hydroxides complex. This fact is clearly observed in the leaching of lead (Fig. 7), which insoluble hydroxide, $Pb(OH)_2$, at pHs higher than 12 forms the corresponding soluble plumbite species, PbO_2H^-. So, the concentration of lead in the leachate increases with the percentage of lime added and therefore always shows concentrations greater than those obtained from non-stabilized polluted soil samples. This behavior is also observed in other metals like zinc or copper, in which the concentration increases in direct proportion to the percentage of lime added. However, in theses cases, the metal concentration of the leachate obtained from the stabilized soil with lime is always lower than those obtained from non-stabilized soil, and the concentration values are low enough to be within the limits established that classify a waste as non-special.

On the other hand, the sulphate concentration in the leachate of most of the samples analyzed decreases inversely with the amount of lime added. However, this results are not as good as expected from the equilibrium solubility of gypsum–$CaSO_4 \cdot 2H_2O$, showing in some stabilized samples, concentrations greater than the limits described in Table 4 (column B) for a non-special residues.

As a consequence of the results obtained, and according to the limits described in Table 1, all polluted soil samples stabilized with lime must be classified as special waste, showing an important release of heavy metals.

4. Conclusions

The mobility of metals and metalloids associated with an exchangeable water or acid soluble phase of the soil and metals adsorbed into solid particles is hindered by the neoformed solid phases and precipitation–dissolution reactions. These attenuation mechanisms depend on factors such as solid–solution equilibrium, or the

Table 6
Results obtained in the leachate (DIN 38414-S4) of the non-stabilized and stabilized polluted soil with lime

Parameters	S1				S2				S3			
Lime (%)	0	5	10	15	0	10	15	20	0	10	15	20
pH	**2.7**[a]	12.0	12.1	12.2	1.7	12.4	**13.1**[a]	**13.1**[a]	3.6	12.6	**13.2**[a]	**13.2**[a]
Cond. (mS cm^{-1})	1.9	8.2	9.2	9.5	4.9	6.6	9.5	9.6	1.8	7.0	8.6	8.1
Zn (mg l^{-1})	**114.98**[a]	**2.54**[a]	**2.65**[a]	**3.56**[a]	**292.19**[a]	*1.30*[b]	*2.00*[b]	*2.45*[b]	**102.44**[a]	*1.57*[b]	**2.53**[a]	**2.64**[a]
Pb (mg l^{-1})	0.08	**1.91**[a]	**2.01**[a]	**3.19**[a]	**2.48**[a]	**6.23**[a]	**13.71**[a]	**15.77**[a]	**2.94**[a]	**14.73**[a]	**14.99**[a]	**15.31**[a]
Mn (mg l^{-1})	2.59	<0.01	<0.01	<0.01	10.16	0.01	0.01	0.01	3.50	<0.01	<0.01	<0.01
Cd (mg l^{-1})	**0.36**[a]	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	**0.25**[a]	<0.01	<0.01	<0.01
Cu (mg l^{-1})	**163.66**[a]	0.98	0.86	1	**155.49**[a]	0.21	0.18	0.24	**41.98**[a]	0.11	0.11	0.20
Cr (mg l^{-1})	0.04	<0.01	<0.01	<0.01	0.53	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
As (mg l^{-1})	**0.13**[a]	0.07	0.07	0.02	*0.26*[b]	*0.11*[b]	*0.13*[b]	0.09	0.07	<0.01	<0.01	<0.01
Mo (mg l^{-1})	<0.01	0.02	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Se (mg l^{-1})	<0.01	0.02	0.02	0.02	0.06	0.18	0.24	0.24	0.01	<0.01	<0.01	<0.01
Sb (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	0.18	0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01
V (mg l^{-1})	<0.01	0.01	<0.01	<0.01	0.08	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni (mg l^{-1})	0.17	0.02	0.03	0.03	0.95	0.02	0.04	0.03	0.13	0.03	0.03	0.03
Hg (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cl$^-$ (mg l^{-1})	50.9	34.9	38.1	10.4	24.7	54.5	53.3	52.2	15.9	34.2	26.3	29.1
NO$_3^-$ (mg l^{-1})	<1.0	<1.0	<1.0	<1.0	<1.0	7.0	7.2	7.3	<1.0	5.0	1.0	1.8
SO$_4^{2-}$ (mg l^{-1})	*697*[b]	*533*[b]	449	153	**2158**[a]	**1226**[a]	**1247**[a]	**1142**[a]	*1052*[b]	*870*[b]	*873*[b]	*711*[b]

[a] Values greater than limits established in column B (Table 1).

[b] Values greater than limits established in column A (Table 1).

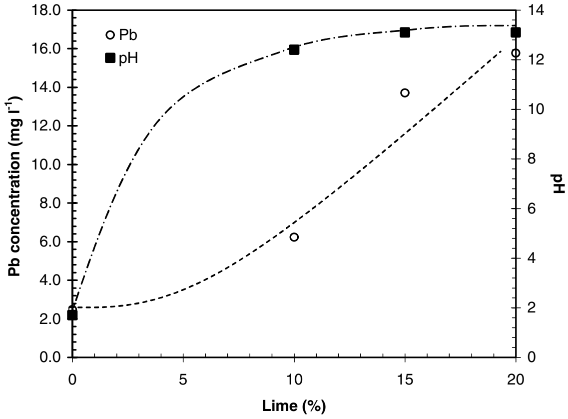


Fig. 7. Lead concentration in the DIN 38414-S4 leached as a function of pH and percentage of lime stabilizer agent added (sample S2).

solubility product (K_{sp}) of the solid phase. In this way, metals and lower oxidation states of metalloids are pH-dependent, and the solubility of most of metal and metalloid (hydr)oxides such as lead, cadmium, zinc and nickel is minimal within pH range 9–11.

The use of low-grade MgO (LG-MgO) acting as a buffering stabilizer agent within the pH 9–11 range may be an economically feasible alternative in the stabilization of heavy metals from heavily contaminated soils. The effectiveness of LG-MgO has been studied in this work as a stabilizer agent of heavily polluted soil contaminated by the uncontrolled deposition of waste generated during the production of inorganic fertilizers, mainly flue-dust from pyrite roasting.

The contaminated soil stabilized with LG-MgO shows, independently of the quantity of stabilizer employed, a pH close to 9.2, which is controlled by the solubility of the magnesium hydroxide. As a consequence, the leachates from the stabilized soil samples show a concentration lower than the limit set to classify the waste as inert, according to Catàleg de Residus de Catalunya (1995). The use of LG-MgO as a reactive medium for the treatment of soils contaminated by heavy metals ensures that significant rates of reduction of metals and metalloids are achieved, greater than 80%, particularly in cases in which there is initially a high concentration where the release remediation is very close to 100%.

The use of a percentage close to 10% of LG-MgO as stabilizer agent, prior to landfill the stabilized polluted soil, has been demonstrated to be enough to diminish the heavy metals and metalloids release and classify the waste as non-special residue. Using greater amounts of LG-MgO an alkali reservoir is provided, that guarantees long-term stabilization without varying the pH conditions and avoiding the redissolution that occurs using lime as stabilizer agent. Only the leaching of sulphates from the stabilized soil samples shows a concentration greater than the limits site to classify the waste as non-special residue using both LG-MgO and lime as stabilizer agents.

According to the results obtained in this work, low-grade MgO was found to be suitable and economically feasible for use as heavy metal stabilizer agent prior to landfill. Similarly, it is possible use LG-MgO for the in situ remediation of soft heavy metal polluted soils.

Acknowledgements

The authors would like to thank the Junta de Residus, Generalitat de Catalunya, the Waste Agency of the Ministry of the Environment of Catalonia (Spain), and Magnesitas Navarras S.A. for their cooperation in financing and supporting this work. The authors also thank Mrs. S. Arosa and Mrs. R. Hernando for their assistance with chemical analysis and data management.

References

Alpaslan, B., Ali Yukselen, M., 2002. Remediation of lead contaminated soils by stabilization/solidification. Water Air Soil Pollut. 133, 253–263.

Catàleg de Residus de Catalunya, 1995. Generalitat de Catalunya Departament de Medi Ambient. Junta de Residus, Barcelona (in Catalan).

Chimenos, J.M., Fernández, A.I., Segarra, M., Fernández, M.A., Espiell, F., 2000. Utilización de Magnesia para la estabilización de tierras contaminadas. Revista Técnica Residuos 55, 69–72 (in Spanish).

Conner, J.R., 1990. Chemical Fixation and Solidification of Hazardous Wastes. Van Nostrand Reinhold, New York.

DIN 38414-S4, 1984. German Standard Procedure for Water, Wastewater and Sludge Analysis, Sludge and Sediments (Group S). Determination of Water Leachability. Benthe-Vertrieb Gmbh, Berlin and Köln, Germany.

Hamon, R.E., McLaughlin, M.J., Cozens, G., 2002. Mechanisms of attenuation of metal availability in in situ remediation treatments. Environ. Sci. Technol. 36, 3991–3996.

Hettiarachchi, G.M., Pierzynski, G.M., Ransom, M.D., 2000. In situ stabilization of soil lead using phosphorus and manganese oxide. Environ. Sci. Technol. 34, 4614–4619.

Holden, T., Newton, J., Sylvestri, P., Diaz, M., Baker, C., Hermann, J.G., Guzman, D., 1989. How to Select Hazardous Waste Treatment Technologies for Soils and Sludges. Noyes Data Corp., Park Ridge, NJ.

Ma, Q.Y., Traina, S.J., Logan, T.J., Ryan, J.A., 1993. In situ lead immobilization by apatite. Environ. Sci. Technol. 27, 1803–1810.

Ma, Q.Y., 1994. Effects of aqueous Al, Cd, Cu, Fe(II), Ni and Zn on Pb immobilization by hydroxyapatite. Environ. Sci. Technol. 28, 1219–1228.

Majid, A., Argue, S., 2001. Remediation of heavy metal contaminated solid waste using agglomeration techniques. Miner. Eng. 14, 1513–1525.

Petit, M.D., Rucandio, M.I., 1999. Sequential extractions for determination of cadmium distribution in coal fly ash, soil and sediment samples. Anal. Chim. Acta 401, 283291.

Smith, C., 1993. Method and mixture for treating electric arc furnace dust. US Patent 5,242,122.

Smith, C., 1996. Buffering of cementations hazardous waste compositions containing electric arc furnace dust. US Patent 5,569,152.

Teringo III, J., 1987. Magnesium hydroxide reduces sludge/improves filtering. Pollut. Eng. 19, 78–83.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.

Wang, Y.M., Chen, T.C., Yeh, K.J., Shue, M.F., 2001. Stabilization of an elevated heavy metal contaminated site. J. Hazard Mater. B 88, 63–74.

Welp, G., Brümmer, G.W., 1999. Adsorption and solubility of ten metals in soil samples of different composition. J. Plant Nutr. Soil Sci. 162, 155–161.

The Environment Agency is the leading public body protecting and improving the environment in England and Wales.

It's our job to make sure that air, land and water are looked after by everyone in today's society, so that tomorrow's generations inherit a cleaner, healthier world.

Our work includes tackling flooding and pollution incidents, reducing industry's impacts on the environment, cleaning up rivers, coastal waters and contaminated land, and improving wildlife habitats.

This report is the result of research commissioned and funded by Environment Agency's Science Programme.

Published by:
Environment Agency, Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol, BS32 4UD
Tel: 01454 624400 Fax: 01454 624409
www.environment-agency.gov.uk

ISBN: 1 844 323 196

This report is printed on Cyclus Print, a 100% recycled stock, which is 100% post consumer waste and is totally chlorine free. Water used is treated and in most cases returned to source in better condition than removed.

Further copies of this report are available from:
The Environment Agency's National Customer Contact Centre by emailing enquiries@environment-agency.gov.uk or by telephoning 08708 506506.

Authors:
B. D. Bone, L H. Barnard, D.I. Boardman, P.J. Carey, C.D. Hills, H.M. Jones, C.L. MacLeod and M. Tyrer

Dissemination Status:
Publicly available

Keywords:
Stabilisation, solidification, immobilisation, remediation, contaminated soil, waste stream, reagent, binder, cement.

Research Contractor:
Centre for Contaminated Land Remediation
School of Science, University of Greenwich
Chatham Maritime, Kent ME4 4TB

Environment Agency's Project Manager:
B.D. Bone, National Groundwater & Contaminated Land Centre, Olton Court, Solihull.

Research Collaborator:
Codes and Standards for Stabilisation and Solidification Technologies (CASSST)

Science Project Number:
SC980003 (P5-064)

Product Code:
SCHO0904BIFP

Science at the Environment Agency

Science underpins the work of the Environment Agency, by providing an up to date understanding of the world about us, and helping us to develop monitoring tools and techniques to manage our environment as efficiently as possible.

The work of the Science Group is a key ingredient in the partnership between research, policy and operations that enables the Agency to protect and restore our environment.

The Environment Agency's Science Group focuses on five main areas of activity:

- **Setting the agenda**: To identify the strategic science needs of the Agency to inform its advisory and regulatory roles.
- **Sponsoring science**: To fund people and projects in response to the needs identified by the agenda setting.
- **Managing science**: To ensure that each project we fund is fit for purpose and that it is executed according to international scientific standards.
- **Carrying out science**: To undertake the research itself, by those best placed to do it - either by in-house Agency scientists, or by contracting it out to universities, research institutes or consultancies.
- **Providing advice**: To ensure that the knowledge, tools and techniques generated by the science programme are taken up by relevant decision-makers, policy makers and operational staff.

Professor Mike Depledge   Head of Science

CONTENTS

APPENDICES

1. INTRODUCTION

1.1 Background

The UK has a long and varied history of industrial development, with an estimated 100-300,000 hectares of potentially contaminated land, equating to about 50-100,000 sites (DETR, 2000). The contaminants present on-site may vary considerably both in terms of their physico-chemical properties and ease of treatment. Appendix 1 contains a list of industry profiles published by the Department of the Environment (now Defra). These profiles are of particular value during a desk study, and enable the reader to determine which types of contamination may be associated with particular industrial activities. It can be seen that contaminants are varied across industrial sectors and that, at any industrial site, residues containing complex mixtures of contaminants may be encountered.

The implementation of the Landfill Directive (Council Directive 1999/31/EC) is likely to encourage the use of alternative forms of disposal or recovery for a number of industrial waste streams, including contaminated soil and hazardous waste by:

- ending the co-disposal of hazardous waste with municipal solid waste;
- requiring pre-treatment of waste before landfill; and indirectly,
- lead to waste minimisation;
- increase the cost of landfill; and
- encourage recovery of waste rather than disposal.

These drivers are likely to create growing markets for both pre-treatment of waste before landfill and for treatment to enable recovery and re-use. Stabilisation/solidification (S/S) is considered to be an effective technology for the commercial treatment of a number of waste streams, including hazardous inorganic waste and contaminated soil, in a number of countries including the USA and France.

This document provides a review of literature on the use of S/S for the remediation of contaminated land and the treatment of hazardous wastes. It provides a reference resource to the "Guidance on the use of S/S for the treatment of contaminated soil" (Environment Agency, 2004), which it accompanies. This review has been completed between 2000 and 2003 and is one of the outputs from the CASSST (Codes and Standards for Stabilisation and Solidification Technologies) work programme produced by the Centre for Contaminated Land Remediation, University of Greenwich.

1.2 Literature Review

In order to review the current status of S/S and the science underpinning this technology a detailed search of the literature has been undertaken. The methodology employed has primarily, involved searching a number of electronic databases augmented by publications such as books and reports provided by a number of key organisations and individuals around the world. Furthermore, as the science review has developed, a number of draft documents have been circulated to approximately 100 active workers in the field of S/S (including the CASSST steering committee and wider CASSST advisory group) for comment. The consultation process extended to approximately 1 year to June 2003 and has resulted in a significant amount of in-depth comment, which has been carefully considered and incorporated where possible in this final review document.

This review, thus, aims to provide a resource of information regarding S/S technology, to inform potential users of the strengths and weaknesses of this technology. This review:

- considers the interactions between contaminants and soil components;
- identifies the fundamental principles underlying S/S and the treatment of inorganic and organic contaminants in soils and wastes;
- presents case studies in which S/S has been used successfully and where problems have occurred;
- discusses appropriate physical and chemical analytical techniques and modelling approaches that may be used; and
- evaluates the long-term durability of S/S waste forms.

1.3 Review Methodology

The databases used during the compilation of this review on S/S are given in Table 1.1. Table 1.2 gives key organisations that have been consulted and who have provided information on S/S to the review process.

At regular intervals during construction of the review electronic information products have been examined and key documents have been obtained and reviewed.

Table 1.1: Electronic databases and search-engines used in this review

Blackwell Synergy
ASCE
Blackwell Publishing
Science Direct
Cambridge Dictionaries Online
Environment Abstracts
Technical Indexes
Ingenta
Kluwer Academic Publishers
Cambridge University press
MIMAS
Oxford University Press
Web of Science
Web of Knowledge
Technical Indexes on-line
SwetsNetNavigator
Clu-in (EPA)
VISIT (EPA)

Table 1.2: Key organisations consulted during the review

ADEME (French Environment Agency)
Arup
Bachy Soletanche
British Nuclear Fuels
Castle Cement
CL:AIRE
CSMA
DEFRA
ECN (Netherlands Energy Research Foundation)
Environment Agency (England and Wales)
Envirotreat
Forkers
INERTEC (France)
Lafarge Cement UK
May Gurney
Powerbetter Environmental Processes
Rugby Cement/RMC
Scottish Environment Protection Agency (SEPA)
SITA
STARNET (EPSRC funded network)
The British Cement Association
The British Lime Association
The Portland Cement Association
TRL/Veridis
UKQAA
US Environment Protection Agency
Weeks Consulting

1.4 How to Use This Document

This electronic review document is a stand-alone document that, when used in conjunction with the guidance, will provide essential information on the use and limitations of S/S within the UK. It is intended for use by parties involved in the remediation of contaminated land and the treatment of hazardous wastes. The relationship between the guidance and this review document is summarised in Table 1.3 below.

Table 1.3: Relationship between the guidance document and the Science Review

Guidance	Science Review
Chapter 1: Introduction - where does S/S fit in the context of remediation of land contamination?	Chapter 1: introduction - review methodology and relationship to guidance
Chapter 2: Screening - is S/S likely to be feasible?	Chapter 2 – soil and contaminant interactions Chapter 3 – binder interactions Chapter 4 – S/S of inorganics Chapter 5 – S/S of organics Chapter 6 – application of S/S
Chapter 3: Design - what binder should be used and how should S/S be applied?	As chapter 2 of guidance
Chapter 4: Construction - what are the key issues for successful implementation?	As chapter 2 of guidance
	Chapter 7 - treatment of waste streams
Chapter 5: Long-term Maintenance and Monitoring - is action required to ensure long-term performance?	As chapter 2 of guidance
Chapter 6: Sampling and Testing Programmes - what tests are required to demonstrate compliance with remedial objectives and predict long-term performance of the treated material (waste form)?	Chapter 8 - physical and leach tests Chapter 9 - durability discussed in terms of analogues - the weathering of concrete and rock and comparison with S/S disposal and re-use scenarios Chapter 10 - modelling approaches to predict the long-term leaching performance of S/S treated material
Chapter 7: Summary	Chapter 11 - concluding remarks

REFERENCES

Council of the European Union. (1999) *Council Directive1999/31/EC Landfilling of Waste*

Department of the Environment, Transport and the Regions (2000*) Environmental Protection Act 1990: Part IIA. Contaminated Land*. DETR Circular 02/2000. The Stationery Office.

Environment Agency (2003). *Guidance on the use of Stabilisation/Solidification for the Treatment of Contaminated Soil*. R&D Technical Report P5-064/TR/1

2 INTRODUCTION TO SOILS, CONTAMINANTS AND THEIR INTERACTIONS

2.1 Introduction

Knowledge of the soil or matrix type and contaminant properties are important factors in the prediction of contaminant partitioning and therefore mobility. Classification of the soil type allows some prediction of soil-binder interactions, which may be beneficial or detrimental to the performance of the S/S waste form, and therefore assists in the selection of the most appropriate binder. A number of excellent textbooks discuss soil processes (e.g. Sposito, 1994, Tan, 1993, Yong *et al.*, 1996, Yong and Mulligan, 2003) and should be referred to for a comprehensive review of the subject. This chapter provides an introduction to the properties and processes that influence the fate and transport of contaminants in soil and may have a bearing on the design of S/S remediation. The properties of commonly used binders are reviewed in Chapter 3 and the interactions that may occur when binders and contaminated soils or wastes are mixed are discussed in Chapters 4 and 5.

2.2 Soils

The primary constituent of the majority of soils is mineral generally derived from the physical and chemical weathering of rock, the parent material. Due to a range of physical and chemical mechanisms and the presence of biota, soils typically consist of a porous mixture of silt, sand, clay, and organic matter. Soil-like deposits may also be formed as a result of man's activities and generally form heterogeneous deposits of mineral and organic matter. Understanding the fundamental factors governing the formation of soil deposits, their composition and subsequent interaction with contaminants is important when considering the application of S/S treatment. Further information on the weathering of rock and soil is provided in Chapter 9. Figure 2.1 illustrates the main constituents of the soil solids.

Soils will react with contaminants to greater or lesser degrees, depending on the physical and chemical properties of the soil and nature of the contaminant. Table 2.1 shows some typical physical and chemical properties of soils measured to support S/S design (after CIRIA, 1995). It should be noted however, that additional information to this might be preferable/required for a particular scheme. Sections 2.3 and 2.4 discuss soil physical and chemical properties in greater detail, and Appendix 2 provides the properties of soil or waste that may require evaluation when S/S is used.

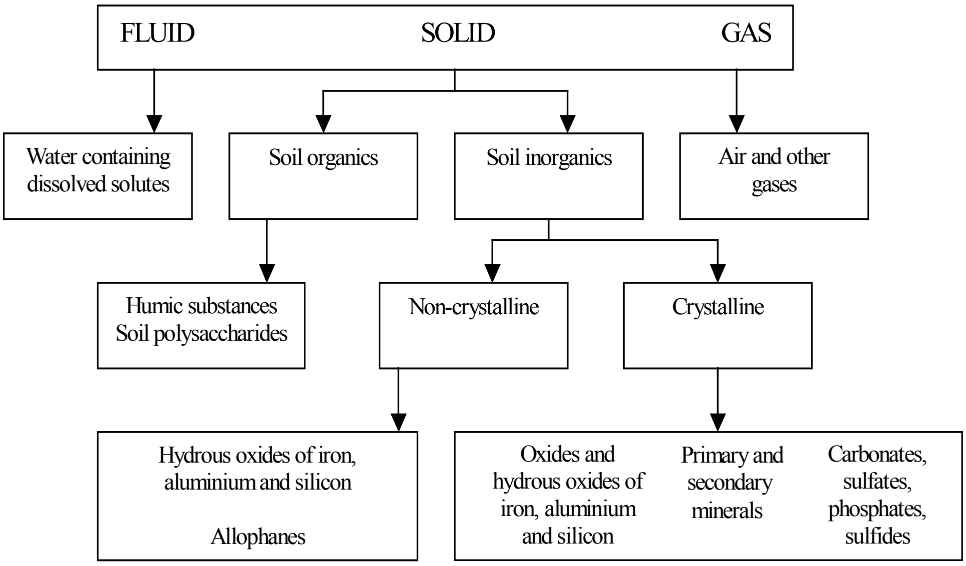


Figure 2.1: Soil constituents, showing the main components of the soil solids (after Yong *et al.*, 1996)

Table 2.1: Typical information requirements for S/S (after CIRIA, 1995)

Parameter	Purpose
Physical characteristics	
Particle size	To determine pre-treatment and materials handling requirements, mixing characteristics, potential environmental impacts.
Moisture content	To determine pre-treatment materials handling requirements, reagent formulation.
Temperature	To determine impact on process performance, curing characteristics.
Chemical Characteristics	
Contaminants (type, concentration, variability)	To determine formulation of reagents, potential environmental impacts through emissions.
Leaching behaviour	To provide measures against which to judge results of treatability studies and full-scale application.
Inhibitory species	To determine compatibility with formulation.
pH	To predict reaction conditions, impact on leaching characteristics.

2.3 Physical Properties of Soils

The physical characteristics of a soil can significantly influence its engineering behaviour and the attenuation of contaminants. The physical tests utilised during S/S design are traditionally selected on the basis of handling/mixing characteristics and the end use of the material (e.g. strength parameters relevant to the loading scenario). However, physical properties can also be used to evaluate the availability of contaminants and the potential effect of remediation on their attenuation.

The sections below discuss some of the more common physical properties in greater detail and Chapter 7 identifies suitable testing methods for these parameters.

2.3.1 Particle size

Particle size is defined as the percentages of various grain sizes present in a material as determined by sieving and sedimentation (British Standard BS 1924: Part 1: 1990).

BS 1924: Part 1: 1990 identifies three classes of stabilised material depending on their particle size. These are shown in Table 2.2. Any material is regarded as belonging to the finest-grained group appropriate under the definitions given.

Table 2.2: Classification of materials before stabilisation, based on particle size distribution (after BS 1924: Part 1: 1990)

Class	Definition
Fine-grained materials	Containing less than 10% retained on a 2mm test sieve
Medium-grained materials	Containing more than 10% retained on a 2mm test sieve but not more than 10% retained on a 20mm test sieve
Coarse-grained materials	Containing more than 10% retained on a 20mm test sieve but not more than 10% on a 37.5mm test sieve.

Materials that contain large or irregular shaped particles can be difficult to test in the laboratory, and in the field they are likely to cause damage to the mixing plant. BS 1924: Part 1: 1990 states that materials containing greater than 10% retained on the 37.5mm test sieve, cannot be fully examined by the majority of test procedures given in that standard. This problem can be overcome by pre-screening to remove the large pieces or crushing the larger particles to within acceptable limits. The fine and medium-grained materials can be further classified as shown in Table 2.3.

Table 2.3: Soil classifications and properties (after Townsend, 1973)

Grain size	**Coarse sand**	**Fine sand**	**Silt**	**Clay**
Maximum (mm)	2	0.2	0.06	0.002
Average number of particles per g	350	350 000	3×10^8	3×10^{11}
Average surface area per g (cm^2)	40	400	4000	60 000
Typical mineralogical make-up	Quartz, felspars, rock fragments	Quartz, felspars, ferro-magnesium minerals	Quartz, felspars, ferro-magnesium minerals, heavy minerals	Quartz, felspars, secondary clay minerals
General characteristics	Loose grained, non-sticky, air in pore space of moist sample. Visible to the naked eye.	Loose grained, non-sticky, no air in pore space of moist sample, visible to the naked eye.	Smooth and flour-like, non-cohesive, microscopic	Sticky and plastic, microscopic to sub microscopic, exhibit Brownian movement
Implications for S/S	Likely to be easily mixed. Potential for increased permeability (over well graded/fine grained soil)	Likely to be easily mixed. Potential for increased permeability (over well graded/fine grained soil). May be moisture sensitive.	Sensitivity to moisture change-needs to be addressed at design.	Uniform mixing may be difficult, but clay is easily stabilised. Clay minerals can react with binders to form cementitious products.

The grading of the material to be stabilised can influence the strength gain properties of the treated material. Well-graded materials have been found to exhibit a linear increase in unconfined compressive strength (UCS) with increased addition of cement binder (and lime binder before all the clay minerals have reacted). The mean particle size is not reported to affect this phenomenon, therefore a linear increase in strength can be expected for either clays or gravels. However, uniformly graded materials are identified as the exception to this linear behaviour when smaller quantities of binder are added. Sherwood (1993) suggests that this is due to the binder acting as a filler in uniformly graded materials. Once the binder has improved the grading of the material Sherwood (1993) reports a linear increase again.

2.3.2 Cohesion and plasticity

The properties of clay minerals give unique engineering properties to clay soils: cohesion and plasticity. Cohesive material can be defined as all material which, by virtue of its clay content, will form a coherent mass. Non-cohesive (granular) material will not form a coherent mass (BS 1924: Part 1: 1990). Where soils that are predominantly coarse-grained contain sufficient fine grains to show apparent cohesion and plasticity, they will be classified as fine soils (BS 5930: 1999). As a consequence, a cohesive soil can comprise less than 10% clay-sized particles.

Knowledge of the cohesivity of a soil assists in the selection of S/S treatment methods. Due to the poor mixing characteristics of cohesive material, treatment using *ex-situ* (e.g.

pugmill) S/S techniques may not be possible, without the inclusion of a lime-treatment step. The addition of lime to cohesive soils can result in a decrease in plasticity due to the flocculation of clay particles as well as a longer-term pozzolanic reaction. The initial change in plasticity can significantly improve the workability of the material, enabling *ex-situ* treatment techniques to be used. Lime treatment is discussed in greater detail in Section 3.2.2.

The plasticity of a fine-grained soil can be measured by its Atterberg limits. The plastic limit, is defined as the moisture content at which soil changes in texture from a dry granular material to a plastic material that can be moulded. With increasing moisture content a cohesive material becomes increasingly sticky, until it behaves as a liquid. The point at which this phenomenon occurs is known as the liquid limit. The range of moisture content between the plastic limit (PL) and the liquid limit (LL) is defined as the plasticity index (PI) i.e. LL – PL = PI. These concepts are illustrated in Figure 2.2.

The transition points are fairly arbitrary, determined by index tests described in BS 1377-2:1990, but they do serve a valuable function in the classification of cohesive soils. With an increase in moisture content, granular soils pass rapidly from a solid to a fluid condition. In these circumstances the PL and LL cannot be identified and such soils are classified as non-plastic (Sherwood, 1993).

Cohesive soils may be classified according to their plasticity properties. Silts have low plasticity indices, which means that they quickly become difficult to handle once the moisture content exceeds the plastic limit. With increasing clay content in a soil, both the plastic limit and the liquid limit increases. The difference between the two limits may widen due to the activity of the clay minerals present (Sherwood, 1993, Cernica, 1995). The activity of clay minerals can be related to plastic index, fineness of clay particles and behavioural tendency to volume changes (Cernica, 1995).

Cohesive soils characteristically have high plasticity indices. Stavridakis and Hatzigogos (1999), states that in soils containing expansive clay minerals with high liquid limits (40-60%), the liquid limit can be used to gauge the amount of cement required to stabilise a soil. Although soils with liquid limits >60% can be stabilised, the amounts of cement required can be uneconomical and result in unacceptable volume increase.

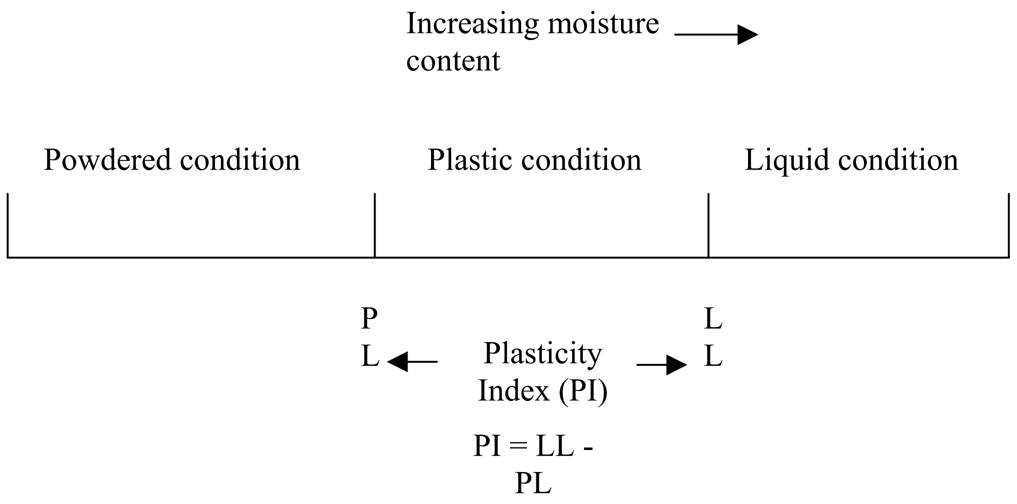


Figure 2.2: Definitions of soil plasticity (after Sherwood, 1993)

2.3.3 Moisture content

The moisture content of a soil is the ratio of the mass of water to the mass of solids in the soil (Craig, 1992). The moisture content is determined as the mass of free water that can be removed from a material, usually by heating at 105°C, expressed as a percentage of the dry mass (BS 1924: Part 1: 1990). If a soil or waste contains too much water then the porosity and permeability are likely to increase. If the amount of moisture present in a soil is above optimum then the density of the compacted product is reduced and this may have an impact on the strength achieved in an S/S product. Figure 2.3 highlights the water content – dry density relationships for eight soils compacted (see Section 2.3.6) according to the standard Proctor method (2.5kg rammer).

It is often necessary to adjust the moisture content in soils prior to S/S and this can be achieved by stockpiling and draining with time, by the addition of lime or by blending contaminated soil with other materials. Alternatively, water can be added to soil that is too dry.

Drying soils with lime is commonly undertaken and it was traditional practice to allow a clay-lime mix to stand for a period of typically 24 h, either in a stockpile or for single layer treatment *in situ*, in order that complete lime distribution could occur. Current thinking, however, suggests that immediate water content adjustment and compaction is more beneficial in achieving a long-term strength gain (Holt and Freer-Hewish, 1996; Glendinning *et al.* 1998).

Boardman (1999) states that immediate compaction would undoubtedly be beneficial for contaminated soil treatment, as long as thorough mixing is possible, since the pozzolanic reaction bonds that form at an early stage would assist with contaminant retention and minimise the flow of water through the stabilised material.

2.3.4 Permeability

The term permeability is used to express the coefficient of permeability or hydraulic conductivity, describing the rate (ms^{-1}) at which water can flow through a permeable medium. Permeability is related to the distribution of particle sizes, particle shape and soil structure. In general, the smaller the particles, the smaller are the average size of the pores and the lower is the coefficient of permeability. The transport of water through a soil will be faster if the soil has a higher coefficient of permeability than if it has a lower value (Craig, 1992). However, it should be noted that the rate of transport of contaminants depends upon a number of factors including solubility and the rate at which contaminants are attenuated in a soil. The determination of the coefficient of permeability using the constant head method or in a cell under known effective stress conditions are described in BS 1377: 1990.

2.3.5 Strength

The strength of a soil measures its capacity to withstand stresses without collapsing or becoming deformed (Brady and Weil, 1996). Soil strength can be considered in terms of the ability of a soil to withstand normal and/or shear stresses.

Shear stress can be resisted only by the skeleton of solid particles, by means of the forces developed at the interparticle contacts. Normal stress may be resisted by the soil skeleton due to an increase in the interparticulate forces. If the soil is fully saturated, the water filling the voids can also withstand normal stress by an increase in pressure (Craig, 1992)

A soil's ability to withstand normal stresses can be influenced by a number of related soil characteristics, amongst which are:

- soil compressibility;
- soil compactability; and
- bearing resistance.

These factors in turn are determined by parameters such as soil moisture content, particle size distribution and the mineralogy of the soil particles. In general, coarser textured materials have greater soil strengths than those with small particle size (Brady and Weil, 1996). For example, quartz sand grains are subject to little compressibility, whereas silicate clays are easily compressed.

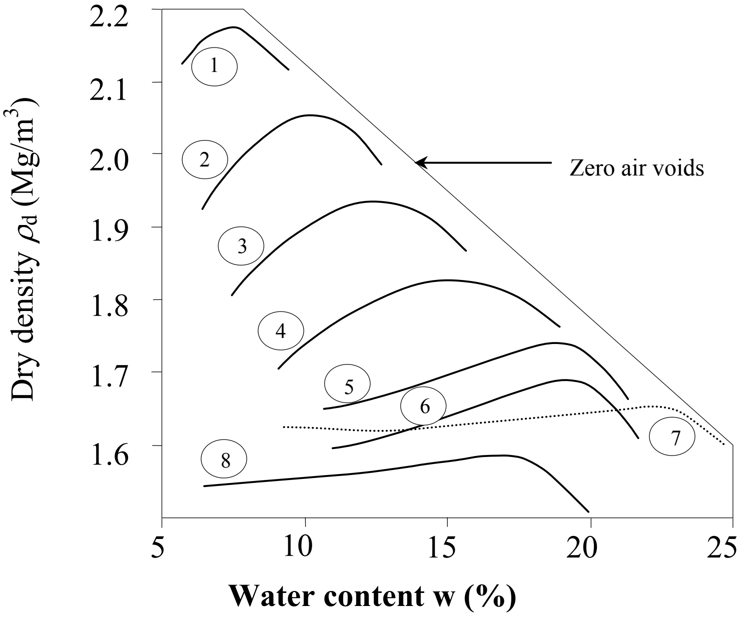
The bearing capacity of the material can be important both in terms of long-term engineering performance to carry loads and also supporting heavy plant in the short-term.

2.3.6 Compaction

Compaction is the process of increasing the density of a soil by packing the particles closer together with a reduction in the volume of air; there is no significant change in the volume of water in the soil. In general, the higher the degree of compaction, the higher the shear strength will be and the lower the compressibility of the soil (Craig, 1992).

The bulk density of a material is defined as the mass of a material (including solid particles, any contained water and any fluid stabiliser) per unit volume including voids. The dry density (ρ_d) is the mass of material after drying to constant mass at 105°C, and after removal of any fluid stabilisers, contained in unit volume of un-dried material (BS 1924: Part 1: 1990). The dry density of a material can be determined for a given compaction at varying moisture contents. This will determine the optimum moisture content at which a specified amount of compaction will produce a maximum dry density.

Standard compaction tests to establish the moisture content - dry density relationship of soils (Figure 2.3) are detailed in BS 1377: Part 4: 1990.



No.	Description	Sand	Silt	Clay	Liquid Limit	Plasticity Index
1	Well-graded loamy sand	88	10	2	16	----
2	Well-graded sandy loam	72	15	13	16	----
3	Mid-graded sandy loam	73	9	18	22	4
4	Lean sandy silty clay	32	33	35	28	9
5	Lean silty clay	5	64	31	36	15
6	Loessial silt	5	85	10	26	2
7	Heavy clay	6	22	72	67	40
8	Poorly graded sand	94	6		----	----

Figure 2.3: Water content-dry density relationships for eight soils compacted according to the standard Proctor method (after Johnson and Sallberg, 1960)

2.3.7 Collapse and swelling

Certain soil formations are prone to volume change due primarily to variation in moisture content. For example, loess deposits are characterised by high void ratio, low unit weight and are incompressible when dry. However, when wet, or subject to shock or dynamic loading they can be prone to sudden collapse. Inundation collapse is also a common phenomenon associated with loose man-made fills.

Soils can swell due to rebound after a period of compression or as a result of the introduction of water. Montmorillonite clays, for example, characteristically swell when saturated leading to significant changes in volume. Swelling may also occur in soil due to the action of frost or from the exposure to air and moisture as in the case of some shale. Here expansion results from the formation of clay minerals. Swelling test requirements also exist for stabilised soils (MacNeil and Steele, 2001).

2.3.8 Frost heave and frost shattering

Sherwood (1992) describes frost heave as an effect that can occur when temperatures are sub-zero for several days. If it is possible for water to move from the water table to the frozen zone easily, it will be drawn up into this zone where it will freeze to form ice lenses. Once this has occurred, further water may be drawn up and be subsequently frozen. It is expansion due to the freezing of transported water that is the primary cause of frost heave, rather than freezing of water originally present. Permeability of the material is identified as the leading factor behind frost heave susceptibility.

Frost shattering is identified as the result of expansion of excess water present in voids of the surface of the material as it freezes (Sherwood, 1992).

2.3.9 Temperature

Table 2.1 indicates temperature as an important factor for consideration when carrying out S/S. The disruption of structure of a waste form can result from the action of frost on freshly solidified materials. Guidance on using concrete in cold weather (American Concrete Institute, 1994) can be used to help mitigate the effects of cold weather on waste form placement.

Whilst temperature does not affect the improvement of plasticity in a lime modified soil, it can adversely affect early age strength development. Sherwood (1992) states for lime, a minimum temperature of 7^oC is stipulated whereas for cement, temperature is less important but a minimum of 3^oC is given.

2.4 Chemical and Mineralogical Composition of Soils

The fate of contaminants in soil is dependent primarily on the surface area available for reaction with contaminants in porewater and the reactivity of such surfaces. As a consequence, the finer-grained solid components play a dominant role in contaminant attenuation.

2.4.1 Soil organic matter (SOM)

Soils contain a large variety of organic matter, usually at concentrations of 0.5-5% by mass in typical soils (Yong *et al.,* 1996). It is a key component in soil particularly in association with attenuation processes, even at such low proportions. Organic-rich soils, such as peat, also occur naturally and can contain more than 80% organic matter (Brady and Weil, 1996).

Soils with an organic content up to 30% and water/solids ratio up to 2.5 will behave largely as mineral soils.

Classification of organic matter can be made according to its state of degradation, or into humic and non-humic material. Classification according to state of degradation allows organic materials to be placed into one of the following classes (Hayes and Swift, 1985):

- unaltered organics (fresh and old non-transformed organic materials such as leaves); and
- transformed organics - bear no morphological resemblance to the original source which may be decayed materials (compounds which belong to recognisable classes, e.g. polysaccharides, lignins, polypeptides, etc.) or amorphous materials (e.g. humic substances).

Alternatively, classification into humic or non-humic materials allows organic materials to be placed in one of the following classes (Yong *et al.,* 1996):

- non-humic compounds (materials which remain un-decomposed, or are only partially degraded); or
- humic compounds (organics arising from the chemical and biological degradation of non-humic materials). Humic materials can be further divided into: humic acids (compounds that are soluble in base, but precipitate in acid), fulvic acids (compounds that are soluble in both base and acid) and humins (insoluble in both acid and alkali)

The humic substances are polymers with molecular weights ranging from hundreds to tens of thousands. They are of particular interest due to their high content of functional groups resulting in variable charge. Figure 2.4 shows a schematic representation of functional groups attached to a generalised picture of soil organic matter represented by a carbon skeleton.

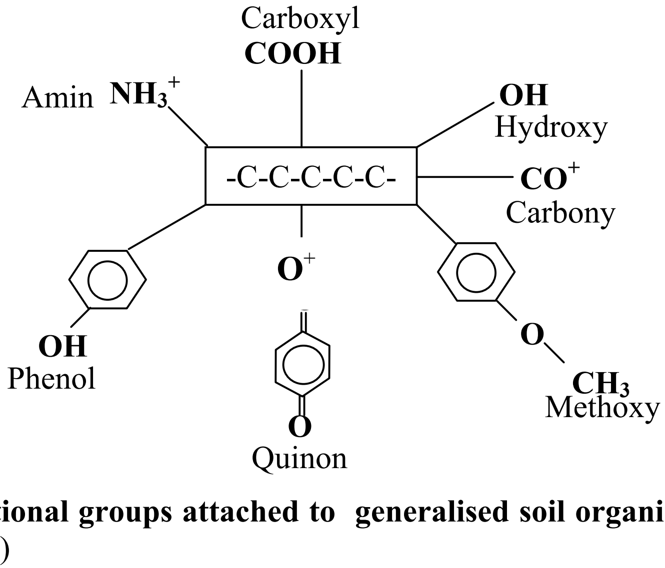


Figure 2.4: Functional groups attached to generalised soil organic matter (after Yong *et al.*, 1996)

The influence of organic matter on contaminant (e.g. heavy metal) mobility depends on whether the material is in a solid or dissolved state. Solid organic matter generally has a retarding effect on heavy metals, but the contaminants can be more mobile due to complexing with dissolved phases (e.g. Cu). Alkaline conditions, as developed when using hydraulic binders, can lead to dissociation of organics that can affect the mobility of contaminants. For example, at pH > 9, carboxylic and phenolic-OH groups can protonate (release a H^+) and the humic molecule attain a high negative charge (Tan, 1993), making it available for complexation with metal cations.

2.4.2 Mineralogy

With the exception of some highly organic soils, the majority of soil material is mineral in character, having been derived from solid geological deposits (Townsend, 1973). Minerals can be conceptually divided into primary and secondary materials.

Primary minerals are those derived in unaltered form from parent rock, generally through physical weathering processes (Yong *et al.,* 1996). They make up most of the sand and silt portion of soils and are usually only a minor constituent in the clay-sized portion. The most common primary minerals in soils are quartz and feldspar. These particles have a relatively low specific surface area, and therefore their role in contaminant interaction and attenuation processes is minimal (Yong *et al.,* 1996).

Secondary minerals are derived as altered products of physical, chemical and/or biological weathering processes. They are layer silicates and account for the majority of the clay-sized portion. Because of their small particle size, they exhibit a large specific surface area. The combination of their large surface area and the fact that they frequently exhibit a surface charge makes the secondary minerals important in the development of contaminant attenuation processes. Clays are also able to react with lime to form cementitious compounds. The most common layer silicates in soils include kaolinite, chlorite, mica, montmorillonite and illite.

2.4.2.1 Clay minerals

Clay minerals are made up of basic silica tetrahedra and alumina octahera units, combined to form sheet-like, or platy, structures. Si and Al may be partially replaced by other elements, such as Al for Si and Fe, Mg for Al. The basic units are one tetrahedron to one octahedron (1:1 layer silicate) and one octahedron between two tetrahedra (2:1 layer silicate). These units are stacked and linked laterally to form the structural building blocks of clay minerals and characterise the nature and properties of the minerals. The clay minerals are commonly amorphous and usually carry a residual negative charge, mainly due to isomorphous substitution of Si and Al or disassociation of hydroxyl ions. The negative charge results in cations from solution being attracted to the particle surfaces, forming a double layer of particle surface and dispersed layer of cations. Such cations are weakly bonded and can be replaced by other cations (cation exchange).

Forces of repulsion and attraction act between clay particles, due to the like charges of the double layers and the characteristics of the layers respectively. An increase in cation valency or concentration can result in a decrease in repulsive forces. The forces of attraction are responsible for the cohesive nature of fine-grained soils.

Kaolinite Group includes kaolinite, dickite and nacrite are isochemical 1:1 layer silicates ($Al_4Si_4O_{10}(OH)_8$) but not isostructural. They are derived from the weathering of alkali feldspars under acidic conditions and contain no exchangeable cations. Residual positive charges can occur on the edge of kaolinite particles in low pH environments, promoting edge-to-face attraction.

Illite Group are 2:1 layer silicates derived from weathering of silicates including micas and alkali feldspars under alkaline conditions. They have a general formula $K_{1-1.5}Al_4(Si, Al)_8O_{20}(OH)_4$ with a non-exchangable cation interlayer of K with subordinate Na and Ca. Illites are non-swelling, but are often present as mixed-layer clays with montmorillonite and/or chlorite.

Montmorillonite (smectite) Group includes montmorillonite, beidelite and nontronite with the general formula: $M\tfrac{2}{3}(X, Y)_{4-6}(Si, Al)O_{20}OH_4.nH_2O$, where M = Na or ½Ca, X = Al or Fe(III), Y = Mg or Fe(II). They are similar in basic structure to illites, but with partial replacement of Al by Mg in the octahedra. Water and exchangable cations occupy the space between combined sheets, in contrast to the non-exchangable K layer of illites. Montmorillonites are particularly important for their ability to adsorb and lose water and their cation exchange capability.

Chlorite Group comprises a heterogeneous group of layer-lattice silicates with a typical formula: $(Mg, Fe)_{10}Al_2(Si, Al)_8O_{20}(OH,F)_{16}$. They are common products of alteration of ferromagnesian minerals and may be present as mixed-layer clays with illite and/or montmorillonite.

Vermiculite Group clays are alteration products of biotite mica by removal of K in the interlayers. Vermiculites may be present as mixed-layer clays with mica and chlorite.

The properties of clay minerals, in particular the reactivity of the particle surfaces, have a significant influence on geochemical processes in soil that affect the attenuation of contaminants (Yong and Mulligan, 2003). Table 2.4 summarises the properties of clay minerals that influence attenuation capacity for the main groups of clay minerals.

2.4.2.2 Carbonates

A number of carbonate minerals may be present in soil including calcite, magnesite, siderite and dolomite. Calcite is the most common form and has a significant influence on the pH of the soil and porewater (see Section 2.4.4). Carbonate minerals may be effective in adsorbing heavy metals and phosphates (Yong and Mulligan, 2003).

Table 2.4: Properties of some clay mineral groups (after Yong and Mulligan, 2003)

Clay group	**Surface area (m^2/g)**	**Cation exchange capacity (meq/100g)**	**Range of charge (meq/100g)**
Kaolinite	10-15	5-15	5-15
Illite	80-120	20-30	20-40
Montmorillonite	800	80-100	80-100
Chlorite	70-90	10-40	20-40
Vermiculite	700	100-150	100-150

2.4.2.3 Oxides and (oxy)hydroxides

Oxides and (oxy)hydroxides are abundant weathering products of parent rock, most commonly iron oxides. The iron forms are amorphous or cryptocrystalline, with the amorphous form having a pH-dependent surface charge. Because of this surface charge, the amorphous forms readily coat solid particles and significantly alter the surface reactivity of the particles.

2.4.3 Sulfates

The presence of sulfates in soil can arise from a number of sources. Sulfur is present in proteins and amino acids bound within the humus and clay fractions. Oxidation of SOM frequently results in the transformation of these sulfur-containing compounds to sulfates. The second source of sulfates in soils comes from the oxidation of:

- sulfides;
- sulfur retained by soils high in Fe-Al oxides and kaolinite; and
- atmospheric sulfur deposited onto soils.

The Building Research Establishment (BRE, 2001) identifies that the presence of naturally occurring sulfates depends on the geological strata, the weathering history of those strata and the groundwater flow patterns. Ancient sedimentary clays are identified as those most likely to have substantial concentrations of sulfates, including:

- Mercia Mudstone;
- Lower Lias Clay;
- Kimmeridge Clay;
- Oxford Clay;
- Wealden Clays;
- Gault Clay; and
- London Clay.

In addition, sulfates can be present in locally significant concentrations in a wide range of strata ranging from Carboniferous mudstones to recent alluvium and peat. Sulfates may also be present in made ground in significant concentrations.

The distribution and concentration of sulfates in both man-made and naturally occurring strata can vary both laterally and vertically. In most geological deposits (except Mercia Mudstone) only the weathered zone (generally upper 2m-10m) is likely to have a significant quantity of sulfates present, although sulfide minerals may be present below this. Within the weathered zone it is usual for the top metre or so to be very low in sulfates due to leaching by rainfall. It is also common to find high concentrations of sulfates at the base of the tree root zone (typically 2-3m) and the base of the weathered zone (typically 3-10m) (BRE, 2001).

2.4.4 pH

The pH of soil has a major influence on the solubility of contaminants by influencing the degree of ionisation and their subsequent overall charge (Pepper, 1996). Stabilisation of very acidic materials can cause rapid heat evolution following binder addition. In materials with excess moisture content, this can be beneficial as a reduction in moisture content is likely. However, in materials with near-optimum moisture contents or the presence of volatile contaminants, staged addition of binder may be required to control the heat evolution.

Materials with low pH can be detrimental to the setting of cement / lime stabilised materials. To overcome this problem the acidic material needs to be neutralised. This can either be achieved by increasing the quantity of lime or cement binder used, or an alternative alkaline material could be used, such as chalk dust.

2.5 Contaminants

A contaminant is a substance which is in, on or under the ground and which has the potential to cause harm or to cause pollution of controlled waters (BS 10175:2001). Contaminants can broadly be divided into inorganic and organic types and may cause harm or pollution irrespective of whether they are present at naturally enhanced concentrations or released from industrial processes or other anthropogenic activities.

Defra/Environment Agency (2002a) published a review of potential contaminants in the UK for the assessment of industrial land. The report provides a selection of key contaminants for Defra to consider in its research work on contaminated land, based on contaminant prevalence and potential risk to humans and other sensitive environmental receptors. The former Department of the Environment published a number of Industry Profiles that describe specific industrial processes and the chemical that may be found (see Appendix 1).

A number of authoritative bodies hold data on the toxicology of chemical substances (e.g. Department of Health, World Health Organisation) and Defra/Environment Agency (2002b) published an overview of international approaches to deriving criteria for the protection of human health. This document contains a number of references and provides background information to the development of intake values for humans for a number of contaminants. These intake values and their derivation are provided as separate TOX reports and have been used to produce Soil Guideline Values for a number of contaminants. The reports are available from the Defra web site.

The following sections contain summary information on the main contaminants types, the key properties and reactions with soil that influence their partitioning and hence mobility.

2.5.1 Inorganic contaminants

Typical inorganic contaminants in soil are dominantly heavy metals and metalloids, but other cations and anions may pose significant risks to environmental receptors. The key inorganic contaminants identified by Defra/Environment Agency (2002a) and their potential receptors are given in Table 2.5. However, contaminants of interest will be site-specific and should be identified following good site investigation practice.

Table 2.5: Potential inorganic contaminants of environmental concern (after Defra/Environment Agency, 2002a)

Contaminants	Receptors			
	Humans	Water	Vegetation and the ecosystem	Construction materials
Barium	X	X		
Beryllium	X	X	X	
Cadmium	X	X	X	
Chromium		X		
Copper	X	X	X	
Lead	X	X	X	
Mercury	X	X	X	
Nickel	X	X	X	
Vanadium	X	X		
Zinc		X	X	
Arsenic	X	X		
Boron		X	X	
Selenium	X	X	X	
Sulfur	X		X	X
Cyanide (complex)	X	X	X	X
Cyanide (free)	X	X	X	
Nitrate		X		
Sulfate		X	X	X
Sulfide		X	X	X
Asbestos	X			
pH (acidity/alkalinity)	X	X	X	X

Heavy metals and metalloids are defined as metals or metalloids having a density greater than 5 g/cm^3 and include lead, copper, nickel, cadmium, platinum, zinc, mercury and arsenic. They readily lose electrons to form cations, and may exist in elemental form, in solution as ions or complexes, in a colloidal suspension phase, partitioned to soil solids, or as low solubility precipitates. Heavy metal cations tend to be strongly sorbed onto organic matter or clay minerals in soil reducing their mobility. In other cases, mobility may be increased by the formation of metal-organic complexes. Heavy metals are generally toxic, and many of them bio-accumulate through food chains, causing detrimental effects in living organisms.

The 38 elements in the periodic table in Groups 3 to 12, including the heavy metals, are called the transition metals. Their chemistry is such that they exhibit several oxidation states, the compounds of which display different properties. Specific chemical tests and thermal analyses may be used to determine the nature of specific compounds in contaminated materials or soil (Brindle *et al.*, 1987).

Yong *et al.* (1996) describes the formation of complexes between heavy metals and ligands in the aqueous phase of soils and competition between this and sorption onto the soil solid phase. For example, cadmium sorption onto soil particles is low where $CdCl_2$, $CdCl_3^-$ and $CdCl_4^{2-}$ compounds are present. This illustrates that the metal salt present can be very important in controlling how the contaminant may behave in the environment.

Metals (and metalloids) such as As, Cr, Mn, Mo, Se, V and U are readily oxidised and form anionic species called oxyanions. Oxyanions have the ability to pass through cell membranes and compete with other anions such as phosphate and sulfate (Bernhard *et al.*, 1986). Examples of oxyanions include arsenite, arsenate, chromate, dichromate and manganite and their ability to interfere with biota is well known.

Although metals form the dominant type of inorganic contaminant, the effects of other contaminants on the environment should not be underestimated. The dominant non-metal inorganic contaminants are listed in Table 2.5. Inorganic compounds may also inhibit cement reactions (see Section 4.2.3 and Appendix 4, and Conner, 1990).

2.5.2 Organic contaminants

Organic substances form a large family of over 1600 natural and anthropogenic chemicals present in natural and polluted environments (Graedel, 1978). Those that are of environmental concern are typically refined petroleum products, chlorinated and non-chlorinated solvents, manufactured biocides and compounds used in a wide range of manufacturing processes. Organic contaminants may be present in waste as a single contaminant, associated with inorganic contaminants, or present as complex mixture, e.g. petroleum hydrocarbons. Many organic contaminants are toxic even at very low concentrations and a number of the more common organic compounds of environmental concern associated with industrial pollution are given in Table 2.6.

Table 2.6: Potential organic compounds of environmental concern (after Defra/Environment Agency, 2002a)

Contaminants	**Receptors**			
	Humans	**Water**	**Vegetation and the ecosystem**	**Construction materials**
Acetone	X	X		
Oil/fuel hydrocarbons	X	X	X	X
Aromatic hydrocarbons	X	X	X	X
Benzene	X	X	X	X
Chlorophenols	X	X	X	X
Ethylbenzene	X	X	X	X
Phenol	X	X	X	X
Toluene	X	X	X	X
o-xylene	X	X	X	X
m,p-xylene	X	X	X	X
Polycyclic aromatic hydrocarbons	X	X		X
Chloroform	X	X	X	
Carbon tetrachloride	X	X	X	
Vinyl chloride	X	X		X
1,2-dichloroethane	X	X	X	X
1,1,1-trichloroethane	X	X	X	X
Trichloroethene	X	X	X	
Tetrachloroethene	X	X	X	X
Hexachlorobuta-1,3-diene	X	X	X	
Hexachlorocyclohexanes	X	X	X	
Dieldrin	X	X	X	
Chlorobenzenes	X	X	X	
Chlorotoluenes	X	X	X	
Pentachlorophenol	X	X	X	
Polychlorinated biphenyls	X	X	X	
Dioxins and furans	X	X	X	
Organolead compounds	X	X	X	
Organotin compounds	X	X		

Nomenclature and classification are important when dealing with such a large group of compounds, and standard nomenclature is provided by IUPAC (1979). However, many compounds have a number of synonyms and Lewis (1992) provides a comprehensive list of synonyms for any chemical substance.

The classification of organic compounds is also important when assessing the properties of individual substances, their fate and transport in the environment and transformation or degradation during remediation. Thurman (1985) proposed a scheme for organic compounds in natural waters based on functional group (e.g. hydroxyl, carbonyl) whereas Garrison *et al.* (1977) proposed a more comprehensive scheme for organic contaminants with 24 major classes and over 100 sub-classes. The latter scheme was condensed to 16 classes by Domenico and Schwartz (1990).

Information on organic contaminants can be found in a number of standard organic chemistry texts, but a number of texts are also available that describe the behaviour of organic compounds in the environment, including Graedel (1978), Lyman *et al.* (1982) and Schwartzenbach *et al.* (1993).

Knowledge of the physical and chemical properties of organic contaminants allows broad predictions to be made about their mobility in the environment, and the likelihood of success of the remediation process. There are a number of key properties that are important when considering their reaction with the soil and porewater, and these are discussed below.

How organic contaminants are bound within S/S-treated soil, and the factors influencing their retention over time, remain to be established. Nevertheless, a considerable body of data now exists to show that a wide range of organic contaminants can be treated by S/S (USEPA, 1986, 1990, 1993, Conner, 1990). The USEPA has also collated publications on the S/S of organic contaminants (USEPA, 1999).

2.6 Key Properties of Contaminants

A number of contaminant properties influence the partitioning of inorganic and organic contaminants, and contaminant mixtures, between the solid, liquid and gaseous components in soil or waste, and hence should be understood when predicting the behaviour of contaminants as a consequence of S/S treatment. The key properties include:

- solubility;
- volatility; and
- immiscibility with water.

2.6.1 Solubility in water

The aqueous solubility of contaminants can be defined as the maximum concentration of a chemical in the aqueous phase when the solution is in equilibrium with the pure compound at a standard temperature and pressure. Solubility thus controls the amount of a chemical that can partition into the aqueous phase and hence be capable of transport through it (e.g. from soil pore water to groundwater).

2.6.1.1 Speciation

The mineral species in which a contaminant is present may have a significant influence on its toxicity and/or mobility in an environmental medium. For example, the solubility of a solid depends on whether the solid (reactant) or products (ions or secondary mineral) are favoured in a dissolution-precipitation reaction. In general, the solubility of a solid increases with increasing ionic strength, and may be reduced in an aqueous solution that contains the ions that would be released when the solid dissolves (the common ion effect). However, the solubility of a substance may be controlled by environmental factors such as pH, Eh and temperature. A number of standard texts are available on mineral equilibrium in aqueous solutions (e.g. Morel, 1983, Stumm and Morgan, 1995).

Modelling of speciation can be carried out using modern computer codes, such as PHREEQC (Parkhurst and Appelo, 1999) that compute equilibria among dissolved, adsorbed, solid and gas phases under specific conditions (e.g. pH, Eh). Further information on thermodynamic equilibrium modelling is given in Chapter 10.

Currently, the main methods of determining the speciation of metals in contaminated soil are by selective means (Table 2.7). Chemical extractions – single, sequential or parallel using selective reagents such as described by Tessier *et al.* (1979) can provide useful information about where metals are bound. Modified sequential extraction procedures have recently been used to establish re-use potential of certain wastes through prediction of leaching performance (Van Herck and Vandecasteele, 2001).

It should also be noted that there are concerns with regard to the severity of extraction methods and that dissolution or degradation of some contaminated solids does not occur (Yong *et al.*, 1996). Methodologies for metals speciation have been reviewed by Morrow *et al.* (1996). In practice, the technical complexity and cost of carrying out the analyses to determine speciation may prohibit these procedures from being routinely used.

Table 2.7: Sequential extraction techniques (after Yong *et al.,* 1996)

Soil constituent	Extraction technique
Exchangeable	Use neutral salts such as $MgCl_2$, $CaCl_2$, and $NaNO_3$ to promote the release of ions physically bound by electrostatic attraction to the negatively charged sites on the soil particle surfaces.
Associated with carbonates	Use the application of an acid to release metal carbonates. Most commonly used extractant is acidified acetate. A solution of 1M HOAc-NaOAc (pH5) appears to be efficient in dissolving calcite and dolomite, and releasing the metals bound to them without dissolving organic matter, oxides, or clay mineral particle surfaces.
Associated with metal oxides	Extract with combination of acid reducing agent (1M hydroxylamine hydrochloride) with 25% (v/v) acetic acid.
Associated with organic matter	Perform oxidation of organic matter to release bound metals. Hydrogen peroxide is a suitable oxidising agent.
Residual fraction	The metals found within the lattice of silicate minerals can only be released by digestion with strong acids at elevated temperatures.

2.6.1.2 Amphoteric metals

Amphoteric metals form compounds that are soluble in both acidic and alkaline solutions (Mackay and Emery, 1993). Some metals, for example, chromium and lead have amphoteric hydroxides and this behaviour is illustrated in Figure 2.5 for a range of heavy metal hydroxides.

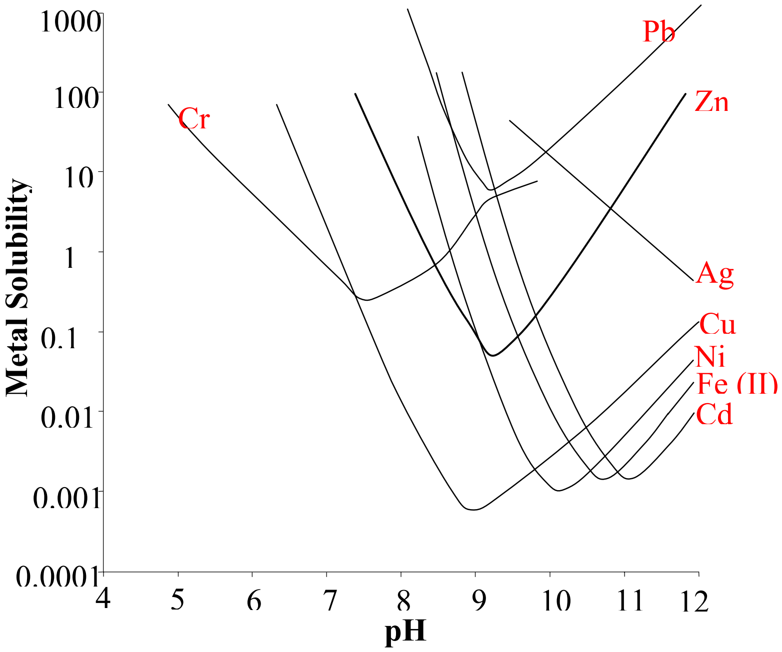


Figure 2.5: Theoretical solubilities of metal hydroxides as a function of pH (adapted from USEPA, 1987 and Wilk, 1997)

2.6.1.3 Organic contaminant solubility

The aqueous solubility of organic contaminants is one of the key factors determining their behaviour and impact on the water environment. For pure substances, aqueous solubility is related to molecular structure and polarity. As a general rule, the more soluble organics are charged or contain oxygen or nitrogen groups that can hydrogen bond with water. Therefore polar organic contaminants (e.g. methanol, phenol) will be soluble in water (itself a polar solvent) and non-polar organic contaminants (e.g. benzo(a)pyrene, PCBs) remain largely insoluble or hydrophobic (Brusseau and Bohn, 1996). In many cases, the solubility of an organic contaminant depends on the pH of the environment in which it is present.

The solubility of most organic substances ranges from <1 to 200,000 mg/l and aqueous solubility data for pure substances can be found in a range of scientific literature (e.g. Verschueren, 1977, Montgomery and Welkom, 1990, Montgomery, 1991).

Organic contaminants are often present as complex mixtures, e.g. fuel oils, and solubility is dependent on the mole fraction of each component in the mixture. The solubility of organic contaminants can also be affected by the presence of other organic compounds that can act as a solvent or reduce the energy requirements for dissolution of the contaminant (cosolvency).

Where reliable solubility data is not available, solubility can be estimate from the octanol/water partitioning coefficient. This is a dimensionless equilibrium constant that characterised the partitioning of a solute between octanol and water, expressed by:

$K_{ow} = C_{oct}/C_{aq}$ where
K_{ow} = octanol/water partitioning coefficient
C_{oct} = concentration of solute in octanol
C_{aq} = concentration of solute in water.

2.6.2 Volatility

Volatility can be defined as the tendency of a compound to partition into the gaseous phase, and is typically measured by the vapour pressure (Keith, 1988). It is a property relevant primarily to organic compounds, although it may influence the partitioning of some inorganic compounds, such as mercury or cyanide. The vapour pressure is a measure of the pressure exerted by the vapour of a compound at equilibrium with its pure condensed phase (either solid or liquid) at a standard temperature. It may range by many orders of magnitude for organic compounds. The composition of a mixture will influence the vapour pressure of any substance present in the mixture.

The volatility of a compound is determined by the strength of the intermolecular forces between molecules. Therefore, solids (with strong intermolecular forces) have lower vapour pressures than liquids and gases that have weaker intermolecular forces (Brusseau and Bohn, 1996).

Organic compounds are normally divided as follows (Keith, 1988):

- volatile organic compounds (VOCs) with a vapour pressure of > 10^{-2} kPa;
- semi-volatile organic compounds (SVOCs), with a vapour pressure of $10^{-2} – 10^{-8}$ kPa; and
- non-volatile organic compounds (NVOCs) with a vapour pressure < 10^{-8} kPa.

2.6.2.1 Volatile organic compounds

Volatile organic compounds (VOCs) include aromatic hydrocarbons, halogenated hydrocarbons, aldehydes and ketones (Keith, 1988). Historically, VOCs have been considered unsuitable for treatment by S/S since the elevated temperatures associated with the cement hydration process are normally sufficient to liberate VOCs into the atmosphere. The role of additives in the successful S/S treatment of VOC-contaminated soils and wastes is discussed in Chapter 5.

It should be noted that the rate of volatilisation of organic compounds from soil is primarily related to the properties of the compound in question, soil capiliarity, the nature of soil-void interface, soil water content and degree of soil heterogeneity (Hantush and Govindaraju, 2003). The sorption of volatile organics to soil may be significant and is discussed by Kobayashi *et al.* (2003), Hwang and Hakura *et al.* (2003) and Cutright (2003).

2.6.2.2 Semi-volatile organic compounds

Semi-volatile organic contaminants include polycyclic aromatic hydrocarbons (PAH) with four or fewer fused rings and their nitro derivatives, chlorobenzenes, chlorotoluenes, polychlorinated biphenyls (PCB), organochlorine, organophosphate pesticides and the various polychlorodibenzo-*p*-dioxins (Keith, 1988).

2.6.2.3 Non-volatile organic compounds

Non-volatile organic contaminants include PAHs with more than four fused rings and their nitrogenous and oxygenated derivatives (Keith, 1988), PCBs and dioxins. In general, the larger and more polar/ionic compounds are considered to be non-volatile and can be more readily treated by S/S (USEPA, 1993a).

2.6.2.4 Henry's law constant

The solubility and vapour pressure of an organic contaminant also determine partitioning between the aqueous phase and air, and the tendency for dissolved phases to volatilise from water is expressed by Henry's law and commonly expressed by the Henry's law constant (HLC):

$K_H = P/C$ where

K_H = Henry's law constant (Pa m^3mol^{-1})
P = partial pressure of compound in the gas phase
C = aqueous solubility as a molar concentration.

Alternatively, a dimensionless form of the HLC can be calculated from the concentration of a contaminant in air over the concentration in water, expressed in the same units. In general, a compound with a HLC (dimensionless) >0.05 (*circa* 50 Pa m^3mol^{-1}) is likely to volatilise from the aqueous phase and if HLC < 0.05 then volatilisation is unlikely.

2.6.3 Immiscibility with water

Liquid phases that are immiscible with water in soil will tend to move through the unsaturated zone as a separate phase, a non-aqueous phase liquid (NAPL). The NAPL will partition in the soil by a combination of (Suthersan, 1997):

- moving through the pore space due to gravity and capillary forces;
- coating the solid matrix;
- dissolving in porewater;
- volatilisation; and
- trapped in pore spaces under capillary forces (at residual saturation).

In general, the residual saturation of a NAPL will tend to increase as the permeability of the matrix decreases, and downward flow cannot take place until the residual saturation is exceeded. The retention capacity is a function of the residual saturation and soil porosity and, for oil in the unsaturated zone ranges from about 3 to 5 lm^{-3} for highly permeable media to 30 to 50 lm^{-3} for low permeability media (Pankow and Cherry, 1996). The NAPL retained in the unsaturated zone will act as a secondary source of contamination due to solution and volatilisation and the attenuating properties of the soil to other contaminants changed because of the surface coating of the matrix. The nature of organic contaminants can substantially increase the intrinsic permeability and subsequent transport properties of contaminants through soils (Kunkel and Anderson, 1999).

2.7 Reactions between Contaminants and Soil

The chemical interactions of contaminants with soil predominantly depend on the phases of the material (solid, liquid or gas), contaminant speciation, soil mineralogy, pH and the amount of soil organic matter present. Interactions between soil and contaminants and their variation with environmental parameters are important to determine the fate of the contaminants present, and therefore the likely risk they will pose to humans, water bodies and the ecology of the surrounding area.

Interactions between sand/silt and contaminants are likely to be limited to reversible sorption on surfaces and trapping of contaminants within pores and cracks in soil particles. Clay minerals and organic matter undergo a range of interactions with contaminants. The following section introduces the main reactions between contaminants, soil and porewater, divided into:

- sorption;
- oxidation-reduction reactions;
- precipitation;
- complexation;
- hydrolysis; and
- biological degradation.

2.7.1 Sorption

Sorption mechanisms can be divided into physical adsorption and chemical adsorption (the word sorption is used as a general term and does not differentiate between chemical and physical processes).

Physical adsorption phenomena occur when contaminants in the soil solution (the aqueous phase or the pore water) are attracted to the soil constituent’s surfaces because of the unsatisfied charges of the soil particles. Chemical adsorption refers to high affinity, specific adsorption, which generally occurs through covalent bonding.

The ability of mineral surfaces to attract or repel chemical contaminants can be considered in terms of their active sites, which are defined by the geometric arrangement of surface atoms and by their chemical composition. Metal speciation and bonding in soils is discussed in Allen *et al.* (1996). The ability of clay minerals to exchange cations is important and is discussed by Ross (1989).

The active sites of clay surfaces can be divided into five groups, each producing different environments for the attraction of pollutants (Allen *et al.*, 1996):

- neutral siloxane surfaces, which occur on 2:1 layer silicates, where isomorphic substitution has not taken place (e.g., talc and pyrophylite) and on the siloxane side of 1:1 layer silicates (e.g., kaolinites);
- isomorphic substitution in the clay lattice of 2:1 layer silicates. This leads to the creation of a permanent negative charge, which attracts cations (organic and inorganic) to its surface;
- polarised water molecules surrounding cations attracted to the clay surface. The polarised water molecules are able to donate protons to adjacent organic compounds and promote a variety of chemical reactions;
- sorption of organic molecules at the clay surface creates a hydrophobic surface suitable for the sorption of other hydrophobic compounds. In many cases, 'organoclays' have been created artificially for use in the remediation of contaminated soil or groundwater; and
- broken edge sites where uncoordinated metal ions (e.g. Si, Al, Fe(III)) react with water to create OH groups. These surface hydroxyl groups can either form inner-sphere complexes with metal species (hydrogen bond to adsorptive or solvent molecules accumulated at an interface), or be influenced by inorganic or organic cations through electrostatic interactions.

Sorption of organics in soil is due to interactions with mineral surfaces and partitioning into organic matter components of a soil. In aqueous systems, partitioning into organic matter is thought to be mainly responsible for uptake of organic contaminants, as sorption on mineral surfaces is suppressed by the presence of water (Sawhney, 1996). However, sorption of non-polar organic compounds from aqueous solutions by mineral surfaces has been observed. For example, Laird *et al.* (1992) and Barriouso *et al.* (1994) determined that smectites adsorbed atrazine from aqueous solutions.

Sorption to soil organic matter (SOM) is thought to account for a large proportion of sorptive processes occurring between hydrophobic organic contaminants and soil components. It is measured by the organic carbon partitioning coefficient (K_{oc}). This coefficient and the fraction of organic carbon together define the soil adsorption coefficient for nonionic organic substances onto the soil matrix, as follows:

$K_d = f_{oc} K_{oc}$ where

K_d = soil adsorption coefficient
f_{oc} = fraction of organic carbon in soil
K_{oc} = organic carbon partitioning coefficient.

One of the easiest ways to determine the K_{oc} values is from the octanol/water coefficient (K_{ow}, see Section 2.6.1.3). The partitioning of a substance to octanol (a non-polar phase) is analogous to partitioning to SOM, and a number of equations are available in the literature to describe the relationship (Knox *et al.*, 1993).

Soil organic matter consists of long chains of carbon atoms, containing OH^- and $COOH^-$ functional groups, coiled into a three-dimensional macromolecular structure (Davis, 1998). At neutral/acidic pH the protonated molecule provides a micelle-like region into which hydrophobic organic contaminants may migrate. However, this situation may change with an alteration in pH. Increasing alkalinity for example has been shown to create negative, repulsive charges on SOM leading to an opening of the macromolecular structure and a release of sequestered organic contaminants.

Many organic compounds can either gain or lose a proton or hydroxyl ion as a function of pH, increasing its solubility in water (a polar solvent). The mechanisms determining their sorption are similar to those governing the sorption of inorganic contaminants. The gain of a proton (or loss of hydroxyl) produces a positively-charged compound that can take part in cation exchange reactions (Knox *et al.*, 1993). Many of the important ionisable organic contaminants (such as the phenols, and chlorophenols) are negatively charged at typical environmental pHs, and because most soil particles have a net negative charge, negatively charged contaminants are repelled and exhibit very little sorption (Brusseau and Bohn 1996).

The sorption of non-polar organic contaminants is often controlled by the amount and type of organic matter associated with the soil and may lead to reduced or increased mobility in the environment, depending on the type of organic matter (large hydrophobic macromolecular structures or smaller, water soluble compounds). The cation exchange capacity, clay content and metal oxide content of the soil are significant for sorption of ionisable and ionic pollutants (Brusseau and Bohn, 1996).

The likelihood of a contaminant undergoing a deprotonation (loss of hydrogen atom to leave a negatively charged species) reaction depends on the presence of ionisable hydrogen atoms within the molecule and is measured by a parameter called pKa. The pKa value for phenol is 10, which means that due to the logarithmic relationship between pKa and pH, at pH 10, both reactant and product are present in equal quantities. Increasing the pH by one unit results in a concentration of product that is ten times greater than the reactant. Increasing the pH by two units results in a concentration of the product that is one hundred times greater than the reactant.

2.7.2 Oxidation-reduction reactions in soils

Stucki *et al.* (1995) have reviewed redox reactions in clay soils. Redox reactions affect chemical weathering, swelling and the properties of clay mineral surfaces. The mechanisms involved are not fully understood but may involve humic materials and micro-organisms.

The oxidation state of Fe has an effect on clay swelling and the capacity of clay to hold water. When Fe is reduced, specific surface area can be lower and this may be accompanied by an increase in the amount of non-exchangable Na, K, Ca, Cu and Zn. Reduction also causes clay to become more consolidated into particles of 40 layers, whereas oxidised clay particles consist of long open ribbons from 1 to 6 layers thick. There is evidence for strong local forces in clay particles when Fe is reduced (Stucki *et al.,* 1995).

It is the redox environment on mineral surfaces that affects the speciation of redox sensitive metals and their chemical behaviour. For example, reduced clay can react with Cr(VI) reducing it to Cr(III), which will be cationic or precipitated as the oxide. In this way Cr may become less toxic and less mobile. However, the size of the ion, its valence state and its availability are also important.

Many organic compounds can either accept or donate electrons, causing transformation of functional groups. This is significant in terms of the environment as the oxidised and reduced species of an organic compound frequently have different toxicological properties. Although oxidation reactions may occur abiotically in natural environments, the reduction of organic compounds is usually microbially catalysed.

2.7.3 Precipitation

Inorganic substances can occur in a wide variety of forms and their stability is dependent on a number of environmental conditions including pH, Eh, and the presence of other inorganic and organic compounds. As environmental conditions change, the speciation may also change causing dissolution or precipitation. Environmental conditions can therefore be altered to promote the precipitation of relatively immobile phases, such as metal hydroxides.

2.7.4 Complexation

Complexation occurs when a metallic cation reacts with an anion that functions as a ligand. Metal ions with this ability include the transition metals and alkaline earth metals. Inorganic ligands able to complex with metal ions include hydroxide, chloride, sulfate and cyanide. The complexes formed between inorganic ligands and metal ions are usually weaker than those formed with organic ligands. Organic ligands include groups such as amines and phenols.

Complexation occurs when a central metallic cation becomes attached to two or more inorganic or organic groups by co-ordinate covalent bonds. Ligands may consist of single atoms or molecules in which one of the atoms contains an un-bonded pair of electrons. If a ligand contains more than one pair of un-bonded electrons, it is referred to as a multidentate ligand. Soil organic matter is an example of a multidentate ligand, since it contains large numbers of COO^- and OH^- groups. Thus, the formation of SOM-metal complexes in soils with a high organic matter content is a significant soil-contaminant interaction process that needs to be considered in assessing the fate and transport of contaminants. By way of example, the presence of humic acids in landfilled material has been shown to significantly enhance metals binding capacity (Bozkurt *et al.,* 2000).

Complexes with multidentate ligands are usually more stable than those with monodentates. With increasing pH, the stability of metal complexes are though to increase because of the increased ionisation of the functional groups and the resulting increased attraction for the cation retained in the complex. The order for the stability of heavy metals complexes according to Jones and Jarvis (1981) is:

$$Cu^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$$

and is dependent upon the ionic radii. In the example shown in Figure 2.6, the formation of the complex contributes to the adsorption of the copper ion by soil organic matter. However in some cases, complexation between a contaminant and a mobile ion results in compounds of a greater solubility than the uncomplexed contaminant as reported by McKinley *et al.* (2001) in respect of metal mobility in S/S sewage sludge. In other cases, the intentional, selective use of chelating agents can facilitate precipitate and remove metals from solution (Aritola, 1996).

The nature of carbon-metal bonds vary widely, ranging from those that are essentially ionic to those that are primarily covalent. Carbon-sodium and carbon-potassium bonds are largely ionic in character whereas carbon-lead, carbon-tin, carbon-thallium (III), and carbon-mercury bonds are essentially covalent. Carbon-lithium and carbon-magnesium bonds fall in between these extremes (Solomons, 1984).

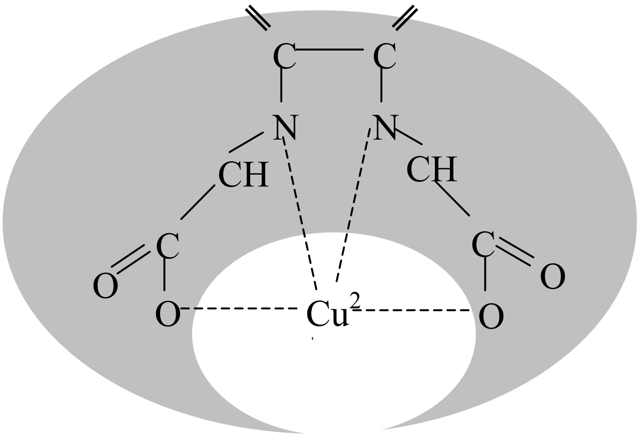


Figure 2.6: Complexation occurring between copper ion and organic substrate (after Yong *et al.,* 1996)

Almost all organometallic compounds are toxic, and covalently bonded complexes of lead, tin, thallium, and mercury are less reactive than their ionic counterparts and therefore more persistent in the environment. Methylmercury and tetraethyllead have been detected in the environment at levels of concern (Solomons, 1984). In some cases, organometallic compounds are produced by organisms in response to exposure to metals that would otherwise harm them. Methylmercury ions (CH_3Hg^+) and gaseous dimethylmercury ($(CH_3)_2$ Hg) for example, are produced by bacteria to protect themselves from the harmful effects of mercury.

Natural organic matter in soils and water bodies frequently form complexes with metals, which contribute either to their sequestration or mobility, depending on the solubility of the resulting compound. Dissolved organic matter in water bodies may form complexes with other contaminants, enhancing their solubility (Williams *et al.*, 2002), whilst humic material in soils may form complexes with contaminants, effectively locking them away and reducing their bio-availability (Bollag *et al.,* 1992).

2.7.5 Hydrolysis

Hydrolysis is a chemical transformation in which an organic compound (RX) reacts with water to form a new covalent bond with OH^-. Functional groups that can be susceptible to hydrolysis, depending on environmental conditions, include amides, carbonates, epoxides, aliphatic and aromatic esters, alkyl and aryl halides, nitriles, ureas and organo phosphorous esters (Lavson and Weber, 1994, Mabey and Mill, 1978). Functional groups relatively resistant to hydrolysis include the alcohols, phenols, glycols, ethers, aldehydes, ketones, biphenyls and pesticides (Lyman *et al.*, 1982).

In many cases hydrolysis reactions can be catalysed under basic or acidic conditions, making hydrolysis a pH-dependent process. If the ROH compound is of a greater solubility than the original RX molecule, then hydrolysis reactions catalysed by the high pH of the cementitious environment may mean that S/S will not be successful in the immobilisation of the RX contaminant. In simple terms, the high pH prevalent in many S/S waste forms can cause organic compounds to degrade by hydrolysis, producing more soluble compounds as degradation products. However, the production of degradation products may take some time and can be difficult to predict.

2.7.6 Biological degradation processes

The range of organisms present in soil that may influence the attenuation of contaminants range from plants and animals (predominantly earthworms) to single cell microbes. The most important microbial components are microbes, divided into two groups, depending on cell structure:

Prokaryotes: simple, single cells <5 µm, e.g. bacteria, cyanobacteria, actinomycetes; and
Eukaryotes: single or more complex multiple cell organisms >20 µm, e.g. fungi, algae.

Table 2.8 gives estimates of the relative populations of bacteria and fungi in soil.

Table 2.8: Abundance of soil biota (after Pepper and Josephson, 1996)

Microbe	Number (per g of soil)
Bacteria	10^8
Actinomycetes	10^7
Fungi	10^6

Micro-organisms require a supply of nutrients and favourable environmental conditions to maintain optimal performance. Nutrient requirements include carbon, oxygen (or other electron acceptor), nitrogen, hydrogen and phosphorus. Key environmental conditions include moisture content, temperature, pH, and salt concentration (affects osmotic uptake of nutrients). Degradation can take place under aerobic or anaerobic conditions, with the rate of degradation generally being faster for the former.

The concentration of carbon dioxide in the gaseous phase of soil is normally in the region of 1% v/v and this reflects the CO_2 generated by soil organisms (Pepper, 1996). Carbon dioxide is a dominant end product of the degradation of organic material under both aerobic and anaerobic conditions, and may result in between 65 - 90% w/w CO_2 in the soil gas (Bozkurt *et al.,* 2000, Lal *et al.,* 1998). The dissolution of CO_2 is also of great importance as it will cause carbonation reactions in binder systems and a consequent drop in pH and this will have an effect upon the immobilisation of both inorganic and organic contaminants.

Many organic contaminants are susceptible to natural degradation processes mediated by soil biota. Microbial decomposers are able to utilise organic compounds as sources of reduced carbon. If microbial degradation runs to completion the resulting products are water and carbon dioxide, although in many cases degradation is only partial, with the formation of potentially toxic long-lived intermediates.

The most common degradation processes involving bacteria are hydrolysis (addition of hydroxyl group) and demethylation (the removal of a methyl group) (Alexander, 1994). Microbial detoxification of pentachlorophenol has also been observed. Other degradation mechanisms available to micro-organisms are anaerobic reductive and aerobic oxidative reactions.

Significant biodegradation has been reported for a large number of contaminants, including: 2-4 D, parathion, carbofuran, atrazine, diazinon, volatile aromatic alkyl and aryl hydrocarbons and chlorocarbons, and surfactants (Manahan, 1994). Cement or lime S/S treatment of soil will cause an increase in pH that may arrest or significantly reduce the rate of biodegradation of organic contaminants. The impact of this must be evaluated when considering S/S treatment for soil with organic or mixed contaminants.

Toxicity of heavy metals to micro-organisms depends upon ability of the organism to bind metals in proteins or nucleic acids. Large metal ions, such as Cu, Ag, Hg and Cd readily bind with sulfhydryl groups whereas, small electropositive metals, such as Cr, Co, Zn and Sn complex with carbonyl, hydroxyl, phosphate and amino groups (Miller, 1996). In interacting with metals in the environment, micro-organisms can bring about a number of important transformations that influence their availability and which are dominated by:

- oxidation/reduction (e.g. the reduction of Cr(VI) to Cr(III));
- complexation; and
- methylation (e.g. As, Hg, Cd, Pb).

Data on the availability of metals as a result of biotic reactions in, for example, contaminated sediments is now available (USEPA, 2002). The effect of biotic reactions on S/S waste forms has been shown to be potentially significant (Idachaba *et al.*, 2001, Knight *et al.,* 2002). In particular, the stability of cementitious matrices appeared particularly affected during these studies.

Bozkurt *et al.* (1999) studied the long-term fate of organics in a variety of landfill environments. For the conditions examined the following times were calculated for all degradable organic matter to degrade:

- partially saturated, without cover = 600 years;
- partially saturated with cover (10% functional) = 3,000 years;
- partially saturated with cover = 30,000 years;
- forced convection with cover = >20,000 years;
- natural convection = 300,000 years;
- fully saturated = >500,000 years.

One important observation from this work is that the state of saturation achieved in the disposal environment is important in determining natural degradation rates, as are the dominant transport processes and total concentration of pollutants in the aqueous phase over geological time. The study involved introduction of oxygen to the landfill after the short initial aerobic and anaerobic phases had taken place (i.e. after the generation of methane had stopped).

Bozkurt *et al.* (2000) estimated that for a northern European exposure environment, the diffusion of oxygen into a landfill (uncovered, unsaturated) will be around 1.5 kg m^{-2} year^{-1} and this is enough to oxidise 1.4 kg m^{-2} year^{-1} of organic substances/matter. In a saturated environment the amount of oxygen ingress is much reduced to 0.005 kg m^{-2} year $^{-1}$ and this will oxidise 4.7 x 10-3 kg m^{2} year $^{-1}$ of organic substances, although this is dependent upon whether the fill is producing CH$_4$ or CO$_2$. An estimate of 700 and 225000 years to complete degradation of organic substances were given for the two disposal environments respectively, indicating the importance of in-service exposure environment to long-term stability.

2.8 Summary

The physical and chemical properties of soils may significantly influence the outcome of S/S treatment. The following conclusions can be made about the nature and interactions of contaminants and soils:

- the variability of soil composition and its ability to interact with contaminants is of fundamental importance to S/S;
- soils are invariably polymineralic systems containing primary and secondary mineral phases, water, soil, gas and organic phases and must be carefully characterised to enable the binder to be optimised and the remediation objectives to be met;
- a detailed examination of a contaminated soil is necessary to determine the likely risks associated with the contaminants present before and after treatment by S/S;

- the physical properties of soils such as grain size, moisture content and plastic properties are important in determining the choice of S/S systems;
- the chemical properties of soils also have a significant influence on the choice of binder system;
- complex reactions between soils and contaminants include sorption, oxidation-reduction reactions, precipitation, complexation, hydrolysis and biological degradation and these govern how contaminants are bound, or mobilised, within a soil;
- biotic degradation processes and the presence of biomass influence the properties and availability of both organic and heavy metal contaminants;
- inorganic and organic complexes are commonly found in soils; and
- the long-term behaviour of organic contaminants is uncertain, but recent work estimates that under certain disposal scenarios recalcitrant organics may persist for thousands of years.

REFERENCES

American Concrete Institute-COMMITTEE 306R-88. (1994) Cold Weather Concreting, Part 2. *ACI Manual of Concrete Practice.*

Alexander, M. (1994). *Biodegradation and Bioremediation*, Academic Press, San Diego.

Allen, H.E., Huang, C.P., Bailey, G.W. and Bowers, A.R. (Eds.). (1996) *Metal Speciation and Contamination of Soil*. Lewis Publishers, Boca Raton.

Alloway, B.J. and Ayres, D.C. (1993) *Chemical Principles of Environmental Pollution*. Blackie Academic and Professional, London.

Aritola, J.F. (1996) Industrial Sources of Pollution. In: *Pollution Science*. (Eds. Pepper, I.L., Gera, C.P. and Brusseau, M.L.). Academic Press. pp. 267-277.

Barriuso E, Laird D.A., Koskinen W.C., Dowdy R.H. (1994) Atrazine Desorption from Smectites. *Soil Science Society of America Journal*, 58, pp. 1632-1638.

Bernhard, M., Brinckman, F.E. and Sadler, P.J. (1986) *The Importance of Chemical "Speciation" in Environmental Processes,* Springer-Verlag, New York, USA.

Boardman, D. I. (1999) *Lime Stabilisation: Clay-metal-lime Interactions*. PhD Thesis. Loughborough University, Loughborough, Leicestershire, UK.

Bozkurt, S. Moreno, L and Neretnieks, I. (1999) Long-Term Fate of Oganics in Waste Deposits and its Effect on Metal Release. *The Science of the Total Environment*, 228, pp 135-152.

Bozkurt, S., Moreno, L. and Neretniks, I. (2000) Long-Term Processes in Waste Deposits. *The Science of the Total Environment*, 250, pp. 101-121.

Bollag, J.M., Myers, C.J. and Minard, R.D. (1992) Biological and Chemical Interactions of Pesticides with Organic Matter, *The Science of the Total Environment,* pp. 123-124, 205-217.

Brady, N.C. and Weil, R.R. (1996) *The Nature and Properties of Soils* (11th Edition), Prentice Hall International, London.

Brindle, T.R., Cote, P.L., Constable, T.W and Fraser J.L. (1987) Evaluation of Heavy Metal Leachability from Solid Wastes. *Water Science and Technology*, 19, pp. 1029-36.

Building Research Establishment (2001) *Concrete in Aggressive Ground.* Building Research Establishment Special Digest 1: Part 1.

British Standards Institution (1990) BS 1377: Part 4. *Methods of Test for Soils for Civil Engineering Purposes. Part 4. Compaction-related tests.*

British Standards Institution (1990) BS 1924: Part 1. *Stabilised Materials for Civil Engineering Purposes. General Requirements, Sampling, Sample Preparation and on Materials before Stabilisation.*

British Standards Institution (1999) BS 5930. *Code of Practice for Site Investigations.*

British Standards Institution (2001) BS 10175. *Investigation of Potentially Contaminated Sites - Code of Practice.*

Brusseau, M.L. and Bohn, H.L. (1996) Chemical Processes Affecting Contaminant Fate and Transport in Soil and Water, In: *Pollution Science*, (Eds. Pepper, I.L., Gerba, C.P. and Brusseau, M.L. Academic Press, London pp. 63-75.

Cernica, J.N. (1995) *Geotechnical Engineering Foundation Design,* Wiley, New York.

CIRIA. (1995) *Remedial Treatment for Contaminated Land*, Volume VII: *Ex situ* Remedial Methods for Soils, Sludges and Sediments. CIRIA Special Publication 107.

Conner, J. R. (1990) *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York.

Craig, R.F. (1992) *Soil Mechanics*, Chapman and Hall, London.

Davis, G. (1998) BTEX Plumes and Vapour Phase Emissions: Can Natural Attenuation Cope? In: *Proceedings of the Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe*. CD-ROM. Warsaw, September, 1998.

DEFRA/Environment Agency (2002a) *Potential Contaminants for the Assessment of Land*. Environment Agency R&D Publication CLR 8.

DEFRA/Environment Agency (2002b) *Contaminants in Soil: Collation of Toxicological Data and Intake Values for Humans*. Environment Agency R&D Publication CLR 9.

Domenico, P.A. and Schwartz, F.W. (1990) *Physical and Chemical Hydrogeology*. John Wiley & Sons, New York.

Garrison, A.W., Keith, L.H. and Shackleford, W.H. (1977) Occurrence, Registry, and Classification of Organic Pollutants in Water, with Development of a Master Scheme for their Analysis. In: *Aquatic Pollutants: Transformation and Biological Effects* (Eds. Hutzinger, O., van Lelyveld, I.H. and Zoeteman, B.C.J.). Pergamon Press, Oxford, pp. 39-68.

Glendinning, S., Rogers, C.D. and Boardman, D.I. (1998) Lime Stabilisation of Inorganic Contaminants in Clays. In: *Contaminated Land and Groundwater: Future Directions.* (Eds. Learner, D. N. and Walton, N. R. G.). Engineering Geology Special Publications, Geological Society, London, England, 14, pp. 19-28.

Graedel, T.E. (1978) *Chemical Compounds in the Atmosphere*. Academic Press, New York.

Hantush, M.H. and Govindaraju, R.S. (2003) Theoretical development of Analytical Solutions for Transport of Volatile Organic Compounds in Dual Porosity Soils. *Journal of Hydrogeolgy* (in press).

Hayes, M.H.B. and Swift, R.F. (1985) The Chemistry of Soil Organic Colloids. In: Greenland, D.J. and Hayes, M.H.B. (Eds.) *The Chemistry of Soil Constituents*. John Wilet and Sons, New York.

Holt, C.C. and Freer-Hewish, R.J. (1996) Lime Treatment of Capping Layers in Accordance with the Current Specification for Highway Works. In: *Lime stabilisation*. (Eds. Rogers, C. D., Glendinning, S. and Dixon, N.). Thomas Telford, London, pp. 51-61.

Idachaba, M.A., Nyavor, K, Egiebor, N.O. and Rogers, R.D. (2001) A Refinement of the Bio-film Formation Method for Waste Form Stability Evaluation. Journal of Hazardous Materials, B24, pp. 95-106.

International Union of Pure and Applied Chemistry (1979) *Nomenclature of Organic Chemistry*.

Johnson, A.W. and Sallberg, J.R. (1960) *Factors that Influence Field Compaction of Soils*. Bulletin 272, Highway Research Board.

Jones, L.H.P., and Jarvis, S.C. (1981) The Fate of Heavy Metal, In: *The Chemistry of Soil Processes* (Eds. Greenland, D.J., and Hayes, M.H.B), John Wiley and Sons, UK.

Keith, L.H. (1988) *Principles of Environmental Cycling*. American Chemical Society.

Knight, J., Cheeseman, C. and Rogers, R. (2002) Microbial Influenced Degradation of Solidified Waste Binder. *Waste Management*, 22, pp. 187-193.

Knox, R.C., Sabatini, D.A. and Canter, L.W. (1993) *Subsurface Transport and Fate Processes*. Lewis Publishers, Boca Raton, FL.

Kobayashi, T., Shimizu, Y. and Urano, K. (2003) Estimation of Adsorbed Amounts of Volatile Chlorinated Organic Compounds to Wet Soil Based on the properties of the Compounds and Soil. *The Science of the Total Environment* (in press).

Kunkel, J.R. and Anderson, D.E. (1999) *Unsaturated Zone Hydrogeology for Scientists and Engineers*. Prentice Hall, New Jersey.

Laird D.A., Barriuso E, Dowdy R.H. and Koskinen W.C. (1992) Adsorption of Atrazine on Smectites. *Soil Science Society of America Journal*, 56, pp. 62-67.

Lal, R., Kimble, J.M., Follett, R.F. and Stewart B.A. (1998) *Soil Processes and the Carbon Cycle*. CRC Press, Boca Raton, Fl.

Lavson, R.A. and Weber, E.J. (1994) *Reaction Mechanisms in Environmental Organic Chemistry*. Lewis Publishers, Boca Raton, FL.

Lewis, R.J. (1992) *Sax's Dangerous Properties of Industrial Materials*. 8th Edition. Van Nostrand Reinhold, New York.
Lyman, W.J., Reehl, W.F. and Rosenblatt, D.H. (1982) *Handbook of Chemical Property Estimation Methods: Environmental behaviour of Organic Compounds*. McGraw-Hill, New York.

Mabey, W.R. and Mill, T. (1978) Critical Review of Hydrolysis of Organic Compounds in Water under Environmental Conditions. *J. Phys. Chem. Ref. Data* 7, 383.

Mackay, M., & Emery, J. J. (1993) Practical Stabilization of Contaminated Soils*, Land Contamination and Reclamation*, 1(3), pp. 149-155.

MacNeil, D.J. and Steele, D.P. (2001) *Swell Test Requirements for Lime Stabilised Materials*. TRL Report 505.

McKinley, J.D., Thomas, H.R., Williams, K.P. and Reid, J.M. (2001) Chemical Analysis of Contaminated Soil Strengthened by the Addition of Lime. *Engineering Geology*, 60, pp.181-192.

Miller, R.M. (1996) Biological Processes affecting Contaminant Fate and Transport. In: *Pollution Science* (Eds. Pepper, I.L., Gerba, C.P. and Brusseau, M.L.) Academic Press, London pp.77-114.

Montgomery, J.H. (1991) *Groundwater Chemicals Desk Reference Vol. 2*. Lewis Publishers, Chelsea, MI.

Montgomery, J.H. and Welkom, L.M. (1990) *Groundwater Chemicals Desk Reference*. Lewis Publishers, Chelsea, MI.

Morel, F.M.M. (1983) *Principles of Aquatic Chemistry*. John Wiley and Sons, New York.

Morrow, D.A., Gintautas, P.A. Weiss, A.D., Piwoni, M.D., and Bricka, R.M. (1996) *Metals Speciation in Soils: A Review of Methodologies*.

Pankow, J.F. and Cherry, J.A. *Dense Chlorinated Solvents and Other DNAPLs in Groundwater.* Waterloo Press, Portland, OR.

Parkhurst, D.L. and Appelo, C.A.J. (1999) *User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse GeochemicalCalculations.* U.S. Geological Survey Water Resources Investigations Report 99-4259, 310pp.

Pepper, I.L. (1996) Abiotic Characteristics of Soil in: *Pollution Science* (Eds. Pepper, I.L., Gerba, C.P. and Brusseau, M.L.) Academic Press, London pp.9-18.

Pepper, I.L. and Josephson, K.J. (1996) Biotic Activity in Soil and Water, In: *Pollution Science*, (Eds. Pepper, I.L., Gerba, C.P. and Brusseau, M.L.) Academic Press, London pp. 31-34

Ross, S. (1989) *Soil Processes: A Systematic Approach*, Routledge, London.

Sawhney, B.L. (1996) Sorption and Desorption of Organic Contaminants by Clays and Soils. In: *Organic Pollutants in the Environment* (Sawhney. B.L., Editor). The Clay Mineral Society, Boulder, Co. pp. 45-68.

Schwarzenbach, R.P., Gschwend, P.N. and Imboden, D.M. (1993) *Environmental Organic Chemistry*. John Wiley & Sons, New York.

Sherwood, P.T. (1992) *Stabilised Capping Layers using either Lime, or Cement, or Lime and Cement*. Transport Research Laboratory, Contractor Report 151.

Sherwood, P.T. (1993) *Soil Stabilisation with Cement and Lime*, HMSO, London.

Solomons, T.W.G. (1984) *Organic Chemistry*, (3rd Edition), John Wiley & Sons, New York.

Sposito, G. (1984) *The Surface Chemistry of Soils*. Oxford University Press, New York.

Stavridakis, E.I. and Hatzigogos, T.N. (1999) Influence of Liquid Limit and Slaking on Cement Stabilised Clayey Admixtures. *Geotechnical and Geological Engineering*, 17, pp. 145-154.

Stucki, J.W., Bailey, G.W. and Gan, H. (1995) Redox Reactions in Phyllosilicates and Their Effects on Metal Transport. In: *Metal Speciation and Contamination of Soil* (Eds: Allen, H, Huang, C.P., Bailey, G.W and Bowers, A.R.) Lewis Publishers, Boca Raton.

Stumm, W. and Morgan, J.J. (1995) *Aquatic Chemistry - Chemical Equilibrium and Rates in Natural Waters*. John Wiley and Sons, New York.

Suthersan, S.S. (1997) *Remediation Engineering: Design Concepts*. CRC Press, Boca Raton, FL.
Tan, K.H. (1993) *Principles of Soil Chemistry*. 2nd Edition. Marcel Dekker, New York.

Tessier, A., Campbell, P.G.C and Bisson, M. (1979) Sequential Extraction Procedure for the Speciation of Particulate Trace Metals, *Analytical Chemistry*, 51, pp. 844 –850.

Thurman, E.M. (1985) *Organic Geochemistry of Natural Waters*. Dortrecht, Martinus Nijhoff/Dr. W. junk.
Tindall, J.A. and Kunkel, J.R. (1999) *Unsaturated Zone Hydrogeology for Scientists and Engineers*. Prentice Hall, N.J.

Townsend, W.N. (1973) *An Introduction to the Scientific Study of Soil*, Butler and Tanner, Frome and London.

United States Environment Protection Agency. (1986) *Handbook of Stabilisation/Solidification of Hazardous Wastes*. EPA/540/2-86/001.

United States Environment Protection Agency (1987) *Federal Register* 52 (155): 29999, August 12, 1987.

United States Environment Protection Agency (1990) *Handbook on In-situ Treatment of Hazardous Wastes-Contaminated Soils*. EPA/540/2-90.

United States Environment Protection Agency (1993) *Solidification/Stabilisation of Organics and Inorganics*. Engineering Bulletin EPA/540/S-92/015.

United States Environment Protection Agency (1999) *Solidification/Stabilization Resource Guide*. EPA/542-B-99-002.

United States Environment Protection Agency (2002) Reachit Database, www.epareachit.org.

Van Herck, P and Vandecasteele, C. (2001) Evaluation of the Use of Sequential Extraction Procedure for the Characterisation and Treatment of Metal Containing Solid Waste. *Waste Management*, 21, pp. 685 –694.

Verschueren, K. (1977) *Handbook of Environmental Data on Organic Chemicals*. Van Nostrand Reinhold, New York.

Wilk, C. M. (1997) *Stabilisation of Heavy Metals with Portland Cement: Research Synopsis*. Waste Management Information, Public Works Department, Portland Cement Association, Skokie, Il.

Williams, C.F., Letey, J. and Farmer, W.J. (2002) Molecular Weight of Dissolved-Organic Matter-Napropomide Complex Transported through Soil Columns. *Journal of Environmental Quality*, 31, 2, pp. 619-627.

Yong, R.N. and Mulligan, C.N. (2003) *Natural Attenuation of Contaminants in Soils*. Lewis Publishers, Boca Raton, Fl.

Yong, R.N., Mohamed, A.M.O. and Warkentin, B.P. (1996) *Principles of Contaminant Transport in Soils*, Elsevier, Oxford.

3 INTRODUCTION TO BINDERS AND THEIR INTERACTIONS WITH SOILS

3.1 Introduction

Binders are used to 'cement' contaminated materials together during S/S to enable disposal, or re-use in a beneficial way. Binders can impart both chemical stability and physical solidity to the treated product. The high pH induced by the addition of the most common binders, such as lime and Portland cement, results in the precipitation of many contaminant species and a corresponding reduction in mobility (stabilisation). Secondly, the ability of the binder to set into a solid mass encapsulating the contaminant results in a physical immobilisation process (solidification). Many binders rely on the presence of *free* CaO for this, although the use of additives is common for modification of the hydration/setting processes.

Binders can be divided into two groups; primary stabilising agents and secondary stabilising agents and their properties and interaction with soils are described below. However, it should be noted that the stabilisation of contaminants in a bound system does depend, to a greater or lesser degree, on the speciation of the contaminants involved (Reid and Brooks, 1999).

3.2 Primary Stabilising Agents

Primary stabilising agents can be used alone to bring about the stabilising action required. A description of the principal stabilisation agents is given below. It is important to note that when using cementitious binder systems, waste or soil particles are both encapsulated chemically and physically (Figure 3.1) in the treated product. Chemical incorporation into hydrated matrices is explored in depth in Chapters 4 and 5.

The interaction of binders with soil is complex. In understanding the interrelationships of hydraulic binders it is recommended that sections 3.2.1 and 3.2.2 on Portland cement and lime, respectively be read in conjunction with one another.

The health and safety implications of using common S/S binders are given in Appendix 3.

3.2.1 Portland Cement

Portland cement is a family of cements introduced in BS EN 197-1: 2000, which are based upon standard strength classes. Class 42.5N, typically has a surface area of 350m^2/kg and equates to Ordinary Portland cement (OPC) of the old British Standard, BS 12. Taylor (1997), provides an authoritative review of cement manufacture, phase chemistry and hydration reactions.

Portland Cement (PC) clinker is produced by calcining a mixture of finely ground limestone and clay in an inclined rotary kiln to a maximum temperature of 1450°C. After cooling, the clinker is ground with 2 – 5% gypsum to control the rate of setting during addition of water. A typical clinker composition is in the region of 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and <3% other components.

A 50µm diameter particle covered with fibrous crystalline growth of ettringite, which is known to chemically incorporate metal contaminants in its chemical structure. The micrograph illustrates the physical encapsulation of a waste particle in the cement matrix.

Figure 3.1: Particle of heavy metal-contaminated material, derived from treatment of metal plating residues, encapsulated in a PC matrix (photograph courtesy of Colin Hills).

The four major phases present are alite, belite, aluminate and ferrite, with alkali, sulfates and free lime present in minor proportions.

Alite

Alite or tricalcium silicate (Ca_3SiO_5 or C_3S[1]) generally constitutes 50 – 70% by mass of a PC clinker. It reacts readily with water to produce calcium silicate hydrate gel (C-S-H) and portlandite ($Ca(OH)_2$). Alite is considered to be the most significant constituent phase of PC and is a major contributor to strength development up to 28 days.

Belite

Belite or dicalcium silicate (Ca_2SiO_4 or C_2S) constitutes 15 – 30% of PC clinker and is normally present as the β–polymorph. It also reacts with water to form C-S-H gel and portlandite, although at a slower rate. At one year of age the compressive strengths of pure alite and belite are comparable.

---

[1] For simplicity, cement chemists nomenclature is used, where: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3 and $\hat{S} = SO_3$

Aluminate
The aluminate phase, tricalcium aluminate ($Ca_3Al_2O_6$ or C_3A) constitutes 5 – 10% of PC clinker. Tricalcium aluminate reacts rapidly with water and may cause undesirably rapid setting in the absence of gypsum.

Ferrite
The ferrite phase, tetracalcium aluminoferrite (Ca_2AlFeO_5 or C_4AF) has a variable Al/Fe ratio and constitutes 5 – 15% of PC clinker. Its reactivity with water is variable.

Proprietary cements are manufactured to address specific problems, such as elevated sulfate, and are now commonly used for S/S. These cements often comprise PC blended with secondary reagents. A review of proprietary cement-based systems is not included in this report.

3.2.1.1 Hydration

On mixing PC and water, the dissolution of alkalis and corresponding initial heat-evolution occurs within minutes, during which time, a semi-permeable film of hydration products coats the surface of the cement grains. The ‘dormant’ or ‘induction’ period follows, during which the rate of hydration is significantly restricted. The breakdown of this film marks the onset of the main period of hydration. After 28 days approximately 65% of the anhydrous cement will have reacted, and hydration is in excess of 95% complete at one year of age.

The rate of reactivity of anhydrous phases of PC with water is in the following general order:

$$C_3A > C_3S > C_2S > C_4AF$$

However, the setting of cement can be divided into four stages involving a series of overlapping reactions as the anhydrous phases hydrate (after Cocke and Mollah, 1993):

Stage 1
$C_3A + 3(C\hat{S}) + 32H \rightarrow C_6A\hat{S}H_{32}$

Stage 2
$2(C_3S) + 4H \rightarrow C_3S_2H_3 + 3CH$

$2(C_2S) + 4H \rightarrow C_3S_2H_3 + CH$

Stage 3
$3(C_3A) + CH + 12H \rightarrow C_4AH_{13}$

$C_4AF + 4CH + 22H \rightarrow C_4AH_{14} + C_4FH_{13}$

Stage 4
$2(C_3A) + C_6A\hat{S}H_{32} + 4H \rightarrow 3(C_6A\hat{S}H_{12})$

The formation of the C-S-H gel is important to the setting of cement and to the S/S process (Cocke and Mollah, 1993), since interference with these reactions will result in an unsatisfactory set.

There are two ways in which the anhydrous components of cement can react with water: the first is through direct addition of molecules of water and the second involves the ionic dissociation of water and is strictly termed hydrolysis. The two reactions are usually termed hydration (Neville, 1995). With reference to the stages of hydration above, the hydration products of C_3S (and C_2S) are the microcrystalline hydrate $C_3S_2H_3$, (referred to as C-S-H because of its variable stochiometry) and CH, normally referred to as portlandite.

The aluminate phase, C_3A hydrates to ettringite, $C_6A\hat{S}H_{32}$, when there is excess sulfate available. When the sulfate is consumed monosulfate, $C_6A\hat{S}H_{12}$, forms. Ferrite (C_4AF) forms similar hydrates but with higher iron contents. Taylor (1997) provides an authoritative description of the chemistry of cement hydration and its products.

Figure 3.2, shows a secondary electron photomicrograph of a cement grain, which is partially hydrated in an S/S Cr-containing plating waste. The grain shows a hydration rim (darker area) in which Cr was associated. In this instance chromium was mobilised during S/S and became incorporated in the C-S-H gel being formed within the original cement grain boundary. The mobilisation of Cr was probably due to the change in pH environment on addition of binder as Cr^{6+} is known to be mobile at high pH. Figures 3.3 to 3.6 show various cement phases.

3.2.1.2 Soil and cement interactions

Although soils are a complex mixture of materials, it may be possible to assess the likely behaviour of a soil upon cement addition by considering its type. As described in chapter 2, soils can be classified according to the proportion of clay, silt and sand in the sample.

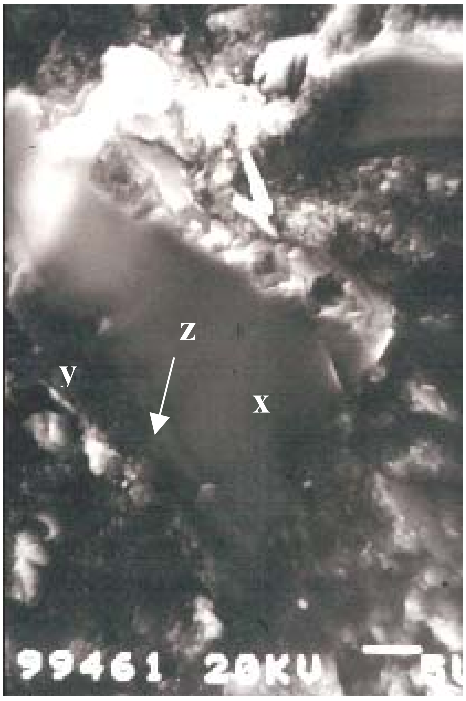
It is well known that organic matter may affect the cementing process in soils (Tremblay *et al.* 2002). Work by these authors has involved different organic substances naturally occurring in soils and has shown some organic acids (see chapter 6) to have significant impact on the properties of the cement-treated product especially where pH conditions in the product were <pH 9. Hebib and Farrell (2003) examined Irish peat, highly organic rich-soil, and found that, with the addition of cement, stabilised media could be formed. However, for apparently similar peat the degree of improvement could vary widely. This work illustrates that in addition to contaminants present, the nature of the soil matrix can influence the efficacy of cementitious binders and that pre-treatment prior to S/S may be required.

Interactions between clays and cements are generally not thought to be detrimental, although in some cases, a stiffening of the mix may occur, requiring the addition of a plasticising agent. In many cases however, clays may sorb organic compounds, which are responsible for retardation of cement set (see below). Clay soils may also present a problem with S/S as a consequence of cohesion and the tendency to form clods rather than a disaggregated mixture.

Pre-treatment of clay with lime can be used to facilitate mixing. Section 3.2.2 discusses the effects of lime addition to soil. There are many similarities in the results of application of cement and lime. However, Stavridakis and Hatzigogos (1999) reported that both PC and lime alone can significantly improve the properties of clayey soils. Bell (1995) discusses the use of PC to improve the properties of a range of soil types.

During hydration of cement the production of C-S-H is accompanied by a raising of pH to 12-13 as alkalis become solubilised. At this high pH, certain hydroxides can react with silica derived from clayey soils. This reaction results in the production of a gel-phase, which cements the soil matrix and is similar to the reaction between soil and lime.

Silt particles act as a substrate for $Ca(OH)_2$ to grow, thus removing it from further hydration reactions. This results in an initial reduction in strength of the cement within the first 3-6 months, although after a year, the strength of cement stabilised soils is likely to be greater than if silt was absent. Strength testing carried out on cement-stabilised silty soils in the initial stages of set may give a value for strength considerably lower than results obtained after a year.



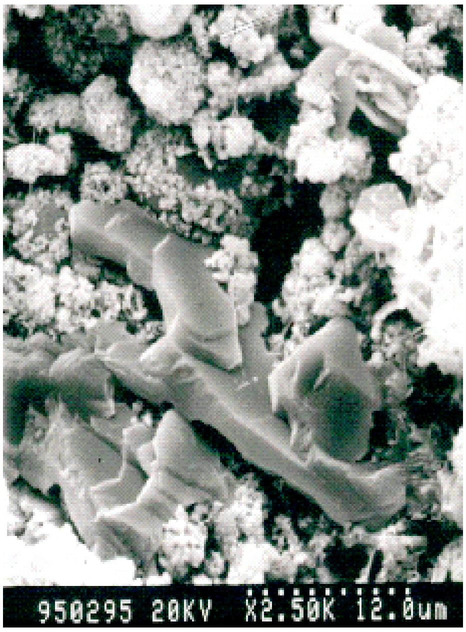
Inner hydration product (y) was associated with higher Cr concentrations in a thin dark band of material (z).

The cement used here was employed in the solidification of a commercially blended hazardous waste. The image shows that pseudomorphic reaction products are also capable of chemically incorporating hazardous constituents of a waste.

Figure 3.2: Secondary electron SEM image of the fractured surface of a cement grain (marked 'x') (Photograph courtesy of Colin Hills).

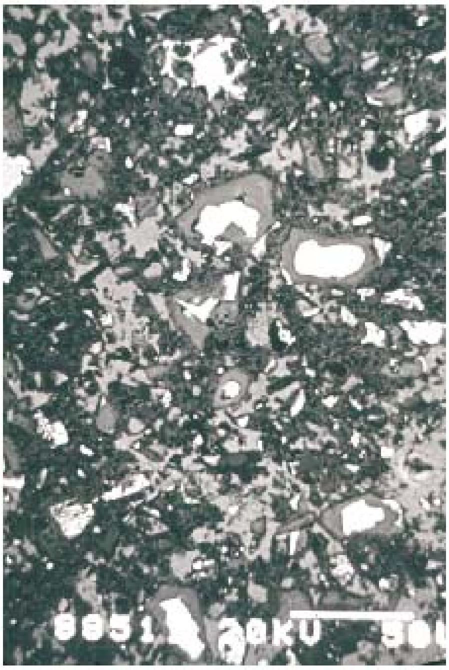
These features are due to the complete dissolution of cement clinker during hydration. Although they form distinct voids, which invariably may remain free of hydration reactions, these features do not have any adverse effect upon the permeability of a cementitious material.

Figure 3.3: Secondary electron photomicrograph of a 'Hadley' grain formed in PC paste (Photograph courtesy of Colin Hills).



A secondary electron photomicrograph of a fracture surface showing C-S-H (fine particulate masses), portlandite (mid grey massive crystals) and platelets of $C_6A\hat{S}H_{12}$ (or monosulfate) in the top right-hand side of image.

Figure 3.4: Secondary electron photomicrograph showing cement hydration products (Photograph courtesy of Colin Hills)



Bright areas are anhydrous cement grains surrounded by darker ‘inner’ hydration product. Portlandite is the mid-grey phase infilling porosity (black). C-S-H is dark grey in colour

Figure 3.5: Backscattered electron photomicrograph of PC paste (Photograph courtesy of Colin Hills).

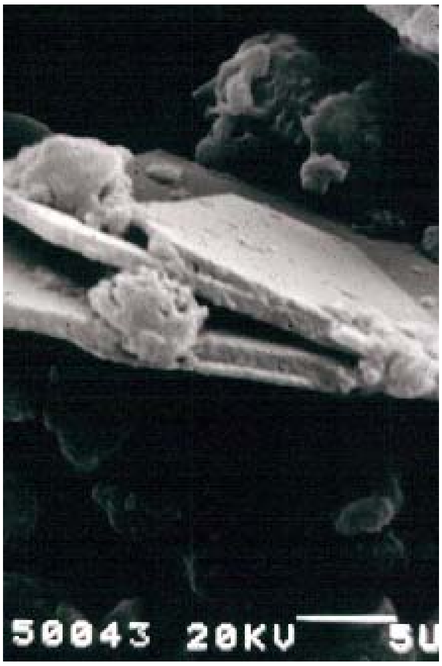


Figure 3.6: Secondary electron photomicrograph of platelets of monosulfate in PC paste (Photograph courtesy of Colin Hills).

Sand particles are thought to be uninvolved in chemical reactions with cement and the precipitation of $Ca(OH)_2$ crystals on the surface of sand grains forming crystals does not appear to be detrimental.

Soil organic matter (SOM) has been shown to sequester significant quantities of contaminants, rendering them immobile. However, increasing the pH of a soil by the addition of cement (or lime) may cause significant morphological change to the organic matter. Andersson and Nilsson (2001) report chemical fractionation in dissolved organic matter as a result of pH change due to the addition of lime to soil. If soil contains metal ions complexed to the humin material, increasing pH will favour the retention of the metal ion by transforming acidic functional groups to their negatively charged forms:

$$\underset{\text{Acidic pH}}{\mathrm{COOH}} \longrightarrow \underset{\text{Alkaline pH}}{\mathrm{COO^-}}$$

The presence of negatively charged groups will therefore increase the attraction between the metal cation and the SOM. On the other hand, where metal ions are complexed to humic or fulvic acids (which are more soluble at alkaline pH) the addition of cement or lime is likely to contribute to an increase in mobility.

If organic compounds are retained in SOM then the creation of negatively charged groups on the SOM may result in the repulsion of neighbouring functional groups, and the release of the sorbed contaminant, as the groups become more hydrophilic. If the contaminant itself contains functional groups that may be deprotonated, the creation of charged species is likely to increase the mobility of the contaminant, leading to retention problems unless suitable compensations are made. Organic contaminants associated with SOM, which are soluble at the pH of the binder system, may also be released as humic and fulvic acids are solubilised.

3.2.2 Lime

Lime is a general term for the various forms of calcium oxide or hydroxide and of lesser amounts of magnesium oxide and/or hydroxide. Soil stabilisation using lime is widely established in the UK (Sherwood, 1993; Chaddock and Atkinson, 1997; Aggregate Advisory Service, 1999). More recently, this process has been extended to include the stabilisation of contaminated soils prior to use for construction purposes, and for the treatment of contaminated wastes (Reid and Brookes, 1997, 1999) and those containing reactive aluminium or silicious components (LaGrega *et al.,* 1994). Lime is used for the stabilisation of laterite roads (Attoh-Okine, 1995) and for modifying the plastic properties of soils (Little, 1987). However the rate of dissolution of lime can vary according to its production process (Robinson and Burnham, 2001).

Lime is used widely in industrial processes (Oates, 1998) and for geotechnical stabilisation of soils. Lime is discussed in detail below, because it illustrates the complex reactions that take place on the addition of a relatively simple material to pozzolans and soils. The interactions of cement and lime on soils are broadly similar, despite cement having a lower free lime content (section 3.2.1.1). Guidance on the various applications of lime in soil stabilisation is readily available (British Lime Association, 1990; Highways Agency, 2003).

3.2.2.1 Soil and lime interactions

The addition of lime, either in the form of quicklime (CaO) or as hydrated or 'slaked' lime ($Ca(OH)_2$), to a soil system initiates a two-stage reaction.

First stage reaction

The interaction of lime with soil results in changes in soil properties on a timescale of minutes to hours. During the first stage of reactivity if added, quicklime reacts with water in the soil according to the following equation:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat} \uparrow$$

This reaction is highly exothermic, producing approximately 17×10^9 joules per kilogram of calcium oxide. The exothermic reaction raises soil temperature driving off further water as vapour or steam. Quicklime is sometimes used purely as a de-watering agent due to the benefits of dehydration of the soil system by reaction and by steam generation.

Within minutes to hours of mixing, there is a decrease in the plasticity of a clay soil caused by the flocculation of the clay particles. This is accompanied by an increase in strength caused by both the dehydration and fundamental changes in the clay particle chemistry. Quicklime chemically combines with free water in a soil and clay minerals undergo cation exchange as Na^+ and H^+ are exchanged for Ca^{2+}. The reaction of soil with $Ca(OH)_2$ is similar, but without the generation of heat and the effect of drying.

Second stage reaction

The second stage of the reaction process, involving solidification, occurs over a period of days and weeks and is the result of pozzolanic reactions (Glendinning and Boardman, 1996). These reactions have been studied and reported in detail by Arman and Munfakh (1970), Eades and Grim (1960) and Diamond and Kinter (1965).

Sherwood (1993) defines a pozzolan as a material that is capable of reacting in the presence of water, at ordinary temperatures, to produce cementitious compounds. The addition of lime to clay in appropriate quantities (generally between 1-7% w/w) raises soil pH to ca. 12.5 and this promotes the dissolution of silica and alumina (particularly at the edge sites of the clay plates). The reaction products are C-S-H and C-A-H gels that are analogous to those produced during hydration of PC (Oates, 1998). The result is a tough, water insoluble gel, which cements the soil particles (McKinley *et al.,* 2001). The dissolution effects of high pH on the basic building 'blocks' of clay minerals including silicon oxides, aluminium oxides and iron oxides is evident from Figure 3.7.

The reaction of quicklime and hydrated lime with clays in cohesive soils results in agglomeration and flocculation of clay particles with a consequent reduction in the plasticity and an increase in shear strength of soils facilitate easier soil handling. Pre-treatment/conditioning of cohesive soils with lime prior to the addition of other binders is common.

The second-stage reaction thus, generally results in continued reduction in plasticity as reported by Lund and Ramsey (1959), Wang *et al* (1963) and Jan and Walker (1963). However, lime affects the liquid limit in various ways. Wang *et al* (1963) and Jan and Walker (1963) reported decreases in the liquid limit, whereas Zolkov (1962) reported substantial increases. Lund and Ramsey (1959) and Taylor and Arman (1960) found increasing and decreasing liquid limits that were dependent on the soil type. Along with changes in Atterberg Limits there is usually an increase in shear strength on addition of lime (Thompson, 1966).

Thompson (1965) showed that organic matter with a high exchange capacity retarded the strength-producing pozzolanic reactions, probably due to the process of Ca attenuation. However, a study by Arman and Munfakh (1970) concluded that organic soil-lime mixtures produce cementitious products similar to those reported for inorganic soil-lime reactions and that the organic matter does not appear to block the reaction that results in an increase in the soil strength. In the context of treating contaminated land, the most significant physical change is in permeability. In the short-term after addition of lime it is expected that the permeability will increase depending on the time between mixing and compaction and curing conditions.

This increase in permeability was hypothesised by Townsend and Klym (1966) when their tests on lime-treated heavy clays exhibited slight increases in permeability. McCallister and Petry (1992) reported on research by Ranganatham (1961) who found a ten-fold increase in permeability after adding lime to expansive clays. Fossberg (1965) however, reported a longer-term tendency for decreased permeability as gel products fill pore spaces between the flocs (El-Rawi and Awad, 1981). Gutschick (1978) reported that the permeability of a lime-fly ash-aggregate canal liner showed an initial increase, which gradually decreased to produce flow rates comparable with the natural clay.

Both quicklime and hydrated lime have been used in many S/S products in the USA as part of a S/S remediation strategy. Lime can be used on its own or in conjunction with other materials. For example, Dermatas and Meng (2001, 2003) describe the application of lime/PFA in the immobilisation of Pb, Cr^{3+} and Cr^{6+} in a contaminated cohesive clay facilitating re-use potential as an engineering medium. Lime has been used to treat sediments but has been noted to cause agglomerations and an increase in porosity despite formation of C-S-H and calcium aluminate hydrate (C-A-H) (Rajasekaran, and Rao, 1996). Rao *et al.* (2001) investigated the effects of cyclic wetting and drying on lime stabilised soil and concluded that the potential for soil collapse was increased significantly after 4 cycles due to the breakdown of cementitious bonds.

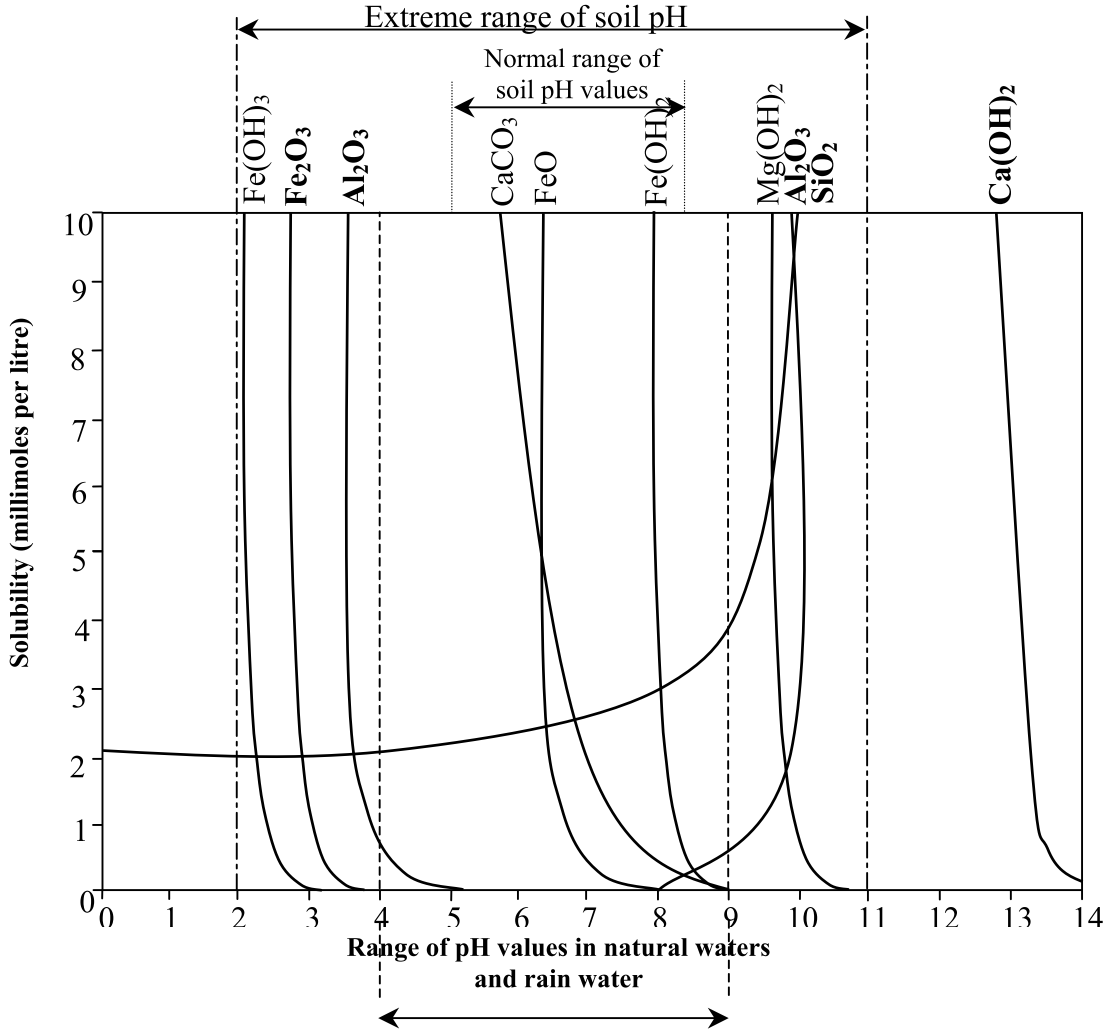


Figure 3.7: Solubility of some soil mineral species in relation to pH (Loughnan, 1969)

Lime can be used in conjunction with PFA or for particular applications. Furthermore, there may be wider beneficial effects resulting from lime use. Rogers and Glendinning (1997) discussed how lime could seep from piles into surrounding soil. Research on lime-treated clays by McCallister and Petry (1992) concluded that lime modification optimum is a central parameter in determining the leaching properties of lime-treated soils. Glendinning (1995) summarised the effects of lime on some of these physical properties for a variety of British clay formations (Table 3.1).

Lime addition to soil also has profound effects on SOM. As described above for cement, the addition of lime to soils and the resultant increase in pH also leads to the solubilisation of humic and fulvic acids.

Lime has the ability to raise pH of a contaminated medium rapidly. In one instance (Bates, 2003 a) this proved to be problematic when lime was used to treat acid tar (<pH4) in a lagoon with the resultant release of SO_2 gas. An alternative approach, raising pH more slowly by the use of agricultural lime ($CaCO_3$) prior to addition of a lime/cement binder, eliminated the evolution of sulfur dioxide gas.

Organic materials have been shown to interfere with the solidification of cementitious binders (Vipulanandan and Krishnan, 1993) and therefore if the soil being treated has a significant organic matter content then the success of the process may be compromised. Furthermore, metals complexed with SOM, which becomes solubilised at high pH, are likely to become mobilised during the S/S process. McKinley *et al.* (2001) observed this phenomenon during treatment of a silt/PFA/metal-contaminated sewage sludge mixture with lime. Copper and nickel leached from the treated material at higher concentrations than from the untreated material. This phenomenon was attributed to the formation of copper and nickel complexes with the organic matter of the sewage sludge, which dissolved on lime addition, bringing the heavy metals out into solution (McKinley *et al.,* 2001). Further information on metal-organic complexation can be found in section 4.3.3.

3.2.3 Thermoplastic materials

Thermoplastic materials have been used for solidifying contaminated materials in the USA. They include bitumen and sulfur polymer cement (Lin *et al.* 1995; Lin *et al.* 1996). The USEPA recognises the usefulness of these materials despite the fact that no chemical stabilisation may be involved during their application. Thermoplastic materials such as bitumen may be used in conjunction with cement (British Cement Association, 2001) or on their own. Haas (1989) describes bitumen being used as a binder and mortar by the Babylonians 5000 years ago, and evidence of its efficacy is still evident. However, the use of many thermoplastics is often precluded in the USA because of price (Bates, 2003b).

Contaminated materials may be encapsulated in thermoplastic materials, which include bitumen, asphalt emulsions, asphalt, paraffin, polyethylene or polypropylene. Prior to mixing with the encapsulating agent, the feedstock material must be dried and heated. The heating step of the treatment process means that this technique may not be suitable for use with volatile contaminants.

Asphalt emulsions consist of fine droplets of asphalt dispersed in water and stabilised by chemical emulsifying agents. They are available in anionic (negatively charged) or cationic (positively charged) forms, and the type most appropriate to the waste being treated should be selected. Following this the appropriate emulsion is added to hydrophilic liquid or semi-liquid contaminated materials at ambient temperature, and mixed. This action causes the emulsion to ‘break’, the water in the waste is released, and the organic phase forms a continuous matrix of hydrophobic asphalt around the solids. In some cases, additional neutralising agents such as lime or gypsum may be required. After setting and curing has occurred, the feedstock solids are evenly distributed through the solid asphalt (CIRIA, 1995).

In the commercial bitumen process, heated bitumen is combined with concentrated slurry of the contaminated feedstock in a heated extruder. This contains screws for mixing the bitumen and the slurry. Water is evaporated from the mixture to about 0.5% moisture to give a homogenous mixture of extruded solids and bitumen. CIRIA (1995) note that large scale plant, such as asphalt manufacturing equipment is potentially available for the treatment of contaminated materials using thermoplastics, and that the high temperatures required (130-230°C) pose certain hazards such as fire, explosion, or the release of volatile toxic substances.

Table 3.1: British clays: properties, mineralogy and effects of lime (Glendinning, 1995)

Formation	LL (%)	PI (%)	Clay fraction $< 2\mu m$ (%)	Average undrained shear strength (kN/m^2)	Effective cohesion c' (kN/m^2)	Effective angle of friction ϕ' (degrees)	Mineralogy	Effects of lime: Author, test, effects
Palaeogene								
London clay	66-100	40-65	40-72	100-173	12-18	17-23	Mainly illite-mica with kaolinite and traces of chlorites, smectites and vermiculite. $CaCO_3$ barytes and gypsum also found	Dumbleton, 1962, mix test, 10% lime. Increase in UCS. Also 5% reduced plasticity.
Cretaceous								
Gault clay	70-92	27-80	38-62	60	----	----	Usually illite-mica, poorly crystallised kaolinite and expanding chlorite/vermiculite. Mixed layer structure.	Dumbleton, 1962, mix test, 10% lime. Increase in UCS. Also 5% reduced plasticity.
Weald clay	42-82	28-32	20-74	----	----	----	Similar to above with impurities of calcite, siderite, pyrite, gypsum, ostracod and ferrous iron	Dumbleton, 1962, mix test, 10% lime. No increase in UCS in 12 weeks; affects to LL and PL
Jurassic								
Kimmeridge clay	----	24-59	57	----	14-67	14-23	Dominantly illitic	Dumbleton, 1962 mix test, 10% lime. Increase in UCS
Oxford clay	----	28-50	30-70	----	0.2	21.5-28	Dominantly illitic	Dumbleton, 1962 mix test, 10% lime. Increase in UCS. Cobbe, 1988 mix test; 2% $Ca(OH)_2$ PL and LL and PI raised 1 hour after mixing.
Upper Lias	56-68	20-39	55-65	30-150	10-17	18-25	Kaolinite-illite with traces of chlorite. Rare mixed layers	Cobbe, 1988, mix test, 2% $Ca(OH)_2$, PI and LL raised 1 hour after mixing.
Lower Lias	56-62	32-37	50-56	----	5	27	Dominantly illitic with impurities of marcite, pyrite, glauconite, fossils; high iron content.	Dumbleton, 1962, mix test, 10% lime, UCS raised.
Triassic								
Keuper Marl	25-60	10-35	10-50	100-150	2-80	25-42	> 40% illite mica, 4-34% dolomite, gypsum, high alkalinity.	Dumbleton, 1962, mix test, 10% lime, UCS raised.

Notes: UCS is the Unconfined Compressive Strength; LL is the Liquid Limit; PL is the Plastic Limit; PI is the Plasticity Index (LL-PL)

A recent development in the use of thermoplastics in S/S has come with the introduction of 'foamed bitumen'. Traditionally, bitumen was made suitable for use by reducing its viscosity by heating it to produce 'hot mix asphalt'. Using the foamed technique however, cold water is introduced to a hot asphalt mix using a specially designed spray-bar. The foamed bitumen expands 10-15 times its original volume and can then be mixed with the contaminated soil to produce mastic that effectively binds soil particles together.

As described above, reactions between bitumen and soils or contaminants are thought to be minimal as the binder acts simply by sticking particles together and preventing the ingress of water (Sherwood, 1993).

3.3 Secondary Stabilising Agents

This group includes materials that are not very effective on their own but can be usefully used in conjunction with lime or cement. Sometimes, only a small proportion of cement or lime is needed as an activator and the 'secondary' agent may comprise the major proportion of the binder. Secondary materials may be added to 'tailor' an S/S system for particular contaminants (with reference to redox environment) or they may be available locally, in quantities that provide an economic binder system, without compromising technical properties. Furthermore, blended S/S systems utilising, for example, lime/PFA or PC/ground granulated blastfurnace slag (ggbs) mixtures can have technical advantages, such as reduced permeability, when the quality criteria selected for S/S waste forms demand higher specifications. Recent developments involving the use of unconventional waste materials with pozzolanic properties, such as spent oil-cracking catalysts (Pacewska *et al.* 2000; Wu *et al.* 2003) illustrates the potential of new materials for use in cementitious applications.

3.3.1 Ground granulated blastfurnace slag

Blastfurnace slag is a by-product from the manufacture of iron, which is tapped from the blast-furnace as a molten liquid. The composition of blastfurnace slag is dominated by calcia, silica, alumina, magnesia and iron (Bijen, 1996). If allowed to cool slowly, it forms a crystalline material with virtually no cementitious properties but if rapidly quenched in water (granulated), it remains in a glassy, non-crystalline state and is a latent hydraulic binder (Taylor, 1997). For use as a binder, the granulated blastfurnace slag (gbs) is ground to a fine powder (ggbs).

BS 6699: 1992 specifies manufacture, chemical and physical properties of ground granulated blastfurnace slag, whereas, BS 1047: 1983 specifies the materials, properties and testing of air-cooled slag for use in construction. BS EN 1744-1: 1998 will cover aspects of chemical testing of slag after December 2003.

Ground granulated blastfurnace slag is used in a third of all UK ready-mixed concrete, with the ggbs comprising between 40 and 70% of the cement content. Whilst ggbs reacts only slowly with water, the rate of reaction increases dramatically when the pH is above about 12. The main hydration product of slag, C-S-H becomes more soil-like as slag content increases. Inner and outer products are different with the latter having higher Ca/(Si +Al) ratio (Richardson and Cabrera, 2000).

Both cement and lime are sufficiently alkaline to activate the cementitious properties of ggbs. Several other materials, including sulfates, chlorides and alkali-silicates, are also activators (Talling and Brandster, 1989). Many waste-streams contain components that will activate ggbs. Shi and Day (1995) showed slag could be activated by different Na-salts including OH, CO_3, SiO_3, PO_4, HPO_4 and F. In this work, the initial pH of the mixture was very important, however at later ages the reaction with Ca became dominant.

According to Talling and Brandster (1989) alkali-activated slag has significant resistance to waste/binder interference effects. For example, the presence of organic compounds known to interfere with PC interaction may be limited to a plasticising effect.

In the stabilisation of soils for road-bases and foundations, it is well established that when Portland cement or lime is used as a binder, the presence of sulfates in the soil can cause expansion and disruption. In this application, unlike in concrete, sulfate-resisting Portland cement provides no protection due to the availability of alumina from the soil to produce ettringite and expansion (Sherwood, 1962). The presence of sulfides may also be disruptive because stabilisation with cement or lime produces an elevated pH at which sulfides are unstable and oxidise to sulfate (Higgins *et al.,* 2002). Stabilisation of sulfates and sulfides using lime and ggbs has been shown to be beneficial in both laboratory (Higgins *et al.,* 1998) and field studies (Higgins and Kennedy, 1999).

Contaminated materials treated using S/S with ggbs include:

- medium- to high-level radioactive waste at Sellafield and Berkley by BNFL over a 10-year period (Fairhall and Palmer, 1992);
- chromium contaminated soils in combination with bentonite and PC (Allan and Kukacka, 1995);
- desulfurisation sludge, where ggbs is activated by the waste;
- used in proprietry S/S systems (see Chapter 6); and
- slurry trench cut-off walls, where typically a blend of about 20% Portland cement with 80% ggbs, is used (Building Research Establishment, 1994).

Ahmed and Buenfeld (1997) note that there are several technical reasons why ggbs-based binders could have enhanced effectiveness for the S/S treatment of wastes:

- enhanced binding/lower diffusion rates in mixes with high ggbs content in comparison to equivalent PC mixes for: Cl (Ayra *et al.,* 1990), SO_4 (Bakker 1981), K (Bakker, 1981) Na (Bakker, 1981), Cs (Roy *et al.* 1986) and Tc (Spence, 1989). This reduced diffusion has been attributed to increased binding of contaminants; and
- lower redox potential of pore solution establishes a reducing environment of around -400mv for mixes containing >70% ggbs, compared with the oxidising environment for Portland cement and Portland cement/PFA mixes, which varies between +100mV and +200mV (Glasser, 1993).

Alkali-stabilised-slag may have enhanced durability performance in comparison with conventional cements according to Talling and Brandster (1989). Byfors *et al.* (1986) have reported a decreases in both hydroxide and chloride contents in the pore water when ggbs is used in combination with PC.

3.3.2 Pulverised fuel ash

Pulverised fuel ash is separated from the flue gases of power stations that burn pulverised coal as a fuel (as distinct from the ash collected from the bottom of the furnace, which is coarser in its composition). The chemical and phase composition of PFA depends on those of the minerals associated with the coal, and on the burning conditions used in the furnace. In general, anthracitic or bituminous coals give ashes high in glass, silica, alumina, iron oxide, and low in calcia, whereas sub-bituminous coals, or lignites give ashes higher in calcia and often also in crystalline phases (Taylor, 1997).

PFA (termed fly ash in Europe and the USA) used in Europe to make blended cements usually contains less than 10% calcia. Factors to take into consideration when determining the suitability of PFA for use with PC include:

- the content of unburned carbon;
- the ability to decrease the water demand of the binder;
- the pozzolanic nature of the product; and
- its ability to influence redox environment.

The use of PFA in concrete is covered by BS EN 450: 1995 and BS 3892, Parts 1-3 (1997a; 1996 and 1997b respectively).

Excessive carbon in PFA may interfere with the action of some concrete admixtures, however, there are advantages when used for S/S of certain contaminants, as they can sorb onto carbon surfaces and become immobilised. The effect of PFA on water demand during S/S may, on occasion, be important during S/S. Because the pozzolanic reaction involving PFA is slower than the hydration reactions of PC, specified 28-day strength may be lower in comparison to PC alone. One way to counteract this effect is to lower the water to solids ratio used (Taylor, 1997). The pozzolanic activity of PFA is important in the development of strength, and reduced permeability in S/S products in the later stages of setting and hardening Figure 3.8 shows PFA particles in a PFA/PC paste surrounded by hydration products.

Partial replacement of PC with a good quality pulverised fuel ash (PFA) has been shown to increase the workability of the composite product. The 28-day strengths of PFA/PC cements and PC may be similar but the strengths at 91 days normally exceed those of PC alone (Taylor, 1997). PFA may also be combined with lime and water to form a pozzolanic concrete. The resulting material may have very low permeability (Tittlebaum *et al.*, 1985).

The surface of individual PFA cenosphere acts as a site for the rapid growth of C-S-H during the reaction with lime-rich water. PFA cenospheres may not always fully react in a cementitious system and may be easily identified years after product hardening has occurred.

Figure 3.8: PFA spheres covered with hydration products (Photograph courtesy of Colin Hills).

The PFA can be supplied either as a high or low lime variety. In the UK at present, PFA is of the low lime variety. High lime fly ash tends to be of inconsistent quality and although they are more common in Europe they are outside the current standard for fly ash in concrete (BS EN 450: 1995). Both types of ash exist in the USA as Class F (low lime) and Class C (high lime) (ASTM, 1995).

Some PFAs are low in their pozzolanic reactivity (CIRIA, 1995). As mentioned above, the carbon content in PFA may be significant to the sorption of organic contaminants during S/S. Barth *et al.*, (1990) carried out a series of experiments and showed the benefits of using S/S with a range of organic compounds. PFA/PC binders have been used to remediate 750 kt of canal sediments containing fuel oil and Hg in the UK (Yates *et al.,* 2002).

PFA may be effectively used with lime but these binders may have higher leaching rates in comparison to cement. It is worth noting that the rate of formation of ettringite (Aft) is higher in pozzolans than in PC because of the propensity for topochemical (mineral surface promoted) formation (Talero, 1996). Furthermore, monosulfate (Afm) can readily exchange anions such as carbonate, chloride and sulfate ions. However depending on anion exchange the resultant phase may be metastable and some expansion attributed to salt exposure may be due to changes in water content in substituted Afm (Glasser *et al.*, 1999).
Duchesne and Reardon (1999) investigated a range of binders including lime/PFA. With ASTM Class F PFA, hydrocalumite was formed which could sorb borate, chromate and

molybdate from waste. However, when ASTM Class C, PFA was used, the mineralogy of the product was dominated by hydrogarnet and Aft and metals were held less readily. This work suggests that the choice of PFA can be used to intentionally engineer the resultant mineralogy of a PFA-based binder system.

Zeolitic structures for stabilisation of Cr and Cd containing residues have been produced from PFA for use with S/S using PC (Fernandez-Pereira *et al.,* 2002). Other work using PFA has involved the successful stabilisation of ferro-vanadium wastes (Potgieter *et al.,* 2002), the alkali activation of PFA in the treatment of Pb and Cr (Palomo and Palacios, 2003) and B (Palomo and Lopez dela Fuente, 2003). However, according to Poon *et al.* (2001) PFA-blended cement-based waste forms have a lower resistance to acid leachates.

3.3.3 Natural pozzolans

Natural pozzolanic materials are primarily volcanic in origin, and possess cementitious properties. Some clays and other materials that are non-cementitious may become pozzolanic if heated (Taylor, 1997). The primary reaction involves water and lime to form a cementitious product, and are therefore frequently used as a partial substitute for cement to economic advantage.

Natural pozzolans contain highly porous glass, high in silica, and/or zeolites. They may also contain varying proportions of minerals such as quartz, feldspars, pyroxenes and magnetite, or materials such as clays or organic materials that may interfere with setting or strength development (Taylor, 1997). Diatomaceous earth is a pozzolan composed of siliceous skeletons of micro-organisms, however, its large surface area limits its use with cement and hence water absorption capacity. Some clays react with lime at ordinary temperatures and whilst their physical properties are unsuitable for use in concrete, they may be suitable for use in soil stabilisation methods (Taylor, 1997).

Table 3.2: Advantages and disadvantages of various S/S techniques (after USEPA, 1989)

Technique	**Advantages**	**Disadvantages**
Portland Cement	Amount of cement used can be varied to produce a geotechnically favourable product or reduce permeability. Reagents are plentiful and inexpensive. Technique is proven and specialised labour is not required. Extensive drying/dewatering of feedstock is not required; cement addition can be adjusted to existing water content or inert fine fillers added. System is tolerant of most chemical variations e.g. low pH, strong oxidisers (nitrates or chlorates etc.) Pre-treatment confined only to substances retarding or interfering in setting process. Leaching properties can be improved where necessary by adding sealant.	Large additions of cement increase the volume of material to be handled. Leaching characteristics may not be acceptable for some contaminant types. Borates, sulfates and other inorganic contaminants may affect setting and strength development. Some organic contaminants e.g. sugars, solvents and oils may impede setting and strength development. Volatile materials (e.g. VOCs, ammonia) may be driven off during processing.
Lime	Lime can be used to de-water and produce a geotechnically favourable product. Permeability is improved in the longer term. Lime is readily available and inexpensive. Technique is proven and specialised labour is not required. System is tolerant of most chemical variations e.g. low pH, strong oxidisers (nitrates or chlorates etc.) Pre-treatment confined primarily to substances retarding or interfering in setting process.	Large additions of lime increase the volume of material to be handled. Leaching characteristics may not be acceptable for some contaminant types. Some inorganic contaminants may affect setting and strength development. Some organic contaminants may impede setting and strength development. Volatile materials (e.g. VOCs, ammonia) may be driven off during processing. Ignition may occur with some organic contaminants with a low flash point. May render waste hazardous.
Pozzolans with lime	Treated product has good handling and permeability characteristics. Reagents are relatively inexpensive and widely available. No specialised equipment is needed for processing. Chemistry of process is well established. Sulfates less likely to cause cracking or spalling. Variations in moisture content of feedstock can be accommodated.	Additives can increase weight and volume of material to be handled. Leaching characteristics may not be acceptable for some contaminant types. Process is temperature sensitive. Feedstocks may require pre-treatment. Setting characteristics sensitive to organic content. Potential for fugitive dust emissions. May render waste hazardous.
Pozzolans with Portland cement	Generally as for Portland cements, but cheaper, and sometimes yielding a less permeable product with greater resistance to chemical attack and freeze/thaw action (depends on formulation).	Generally as for Portland cements. May exhibit slower rate of setting and strength development.
Thermo-plastics (incl bitumen)	Because feedstocks are dried before processing, overall volumes are reduced. Treated material is resistant to attack by aqueous solutions. Microbial degradation of treated material is insignificant. Compressive strength/shear strength of final product can be high if good mixing is achieved and approach those of cement treated materials while remaining flexible Lower moisture content is required compared to bitumen emulsion stabilisation and hence wet spots are minimised. After construction, the bitumen product can tolerate heavy rainfall, and is less susceptible to damage than other forms of stabilisation. Foamed bitumen layers can be constructed even in adverse weather conditions, such as cold or light rain without affecting the quality of the finished layer. It can be carried out *in situ.*	Equipment, materials and processing complex and can be expensive. Plasticity of material may require use of containers during transport and disposal. Energy intensive. High initial moisture content affects leaching characteristics. Organic components (e.g. plastics) may decompose during treatment. Volatiles and odours may be released during processing. Elevated temperatures and strong oxidisers pose a fire risk with some binders (e.g. bitumen) Iron and aluminium salts may cause premature hardening. Rehydration of salts on wetting may crack treated block and expose contaminants to leaching. Not suitable for all soil types. Design methodologies for foamed bitumen are relatively new, as a rapid evolution of the technology associated with foamed bitumen stabilisation has only just occurred The process requires hot bitumen (180°C) for the foaming action to be successful, thus there is a risk of burning. Purpose-built foamed bitumen stabilising equipment is required.

3.3.4 Polymers

Daniali (1990) observed that one of the shortcomings of cement-only encapsulation was the relatively high porosity of cement matrices and the resultant leaching of physically retained contaminants that may ensue. He examined the potential of latex modified cement in the immobilisation of both organic and inorganic wastes to test the hypothesis that organic polymers, with their high corrosive resistance and good adhesive properties have the potential for S/S of hazardous substances. Daniali's study concluded that the technique showed more promise for the S/S of inorganic than organic wastes.

Many proprietary formulations are based on rubber particulates (obtained from ground scrap tyres for example), and were found to be successful in the immobilisation of semi-volatile organics (Conner, 1995). One particular proprietary system involving re-use of a problematic waste worked best on mixtures of VOCs and SVOCs, as well as pesticides and herbicides.

3.3.5 Silica fume (condensed silica fume, or microsilica) and soluble silicates

Silica-fume is a by-product of the smelting process for silicon metal and ferrosilicon alloy production. It has an amorphous structure and a high SiO_2 content, coupled with a large surface area (20 m^2 g^{-1}). High quality silica fume contains spherical particles of glass, around 100 nm in diameter (Taylor, 1997). It can be added to cement in quantities up to 5% w/w but is limited by its high demand for water, although this property can be modified by the use of superplasticisers. The benefits from the addition of silica fume to PC include acceleration of clinker phase reactions; filling of fine spaces between clinker grains (resulting in a denser paste), increased strength, and reduced permeability.

A 24% silica-fume by weight substitution of PC has been shown to eliminate $Ca(OH)_2$ in the silica-fume/cement paste, which indicates the high pozzolanic reactivity of the compound. Fine silica-fume is thought to be an efficient filler and acts by distributing the binder phase (C-S-H) more homogeneously into the available space. This does not decrease the total porosity but results in the production of smaller pores, which leads to very slow moisture transport.

Shin and Jun (1995) examined the use of silica fume in combination with sodium bentonite and briquette ash adsorbents. They found the solidification of waste/clay/silica-fume cementitious mixes produced a monolithic mass with high strength that showed low leaching of organic compounds. The addition of silica fume produced solid products that set rapidly and resulted in stronger homogenous products than with cement-only S/S. Leaching of organics was reduced by 78% and 95% when compared with cement and non-solidified waste, respectively.

The addition of silica-fume may be possible in conjunction with other additives in order to improve the properties of cement (for example by decreasing the pore size and setting time, and increasing the strength of the cement).

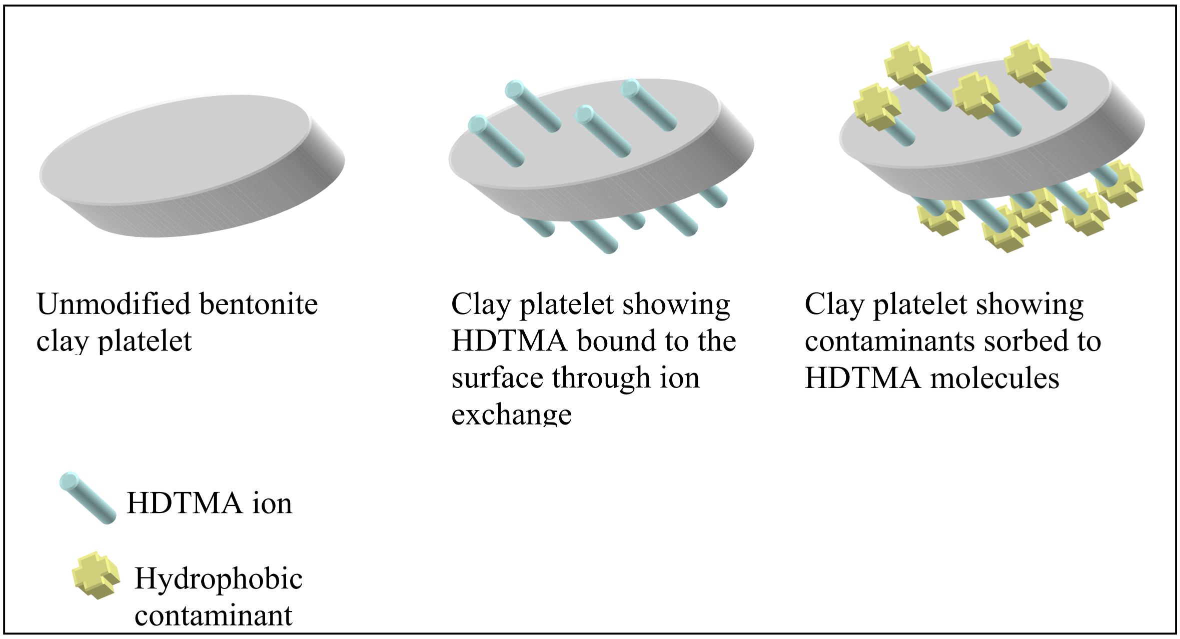
Soluble silicates (waterglass) have been added to PC to produce a solid matrix in a controlled manner, with additional immobilisation of metallic compounds. The reaction involves silicates and polyvalent metal ions in the production of low solubility metal silicates, which may be difficult to solubilise once formed.

3.3.6 Rice husk ash

Rice husks are the outer husks of rice grains discarded in the preparation of rice for food consumption. The husks were found to contain pozzolanic materials and as such, rice husks make good fillers and pozzolans for addition to cement (Ajiwe and Okeke, 2000; Cisse *et al,* 1998; Mehta, 1983; Real and Alcala, 1996; Riveros and Garza, 1986). Their use may improve the physical properties of cement that would otherwise be compromised by the addition of organics. Commercial supplies of rice husk ash are not currently available in the UK.

3.3.7 Organoclays

The ability of clays to bind charged species on their surfaces, coupled with their large surface area, has led to the development of organically modified clays, or organoclays. Organoclays are prepared by exchanging cationic quartenary ammonium compounds of the general form $[(CH_3)_3NR]^+$ (e.g., hexadecyltrimethylammonium; HDTMA), where R is an aromatic or alkyl hydrocarbon group (Sheng *et al.*, 1996), for the mineral cations normally associated with negatively charged clays (Gullick and Weber Jr., 2001). In turn, these hydrophobic species are able to sorb organic contaminants prior to inclusion in a S/S binder such as cement. This principle is illustrated in Figure 3.9.



Unmodified bentonite clay platelet

Clay platelet showing HDTMA bound to the surface through ion exchange

Clay platelet showing contaminants sorbed to HDTMA molecules

Figure 3.9: The modification of natural clays to produce organoclays capable of sorbing organic contaminants

Operative sorption mechanisms for the organoclays depend on the size of the organic modifier (Gullick and Weber Jr., 2001). If the R group is small (e.g. R = CH_3, C_6H_5) then the organic cations in the interlamellar region of smectite are isolated from each other. Such organoclays have relatively high surface areas and display characteristics of surface adsorbents. When the R is a large alkyl group, (e.g. R= $C_{16}H_{33}$), the resultant organoclays have low surface areas and act as partitioning media in the sorption of organic contaminants from water (Sheng *et al.*, 1996).

Organoclays have been shown to be effective for the absorption of a variety of PAHs (Ake *et al.*, 2003), phenols (Wilbulswas *et al.*, 1999), VOCs (Sheng *et al.*, 1996; Redding *et al.*, 2002), PCPs and toxic metals (Brixie and Boyd, 1994, Mercier and Detellier, 1995, Baeyans and Bradbury, 1997, Vengris *et al.*, 2001, Krishna *et al.*, 2001). HDTMA-modified clay minerals have been used for the sorption of oxyanions such as chromate and nitrate (Li, 1999). Lo *et al.* (1997) used bentonite clays modified by the above method for the removal of a range of organics.

Different clay will interact with cement hydration processes differently. Dweck *et al.* (2001) compared Na-bentonite and an organophilic clay and showed these differences to be only short term (<1 week) as they appear not affect the properties of mature S/S products containing Cr-tannery wastes.

Gitipour *et al.* (1997) examined modified bentonite for the removal of aromatic organics from contaminated soil, prior to solidification with PC. They found that benzene, toluene, ethylbenzene and o-xylene were successfully sorbed with removal rates of 88-92% preventing them from interfering with the cement hydration. Faschan *et al.* (1993) examined non-ionic organic partitioning onto organoclays through the sorption of nitrobenzene and 1,2 dichlorobenzene and found that the extent of partitioning onto different clays could be expressed by the following equation:

$$\text{Log } K_{om} = 0.988 + 0.840 \text{ Log } K_{ow} \quad \text{where}$$

K_{om} = K_p/% organic matter of the clay
K_p = partition coefficient of the compound between water and the organoclay
K_{ow} = partition coefficient of the compound between water and 1-octanol

provided that the cation exchange sites are completely occupied by quaternary ammonium compounds containing at least one chain 17-18 carbons in length.

This finding has been repeated by many workers including Shin and Jun (1995), even though organoclays have been criticised for their high specificity, necessitating the development of a particular clay formulation for a particular application.

Clays can also be modified by the addition of hydroxy-aluminium polymers that alter the chemical structure and morphology of the clay by intercalating between the platelets. The resultant products possess increased surface areas and zeolite-like structures, which results in a high binding affinity and capacity for dioxins and polychlorinated biphenyls (Srinivasan *et al.*, 1985). Pires *et al.* (2001) used pillared interlayered clays for the sorption of VOCs. They found that the total amount of VOC sorbed was related to the total microporous volume or surface area of the media and compared favourably to sorption by zeolites.

Smith (1998) discusses the effectiveness of emerging S/S technologies in a NATO/CCMS pilot study evaluation. This work included the use of organoclays.

3.3.8 Other proprietary mixtures

The evaluation of proprietary mixtures in the S/S of contaminated soils and wastes is problematic since the available information is often deliberately vague. In most cases, it has not been possible to perform independent scientific analyses on the performance of proprietary mixtures, and one must turn to the manufacturers themselves for information. Many organisations claim to have developed successful mixtures for the remediation of organic contaminated sites and wastes. At least one S/S vendor claims to have developed a proprietary material capable of incorporating large organic molecules into a clathrate (Wiles and Barth, 1992).

Clathrates are a class of solids whereby guest molecules occupy an empty region of the structure, and contribute to the overall stability of the product. They are normally held in place by hydrogen bonding, and consequently clathrates are able to include a variety of compounds from noble gases to large polar organic molecules.

Table 3.3 identifies some of the pre-treatments and additives used in some of the proprietary systems available for treating contaminated wastes. Appendix 4 lists substances known to interfere with cement reactions (see Chapter 4), whereas Appendix 5 gives further examples of the additives that might be used during waste treatment.

Table 3.3: Additives in many proprietary S/S processes (after Conner, 1990)

Method or Material	Mechanism
Flocculant	Aggregation of fine particles and film formers
Wetting agent	Dispersion of oils and greases and fine particulates away from reacting surfaces
PH adjustment	Removal of interfering substances from solution; destruction of gels and film formers
Fe^{+2}/Fe^{+3} addition	Precipitation of interfering substances
Ion exchange	Removal of interfering substances from solution
Sorbent addition	Removal of interfering substances from reacting surfaces
Redox potential	Destruction/conversion of interfering substances
Aeration	Alteration of biological status; removal of interfering volatiles
Temperature adjustment	Acceleration of reaction rate to counter retarding effect
Lime addition	Supplies additional calcium for reaction; reacts with certain interfering organics; pH adjustment
Sodium silicate	Reacts with interfering metals; causes acceleration of initial set
Calcium chloride	Accelerates set in Portland cement systems
Sodium hydroxide	PH adjustment; may solubilise silica for quicker reaction with calcium ion (low concentration)
Amines, other organics	Mechanism unclear
Metal ions	Mechanism unclear
Miscellaneous Cement Additives $^{\gamma}$	
Sodium lignosulfonate	Surfactant
Calcium lignosulfonate	Surfactant
Polyoxyethylene	Surfactant
Calcium aluminate	Accelerator
Silica fume	Hardener
Polyvinyl acetate	Decreases permeability
Aluminium stearate	Makes product hydrophobic
Magnesium oxide	Accelerator
Sodium bicarbonate	Accelerator
Isocyanate-thio-urea polymer	Decreases permeability, improves mechanical properties
Polyvinyl alcohol	Hardener
Paraffin	
Slag/gypsum	Accelerator; improved strength
Vermiculite	Sorbent
Gypsum/sulfate	Anti-inhibitor

$^{\gamma}$ Described in the literature especially in patent literature. Most have not been used commercially, or have found narrow use for specific projects

3.4 Summary

On the addition of binders such as lime or cement, and at high pH, soils can undergo a 2-stage reaction process, which results in the immobilisation of contaminants. Contaminants are sorbed, precipitated, physically trapped and/or incorporated into crystalline phases that result from the addition of binder. A number of pre-treatment options exist for contaminants that are difficult to stabilise and solidify. Bench testing can be used to ensure that optimum mix designs are produced and that unforeseen reactions are evaluated and eliminated where possible. The key conclusions from this chapter are summarised below:

- primary binding agents, such as cement and lime are widely applied in the remediation of contaminated soils abroad;
- lime and cement will undergo a primary reaction process where the plasticity of soils is affected and strength is increased by cation exchange reactions;
- a second stage reaction involving solidification occurs over days by reaction of lime and alkalis with clays in the production of a gel-phase, which can cement the soil particles together;
- cement and lime can be blended with, for example, PFA or ggbs to modify physical and chemical properties of S/S waste forms. This enables optimisation of the binder to a contaminated medium;
- alternative binders such as bitumen and organoclays may be used, however they may not involve use of stabilisation and solidification processes together;
- a considerable body of evidence supports the use of S/S for managing the risks associated with contamination, in a range of scenarios;
- a range of additives may be used in S/S to improve the performance of binder systems. These include surfactants, accelerators and sorbents; and
- S/S can be used as part of a combined remediation operation whereby it is used in conjunction with other technologies.

REFERENCES

Aggregates Advisory Service (1999) *Improving Poor Ground Conditions. Lime and Cement Stabilisation of Weak Clay Soils*. Aggregates Advisory Service Digest 058.

Ahmed Y.H. and Buenfield N.R. (1997) An Investigation of GGBS as a Toxic Waste Solidification/Stabilisation Reagent. *Environmental Engineering Science* 14, pp. 113-132.

Ajiwe, V.I. and Okeke, C.A. (2000) A Preliminary Study of Manufacture of Cement from Rice Husk Ash. *Bioresource Technology* 73, pp. 37-39.

Ake C.L., Wiles M.C., Huebner H.J., McDonald T.J., Cosgriff D., Richardsons M.N., Donnelly K.C. and Phillips T.D. (2003) Porous Organoclay Composite for the Sorption of Polycyclic Aromatic Hydrocarbons and Pentachlorophenol from Groundwater. *Chemosphere* 51, pp. 835-844.

Allan, M.L. and Kukacka, L.E. (1995) Blast Furnace Slag-Modified Grout for *In Situ* Stabilisation of Chromium-Contaminated Soil. *Waste Management* 15, pp. 193-202.

Andersson, S. and Nilsson, S.I. (2001) Influence of pH and Temperature on Microbial Activity, Substrate Availability of Soil Solution Bacteria and Leaching of Dissolved Organic Carbon in a Mor Humus. Soil *Biology and Biochemistry* 33, pp. 1181-1191.

Arman, A. and Munfakh, G.A. (1970) *Stabilization of Organic Soils with Lime*. Louisiana State University, Baton Rouge, USA, Engineering Research Bulletin 103.

ASTM (1995) D5759-95. *Standard Guide for Characterization of Coal Fly Ash and Clean Coal Combustion Fly Ash for Potential Uses*.

Attoh-Okine, N.O. (1995) Lime Treatment of Laterite Soils and Gravels-Revisited. *Construction and Building Materials* 9, pp.283-287.

Ayra C., Buenfield N.R. and Newman J.B. (1990) Factors Influencing Chloride-Binding in Concrete. *Cement and Concrete Research* 20, pp. 291-300.

Baeyens B. and Bradbury M.H. (1997) A Mechanistic Description of Ni and Zn Sorption on Na-Montmorillonite. Part 1: Titration and Sorption Measurements. *J. Contam. Hydrol.* 27, pp. 199-222.

Bakker R.F. (1981) About the Resistance of Blastfurnace Cement Concrete to the Alkali-Silica Reaction. *Conference on Alkali-Silica Reaction in Concrete*, Cape Town, South Africa.

Barth, E.F., Percin, P., Arozarena, M.M., Zieleniewski, J.L., Donazi, M., Maxey, H.R., Hokanson, S.A., Pryateley, C.A., Whipple, T., Kravitz, R., Cullinane, M.J., Jones, LW. and

Malone, P.G. (1990) *Stabilisation and Solidification of Hazardous Wastes*. Noyes. Data Corporation, N.J.

Bates, E.R. (2003a) USEPA. Personal Communication, January 2003
Bates, E.R. (2003b) USEPA. Personal Communication, March 2003

British Cement Association (2001) *Cement-Based Stabilisation and Solidification for the Remediation of Contaminated Land. Findings of a Study Mission to the USA*. British Cement Association Publication 46.050. Also available from: www.cassst.co.uk (output).

Bell, F.G. (1995) Cement Stabilisation and Clay Soil, with Examples. *Environmental and Engineering Geoscience* 1, pp. 139-151.

Bijen, J. (1996) *Blast Furnace Slag Cement for Durable Marine Structures*. Stichting BetonPrisma, The Netherlands.

British Lime Association. (1990) Lime Stabilisation Manual.

British Standards Institution BS 12. (1996) Specification for Portland Cement (Withdrawn, superseded). British Standards Institution.

British Standards Institution BS EN 197: Part 1. (2000), Cement, Composition, Specifications and Conformity Criteria for Common Cements. British Standards Institution.

British Standards Institution BS EN 450. (1995). Fly ash for Concrete. Definitions, Requirements and Quality Control. British Standards Institution.

British Standards Institution BS 1047. (1983). Specification for Air-Cooled Blastfurnace Slag Aggregates for use in Construction.

British Standards Institution BS EN 1744: Part 1. (1998). Tests for Chemical Properties of Aggregates, Chemical Tests

British Standards Institution BS 3892: Part 1. (1997a). Specification for Pulverised Fuel Ash for use with Portland Cement.

British Standards Institution BS 3892: Part 2. (1996). Specification for Pulverised Fuel Ash to be Used as a Type 1 Addition.

British Standards Institution BS 3892: Part 3. (1997b). Specification for Pulverised Fuel Ash for Use in Cementitious Grouts.

British Standards Institution BS 6699. (1992). Ground Granulated Blastfurnace Slag for use with Portland Cement.

Brixie J.M. and Boyd S.A. (1994) Organic Chemicals in the Environment: Treatment of Contaminated Soils with Organoclays to Reduce Leachable Pentachlorophenol. *J. Environ. Quality* 23, pp. 1283-1290.

Building Research Establishment (1994) *Slurry Trench Cut-Off Walls to Contain Contamination*. Building Research Establishment Digest 395.

Byfors, K., C. M. Hansson, and J. Tritthart. (1986) Pore Solution Expression as a Method to Determine the Influence of Mineral Additives on Chloride Binding. *Cement and Concrete Research* 16 (5) pp. 760-770.

Chaddock, B.C. and Atkinson, V.M. (1997*) Stabilised Sub-Base in Road Foundations: Structural Assessment of Benefits*. Transport Research Laboratory Report 248.

CIRIA. (1995). *Remedial Treatment for Contaminated Land, volume VII: Ex situ Remedial Methods for Soils, Sludges and Sediments*. CIRIA, Special Publication 107.

Cisse, I., J., Temimi, M. and Laquerbe, M. (1998) Addition of Rice Husk Ash as Filler in Concrete. *Indian Concrete Journal* 72, pp. 241-242.

Cobbe, M.I. (1988) Lime Modification of Kaolinite-Illite Clays. *Civil Engineering Technology*, February 1988.

Cocke, D. L. and Mollah, M. Y. (1993). The Chemistry and Leaching Mechanisms of Hazardous Substances in Soldification/Stabilisation Systems. In: *Chemistry and Microstructure of Solidified Waste Forms.* Spence, R. D. (ed.), Lewis Publishers, Boca Raton.

Conner, J. R. (1990) *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York.

Conner, J.R. (1995) Recent Findings on Immobilisation of Organics as Measured by Total Constituent Analysis. *Waste Management* 15, pp. 359-369.

Daniali, S. (1990) Solidification Stabilization Of Heavy-Metals In Latex Modified Portland-Cement Matrices. *Journal of Hazardous Materials* 24, pp. 225-230.

Dermatas, D. and Meng, X. (2001) Utilization of Fly Ash for Stabilisation/Solidification of Heavy Metal Contaminated Sites. Geoenvironmental Engineering. *Geoenvironmental Impact Management* (Eds. Yong, R.W. and Thomas, H.R.) Proc. 3rd Conf. Organised by the British Geotechnical Association and Cardiff School of Engineering, Edinburgh, 17th–19th September 2001.

Dermatas, D. and Meng, X. (2003) Utilisation of Fly Ash for Stabilisation/Solidification of Heavy Metal Contaminated Soils. *Engineering Geology*, 70, pp. 337-394

Diamond, S. and Kinter, B. (1965) *Mechanisms of Soil Stabilisation*. Highway Research Record 92. National Research Council, Washington.

Duchesne, J and Reardon, E.J. (1999) Lime Treatment of Fly Ash: Characterization of Leachate Composition and Solid/Water Reactions. *Waste Management* 19, pp. 221-231.

Dumbleton, M.J. (1962) Investigations to Assess the Potentialities of Lime for Soil Stabilisation in the United Kingdom. Road Research Technical Paper. Number 64. TRL, Crowthorn

Dweck, J., Buchler, P.M. and Cartledge, F.K. (2001) The Effect of Different Bentonites on Cement Hydration During Solidification/Stabilisation of Tannery Wastes. *Journal of Thermal Analysis and Calorimetry* 64, pp. 1011 –1016.

Eades, J.L. and Grim, R.E. (1960) *Reaction of Hydrated Lime with Pure Clay Minerals in Soil Stabilization*. Highway Research Board. Bulletin 262, pp. 51-63.

El-Rawi, N.M. and Awad, A.A. (1981) Permeability of Lime Stabilized Soils. *Transportation Engineering Journal*, January 1981, pp. 25-35.

Fairhall, G.A. and Palmer, J.D. (1992) The Encapsulation of Magnox Swarf in Cement in the United Kingdom. *Cement and Concrete Research* 22, pp. 293-298.

Faschan, A., Tittlebaum, M. and Cartledge, F. (1993) Nonionic Organic Partitioning Onto Organoclays. *Hazardous Waste and Hazardous Materials* 10, pp. 313-322.

Fernandez-Pereira, C., Galiano, Y.L., Rodriguez-Pinero, M.A., Vale, J. and Querol, X. (2002) Utilisation of Zeolitised Coal Fly Ash as Immobilising Agent of a Metallurgicam Waste. *Journal of Chemical Technology and Biotechnology* 77, pp. 305-310.

Fossberg, E. (1965) Some Fundamental Engineering Properties of Stabilized Clay. In: *Proceedings of the 6th International Conference of Soil Mechanics and Foundation Engineering*, Montreal, Canada.

Gitipour, S.B. Bowers, M.T. and Bodocsi, A. (1997) The Use of Modified Bentonite for Removal of Aromatic Organics from Contaminated Soil. *Journal of Colloid and Interface Science* 196, pp. 191-198.

Glasser F.P. (1993) Chemistry of Cement-Stabilised Waste Forms. In: *Chemistry and Microstructure of Solidified Waste Forms.* R D Spence (ed). Lewis Publishing, Boca Raton, Fl., pp. 1-40.

Glasser, F.P., Kindness, A. and Stronach, S.A. (1999) Stability and Solubility Relationships in Afm Phases. Part 1: Chloride, Sulfate and Hydroxide. *Cement and Concrete Research* 29, pp 861-866.

Glendinning, S. and Boardman, D.I. (1996) Lime Treatment of Metal Contaminated Clay Soils. In: *Proceedings of the 32nd Annual Conference of the Engineering Group of the Geological Society and the Hydrogeological Group*. (Eds. Lerner, D. N., and Walton, N.), University of Portsmouth, UK, pp. 249-258.

Glendinning, S. (1995) *Deep Stabilization of Slopes Using Lime Piles*. PhD. Thesis, Loughborough University, Leicestershire, UK.

Gullick, R.W. and Weber Jr., W.J. (2001) Evaluation of Shale and Organoclays as Sorbent Additives for Low Permeability Soil Containment Barriers. *Environ. Sci. Technol*. 35, p. 1523-1530.

Gutschick, K.A. (1978) Lime Stabilization Under Hydraulic Conditions. Presented at the *4th International Lime Congress*, Hershey, PA. Available from the National Lime Association, Washington, DC, USA.

Haas, H. (1989) Zur Eignung von Deponieabdichtungen aus Asphaltneton. *Kommunalwirtschaft* 1, pp. 1-8.

Hebib, S. and Farrell, E.R. (2003) Some Experience on the Stabilisation of Irish Peat. *Canadian Geotechnical Journal* 40, pp. 107-120.

Higgins, D.D., Kinuthia, J.M. and Wild, S. (1998) Soil Stabilisation using Lime-Activated GGBS, In: *Proceedings of the 6th CANMET/ICI International Conference on Fly ash, Silica fume, Slag and Natural Pozzolans in Concrete* (Ed.: Malhotra V.M.) Bangkok Thailand. ACI Publication SP 178-55 pp. 1057-1073.

Higgins, D.D. and Kennedy, J. (1999) Lime and Ground Granulated Blastfurnace Slag Stabilisation of Boulder Clay on the A421 Tingewick Bypass. *Third European Symposium on the Performance and Durability of Bituminious Materials and Hydraulic Stabilised Composites*. Leeds, UK.

Higgins D.D., Thomas, B., and Kinuthia J.M. (2002) Pyrite Oxidation, Expansion of Stabilised Clay and the Effect of GGBS. *Fourth European Symposium on the Performance of Bituminous and Hydraulic Materials in Pavements*, University of Nottingham, UK.

Highways Agency. (2003), *Specification for Highway Works*, Section 600: Use of Lime for Roads.

Jan, M.A. and Walker, R.D. (1963) *Effect of Lime, Moisture, and Compaction on a Clay Soil*. Highway Research Record 29, pp.1-12.

Krishna B.S., Murty D.S.R. and Prakash B.S.J. (2001) Surfactant-Modified Clay as Adsorbent for Chromate. *Applied Clay Science* 20, pp. 65-71.

LaGrega, M.D. Buckingham, P.L. and Evans, J.C. (1994) Stabilisation and Solidification. In: *Hazardous Waste Management*, McGraw Hill, pp. 641-704.

Li Z. (1999) Oxyanion Sorption and Surface Anion Exchange by Surfactant-modified Clay Minerals. *J. Environmental Quality* 28, pp. 1457-1463.

Lin, S-L., Lai, J.S. and Chian, E.S.K. (1995) Modifications of Sulfur Polymer Cement (SPC) Stabilization and Solidification (S/S) Process. *Waste Management* 15, pp. 441-447.

Lin, S.L., Cross, W.H., Chian, E.S.K., Lai, J.S., Giabbai, M. and Hung, C.H. (1996) Stabilisation and Solidification of Lead in Contaminated Soils. *Journal of Hazardous Materials* 48, pp. 95-110.

Little, D.N. (1987) *Fundamentals of Stabilisation of Soil with Lime*. National Lime Association Bulletin 332.

Lo I.M., Mak R.K.M. and Lee S.C.H. (1997) Modified Clays for Waste Containment and Pollutant Attenuation. *J. Environ. Engineering* ACSE 123, pp. 25-32.

Loughnan, F.C. (1969) *Chemical Weathering of Silicate Materials*. Elsevier, New Year.

Lund, O.L. and Ramsey, W.J. (1959) *Experimental Lime Stabilization in Nebraska*. Highway Research Board, Bulletin 231, pp. 24-59.

McCallister, L.D. and Petry, T.M. (1992) Leach Tests on Lime-treated Clays. *Geotechnical Testing Journal* 15, pp. 106-114.

McKinley, J.D., Thomas, H.R., Williams, K.P. and Reid, J.M, (2001) Chemical Analysis of Contaminated Soil Strengthened by the Addition of Lime. *Engineering Geology*, 60, pp. 181-192

Mehta, P.K. (1983) Technology Alternatives for the Use of Rice Husks. *Appropriate Technology* 9, pp. 7-9.

Mercier L. and Detellier C. (1995) Preparation, Characterization and Applications as Heavy Metal Sorbents of Covalently Grafted Thiol Functionalities on the Interlamellar Surface of Montmorillonite. *Environmental Science and Technol*ogy 29, pp. 1318-1323.

Neville, A.M. (1995). *Properties of Concrete* (4th Edition) Longman Group, London.

Oates, J.A.H. (1998) *Lime and Limestone: Chemistry and Technology, Production and Uses*, Weinheim, Chichester.

Pacewska, B., Wilinacuteska, I. and Bukowski, M. (2000) Hydration of Cement Slurry in the Presence of Spent Cracking Catalyst. *Journal of Thermal Analysis and Calorimetry,* 60, pp. 71-78.

Palomo, A. and López de la Fuente J. I. (2003) Alkali-Activated Cementitious Materials: Alternative Matrices for the Immobilisation of Hazardous Wastes: Part I. Stabilisation of Boron, *Cement and Concrete Research* 33, pp. 281-288.

Palomo A. and Palacios M. (2003) Alkali-activated Cementitious Materials: Alternative Matrices for the Immobilisation of Hazardous Wastes: Part II. Stabilisation of Chromium and Lead, *Cement and Concrete Research* 33, pp. 289-295.

Pires J., Carvalho A. and de Carvalho M.B. (2001) Adsorption of Volatile Organic Compounds in Y Zeolites and Pillared Clays. *Microporous and Mesoporous Materials* 43, pp. 277-287.

Poon, C.S. Lio, K.W. and Tang, C.I. (2001) A Systematic Study of Cement/PFA Chemical Stabilisation/Solidification Process for the Treatment of Heavy Metal Waste. *Waste Management and Research* 19, pp. 276-283.

Potgieter, J.H., Potgieter, S.S., Loubser, M., Kearsley, E and Strysom, C.A. (2002) Stabilisation of Ferro-industry Waste in Various Solid Matrices. *Journal of Chemical Technology and Biotechnology* 77, pp. 311-314.

Rao, S.M., Reddy, B.V and Muttharam, M. (2001) The Impact of Cyclic Wetting and Drying on the Swelling Behaviour of Stabilised Expansive Soils. *Engineering Geology* 60, pp. 223-233.

Rajasekaran, G. and Rao, S.N. (1996) The Microstructure of Lime Stabilised Marine Clay. *Ocean Engineering* 24, pp. 867-878.

Ranganatham, B.V. (1961) Soil Structure and Consolidation Characteristics of Black Cotton Clay. *Geotechnique* 11, p.331.

Real, C. and Alcala, M.D. (1996) Preparation of Silica from Rice Husks. *Journal of the American Ceramic Society* 79, pp. 2012-2016.

Redding A.Z., Burns S.E., Upson R.T. and Anderson E.F. (2002) Organoclay Sorption of Benzene as a Function of Total Organic Content. *J. Colloid and Interface Science* 250, pp. 261-264.

Reid, J.M and Brookes, A.H. (1997) Proving Ground. *Ground Engineering* 30, pp.18-19.

Reid, J.M. and Brookes, A.H. (1999) Investigation of Lime Stabilised Contaminated Materials. *Engineering Geology* 53, pp. 217-231.

Richardson, I.G. and Cabrera, J.G. (2000) The Nature of C-S-H in Model Slag-Cements. *Cement and Concrete Composites* 22, pp. 259-266.

Riveros, H. and Garza, C. (1986) Rice Husks as a Source of High-purity Silica. *Journal of Crystal Growth* 75, pp. 126-131

Robinson, R.B. and Burnham, J. (2001) Relative Dissolution Rates of Several Hydrated Limes. *Journal of Environmental Engineering*, June, pp. 565-568.

Rogers, C.D. and Glendinning, S. (1997) Improvement of Clay Soils *in-situ* Using Lime Piles in the UK. *Engineering Geology* 47, pp. 243-257.

Roy, D.M. Kumar, A. and Rhodes, J.P. (1986) Diffusion of Chloride and Cesium ions in Portland Cement Pastes and Mortars Containing Blastfurnace Slag and Fly Ash, *American Concrete Inst*. SP 91-70, pp. 1423-1444.

Sheng G., Xu S., Boyd S.A. (1996) Cosorption of organic contaminants from water by hexadecyltrimethylammonium-exchanged clays. *Water Research* 30: pp. 1483-1489.

Sherwood, P.T. (1962) The Effect of Sulfates on Cement-and Lime-Stabilised Soils. *Roads and Road Construction* 40 (470), pp. 34-40.

Sherwood, P.T. (1993) *Soil Stabilisation with Cement and Lime*, HMSO, London.

Shi, C. and Day, R.L. (1995) A Calorimetric Study of Early Hydration of Alkali-Slag Cements. *Cement and Concrete Research* 25, pp. 1333-1346.

Shin, H.S. and Jun, K.S. (1995) Cement Based Stabilization/solidification of Organic Contaminated Hazardous Wastes using Na-bentonite and Silica-fume. *Journal of Environmental Science and Health* Part A 30, pp. 651-668.

Smith, M.A. (1998) Stabilisation/solidification Processes. In: *NATO/CCMS Pilot Study-Evaluation of Demonstrated and Emerging Technologies for Treatment and Clean-up of Contaminated Land and Groundwater*. EPA542-R-98-001a.

Spence, R.D. (1989) Immobilisation of Technetium in Blastfurnace Slag Grouts. In: *Proceedings of the 3rd CANMET/ICI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*. Trondheim Norway. Malhotra V.M. (Ed.). ACI Publication, SP 114, pp. 1579-1596.

Srinivasan, K.R., Fogler, H.S., Gulari, E., Nolan, T. and Schultz J.S. (1985) The Removal of Trace Levels of Dioxins from Water by Sorption on Modified Clay. *Environ. Prog*. 4, pp. 239-244.

Stavridakis, E.I. and Hatzigogos, T.N. (1999) Influence of Liquid Limit and Slaking on Cement Stabilised Clayey Admixtures. *Geotechnical and Geological Engineering* 17, pp. 145-154.

Talero., R. (1996) Comparative XRD Analysis of Ettringite Originating from Pozzolan and From Portland Cement. *Cement and Concrete Research* 26, pp. 1277-1283.

Talling, B. and Brandster, J. (1989) *Present State and Future of Alkali-Activated Slag Concretes*. American Concrete Institute Special Publication, SP-114, pp. 1519-1545.

Taylor, W.H. and Arman, A. (1960) Lime Stabilization using Pre-conditioned Soils. *Highway Research Board Bulletin* 262, pp.1-19

Taylor, H.F.W. (1997) *Cement Chemistry*, (Second Edition), Thomas Telford Press, London

Thompson, M.R. (1965) Influence of Soil Properties on Lime-soil Reactions. *Public Works* 96, No. 8 (August).

Thompson, M.R. (1966) Shear Strength and Elastic Properties of Lime-soil Mixtures. *Highway Research Record* 139, pp.1-14.

Tittlebaum, M.E., Seals, R.K., Cartledge, F.K. and Engles, S. (1985) State of the Art on Stabilisation of Hazardous Organic Liquid Wastes and Sludges. *Critical Reviews in Environmental Control* 15, pp.179-211.

Townsend, D.C. and Klym, T.W. (1966) *Durability of Lime-stabilized Soils*. Highway Research Record No. 139. Highway Research Board, National Research Council, Washington, DC, pp. 25-41.

Tremblay, H., Duchesne, J., Locat, J and Leroueil, S. (2002) Influence of the Nature of Organic Compound on Fine Soil Stabilization with Cement. *Canadian Geotechnical Journal* 39, pp. 535-546.

United States Environmental Protection Agency (1989) *Corrective Action: Technologies and Applications*. Seminar Publication, US Environmental Protection Agency, EPA/625/4-89/020.

United States Environmental Protection Agency (1993) *Remediation Technologies Screening Matrix and Reference Guide*. Report Number EPA 542-B-93-005, United States Environmental Protection Agency.

United States Environmental Protection Agency (2001) *Treatment Technologies for Site Cleanup: Annual Status Report (10th Edition)*. Report Number EPA-542-R-01-004, United States Environmental Protection Agency.

Vengris T., Binkiene R. and Sveikauskaite A. (2001) Nickel, Copper and Zinc Removal from Waste Water by a Modified Clay Sorbent. *Applied Clay Science* 18, pp. 183-190.

Vipulanandan, C. and Krishnan, S. (1993) Leachability and Biodegradation of High Concentrations of Phenol and O-cholorophenol. *Hazardous Waste and Hazardous Materials* 10, pp. 27-47.

Wang. J.W., Matoes, M. and Davidson, D.T. (1963) Comparative Effects of Hydraulic, Calcitic, and Dolomitic Limes and Cement in Soil Stabilization. *Highway Research Record* 29, pp. 42-54.

Wilbulswas R., White D.A. and Rautiu R. (1999) Adsorption of Phenolic Compounds from Water by Surfactant-modified Pillared Clays. *Trans. I. Chem. Eng*. 77, pp. 88-92.

Wiles, C.C. and Barth, E. (1992) Solidification/Stabilization: Is it Always's Appropriate? In: *Stabilisation and Solidification of Hazardous, Radioactive, and Mixed Wastes,* (Eds. T.M. Gilliam and C.C. Wiles) 2nd Volume, ASTM STP 1123.

Wu, J-H., Wu, W-L and Hsu, K-C. (2003) The Effects of Waste Oil-Cracking Catalyst on the Compressive Strength of Cement Pastes and Mortars. *Cement and Concrete Research* 33, pp. 245-253.

Yates, E.P., Hills, C.D. and MacLeod, C.L. (2002) Remediation of Contaminated Sediments by Stabilization and Solidification Technology in the USA and UK. In: *Proceedings of Waste 2002: Integrated Waste Management and Pollution Research, Policy and Practice*. 24th-26th September, Stratford-on-Avon, UK. (Eds. Elvera Lencioni and Raminder Dhanda).

Zolkov, E. (1962) Influence of Chlorides and Hydroxides of Calcium and Sodium on Consistency Limits of Fat Clay. *Highway Research Board Bulletin* 309, pp.109-115.

4 STABILISATION/SOLIDIFICATION OF INORGANIC CONTAMINANTS

4.1 Introduction

Stabilisation/solidification (S/S) is routinely used outside the UK for the treatment of industrial wastes and remediation of contaminated soil. Stabilisation and solidification processes can be used together to encapsulate the contaminants in the treated product. The contaminants are chemically immobilised in the matrix of the treated waste form by adsorption, hydrolysis and precipitation reactions.

The S/S system should have sufficient resistance to aggressive agents, such as acid groundwater or rainfall, to maintain the chemical environment promoting stabilisation of contaminants. However, the appropriate choice of binders can aid production of low permeability waste forms in which contaminants are physically isolated from aggressive agents.

The effective use of S/S has been demonstrated with a range of inorganic contaminant groups (USEPA, 1993, 2000), including:

- volatile metals;
- non-volatile metals;
- radioactive materials;
- asbestos;
- inorganic corrosives; and
- inorganic cyanides.

This chapter provides a review of the fixation of inorganic compounds in S/S waste forms and aims to identify why S/S is routinely used in many countries around the world as a method of managing the risk associated with contaminated soil and hazardous waste.

4.2 Inorganic Contaminant -Binder Interactions

The physical and chemical processes by which anions and cations interact with cementitious binders enable useful predictions to be made regarding the treatment of waste. For the treatment of contaminated soils, the influence of soil components on the immobilisation of contaminants must also be considered if remedial targets are to be met and maintained and effective remediation is to be carried out (see Section 2.4).

There are several processes that combine to facilitate chemical stabilisation of inorganic contaminants in soils. These will have a large effect on S/S and are dominated by the clay fraction of a soil. The reaction of clay soil particles and binders provides a long-term stabilising process that encourages adsorption and metal precipitation.

The aqueous phase present in the pore structure of cement-based waste forms is alkaline and promotes the precipitation of insoluble species, particularly metal hydroxides (Li *et al.* 2001). However, the high pH of pore fluids is not dependent on the amount of hydrated phases but on the maintenance of a quasi-equilibrium between solid and aqueous phases (Glasser, 1993) and this results in continued retention of metallic contaminants in a waste form.

The disruption of equilibrium by intrinsic (internal) or extrinsic (external) effects will eventually result in the release of contaminants. This important observation tells us that over time and in response to changing conditions of service, a reduction in pore fluid pH will occur resulting in the mobilisation of some contaminants.

The interaction of contaminants with soil and/or binder involves a number of fixation mechanisms and these are discussed below:

- adsorption to binder-soil matrices;
- pH-dependent precipitation;
- redox-controlled precipitation of insoluble compounds;
- absorption/encapsulation into and onto nano-porous C-S-H gel; and
- incorporation into crystalline components of the cement matrix.

4.2.1 Adsorption to binder-soil matrices

Adsorption in binder-soil matrices is achieved at high pH in order to bring enhanced surface adsorption at the mineral edge sites. Mollah *et al.* (1995a) described near-surface interfacial phenomena during S/S and showed that metals have a strong affinity to the surface of clays. The presence of oxyhydroxide species and a surface charge were also found to be important. The effectiveness of sorption processes depends on both soil mineralogy and maintaining a high pH environment. However, continuation of a high pH in the long term may be problematic because natural groundwater tends towards acidity rather than alkalinity. In this respect, the neutralising capacity afforded by binder systems is very important, as illustrated by the work of Astrup *et al.* (2001) who investigated the landfilling of air pollution control (APC) residues from municipal solid waste incineration. They concluded that the waste forms were capable of performing (retaining pH >9) for ca. 100,000 years (see further discussion in Chapter 10).

The process of cation exchange inherently results in the displacement of the host cations from a clay soil. Griffin and Shrimp (1975) noted this whilst investigating the attenuation of metals from landfill leachate by kaolinite, montmorillonite and illite. The levels of leachable Ca recorded were attributed to exchange of Ca for metals, as Ca was the predominant exchangeable cation present on the clays. In respect of Mn leaching, this was attributed to desorption from the surface of the clay. Griffin and Shrimp (1976) observed that Mn is three times more abundant on the surface of kaolinite than montmorillonite. According to Glendinning *et al.* (1998) surface sorption of metals is one of the important factors in metal immobilisation mechanisms of lime-stabilised soils. Table 4.1 gives adsorption selectivity of heavy metals in different soils.

Table 4.1: Adsorption selectivity for metals on different soils (after Yong *et al.,* 1996)

Material	Selectivity order
Kaolinite clay (pH 3.5-6)	Pb > Ca > Cu > Mg > Zn > Cd
Kaolinite clay (pH 5.5 – 7.5)	Cd > Zn > Ni
Illite clay (pH 3.5 – 6)	Pb > Cu > Zn > Ca > Cd > Mg
Montmorillonite clay (pH 3.5 – 6)	Ca > Pb > Cu > Mg > Cd > Zn
Montmorillonite clay (pH 5.5 – 7.5)	Cd = Zn >Ni
Al oxides (amorphous)	Cu > Pb > Zn > Cd
Mn oxides	Cu > Zn
Fe oxides (amorphous)	Pb > Cu > Zn > Cd
Goethite	Cu > Pb > Zn > Cd
Fulvic acid (pH 5.0)	Cu > Pb > Zn
Humic acid (pH 4 – 6)	Cu > Pb > Cd > Zn
Mineral soils (pH 5.0; with no organics)	Pb > Cu > Zn > Cd
Mineral soils (containing 20 – 40 g/kg organics)	Pb > Cu > Cd > Zn

4.2.2 pH-dependent precipitation

The precipitation of salts from solution is pH dependent (Chapter 2). As well as facilitating the surface adsorption of metal ions, an increase in the concentration of OH^- ions in solution can ultimately result in the formation of metal complexes and precipitation of metal salts will occur.

Griffin and Shrimp (1976) considered the precipitation reactions of lead (Pb) from landfill leachate and showed that species other than Pb^{2+} were relatively insignificant at pH values of less than 6. It was evident that at pH values above 6, adsorption of Pb coincided with the formation of hydroxyl Pb (Figure 4.1). Thus, metal speciation, availability and factors such as pH, E_h ion exchange capacity, and complexation/chelation with organic matter directly affect metal solubility in cement-bound soil.

Investigations by McWhinney and Cocke (1993) showed that for Zn and Cd-stabilised wastes precipitation of hydroxides or oxides occurred, whereas for Hg physical encapsulation was identified as being important. With the former two metals, pH dependent precipitation was particularly important at early ages, but on exposure to the effects of carbonation, changes in pH and speciation of precipitates occurred. Later work by Mollah *et al.* (1995b) used a charge dispersal model to show that Zn and Cd would not form calcium zincate and Ca-Cd hydroxide and would be physically encapsulated during S/S. Investigations of this nature illustrate the complex interaction of contaminants in S/S systems.

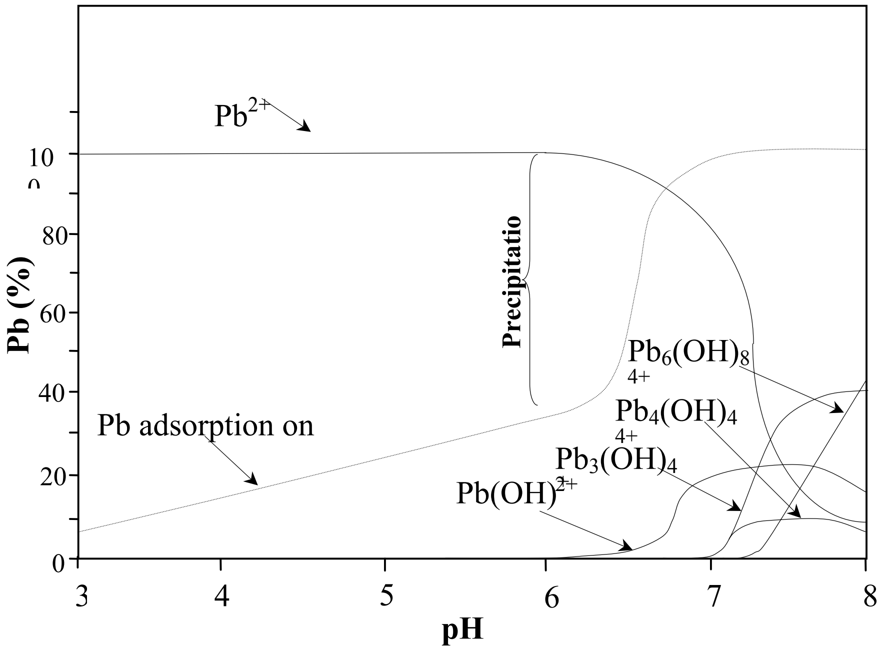


Figure 4.1: Distribution of Pb (II) species in $4x10^{-4}$M $Pb(NO_3)_2$ and uptake by 0.1g kaolinite from 60ml of solution (after Griffin and Shrimp, 1976)

4.2.3 Redox-controlled precipitation

Binder systems can be tailored to produce an oxidising or reducing environment in the pore fluids of a treated waste form. Generally however, cements typically used are produced under oxidising conditions with typical E_h values between +100 and +200 mV due primarily to dissolved oxygen (Taylor 1997).

When ground granular blastfurnace slag (ggbs) (see section 3.3.1) is introduced to the binder system at higher addition rates, typically >40-50%, chemically reduced sulfur, which is present in the glassy structure of a slag, is released over time. Low E_h values, in the order of –350 to –450 mV, are recorded for sulfur-containing slag (Macphee *et al.*, 1989). Therefore, slag-blended binders can be reliably used to control the mobility of metals such as Cr and Mn because they reduce them to compounds of lower solubility and increase sorption onto C-S-H gel.

Considering that binder addition rates are generally quite low during S/S, the potential for a contaminated material to influence the redox environment in a treated waste form should not be underestimated. Glasser (1993) suggests that the presence of, for example, steel or organics can induce E_h values as low as –600mV. The most favourable environment for immobilisation of contaminants would appear to involve maintenance of a lower E_h environment so that multivalent anionic metals can be reduced to less soluble cationic species. In practice, kinetic considerations and the depletion of oxygen by bioactive soil may result in persistent lower E_h values and thus appropriate disposal conditions over the longer term (Glasser, 1993).

4.2.4 Adsorption/encapsulation into and onto nanoporous C-S-H gels

Calcium silicate hydrate (C-S-H) gels are known to be persistent under geological conditions for a long time i.e. thousands of years and thus, are very important where retention of metals in S/S waste forms are concerned (McConnell, 1955). C-S-H gels have a nanoporous structure, which confers a high specific surface area (between 10 and 50 m^2g^{-1}) to which both anions and cations may be sorbed. The sorption potential of cement hydrates is dominated by the properties of the C-S-H gel. Indeed, Cheng and Bishop (1992) showed cement-based waste forms had sorption characteristics for heavy metals analogous to amorphous silica gel, although the behaviour observed was very pH dependent. This was illustrated by the fact that above pH 9 desorption of metals did not occur to any large extent.

The nano-structure of the gel phase is disordered, but based upon a layered structure of calcium silicate, typically of 10 to 100 nm in size. Silicon is in a state of low polymerisation and the stacked structure of gel facilitates a high surface charge, which causes irregular bonding to water molecules and a high degree of micro-porosity. Although the sorption potential of C-S-H is of importance where cations are concerned, it is relatively small when compared to that of industrial adsorbents.

The surface charge of C-S-H gel varies with its composition and is about zero when the calcium:silicon ratio (c/s) is about 1.2. Glasser (1993) states that even at early stages of hydration, the effect of gel production on metals immobilisation is high and this is due to colloid generation and coalescence prompting sorption processes. He further added that this could be enhanced by the use of additives such as sodium silicate.

Preferential binding for either anions or cations can be achieved by altering the c/s ratio of the C-S-H gel and this can be done by carefully choosing the binder system. Calcium-rich C-S-H gel possesses a positive surface charge to which preferential sorption of anions may occur, whereas silicon-rich C-S-H gel favours the sorption of cations. Alteration of the c/s ratio can be easily performed by the choice of binder. For example, when ggbs-blended binders are used, c/s ratios of <0.8 may be formed, favouring the sorption of cations (Harris *et al.*, 2002).

In addition to reversible sorption and exchange on C-S-H gel surfaces, isomorphic substitution of calcium ions for other divalent cations of similar size including, strontium, barium and lead are possible. Ivey *et al.* (1990) proposed that Cr^{3+} will substitute for silicon and is chemically incorporated into the C-S-H gel. Other work by Lin *et al.* (1997) shows that in the case of Cr substitution for Si, this may be accompanied by promotion of hydration of C_3S. Omotoso *et al.* (1998) concluded that Cr was effectively stabilised by local incorporation in a stable C-S-H phase, however, Diet *et al.* (1998) concluded that a distinctive phase (U-phase) might be formed due to the presence of chromate ions.

Bonen and Sarkar (1995) indicated that heavy metals are more likely to be physically encapsulated in C-S-H. This work indicated that for Cd and Ni hydroxide speciation and precipitation may dominate, whereas for Hg formation of the oxide salt was favoured. Komarneni *et al.* (1988) showed Cu could substitute for Ca in C-S-H, but was more likely to be present as hydroxy-carbonates or incorporated into sulfoaluminate phases (Aft/Afm) which may exhibit cation and anion exchange with carbonate, chloride and sulfate. Similarly, Zn, may substitute for Ca in C-S-H, although calcium zincate may also be formed (Yousuf *et al.*, 1995). Li *et al.* (2001) concluded from sequential leaching tests that Cu and Zn might precipitate on the surface of C-S-H or on PFA particles as hydroxide or metal-hydrated phases.

It is very clear that the abundant C-S-H produced during hydration of Portland cement has a dominant influence on the retention of metals in solidified waste forms. There is much evidence to show that immobilisation is through both sorption processes and by substitution for Ca or Si in the gel phase. Park and Batchelor (1999) showed sorption processes are significant in the retention of Cr^{6+}, Cd, Pb and other metals.

Physical encapsulation of contaminants by C-S-H gel also provides another simple mechanism for the effective retention of pollutants. Furthermore, the chemical nature of the gel phase may be manipulated by design, by the addition of slag and other additives, to optimise gel properties in terms of E_h and chemistry for certain contaminants. The physical structure of C-S-H, which also changes with slag addition, illustrates effectiveness of this approach, as observed by Richardson and Cabrera (2000). The authors noted that the results of studies of blended cements are in good agreement with model systems involving C_3S.

The speciation of metallic pollutants during S/S is important and chemical equilibrium models can be effective in describing their behaviour in a cement system. However, the influence of Na ions in the pore water of cementitious products may be an important factor in determining the retention of contaminants in C-S-H by sorption. Langmuir isotherm studies (Park and Batchelor, 1999) support the assumption that Na sorbed onto the surface of C-S-H imparts a net positive surface charge that facilitates the removal of anionic metals, such as CrO_4^{2-}, $Pb(OH)_4^{\ 2-}$ and $Cd(OH)_4^{2-}$ from pore water.

Solid state nuclear magnetic resonance spectroscopy (NMR) studies carried out by Katz *et al.* (2001) on simulated low-level radioactive waste residues, showed that the nature of C-S-H remained similar in PC on its own or blended with PFA or slag. However, in the blended systems longer silica chains with a higher degree of Al substitution for Si (in tetrahedral sites) was reported. The higher degree of polymerisation obtained reflects the increase in Al content in blended systems and may reflect improved stability of the gel phase. The higher degree of substitution of Al for Si reported will be linked to a higher degree of disorder in the gel phase produced by blended cement systems. Bakharev *et al.* (1996) showed that resistance to chemical transport in these blended systems was primarily due to an inherent low porosity and high tortuosity in the pore networks.

The nature of the early production of amorphous co-precipitated hydrated silicates probably changes with time after mixing increases, as they ‘transform’ into phases with a higher degree of crystallinity which should be more thermodynamically stable in the longer term.

4.2.5 Incorporation into crystalline components of the cement matrix

Chemical immobilisation of contaminants by S/S is successful due to the fact that contaminants can become incorporated into the solid, crystalline phases of the cementitious matrix. The various phases of cementitious binders (detailed in Chapter 3) and their interactions with contaminants are described below. However, it is important to note that a considerable amount of work has been undertaken in the past to investigate the effect of metallic and other compounds on the hydration of cements and their constituent phases (Tashiro, *et al.* 1977; Kantro, 1975; Forsen, 1933a, 1933b). This body of work clearly illustrates that compound-specific interactions are possible.

4.2.5.1 Portlandite

Portland cements generally contain 0.5 – 1.0 wt % of Na_2O and K_2O which concentrates in the pore fluid such that a pore solution pH of 13 to 14 is achieved. The high hydroxide ion concentration afforded by the dissolved alkali metals suppresses the solubility of calcium. The role of portlandite is predominantly by buffering of the pore solution pH in the event of leaching of alkalis. It generally appears that chemical interactions between contaminants and portlandite are minimal.

4.2.5.2 Ettringite

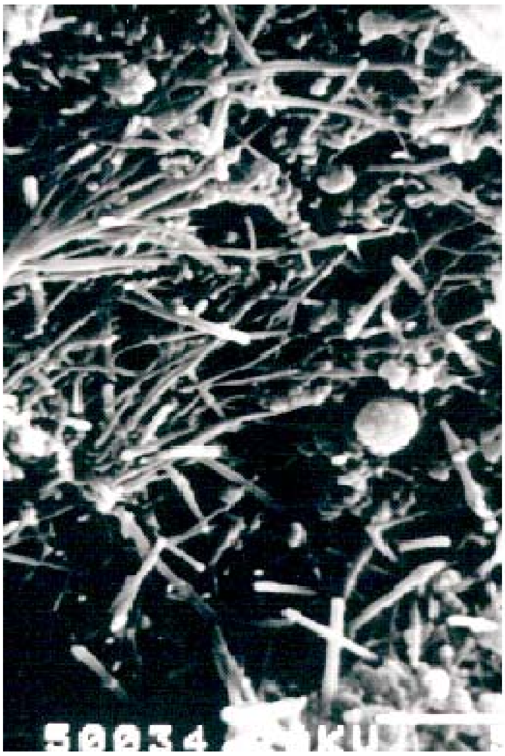
Interactions between inorganic contaminants and ettringite are numerous. Ettringite exhibits extensive ionic substitution potential. Simple trivalent metal cations such as Fe^{3+}, Cr^{3+}, Mn^{3+}, and Ti^{3+} can replace Al^{3+} in the ettringite crystal lattice. In addition, cationic substitution of Ca^{2+} by Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+}, to variable extents have been reported (Poellmann *et al.*, 1993; Glasser, 1993; Albino *et al.*, 1996). Furthermore, replacement of SO_4^{2-} by a range of oxy-metal anions such as CrO_4^{2-}, AsO_4^{3-}, SeO_4^{2-}, IO_3^-, CO_3^{2-}, NO_3^- can take place (Omotoso *et al.* (1998). There is also a limited amount of evidence to suggest that small organic molecules may occupy the channel sites within the ettringite structure (Glasser, 1993). Other workers such as Hassett and McCarthy (1992) and Tashiro *et al.* (1979) have shown that metals may be incorporated in ettringite. Figure 4.2 shows ettringite development in voids of an S/S treated metal-plating residue.

4.2.5.3 Monosulfate and tetracalcium aluminate

Monosulfate and tetracalcium aluminate hydrate demonstrate a similar range of crystallochemical substitutions to those observed in ettringite with respect to the replacement of Al^{3+} and Ca^{2+} in the lattice.

Interlayer and interstitial anionic substitution for SO_4^{2-} and OH^- also occurs, however, the capacity of these phases to incorporate monovalent and simple spherical anions, such as I^- is superior to that of ettringite (Glasser, 1993).

Lin *et al.* (1993) investigated hydration of C_3A in the presence of Cu compounds and found that Cu dissolved and bound in a heterogeneous solid solution series with C_3A hydrates. Tashiro and Oba (1979) investigated the effect of Cu, Zn, Pb and Cr compounds on mechanical properties of C_3A cement and showed them to be dependent on the metal concerned.



In this particular waste form, ettringite prisms were found to fill voids/air bubbles. In addition, ettringite coated larger grains of contaminated material. It was thought that loss of water from grains resulted in shrinkage during setting/hydration causing a void in which ettringite was able to grow.

Figure 4.2: Secondary electron photomicrograph of ettringite formation in S/S metal-plating waste (Photograph courtesy of Colin Hills).

4.3 Interactions with Inorganic Contaminants

4.3.1 Transition metals including heavy metals

Generally, in the treatment of contaminated soil or wastes containing transition metals, reduction in oxidation state is required to produce compounds that are insoluble. Guidance on this subject can be obtained from USEPA (1990a) and is discussed by Anderson (1994).

When cement or lime-based systems are used during S/S, the high pH environment favours the precipitation of many metals as hydroxides, hydrous oxides or carbonates (Bonen and Sarkar, 1994). However, only soluble salts will be incorporated into the structure of the cementitious hydrated phases. Thus, the particular nature of contaminants present will, to a large extent, govern how they can be ‘fixed’ within an S/S treated waste form. Table 4.2 shows the effect of high pH on the solubility of selected transition metals in their usual oxidation states.

Work has been carried out to investigate the effects of blended binders on simulated and real mixed metal systems containing transition metals. One such study, (Olsen *et al.* 1997), aimed at the nuclear waste industry, used hot alkaline mixed waste, and concluded that in PC/attapulgite and PFA blends, hydration phases including zeolite, apatite, calcite, quartz and monosulfate were formed in a stable matrix. This study illustrates that S/S can be used with complex binder systems to achieve stable products, even for mixed wastes.

Table 4.2: Classification of aqueous species at high pH for common oxidation states (after Glasser, 1997)

Group	Element	Behaviour
III	Sc, Y, La, Ac	Precipitates
IV	Ti, Zr, Hf	Precipitates
V	V Nb, Ta	Amphoteric (may be soluble as complex) Precipitates
VI	Co, Mo, W	Amphoteric (may be soluble as complex)
VII	Mn, Tc Re	Precipitates Amphoteric (may be soluble as complex)
VIII	Fe, Ru	Precipitates
IX	Co Rh	Precipitates Precipitates as hydrous oxide or metal
X	Ni Pd	Precipitates Precipitates as hydrous oxide or metal
XI	Cu Ag	Precipitates Precipitates as hydrous oxide or metal
XII	Zn Cd, Hg	May be soluble as complexes Precipitates as hydrous oxide or metal

The use of PC, or blended-cement systems for treatment and conditioning of heavy metal-bearing liquids, sludges and particulate wastes is well established (Conner, 1990; Glasser, 1997; Conner and Hoeffner, 1998). Lime has been used to successfully treat soils contaminated with heavy metals from mining activities (Yukselen and Alpaslan, 2001). McKinley *et al.,* 2001 describe the successful application of lime to soils contaminated by a variety of industrial activities. Different binder systems incorporating carbonate or clay may also be appropriate for specific treatment purposes (Dweck *et al.*, 2001).

Pb and Ba have been found to be present in cement-solidified wastes as sulfate or carbonate compounds, whereas Hg may be present as mercury oxide sorbed onto cement surfaces (Ortego *et al.*, 1989; McWhinney *et al.*, 1990a, 1990b; Cocke *et al.*, 1989, 1993).

Thevenin and Pera (1999) showed that with PC, Pb is stabilised by the following mechanisms:

C-S-H + Pb → Pb-C-S-H (chemisorption)
C-S-H + Pb → Pb-S-H + Ca (substitution)
Pb + OH + Ca + SO_4 → mixed salt (precipitation)

There are implications for durability performance in the way contaminants are incorporated in waste forms. These are dealt with in more detail in Chapter 9.

Janusa *et al.* (1998) state that, although the rate of cement hydration is rather insensitive to temperatures in the range 0 – 40°C (Glasser, 1997), the retarding effects of lead salts is increased at lower curing temperatures. Consequently, the leaching of lead is increased in waste forms cured at low temperatures. Whether the waste/cement matrix is cured during winter or summer months affects the extent that the waste is solidified/stabilised.

Barna *et al.* (1997) examined the solidification of an air pollution control residue originating from Pb-slag production with PC, slag, and metakaolin-based binders. They concluded that for amphoteric metals, sensitivity to pore water chemistry could be described using solubilisation/diffusion models. For metals, which are not sensitive in this way, a shrinking core model can be used to describe leaching.

Park (2000) investigated a number of blended binders for S/S of metals and showed that in comparison to PC, leaching was lower for Cr, Cd and Pb during testing. Similar results using ggbs and silica fume with heavy metals are reported by Rha *et al.* (2000) and Asavapisit *et al.* (2001).

De Angelis *et al.* (2002) investigated a slag containing 16% Pb and showed leaching to be problematic. Alpaslan and Yukselen (2002) investigated lead contaminated soil which could not be effectively treated by zeolite, activated carbon, clay or sand. However, simple PC and lime mixes were successful with 88% removal of Pb from leachates (1:21 lime/soil mix) and 99% removal (1:15 cement/soil) respectively. Carey and Nagelski (1996) discussed successful case studies of lead S/S by PC and phosphate addition.

Lin *et al.* (1995) used sulfur polymer cement to S/S Pb-contaminated soil with additions of certain additives: Na_2S, Na_2SO_3, to improved retention in the waste form. The use of $NaNO_2$, a strong reducing agent, was found to be ineffective in this study. In a further study, Lin *et al.* (1996) used a variety of binders including PC and found Pb-contaminated soil could be treated successfully by all the binders employed. Janusa *et al.* (1998) showed that curing temperature had a significant effect on the fixation of Pb at 28 days. The amount of leachable Pb differed by a factor of 25 when cured at 2°C (high Pb leaching) in comparison to 40°C (low Pb leaching).

Zn may be present as the crystalline compounds zinc hydroxide or calcium zincate (Poon and Perry, 1986). Palomo and Palacios (2003) used activated fly ash and PC to solidify Pb and obtained an amorphous product consisting of Pb_3SiO_5 and herschelite, a zeolite mineral phase.

When a soluble metal salt is encapsulated in cement it may re-speciate to form a more stable, lower solubility, compound. In respect of Cd, Cartledge *et al.* (1990) suggest that in cement-based systems the insoluble hydroxide salt is readily formed. However, the binder used must have physical properties that reduce the mobility of contaminants, for example, Poon *et al.* (1986) showed how the increased permeability of a cementitious matrix can significantly reduce the retention of certain metal contaminants.

Hg compounds may be volatile in nature. Options for mercury S/S include formation of insoluble salts by using pre-treatment or sorption into matrices prior to, or during S/S. Zhang and Bishop (2002) used powdered activated carbon (soaked in CS_2 (aq.)) to S/S HgCl and hypothesised that a precipitate of HgS formed on activated carbon surfaces and was responsible for reduced leaching of Hg and Cl.

Pre-treatment of Hg-containing residues from the chlor-alkali industry resulted in successful S/S using PC and PFA (Chang *et al.,* 1993). In this case, additional treatment by sodium sulfide and ferrous sulfate in a 2-stage step was required. Fuhrmann *et al.* (2002) investigated radioactive Hg metal combined in sulfur polymer cement. Mercury was converted to insoluble HgS and subsequent release was shown to be diffusion controlled (at $7.6 \text{ x}10^{-18}$ cm s^{-1}). Measurement of vapour release in the S/S waste form was shown to be less than 0.6 mg/m^3.

Hamilton and Bowers (1997) used HgO, HgS and Hg metal to dope PC and recorded volatilisation with time and temperature. Mercury sulfate was not mobilised whereas HgO vapourised the most. Mercury metal vapourisation was limited by the mass transfer resistance of the binders, through the kinetic control of Hg dissolution into the pore solution. Thus, if a volatile salt of Hg is presented for S/S it may be lost from a waste form by diffusion controlled processes with time.

Cioffi *et al.* (2002) used a modified binder consisting of C_2S and sulfoaluminate to S/S galvanising sludge. They showed that during S/S of a galvanic sludge, Cd was physically trapped in the matrix of the waste form, whereas Cr and Ni were chemically encapsulated.

Wastes can interact with PC to form new phases to incorporate pollutants. In a study by Puertas *et al.* (1999) Fiedels salt ($Ca_4Al_2Cl_2O_6.10H_2O$), stratlingite and Si-hydrogarnet formed in a stable product during S/S of an aluminium-smelting residue. Van Jaarsveld and van Deventer (1999) and van Jaarsveld *et al.* (1999) tried to synthesis a binder from PFA and kaolin and found that its production was affected by nitrate salts of Pb, Cu, (mainly) and $Fe^{(3+)}$, Cd, As and Hg. The production of amorphous phases was influenced by the ionic size and valence of metals and they concluded that in general, the larger the atomic radii of contaminants the lower the levels of leaching likely to be achieved.

Knowledge of the nature and speciation of metals in contaminated materials is important in the prediction of metal behaviour during S/S, and in the selection of suitable binder systems. Studies on Cr leaching of S/S treated soils highlight that mobility may be closely related to speciation (Rinehart *et al.*, 1997), however the influence of other variables such as binder type and soil cation exchange capacity may also important. In respect of binder choice, the authors state that with OPC, Cr^{6+} will leach out of the S/S product.

According to Park and Batchelor (1999) equilibrium models may be used to predict speciation of metals in waste forms. However, it should be emphasised that interaction of contaminants with binders also has an important influence on mobility of contaminants from S/S products (Poon *et al.,* 2001). This was illustrated by Stegemann *et al.,* (2000), who investigated the effects of metal salts on the acid nutralisation curve of S/S products.

They concluded, especially for Cr^{3+} and Zn, that metals had the ability to change the shape of the curve obtained by changing the hydration products formed.

Other work by Sanchez *et al.* (2002) investigated cement-based binders and showed different effect of carbonation during wetting/drying for S/S products containing Cd, As and Pb. The authors concluded that release was affected by reducing pH and degree of carbonation for As but not for Pb. Only As was found to re-speciate during the study, indicating that when predicting the performance for a waste form the influence of extrinsic factors may be significant and need to be considered during S/S of particular contaminants.

Table 4.3 gives stabilisation experience for a number of metals including any pre-treatment steps that may be necessary.

4.3.2 Oxyanions

Oxyanions may require pre-treatment prior to S/S because they can be highly soluble and difficult to solidify, depending on the species prevalent. Conner (1990) describes a number of systems that have been specifically formulated for treating oxyanions. Table 4.7 gives pre-treatment options that are available (Conner, 1990).

Chromates and dichromates are highly soluble and are often associated with metal finishing operations or pigment production. Treatment generally involves reduction prior to S/S. Palomo and Palacios (2003) described treatment of hexavalent chromium by PC and fly ash. In this work $Na_2CrO_4.4H2O$ and a zeolite (hydroxisodalite) were formed. Concentrations of Cr above 2.6% w/w caused severe retardation of setting.

Spence (1998) investigated the S/S of a range of radioactive contaminants including chromate and concluded that use of ggbs was advantageous by providing a reducing environment. Allan and Kukacka (1995) investigated slag-based binders for S/S of Cr^{6+} and Cr^{3+} salts. Use of ggbs meant that a reduction of Cr^{6+} to Cr^{3+} was achieved without the use of lime or PC. Strengths in the range 3-36 MPa and permeabilities of 10^{-11} to 10^{-7} m s^{-1} were recorded. Up to 1000 mg kg^{-1} Cr were successfully S/S however, there was evidence that exposure to air gave increased Cr leaching after 14 months.

Multiple speciation of As may be present at any one time depending on binder choice, although the phase $Ca_3(AsO_4)_2$ may be thermodynamically the most stable in PC (Type V, sulfate resisting) according to Mollah *et al.* (1998). In studies utilising blended OPC/PFA binder, re-speciation of As was noticed during curing leading to increased As leaching (Akhter *et al.*, 1997). Sanchez *et al.* (2003) investigated additions of As^{3+} contaminated soil to PC and compared the results to a laboratory doped soil. They showed that diffusion and solubility of the As compound present dominated leaching characteristics in soil, whereas in PC, As release was controlled by solubilisation at the solid-leachate interface.

Table 4.3: Stabilisation experience for selected metals (after Conner, 1997)

Metal	Common compounds include	Comments
Antimony	Forms inorganic and organic compounds	Easy to treat by S/S. No problems encountered [1]
Arsenic	Metal arsenates, metal arsenites, e.g. $Ca_3(AsO_4)_4$, sodium arsenite (NaAsO2), and arsenic sulfides and oxides	Normally chemical methods are suitable for immobilising As. Some species e.g. As_2S_3 need alkaline oxidation to produce insoluble species e.g. calcium arsenate [2,3,4,5]. As may respeciate under influence of carbonation [10].
Barium	Present in many wastes	Addition of gypsum will precipitate insoluble barium sulfate.
Beryllium	Limited data	Spiked soils treated by cement effectively [1]. Building blocks produces from some wastes [8].
Cadmium	Cadmium arsenates, borates, carbonates, halides, hydroxides and oxides	Compounds generally have low solubility in alkali and can be treated with lime or cement. Cd may require additional treatment step [6]. Cd may be physically encapsulated in some binders [11].
Chromium	Pigments with chromium, chromium sulfate, copper arsenate, chromic acid, nitrate, sodium or potassium dichromate and ammonium dichromate,	Cr is amphoteric and may form basic or acidic compounds. Reduction of $Cr^{(6+)}$ salts produces $Cr(OH)_3$ of low solubility. Soils contaminated with $Cr^{(6+)}$ may require a two-step treatment regime [7]. $Cr^{(6+)}$ may remain mobile if PC binder used [9].
Lead	Lead halides, oxides, sulfates, nitrates, carbonates and silicates	Pb is amphoteric and forms soluble anionic compounds. Control of pH is important. Additives such as carbonates give e.g. $Pb_3(CO_3)_2(OH)_2$ insoluble precipitates in treated soils. Lead may be sorbed onto C-S-H [13] and treated with lime and PC [14].
Mercury	Mercuric chloride, oxide, nitrate, sulfate and sulfides	Most S/S binders effective. Elemental sulfur or organic sulfides additives can be used. Organo-mercury compounds may prove difficult. Sorbents may be used [12].
Nickel	Nickel oxide, sulfate, nitrate, halides, carbonates, hydroxides, cyanide, sulfide	Good pH control generally effective for nickel. Under some circumstances organo-sulfur compounds are required. Ni may be chemically encapsulated by sulfoaluminate binders [11].
Thallium	Limited data	Spiked soils treated by cement effectively [7]
Vanadium	Limited data	Spiked soils treated by cement effectively [1]
Zinc	Commonly encountered	Control of pH effective. CN complexes may prove difficult

References [1] Chemical Waste Management (1992), [2] Conner and Lear (1992), [3] Conner (1993), [4] Young 1979, [5] Mollah *et al.* (1998), [6] Weiner (1967), [7] Cote (1986), [8] Bhat and Pillai (1997), [9] Rinehart *et al.* (1997), [10]Sanchez *et al.* (2002), [11] Cioffi *et al.* (2002), [12] Zhang and Bishop (2002), [13] Thevenin and Pera (1999), [14] De Angelis *et al.* (2002)

Van der Sloot (2002) showed that Aft is an important phase for the S/S of low levels of oxyanions at >pH 12. In high waste loading, sulfate reduces the binding of oxyanions in PC because of site competition in the Aft phase. In an assessment of performance using the tank test, the **ratio** of leaching of oxyanions and other compounds in cement mortar at pH

10 and pH12 gave the following results, indicating the importance of matrix retention attributable to Aft:

BO_3 = 300
CrO_4 = 20
MoO_4 =10
PO_4 =10
SO_4 =500
Sb =5
VO_4 = 1000

4.3.3 Organo-metallic complexes

A variety of pre-treatment methods may be used to transform contaminant complexes into a form that are easier to treat using S/S systems. For example, Pb has been successfully treated by trisodium phosphate at a former waste oil recycling plant (BCA, 2001). Table 4.4 gives some of the options available for a number of organo-metallic compounds.

In the selection of pre-treatment methods, careful consideration must be given to the effects on other contaminants present. For example, the strong oxidants used to destroy cyanide complexes transform Cr into its anionic, highly soluble, hexavalent form. Other simple pre-treatment steps such as the addition of soluble phosphate (Cannell *et al.*, 2000) or selective precipitation to metal sulfide compounds (Cheeseman *et al.*, 1993) have been shown to be useful in the stabilisation of metals in waste streams. Table 4.4 gives properties of some organo-metallic compounds presented for S/S.

4.3.4 Amphoteric metals

Amphoteric metals form compounds that are soluble in both acidic and basic solutions (Mackay and Emery, 1993). There are a number of metals, which form amphoteric compounds, including Zn, Cr and Pb. For precipitation to occur with optimum effect, the binding reagent should be added in such proportions as to ensure the optimum pH conditions are maintained for the main contaminants present (Wilk, 1997).

Table 4.4: Properties of organo-metallic complexes (after Conner, 1990, 1997)

Compounds	Comments
Organo-arsenic	Arsenic readily combines with carbon to form compounds that are used commercially. Organo-arsenic compounds are often found at remediation works at lagoons and disposal sites. Complexes may be destroyed by oxidation or sorbed onto activated carbon during S/S.
Organo-cadmium	Organic complexes involving cadmium include: acetic acid, EDTA, oxalic acid, pyridine and tartaric acid. Dialkyl cadmium compounds are used organic polymer synthesis. Cyanide complexes are found associated with electroplating operations. Organo cadmium complexes can be destroyed by e.g. alkaline chlorination prior to treatment by S/S.
Organo-lead	The most common organo-lead compound has been tetraethyl lead (TEL). The low solubility of TEL has contributed to its successful immobilisation by S/S. Can be pre-treated and precipitated as e.g. PbOH prior to S/S. Specific systems including phosphate have been applied to lead
Organo-nickel	Complexes include acetate, formate, oxalate and stearate. Nickel acetate is found in metal finishing operations and electroplating. Soluble chelates can cause problems during S/S. Cyanide complexes can be treated to leave nickel residues suitable for cement-based treatment. Organo-nickel compounds are stable and difficult to pre-treat to form compounds with low solubility prior to S/S.
Organo-silver	High levels of silver compounds can be treated with $MgSO_4$ and lime to produce mixed sulfate oxide. Sulfides and hydrosulfides can also be used to pre-treat silver complexes. Can be treated by S/S following simple pre-treatment steps.
Organo-tin	Found in contaminated sediments. Can be oxidised by hydrogen peroxide/perchlorate. Organo-tin can be successfully treated by S/S, with or without pre-treatment

4.3.5 Other inorganic compounds

Lime and cement have been widely used for stabilisation of soils in highway and foundation construction. However, in a number of cases serious problems involving swelling and heave have occurred. These have been associated with the formation of ettringite. For example, Mitchell (1986) reported heave in excess of 100% leading to pavement failure in the Stewart Avenue lime-treated sub-base in Las Vegas, USA. Snedker and Temporal (1990) reported at least 60% heave on the M40 Motorway between Oxford and Birmingham in the UK. Common to both of these cases was the ingress of water into sulfate bearing clay and the consequent formation of ettringite and thaumasite.

The detection of sulfates in soils, wastes and groundwater is of importance if cement or lime based S/S is to be used. Whilst sulfates do not have any detrimental effect on the improvement of plasticity qualities following the addition of lime, in the presence of excess water sulfates can react with hydrated cement or cementitious material. This leads to the production of excess ettringite and/or thaumasite, which occupy a greater volume than the reactants and may result in heave or cracking of the S/S waste form. Sherwood (1962) showed that in the case of cohesive soil, serious loss of strength and considerable volume expansion could occur if the stabilised soil was soaked in water and the total sulfate content exceeded 0.25% SO_4. Furthermore, bound waste forms may then be exposed to ingress of sulfate bearing groundwater with similar consequences (Sherwood, 1962, 1992). However, there are no reported releases from affected materials.

Guidance on potential for expansion caused by the presence of sulfates is available (Highways Agency, 2000). It should be noted however, that expansion caused by sulfates in soil might not result in the failure of a waste form treated by S/S over time. In practice, any heave expected by sulfate induced expansion, may not necessarily result in the presence of cracking or the ingress of aggressive solutions. During S/S simple procedures such as the use of ggbs/lime additions can be used to mitigate the effects of high sulfate-bearing soils.

Fluoride, when present as calcium fluoride, is highly insoluble in cement matrices and only sparingly soluble in acids. Conner (1990) reviews the treatment options available for fluoride, cyanide and other inorganic compounds. Very soluble salts of fluoride exist and when present may be difficult to S/S on account of their mobility during leaching.

Chlorides are a problem for cement-based systems in that during subsequent leaching, chloride levels can easily be above regulatory limits. Chloride ions can have an accelerating effect on cement setting. Cheeseman and Assavapisit, (1999) investigated cement retarded with $Pb(OH)_2$ and showed that retardation could be noticeably reduced by adding calcium chloride, however resistance to leaching (by weight loss) and the retardation of hydration achieved in mixes were not fully overcome.

Rossetti *et al.* (2002) used grout formulations produced with heavy metal chloride salts and dropped these into 20% NaOH (aq.) solution. The chloride salts containing the following metals, Zn, Cr, Pb and Li, rapidly solidified to form pellets with low leachability. The use of silica fume in the grout gave the best results for, for example, Cr^{3+} where leaching was reduced by 98%.

Bhat and Pillai (1997) examined the disposal of Be-contaminated residues and showed they could be effectively treated with PC. Leaching results showed a reduction in leachability of 4 orders of magnitude and the authors concluded the waste could be incorporated into cement-block production.

Valls and Vazquez (2002) used $CaCl_2$ as an accelerator during S/S of sewage sludge by PC and PFA mixes in order to overcome retardation by organic compounds. The leachates obtained did not exceed Dutch leaching limits for chloride except where $CaCl_2$ was used. Rossetti and Medici (1995) added metal chloride salts to white PC during S/S and found that waste/binder interference (involving other compounds) were much reduced.

Sulfides of Hg or As appear to be stable in highly alkaline cement-based S/S products. Vale (1995) showed that a high sulfate PFA from a desulfurisation operation could be used to solidify liquid wastes. Other sulfate-contaminated materials produced from TiO_2

manufacture were S/S-treated using an ash product of coal combustion (Vondruska *et al.*, 2001). In this work a solid with acceptable leaching properties was readily formed. Sulfates are often encountered during S/S and can be treated using a variety of binders including lime/ggbs.

Nitrate salts are highly soluble and have been used in the laboratory to study the effects of metals on S/S binder systems (Hills *et al.,* 1994a). Ouki and Hills (2002) examined the microstructure of Portland cement doped with metal nitrate salts and showed that low dosages of salts can significantly affect the microstructure of the solidified medium. However, Gervais and Ouki (2002) showed that for blended cements the choice of binder was important in maintaining the properties of S/S metal nitrate salt-containing products.

Boardman *et al.* (1998) investigated clays stabilised with quicklime containing Pb and Fe nitrates. Results indicated that contaminants were sorbed into reaction products. Small doses of $Pb(NO_3)_2$ improved strength development in sodium bentonite, whereas the Fe salt was detrimental to strength development.

Cyanides readily combine with a number of metals and form simple compounds of Na, K, Ca, Zn and Cu. Cyanide complexes involve organic and inorganic molecules. Limited data exists on the effects of cyanide on binders, but a study by Hills *et al.* (1994b) showed that interference with setting of PC was possible. Because of the toxic nature of cyanide compounds they are often subject to chemical destruction by oxidation prior to S/S.

4.3.6 Waste streams

High volume waste streams, such as municipal solid waste (MSW) incinerator residues have been treated with cementitious binders for re-use in construction (Hudales, 1994; Triano and Frantz, 1992, Redmond *et al.*, 2002a; 2002b). Options for MSW ash (Reich *et al.* 2002) include blending with limestone and sintering to produce a slag with metals solubility minima 15% CaO and pH 10, or by blending with coal dust and cement (Kamon *et al.* 2000). However, metals solubility in MSW ash is problematic and to overcome this Eighmy *et al.* (1998) used PO_4, to form tertiary insoluble phosphates. Further work by Crannell *et al.* (2000) confirmed improved leaching properties for a range of metals and anionic contaminants using this method.

Metals such as Zn, Cd and Pb, found in residues of this type, have been reported to be readily immobilised by blended binders containing slag or PFA (Alba *et al.*, 2001). Similar results have also been achieved with steel foundry waste (Skvara *et al.*, 2002) where, despite retardation of PC setting, up to 70-80%wt. ZnO content of steel foundry dust could be solidified with improved long-term strength and lower leachable heavy metals. The results showed that these foundry dusts behaved similarly to silica fume additions to concrete and suggested potential for use as a cement replacement material.

Vandecasteel *et al.* (2002) showed successful immobilisation of As in a Cu smelting residue was due to the formation of the insoluble $Ca_3(AsO_4)_2$ in the presence of portlandite. The degree of fixation achieved was improved by an order of magnitude by an oxidation step prior to S/S illustrating the potential importance of pre-treatment steps for difficult wastes.

Filipponi *et al.* (2003) examined the physical and chemical properties of cement-based waste forms containing municipal and hospital waste derived MSW ash. They concluded that these residues had a low pozzolanic reactivity with PC and would require activation if their addition to cement were to be optimised. An alternative, but relatively expensive, approach to MSW ash utilisation is described by Nishida *et al.* (2001) where a melting step was used to produce stone suitable for use in asphalt and block manufacture.

As described above, stabilising reagents such as soluble phosphates, soluble silicates or kiln dusts may be added prior to or during mixing with binders to improve performance (Conner and Hoeffner, 1998). Nevertheless, with binders based on PC the chemistry of the product can be expected to be dominated by the dissolution of portlandite and C-S-H (Harris *et al.*, 2002).

Bone *et al.* (2003) demonstrated a dramatic reduction in leachable Pb and Zn (up to 3 orders of magnitude) using accelerated carbonation of bottom ash and APC residues from MSW incinerators without binder addition. The method made no significant difference to the leaching of soluble salts, such as chlorides. However, research has been carried out on bottom ash from MSW incinerators using a pre-wash step to remove soluble salts prior to carbonation with or without phosphate addition to immobilise Pb (Hjelmar *et al.*, 2000, 2001).

Lo *et al.* (2000) investigated S/S of Zn sludge containing Cu, Pb, Co and other metals. Zincite (ZnO) was detected with both PC and PC/PFA based binders showing that portlandite was clearly involved with the fixation of Zn. A number of other investigations have been carried out on the incorporation of metallic species in S/S systems. Tashiro *et al.*, (1979) and Tashiro and Oba (1980) reported on a number of metals including Cr, Cu, Zn and Pb. They showed that many metals interact strongly with cement hydrates. Other metal salts were shown to produce complexes (Stepanova, 1981; Cartledge *et al.*, 1990; Ortego *et al.*, 1989).

Thevenin and Pera (1999) investigated the interaction of lead nitrate with PFA and ggbs blended cements. They showed PFA was best placed for S/S of lead nitrate with ultrafine ggbs cement producing the best results. Roy and Cartledge (1997) examined synthetic electroplating waste containing copper nitrate and showed that although the microstructure of S/S products remained largely unchanged over an eight-year period, observable changes in microchemistry had occurred.

Nitrate salts often retard hydration and curing temperature may also be a factor in controlling their release (Janusa *et al.,* 1998). Further studies by Janusa *et al.* (2000) involved use of bagasse (sugar cane residue with high lignin content) as an additive in PC for S/S of lead nitrate. In this work leaching of lead was reduced at high (15% w/w) loading of $Pb(NO_3)_2$ from 45 mg l^{-1} to 0.5 mg l^{-1}.

Polettini *et al.* (2002) examined the effect of different compounds on the properties of cementitious waste forms by factorial design analysis. They concluded that sulfate and chloride ions had a major influence on the strength and acid neutralisation capacity of cementitious products.

Sulfates are known to promote expansive reactions in cement whereas chloride ions are known to replace OH- in cement hydrates (Glasser, 1997). Malone *et al.* (1997) used salt water during S/S using OPC. The salt loading was 39% and the products were cured at different temperatures to 55°C. The waste forms broke up after thermal loading between 1 and 25°C. Expansion was due to recrystallisation of confined salts and suggested that the durability of waste forms would be significantly impaired if such high salt loadings (ca. 40% w/w) were used in practice.

4.4 Interference of Inorganic Contaminants During S/S

The successful use of S/S to treat specific waste/contaminated soil containing organic or inorganic compounds depends upon whether any specific constituents compromise the strength or durability of the waste form or are highly leachable (Trussell and Spence, 1994). Retardation of setting and hardening of binder systems may not necessarily result in an increase in leaching of contaminants as the buffering capacity of waste forms may not be affected.

4.4.1 Technology limitations

From Table 4.7 it can be seen that the effectiveness of S/S for a particular contaminant may depend on both the use of pre-treatment and an appropriate choice of binder. However historical information suggests the application of S/S may prove difficult for some inorganic materials because of the complex nature of chemical and physical interference effects outlined.

4.4.2 Physical limitations

Physical limitations may be imposed by a number of influences:

- the physical characteristics of the soil/waste being treated;
- the environment into which the treated material is to be placed (*ex-situ* treatment) or that it exists in (*in-situ* treatment); and
- logistical/economic/time constraints.

Physical limitations in relation to the characteristics of the material/plant can lead to problems such as inadequate mixing of binder and contaminated material, too high moisture content or aggregation into clumps (Jones, 1990; USEPA 1993). These issues are considered in Chapters 2 and 5.

4.4.3 Chemical interference mechanisms

Chemical mechanisms that interfere with S/S primarily involve sorption, complexation and precipitation reactions. Complexation of Ca in solution is not an effective retarding mechanism according to Young (1972). It is most likely that in practice retardation is primarily via adsorption onto C-S-H due to hydrogen bonding to form an impervious coating that stifles further hydration. Chelation of carboxyl or hydroxyl oxygen and metal ions on the surface of hydration products may also be important. Taylor (1997) considers retarding and accelerating admixtures for use with cement in the application of concrete.

Figure 4.3 shows an S/S waste in which interference effects could be observed. In this S/S product the absence of hydration products was correlated with the low strengths recorded at the expected time of maturity.

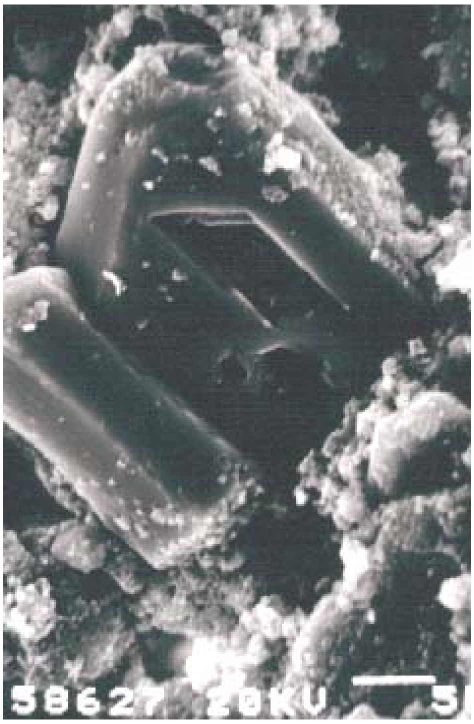
Hydration products are absent in this mature waste form. The waste form did not set nor harden. Unreacted spherical PFA particles can be clearly seen set in a friable matrix.

The waste involved contained a wide range of inorganic contaminants. Secondary electron SEM image.

Figure 4.3: An S/S waste form where interference effects can be observed (photograph courtesy of Colin Hills).

Figure 4.4 shows gypsum development in a solidified product comprised of commercially blended wastes. The high sulfate content of the waste induced gypsum crystals to form, which could cause significant dimensional changes in the waste form in the longer term.

A number of inorganic compounds, including Cu, Pb, Zn, borates, phosphates and iodides, are known to interfere with S/S processes employing cement (USEPA, 1986; Wiles and Barth, 1990; Bhatty and West, 1996; Hills and Pollard, 1997). Appendix 4 lists substances known to affect cement setting/hardening and Appendix 5 gives additional information on how to stabilise metal contaminants. Table 4.5 summarises the effects of a range of inorganic materials, which include fine inorganic particulates, heavy metal salts and gypsum, and Table 4.6 summarises the effects of some commonly encountered metals on cement-based binder systems. Table 4.7 lists common additives used to treat problem metals.



Gypsum crystals formed in S/S blended industrial hazardous waste. It is not clear whether the gypsum was present in the waste or formed after the addition of cement.

The presence of gypsum may lead to expansion and to physical degradation of a S/S waste form. Secondary electron SEM image.

Figure 4.4: Gypsum crystal formation in an S/S waste form (photograph courtesy of Colin Hills).

The immobilisation of B on hydration was improved by the use of activated PFA during S/S (Palomo and da la Fuente, 2003) by forming a precipitate of $NaB(OH)_4$ which was physically encapsulated in the treated product . The use of PFA reduced leaching by 100x and by treating B (aqueous) with lime, Ca meta–borate was formed which did not interfere with PC hydration.

The effect of anions may also be of importance (Hills and Pollard, 1997). Sulfate in waste can react with cement-hydrates to cause delayed ettringite formation, which may lead to problems of expansion. Chloride ions promote dissolution of portlandite, changes in both porosity and permeability and promote sulfate attack (Trussell and Spence, 1994).

The amount of a particular contaminant required to interfere with setting, or to promote leaching in unacceptable quantities will be compound dependant. Furthermore, some compounds that retard at lower dosage rates may accelerate setting at higher additions. In addition, compounds that do not cause interference on their own may cause problems when combined within a contaminated material presented for S/S (Hills and Pollard, 1997). The appropriate use of bench trials will enable the interference effects to be identified and eliminated.

In practice, materials to be treated by S/S will often contain a mixture of inorganic and organic contaminants. Trussell and Spence (1994) described a number of studies where mixed wastes have been successfully treated using blended-cement, lime and zeolite and clay additives. Bates *et al.* (1999) report treatabilty data for a range of proprietary S/S systems from a number of wood preserving sites and shows that despite the mixture of metals (including As, Cr, Cu, Pb, Zn) and organics present solidification was effectively carried out.

Bettekler *et al.* (1986) showed Portland cement to be effective at treating As and PCBs, to below detection in the leachate of cement-solidified sediment. On only a few occasions were PCBs measured in the leachate at levels >1 ug l^{-1}. For Zn, Cd and Pb these were contained most effectively by the pozzolanic binders, with no detectable concentrations of the metals in any of the leachates. Landreth (1982) carried out similar investigations, producing similar conclusions. However, Fleming *et al.* (1992) reported that efforts to stabilise and solidify Buffalo River sediments containing inorganic and organic contaminants using PC, PFA and cement kiln dusts failed to meet the design properties required for successful treatment. The reasons for this were not dealt with in detail.

Cement S/S research carried out by Wilk (1997) on Pb, Cr, Cd, As and Hg, using sequential batch leaching on mature cement pastes, concluded that the metal mobility generally was a function of pH. However, leaching was in general far lower than would be predicted by the theoretical solubility of the corresponding metal hydroxides, particularly for lead. The behaviour observed was partially attributed to the incorporation of the metals into the cement hydration products, reinforced by the fact that there appeared to be a correlation between increasing Pb leachability with increasing alumina leachability as well as a similar correlation between Cr and Si.

This work also suggested that combinations of the metals were stabilised more effectively in a cement matrix than were the individual metals. However, in a study by Hills *et al.* (1994a), a combination of metal salts was shown to completely inhibit cement setting whereas the individual metals concerned did not. This work is supported by the findings of Fernandez Olmo *et al.* (2001) who investigated Pb, Fe^{3+}, Zn and Cr^{3+} at levels found in wastes from thermal processes. The authors showed Zn retardation reduced strength development and that Cr_2O_3 did not interfere except when in association with other metals.

Adbelrazig *et al.* (1999) investigated different calcium salts and showed that Aft formation was often affected when cement grains became starved of water due to changes in pore solution chemistry as complex species formed. They concluded that on the basis of these observations interference effects will remain difficult to predict.

As has been effectively treated at a number of sites in the USA (USEPA, 1990b; 1992, 1997, 2001), by cement (22 times), lime (4 times), pH adjustment and phosphate (3 times each), ferric sulfate (twice) and asphalt (once). The variety of systems employed illustrates the site-specific approach that is often needed to successfully treat contaminated materials.

As discussed, most inorganic contaminants can be solidified using cement and lime-pozzolan-based S/S systems. An understanding of the processes being employed and, where necessary, the use of appropriate pre-treatment or other simple precautions, such as dilution or blending, can normally be used to reduce the critical amounts of interfering compounds. In this way interfering contaminants will cease to pose a threat to the integrity of S/S waste forms.

Table 4.5: Inorganic contaminants affecting solidification (after Conner, 1990)

Compound or Factor	
Inorganics, general	**Fine particulates**
Acids	Ion exchange materials
Bases	Metal lattice substitution
Borates	Gelling agents
Calcium compounds	
Chlorides	**Inorganics, specific**
Chromium compounds	Calcium chloride
Heavy metal salts	Copper nitrate
Iron compounds	Gypsum, hydrate
Lead compounds	Gypsum, semihydrate
Magnesium compounds	Lead nitrate
Salts, general	Sodium hydroxide
Silicas	Sodium sulfate
Sodium compounds	Tin
Sulfates	Zinc nitrate
Tin compounds	

Table 4.6: Summary of effects of some metals on cement-based mixtures (after Conner and Hoeffner, 1998)

Metal	Interference effect
Pb	Precipitates on cement surfaces and forms impermeable coating. Retardation effects common. High concentrations (>5% w/w) may cause weak S/S product. Silica has lower degree of polymerisation [1]. Lead weakens lime-fly ash and cement-fly ash mixtures [2]
Zn	Zinc prevents hydration at high concentrations [3], lime and cement-fly ash mixtures have reduced strength (2% w/w) [2]. Ettringite formation is promoted and porosity reduced [4, 5].
Hg	Does not retard, however, carbonate formation in cement is enhanced [1]. Sorption onto cement grains possible, however presence of some organics will promote Hg leaching from cement, lime- and cement-fly ash mixtures [6]
Cd	Associated with increased ettringite formation, expansion and strength loss [5, 7]
Cr	Associated with increased ettringite formation, expansion and strength loss [5, 7]

[1] Cocke *et al.* (1989; 1992); [2] Cullinane *et al.* (1987); [3] Ortego *et al.* (1989); [4,5] Poon *et al.* (1985a,b); [6] Jones *et al.* (1992); [7] Tashiro *et al.* (1979), Tashiro and Oba (1979)

Table 4.7: Additives used to treat problem metals (after Conner 1997)

	Additive												
Contaminant	Fly/bed ash	$Ca(OH)_2$	$FeSO_4$	$CaCO_3$	$NaCO_3$	NaCl	Na_2SO_4	Organo sulfur	Carbon	$Ca(OCl)_2$/ NaOCl	$KMnO_4$	$Na_2S_2O_4$	Na_2S/ Sulfur
Antimony													
Arsenic $^{(5+)}$	x												
Arsenic $^{(3+)}$	x	x								x	x		
Arsenic-organo Compounds	x	x							x		x		
Barium	x						x						
Barillium													
Cadmium	x	x											
Chromium $^{(3+)}$	x												
Chromium $^{(6+)}$	x		x									x	
Chromium complexes									x				
Lead, conventional	x		x	x	x			x					
Lead-organo compounds									x	x	x		
Lead elemental				x									
Mercury - conventional	x							x					x
Mercury-organo compounds												x	x
Mercury elemental	x												
Nickel conventional	x							x					
Nickel cyanide complexes	x								x	x			
Nickel organo complexes	x								x		x		
Selenium Conventional	x												
Selenium/ selenate			x										
Silver						x							
Thallium													

4.5 Summary

To date, much of the work involving inorganic contaminants and their interactions with binder systems has been carried out with simple, single contaminant systems. Considering that hazardous wastes and contaminated soils are complex mixtures, a treatabilty trial prior to S/S is a vital part of the process of selecting S/S as a risk management strategy.

A considerable body of evidence now supports the effective use of S/S for a wide range of inorganic pollutants. Treatment may involve the use of specific reagents to modify the behaviour of difficult contaminants prior to S/S, or by the addition of binders in a single treatment step. A number of contaminants are known to interfere with cement-based processes, however it is now possible to eliminate these through careful choice of the S/S treatment options now available. Key conclusions from this chapter include:

- the treatment of both metallic and anionic contaminants by S/S is well established;
- the speciation of heavy metals in the contaminated medium and in the resultant waste form will influence the extent of immobilisation achieved in the longer-term;
- metals are immobilised in solidified waste forms through a number of mechanism including- pH control, sorption, precipitation and by physical encapsulation in pores;
- the binder system used for S/S can be tailored for the contaminants to be treated. The redox environment of a binder-system can be altered by design to optimise S/S performance;
- pre-treatment steps for difficult inorganic contaminants such as organo-metallic compounds and amphoteric metals are used to facilitate treatment by S/S;
- chemical fixation is the most important factor in the successful long-term treatment of inorganic contaminants. Permanence however, can be variable and is not well researched;
- interference effects from some inorganic or combinations of inorganic contaminants can affect the performance of S/S; and
- knowledge of contaminants to be treated and their likely interactions with available binders can remove any threat of interference on binder setting and hardening.

REFERENCES

Adbelrazig, B.E. and Bonner, D.G., Nowell, C.V., Dransfield, J.M. and Egan, P.J. (1999) The Solution Chemistry and Early Hydration of Ordinary Portland Cement Pastes With and Without Admixtures. *Thermochemica Acta* 340, pp. 417-430.

Akhter, H., Cartledge, F.K., Roy, A. and Tittlebaum, M.E. (1997) Solidification/Stabilisation of Arsenic Salts: Effects of Long Cure Times. *Journal of Hazardous Materials* 52, pp. 247-264.

Alba, N., Vazquez, E., Gasso, S. and Baldasano, J.M. (2001). Stabilisation/solidification of MSW Incinerator Residues from Facilities with Different Air Pollution Control Systems. *Durability of Matrices Versus Carbonation* 21, pp. 313-323.

Albino, V., Cioffi, R., Marroccoli, M., and Santoro, L. (1996) Potential Application of Ettringite Generating Systems for Hazardous Waste Stabilisation. *Journal of Hazardous Materials* 51, pp. 241-252.

Allan, M.L. and Kukacka, L.E. (1995) Blast Furnace Slag-Modified Grout for *In Situ* Stabilisation of Chromium-Contaminated Soil. *Waste Management* 15, pp. 193-202.

Alpaslan, B. and Yukselen, M. (2002) Remediation of Lead Contaminated Soil by Stabilization/Solidification.*Water, Air and Soil Pollution* 133, pp. 253-263.

Anderson, W.C., (Ed.). (1994) *Innovative Site Remediation Technology: Stabilisation and Solidification*. EPA/542-B-94-001.

Asavapisit, S., Nanthamonty, W. and Polprasert, C. (2001) Influence of Condensed Silica Fume on the Properties of Cement-Based Solidified Wastes. *Cement and Concrete Research* 31, pp. 1147-1152.

Astrup, G., Hansen, J.B., Hjelmar, O. and Christiansen, T.H. (2001) Long-Term Development in APC Ash Landfills with Respect to pH. In: *Proceedings of Sardinia 2001, 8th International Waste Management and Landfill Symposium*, Cagliari, Italy, 1st –5th October. CISA, Environmental Sanitary Engineering Centre, Italy.

Bakharev, T, Brough, A.R., Kirkpatrick, R.J., Struble, L.J. and Young J.F. (1996) Chemical Evolution of Cementitious Materials with High Proportions of Fly ash and Slag. In: *Mechanisms of Chemical Degradation of Cement-Based Systems*. (Young, J.F., Scrivener, K.L, Eds.), pp. 307-314.

Barna, R., Sanchez, F., Moszkowicz, P and Mehu, J. (1997) Leaching Behaviour of Pollutants in Stablized/Solidified Wastes. *Journal of Hazardous Materials* 52, pp. 287-310.

Bates, E.R., Sahle-Demessie, E. and Grosse, D.W. (1999) *Solidification /Stabilization for Remediation of Wood Preserving Sites: Treatment for Dioxins, PCP, Creosote and Metals*. Portland Cement Association Publication RP371, Skokie, Il.

Bettekler J. M., Sherrard, J. H., and Ludwig, D. D. (1986) Solidification/Stabilisation of Contaminated Dredged Material. In: *Mid Atlantic Industrial Waste 18th Conference*, Virginia, USA, pp. 253-273.

Bhat, P.N. and Pillai, K.C. (1997) Leaching and Immobilisation of Beryllium from Solid Waste (Red-Mud) Generated in Processing Beryl. *Water, Air and Soil Pollution* 94, pp. 297-306.

Bhatty, J.I and West, P.B. (1996) Stabilisation of Heavy Metals in Portland Cement Matrix: Effects on Paste Properties. In: *Stabilisation and Solidification of Hazardous, Radioactive and Mixed Wastes*: 3rd Volume ASTM STP 1240. (Eds. M.T.Gilliam and C.Wiles), pp. 147-162. ASTM.

Boardman, D.I., Glendinning, S. and Rogers, C.D. (1998) Lime Treatment for Clean up of Contaminated Soil. In: *Proceedings of the 4th. International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe*.

Bone, B.D., Knox, K., Picken, A. and Robinson, H.D. (2003) The Effect of Carbonation on Leachate Quality from Landfilled Municipal Solid Waste (MSW) Incinerator Residues. In: *Proceedings of Sardinia 2003, 9th International Waste Management and Landfill Symposium*, Cagliari, Italy, CISA, Environmental Sanitary Engineering Centre, Italy.

Bonen, D. and Sarkar, S.L. (1994) The Present State of the Art of Immobilisation of Hazardous Heavy Metals in Cement-Based Materials. In: *Advances in Cement and Concrete* (Eds. M.W.Grutzeck and S.L. Sarkar). American Society of Civil Engineers, pp. 481-495.

Bonen, D. and Sarkar, S.L. (1995) The Effects of Simulated Environmental Attack on Immobilisation of Heavy Metals Doped in Cement-based Materials*, Journal of Hazardous Materials* 40, pp. 321-335.

British Cement Association. (2001) *Cement-based Stabilisation and Solidification for the Remediation of Contaminated Land: Findings of a Study Mission to the USA*. British Cement Association, Publication 46.050.

Carey, M.J. and Nagelski, D. (1996) Treatment Alternatives for Lead Impacted Media: Case Studies. *Waste Management* 16, pp. 263-270.

Cartledge, F.K., Butler, L.D., Chaslani, D., Eaton, H.C., Frey F.P, Herrera, E., Tittlebaum, M.E., and Yang, S.L. (1990). Immobilization Mechanisms in Stabilisation/Solidification of Cd and Pb Salts using Portland Cement Fixing Agents. *Environmental Science and Technology* 24, pp. 867 –873.

Chang, C-Y., Hsu, C.P., Jann, J.S., Chen, Y.W., Shih, Y.C., Mao, C.F., Lin, W.Y., Yin, K.L. and Wu, Y.M. (1993) Stabilisation of Mercury Containing Sludge by a Combined Process of Two-Stage Pre-treatment and Solidification. *Journal of Hazardous Materials* 35, pp. 73-88.

Cheeseman, C.R. and Assavapisit, S. (1999) Effect of Calcium Chloride on the Hydration of Lead Retarded Cement. *Cement and Concrete Research* 29, pp. 885-892.

Cheeseman, C.R., Butcher, E.J., Sollars, C.J. and Perry, R. (1993) Heavy Metal Leaching from Hydroxide, Sulfide and Silicate Stabilised/Solidified Wastes. *Waste Management* 13, pp. 545-552.

Chemical Waste Management. (1992) *Stabilisation of Sb, Be, Tl and V*. Geneva Research Centre, Geneva, Illinois.

Cheng, K.Y. and Bishop, P.L. (1992) Sorption, Important in Stabilised/Solidified Waste Forms. *Hazardous Waste and Hazardous Materials* 9, pp. 289-296.

Cioffi, R., Lavorgna, M. and Santoro, L. (2002) Environmental and Technological Effectiveness of a Process for the Stabilisation of Galvanic Sludge. *Journal of Hazardous Materials* B89, pp. 165-175.

Cocke, D.L., Ortego, J.D., McWhinney, H., Lee, K and Shukla, S.A. (1989) A Model for Lead Retardation of Cement Setting. *Cement and Concrete Research* 19, pp. 156-159.

Cocke, D.L., Mollah, M.Y., Parga, J.R., Hess, T.R. and Ortego, J.D. (1992) An XPS and SEM/EDS Characterisation of Leaching Effects on lead-Doped and Zinc-Doped Portland Cement. *Journal of Hazardous Materials* 30, pp. 83-95.

Cocke, D.L. and Mollah, M.Y.A. (1993) The Chemistry and Leaching of Hazardous Substances in Cementitious Stabilisation/Solidification Systems. In: *Chemistry and Microstructure of Solidified Waste Forms*, (Ed R.D. Spence), Lewis Publishers, Ann Arbor, Mi.

Conner, J. R. (1990). *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York.

Conner, J.R. (1993) Advanced Stabilisation Methods for Treatment of Hazardous Wastes. *Conference on Chemical-Physical Treatment of Industrial Wastes*, University of Brescia, Italy, Jun 17th-18th.

Conner, J.R. (1997). *Guide to Improving the Effectiveness of Cement-based Stabilisation/Solidification*. Portland Cement Association, Skokie, Illinois.

Conner, J.R. and Lear, P.L. (1992) Treatment of Landban-Varianced Arsenic Wastes at TSDFs, *Chemical Waste Management*, Geneva, IL.

Conner, J. R. and Hoeffner, S. L. (1998) The History of Stabilisation/Solidification Technology. *Critical Reviews in Environmental Science and Technology* 28, pp. 397-462.

Cote, P. (1986) *Contaminant Leaching from Cement-Based Waste Forms Under Acidic Conditions*. PhD Thesis. McMaster University. Hamilton, ON, Canada.

Crannell, B.S., Eighmy, T.T., Kranowski, J.E., Eusden, J.D., Shaw, E.L. and Francis, C.A. (2000). Heavy Metal Stabilization in Municipal Solid Waste Combustion Bottom Ash using Soluble Phosphate. Waste Management, 20, pp 135-148.

Cullinane, M.J., Brica, R.M. and Francingues, N.R. (1987). An Assessment of Materials That Interfere with Solidification/Stabilisation Processes. In: *Proc. 13th Annual Research Symposium*, pp. 67-71, United States Environmental Protection Agency.

De Angelis, G., Medici, F, Montereali, M.R. and Pietrelli, L. (2002) Reuse of Residues Arising from Lead Batteries Recycle: A Feasibility Study. *Waste Management* 22, pp. 925-930.

Diet, J.N., Moszkowicz, P. and Sorrentino, D. (1998). Behaviour of Ordinary Portland Cement during the Stabilisation/Solidiffication of Synthetic Heavy Metal Sludges: Macroscopic and Microscopic Aspects. *Waste Management* 18, pp. 17-24.

Dweck, J, Buchler, P.M. and Kartledge, F.K. (2001) The Effect of Bentonites on Cement Hydration During Solidification/Stabilisation of Tannery Wastes. *Journal of Thermal Analysis and Calorimetry* 64, pp. 1011-1016.

Eighmy, T.T., Crannell, B.S., Krzanowski, J.F., Butler, L.G., Cartledge, F.K., Emery, E.F., Eusden, J.D., Shaw, E.L. and Francis, C.A. (1998) Characterisation of Phosphate Stabilistaion of Dusts from the Vitrification of MSW Combustion Residues. *Waste Management* 18, pp. 513-524.

Fernandez Olmo, I, Chacon, E. and Irabien, A. (2001) Influence of Lead, Zinc, Iron (III) and Chromium (III) Oxides on Setting Time and Strength Development of Portland Cement. *Cement and Concrete Research* 3, pp 1213-1219.

Fleming, E, Averett, C.D., Channell, M.G. and Perry, B.D. (1992) *An Evaluation of Solid-state Technology for Buffallo River Sediment*. Miscellaneous Paper EL-91-11, Vicksburg, Miss, US Army Engineer Waterways Experimental Station.

Filipponi, P., Polettini, A., Pomi, R and Sirini, P. (2003) Physical and Chemical Properties of Cement-Based Products Containing Incinerator Bottom Ash. *Waste Management* 23, pp. 145-156.

Forsen, L. (1933a) Die Chemie des Portlandzments in Komplexchemischer Darstellung. *Zement* 6, pp. 73-78.

Forsen, L. (1933b) Die Chemie des Portlandzments in Komplexchemischer Darstellung. *Zement* 7, pp. 87-91.

Fuhrmann, M., Melamed, D., Kalib, P.D. Adams, J.W and Milian, L.W. (2002). Sulfur Polymer Solidification/Stabilisation of Elemental Mercury Waste. Waste Management 22, pp. 327-333.

Gervais, G. and Ouki, S.K. (2002) Performance Study of Cementitious Systems Containing Zeolite and Silica Fume: Effects of Four Metal Nitrates on Setting Time, Strength and Leaching Characteristics. *Journal of Hazardous Materials* 93, pp. 187-200.

Glasser, F.P. (1993) Chemistry of Cement-Solidified Waste Forms. In: *Chemistry and Microstructure of Solidified Waste Forms*, (Ed. R.D. Spence), Lewis Publishers. Ann Arbor,

Glasser, F.P. (1997) Fundamental Aspects of Cement Solidification and Stabilisation. *Journal of Hazardous Materials* 52, pp.151-170.

Glendinning, S., Rogers, C.D. and Boardman, D.I. (1998) Lime Stabilisation of Inorganic Contaminants in Clays. Contaminated Land and Groundwater: Future Directions. *Engineering Geology* 14, pp. 19-28

Griffin, R. A., and Shrimp N. F. (1975) *Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals*, Final Report for EPA Contract 68-03-0211, Cincinnati, Oh.

Griffin, R. A., and Shrimp, N. F. (1976) Effect of pH on Exchange-Adsorption or Precipitation of Lead from Landfill Leachates by Clay Minerals. *Environmental Science and Technology* 10 (13), pp.1256-1261.

Hamilton, W.P. and Bowers, A.R. (1997) Determination of Acute Hg Emissions from Solidified/Stabilised Cement Waste Forms. *Waste Management* 17, pp. 25-32.

Harris, A.W., Manning, M.C., Tearle, W.M. and Tweed, C.J. (2002) Testing Models of the Dissolution of Cements and Leaching of Synthetic C-S-H Gels. *Cement and Concrete Research* 32, pp. 731-746.

Hassett, D.J. and McCarthy, G.J. (1992) Fixation of Trace Elements by Ettringite: A Screening Study Final Topical Report. N. Dakota University (1990). In: *NTIS Environmental Pollution and Control*, No 21.

Highways Agency. (2000) *Treatment of Fill and Capping Materials using either Lime or Cement or Both*. Design Manual for Roads and Bridges, HA74/00.

Hills, C.D., Sollars, C.J and Perry, R. (1994a) Calorimetric and Microstructural Study of Solidified Toxic Wastes: Part 1 -A Classification of OPC/Waste Interference Effects. *Waste Management* 14, pp. 589 -599 and Part 2 -A Model for Poisoning of Hydration. *Waste Management* 14**,** pp. 601 -612.

Hills, C.D., Sollars, C.J. and Perry, R. (1994b) Solidification of Hazardous Wastes Containing Cyanide. *Cement and Concrete Research* 24, pp. 707 –714.

Hills, C.D. and Pollard, S.J.T. (1997) The influence of Interference Effects on the Mechanical, Microstructural and Fixation Characteristics of Cement-Solidified Waste Forms. *Journal of Hazardous Materials* 52, pp. 171-191.

Hjelmar, O., Birch, H. and Hansen, J.B. (2000) Further Development of a Process for treatment of APC Residues from MSW Incinerators. In: Woolley, G.R., Goumans, J.J.J.M. and Wainwright, P.J. (editors). *Waste Materials in Construction*, 872-883. Elsevier Science Ltd.

Hjelmar, O., Birch, H. and Hansen, J.B. (2001) Treatment of APC Residues from MSW Incineration: Development and Optimisation of a Treatment process in Pilot Scale. In: *Proceedings of Sardinia 2001. Eighth International Waste Management and Landfill Symposium*. 1-5 October 2001, Margherita de Pula, Cagliari, Italy.

Hudales, J.M.B. (1994) The Use of M.I.W Fly Ash in Asphalt for Road Construction. In: *Environmental Aspects of Construction with Waste Materials*. (Eds. Goumans, J., Van der Sloot, H.A., Aalbers T.G.) Elsevier Science B.V. pp. 227-232.

Ivey, D.B., Heinmann, R.B., Neuwirth, M., Shumborski, D., Conrad, Mikula, R.J. and Lam, W.W. (1990) Electron Microscopy of Heavy Metal Waste in Cement Matrices. *Journal Materials Science Letters* 25, pp. 5055-5062.

Janusa, M.A., Heard, G.E., Bourgeois, J.C., Kliebert, N.M. and Landry, A.A. (1998) Effects of Curing Temperature on the Leachability of Lead Undergoing Solidification/Stabilisation with Cement. *Microchemical Journal* 60, pp 193-197.

Janusa, M.A., Champagne, C.A., Fanguy, J.C.Heard, G.E. Laine, P.L. and Landry, A.A. (2000) Solidification/Stabilisation of Lead with aid of Bagasse as an Additive to Portland Cement. *Microchemical Journal* 65, pp 255-259.

Jones, L.W. (1990) *Interference Mechanisms in Waste Stabilisation/Solidification Processes- Project Summary*. USEPA Risk Engineering Laboratory. EPA/600/S2-89/067.

Jones, L.W., Brica, R.M. and Cullinane M.J. (1992) Effects of Selected Waste Constituents on Solidified/Stabilised Waste Leachability. In: *Stabilisation and Solidification of Hazardous, Radioactive, and Mixed Wastes,* (Eds. T.M. Gilliam and C.C. Wiles) 2nd Volume, pp. 193-203 ASTM STP 1123.

Kamon, M., Katsumi, T. and Sano, Y. (2000) MSW Fly Ash Stabilised with Coal Ash for Geotechnical Applications. *Journal of Hazardous Materials* 76, pp. 265-283.

Kantro, D.L. (1975) Tricalcium Silicate Hydration in the Presence of Various Salts. *Journal of Testing and Evaluation* 3, pp. 312-321.

Katz, A., Brough, A.R., Kirkpatrick, R.J., Struble, L.J., Sun, G.K. and Young, J.F. (2001) Cement Solidification of Simulated off-Gas Condensates from Vitrification of Low-Level Nuclear Waste Solutions. *Waste Management*, 21, pp. 543-553.

Komarneni, S. Breval, E. and Roy, R. (1988) Reactions of Some Calcium Silicates with Metal Cations. *Cement and Concrete Research* 18, pp. 204-220.

Landreth, R. E. (1982) *Physical Properties and Leach Testing of Solidified/Stabilised Industrial Wastes*. Report Number EPA-600/2-82-099, US Environmental Protection Agency, Cincinnati, Oh. 45268, USA.

Li, X.D., Poon C.S., Sun, H., Lo, I.M.C. and Kirk, D.W. (2001) Heavy Metal Speciation and Leaching Behaviour in Cement Based Solidified/Stabilized Waste Materials. *Journal of Hazardous Materials* A82, pp. 215-230.

Lin, C.K., Chen, J.N. and Lin, C.C. (1997) An NMR, XRD and EDS Study of Solidification/Stabilisation of Chromium with Portland Cement. *Journal of Hazardous Materials* 56, pp. 21-34.

Lin, S-L., Lai, J.S. and Chian, E.S. (1995) Modification of Sulfur Polymer Cement (SPC) Stabilization and Solidification (SS) Process. *Waste Management* 15 pp. 441-447.

Lin, S-L., Cross, W.H., Chian, E.S., Lai, J.S., Giabbai, M. and Hung, C.H. (1996) Stabilization and Solidification of Lead in Contaminated Soils. *Journal of Hazardous Materials* 48, pp. 95-110.

Lin, T.T., Lin, C.F., Wei, W.C. and Lo, S-L. (1993) Mechanisms of Metal Stabilisation in Cementitious Matrices: Interactions of Tricalcium Aluminate and Copper Oxide/Hydroxide. *Environmental Science and Technology* 28, pp. 1312-1318.

Lo, I.M.C., Tang, S.I., Li, K.D. and Poon, C.S. (2000) Leaching and Microstructural Analysis of Cement-Based Solid Waste. *Environmental Science and Technology* 34, pp. 5038–5042.

Mackay, M., and Emery, J.J. (1993) Practical Stabilization of Contaminated Soils. *Land Contamination and Reclamation* 1 (3), pp. 149-155.

Macphee, D.E., Atkins, M. and Glasser, F.P. (1989) *Scientific Basis for Nuclear Waste Management VII*. Materials Research Society, Pittsburgh, pp. 475-480.

Malone, P.G., Poole, T.S., Wakeley, L.D. and Burkes, J.P. (1997) Salt-Related Expansion in Portland-Cement-based Wasteforms. *Journal of Hazardous Materials* 52, pp. 237-246.

McConnell, J.D.C. (1955) The Hydration of Larnite (B-Ca_2SiO_4) and Bredigite (A1-Ca_2SiO_4) and the Properties of the Resulting Gelatinous Plombierite. *Mineral Magazine* 30, pp. 672-680.

McKinley, J.D., Thomas, H.R., Williams, K.P. and Reid, J.M. (2001) Chemical Analysis of Contaminated Soil Strengthened by the Addition of Lime. *Engineering Geology* 60, pp. 181-192.

McWhinney, H.G. and Cocke, D.L. (1993) A Surface Study of the Chemistry of Zinc, Cadmium and Mercury in Portland Cement. *Waste Management* 13, pp. 117-123.

McWhinney, H.G., Cocke, D.L., Balke, K and Ortego, J.D. (1990a) An Investigation of Mercury Solidification and Stabilisation in Portland Cement Using X-ray Photoelectron Spectroscopy and Energy Dispersive Spectroscopy. *Cement and Concrete Research* 20, pp. 79-91.

McWhinney, H.G., Rowe, M.W., Cocke, D.L., Ortego J.D. and Yu, G.S. (1990b) X-ray Photoelectron and FTIR Spectroscopic Investigation of Cement Doped with Barium Nitrate. *Journal of Environmental Science and Health* A25, pp. 463-477.

Mitchell, J.K. (1986) Delayed Failure of Lime-Stabilised Pavement Bases. *Journal of Geotechnical Engineering*, 112, pp. 274-279.

Mollah, Y.M., Vempati, R.K., Lin, T.C. and Cocke, D.L. (1995a) The Interfacial Chemistry of Solidification/ stabilisation of Metals in Cement and Pozzolanic Material Systems. *Waste Management* 15, pp. 137-148.

Mollah, M.Y., Palta, P. and Hess, T.R. (1995b) Chemical and Physical Effects of Sodium Lignosulfonate Superplasticiser on the Hydration of Portland Cement and Solidification/Stabilisation Consequences. *Cement and Concrete Research* 25, pp. 671-682.

Mollah, M.Y., Lu, F. and Cocke, D.L. (1998) An X-ray Diffraction (XRD) and Fourier Transform Infared Spectroscopic (FT-IR) Characterisation of Speciation of Arsenic (V) in Portland Cement Type-V. *The Science of the Total Environment* 224, pp. 57-68.

Nishida, K., Nagayoshi, Y., Ota, H. and Nagasawa, H. (2001) Melting and Stone Production of MSW Incinerator Ash. *Waste Management* 21, pp. 443-449.

Olsen, R.A., Tennis, P.D., Bonen, D., Jennings, H.M., Mason, T.O., Christensen, B.J., Brough, A.R., Sun, G.K. and Young, J.F. (1997) Early Containment of High-Alkaline Solution Simulating Low-Level Radioactive Waste in Blended Cement. *Journal of Hazardous Materials* 52, pp. 223-236.

Omotoso, O.E., Ivey, D.G. and Mikula, R. (1998) Containment Mechansism of Trivalent Chromium in Tricalcium Silicate. *Journal of Hazardous Materials* 60, pp. 1-28.

Ortego, J.D., Jackson, S., Yu, G.S., McWhinney, H.G. and Cocke, D.L. (1989) Solidification of Hazardous Substances – a TGA and FTIR Study of Portland Cement Containing Metal Nitrates. *Journal of. Environmental Science and Health* A24, pp. 589-602.

Ouki, S.K. and Hills, C.D. (2002) Microstructure of Portland Cement Pastes Containing Metal Nitrate Salts. *Waste Management* 22, 2, pp. 147-151.

Palomo A. and López de la Fuente J. I. (2003) Alkali-activated Cementitious Materials: Alternative Matrices for the Immobilisation of Hazardous Wastes: Part I. Stabilisation of Boron. *Cement and Concrete Research* 33 (2), pp. 281-288.

Palomo A. and Palacios M. (2003) Alkali-Activated Cementitious Materials: Alternative Matrices for the Immobilisation of Hazardous Wastes: Part II. Stabilisation of Chromium and Lead. *Cement and Concrete Research* 33, pp. 289-295.

Park, J.Y. and Batchelor, B. (1999) Prediction of Chemical Speciation in Stabilised/Solidified Wastes Using a General Chemical Equilibrium Model. Part 1: Chemical Representation of Cementitious Binders. *Cement and Concrete Research* 29, pp. 361-368.

Park, C-K. (2000) Hydration and Solidification of Hazardous Waste Containing Heavy Metals Using Modified Cementitious Materials. *Cement and Concrete Research* 30, pp. 429-435.

Poellmann, H., Kuzel, St. A., Kuzel, H.J. and Wenda, R. (1993) Solid Solution in Ettringites, Part II: Incorporation of $B(OH)_4^-$ and $Cr_2O_4^{2-}$ in $CaO.Al_2O_3.3CaSO_4.32H_2O$. *Cement and Concrete Research* 23, pp. 422-430.

Polettini, A., Pomi, R and Sirini, P. (2002) Fractional Factorial Design to Investigate the Influence of Heavy Metals and Anions on the Acid Neutralisation Behaviour of Cement-Based Products. *Environmental Science and Technology* 36 (7), pp 1584-1591.

Poon, C.S., and Perry, R. (1986) Studies of Zinc, Cadmium and Mercury Stabilisation in OPC/PFA Mixtures. In: *Proceedings of the Materials Research Society Symposium*, Massachusetts, 86, pp. 67-76.

Poon, C.S., Peters, C.J., Perry, R., Barnes, P and Barker, A.P. (1985a) Mechanisms of Metal Stabilisation by Cement-Based Fixation Processes. Science of the Total Environment, 41, pp. 55-71.

Poon, C.S., Clarke, A.I., Peters, C.J., and Perry, R. (1985b). Mechanisms of Metal Fixation and Leaching by Cement Based Processes. Waste Management and Research, 3, pp. 127-142.

Poon, C.S., Clark, A.I. and Perry, R. (1986) Permeability Study of the Cement Based Solidification Process for the Disposal of Hazardous Wastes. *Cement and Concrete Research* 16, 1, pp. 61-172.

Poon, C.S., Chen, Z.Q. and Wai, O.W. (2001) The Effect of Flow-Through Leaching on the Diffusivity of Heavy Metals in Stabilised/Solidified Waste. *Journal of Hazardous Materials* 81, pp. 179-192.

Puertas, F., Blanco-Varela, M.T. and Vazquez, T. (1999) Behaviour of Cement Mortars Containing an Industrial Waste from Aluminium Refining. Stability in Ca(OH)2 Solutions. *Cement and Concrete Research* 29, pp. 1673-1680.

Redmond, S., Pimienta, P and Bentz, D.P. (2002a) Effects of Incorporation of Municipal Solid Waste Incineration Fly Ash in Cement Pastes and Mortars: I Experimental Study. *Cement and Concrete Research* 32, pp. 301-311.

Redmond, S., Pimienta, P and Bentz, D.P. (2002b) Effects of Incorporation of Municipal Solid Waste Incineration Fly Ash in Cement Pastes and Mortars: II Modelling. *Cement and Concrete Research* 32, pp. 565-576

Reich, J., Pasel, C., Herbell, J-D. and Luckas, M. (2002) Effects of Limestone Addition and Sintering on Heavy Metal Leaching from Hazardous Waste Incineration Slag. *Waste Management* 22, pp. 315-326.

Rha, C.Y., Kang, S.K. and Kim, C.E. (2000) Investigation of the Stability of Hardened Slag paste for the Stabilisation/Solidification of Wastes Containing Heavy Metal Ions. *Journal of Hazardous Material* B73, pp. 255-267.

Richardson, I.G. and Cabrera, J.G. (2000) The Nature of C-S-H in Model Slag-Cements. *Cement and Concrete Composites* 22, 4, pp. 259-266.

Rinehart, T.L., Sculze, D.G., Bricka, R.M., Bajt, S. and Blatchley, E.R. (1997) Chromium Leaching vs. Oxidation State for a Contaminated Solidified/Stabilised Soil. *Journal of Hazardous Materials* 52, pp. 213-221.

Rossetti, V.A. and Medici, F. (1995) Inertization of Toxic Metals in Cement Matrices: Effects on Hydration, Setting and Hardening. *Cement and Concrete Research* 25, pp. 1147-1152.

Rossetti, V.A., Di Palma, L and Medici, F (2002) Assessment of the Leaching of Metallic Elements in the Technology of Solidification of Aqueous Solution. *Waste Management* 22, pp. 605-610.

Roy, A. and Cartledge, F.K. (1997) Long-Term Behaviour of a Portland Cement-Electroplating Sludge Waste Form in Presence of Copper Nitrate. *Journal of Hazardous Materials* 52, pp 265-286.

Sanchez, F., Gervais, C., Garrabrants, A.C., Barna, R. and Kosson, D.S. (2002) Leaching of Inorganic Contaminants from Cement-Based Waste Materials as a Result of Carbonation During Intermittent Wetting. *Waste Management* 22, pp. 249-260.

Sanchez, F., Garrabrants, A.C., Vandercasteel, C, Moszkowicz, P. and Kosson, D.S. (2003) Environmental Assessment of Waste Matrices Contaminated with Arsenic. *Journal of Hazardous Materials* 96, pp. 229-257.

Skvara, F., Kastanek, F., Pavelkova, I., Solcova, O., Maleterova, Y and Schneider, P. (2002) Solidification of Waste Steel Foundry Dust with Portland Cement. *Journal of Hazardous Materials* B 89, pp. 67-81.

Sherwood, P.T. (1962) The Effect of Sulfates on Cement-and Lime-Stabilised Soils. *Roads and Road Construction*, 40 (470), pp. 34-40.

Sherwood, P.T. (1992) *Stabilised Capping Layers using either Lime, or Cement, or Lime and Cement*. Transport Research Laboratory, Contractor Report 151.

Snedker, E.A. and Temporal, J. (1990) M40 Motorway Banbury IV Contract - Lime Stabilisation. *Highways and Transportation*, December 7th – 8th , 1990.

Spence, R.D. (1998) Immobilisation of Technetium in Blastfurnace Slag Grouts. In: *Proceedings of the 3rd CANMET/ICI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*. Trondheim Norway. (Ed. Malhotra V.M.). ACI Publication, SP. 114 pp. 1579-1596.

Stepanova, I.N. (1981) Hardening of Cement Pastes in the Presence of Chloride of 3d Elements. *Journal of Applied Chemistry* 54, p.885

Stegemann, J.A., Perera, R., Cheeseman, C. and Buenfeld, N.R. (2000) 1/8 Factorial Study of Metal Effects on Acid Neutralisation by Cement. *Journal of Environmental Engineering*, October, pp. 925-933.

Taylor, H.F.W. (1997) *Cement Chemistry*, (Second Edition), Thomas Telford Press, London.

Tashiro, C., Takahashi, H., Kanaya, M., Hirakida, I and Yoshida, R. (1977) Hardening Properties of Cement Mortar Adding Heavy Metal Compounds and Solubility of Heavy Metal Hardened Mortar. *Cement and Concrete Research* 7, pp. 283-290.

Tashiro, C., Oba, J. and Akama, K. (1979) The Effect of Metal Oxides on the Formation of Ettringite and the Microstructure of Hardened Ettringite. *Cement and Concrete Research* 9, pp. 303-308.

Tashiro, C. and Oba, J. (1979) The Effect of Cr_2O_3, $Cu(OH)_2$, ZnO and PbO on the Compressive Strength an Hydrates of Hardened C_3A Paste. *Cement and Concrete Research* 9, pp. 253-258.

Tashiro, C and Oba, J. (1980) The Effect of Cu $(OH)_2$ on the Hydration of C3A. In: *Proceedings of the Seventh International Congress of Cement Chemistry*, Vol. 2 (II), Paris, France pp. 59-63.

Thevenin, G. and Pera, J. (1999) Interactions Between Lead and Different Binders. *Cement and Concrete Research* 29, pp. 1605-1610.

Triano, J.R., Frantz, G.C. (1992) Durability of MSW Fly Ash Concrete. *Journal of Materials in Civil Engineering* 4, pp. 369-384.

Trussell, S and Spence, R.D. (1994) A Review of Solidification/Stabilisation Interferences. *Waste Management* 14, pp. 507-519.

United States Environmental Protection Agency. (1986) Handbook of Stabilisation/Solidification of Hazardous Wastes. EPA/540/2-86/001.

United States Environmental Protection Agency. (1990a) *Handbook on In-situ Treatment of Hazardous Wastes-Contaminated Soils*. EPA/540/2-90.

United States Environmental Protection Agency. (1990b) *Final Best Demonstrated Available Technology Background Document for K031, K084, K101, K102, Characteristic Arsenic Wastes (D004), Characteristic Selenium Wastes (D010) and P and U Wastes Containing Arsenic and Selenium Listing Constituents*. Office of Solid Waste.

United States Environmental Protection Agency. (1992) *Arsenic and Mercury- Workshop on Removal, Recovery, Treatment and Disposal*. EPA-600-R-92.

United States Environmental Protection Agency. (1993*) Solidification/Stabilisation of Organics and Inorganics*. Engineering Bulletin EPA/540/S-92/015.

United States Environmental Protection Agency USEPA. (1997) *Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg and Pb*. Engineering Bulletin. EPA/540/S-97/500.

United States Environmental Protection Agency (2000) *Solidification/Stabilisation use at Superfund Sites*. EPA-542-R00-010

United States Environmental Protection Agency. (2001*) National Risk Management Research Laboratory. Treatabilty Database*. http://www.epa.gov/tdnrmrl.

Vale, J. (1995) Stabilisation/Solidification of Industrial Inorganic Wastes using Coal Fly Ashes from Desulfurisation Processes. *Coal Science and Technology* 24, pp. 1955-1958.

Valls, S and Vazquez, E. (2002) Leaching Properties of Stabilised/Solidified Cement-Admixtures-Sewage Sludge Systems. *Waste Management* 22, pp. 37-45.

Vandecasteel, C., Dutre, V. Geysen, D and Wauters, G. (2002) Solidification/Stabilisation of Arsenic bearing Fly Ash from the Metallurgical Industry. Immobilisation Mechanism of Arsenic. *Waste Management* 22, pp. 143-146.

van der Sloot, H.A. (2002) Characterisation of Leaching Behaviour of Concrete Mortars and Cement-Stabilised Wastes with Different Waste Loading for Long Term Environmental Assessment. *Waste Management* 22, pp. 181-186.

van Jaarsveld, J.G. and van Deventer, J.S. (1999) The Effect of Metal Contaminants on the Formation and Properties of Waste-Based Geopolymers. *Cement and Concrete Research* 29, pp. 1189-1200.

van Jaarsveld, J.G., van Deventer, J.S. and Schwartzman, S. (1999). The Potential use of Geopolymeric Materials to Immobilise Toxic Metals: Part II. Materials and Leaching Characteristics. *Materials Engineering* 12, pp. 75-91.

Vondruska, M. Bednarik, V and Sild, M. (2001) Stabilisation/Solidification of Ferrous Sulfate from Titanium Dioxide Production by Fluidised Bed Combustion Product. *Waste Management* 21, pp. 11-16.

Weiner R.F. (1967) Acute Problems in Effluent Treatment. *Plating* 54, pp. 1354-1356.

Wiles, C.C and Barth, E. (1990) *Solidification/Stabilisation: is it Always Appropriate*. ASTM, Pa.

Wilk, C. M. (1997) *Stabilisation of Heavy Metals with Portland Cement: Research Synopsis*. Waste Management Information, Public Works Department, Portland Cement Association, Skokie, Il.

Yong, R.N., Mohamed, A.M.O. and Warkentin, B.P. (1996) *Principles of Contaminant Transport in Soils*, Elsevier, Oxford.

Young D.A. (1979) US Patent 4, 142912.

Young, D.F. (1972) A Review of Mechanisms of Set Retardation in Portland Cement Pastes Containing Organic Admixtures. *Cement and Concrete Research* 2, pp. 415-433.

Yousuf, M., Vempati, R.K., Lin, T-C., Cocke, D.L. and Mollah, A. (1995) Interfacial Chemistry of Solidification/Stabilisation of Metals in Cement and Pozzolanic Systems. *Waste Management* 15, pp. 137-148.

Yukselen, Y.A. and Alpaslan, B. (2001) Leaching of Metals from Soils by Mining Activities. *Journal of Hazardous Materials* B87, pp. 289-300.

Zhang, J and Bishop, P.L. (2002) Stabilisation/Solidification (S/S) of Mercury Containing Wastes Using Reactivated Carbon and Portland Cement. *Journal of Hazardous Materials* 92, pp. 199-212.

5 STABILISATION/SOLIDIFICATION OF ORGANIC CONTAMINANTS

5.1 Introduction

The S/S of soil or waste containing organic contaminants presents more of a challenge, and has a shorter track record than the S/S of inorganicl-contaminated soils and wastes. Although unsatisfactory results have been achieved with cement alone, considerable progress has been made with the use of additives blended with the cement.

This chapter discusses the treatment of organics using S/S, looking at a variety of examples where the treatment has worked effectively. It also identifies problematic applications and considers the use of additives to combat the effects of interference.

5.2 Organic Reaction Principles

Many hazardous organic wastes lend themselves primarily to destructive or degradative treatments rather than S/S. However, many contaminated materials contain small amounts of organic material (Conner, 1990), and S/S has been used at a significant number of Superfund sites in the USA (USEPA, 2000). Some examples of these are given in section 5.3. There is no doubt that many of the issues that influence the choice of binder system for inorganic contaminants also pertain to organic contaminants. Issues related to the retention of soluble compounds, the effect of interference reactions and the presence of recalcitrant compounds will need to be addressed and dealt with in a cost-effective manner, if satisfactory S/S is to be carried out.

Cement based systems operating at ambient temperatures and pressures in aqueous environments are involved in a few organic reactions. Aside from adsorption and volatisation the most likely reactions involving organics are (Conner, 1990):

- hydrolysis;
- oxidation;
- reduction; and
- salt formation.

Some general and specific reactions within these categories are shown in Table 5.1. The reaction products are not all shown in some cases and the stoichiometry is not necessarily as stated. Appendix 5 lists additives that might be used to treat organic compounds together with their likely effectiveness based on the classification of organics.

5.2.1 Hydrolysis

Hydrolysis involves the reaction of a contaminant with water and usually involves exchange of the hydroxyl group with another functional group (Conner, 1990). Compounds less resistant to hydrolysis include alkyl halides, polymethanes and aliphatic acid esters. Compounds resistant to hydrolysis include amides, nitriles and carbamates.

Table 5.1: Some organic reactions in cement systems (after Conner, 1990)

Reactants	**Products**
Hydrolysis	
$RX + H_2O$	$ROH + HX$
Organoaminos	Organics + NH_3
Oxidation	
Phenol + $14H_2O_2 + Fe^{2+}$	$6CO_2 + 17H_2o$
$R\text{-}CH_3$	R-COOH
$R\text{-}CH_2OH$	R-COOH
RCHOH-CHOHR’	R-COOH + R’ –COOH
R-CHO	R-COOH
R_2CH_2	R_2CO
$R_2CH(OH)$	R_2CO
R_3CH	$R_3C(OH)$
$R_3CH + HCR'_3$	$R_3\text{-}C\text{-}C\text{-}R'_3$
$R_2N\text{-}H + H\text{-}NR'_2$	$R_2N\text{-}NR'_2$
RCH=CHR’	RCHOH-CHOHR’
2R-SH	R-S-S-R
R-S-S-R’	$R'SO_3H + RSO_3H$
Reduction	
$Fe + 2H_2O + 2RCl$	$2ROH + Fe^{+2} + 2Cl^- + H_2$
Salt Formation	
Oxalic acid	Calcium oxalate

5.2.2 Oxidation

Oxidation of organic contaminants involves attack by an electrophilic agent in which one or two electrons are removed creating a free radical. These reactions can be catalysed at ambient temperatures in clays and soils and involve iron, aluminium and trace metals (Conner, 1990).

A number of substituted aromatic compounds undergo free radical oxidation and these include benzene, benzadiene, naphthalene and phenol. Compounds resistant to oxidation include chlorinated aromatic and polynuclear organics.

5.2.3 Reduction

Reduction occurs when there is a transfer of electrons from an electron donor to the contaminant (an electron acceptor in this case). Reduction of organics involves an increase in the hydrogen content of a compound and a decrease in its oxygen content.

Many organic compounds are stable under reducing conditions, but reductive transformation is an important degradative process, for example for chlorinated hydrocarbons. Examples of reductive transformation processes include reductive dehalogenation or dealkylation, nitroaromatic reduction, and sulfoxide reduction. The degradation is a charge transfer process, utilising electrons from an external source.

5.2.4 Salt formation

A number of compounds are capable of forming salts of lower solubility than their acid forms. Conner (1990) suggests that the formation of organic salts is an important area for future development. However, at this time little work has been carried out.

5.3 Reported Treatment of Organic Contaminated Sites

There are a number of high profile, Superfund remediation operations involving S/S of primarily organic contamination in the USA. These are testament to the appropriate use of inorganic S/S systems to treat soils contaminated with organic substances. State regulated cleanup operations also routinely employ S/S.

Bates *et al.* (1999) describe S/S treatment at wood preserving sites (at Selma, California and Jackson, Tennessee) containing dioxins, pentachlorophenol (PCP), and creosote. Table 5.2 below, shows the effects of treatment for selected compounds at the Selma site. Data given also includes results from archived sample testing. Aspects of treatment of this site, which also contained high levels of Cr, are discussed in Bates and Lau (1995).

Table 5.2: Treatment of the Selma site by S/S (after Bates *et al.*, 1999)

Parameter	Untreated	Treated	Target
PCP Total	3000 (mg/kg)		
PCP (TCLP)	3.1 (mg/l)	<0.1 (mg/l)	0.30 (mg/l)
PCP (SPLP)	39 (mg/l)	<0.1 (mg/l)	-
Dioxin/Furan Total (TCDD-TEQ) archived samples	12 (μg/kg)	-	-
Dioxin/Furan (TCLP)	28 (pg/l)	<0.025 (pg/l)	-
Dioxin/Furan (SPLP)	144 (pg/l)	<0.01 (pg/l)	-
PCP Total Archived samples	1100 (mg/kg)	-	-
PCP (TCLP) Archived samples	3.1 (mg/l)	<0.1 (mg/l)	-
PCP (SPLP) Archived samples	38.5 (mg/l)	<0.1 (mg/l)	-

TCLP = Toxicity Characteristic Leaching Procedure
SPLP = Synthetic Precipitation Leaching Procedure
TCDD-TEQ = tetrachlorodibenzo-p-dioxin toxicity equivalent

Table 5.3 below gives the specification data developed for the American Creosote site in Jackson, which contained PAHs including dibenzo (a,h) anthracene. The treatment formulation was 1.3% powdered carbon, 5% Portland cement and 4.5% fly ash, determined as weight % of untreated soil. This project demonstrated that a highly contaminated wood preserving site containing dioxins, PCP and creosote can be remediated at moderate cost using S/S technology.

Table 5.3: Specification treatment levels at Jackson after S/S (after Bates *et al.*, 1999)

Parameter	**Target (average)**
Creosote PAHs (B(a)p) potency estimate	<10μg/l
Dibenzo (a,h) anthracene	<4.4 μg/l
PCP	<200 μg/l
Dioxin TCDD-TEQ	<30 pg/l

Table 5.4 below gives a summary of the physical properties from 4 particular sites discussed by Bates *et al.* (1999). Site 1 refers to the Jackson site in California.

Table 5.4: Properties of soils from treatability trials (after Bates *et al.,* 1999)

Property	**Site 1**	**Site 1**	**Site 2**	**Site 2**	**Site 3**	**Site 4**
Cost ($) / Ton soil	39	62	66	54	50	50
28 day UCS (MPa)	9.89	8.55	2.34	4.27	1.17	0.69
Permeability (cm/sec)	1.1×10^{-6}	4.1×10^{-7}	1.4×10^{-7}	5.6×10^{-7}	2.2×10^{-7}	3.1×10^{-7}
Dilution factor	1.32	1.26	1.24	1.35	1.2	1.2

The British Cement Association (2001) reported a number of sites visited on a Department of Trade and Industry-sponsored mission to the USA. The sites contained mixed inorganic and organic contaminants that were treated with cement-based binder systems, as summarised in Table 5.5 below. In practice, mixed inorganic/organic contaminants are frequently encountered and a number of examples of sites treated in the UK are available (Al-Tabbaa and Evans, 1996; 1998, Sansom and Jardine, 1997).

Table 5.5: Summary of sites visited during dti study visit (after British Cement Association, 2001)

Site	Contaminants	Binder system and process
Harrison Ave. former power station, Boston, MA	Pb and oil	Asphalt emulsion pre-treatment, cement-based binder; ex-situ pugmill.
Third Street former gasworks, Cambridge, Boston, MA	Coal tars and diesel	Cement-bentonite binder; in-situ augering.
Former wood processing site, Port Newark, NJ	As, Cr and creosote	Cement-based; "in-situ" mixing of redeposited soil using rotary mixing head.
Jersey Garden Mall, Port Elizabeth, NJ	Mixed contaminants (PCBs, metals) - port dredging	Cement-based; in-barge mixing using rotary mixing head. Treated product used as engineering fill.
Closed landfill site, Salem, NJ	Petroleum fuels from filling stations and road spillage clean-up	Cement-based binder; ex-situ pugmill. Treated product used in capping system.
Peak Oil Superfund site, Tampa, Florida	Pb, PCBs and trichloroethene	Pre-treatment with phosphate, cement-based binder; ex-situ pugmill.

5.4 Contaminant-Binder Interference

Many authors have reported difficulty with cement or lime alone in the treatment of organics contaminants (USEPA, 1993). This is because many organic compounds interfere with the hydration of cement/lime, resulting in retardation of set and a reduction in strength. Mixed wastes are typically presented for S/S and the direct consequences of interference from one contaminant or another are difficult to isolate. However, it should be noted that the successful treatment of difficult organic compounds in contaminated soil, has been carried out as described above and by Tuncan (1996) who showed that petroleum-drilling wastes could be treated with cement, lime and fly ash to facilitate re-use as a sub base material for roads.

Trussell and Spence (1994) review interference effects between a range of inorganic and organic compounds and identify potential interference mechanisms. It should be noted that the effects of organic compounds may be dependent on both concentration and the presence of other contaminants. For example, Rteil *et al.* (2003) dosed new and used engine oil into fresh concrete and found that properties such as strength could be significantly improved. However, Minocha *et al.* (2003) found that a range of organic compounds including grease and oil retarded setting and strength development and adversely influenced the retention of metals in solidified heavy metal sludge.

Organic acids may occur from a variety of sources and be present in soils and some substances, e.g. acetic compounds, may be very aggressive to cement Zivica and Bajza (2001). The aggressiveness of organic acids is related to the solubility of their calcium salts, and the effects of acid attack on binders can be realised, for example, from phenolic compounds, amines, amides and esters. The results can be the formation of alcohol and carboxylic acids.

Conner (1990) has compiled a list of organic compounds that have been found to interfere with S/S systems. Table 5.6, which is taken from this work, illustrates the varied nature of the organic compounds involved.

Table 5.6: Organic contaminants known to affect the outcome of solidification (after Conner, 1990)

Compound	
Organics, general	**Organics, specific**
Acids, acid chlorides	Adipic acid
Alcohols, glycols	Benzene
Aldehydes, ketones	EDTA
Amides	Ethylene glycol
Amines	Formaldehyde
Carbonyls	*p*-Bromophenol
Chlorinated hydrocarbons	Hexachlorobenzene
Ethers, epoxides	Methanol
Grease	NTA
Heterocyclics	Phenol
Hydrocarbons, general	Trichloroethylene
Lignins	Xylene
Oil	
Starches	
Sulfonates	
Sugars	
Tannins	

Hanna *et al.* (1995a; 1995b) investigated a mixed waste by a range of investigative techniques and concluded that some organics impeded silica polymerisation during S/S, resulting in severe retardation. Also, C_3S reactivity and the consequent production of $Ca(OH)_2$ were markedly reduced. In a separate study by Hills *et al.* (1995), seven toxic organic compounds were added to OPC and strength and setting characteristics were monitored. Although all organics had an effect on early-age properties of waste forms, differences in mature samples were less significant.

Five possible mechanisms of organic retardation of cement set have been hypothesised (Young, 1972, Thomas and Double, 1981):

- adsorption of the retarding compound on the surface of cement particles, forming a protective skin which slows down the hydration reactions;
- adsorption of the retarding compounds on the nuclei of calcium hydroxide, poisoning their growth, which is essential for continued hydration of cement after the end of the induction period;
- formation of complexes with calcium ions in solution, increasing their solubility and discouraging the formation of nuclei of calcium hydroxide;
- precipitation around cement particles of insoluble derivatives of the retarding compound formed by a reaction with the highly alkaline aqueous solution, forming a protective skin; and
- incorporation of the retarder in the protective membrane, which rapidly forms around cement particles in water and reduces its permeability, thereby lengthening the time taken for the hydrostatic pressure generated by osmosis to reach a level high enough for rupture and continued growth of hydration products.

Table 5.7 below shows the interactions of different groups of organic compounds on some commonly used S/S binder systems. It shows that the nature of the organic contamination concerned may be significant in determining setting and hardening reactions. It is also worth noting here that the use of alkaline materials to treat acid tars can be problematic (Bates, 2003). At one location in the USA, quick lime was used to treat a tar lagoon with a pH of <4 and SO_2 was evolved. An alternative approach used for the remainder of the operation involved treatment with calcium carbonate to raise pH prior to further additions of lime/cement.

In addition to retardation of set, problems with the retention of organic compounds are also encountered. This is believed to occur because organic compounds do not generally form chemical interactions to the extent that inorganics do, which results in physical rather than chemical immobilisation. Compounds that are retained purely by physical mechanisms may leach from the waste form more readily, since their entrainment depends on the physical characteristics of the solid. This situation is exacerbated if the organic contaminant is soluble in water and/or has a low pKa, which suggests that transformation to a water-soluble species would occur at the pH of the cementitious system

For the purpose of this review, organic compounds are presented in 3 broad classes of compounds, and the important characteristics of each is discussed in turn:

Table 5.7: Interactions between organic chemical groups and stabilisation/solidification binders (After CIRIA, 1995)

Chemical group	OPC Type I	OPC Type II and V	Bentonite	Clay-cement
Alcohols and glycols	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)
Aliphatic and aromatic hydrocarbons	Set time: increase (lengthen or prevent from setting) Durability: no significant effect.	Set time: increase (lengthen or prevent from setting)	Durability: decrease (destructive action occurs over a long time period)	D/U
Chlorinated hydrocarbons	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action occurs over a long time period)	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action occurs over a long time period)	D/U	D/U
Heterocyclics	D/U	D/U	Durability: decrease (destructive action occurs over a long time period)	D/U
Organic acids and acid chorides	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action occurs over a long time period)	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)

Phenols	Set time: no significant effect. Affects strength development Durability: decrease (destructive action occurs over a long time period)	D/U	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)

Key
D/U = Data unavailable
ASTM Type I and II are generally equivalent to OPC and type V to sulphate resisting cement.

5.4.1 Aromatic compounds

There is a reasonable volume of literature on the S/S of aromatic contaminants, most notably for phenols. Other contaminants studied include PAHs and BTEX compounds, with full-scale treatment of PCP and dioxins/furans reported (see section 5.3 above). Zivica and Bajza (2001) reviewed the aggressiveness of phenolic compounds to concrete and showed them to be in the following increasing order: hydrochinone, pyrokatechine, *p*-cresol, phenol, pyrogalole and resorcinole and that their solutions were deleterious to PC and slag-blended binders, resulting in expansion and deterioration of hardened materials. Furthermore the effects of oxidation were noted with hydrochinone, pyrokatechine, pyrogalole and resrcinole when hardened specimens displayed a brow or black discolouration, with the latter being accompanied by dense black reaction products.

Vipulanandan and Krishnan (1993) examined the effects of phenol and *o*-chlorophenol on the properties of cement using two concentrations (2000ppm and 40,000ppm). The authors found that both concentrations inhibited the setting time of cement, decreased its strength, formed complexes with $Ca(OH)_2$ and were leachable from the cement at concentrations inversely proportional to the curing time. The chlorophenol-treated samples also showed greater concentrations of ettringite than in control samples suggesting that chlorophenol also interfered with the conversion of ettringite to monosulphate. Vipulanandan (1995) later concluded from leaching studies that phenol reacted with cement and that up to 400ppm phenol could be treated effectively using S/S.

Montgomery *et al.* (1991) examined the interferences of chlorophenol on hydration processes of cement and found that unhydrated C_3S was 40% greater in chlorophenol-dosed samples than in the untreated pastes. They suggested that the chlorophenol interfered with the reactions that resulted in the conversion of C_3S to C-S-H and $Ca(OH)_2$.

Sheffield *et al.,* (1987) studied the effects of p-chlorophenol (PCP) and p-bromophenol (PBP) on the setting time, compressive strength and leachability of PC. They found that PCP retarded the setting time of the cement, decreased its compressive strength and was readily extracted into water from the solidified cement. PBP had a lesser effect on setting times, did not decrease the compressive strength significantly, and had a lower recovery by extraction. The PCP was detected predominantly in the C-S-H gel phase. The brominated phenol was primarily associated with localised equiaxed and irregular shape grains indicating a strong association with cement hydrates, possibly through strong hydrogen bonding. In addition to this, Cioffi *et al.*, 2001 found that when PC is used in conjunction with organoclay, chlorophenol retention is enhanced.

Vipulanandan and Krishnan (1993) suggested that the phenol used in their work became ionised (as would be predicted by the pKa of phenol) and subsequently reacted with calcium ions released by the initial dissolution of cement to form a complex. This explained the linear relationship observed between the concentration of phenol present in the mixture and the setting time. It also suggests that at sufficiently high concentrations of phenols, cement setting may be prevented altogether. However, the formation of crystalline phenol-calcium hydroxide complexes is consistent with the ready leachability of phenol reported by most workers (Hills *et al.* 1995).

Eaton *et al.* (1986) acknowledge that in principle at least, phenols (present in cementitious matrices as their phenoxide ions) could be incorporated into ionic crystal lattices. The authors state that the participation should be dependent on size relationships, and phenols are probably too large to substitute effectively without causing major deformations of the crystalline lattices. This may provide an explanation as to why, even though phenol has the potential to enter the crystalline phases of the cement; the majority of it is still mobile and readily leachable from the S/S waste form.

Many organic compounds exhibit ready leachability because they don't form stable, insoluble compounds within the cement matrix. For example, a mixture of 2-chloroaniline and methanol was added to fresh cement paste by Sora *et al.* (2002), causing significantly retardation of hydration. Subsequent leaching studies on mature products indicated that >75% of the 2-chloroaniline was readily leached from some samples indicating that it was not readily bound in cementitious matrices.

Indeed, few studies involving the treatment of organic contaminants with cement or lime alone report successful immobilisation at any significant concentration. To improve this situation, additives that provide surfaces for interaction with the contaminant and/or improve the physical properties of the cement have been developed.

Cote *et al.,* (1990) developed a method to differentiate between the physical and chemical components of containment for different contaminants in cement-based waste forms. The method was demonstrated using seven mixtures containing three aromatic organic compounds – phenol, aniline, and acenaphthene. These mixtures contained various additives purported to improve the performance of the S/S process. Unfortunately, full descriptions of the nature of the additives were not given. However activated carbon, hydrated lime, silica fume and PFA were used.

The authors calculated the proportion of chemical and physical containment by a comparison of the leaching of lithium (which was assumed to be retained only by physical methods) to the leaching of the contaminant in question. Table 5.8 summarises the results of this work. The degree of chemical containment can be obtained by subtracting the physical containment factor from the total containment factor. The authors noted that determination of the physical and chemical containment factors can be used to assess the importance of waste form durability for the long-term containment of contaminants. Total containment factors were highest for acenaphthene, which may be consistent with the fact that it has no ionisable hydrogen atoms, and does not form ions of greater solubility at the pH of the cementitious systems.

The authors concluded that activated carbon was the best additive for chemical containment, and that silica fume was the best additive for improving the physical containment of the contaminants studied; however, the dosage of activated carbon used in preparing the formulation was unlikely to be cost effective in practice.

Additives such as activated carbon can be used as part of a binder mixture used to S/S contaminated material or as a pre-solidification adsorbent, whereby, the activated carbon is mixed with material prior to the addition of binders. Other pre-solidification absorbents involving spent bleaching earth have been used by Pollard *et al.* (1990).

The cost associated with using activated carbon as a sorbent for the S/S of organics was considered by Arafat *et al.* (1999). The authors reported that reactivated carbon has been shown to be a promising additive for phenol, and that the capacity of the virgin and the less expensive reactivated forms of the carbon were comparable. Other work by the same authors found that reactivated carbon could also be used in the successful immobilisation of aniline and naphthalene (Franz *et al.,* 2000).

Rho *et al.* (2001) used a catalytic activation process involving activated carbon and hydrogen with cement-based S/S for phenol and 2-chlorophenol. The levels of leachable phenol using the aggressive TCLP leach test were significantly reduced as the process resulted in breakdown of the aromatic phenolic structure. Less hazardous organic compounds such as alcohol were detected in leachates suggesting the C-N bond on the catalytic carbon were involved in degradation reactions.

Table 5.8: Containment factors of acenaphthene, aniline and phenol by 7 different S/S formulations (after Cote *et al*., 1990)

Formulation	Additives	Physical containment factor	Acenaphthene	Aniline	Phenol
A	Portland cement type 1 + proprietary	1.8	4.9	3.1	2.7
B	Proprietary	1.4	5.1	2.9	1.6
C	Proprietary	1.3	3.8	2.2	1.3
D	Portland cement type 2 + proprietary	2.3	5.4	3.4	2.8
E	Portland cement type 2 + proprietary	2.6	5.7	4.7	4.1
F	Activated carbon and Portland cement type 2	1.8	>5.4	>5.4	5.6
G	Hydrated lime, Portland cement type 2 + silica fume	3.2	6.4	5.6	3.9

Other work involving 2-chlorophenol and chloronaphthene (Cioffi et al., 2001) involved mixing organoclay and ggbs. In this study organoclay was used as a pre-solidification adsorbent, thereby overcoming retardation/interference effects on the setting and hardening of the ggbs-based binder. 2-chlorophenol was less effectively retained in the S/S waste form than chloronaphthene. Earlier studies by Montgomery et al. (1991) showed the need for optimisation of organoclays for use in S/S.

Mulder *et al.,* (2001) examined the possibility for the S/S of a range of PAHs in order to produce a material suitable for use as road-base construction material. Ten PAHs were used in this study, with varying water solubilities, with the two end members being naphthalene (most soluble) and indeno[123cd]pyrene (least soluble). The authors considered two proprietary additives – a clay modifier and an adsorbent. The adsorbent was able to bind the PAHs in such a way that the leaching was largely reduced and the product was solidified with a hydraulic binder. The leaching of the lighter (and more water-soluble) PAHs was especially improved in this way.

Gitipour *et al*., (1997) examined treatment of aromatic organics from contaminated soil using modified bentonite during S/S treatment with PC. Benzene, toluene, ethylbenzene and o-xylene were treated successfully with reductions in leachates from the soil of 88-92%. Organoclay addition prevented interference with cement hydration. Faschan *et al.* (1993) examined non-ionic organic partitioning onto 5 different organoclays for nitrobenzene and 1,2 dichlorobenzene and found that the extent of partitioning of the contaminant onto the organoclay could be expressed mathematically (Section 3.3.7). Shin and Juan (1995) found similar results, however organoclays are often criticised for their high specificity, necessitating the development of modified clay for a particular application.

Uribe *et al.* (2002), however, found that pH influenced the adsorption behaviour of organoclays and that desorption of phenol and chlorophenol was promoted by high pH found in cement. Thus caution must be exercised when choosing modified clays for sorption of organic compounds prior to or during combination in cementitious systems.

5.4.2 Non-aromatic compounds

Significantly less work has been reported on the treatment of non-aromatic contaminants, with much of the research based on aliphatic alcohols. Limited work is also reported for trichloroethene.

The effects of primary aliphatic alcohols such as methanol on hydration of alite and belite pastes are not clear (Sora *et al.,* 2002). Primary aliphatic alcohols such as methanol may react with calcium hydroxide to give calcium methoxone however alternative this is not universally agreed.

Acetate groups of ethylene vinyl copolymer undergo alkaline hydrolysis in cement to form calcium acetate ($Ca(CH_3COO)_2$) according to Silva *et al.* (2002). Janotka *et al.* (1996) considered that complex structures can be formed in hydrating cement containing styrene-acrylate dispersants, which also involve portlandite.

Eaton *et al.* (1987) examined the interactions between ethylene glycol and cement. Ethylene glycol (EG) is water soluble, and because of its OH groups, is capable of extensive hydrogen bonding. The formation of hydrogen bonds between the contaminant and the cement phases is one of the mechanisms suggested to be influential in set retardation. The authors concluded that EG, and other large organic molecules, associate themselves with the C-S-H rather than with ettringite or $Ca(OH)_2$.

The effects of EG on the physical properties of PC were examined by Sheffield *et al.,* (1987) at organic to cement weight ratios of 1:5, 1:10 and 1:25. The authors found that at the moderate and high concentrations, the compound inhibited the set of PC and significantly decreased its compressive strength. EG leached from the samples readily, with recoveries of over 80% recorded.

Other workers reported that EG forms small cubic crystals thought to be a complex of EG and C_3A (Chou *et al.,* 1986). Most abnormal setting phenomena can be traced to chemical reactions involving the aluminates such as C_3A in the early hydration period (Lea, 1971), and Eaton *et al.* (1987) suggest that EG may sorb to the C_3A via hydrogen bonding processes.

Ethylene glycol has also been shown to interfere with the hydration of C_3S. Chou *et al.,* (1986) used transmission electron microscopy to examine the interaction of EG with the various hydration phases of cement. They found that it combined with calcium hydroxide crystals. The formation of C-S-H is thought to involve the deposition of silicate anions on the surface of the preformed calcium hydroxide lattice (Birchall and Thomas, 1984). Eaton *et al.,* (1987) hypothesised that the presence of EG interfered with the deposition of C-S-H by interacting with its precursor, calcium hydroxide.

El Korchi *et al.,* (1986) examined the effects of methanol and trichloroethene on the microstructure of cement-stabilised hazardous wastes. They found that the growth of ettringite crystals had been stunted in the presence of methanol, whilst trichloroethene had the opposite effect and resulted in the excess formation of ettringite. The authors noted that the retardation effect of organics on the hydration correlated approximately with the number of hydroxyl, carboxyl, and carbonyl groups in the organic molecules, accounting for the minimal negative effects of trichloroethene.

The above hypothesis correlates with the suggestion of Eaton *et al.* (1987) that compounds with the ability to form hydrogen bonds are likely to interfere with the normal hydration of cement. Minorcha *et al.* (2003) investigated a range of organic compounds and showed that trichloroethene was also responsible for influencing the efficacy of fixation of metals in the solidified product.

The groups of additives that have been used to address the problems associated with aromatic organics, have also been used with their non-aromatic counterparts in S/S systems. In the seven formulations examined by Cote *et al.,* (1990), bis(2-chloro-ethyl) ether showed total containment factors ranging from 3.3 to 5.6, with the best containment in formulations E (proprietary, Portland cement Type II, PFA), F (activated carbon, Portland cement, Type II), and G (Hydrated lime, Portland cement Type II, silica fume). In all the formulations examined, physical containment mechanisms accounted for between 33-57% of the total containment of the compound within treated samples.

5.4.3 Volatile organic compounds

Volatile organic compounds (VOCs) present a significant challenge to the S/S of a contaminated soil or waste, as the temperature elevations encountered during the hydration of cement and lime frequently assists in the volatilisation of volatile or semi volatile compounds. These compounds frequently occur alongside contaminants that are well suited to S/S remediation. Volatile organic compounds interfere with setting and can be emitted during mixing subsequent solidification (Arocha *et al.,* 1996). Research on S/S of volatile organic contaminants has focussed on the influence of additives to reduce the volatilisation of organic contaminants from contaminated soil and waste during S/S.

Arocha *et al.,* (1996) examined the feasibility of various binder systems and additives in the reduction of VOC emissions during S/S treatment of contaminated soil. They noted that when PC based S/S methods are used in the remediation of contaminated soil, a minimum of 0.4 water/cement ratio must be available for PC hydration and mixing (Conner, 1990). If the original soil water content is less than the PC requirement, and water is added, a significant amount of the adsorbed VOCs may be released into the air, since water displaces VOCs from adsorption sites. Thus, adsorbents may need to be used to counteract VOC desorption, if an increase in water content is required.

Arocha *et al.* (1996) also measured retention of toluene by PC and sodium silicate systems using rice hull ash and shredded tyre particles. The authors found that the immobilisation of toluene was best when shredded tyre particles were encapsulated with a sodium silicate binder system. They noted that the product was an economic and environmentally safe soil-like material.

In other cases, organoclays have been used to reduce the volatilisation of organic compounds during S/S treatment. Faschan (1992) examined the ability of organoclays to reduce the volatilisation of nitrobenzene (NB) and 1,2-dichlorobenzene (DCB) from cement-solidified samples. The results indicated that the incorporation of organoclays reduced the volatilisation caused by cement-based solidification of NB and DCB to 1/6 and 1/10 of their original values respectively (DCB is a more volatile compound than NB). Leaching results were also improved compared with cement-alone samples. The amount of DCB remaining in the samples containing organoclays being approximately three times that of samples using cement alone (Faschan, 1992).

In other cases, where unacceptably high concentrations of VOCs are released during treatment, the use of an extraction hood and carbon filter trap is common, but this represents secondary rather than primary treatment and may not be desirable at sensitive sites, for example with housing in close proximity.

5.5 Summary

Stabilisation/solidification of organic-contaminated soil and waste has been regarded with scepticism in the UK in the past. Organic compounds may vary considerably in their properties and many, such as those that are volatile, will be difficult to immobilise in cement or lime based binder systems. However, an increasing body of research, supported by field evidence, can be used to show that organic contaminants can be successfully treated by inorganic S/S systems.

Additives, to adsorb/retain organic components in S/S treated products may also be used. Many of these additives are waste products of industrial processes themselves. As with inorganic compounds, characterisation of materials presented for S/S will ensure that optimal binder systems are used to treat organic contaminants. Key conclusions from this chapter include:

- when dealing with organic contaminants in the S/S process, it is important to be aware that they may interfere with the hydration and setting process of cementitious systems;
- the retarding effect of organics on the hydration of cement paste has been correlated with the number of hydroxyl, carboxylic, and carbonyl groups in the organic molecules, since the ability to form hydrogen bonds with cementitious constituents is thought to be a pre-requisite for interference in hydration mechanisms;
- as a rule of thumb, compounds that are volatile, water soluble, and have pKa below 12 are likely to readily leach from cement or lime-based binder systems;

- the use of additives may improve the immobilisation of organic contaminants in S/S waste forms;
- additives such as activated carbon, shredded tyre particles and organoclays (sorbents) can increase the chemical containment of the contaminant; and
- additives such as silica fume and fly ash can improve the physical containment of organic compounds by reducing waste form porosity and permeability.

REFERENCES

Al-Tabbaa, A. and Evans, C.W. (1996). In-situ Treatment of Contaminated Ground using Soil Mixing. Research Development Article. *Ground Engineering* 29 (7), p. 37.

Al-Tabbaa, A. and Evans, C.W. (1998). Pilot In-situ Auger Mixing Treatment of a Contaminated Site: Part 1. Stability Study. *Proc. Institution of Civil Engineers* 131, pp. 52-59.

Arafat, H.A., Hebatpuria, V.M., Rho, H.S., Pinto, N.G., Bishop, P.L. and Buchanan, R.C. (1999). Immobilization of Phenol in Cement-based Solidified/Stabilized Hazardous Wastes using Regenerated Activated Carbon: Role of Carbon. *Journal of Hazardous Materials* B70, pp. 139-156.

Arocha, M.A., McCoy, B.J. and Jackman, A.P. (1996) VOC Immobilisation in Soil by Adsoption, Absorption and Encapsulation. *Journal of Hazardous Materials* 51, pp. 131-149.

Bates, E. R. and Lau, M. C. (1995) Full Scale Stabilisation of Soils Contaminated with CCA and PCP at the Selma Pressure Treating Site, Selma, Ca. In: *Air and Waste Management Association Proceedings, 88th Annual Meeting* Vol. 15, San Antonio, TX, 95-RP130.02.

Bates, E.R., Sahle-Demessie, E. and Grosse, D.W. (1999) *Solidification /Stabilization for Remediation of Wood Preserving Sites: Treatment for Dioxins, PCP, Creosote and Metals*. Portland Cement Association Publication RP371, Skokie, Il.

Bates, E.A. (2003) Personal Communication.

British Cement Association. (2001) *Cement-based Stabilisation and Solidification for the Remediation of Contaminated Land. Findings of a Study Mission to the USA*. British Cement Association Publication 46.050.

Birchall, J.D. and Thomas, N.L. (1984). The Mechanism of Retardation of the Setting of OPC by Sugars. In: Glasser, F.P. (Ed*) The Chemistry and Chemically-Related Properties of Cement*. British Ceramic Proceedings, No. 35, pp 305-315.

Cioffi, R., Maffucci, L., Santoro, L and Glasser, F.P. (2001) Stabilisation of Chloro-Organics using Organophilic Bentonite in a Cement-Blast Furnace Slag Matrix. *Waste Management* 21, pp. 651-660.

Construction Industry Research and Information Association (1995) *Remedial treatment of contaminated land. Ex-situ remedial methods for soils, sludges and sediments,* Volume VII. Construction Industry Research and Information Association Special Publication 107.

Chou, A.C., Eaton, H.C., Cartledge, F.K and Tittlebaum, M.E. (1986) A TEM Study of the Interactions Between Certain Organic Hazardous Wastes and Type I Portland Cement. In: *8th International Congress on the Chemistry of Cement*, Rio de Janerio, Brazil, September.

Conner, J.R. (1990) *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York.

Cote, P.L., Caldwell, R, and Chao, C.C. (1990) Physical and Chemical Containment of Organic Contaminants in Solidified Wastes. *Waste Management* 10, pp. 95-102

Eaton, H.C., Walsh, M.B., Tittlebaum, M.E., Cartledge, F.K. and Chalasani, D. (1986) Organic Interference or Solidified/Stabilized Hazardous Wastes. *Environmental Monitoring and Assessment* 9, pp. 133-142.

El Korchi, T., Melchinger, K., Kolvites, B., and Gress, D. (1986) The Effect of Heavy Metals and Organic Solvents on the Microstructure of Cement Stabilized Hazardous Waste. In: *Proceedings of the 8th International Conference on Cement Microscopy*, April Orlando, Florida. pp. 132-144.

Faschan, A. (1992). The Use of Organoclays to Reduce Organic Waste Volatilisation during Solidification, *Hazardous Waste and Hazardous Materials* 9, 4, pp. 45-354.

Faschan, A., Tittlebaum, M. and Cartledge, F. (1993) Nonionic Organic Partitioning Onto Organoclays. *Hazardous Waste and Hazardous Materials* 10, pp. 313-322.

Franz, M., Arafat, H.A. and Pinto, N.G. (2000) Effect of Chemical Surface Heterogeneity on the Adsorption Mechanism of Dissolved Aromatics on Activated Carbon. *Carbon* 38 (13), pp. 1807-1819.

Gitipour, S., Bowers, M.T. and Bodocsi, A. (1997) The Use of Modified Bentonite for Removal of Aromatic Organics from Contaminated Soil. *Journal of Colloid and Interface Science* 196, pp. 191-198.

Hanna, R.A., Barrie, P.J., Cheeseman, C.R., Hills, C.D., Buchler, P.M. and Perry, R. (1995a) Solid-State Si-29 and Al-27 NMR and FTIR Study of Cement Pastes Containing Industrial Wastes and Organics. *Cement and Concrete Research* 25, pp. 1435-1444.

Hanna, R.A., Cheeseman, C.R., Hills, C.D., Sollars, C.J., Buchler, P.M. and Perry, R. (1995b) Calcium Hydroxide Formation in Cement Solidified Industrial Wastes. *Environmental Technology* 16, pp. 1001-1008.

Hills, C.D., Sollars, C.J. and Perry, R. (1995) A Calorimetric Study of the Effect of Organic Compounds on the Initial Behaviour of Cement-Based Solidified Wastes. *Waste Management and Research* 13, pp. 21-36.

Janotka, I, Madejova, L., Stevula, D.M. and Frt'alova. (1996) Behavour of $Ca(OH)_2$ in the presence of set Styrene-acrylic Dispersion. *Cement and Concrete Research* 26, pp.1727-1735.

Lea, F.M. (1971) *The Chemistry of Cement and Concrete*. Chemical Publishing, New York.

Minocha, A.K., Jain, N, Varma, C.L. (2003) Effect of Organic Materials on the Solidification of Heavy Metal Sludge. *Construction and Building Materials* 17, pp. 77-81.

Montgomery, D.M., Sollars, C.J. and Perry, R. (1991) Optimisation of Cement Based Stabilisation/Solidification of Organic-Containing Industrial Wastes using Organophilic Clay. *Waste Management and Research* 9, pp. 21-34.

Mulder, E., Brouwer, J.P., Blaakmeer, J. and Frenay, J.W. (2001) Immobilisation of PAH in Waste Materials. *Waste Management* 21, pp. 247-253.

Pollard, S.J., Sollars, C.J. and Perry, R. (1990) The Reuse of Spent Bleaching Earth for Stabilisation/Solificiation of Mixed Waste Streams. *Environmental Technology* 11, pp. 1113-1122.

Rho, H., Arafat, H.A., Koutntz, B., Buchanan, R.C., Pinto, N.G. and Bishop, P.L. (2001) Decomposition of Hazardous Organic Materials in the Solidification /Stabilisation Process Using Catalytic-Activated Carbon. *Waste Management* 21, pp. 343-356.

Sansom, M.R. and Jardine, F.M. (1997) CIRIA's Case Study Demonstration Programme: Remedial Technologies for Treating Contaminated Land. In: *1st BGS Geo-environmental Engineering Conference*. Thomas Telford, pp. 490-495.

Sheffield, A, Makena, S, Tittlebaum, M, Eaton, H, and Cartledge, F. (1987) The Effect of Three Organics on Selected Properties of Type 1 Portland Cement. *Hazardous Waste and Hazardous Materials* 4, pp. 273-286.

Shin, H.S. and Jun, K.S. (1995) Cement-Based Stabilization/Solidification of Organic Contaminated Hazardous Wastes using Na-Bentonite and Silica-Fume. *Journal of Environmental Science and Health* A30, pp. 651-668.

Silva, D.A., Roman, H.R. and Gleize, P.J.P. (2002) Evidences of Chemical Interaction between EVA and Hydrating Portland Cement. *Cement and Concrete Research* 32, pp. 1383-1390.

Sora, I.N., Pelosato, R., Botta, D. and Botelli, G. (2002) Chemistry and Microstructure of Cement Pastes Admixed with Organic Liquids. *Journal of European Ceramic Society* 22, pp. 1463-1473.

Rteil, A.A., Hamad, B.S. and El-Fadel, M. (2003) Effect of used Engine Oil on the Properties of Fresh and Hardened Concrete. *Construction and Building Materials* 17, pp.311-318

Thomas, N. L. and Double, D.D. (1981) Calcium and Silicon Concentrations in Solution during the early Hydration of Portland Cement and Tricalcium Silicate. *Cement and Concrete Science* 11, pp. 675-687.

Trussell, S. and Spence, R.D. (1994) A Review of Solidification/Stabilisation Interferences. *Waste Management* 14, pp. 507-519.

Tuncan, M. (1996). Pilot Field Study of Petroleum Contaminated Wastes Stabilization. In*: Environmental Technology, Proceedings of the 3rd International Symposium*. (Eds. Fang, H.Y. and Inyang, H.I.) Technomic Press, Lancaster, Pa.

Uribe, A, Bishop, P.L. and Pinto, N.G. (2002) The Influence of pH and Temperature Changes on the Adsorption Behaviour of Organophilic Clays used in Stabilisation/Solidification of Hazardous Wastes*. Journal of Environmental Engineering and Science* 1, pp. 123-133.

United States Environmental Protection Agency. (1993*) Solidification/stabilisation and its Application to Waste Materials*. Report number EPA/530/R-93/012. pp. 2-59.

United States Environmental Protection Agency. (2000) *Solidification/Stabilisation use at Superfund Sites*. EPA-542-R-00-010.

Vipulanandan, C. (1995) Effect of Clays and Cement on the Solidification/Stabilisation of Phenol-Contaminated Soils. *Waste Management* 15, pp. 399-406.

Vipulanandan, C. and Krishnan, S. (1993) Leachability and Biodegradation of High Concentrations of Phenol and O-cholorophenol*. Hazardous Waste and Hazardous Materials* 10, pp. 27-47.

Zvica, V. and Bajza, A. (2001) Acid Attack of Cement Based Materials – A Review. Part 1. Principles of Acid Attack. *Construction and Building Materials* 15, pp. 331-340.

Young, D.F. (1972) A Review of Mechanisms of Set Retardation in Portland Cement Pastes Containing Organic Admixtures. *Cement and Concrete Research* 2, pp. 415-433.

6 SITE-SPECIFIC APPLICATION OF S/S

6.1 Introduction

Once stabilisation/solidification technology has been selected as the remediation method for contaminated soil or waste, optimisation of the process is an essential step in the production of a high quality product. This chapter deals with the factors that must be considered in the selection of S/S, and discusses the various methods available.

6.2 Effectiveness of S/S

The effectiveness of S/S in practice is likely to depend upon:

- good characterisation of the material to be treated;
- selection of the most appropriate binder formulation;
- effective contact between the contaminants and treatment reagents;
- a high degree of chemical and physical consistency of the feedstock;
- the use of appropriate mixing equipment and good working practice;
- control over external factors such as temperature, humidity, and the amount of mixing since these affect setting, strength development and durability of the product; and
- the absence (or control) of substances which inhibit the S/S process and affect the product properties.

However, optimisation of S/S processes for a particular site is complicated by the fact that it is not possible to model all of the dynamic processes that may occur in the field (CIRIA 1995a).

Reluctance of many clients to choose S/S as a remediation method is frequently due to the lack of information on where and how S/S has been used successfully (and unsuccessfully) in the past. In the UK, this problem is currently being addressed, and a number of organisations are working to improve information dissemination with respect to S/S technology, including the CASSST (www.cassst.co.uk) and STARNET (www-starnet.eng.cam.ac.uk) initiatives. A European project involving UK participants compiled a database of published data on S/S (Stegemann and Buenfeld, 2002) involving 1506 literature references and information on the properties of 7953 cement-based products containing impurities.

Outside the UK, particularly in the USA, a large amount of work on the application of S/S to contaminated soil has been undertaken. Figure 6.1 illustrates the percentage of contaminated soil treated by various remediation techniques under the Superfund programme. It can be seen that S/S is one technology amongst a number of routinely used remediation techniques. Appendix 6 lists previous applications of S/S treatment.

Metal-contaminated sites have been treated almost exclusively by S/S. However, much work has been done to expand the usefulness of S/S beyond metal-only contaminated sites (e.g. Arocha *et al.,* 1996; Bates *et al.,* 1999).

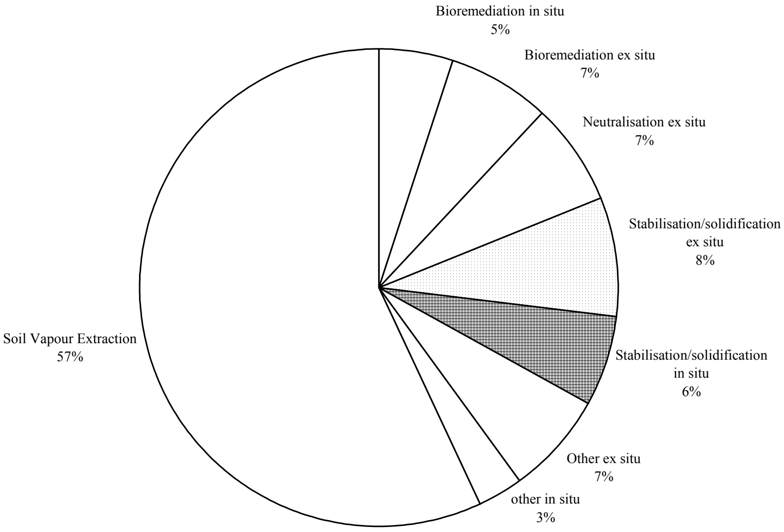


Figure 6.1: Superfund remedial actions by technology type (after USEPA, 2001)

The USEPA reported that at Superfund sites, S/S has been implemented (or is currently planned for use) in 183 instances, 137 of which were *ex-situ*, with the remaining 46 being *in-situ* (USEPA, 2001). The binders used in Superfund projects included cement, phosphate, lime, pH buffering agents, proprietary additives and other inorganic and organic components, including polymers, iron salts, silicates and clays (Table 6.1).

Table 6.1: Binders and reagents used for S/S projects (after USEPA, 2000; 2001)

Binder or reagent	Number of instances of use
Cement	50
Proprietary reagents	22
Other inorganic	20
Phosphate	14
pH controls*	12
Other inorganic	6
Fly ash	10
Lime	10
Sulphur	4
Asphalt	4

*pH buffering and adjustment agents, such as sodium hydroxide are sometimes added during stabilisation processes to decrease post-treatment contaminant leachability.

At many contaminated sites, the range of contaminants present may prove difficult to treat. In some cases, the use of ‘treatment trains’ may be practicable, where two or more remediation processes are used in sequence to achieve the desired objectives. The use of treatment trains is more common in the USA, where disposal of contaminated material to landfill is significantly more expensive than in the UK. In Table 6.1, treatment trains were used in several cases (which is why the total number of instances of use in column two exceeds the number of projects documented).

Table 6.2 shows the type of contaminants for which S/S has been used in the USA (USEPA, 2000). The data shows that S/S has been used predominantly for the treatment of metals, and combinations of metals and organics, with other uses being relatively minor. The low incidence of use in the remediation of organic-only contaminated soils has risen from concerns relating to volatilisation of organics, and their role in impeding cement and other binders setting. These issues are discussed in greater detail in Chapter 5.

Table 6.2: Contaminant types treated by S/S (after USEPA, 2000)

Contaminant type	Number of projects (%)
Metals only	92 (56%)
Organics only	10 (6%)
Radioactive metals	3 (2%)
Radioactive metals and metals	4 (2%)
Metals and organics	50 (31%)
Radioactive metals and organics	1 (1%)
Non-metals only	2 (1%)
Organics and non-metals	1 (1%)

The Superfund statistics have been recently updated by the USEPA for the period 1982 to 2002 (USEPA, 2004) and indicate the use of S/S as follows:

	Completed	Not completed	Total
Ex-situ	105	52	157
In-situ	33	15	48
			205

In contrast to the data published in 2000, this shows a rising trend in S/S, with 24% of all source treatment projects using S/S, as opposed to 14% in Figure 6.1.

6.3 Treatability Studies

As S/S does not remove or destroy the contaminants present, the selection of binders must address:

- compatibility between the binders and the materials being treated (Chapter 3);
- the presence of chemicals which interfere with the setting and durability of the product (Chapters 4 and 5); and
- anticipated ground and groundwater conditions over the long-term.

Because of the variable nature of contaminated soil encountered, bench-scale testing to evaluate the effectiveness of potential binder systems is an essential pre-requisite to S/S in the field. The nature of contaminants may vary across a site requiring remediation and this may mean that more than one binder formulation may be required for use during an S/S operation. Furthermore, the effects of otherwise unforeseen contaminant/binder interactions can be identified during treatability studies. Appendix 7 gives mix design criteria and their engineering implications.

It is essential that the objectives of S/S remain clear during the treatability study. These objectives will allow optimised pre-treatment steps and binder-formulations that are cost effective to be developed for a particular contaminated site.

Specific objectives of a S/S-specific treatability study may include:

- determination of the most economical mix design;
- identification of handling problems such as oversize material;
- identification of whether volatile emissions are a concern;
- assessment of physical and chemical uniformity of the waste; and
- determination of volume increase associated with the S/S process (United States Army Corps of Engineers, 1995).

Treatability studies may be divided into three stages: the desk study, the laboratory study, and the field trial.

6.3.1 Desk study

The desk study may be used to identify suitable mix designs by considering factors such as soil types and the types of contaminant present. It can also identify variable site conditions and likely quantities or depths of material that may also influence the design process. This should reduce the number of mix designs going forward to the laboratory study stage to a manageable level. For example, the use of lime as a hydraulic binder will not be appropriate on soils with a very low clay content, and cement would not be suitable for treatment of wastes with high concentration of organic compounds without the presence of a suitable binder additive. Appendix 8 identifies the environmental considerations of carrying out S/S treatment. Appendix 9 gives guidance on typical COSHH assessment scenarios for handling the various materials associated with S/S.

6.3.2 Laboratory study

The importance of bench-scale testing of binder systems to enable comparison and evaluation of the optimum mix should not be underestimated. Following bench-scale testing, it should be possible to demonstrate an understanding of the factors that affect the performance of the mix and have confidence that the proposed approach to full-scale treatment is suitable.

The US Army Corps of Engineers (USACE, 1995) noted that sampling, handling and waste characterisation must be carefully considered so that a treatability study is run on material that is representative of the soil to be treated. Currently, the issue of which tests best represent on-site conditions is a matter of debate. Nevertheless, a number of standard (and non-standard) testing procedures can be employed to evaluate the optimum full-scale treatment option. Some examples of commonly used chemical testing methods are given in Table 6.3.

Table 6.3: Chemical test methods (after Weitzman *et al*., 1990)

Total waste analysis
Metals by inductively coupled plasma spectrometry or atomic absorption
Organics by gas chromatography (GC) and mass spectrometry (MS)
Total organic carbon
Loss on ignition
pH
Fourier transform infrared spectra (FTIR)
Differential scanning and thermal gravimetric analysis

When deciding which tests to use, it is important to consider the short and long term environmental conditions that the material may be subjected to and any performance criteria that the material is required to meet. Test methods can then be chosen that are appropriate to the particular material and application. ENV 12920 (1998) provides a draft methodology for the determination of the leaching behaviour of a waste under specified conditions i.e. in a disposal or utilisation scenario, within a specified time period. It is designed to ensure that waste specific properties and environmental conditions are taken into account.

In the past standard leaching test methods have been used, which were not necessarily appropriate for testing all materials. One of the most commonly used tests in the USA (and elsewhere) has been the Toxicity Characteristic Leaching Procedure (TCLP), which involves grinding the sample and exposing it to an aggressive, low pH leachant. This characteristic test was widely used to define the nature of the contaminated materials and to propose a method of treatment. Many argued, however, that such a test is unrepresentative of many disposal situations, particularly because in many cases S/S remediation of contaminated land is used as an alternative to landfill, and therefore the S/S waste form is less likely to be exposed to low pH leachant. A number of legal challenges have since led to the Science Advisory Board (SAB) criticising the widespread application of the TCLP test. It further recommended that leach tests should reasonably relate to conditions that govern leaching mechanisms under actual disposal conditions (USEPA, 1999).

In Europe over the past decade a series of leaching tests have been developed to link testing with ultimate disposal scenario (van der Sloot *et al*., 2002). These CEN leaching tests are discussed in more detail in Chapter 8. The Network on Harmonization (www.leaching.net) was also established and has conducted a thorough review of leaching tests and inter-laboratory comparisons of some of these CEN tests (van der Sloot *et al*., 1997).

6.3.3 Site trial

A number of treatability trials and case studies have been reported in the literature. These include Barker *et al.* (1996), Carey and Nagelski (1996), Bates *et al.* (1999) and Evans and Al-Tabbaa (1997). In the latter work treatability trials resulted in the selection of 7 mix designs based on PFA, lime and bentonite clay in the following proportions (by mass):

Soil	75-84%	Cement	1-7%
PFA	0-16%	Lime	0-0.5%
Bentonite	0-1%	Water	3-13%

The authors reported on a comparison between the unconfined compressive strength of stabilised made ground and granular soils, and showed that the latter soils achieved higher strengths for the same mix, and that a minimum cement to PFA ratio of 2.5 to 8 by weight was required to achieve the 28 day strength criteria of 350kPa for both soil types.

A correlation made during this work indicated that the use of 'model' laboratory stabilised soils enabled predictions to be made during laboratory-scale treatability studies for actual site specific contaminated soils (Evans, 2003).

Bates *et al.* (1999) summarised the treatability study data for 4 sites in the USA, contaminated with residues from wood preserving operations, including arsenic and creosote contaminants. Table 6.4 gives data on the mix components investigated for these sites.

In the treatability studies, 2 or 3 rounds of testing comprising 3 to 6 formulations each round were conducted for each specific site before formulations meeting the remedial targets were identified. The authors noted that valuable information was gained from the formulations that failed, most commonly on leachability of pentachlorophenol and permeability.

Table 6.4: Trial formulations for contaminated sites (after Bates *et al.* 1999)

Formula (w/w)	**Site 1**	**Site 1**	**Site 2**	**Site 2**	**Site 3**	**Site 4**
Soil	1	1	1	1	1	1
PC (Type 1)	0.2		0.1	0.2	0.08	0.08
PFA (Type F)	0.1		0.1	0.1		
Activated Carbon	0.02		0.02	0.05		
PA1				0.02		
PA2		0.02				
PA3		0.06			0.12	0.12
Water added			0.15	0.2		
Dilution factor	1.32	1.26	1.24	1.35	1.2	1.2

PA = proprietary additive

The USEPA (1993) reported a number of trials, involving S/S of inorganic and organic contaminants and identified uncertainties associated with scale-up from bench-scale to site implementation. This was illustrated with reference to a stabilisation operation involving a sludge lagoon treated with lime. Approximately 3 weeks after treatment, the strength of samples (which should have been ≥25 psi (172 kPa)) ranged between 2.4 and 10 psi (16.5 and 68 kPa).

TREATABILITY TRIAL CASE STUDY

The number of S/S operations carried out in the UK to date is limited. Nevertheless, from those remedial actions that are cited in the literature, there is enough information to be able to present an example of a treatability study from a well-executed remedial action in Scotland. The following case study is from work described by Barker *et al.,* 1996 and CIRIA, 2000.

Treatability Trial for *In-situ* Remediation-Ardeer, Scotland

This case study describes the laboratory and field trials carried out to select the optimum remediation process for a contaminated site owned by ICI in the UK.

The remediation of the Ardeer site in Scotland is an excellent example of good practice, since the site had been fully characterised, and information collected at every stage of the remediation process. The site was an unlined landfill site, in operation until 1993. Monitoring investigations revealed that the volume of groundwater discharging into the Garnock estuary from the area of the landfill was about 15 000 litres per day. The groundwater beneath the landfill was found to be acidic with elevated metal concentrations and formed an attenuated plume of contamination flowing in the direction of the estuary. The groundwater quality up-gradient of the landfill was found to be good. Information on the quality of groundwater down-gradient was not available.

Consequently, the risk assessment indicated that there was a long-term, low-level risk to the flora and fauna likely to be in or on the mud flats. S/S was chosen as a remedial option because it was capable of neutralising the low pH, and immobilising metals in the former landfill.

A number of cement-based slurry compositions were bench-tested. Setting time, strength development and permeability were measured, and two leaching tests were carried out; the acid neutralisation capacity (ANC) test and a French leaching test, NFX31211 (Barker *et al.,* 1996). Three potential mixes were selected to stabilise the waste using the following binder reagents:

- lime as a neutralisation agent;
- OPC as a hydraulic binder to provide an unconfined compressive strength (UCS) of at least 100kPa at 7days; and
- PFA as a filling agent to stabilise of the slurry and improve leaching performance.

Following bench-scale testing and preliminary site trials, 10% of the site was used for a full-scale site trial using the Colmix process with mixing by multiple, overlapping counter-rotating augers. The binder slurry was introduced into the soil at a rate of 230 litres per metre of column for a 4 x 500mm column. When the required depth was reached, the augers were rotated in the opposite direction and slowly withdrawn to further mix and compact the treated column.

After the columns had been prepared, the pH was measured 1 metre from the top, at the midpoint and 1 metre from the bottom of the column. This was carried out for the first 20 columns constructed to confirm that the required pH (greater than or equal to 9.0) had been achieved.

In addition, samples were taken daily from a completed column, using the auger to re-drill to mid-column height. The rig was then lifted without rotation and three samples were taken from the auger blades. These samples were compacted in layers in a similar manner to concrete cubes and tested. The acceptable limits for these tests were:

pH at time of sampling	>9
UCS at 7 days	> 100kPa
UCS at 28 days	> 200kPa
ANC at 14 days	> 2meq. H^+/g at pH 9
Permeability	<1 x 10^{-7} ms $^{-1}$

Two lab-cured samples were taken every 5th and 6th day of the operation, for testing at 28 days of age for permeability and leachability. At least 28 days after the completion of the site trial, 100mm diameter samples were obtained from the stabilised waste and tested as follows:

UCS	> 200kN/m^2 (70 samples)
ANC	> 2meq/H^+/g at pH 9, (4 samples)
Permeability	1 x 10^{-7} ms $^{-1}$, (4 samples)

6.4 Application of Binder

Binders may be added to a soil or waste in a number of ways, although the common objective of all methods is to produce a system whereby the contaminated medium and the binder are consistently and intimately mixed.

The application of binders to contaminated soil can be undertaken in two ways: *ex-situ*, where contaminated material is removed from its original location, treated and replaced or transported elsewhere; or *in-situ*, where the mixing of waste and reagent occurs in place without prior excavation.

Cement or lime can be added in either a dry or a slurry form. When added dry, the binders rely on the water present in the soil/waste to enable hydration reactions to occur. Alternatively, the binder may be prepared as liquid slurry, which can be pumped from an *in-situ* mixing device, such as an auger system, whilst being mixed with the contaminated material. Al-Tabbaa and Evans (1999) found that dry *in-situ* soil mixing required more vigorous mixing compared to wet soil mixing to achieve the same level of homogeneity of the soil-grout material.

6.4.1 Binder/Reagent delivery

Binder/reagent delivery systems are often system built for a specific site. When multiple components are required for the binder system they may be blended or part blended off site or blended on-site. Table 6.5 details a range of delivery/transfer systems used for lime.

Figures 6.2 and 6.3 show a number of silos for a multi-component binder system formulated for S/S of an oil sludge lagoon. Reagent delivery will invariably involve a weigh batching operation to ensure correct proportioning of reagents.

Figure 6.2: Reagent silos/batching equipment for a multi-component binder (Photograph courtesy of Colin Hills)

Figure 6.3: Close-up of the above illustrating the reagent delivery systems (Photograph courtesy of Colin Hills)

Table 6.5: Examples of binder transfer equipment available
(from Buxton Lime Industries, 1999)

EQUIPMENT	BINDER TYPE	COMMENTS
Skip hoists	Granular and lump grade quicklime	Can be used with all grades, but more suitable for pieces larger than 100mm.
Elevators	All grades of quicklime	Belt and bucket type or chain and bucket have been used successfully.
Drag link conveyors	Granular and fine grain quicklime	They may be employed quite successfully for horizontal or inclined transfer.
Conveyor belts	Granular and lump grade quicklime	Suitable for transferring material horizontally and on an upwards slope providing the angle of inclination does not exceed 17º. It is possible to transfer at a steeper angle than this if specialised types of conveyor belt are employed.
Vibrating troughs	Finer grades of lump quicklime (<40mm) and granular quicklime	May also be used with coarser grades of fine quicklime where there is a slight downhill slope between the storage bunker and the use point. The troughs should be totally enclosed.
Screw conveyors	Mainly fine quicklime and hydrated lime and cement	Screw conveyors should be totally enclosed. If measurement of quantity is needed, tubular conveyors should be employed, otherwise U-trough conveyors may be equally suitable. .
Air conveyors	Hydrated lime and cement	The quantity of air required for fluidisation depends on the area of the conveyor, its slope and the quantity of powder to be conveyed. The flow of the product should be controlled by a positive cut-off at the discharge end of the conveyor.
Pneumatic transfer	Quicklime, hydrated lime and cement	This can be achieved using a Rootes type of blower as a source of air, in conjunction with a rotary blowing seal. Alternatively, proprietary units are available which operate using a pressurised vessel that transfers batches of product through a suitably designed pipeline. Pneumatic transfer of pieces of quicklime up to 50mm in size has been achieved. In practice however, the method is much more suitable for transferring the granular and fine quicklime grades and powder products.
Powder pumps	Hydrated lime and cement	These have been used successfully for conveying through a pipeline at rates between hundreds and thousands of kilograms per hour. Rather smaller quantities of air are used than with fully pneumatic systems.

6.5 *Ex-Situ* Treatment Techniques

Despite the apparent complexity of operational requirements, *ex-situ* methods can be divided into three broad groups:

- direct mixing;
- in-drum processing; and
- plant processing.

Tables 6.6 and 6.7 show some of the key issues when considering use of an *ex-situ* application method at a particular site. They focus in particular on plant processing.

Ex-situ treatment generally enables good control over reagent delivery and mixing. Operations of this type are tolerant of ground obstructions as the soil is excavated before treatment. *Ex-situ* plant may be included as a process in a treatment train at a particular site (e.g. for stabilisation of fine residues following soil washing). Alternatively plant may be located at a central location to treat material from different sources to minimise plant-operating costs. Figures 6.4 and 6.5 show mobile plant used to treat contaminated soil.

As *ex-situ* treatment requires excavation of material, it is feasible to include a screening stage in the treatment train to improve the grading properties of the material. Figure 6.4 shows mobile screening and conveying plant.

Table 6.6: Examples of site requirements for mobile *ex-situ* S/S (after CIRIA, 1995a)

Site Requirements	Examples
Access	Suitable for plant delivery and any material movements or deliveries Height restrictions
Space requirements	Reagent storage. Pre-treatment, mixing and curing areas. Decontamination areas (for equipment and personnel). Disposal area for treated material.
Services	Water (for mixing, dust suppression, etc). Electricity supply (for process and support equipment). Diesel fuels for on-site generators. Telephone communications. Drainage.
Auxiliary equipment	Lifting and earth moving equipment, e.g. cranes, forklifts, front-end loaders. Decontamination equipment, e.g. steam cleaners, storage tanks, basins, plastic sheeting.

Table 6.7: Typical plant and equipment needs for *ex-situ* S/S (after CIRIA, 1995a)

Unit process	**Equipment type**	**Purpose**
Pre-treatment preparation	Crusher Screens Blending plant De-watering and drying plant	To optimise the particle size and/or handling characteristics of the feedstocks If moisture content exceeds that suitable for processing
Feeding	Feed hoppers Conveyors, etc. Weigh feeder	Reception, transfer and measurement of feedstocks.
Dosing mixing	Liquid / dry reagent tank / silos Mixers (e.g. pugmill, pan mixers, rotary drum, high energy)	Storage of feed and reagents prior to mixing. Mixing of contaminated soil with reagents.
Containment measures	Adsorption incinerator / unit for gaseous emissions Leachate collection systems Liquid-phase treatment system Bunded storage areas	Removal of volatiles, ammonia etc. that may be released during the S/S process. For leachates generated during curing. To treat contaminated water arising from dewatering or leachate from treatment process. To contain any leaks/spillages from reagent storage, generators etc.
Product storage / disposal	Pits/moulds Compacting equipment	Curing of treated material prior to removal from/or replacement at site. Required when material is to be placed for disposal or as reclamation material to predetermined standards
Testing	Physical / chemical	To ensure compliance with specification, on feedstock and products.

Figure 6.4: Mobile screening and conveying plant (Photograph courtesy of Colin Hills)

Figure 6.5: *Ex-situ* operation using mobile plant in centralised manner for treating petroleum-contaminated soils (Photograph courtesy of Keith Bradshaw)

The depth of required treatment may preclude use of *ex-situ* methods at some sites due to the space required to manoeuvre large quantities of material. Nevertheless, the choice of treatment is sensitive to site circumstances and *ex-situ* methods are versatile and widely used.

6.5.1 Direct mixing plant

With direct mixing plant the contaminated soil is generally excavated and transported to a designated area of the site. The soil is then spread out in layers, usually about 200-400mm thickness. The reactive ingredients are then spread on the surface, mixed-in using mechanical plant (essentially a tiller or rotavator) and then compacted and left to cure. Figure 6.6 shows one kind of dedicated direct mixing plant, often used in road construction, which is capable of treating 400mm layers of material at a time. Figure 6.7 shows grading of an S/S treated area.

Figure 6.6: **A direct mixing plant (rotovator)** (Photograph courtesy of the machine manufacturer, Wirth)

Figure 6.7: **Grading of recently S/S creosote contaminated soil** (Photograph courtesy of Portland Cement Association)

6.5.2 In-drum processing

In-drum processing involves the addition of binders to a contaminated material, which is stored in a drum or other suitable container. When mixing and setting are complete, the drum and its contents are disposed of in an appropriate manner. This may be a suitable decommissioning method where many drums of incompatible wastes are present. One drawback of this method is that it tends to be expensive due to high labour costs (CIRIA, 1995a). It has however been used in the UK for the disposal of low-level radioactive waste, fibrous asbestos and other hazardous wastes. Figure 6.8 shows an in-drum mixed S/S product containing the mixing paddle, with the drum removed for inspection.

Figure 6.8: In-drum S/S of radioactive waste processing (Photograph courtesy of BNFL)

6.5.3 Plant processing

Plant processing is probably the most commonly used method practised in the USA for the treatment of contaminated soil and is widely used for the treatment of hazardous waste streams at fixed installations. The contaminated material is excavated, pre-treated if necessary and mixed with binder in a plant specifically designed for the purpose (e.g. a pugmill mixer), or adapted from other applications (e.g. a concrete batching and mixing plant; CIRIA, 1995a). Following mixing the mixed binder may be discharged to a slurry pump and piped to the point of delivery or be conveyed using a series of belts.

In general, plant-processing techniques are preferred as they can be adjusted to ensure thorough mixing, and reduced environmental impact resulting from the release of particulates and vapours. The principle steps involved in plant processing are:

- pre-treatment (e.g. de-watering, screening, homogenisation of material to be treated, addition of modifier);
- mixing of waste with active ingredients. This may take the form of a pumped slurry, or a material that can be placed using standard earthworks equipment; and
- placement and curing.

Mixing plants may be permanent installations or may be mobile, allowing flexibility of use around a site or sites. Figures 6.9 and 6.10 show a mobile mixing plant and slurry pump.

Figure 6.9: Mobile mixing plant to slurry pump by conveyor (Photograph courtesy of Keith Bradshaw)

6.5.3.1 Pugmill mixers

Pugmill mixers are used to mix materials, usually one dry and one liquid. The amount of mixing is controlled by the rate of rotation of the two screw sections in the mixer, as well as the angle at which the adjustable paddles on the rotating sections are set. This allows the amount of mixing to be fine-tuned, making the pugmill mixer very versatile.

Figure 6.10: Mobile slurry pump (Photograph courtesy of Portland Cement Association)

Figure 6.11: Single shaft pugmill mixer with safety screen removed under inspection (Photograph courtesy of The British Cement Association)

The longer the retention time of the regents and soil in the pugmill mixer, the better the mixing achieved. To extend the retention time, two or more mixers can be stacked vertically. The speed of the mixing action can also be modified to achieve optimum conditions for the blending of binder and contaminated material. The position of the mixing paddles and flow rate of reagents and soil/waste through a pugmill mixer may also be adjusted to ensure the best mixing action.

Figure 6.12 shows a twin shaft pugmill mixer. Wear-resistant paddles rotate and mix binder and contaminated materials, which are loaded into one end of the mixer. The paddles are angled, which forces the mixture along the length of the set-up towards the exit-gate.

Figure 6.12: Twin shaft Pugmill mixer with exposed mixing blades during inspection (Photograph courtesy of British Cement Association)

6.6 *In-Situ* Treatment Technologies

In-situ treatment involves adding the binder/reagent to the contaminated soil/waste without removing the material from its original location. CIRIA (1995b) noted that *in-situ* S/S processes involving soil mixing have two main components; the S/S reagents and the mixing process used to apply the reagents to the contaminated material. Table 6.8 gives the typical requirements for consideration when utilising *in-situ* S/S operations.

The cost of *in-situ* operations is generally lower where large, deep site remediation operations are concerned. More recent developments in mixing plant allow controlled binder delivery and control over volatile or dust emissions (CIRIA 2001). Other considerations are the reduced levels of spoil that require handling, low levels of noise production, and the ability to treat contamination close to existing structures without the need to excavate or control groundwater.

A number of factors that may restrict the use of *in-situ* soil mixing techniques include (CIRIA, 1995b):

- oily sands and cohesive soils may reduce auger penetration rate and depth of operation (due to the excessive torque required);
- the potential for increase in bulk volume of treated materials, especially where soil conditions (oily sludges etc) require an increase in the quantity of additives used. Volume increases may restrict the use of the technology in areas where land contours may be seriously affected;
- debris, such as rocks and buried drums, would need to be excavated prior to mixing as they are likely to impede operations;
- very low ambient temperatures (below $-12^{o}C$) may cause freezing of the feed slurry before injection (although this could be heated);
- small sites may not accommodate the necessary equipment and batching plant;
- the bearing capacity of the ground must be sufficient to support the equipment;
- presence of underground services, buried foundations etc.;
- ability to apply active reagents in slurry form without plugging;
- ability to achieve adequate mixing throughout column depth and response to physical/chemical changes in the ground profile;
- quality control of the process;
- need to ensure alignment of columns and provide adequate overlapping to avoid forming pockets of untreated soil; and
- difficulty in determining the effectiveness of the method.

Stabilisation/solidification reagents may be directly introduced to contaminated soil and waste using a variety of techniques. These include:

- direct mixing plant;
- augers; and
- pressured injection systems.

6.6.1 Direct Mixing Plant

If the depth of contamination is not greater than 0.5m, then rotavators may be used in the S/S treatment of contaminated soil without the need for prior excavation (see Section 6.5.1).

Table 6.8: Typical data requirements associated with *in-situ* S/S methods (after CIRIA, 1995b)

Parameter	Purpose
Physical:	Physical testing procedures are used to:
Particle size distribution Moisture content Density Permeability Strength testing Unconfined compressive strength testing Flexural strength Cone index Durability testing Freeze/thaw characteristics Wet/dry durability	a) Predict mixing behaviour, reagent needs and volume increases b) Compare treated and untreated materials in terms of their strength and durability
Chemical:	Chemical testing procedures are used to:
PH Alkalinity Interfering compounds Indicator compounds Leach testing Heat of hydration	a) determine the applicability of the reagents b) determine the leaching behaviour of the treated product.

Direct addition and mixing may also be used to treat contaminated sludge and sediments present in lagoon areas and ponds (CIRIA, 1995a), or for direct mixing of contaminated soils *pseudo in-situ*. Figures 6.13 to 6.15 show a rotary tiller, adapted from shredding plant used by the forestry industry. It is mounted on the arm of a backactor and uses a supplementary hydraulics system powered by a generator. This equipment has been used in the USA to treat dredged sediments in-barge and creosote-contaminated soil at Port Newark, New Jersey (BCA, 2001).

Figure 6.13: ***In-situ* blender** (Photograph courtesy of Colin Hills)

Figure 6.14: ***In-situ* blender in use** (Photograph courtesy of Colin Hills)

Figure 6.15: ***In-situ* mixer treating a tar lagoon** (Photograph courtesy of Colin Hills)

6.6.2 Augers

The use of augers in S/S derived from the construction of lime columns using a deep mixing process that has been used in Scandinavian countries for many years (Barker *et al.,* 1996).

The Swedish method of forming lime columns involves the introduction of quicklime by hollow stem auger at depth so that it will be mixed with the soft, fine-grained soil as the auger is rotated and raised. Lime columns were originally developed as an alternative to piles for houses founded on clays with shear strengths of about 10-20 kN/m^2. In this method, a hollow-stemmed auger with a special blade for mixing is drilled into the ground to the required depth. Rotation is reversed, so that the soil is not lifted on the flights of the auger, and the tool is withdrawn slowly at about 25mm/revolution to ensure thorough mixing of lime and soil. During extraction, lime is pumped down the hollow stem by compressed air through a hole just above the auger blade to mix with the soil. To prevent clogging of the discharge point, pure lime, with a particle size of less than 0.2mm is used (CIRIA, 2002).

Figure 6.16: A quadruple auger penetrating contaminated soil (Photograph courtesy of Bachy Soletanche)

Lime columns, used for increasing the strength of soils, are appropriate for soils containing at least 20% clay, and the content of silt and clay should be at least 35% (Broms and Boman, 1984). The plasticity index should also be greater than 50%. Gypsum can be added to help stabilise organic soils with moisture contents of up to 180%. Calcium silicate or calcium aluminate may be used to accelerate the pozzolanic reaction between the lime and clay (CIRIA, 2002).

Figure 6.17: Large single auger (10ft diameter) with vapour extraction hood (and auger detail) (Photograph courtesy of Portland Cement Association)

More recently, augers have been used to introduce cement-slurries into contaminated land as part of an *in-situ* S/S process. Augers may be used singly, or in multiples as shown in Figures 6.16 to 6.18. The quality of mixing can be investigated by using intrusive methods such as coring, on a representative number of columns of treated material. One important advantage of column mixing is the ability of augers to key treated columns into underlying strata, providing the sub-strata is of a suitable lithology. Furthermore, the ability of the auger to deliver grout-based binder to the mixing blades and the reverse flight configuration of many augers, promotes intimate mixing and compaction of each overlapping column.

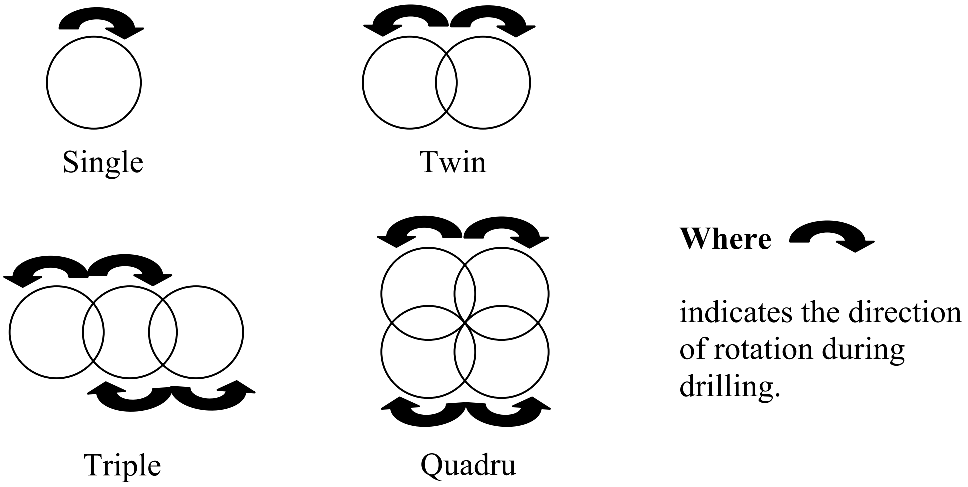


Figure 6.18: Drilling auger configurations for the introduction of binders in slurry form to contaminated land.

Research using laboratory-scale augers has shown that the shape of the auger head can influence mixing characteristics, particularly for layered soils (Al-Tabbaa *et al.,* 2000, Al-Tabbaa and Evans, 1999). The depth of mixing achievable often depends on the material type and plant available. Also, the presence of buried objects can prove problematic; stopping, breaking or preventing withdrawal of the auger. In addition, it may not always be possible to key columns into underlying strata especially where hard rock is encountered.

6.6.3 Pressured Injection Systems

CIRIA, 1995b identifies a jet grouting technique where soil is loosened by the high pressure action of water often sheathed in a cone of air (jet cutting). The loosened soil is partially removed to the surface by air-lift pressure as the remaining soil is simultaneously mixed with cement or cement/bentonite grout. Columns can be made to overlap so treating all the soil. The columns have diameters of 0.5m – 1.8m depending on the soil type.

6.7 Summary of Techniques

S/S has been successfully used on many projects around the world. Figures 6.19 and 6.20 show a site on completion of the remediation works and a case study of a successful treatment is given below. Selection of an appropriate treatment technique is often fundamental to the success of a project. Table 6.9 provides a comparison of some of the treatment techniques available.

Figure 6.19: Sub-base placed on S/S treated soil (Photograph courtesy of Portland Cement Association)

Figure 6.20: Site following completion of wearing course (Photograph courtesy of Portland Cement Association)

Table 6.9: Comparison of S/S techniques

Method	Benefits	Issues for consideration
Ex-situ		
Direct plant mixing	Can be used on sites with restricted headroom Can be used as bulk fill Good quality control Easy to visually inspect treated product Possible to achieve good compaction of end product	~300mm maximum depth of layers for good compaction depending on type and loading of plant used Dust if spreading binder in powdered form prior to mixing Maximum size of material for plant Requires relatively large and level area for spreading, mixing and compaction Not suitable for treating materials with very high moisture contents
In-drum mixing	Easy to control volumes and mix proportions Good quality control No direct contact of material being treated with the environment	Labour and plant intensive High materials requirement due to the disposal of the drum and mixing paddle with each treatment Integrity of the drum should not be considered in determining long-term performance Low rate of production
Plant processing (static)	Promotes consistent mixing Can be set up to reduce environmental impact from release of particulates and vapours Mobile equipment enables flexibility of location on site Can accommodate a high rate of production – up to several thousand m^3 per day	Transportation of wastes around site or off site Time to place, compact, cure material and turn around time of vehicles needs to be considered when evaluating rate of processing Volume increase

Method	Benefits	Issues for consideration
In-situ		
Augers	Can work in saturated ground and difficult weather conditions Can be used on difficult ground and where space is restricted Tolerates most soil conditions and can drill through hard ground Reverse auger withdrawal can provide compaction	Generally 200-1200mm dia. And can treat down to 35m depth Accuracy of treatment at depth can be poor and difficult to assess. May require separate drilling operations Requires considerable headroom Heavy plant required Compaction capabilities of particular equipment Buried structures or underground obstacles can damage plant and can increase complexity of treatment
Direct plant mixing	Can be used on sites with restricted headroom Good quality control Easy to visually inspect treated product Possible to achieve good compaction of end product	~300mm maximum depth of treatment for good compaction depending on type and loading of plant used Dust of spreading binder in powdered form prior to mixing Maximum size of material for plant Buried structures or over-sized particles can damage plant Not suitable for treating materials with very high moisture contents

CASE STUDY OF S/S IMPLEMENTATION

The Nantieux landfill site accepted waste from a nearby industry producing cobalt and sodium between 1955 and 1966 (iron arsenate) and 1966 to 1989 (sodium sludge). The landfill was closed by the local authority in September 1989 and classified as potential contaminated land in the inventory published by the French Ministry of Environment in 1994. Studies to assess the potential impact of the landfill were launched in 1995.

The site of the closed landfill was on a steeply sloping mountainside (40% gradient) above a river. The site dimensions were 130m in length and 35 m in height. It was estimated that the volume of the landfill was 50,000m^3 (approx 100,000 tonnes)

Site remediation commenced in 1998, with the protection of the surrounding area carried out by placing rocks (rip-rap) at the bottom of the landfill. The main phase of remediation commenced in 1999.

There were a number of specific problems associated with the site:

- chemical stability: de-stabilisation of the iron arsenate due to the disposal of highly basic sodium sludge that was not evenly distributed on the site resulting in increased solubility of arsenic with increasing pH;
- heterogeneous materials in the landfill;
- mechanical stability: the landfilled wastes had weak mechanical characteristics and there was significant risk of instability with materials sliding towards the river;
- the edge of the landfill is located in an erosion curve of the river (Figure 6.21); and
- presence of drums containing a mix of sodium and potassium that were not precisely located within the landfill presenting risks during remediation.

The objectives of the treatment design, at the site, where to achieve chemical stability, measured in terms of the leachable arsenic below 10 mg/kg and mechanical stability, defined as a uniaxial compressive strength of more than 1 MPa.

Figure 6.21: Proximity of the Nantieux Landfill site to the river (Photograph courtesy of INERTEC)

The material had to be treated on site despite difficult access, because the nearest hazardous waste landfill was some distance away. The project was carried out by INERTEC (France). (Figures 6.22 and 6.23 show stages of the remediation)

The proposed treatment was validated at a pilot scale by treating 50-ton batches. The treatability was assessed via a risk assessment methodology using ENV 12920 where the leaching behaviour was tested for the infiltration of rain through a vegetated layer. The release of pollutants as a function of time was modelled, in terms of impact on the river below the site. The river water was required to meet the European/World Health Organisation drinking water standards.

An automated batch treatment system was able to cope with the heterogeneity of the materials to be treated on site. Between 180 and 250 tonne of reagents was consumed per day, when the plant was running at between 15 and 20 hours per day.

Figure 6.22: Nantieux landfill during remediation (Photograph courtesy of INERTEC)

There was a three stage quality control process involving an on site laboratory, the vendors central laboratory and an external laboratory named by local authority. Treated materials were evaluated for leaching and strength. In all, 98500 m^3 of waste and soil were treated representing 90% of the extracted materials.

Figure 6.23: Nantieux landfill remediation operation nearing completion (Photograph courtesy of INERTEC)

Post-completion monitoring was specified by the local regulatory authority. Surface water monitoring points were located upstream, at the downstream edge of the landfill and further downstream. There were periodical measurements of the slope of the final profile of the site (Figure 6.24).

Figure 6.24: The completed project at Nantieux (Photograph courtesy of INERTEC)

6.8 Summary

The remediation of contaminated soil by S/S can be carried out using a range of equipment that involve either *in-situ* or *ex-situ* application. Mobile plant and reagent delivery systems can be configured to meet most site-based and ground conditions. Fixed or mobile plant options can be used to treat waste streams.

The use of bench-scale testing followed by pilot-scale application is an important part of an S/S remedial plan and demonstrates that a robust approach to risk management has been used. Following this, the full remediation operation can be carried out with confidence. The main findings of this chapter are:

- the use of S/S requires good information on the material to be treated and thorough mixing between the soil/waste and the binder;
- control over external factors such as humidity and temperature, and the absence of compounds that may interfere with the S/S process are an essential part of a successful remediation plan employing S/S;
- bench-scale testing is an essential part of the remediation plan and should be used to demonstrate that an optimised remedial solution has been established;
- a wide variety of S/S methods are available to enable the treatment criteria to be met. Broadly, these may be divided into *in-situ* and *ex-situ* applications;
- *in-situ* operations include augers and rotavators and blend binders directly with contaminated materials in the ground or in lagoons or ponds;
- *ex-situ* operations include pugmill and direct mixing plant, and involve the removal of contaminated soil, mixing with binders and then transportation to the site of placement; and
- complex formulations of binders can be accommodated at the site of the remediation operation and pre-mixed binders can be transported over considerable distances for immediate use.

REFERENCES

Al-Tabbaa, A and Evans, C.W. (1999) Laboratory-scale Soil Mixing of a Contaminated Site. *Journal of Ground Improvement* 3, pp 119-134.

Al-Tabbaa, A, Ayotamuno, J.M., and Martin, R.J. (2000) Soil Mixing of Stratified Contaminated Sands. *Journal of Hazardous Materials* 72, pp. 53-75.

Arocha, M.A., McCoy, B.J., and Packman, A.P. (1996) VOC Immobilisation in Soil by Adsorption, Absorption and Encapsulation. *Journal of Hazardous Materials* 51, pp. 131-149.

Barker, P., Wyllie, P.J.M., and Esnault, A. (1996) Investigation, Planning and Execution of the Remediation of the Ardeer Landfill, Scotland. In: *Polluted and Marginal Land – 96: Re-use of Contaminated Land and Landfills.* Preprints of Conference held at Brunel University, London, July, pp. 153 – 166.

Bates, E.R., Sahle-Demessie, E. and Grosse, D.W. (1999) *Solidification /Stabilization for Remediation of Wood Preserving Sites: Treatment for Dioxins, PCP, Creosote and Metals*. Portland Cement Association Publication RP371, Skokie, Il.

British Cement Association. (2001) *Cement-based Stabilisation and Solidification for the Remediation of Contaminated Land. Findings of a Study Mission to the USA*. British Cement Association Publication 46.050.

Broms. B.B and Boman, A. (1984) *Stabilisation of Soil with Lime Columns, Design Handbook*, (Second Edition) Royal Institute of Technology, Soil and Rock Mechanisms Dept, Oslo.

Buxton Lime Industries. (1999) *Delivery, Storage and Handling of Quicklime, LIMBUX hydrated lime and Portland cement*. Technical Service Note TS1/1999. Buxton Lime Industries Ltd.

Carey, M.J. and Nagelski, D. (1996) Treatment Alternatives for Lead Impacted Media: Case Studies. *Waste Management* 16, pp. 263-270.

Construction Industry Research and Information Association (1995a) *Remedial Treatment of Contaminated Land. Ex-situ Remedial Methods for Soils, Sludges and Sediments,* Volume VII, CIRIA Special Publication 107.

Construction Industry Research and Information Association (1995 b) *Remedial Treatment for Contaminated Land*, *In-situ Methods of Remediation*, Volume IX, CIRIA Special Publication 109.

Construction Industry Research and Information Association (2000) *In-situ* Stabilisation of Chemical Waste. CIRIA Report 37.

Construction Industry Research and Information Association (2001) *Remedial Processes for Contaminated Land: Principles and Practice*. CIRIA Report C549.

Construction Industry Research and Information Association (2002) *A Guide to Ground Treatment*. CIRIA Report C573.

Evans, C.W. (2003) Personal Communication, December 2003

Evans, C.W. and Al-Tabbaa, A. (1997) Treatability Study on the Solidification of Two Soils. In: *Geoenvironmental Engineering Conference, Contaminated Ground: Fate of Pollutants and Remediation*. Thomas Telford Press, pp. 293-298.

Stegemann, J.A. and Buenfeld, N.R. (2002) Prediction of Leachate pH for Cement Paste Containing Pure Metal Compounds. *Journal of Hazardous Materials* 90 (2), pp. 169-188.

United States Army Corps of Engineers (1995) *Engineering and Design Treatability Studies for Solidification/Stabilization of Contaminated Material*. Department of the Army, U.S. Army Corps of Engineers, Washington, D.C. 20314-1000.

United States Environmental Protection Agency. (1993) *Solidification/Stabilisation of Organics and Inorganics*. Engineering Bulletin EPA/540/S-92/015.

United States Environmental Protection Agency. (1999) *Waste Leachability: The Need for Review of Current Agency Procedures*. EPA Science Advisory Board Environmental Engineering Committee Commentary EPA-SAB-EEC-COM-99-002, February 26th.

United States Environmental Protection Agency. (2000) *Solidification/Stabilization Use at Superfund Sites*. EPA-542-R-00-010.

United States Environmental Protection Agency. (2001) *Treatment Technologies for Site Cleanup: Annual Status Report (10th Edition).* Report Number EPA-542-R-01-004.

United States Environmental Protection Agency. (2004) *Treatment Technologies for Site Cleanup: Annual Status Report (11th Edition)*. Report Number EPA-542-R-03-009. http://cfpub.epa.gov/asr

van der Sloot, H. A., Heasman, L. and Quevauviller, Ph. (1997) *Harmonisation of Leaching Extraction Tests.* Studies in Environmental Science 70. Elsevier, Amsterdam.

van der Sloot, H.A., Hjelmar, O., Bjerre Hansen, J., Woitke, P., Lepom, P., Leschber, R., Bartlet, B. and Debrucker, N. (2002*) Validation of CEN/TC292 Leaching Tests and Eluate Analysis Methods PrEN 12457-1 to 4, ENV 13370 and ENV 12506 in Co-operation with CEN/TC308*. Summary Report ECN-C—01-117, ECN, The Netherlands.

Weitzman, L.H., Hamel, L.E. and Barth, E.F. (1990) *Evaluation of Solidification/Stabilisation as a Best Demonstrated Available Technology for Contaminated Soils*. EPA/600/52-89/013.

7 CENTRALISED TREATMENT OF WASTE STREAMS

7.1 Introduction

Changes in European waste legislation at the beginning of the 21st century will have a profound influence on the classification of waste and its treatment, including the remediation of contaminated soil. The most significant changes relate to the revision of the European Waste Catalogue (EWC) and introduction of the Landfill Directive (LFD).

In some countries, such as North America, Japan and some EU member states, S/S technology is well established through 20-30 years of use to treat a variety of wastes and contaminated soil. This chapter gives a brief history of the development of S/S technology for the treatment of wastes in the USA, Europe and the UK and summarises the key changes that may affect the use of S/S in the UK. It makes reference, in some detail, to the development of S/S in the USA, because this is where S/S is widely used and where details are publicly available.

7.2 Implementation of Waste Treatment

There are two routes for the treatment of waste streams by S/S:

- treatment at the site of production as part of the waste-generating process, dealing with a specific waste stream; and
- treatment at a central processing plant, where a variety of wastes are treated, for example the former processing plant at Thurrock, Essex.

In both cases the S/S wastes are disposed of at a landfill site, although exceptionally the treated wastes may be suitable for use as general fill or road sub-base.

Solidification/stabilisation processes involving mobile or small-scale plants where the stabilised materials (soil or dredgings) are generally re-used on or near the site from which they were excavated are not included here but are described in Chapter 6.

7.2.1. Treatment processes

There are a large number of S/S waste treatment processes available to treat hazardous wastes including at least seventy processes, which were patented in the USA by the 1980s (Clements and Griffiths, 1985). More than half of those processes involved different combinations of cement, lime and PFA in the binders. The remaining processes involve the use of organic compounds to form organic polymers or inorganic materials that rely on the formation of silicate polymers. The widespread use of organic processes for the S/S of hazardous wastes is hampered by their high cost, high-energy consumption or their specialised application (USEPA, 1989). Many of the S/S processes remain as 'blackbox' solutions to the treatment of wastes and the formulations are unknown, which has led to a lack of confidence in the technology.

The six main binder systems employed in 1985 are described in Table 7.1, however, it should be noted that these systems may no longer be available and that a number of commercially confidential new binders have been developed.

Table 7.1: Typical cement based stabilisation processes (modified from Clements and Griffiths, 1985)

Principal binder components	**Other additives/pre-treatments**	**Application**
Sodium silicate	Calcium chloride Calcium sulphate Cement	America Canada Japan France UK (Mobile plant)
Cement	Number of silicate waste materials Lime or alkali metal hydroxide	Belgium UK – Southampton France – Mitry Paris Norway Canada
Blast furnace slag	Alkaline activator	France UK
PFA, coal ash and lime	cement	France US
Cement/fly ash	variety	Canada Japan UK – West Midlands, Thurrock
Mixture of organic & non-organic chemicals	Variety of reducing agents or complexing agents as required	Switzerland UK (Mobile plant)

Most S/S operators can refer to an extensive database of binder formulations previously used to treat characterised waste streams. Such a system, however, does not remove the need for waste stream-specific characterisation and treatability trials before a waste is accepted for treatment, as concluded in Chapters 4 and 5.

Lime kiln dust and cement kiln dust have also been used extensively at central hazardous waste management plants as absorbents, bulking agents or neutralizing agents for acidic wastes. These systems have also been utilised for organic waste streams, for example a mixture of quick lime and cement kiln dust was used to stabilize more than 190,000 m^3 of oily sludge in a waste lagoon (Conner and Hoeffner, 1998).

Lime kiln dust and cement kiln dust are examples of materials added to the waste in a pre-treatment phase. Consideration of a pre-treatment phase is an important aspect in the selection of treatment options as are: 1) whether the waste will benefit from proprietary agent addition and 2) what influence the site has on the selection of a treatment process (USEPA 1989). Different pre-treatment options are discussed in Chapters 4 and 5.

Apart from the benefits of S/S in terms of contaminant immobilisation, S/S systems generally make the waste easier to handle and improve their engineering and structural properties. The wastes that result from the variety of S/S treatments, may take the form of:

- slurries which can be pumped into solidifying bays or engineered cells within a landfill site;

- granular materials which can be reused as fill or road sub-base, or landfilled; or
- monoliths which are subsequently landfilled.

7.2.2. History of the development of S/S of wastes in the USA

S/S is a technology that has developed from the stabilisation of soils within the construction industry, the treatment of radioactive nuclear waste, and the stabilisation of mine tailings or back-filling of mines. The use of S/S technology for waste residues dates only from about 1970 (Conner, 1990).

In the USA, shortly after the Second World War, it was realised that nuclear waste needed to be solidified in drums or other containers prior to shipping to, and burial at, government controlled disposal sites simply in order to facilitate handling of the material. Liquid waste containing low-level radioactivity was absorbed into mineral sorbents, such as vermiculite or solidified with large quantities of PC (Conner and Hoeffner, 1998).

Many waste producers and waste disposal operators, prior to 1970, probably used PC, lime, PFA and other S/S reagents, but as there was little or no regulation controlling these processes, there is little documentation available. Lime/PFA S/S processes were used for concentrated wastes produced directly from processes such as steel pickling. Lime neutralised the acid content and PFA, soil or PC was added to produce a solid that could be landfilled. Oily sludges from petroleum refining were also incorporated into a lime-PFA system to produce a solid with physical properties sufficient to allow the material to be landfilled.

In the 1960s, Chemfix Inc. developed a method based on the combination of soluble silicates and silicate setting agents such as sodium silicate and PC in order to stabilise and solidify sludge from the treatment of acid coal mine drainage water. The method was deemed unsuitable for the vast volumes of mine drainage sludge, for which it was developed, but was applied to other process wastes and wastewater treatment residues such as sludge from metal finishing and metal producing operations and eventually sludge containing organics. By the early 1990s, 500 million gallons of sludge had been solidified using the Chemfix process. Mobile treatment units could be set up next to a storage lagoon and the waste treated in a matter of days, weeks or months before moving onto the next site (Conner and Hoeffner, 1998).

In the mid 1970s, Conversion Systems Inc. developed a lime/PFA process for the treatment of calcium sulfate and sulfate sludge from the scrubbing of power plant flue gases and lime or limestone. This process was also deemed suitable for the treatment of sludges produced from neutralisation of sulfuric acid pickle liquor and from the battery industry. The solids produced were commonly used as structural fill or road base. The Dravo Corporation used granulated blast furnace slag for the combined dewatering, compaction and solidification of sludge from electric power plants.

There appears to have been no major studies on the leachability, environmental degradation or other performance characteristics of solidified wastes until the mid 1970s as there were few laws or regulations in the USA or elsewhere concerning the disposal of waste residues (Conner and Hoeffner, 1998).

Since 1976, S/S technology in the USA has been controlled by two main pieces of legislation:

- Resource Conservation and Recovery Act (RCRA) and subsequent Hazardous and Solid Waste Amendments (HSWA, 1984) and the Land Disposal Restrictions (LDR, 1985); and
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or “Superfund.” (1980) and its reauthorisation in 1986 (SARA)

The introduction of RCRA in 1976 provided an impetus for S/S treatments in the US. This was achieved by developing criteria for the definition of hazardous waste, establishing standards for the siting, design and operation of disposal and recovery facilities and encouraging individual states to develop their own regulatory programs (Conner, 1990). The number of vendors of hazardous waste treatment technologies increased dramatically with considerable technical developments. However, vendors are reluctant to share their knowledge with competitors and little detail of this work has been published other than in the patent literature.

Between 1982 and 1992, S/S techniques were cited in 28% of Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) records of decisions indicating that S/S was the most widely used technology for waste sites in the USA (Powers and Zander, 1996). The technology is used extensively for the treatment of industrial wastes, especially liquids, sludges and incinerator ash. The major waste streams treated in the USA are listed in Table 7.2.

Table 7.2: Major waste streams treated by S/S in the USA (after Conner and Hoeffner, 1998)

Metal finishing sludges
Metal refining sludges and emission control dusts
Mining wastes
Petrochemical industry sludges
Inorganic chemical industry sludges and dusts
Hazardous waste incinerator ash
Municipal waste ash
Various solutions, sludges and dry solids hazardous by characteristic for metals
Contaminated soils and sludges form CERCLA/RCRA remedial actions
Non-hazardous sludges and slurries, including municipal sewage sludge

Hazardous and Solid Waste Amendments and Land Disposal Restrictions (LDRs) introduced the statutory "landbans" under which land disposal of hazardous waste was no longer permitted. The "landbans", introduced in three phases, include the following wastes:

- bulk hazardous waste liquids, unless solidified by a 'chemical reaction';
- non hazardous bulk liquids, including water, unless the operator can demonstrate that landfill is the only safe alternative;
- dioxins and solvents; and
- sludge containing concentrations of cyanides, As, Cd, Pb, Hg, Ni, Se, PCBs, Tl and halogenated organic compounds (known as the California list).

Stabilisation/solidification is specified as best demonstrated available technology (BDAT) for the treatment of RCRA-listed hazardous wastes that need to be treated prior to disposal to landfill, and RCRA-characteristic hazardous wastes.

The LDRs deal primarily with the operations at waste generators' facilities and at central treatment facilities known as Treatment, Storage and Disposal Facilities (TSDFs). The LDRs have brought many new waste streams to S/S treatment. These include solid hazardous wastes, that were going to direct landfill in secure cells at TSDFs, and wastes that had previously been considered to be non-hazardous, such as bottom ash, oil and gas drilling mud and flue gas emission control wastes.

The acceptability of S/S treatment is evaluated through a combination of prescribed physical and chemical tests as shown in Table 7.3. The standards and criteria are specified in Federal, state or local regulations or by regulatory agencies for individual projects.

Table 7.3: Testing regime for S/S wastes in the USA (from Wilk, 2002)

Physical Tests	**Chemical tests**
Paint filter test (PFT)	Toxicity characteristic leaching procedure (TCLP)
Liquid release test (LRT)	Synthetic precipitation leaching procedure (SPLP)
Moisture content	Acid neutralization capacity
Density	Multiple extraction procedure
Hydraulic conductivity	Equilibrium leach
Unconfined compressive strength	Dynamic leach
Freeze-thaw and wet-dry durability	

Typical waste acceptance criteria for disposal in non-hazardous landfill in the USA are shown in Table 7.4.

Table 7.4: Typical USA waste acceptance criteria (after Al-Tabbaa and Perera 2002a)

Unconfined Compressive Strength	>350 kPa soaked at 28 days	USEPA 1986
Leachate pH	7 - 11	Conner, 1990;
Leachability TCLP or NRA tests	100 x drinking water quality standards	Conner 1990
Permeability	$< 10^{-9}$ m/s	
Freeze – thaw and wet – dry durability	Pass in ASTM tests	
Acid Neutralisation Capacity Environment Canada test method		Stegemann and Cote 1991

Further information on these and other tests can be found in Chapter 8.

7.3 Stabilisation/Solidification Developments in Europe

In Europe, S/S technology developed in the early 1950s to treat radioactive wastes. These wastes were solidified in drums using concrete and buried at sea. However, the use of large quantities of PC resulted in large increases in volume with consequential difficulties in transport and storage. There were also problems of the waste retarding the setting of the PC. More recently intermediate level, inertised (treated) radioactive wastes were deposited in deep underground repositories after mixing with cement/PFA and clay.

High level radioactive wastes were initially stabilised with cements, but because of the large volume increase and the premium on storage space, calcination and vitrification became the preferred stabilisation techniques.

In the late 1950s the French government introduced the addition of sodium silicate to PC producing a quick gelling system for low solids waste streams. (Conner, 1990).

S/S is currently carried out principally in Austria, the Netherlands, France and Portugal and has been developed in relation to the disposal of wastes to landfill. There have been few applications related to soil treatment (less than 10 applications in France, although 200,000 m^3 soil has been treated) and most S/S has been applied to Air Pollution Control (APC) residues from Hazardous Waste Incinerators (HWI) or Municipal Waste Incinerators (MWI).

In France, S/S has been mainly related to disposal to landfill of industrial wastes, with stabilisation being the only treatment that will comply with the acceptance limit values required by French Orders dated December 1992. There are twelve central processing plants in France, treating 400,000 tonnes of waste per year of which 50-60% are air pollution control residues (APC) (Magnie, 2003) and 40-50%% are industrial sludges; metallic residues and other wastes.

In contrast to legislation in a number of other countries, in France the S/S treatment does not remove the hazardous classification of the waste. Acceptance criteria for the deposit of stabilized waste in a hazardous waste landfill (pre-Landfill Directive) are written into legislation and reproduced in Table 7.5.

Table 7.5: Waste acceptance criteria (pre-LFD) to allow stabilized and solidified waste to be landfilled in inorganic hazardous waste landfill

	Leachable contaminants	
Dry Matter > 35%	Phenols <100 mg/kg	CN <5 mg/kg
Soluble fraction <10% dry mass waste	As<10 mg/kg	Hg < 5 mg/kg
	Cd <25 mg/kg	Ni <50 mg/kg
pH between 4 – 13	Cr < 50 mg/kg	Pb <50 mg/kg
COD <2000 mg/kg,	Cr^{6+} <5 mg/kg	Zn <250 mg/kg
>1 MPa compressive strength		

Note - Leaching test carried out to NF X 31-211French standard,

Waste management and treatment in France is overseen by the French Ministry of the Environment and Durable Development (MEDD) and local authorities (DRIRE). The Agency for Environment and Energy Management (ADEME), in particular the Impact and Contaminated Land Department of the Industry Division, is charged with the development of new processes (Magnie, 2003).

Between 1993 and 2000, ADEME have examined the S/S of 14 waste streams (including 12 hazardous wastes) and developed Stabilisation Assessment Procedures (SAP), to establish whether the chemical fixation of the contaminants occurs and whether the process is sustainable. The wastes tested contained only inorganic contaminants. The performance of the S/S wastes was assessed by subjecting the waste forms to wetting/drying or to freezing/thawing cycles and then carrying out a variety of leaching and strength tests at different ages (Chateau, 2002). The results of this work are not yet published.

7.4 The S/S of Waste Streams in the UK

The UK saw a fairly active market in the treatment of waste using S/S in the late 1970s and 1980s. However, there are currently few centralised waste processing plants in the UK with the capacity to use S/S technology. Two former centralised treatment plants are described in the boxes below; one of which highlights the consequences of failure of the treatment process.

The Sealosafe process was patented in 1973 as a method of treating waste and subsequently immobilising it in a 'synthetic rock' known as Stablex. Clements and Griffiths (1985) describe the process and wastes treated in some detail. In addition, other processes operating at that time in the UK (and elsewhere) are also described.

Sealosafe involved a two-stage process: a pre-treatment step (where waste was converted to a form suitable for solidification); and solidification using a cement/PFA-based system primarily designed for the treatment of inorganic wastes specifically metal plating wastes). Two plants using this process operated in the West Midlands and in Essex, with the latter ceasing operation in mid 1990s. The standard formulation used is shown in Table 7.6.

Table 7.6: Standard formulation for the production of Stablex (after ERL, 1989)

Ingredient	Parts by weight
Portland cement	1
PFA	5
Waste	14

CASE STUDY 1

The Sealosafe Process, Aldridge, West Midlands.

Leigh Interests plc constructed a plant adjacent to old clay pits in the Aldridge area, West Midlands to use the Sealosafe process for the treatment of difficult waste streams in the 1970s and 1980s. The waste was pre-treated to contain 34% solids.

Two patents, filed in the late 1970s, allowed the incorporation of up to 10% by weight organic compounds, including latex, acid tars, oily wastes and pharmaceutical wastes. Following this the plant began to accept organic-contaminated wastes and problems with the physical and chemical characteristics of the product were reported.

From the data that is publicly available, it is not clear if detailed laboratory trials into the suitability of the organic waste streams to be treated by the Sealosafe process were undertaken. In any event, disposed treated waste was found to be unstable and this resulted in problems including:

- retarded setting characteristics of the Stablex;
- unsatisfactory leaching characteristics;
- surface water ponding in the landfill led to set retardation and water contamination;
- collapse of retaining wall led to outflow of thixotropic Stablex.

Failure of the Sealosafe process at this site appear to have been as a result of both poorly controlled process and waste disposal practices, including:

- high levels of organics, possibly as a result of poor waste stream characterisation and/or treatability trials;
- insufficient cement or lime used to neutralise acid wastes, resulting in a low pH product;
- insufficient solids, resulting in excessive setting rate;
- deposit into ponded water, resulting in leaching and excessive setting rates;
- absence of a leachate collection system;
- absence of surface water drainage to control ingress into the landfills; and
- instability of retaining wall, probably due to high pore water pressures.

The failure at Aldridge was widely reported in the environmental press and it was estimated that around 50% of the Stablex deposited were in a semi-liquid state. The company was subsequently convicted of seven charges under the Trade Descriptions Act 1968 (ENDS, 1992).

The publicity surrounding the failures at the Sealosafe plant possibly put back the development of S/S in the UK by several years, but the failures at the site can be attributed to poor working practices and emphasise the need for:

- waste characterisation;
- treatability trials for all new waste streams;
- compliance testing and batch testing; and
- adequate engineering of the landfill sites that are accepting the S/S waste.

CASE STUDY 2

The West Thurrock Treatment Plant

From 1978 to 1996 Crossford Pollution Control (later Stablex) began solidifying industrial inorganic waste streams at a central treatment site at West Thurrock in Essex. This plant had the capacity to process 400,000 tonnes of hazardous waste per year, using an PC/PFA blend as a derivative product of Stablex. 30,000 tonnes per annum were treated.

Table 7.7 illustrates the variety of wastes processed at this plant during the 1980s. All incoming wastes were pre-treated (Table 7.8) and converted to alkaline slurry before solidification. The incoming waste (Figure 7.2), therefore, had to be well characterised, both physically and chemically, so that the correct handling procedures could be followed. Figure 7.1 is a schematic diagram of the process operating at Thurrock.

Table 7.7: Summary of waste types received at Thurrock during July - December 1980. (after Conner 1990)

Type of Waste	% of waste received	Type of Waste	% of waste received
Sulphuric acid	4.7	Neutral Sludge	10.4
Hydrochloric acid	4.6	Lime sludges	14.0
Chromic acid	0.6	Other sludges	0.8
Mixed/other acids	6.6	Filter cakes	1.1
Al-chloride solutions	16.6	Paint stripper washings	1.7
Fe-Chloride solutions	0.9	Ferrous sulphate	1.0
Solid/Liquid cyanides	3.7	Others	3.0
Caustic solutions	30.5		

Table 7.8: Pre-treatment requirements for general wastes types accepted at Thurrock (from Hills, 1993).

Type of waste	Pre-treatment
Acid Wastes	Neutralised by the addition of lime or waste alkaline to increase pH to 9-10
Alkaline Wastes	Neutralised by addition of acidic wastes
Cyanide Wastes	Oxidation with ozone or hydrogen peroxide
Organic Wastes	Generally avoided as difficult to characterise and pre-treatment difficult to optimise

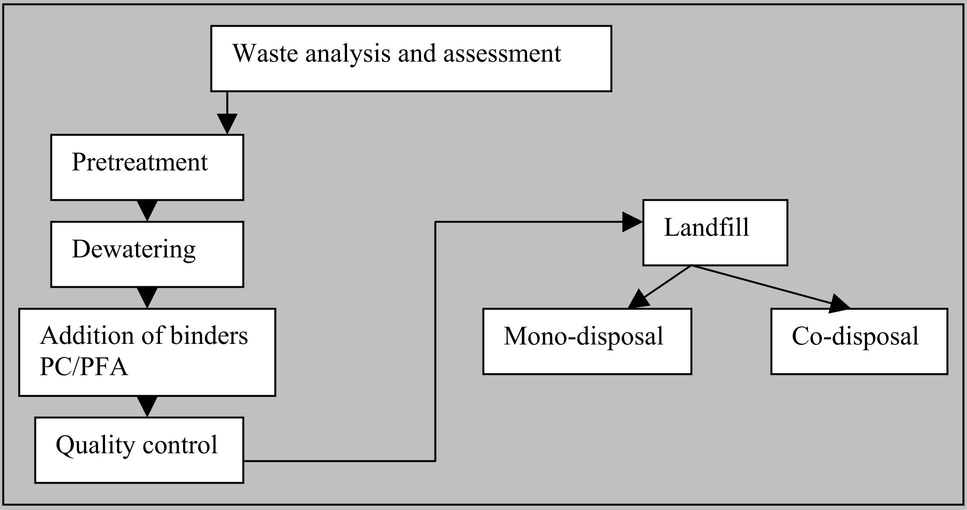


Figure 7.1: Schematic of the Thurrock processing route (from Hills, 1993)

Once the wastes had been pre-treated they were blended, pH adjusted and the solids content of the slurry controlled by the addition of chalk, PFA or diluted with water (Figure 7.3). Vacuum filter pressing and microfiltration techniques (Figure 7.4) were then used to dewater the slurry, with the wastewater discharged to the sewer. The de-watered solids, at a solid content of 50%, were mixed with PC and PFA in a batch-like mixing operation.

The solid waste was discharged to a storage area so that the hardening could be monitored. From the storage area, the granular, solidified wastes were transported, by lorry, to the Mucking landfill site, where they were tipped into designated pits excavated in compacted domestic refuse (Hills, 1993).

Figure 7.2: Collection point for incoming wastes at Thurrock (photograph courtesy of Colin Hills).

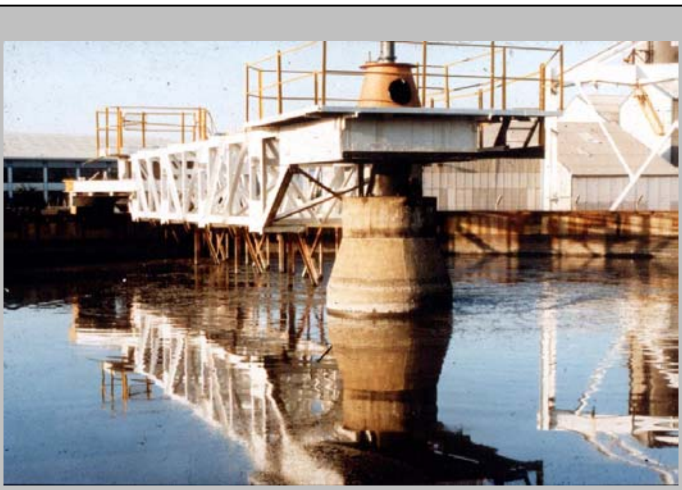


Figure 7.3: Lagoon for blending and dewatering wastes at Thurrock (photograph courtesy of Colin Hills).

Figure 7.4: Vacuum filtration and production of filter cake at Thurrock (photograph courtesy of Colin Hills).

The quality of the solidified product was assessed on its ability to satisfy the requirements set by the Waste Regulation Authority (Table 7.9). These requirements were based upon simple dissolution/leach tests using distilled water and the development of strength as a measure of the effective hydration of the cementitious binders (Hills, 1993).

The operation was considered to be successful and continued in operation until 1996, when it closed, principally because the process was considered uneconomic whilst wastes could still go untreated to landfill.

Table 7.9: Specification for solidifying chemically fixed material

1	At 28 days, the UCS from any 1 day of production will not be less than 700 kPa. No individual sample will have a UCS of less than 350 kPa.
2	The co-efficient of permeability after 28 days, will be less than 1×10^{-7} m s^{-1}
3	No supernatant will be present after the solidified material is left standing for 24 hours
4	After 28 days of curing, the filtrate produced when 50 g of finely ground solidified material is mixed for 1 hour at 20°C with 500 ml distilled/deionised water then filtered through Whatman GF/C or equivalent paper, must on analysis conform to the following: a) pH between 8 and 12.5 b) TOC < 100 mg/l c) Total cyanide < 2 mg/l d) Total Phenol < 5 mg/l e) Ammonia < 40 mg/l f) Toxic heavy metals (mg/l) Zn < 5.0 Hg < 0.5 Cr < 2.0 Others (including Cd, Sn, As, Se, An and Be) < 5.0 in total g) Total organic or organometallic pesticides < 0.005 mg/l

7.4.1 Current and recent S/S activites in the UK

There have been a number of field trials and associated laboratory work on the S/S of industrial wastes; summarised by Al-Tabbaa and Perera (2002b) and outlined in Table 7.10. None of these field trials involved the placement of the treated wastes in a landfill, although leachate samples were taken from the test cells and samples will be taken from the drainage from the road constructed during the MARS (Manufactured Aggregates for Reclamation Sites) trials.

The MARS project utilised the Geodur immobilisation process (Geodur CIS AG), whereby the binder is formulated on a site by site basis from the results of chemical and physical testing of the input materials. This system consists of a mixture of organic and inorganic binders including where necessary hydrophobic compounds and surfactants. Complexing and reducing agents can also be used (Reid 2002).

Landfill drainage material, fill (Type 1), capping materials and aggregates for lightweight masonry blocks have been produced using the Geodur process. Processing can involve using an excavator bucket with internal blades (an ALLU bucket) for a period of several hours.

A field trial involving construction of a 200m stretch of unsurfaced road is planned using treated materials in the capping and sub-base layers. The performance of the planned road will be monitored according to the Specification for Highway Works and drainage from the road will be sampled to assess whether any leaching from the S/S materials is taking place and the results of this work is intended to be published (Reid, 2002).

Table 7.10: Example field trials in the UK involving the S/S of wastes (from Al-Tabbaa and Perera, 2002b)

Waste	**Process**	**Disposal/Use**	**Reference**
Electric arc furnace dust	Sodium silicate activated blast furnace slag,	Inverted pyramid, test cell	Stegemann *et al.* 1997
Metal smelting residue	10% cement and 0.15% Geodur Traceloc	300 mm thick slab, part of which was crushed for aggregate after 1 year	Jardine and Johnson, 2000; Board *et al.,* 2000
Soil/slag wastes from a metal recycling site			
Lead/zinc slag from smelting			
Foundry sand	Geodur (MARS)	Re-use as landfill drainage, Type 1 sub-base, Class 6F1 capping and aggregate for masonry blocks	Reid, 2002
Water treatment sludge			
Metal refining residues			
Incinerator bottom ash			
Steel slag			

Both intermediate and low level waste generated by BNFL at the Sellafield Site, have been treated using cement stabilisation. The intermediate waste is treated using blends of PC with either blast furnace slag or PFA at four plants on site in order to ensure long-term product stability whilst keeping the final volume at a minimum. Two processes are used; one involving encapsulation of wastes outside the container and the other involving in-drum mixing with a sacrificial paddle. The treated wastes along with the containers are disposed of in a designated intermediate level waste repository. The low level waste is treated at the centralised low level waste treatment site in Drigg, via encapsulation and mixing outside the container. The treated wastes and containers are then placed in an engineered vault at Drigg.

Several small-scale commercial applications have also been reported, as shown in Table 7.11.

Table 7.11: Recent commercial applications of S/S treatment of wastes in the UK

Waste	**Process**	**End Use**	**Reference**
Lightly contaminated silt dredgings	PFA and lime	Lightweight embankment fill	Al-Tabbaa and Perera, 2002b
Water treatment sludge	Envir**O**ceM[*1] **SSP**	Landfill	Blue Circle Industries, 2001
Intermediate level radioactive Waste (ILW) and low level radioactive Waste (LLW)	PC and Blast furnace slag or PFA	Stored in designated repository	Al-Tabbaa and Perera, 2002b
Mercury contaminated dredgings	PC and PFA blend	Disposed of to landfill	Guha, 2002
Diesel contaminated canal dredgings	PC and PFA blend	Used to strengthen Canal Tow Path	MacLeod *pers comm.* 2002

*1 EnvirOceM is a special cement produced by Blue Circle/Lafarge for the treatment of contaminated soil/wastes

Mercury contaminated dredgings from the Union Canal in Glasgow, have been treated using a PC and PFA blend (Guha, 2002). Because of the toxic nature of mercury, these dredging have not been reused on site but disposed of to a HDPE lined cell at an appropriate landfill. The treated materials had to meet physical criteria for acceptance, principally UCS rather than chemical criteria (Gush, per comm., 2002).

7.5 Significant Changes in the S/S of Waste Streams in the UK Following Implementation of the Landfill Directive

The landfilling of waste in the UK will go through some significant changes as a consequence of updating waste classification and implementation of EC directives, in particular the Landfill Directive (LFD). The LFD encourages the recycling and recovery of waste and places stringent controls on landfill activities. With respect to the treatment of waste by S/S, the most significant implications of the LFD will be the classes of landfill, requirement for pre-treatment before landfill, and the waste acceptance criteria. Technical and regulatory guidance on the LFD implementation is available from the Environment Agency's web-site.

7.5.1 European Waste Catalogue

In 1994 a comprehensive list of wastes, the European Waste Catalogue (EWC), was produced under the European Council Directive on Waste 75/442/EEC (as amended by Council Decision 91/156/EEC). Council Decision 94/904/EC then identified a list of wastes from the EWC deemed to be hazardous, known as the Hazardous Waste List (HWL), as required by the Hazardous Waste Directive (European Council Directive 91/689/EC). Contaminated soil was not identified on the HWL and was evaluated as a special waste only against hazards H3a (1st indent) and H4 to H8 inclusive.

The EWC is subject to periodic review and has recently been updated and combined with the HWL (European Commission Decision 2000/532/EC as amended). Hazardous wastes in the revised EWC appear as "absolute" or "mirror" entries:

- absolute entries are hazardous regardless of chemical composition; and
- mirror entries may be hazardous or non-hazardous, depending on whether they contain dangerous substances. Mirror entries must be evaluated against hazards H1 to H14 inclusive.

The revision to the EWC has resulted in a wider range of wastes, not previously on the HWL, being evaluated against ecotoxic criteria (H14), including contaminated soils (EWC entry 17 05). This is likely to increase the quantity of contaminated soil classified as hazardous waste, in comparison to special waste, as many heavy metals will have lower threshold concentrations against the ecotoxic hazards than human health hazards (Naisbitt *et al.*, 2002). For example, the presence of copper compounds would make contaminated soil a special waste at between 10 and $25\%_{w/w}$, depending on hazard and risk phrases. However, copper contaminated soil can be hazardous at a Cu concentration of $> 0.25\%_{w/w}$ (2,500 mg/kg) by H14.

Furthermore, there are additional criteria introduced with the new EWC. The main impact for contaminated soil is that category 3 carcinogens are now evaluated (they are not within the scope of the definition of special waste). The threshold is 1% and diesel contaminated soils may be hazardous wastes that were previously not special.

Stabilised/solidified wastes (EWC entry 19 03) also appear as mirror entries in the EWC. Stabilised wastes are defined as wastes that have been treated so that they are no longer hazardous (European Commission Decision 2001/118/EC amending Decision 2000/532/EC).

Partially stabilised wastes are those where, after stabilisation, the dangerous constituents have not been completely changed into non-hazardous constituents and could be released into the environment in the short, medium or long term. Solidified wastes are those whereby treatment has changed the physical state of the waste without changing the chemical properties. Partly stabilised and solidified wastes can be hazardous or non-hazardous, depending on the presence of dangerous substances. The implication is that hazardous waste treated by S/S may remain hazardous. Such treated wastes may be defined as "stable non-reactive" whereby they are still classified as hazardous wastes but may be deposited with inorganic non-hazardous wastes in non-hazardous landfills as their hazardous properties are no longer manifest. The draft Landfill (England and Wales)(Amendment) Regulations 2004 (consultation closed 17 December 2003) is available from: www.defra.gov.uk/corporate/consult/landfill-regs/index.htm) and define this to mean:

where the leaching behaviour will not change adversely in the long-term, under landfill design conditions or foreseeable accidents:

(a) *in the waste alone (e.g. by biodegradation);*

(b) *under the impact of long-term ambient conditions (e.g. water, air, temperature, mechanical constraints); or*

(c) by the impact of other wastes (including waste products such as leachate and gas).

The use of hydraulic binders for waste treatment may result in the treated waste being assessed as hazardous by H4 (irritant) or H8 (corrosive) where the pH of the leachate is 11.5 or greater. An alkali reserve test can also be carried out that, when combined with pH, provides a measure of corrosivity (Young *et al.*, 1988). The pH can only be used for this purpose where the waste is a complex mixture of substances whose composition is not determined (Environment Agency, 2003). The risk phrase for CaO and CaOH is R41 (H4) - risk of severe damage to the eyes - and the threshold concentration associated with this phrase is 10%.

7.5.2 Article 4 of the LFD: Classes of landfill

The LFD divides landfill into three classes:

- landfill for hazardous waste;
- landfill for non-hazardous waste; and
- landfill for inert waste.

Article 5 includes information on wastes that will no longer be accepted in a landfill, including:

- liquid waste;
- explosive, corrosive, oxidising, highly flammable or flammable waste (under the conditions in the landfill);
- hospital and other clinical wastes that are infectious;
- whole and shredded used tyres; and
- any other waste that does not comply with acceptance criteria (see section 7.5.4).

The mixing of waste solely to meet the acceptance criteria is also prohibited.

Article 6 provides further detail on what types of waste may be deposited in each class of landfill as follows:

- landfill for inert waste may only accept inert wastes;
- landfill for non-hazardous waste may accept municipal waste and other non-hazardous wastes (including inert wastes). They may also accept stable, non-reactive hazardous wastes provided that they are not deposited in cells containing biodegradable waste; and
- landfill for hazardous waste may only accept hazardous waste that satisfy acceptance criteria.

The main implications for S/S are the prohibition of liquid wastes, many of which may be successfully treated by S/S, and the prohibition of co-disposal of hazardous wastes with non-hazardous waste.

7.5.3 Article 6 of the LFD: requirement for treatment of waste

Article 6 requires member states to take measures in order that only waste that has been subject to treatment is landfilled. In addition to the Article 6 requirement, treatment can also be carried out to:

- enable waste to be recovered;
- meet acceptance criteria for a particular class of landfill;
- permit deposit in a lower class of landfill, e.g. the deposit of stable, non-reactive hazardous waste in a non-hazardous waste landfill; or
- to reclassify mirror entry wastes (e.g. treat a hazardous waste to remove the hazardous properties).

The Environment Agency has published a consultation draft document "Guidance for the recovery and disposal of hazardous and non hazardous waste. IPPC S5.06, Issue 5, 13 October 2003" that provides high level guidance on indicative standards and environmental performance relevant to waste treatment techniques for hazardous and non-hazardous wastes.

7.5.4 Article 11 of the LFD: waste acceptance procedures

Article 11 requires Member States to take measures to ensure that waste is demonstrated to be acceptable before being accepted at a landfill site. Annex II of the LFD describes general principles and guidelines for acceptance of waste at various classes of landfills, to be implemented in England and Wales by the Landfill (England and Wales)(Amendment) Regulations 2004. The Environment Agency has published a consultation draft document "Guidance on sampling and testing of wastes to meet landfill waste acceptance procedures. Version 4.3a, December 2003" that includes a proposed approach to determining compliance with the waste acceptance procedures for both granular and monolithic wastes. Acceptance criteria for monolithic wastes are yet to be published (as of December 2003).

In view of the draft status of both regulations and key guidance at the time of writing (December 2003) the following presents only a brief overview of the proposed approach.

7.5.4.1 Basic characterisation of a waste stream

Annex II of the LFD requires general characterisation and testing of waste to be based on three levels:

Level 1: Basic characterisation
Level 2: Compliance testing
Level 3: On-site verification

The producer of the waste, or the person responsible for its management, must ensure that the waste has undergone basic characterisation. This includes the type and origin of the waste, its composition, consistency, leachability and other characteristic properties, which enable an understanding of its behaviour in landfills and the options for its treatment (Table 7.12). The requirement for level 1 testing may be waived for certain wastes or under certain circumstances.

Table 7.12: Basic requirements for characterisation of waste (COM(2002) 512 final, draft Landfill (England and Wales)(Amendment) Regulations, 2004).

Source and origin
Information on the process producing the waste
Description of the waste treatment applied in compliance with Article 6 or a statement of reasons why such treatment is not considered necessary
Data on the composition of the waste and its leaching behaviour
Appearance of the waste in terms of colour, smell etc
Code according to the European Waste List (Decision 2001/118)
For hazardous wastes – the relevant hazard properties according to Annex III of the Directive 91/689
Information to prove the waste does not fall under the exclusions of Article 5.3 of Directive 91/31
The landfill class at which the waste may be accepted
Additional precautions to be taken at the landfill
A check if the waste can be recycled or recovered
Understanding of likely behaviour of the waste in a landfill
Assessment of the waste against relevant limit values
Identification of key variables for compliance testing and options for simplification of such testing

The compliance test to be used to routinely test the waste against acceptance criteria should be used during basic characterisation to determine the class of landfill in which the waste can be disposed. However, basic characterisation testing should also be used to assess its leaching behaviour. The long-term performance of the waste stream under most likely and worst-case scenarios within the landfill may be assessed and key questions addressed, such as:

- how much of the available contaminant will remain after flushing with a known number of bed volumes?
- what effect will weathering (exposure to air, water) have on the release of contaminants (as a result of a change in pH)?
- is the predicted rate of release likely to pose a problem?
- what is the likely timescale to final storage quality?

A range of standard leach tests are available or in draft to facilitate performance testing (Environment Agency, in prep.).

Characterisation test data may also be used to identify treatment options to ensure that waste acceptance criteria are met, to result in a lower classification, or to enable recovery.

7.5.4.2 Waste acceptance criteria for landfill

Waste acceptance criteria (WAC) have been set for each class of landfill. With regard to S/S treated wastes the most significant criteria are likely to be those for stable non-reactive hazardous waste and hazardous waste, for both granular and monolithic waste forms. Criteria for monolithic wastes have yet to be set in the UK (as of December 2003). A summary of the WACs using the BS EN 12457-3: 2002 at a cumulative liquid:solid (L/S) ratio of 10 is given in Table 7.13.

Table 7.13: Leaching limit values for granular wastes at L/S10 (COM(2002) 512 final)

Component	Inert landfill	Stable non-reactive hazardous waste	Hazardous landfill
As	0.5	2	25
Ba	20	100	300
Cd	0.04	1	5
Cr_{total}	0.5	10	70
Cu	2	50	100
Hg	0.01	0.2	2
Mo	0.5	10	30
Ni	0.4	10	40
Pb	0.5	10	50
Sb	0.06	0.7	5
Se	0.1	0.5	7
Zn	4	50	200
Chloride	800	15000	25000
Fluoride	10	150	500
Sulfate	1000*	20000	50000
phenol index	1	N/A	N/A
DOC**	500	800	1000
TDS***	4000	60000	100000

All units in mg/kg dry weight

N/A Not applicable

* this limit value for sulfate may be increased to 6,000mg/kg, provided that the value of C_0 (the first eluate of a percolation test at L/S = 0.1 l/kg) does not exceed 1,500 mg/l. It will be necessary to use the percolation test (prEN 14405) to determine the limit value at L/S = 0.1 l/kg under initial equilibrium conditions.

** if the waste does not meet this value for Dissolved Organic Carbon (DOC) at its own pH value, it may alternatively be tested at L/S = 10 l/kg and a pH between 7.5 and 8.0. The waste may be considered as complying with the acceptance criteria for DOC, if the result of this determination does not exceed the limit value. (A draft method based on prEN 14429 is available).

*** the value for Total Dissolved Solids (TDS) can be used alternatively to the values for sulfate and chloride.

Limit values for the total content of some organic parameters have also been set for inert wastes as shown in Table 7.14.

Table 7.14: Limit values for total organic parameters for inert wastes

Parameter	**Value mg/kg**
TOC	30000*
BTEX	6
PCBs (7 congeners)	1
Mineral oil (C10 to C40)	500
PAHs	Member states to set limit values

* in the case of soils a higher limit value may be admitted by the competent authority; provided the Dissolved Organic Carbon at pH 7 (DOC7) value of 500 mg/kg is achieved.

Stable non-reactive hazardous wastes must also meet the criteria set out in Table 7.15 if they are to be deposited in a cell at a non-hazardous landfill.

Table 7.15: Additional criteria for stable, non-reactive hazardous wastes deposited in non-hazardous landfill

Parameter	Value
TOC	5%*
pH	Minimum 6
ANC	Must be evaluated

* if this value is not achieved, a higher limit value may be admitted by the competent authority, provided that the Dissolved Organic Carbon value at pH 7 (DOC7) of 800 mg/kg is achieved.

Hazardous wastes disposed of in hazardous landfills must meet the additional criteria set out in Table 7.16.

The procedures for accepting waste at landfill sites will come into force on 16th July 2004 and the waste acceptance criteria must be applied in England and Wales from 16th July 2005.

Table 7.16: Additional criteria for hazardous wastes deposited in hazardous Landfill

Parameter	Value
TOC*	6%**
LOI*	10%
ANC	Must be evaluated

* either LOI or TOC must be used

** if this value is not achieved, a higher limit value may be admitted by the compentent authority, provided that the DOC7 value of 1000mg/kg is achieved.

7.6 Summary

Solidification/stabilisation systems have been used in the UK to treat hazardous wastes for at least 15 years, although problems with centralised treatment centres has led to the technology having a poor reputation. In North America, Japan and some EU member states S/S has been used successfully for 20-30 years to treat a variety of wastes. Although there have been some reported failure of S/S in the past it is unlikely that these would occur again. This is for the simple reasons that regulation and guidance are much more effective than in the past and that there is a greater appreciation of limitations of treatment technologies including S/S.

The following conclusions can be made about the centralised treatment of wastes by S/S:

- S/S treatment of waste streams is an accepted technology in the USA, Europe and elsewhere for the treatment of hazardous waste prior to disposal in landfill;
- in the USA industrial wastes have been treated by S/S since the 1960s;

- the technology has been used for the treatment of hazardous wastes in France since 1975 and legislated since 1995;
- clear criteria for judging the success of treatments have been developed and supported by the EPA in the USA and ADEME in France;
- there have been some past failures of the technology but these are greatly outweighed by successful treatment of large volumes of waste;
- many waste streams require pre-treatments or special additives prior to S/S and it is important to characterise a waste stream fully and conduct treatability trials before accepting the waste for treatment;
- under the provisions of the Landfill Directive, S/S of hazardous wastes may allow them to be deposited in non-hazardous landfills provided that they meet the acceptance criteria and are not deposited in the same cell as biodegradable waste; and
- stabilised treated wastes are also used in road construction and as an engineering fill. A number of projects are being carried out to identify *bona fide* uses for stabilised wastes, particularly in association with construction.

Changing legislation in Europe will have a significant impact on waste management practices in the UK through:

- changes to the classification of waste;
- change to classes of landfill, including prohibition on co-disposal of biodegradable and inorganic wastes;
- the requirement to pre-treat wastes prior to landfill; and
- a new regime of waste acceptance procedures.

The changes will increase substantially the volume of waste subject to treatment, either to satisfy Article 6(a) of the LFD, to permit treated waste to be disposed of at a lower class of landfill, to satisfy waste acceptance criteria, or to enable recovery.

The strict regulatory controls over the management of hazardous wastes, including waste treatment, make it unlikely that dramatic failure of a centralised waste treatment process as illustrated by the Sealosafe case study, is much less likely to occur in the UK.

REFERENCES

Al-Tabbaa, A. and Perera, A.S.R. (2002a) State of Practice Report UK Stabilisation/ Solidification Treatment and Remediation: Binders and Technologies – Basic principles. STARNET REPORT II.

Al-Tabbaa, A. and Perera, A.S.R. (2002b) State of Practice Report UK Stabilisation/ Solidification Treatment and Remediation: Binders and Technologies – Applications. STARNET REPORT III.

Blue Circle Industries. (2001) Company Information Sheet 'Envirocem' (available from www.lafargecement.co.uk/data-pdfs/envirocem/pdf)

Board, M.J., Reid, J.M., Fox, D.S.J. and Grant, D.I. (2000*) The Effects of Age on Cement Stabilised/solidified Contaminated Materials*. TRL Report 451. Transport Research Laboratory, Crowthorne

Bone, B. (2000). Cement Stabilisation/solidification of Contaminated Soil: A Regulator's View. BCA Symposium: Recycling Contaminated Land with Cement. University of Greenwich, June 2000 (available from www.cassst.co.uk)

Chateau, L. (2002) The European Perspective on S/S. Focusing on the French experience. Symposium: Recycling Contaminated Land with Cement-Issues Facing Stakeholders in the UK. University of Greenwich, April 2002 (available from www.cassst.co.uk)

Clement, J.A. and Griffiths, C.M. (1985) Solidification Processes. In: Porteous, A. (Ed.) *Waste Management Handbook*. Butterworths, London.

COM (2002) 512 final. Proposal for a Council Decision Establishing Criteria and Procedures for the Acceptance of Waste at Landfills.

Conner, J.R. (1990) *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold. P. 692.

Conner J.R. and Hoeffner S.L. (1998) The History of Stabilisation/Solidification Technology. *Critical Reviews in Environmental Science and Technology* 28, pp. 325-396.

Council Directive 1999/31/EC The Landfill of Waste. The Council of the European Union.

Council of the European Communities (2002 a) European Waste Catalogue European Commission Decision 2000/532/EC as amended by European Commission Decisions 2001/118/EC, 2001/119/EC and 2001/573/EC.

Environment Agency (2003) *Hazardous Waste: Interpretation of the Definition and Classification of Hazardous Waste*. Environment Agency Technical Guidance WM2.

Environment Agency (*in prep.*) Guidance on Sampling and Testing of Wastes to Meet Landfill Waste Acceptance Procedures, External Consultation Document, Version 4.3a, December 2003.

Environmental Data Services (1992) *Leigh Convicted of False Claims for Waste Solidification Process*. ENDS No. 206, March 1992.

ERL (1989*) Environmental Impact Assessment of Waste Disposal Activities at Leigh Interests plc*. Walsall Metropolitan Borough Council, Environmental Health and Consumer Services Department.

European Council Directive on Waste 75/442/EEC (as amended by Council Decision 91/156/EEC).

European Commission Decision 2000/532/EC (as amended) Revision of the European Waste Catalogue

European Council Directive 91/689/EC, Hazardous Waste Directive.

European Council Directive on Waste 75/442 EEC (as amended by Council Decision 91/156/EEC) European Waste Catalogue.

Guha, B. (2002) Design for the In-situ Remediation of Mercury Contaminated Sediment Using Solidification/stabilisation. Unpublished MSc Research Thesis, University of Greenwich, UK.

Gush, B. (2002) Personal communication.

Hills, C.D. (1993) *The Hydration of Ordinary Portland Cement during Cement-Based Solidification of Toxic Wastes*. Unpublished PhD Thesis, University of London.

Jardine, F.M. and Johnson, S.T. (2000*) Demonstration of the Geodur Stabilisation/solidification System*. CIRIA Project Report, 14.

MacLeod, C.L. (2003) Personal communication, January 2003, University of Greenwich, UK.

Magnie, M-C. (2003) Personal communication, June 2003, INERTEC, Nanterre, France.

McKinley, J.D., Thomas, H., Williams, K. and Reid, J.M. (1999) Detailed Chemical Analysis of Lime Stabilised Materials. TRL Report, 424. Transport Research Laboratory, Crowthorne

Means, J.L., Smith, L.A., Nehring, K.W., Brauning, S.E., Gavaskar, A.R., Sass, B.M., Wiles, C.C. and Mashni, C.I. (1995) The Application of Stabilisation/solidification to Waste Materials. Lewis Publishers.

Naisbitt, N.J., Bethel, N., Gregory, R.G. and Davies, J.N. (2002) Redefining Special Waste. In: *Proceedings of Waste 2002. Integrated Waste Management and Pollution*

Control: Research, Policy and Practice. Stratford-upon-Avon, UK, 24-26 September 2002, pp. 3-9.

Powers S.E., and Zander A.K. (1996) Stabilisation of a Mixed Waste Sludge for Land Disposal. *Hazardous Waste and Hazardous Materials* 13, pp.515-524.

Reid, J.M. (2002) Manufactured Aggregates for Reclamation Sites (MARS). *Starnet News* Issue 2.

Reid, J.M. and Clarke, G.T. (2001) The Processing of Contaminated Land in Highways Works. TRL Report 489. Crowthorne, Transport Research Laboratory.

Stegemann, J.A. and Cote, P.L. (1991*) Investigation of Test Methods for Solidified Waste Evaluation*. Appendix B: Test Methods for Solidified Waste Evaluation. Environment Canada. Unpublished Manuscript Series Document TS – 15.

Stegemann, J.A., Caldwell, R.J. and Shi, C. (1997) Variability of Field Solidified Waste. *Journal of Hazardous Materials* 52, pp. 335-348

United States Environmental Protection Agency (1986) *Prohibition on the Disposal of Bulk Liquid Hazardous Waste in Landfills – Statutory Interpretive Guidance*. Office of Solid Waste and Emergency Response Policy Directive No. 9487.00-2A. EPA/530-SW-016, Washington, DC.

United States Environmental Protection Agency (1989) *Stabilisation/Solidification of CERCLA and RCRA Wastes. Physical Tests, Chemical Testing Procedures. Technology Screening and Field Activities*. EPA/625/6-89/022

Wilk, C. (2002) Application of S/S in the U.S.A. British Cement Association Symposium: Recycling Contaminated Land with Cement-Issues Facing Stakeholders in the UK. University of Greenwich, April 2002 (available from www.cassst.co.uk)

Young, J.R., How, M.J., Walker, A.P. and Worth, W.H.M. (1988) Classification as Corrosive or Irritant to Skin pf Preparations Containing Acidic or Alkaline Substances, Without Testing on Animals. *Toxic In Vitro* 2(1), pp. 19-26.

8 TESTING OF MATERIALS BEFORE, DURING AND AFTER STABILISATION/SOLIDIFICATION

8.1 Introduction

This chapter discusses appropriate methods for testing contaminated soil, sediment and waste, and for evaluating such materials treated using S/S. The test methods are presented under three broad headings:

- leaching tests;
- physical tests; and
- mineralogical/micro-structural tests.

This chapter does not discuss analytical methods used to determine the concentration of chemical substances or other sampling, testing and monitoring activities (e.g. groundwater monitoring) carried out in association with but not on S/S treated material.

Sampling and testing of materials is a fundamental part of the design and implementation of S/S treatment. There are a number of key stages when sampling and testing of the material before or after treatment may be required, as set out below. Appendices 10 to 12 list key considerations and test methods used prior to and following treatment by S/S.

8.2 Leaching Tests

A simple definition of leaching is the transfer of a substance or compound from a solid to a liquid phase when the two are in contact. It is a complex phenomenon and occurs in nature as a result of physical and chemical weathering processes involving the interaction between a soil or rock and water (see Chapter 9).

The amount, or rate, of leaching of a particular substance from a solid matrix, can be influenced by a large number of physical, chemical and biological factors, including (from van der Sloot *et. al.*, 1997):

Physical:
- particle size and shape;
- mineralogy of the solid matrix;
- time frame of interest;
- leachant flow rate;
- temperature;
- porosity and permeability of the solid matrix; and
- hydrogeological conditions;

Chemical and biological:

- equilibrium or kinetic control of release;
- potential leachability of substances;
- pH of the material or that imposed by its surroundings (e.g. carbonation, acid rain);
- complexation;
- redox conditions;
- sorption processes; and
- biologically mediated processes.

Although it may be tempting to recommend a standard test method for S/S treated materials, this would not allow consideration of the likely leaching mechanisms or the site-specific conditions where the material will be deposited. For example, the Toxicity Characteristic Leaching Procedure (TCLP) was developed in the USA to characterise the toxicity of wastes under standard worst-case conditions (co-disposal with biodegradable waste and exposure to landfill leachate). This test was then widely used by regulators and industry as a standard test until a number of legal challenges led to the Science Advisory Board (SAB) criticising the widespread application of the TCLP test. It further recommended that leach tests should reasonably relate to conditions that govern leaching mechanisms under actual disposal conditions (USEPA, 1999). A draft European Standard has been developed that provides a framework for evaluating leaching performance having regard to the disposal or re-use scenario (CEN, 1997).

The number of variables that control leaching processes in reality cannot be replicated under test conditions, and a range of tests will be required to predict the leaching behaviour of the waste form in the environment of deposition. The main parameters that control leaching of a substance, during a leach test are given below:

- sample heterogeneity;
- sample preparation (e.g. size reduction);
- presence and composition of organics;
- composition of the leachant;
- liquid to solid ratio (L/S);
- contact time;
- environmental conditions (e.g. temperature);
- redox conditions;
- solid and leachate separation method; and
- sample storage, preservation and method of analysis.

8.2.1 Sample heterogeneity

When carrying out any tests, including leach tests it is important to know that the samples that are being tested are representative of the materials to be treated. Sampling methodology, frequency and presentation for testing are dealt with in a number of reports including BS1924 (1990), BS10175 (2001), CEN (2002a) and Environment Agency (in prep.).

Depending on the heterogeneity of material to be treated at a site, it may be necessary to segregate the materials on site, for example for separate treatment or disposal routes. Alternatively, it may be preferable to blend variable materials on site to produce a more uniform feedstock for treatment. This needs to be reflected in the sampling plan to ensure that a like-for-like comparison can be made between test and full-scale treatment.

8.2.2 Sample curing and preparation

Before samples are tested they need to be cured for a period of time. Guidance exists on curing conditions for concrete (e.g. BS EN 12390-2, 2000) and conditions may vary depending on the tests to be undertaken (e.g. BS 1924-2, 1990). The US Army Corps of Engineers (1995) recommends a curing procedure of 95-100% relative humidity at 20-25ºC in a temperature-humidity controlled chamber. For concrete curing BS EN 12390-2 (2000) recommends curing in water or at a relative humidity ≥95% at 20°C ± 2°C. The sample will usually be cured under conditions that will retain the original moisture content and prevent ingress of air. This may be achieved by sealing the sample in wax or a sealed container.

The relationship between curing time and chemical or physical properties may not be straightforward, particularly in view of the complex chemistry of contaminated materials. BS 1924-2 (1990) recommends, for compressive strength testing, that cement stabilised materials may be tested at 3, 7, 14 and 28 days, and lime stabilised materials for 7, 28, 56 and 112 days to determine whether strength is increasing satisfactorily. A 90 day cure has also been used to determine longer-term strengths, and leachability, within reasonable timescales. The determination of variability over various curing periods can also be used to select an appropriate curing period for compliance testing.

In 1995 the Harmonization Network undertook an inter-comparison study of leaching tests for stabilised wastes. The specific objectives of the study were to determine the available release potential, gain a better understanding of the solubilities at equilibrium and to assess the release dynamics. The findings of this study are a typical example of the specific conditions that need to be considered in relation to the testing of a S/S treated soil or waste. Cement reactions were found to continue beyond a 28-day curing time, which is a standardised curing period within the cement and concrete industries. Because hydration continues there may be changes in release rates of contaminants from the treated material beyond this time period and these must be considered when evaluating any leaching data.

Sample preparation techniques e.g. drying, screening and/or crushing may be required to satisfy the criteria of specific tests. The potential impact of sample preparation must be considered, in particular with regard to the objectives of the test. For example, if the material to be tested consists of large particle size (> gravel), it may be appropriate to crush the sample to increase surface contact with the leachant. However, for solidified products resulting from lime or cement addition the objective may be to assess the diffusive release of contaminants when the monolith is in contact with water and it would therefore not be desirable to crush the sample. In general a worst-case leaching scenario will be tested as the maximum particle size is reduced.

Although it is usually considered standard practice to dry material in an oven at 105 ±0.5 ^{o}C, in circumstances where a contaminated material has been stabilised or solidified, drying may significantly change the chemistry of precipitates or other chemical species. This hypothesis is based on the fact that some reactions are exothermic (produce energy) or endothermic (require energy). Therefore by applying energy in the form of heat, exothermic reactions may be inhibited and endothermic reactions may be promoted. In addition to hydration products, this may be significant in terms of cation exchange, surface adsorption and the structure and properties of clay minerals.

A standard test method for wetting and drying of solid wastes (ASTM D4843, 1999) requires a drying temperature of 60ºC to minimise the loss of VOCs. However, forced drying may still cause changes to the nature of the material being investigated.

Sample preparation by air drying may also have a significant affect on the chemistry of an S/S treated material in that it may promote carbonation and affect the rate of hydration reactions.

It should be noted that the way samples are collected and stored can also have a significant affect on the results obtained from leach tests and that recommended procedures for sample storage should be followed.

8.2.3 Redox status and presence of complexing agents

Organic compounds may be present in the sample as contaminants or as soil organic matter. The dissolution of organic compounds may have an influence on leachant pH, the solubility of inorganic contaminants (e.g. heavy metals) due to complexation, and the solubility of organic contaminants. Chapter 2 discusses redox and complexation reactions.

8.2.4 Leachant composition

Leachant composition is critical when determining contaminant release. A large number of leachants have been used to suit specific objectives including the level of aggressiveness required (e.g. total, available and actual leaching under specified conditions), the nature of the material being leached, and the receptor (e.g. groundwater, plant uptake). Table 8.1 provides example leachants used to assess different leaching scenarios (after van der Sloot, *et. al.*, 1997). In terms of practical application for prediction of behavioural characteristics, surface water or groundwater from the site may be the preferred leachant. However, the groundwater quality may be subject to significant variation, be difficult to store and transport in bulk without chemical change and may have a limited 'shelf' life.

Table 8.1: Typical leachants used to assess different leaching scenarios (after van der Sloot, *et al.*, 1997)

Level of aggressiveness	Soil	Sediment	Waste	Construction materials
Total	Aqua regia	Aqua regia	Aqua regia	Aqua regia
Available for leaching	Acetic acid EDTA	Acetic acid (sequential extraction)	2 step batch test at pH7 and pH4	Not defined
Leaching to reflect environmental conditions	Mild leachants, e.g. $CaCl_2$ NH_4NO_3 $NaNO_3$	$MgCl_2$ $CaCl_2$	Deionised water $5 < pH < 7.5$	Deionised water (tank test)

Many leaching tests in the past have utilised aggressive leachants that contain organic acids such as acetic acid, strong inorganic acids such as nitric acid/hydrochloric acid mixtures or complexing agents which have a high affinity for specific elements, essentially stripping contaminants from the waste or soil. Aggressive acids are usually added either as a fixed quantity at the beginning of a test or added gradually throughout the entire test to retain a specific constant pH. Aggressive acids will dissolve precipitates and the high hydrogen ion concentration could exchange with contaminants at potential cation exchange site. The implication of adding such acids are especially detrimental to stabilised materials since the strong acid has the potential to neutralise the pH-dependent benefits of some stabilisation and solidification methods. The stabilisation and solidification methods directly affected include, lime stabilisation, cement stabilisation, adsorption stabilisation such as modified clays and any combination of these methods.

It may therefore be important to investigate leaching properties with varying pH conditions. CEN have developed a pH dependence test, pr EN 14429 (CEN, 2002d), that evaluates the effect of falling or increasing pH conditions on the leachability of granular waste. The acid neutralising capacity (ANC) of the treated material can also be assessed using this test.

The buffering capacity, or ANC, of S/S treated material is important in predicting the durability of the treated material. If the pH falls rapidly on addition of acid it can be predicted that the treated material has poor capacity to buffer acidic infiltrates and therefore are likely to leach contaminants sensitive to pH change. The buffering capacity will be dependent on the mineralogy and pH of the system, and thermodynamic modelling can be used to predict buffering mineral phases over a pH range. For example, hydroxides show strong buffering of strong acids in alkaline systems and some silicates, carbonates and gibbsite (aluminium hydroxide) have a strong buffering capacity to strong acids at slightly alkaline to slightly acid conditions (Yong *et al.*, 1992).

A S/S treated system with a high buffering capacity is more likely to be durable, i.e. "permanently" fix the contaminants over a significant time scale. The ANC was assessed during treatability studies for *in-situ* treatment of heavy metal contaminated soil at Ardeer, Scotland (Sansom, 2000). Once the optimum binder was selected, an ANC of 2 meq H^+g^{-1} at pH9 was set as a remediation criterion.

8.2.5 Liquid to solid (L/S) ratio

Liquid to solid ratio is usually defined as the ratio of the contact liquid and dry mass of solid. Either the sample is air-dried or a moisture content is measured and the dry mass calculated. The ratio of liquid to solid in a leaching test is usually significantly greater than that in soil pores *in-situ* and consequently chemical equilibria are significantly different. This will affect the quantities of soluble contaminants detected and does not represent the true *in-situ* leaching characteristics.

Liquid to solid ratio is important because it can relate to a time scale through the rate of infiltration, density and thickness of treated material. Bordas and Bourg (2001) investigated the effect of L/S on the remobilisation of heavy metals from polluted river sediment. They found that when sediment is left *in-situ* with low L/S the mobility of the pollutants was low, re-suspending the sediment with a high L/S caused increased dissolution of contaminants from the sediment surfaces. This is because in a dynamic system with sediment suspended within the liquid, more surface area is exposed and hence desorption or dissolution can occur. Thus, performing leaching tests with different L/S ratios and the same leachant may give an indication of the overall solubility of the contaminants in the material tested.

It is necessary to consider how the L/S used in the leach tests represents this *in-situ* condition and how the differences in L/S ratio may affect the results and prediction of long-term performance.

8.2.6 Contact time

The contact time will influence the concentration of leached substances at fixed L/S, until equilibrium conditions are reached, when a maximum concentration will occur. Equilibrium is a unique thermodynamic state of a system depending only on temperature. As such, this state provides a framework within which comparisons to other systems may be made. True equilibrium, or even steady state conditions are unlikely to be reached in natural systems. For such systems, the extent of the reaction, related to equilibrium, may be a more useful concept (Löwenbach, 1978). Equilibrium conditions will exist in a test when the total dissolved solids have reached steady state conditions. This can be measured indirectly by monitoring conductivity and/or pH. Both these methods are particularly useful when considering lime or cement stabilised materials due to the high calcium ion content and the very high pH induced by reagent addition.

The leaching period is also important when the contaminated material is continually or sequentially subjected to fresh leachant over a time period, dependent on pore volume and permeability. Therefore the driving force for desorption is constant, resulting in time dependent desorption curves. Such methods may be useful where a material will be exposed to rainfall, particularly in a wet climate.

8.2.7 Contact method

The contact method is directly linked to the leaching period in the sense that the two together affect particle abrasion and subsequent breakdown. The level to which a container is filled is also relevant because this governs the amount of air and also CO_2 (g) present, and the degree to which the solid and liquid can be agitated within the confined space.

The contact method is also of importance in flow-through tests because the shape and orientation of the confined material, as well as the pressure at which the leachant is passed though the sample, governs the sample structural breakdown. Sample shape (height to diameter ratio) can have a large influence on end effects that result in non-uniform flow through the ends of the sample. This can directly affect the quantities of contaminant removed from a sample.

8.2.8 Test environmental conditions

Probably the most important environmental condition is temperature, which affects the results of both equilibrium and kinetic tests. Temperature affects both the solubility of the test species and the rate of reactions. Thus changes in the temperature of a system may change the reaction mechanism. For convenience most leaching tests are performed at room temperature without any temperature control, although raised temperatures are sometimes applied to simulate the effects of self-heating radioactive wastes or biological activity in landfill sites. It is clear however that large changes in temperature from summer to winter in the laboratory will affect attenuation and desorption reactions. Hence it is important when evaluating or comparing leach test results to ensure that the laboratory conducting the tests control the temperature in which they are carried out.

It may also be possible to specify the temperature at which tests are undertaken, to eliminate the difference in test conditions from those present on site. If this is not done, leach tests carried out at room temperature may provide conservative results.

8.2.9 Solid and leachate separation methods

This is generally not a significant factor for samples where solids settle within a few minutes and the solution can be decanted through filter 'papers'. Lewin *et al.* (1994) state that glass fibres should be used when hydrophobic, low solubility organic molecules are expected in the leachate because they could have a high affinity for filters composed of an organic polymer. Membrane filters with a pore size of 0.45 μm, such as cellulose acetate, should be used for metal species in place of glass. Pore size is important as the less than 0.45 μm fraction is operationally considered to contain dissolved species. Filter 'papers' do pose a particular problem for sequential rapid extraction batch tests because the material on the filter must be placed in a fresh container with fresh leachant. In some cases the filter is also placed in the fresh container. It is therefore especially desirable to use a filter that does not contain elements that may be released into solution or alternatively attenuate elements from the waste.

Centrifugation is often used for separation of solid and liquid components, e.g. where the leachate contains a high humic content or losses by absorption are likely. However, the action of centrifugation can cause particle abrasion and, if not refrigerated, significant heat is produced which may affect the leachate chemical composition. Furthermore, each solution must be considered independently since the speed of revolution and duration of centrifugation required to separate the solid from the liquid will vary from sample to sample. In circumstances involving thixotropic material, centrifugation may be the only method capable of separating the liquid from the solid. However, it must be remembered that in these circumstances the separation technique is particularly aggressive and perhaps produces a leachate that does not reflect the true quantitative properties of the original material-solution mixture. It is also important that flocculating agents are not added to force solid - liquid separation since this will clearly alter the chemistry of the mixture.

8.2.10 Sample storage, preservation and sample analysis method

There are many standards including ASTM and BS procedures for appropriate sample storage methods that largely depend on the types of contaminants present. For example, leachate sub-samples to be analysed for metals should be acidified using very pure acids to pH <4 and stored at 4^{o}C to prevent biological activity. Instrumental methods such as Inductively Coupled Argon Plasma Atomic Emission Spectroscopy (ICP), Atomic Absorption spectrometry (AA) or Graphite Furnace (GF) are often used for analysis of metals.

If the leachate sample contains organic compounds, these are usually stored in amber glass bottles that have been previously rinsed in a solvent and baked to drive off any organic residues. These solutions usually require some further extraction, derivitisation and pre-concentration of analytes prior to analysis via Gas Chromatography (GC), Gas Chromatography–Mass Spectrometry (GC-MS) or High Pressure Liquid Chromatography (HPLC).

8.2.11 Further significant factors affecting leachate generation

Table 8.2 (after Löwenbach, 1978) summarises the significance of pH, redox potential, buffering capacity, complexation capacity, ionic strength, dielectric constant and surface area, and suggests how these variables may affect leachate generation. Table 8.4 highlights the advantages and disadvantages of extraction (batch) tests, flow-around (diffusion) tank tests and flow-through (column) tests.

8.2.12 Leaching of organic contaminants

Most leach tests have been developed and validated for leaching of inorganic compounds, yet they are often used to assess the leachability of a wide range of organic compounds. Few tests available are validated for organic compounds due to the large range of compounds and their diverse properties (e.g. volatility, degradability, solubility), and factors controlling their distribution (see Sections 2.5 and 2.6). Some of these factors can make many compounds difficult to preserve and handle in simple test systems.

Any test data presented on organics using tests developed for inorganic compounds should be viewed with caution, primarily because of:

- sampling and preparation methods required by a standard method may not be conducive to preservation of volatile and semi-volatile organics;
- desorption of low solubility organics from the solid matrix may take significantly longer than a standard equilibrium test permits;
- influence of oxygen (degradation) during testing;
- dilution effects of liquid: solid ratio;
- influence of headspace on volatile organics;
- sorption onto container walls; and
- resorption during filtration.

The Industrial Waste Division of the Danish Environmental Protection Agency has investigated the development of a standard leach test method for organics. Such a test would be used to assess the re-use of residual products and soil in association with building and engineering works where the material is to be re-used "not near the surface" (www.mst.dk/project/NyViden/2001/10030000.htm). The Danish EPA divide organic contaminants into three groups in relation to likely leaching properties from soil and residual products:

- substances that sorb strongly to the soil, are only partially soluble in water and are non-volatile (e.g. higher PAHs, PCBs);
- volatile substances with a relatively high solubility in water (e.g. BTEX and chlorinated solvents); and
- substances that are highly soluble in water (e.g. phenols, MTBE).

The relevance of leach testing to each of the groups will be variable. For the first group, the separation of the contaminant from the solid phase (including materials used in the test) will be critical during testing. Loss of contaminant to air will be a key consideration in the design of a leach test for the second group, and a leach test will be of limited use for contaminants that strongly partition to the aqueous phase since they are rarely sorbed.

The Harmonisation Network reported the outcome of a workshop on leaching of organic contaminants on 2 December 1998, attended by 17 specialists from 8 countries (Newsletter No. 5, www.leaching.net/newslett/mrt99.html). The workshop concluded that:

- leaching of organics is considered to be a key issue in evaluating the impact of organic contaminants as opposed to use of total concentrations;
- stronger focus on the behaviour of DOC, its relevant sub-fractions and properties, and colloids is needed, particularly when evaluating the strongly water-insoluble organics (e.g. PCBs and higher PAHs);
- a longer-term experiment is needed to examine DOC and PAH concentration and speciation in leachate generated from soil undergoing active biodegradation;
- a study on the interaction of poorly water soluble and/or DOC-associated organics with materials, such as filtration media, container walls is needed to better understand limitations of potential test methods and materials;
- where S/S is applied to waste, the role of DOC generated by chemical degradation of organic matter present in the waste may lead to limitations on the tolerable amount of degradable organic matter; and
- the use of leaching tests for evaluating treatment performance of soil and sediment remediation is recommended.

An EU project (ECN Contract SMT4-CT97-2160) was commissioned to develop scientifically-based and practical procedures to test the leaching of organic contaminants from contaminated soil, sediments and granular waste materials (www.leaching.net/newslett/mrt99.html). The project considered three environmentally significant classes of relatively non-volatile contaminants; PAHs, chlorophenols and PCBs, and evaluated the influence of key factors that control the leaching from contaminated soil and waste materials.

A set of standardised test methods is proposed for non-volatile organic contaminants in soil and waste, adapted from the standard CEN tests published or under development for inorganic contaminants (see Section 8.4). The tests developed during the project are:

- an availability test, to assess total availability for leaching;
- a dynamic column test, to assess emission over time; and
- a batch test, for compliance purposes.

The availability and batch leaching test, the latter for compliance, have been developed and detailed procedures are presented in Comans (2001). The factors that were considered and their implications for developing standard availability and batch leach tests are presented in Table 8.3. However, further work is needed to develop a standard column test for non-volatile organics.

Findings from the project have partly been published for PCBs and chlorophenols (Wahlström, *et al.*, 2000) and PAHs (Comans and Roskam, 2002). Key factors that influence the leaching of organics from contaminated soil and wastes were evaluated and leaching methods developed for PAHs using three materials (gasworks soil, asphalt granulate and an organic-rich, mechanical and biological separated fraction of municipal waste). The leach tests were also applied to a range of contaminated and spiked soils for chlorophenols and PCBs.

A key factor in influencing the partitioning of strongly hydrophobic organics is the nature and concentration of DOC (Chin *et al.*, 1990). Comans *et al.* (2000) have confirmed that the increased solubility of DOC with pH applies for a wide range of soil, sediment and waste materials, with a plateau of around pH12-13. This is a significant factor when considering the S/S of material containing hydrophobic organic contaminants. Currently no standard leach test is available in Europe for organic contaminants in soil and waste material and the above approach, reported by Comans (2001) represents the state of research in Europe. Any leach test proposed for organic contaminants must address the factors likely to influence the results, having regard to the nature of the contaminants.

Table 8.2: Definition and significance of factors affecting leachate generation (after Löwenbach, 1978 and reported by Lewin *et al.,* 1994)

FACTOR	DEFINITION	SIGNIFICANCE	REMARKS
pH	pH is defined as the negative log of hydrogen ion concentration. pH is an indirect measure of the electrochemical potential of protons.	The hydrogen ion concentration is an important factor affecting reaction rate and thus pollutant solubilities.	The pH of rainwater is controlled primarily by dissolved CO_2. With rare exceptions, proton exchange and associated processes occur so rapidly that such systems may be treated in terms of shifts of true equilibrium.
Redox potential	The redox potential of a system as defined by Nernst equation. In natural systems redox potential is taken as the measured potential differences between an inert electrode and a reference electrode.	The redox potential is a measure of the oxidising capacity of a system and provides a framework within which redox and hydrolysis reactions may be compared.	Redox potential determines, in part, the aerobic conditions under which a material is leached. Low electron activity represents strong oxidising conditions while high electron activity corresponds to strong reducing conditions.
Buffer capacity	The buffer capacity of a system is defined as the response of that system, in terms of pH change, to the addition of an acid or a base.	Buffer capacity defines the resistance of a system to changes in pH upon the addition of acids or bases.	Naturally occurring leachate exists as a highly buffered system. Total acidity and alkalinity together with pH operationally define buffering capacity.
Complexation capacity	Complexation is defined as the formation of a complex from a metal ion with a natural or negative ion by means of one or more chemical bonds.	The effects of complexation vary from the solubility of specific metals to causing their precipitation, depending on the complexing agent and metal ion. Complexation affects the solubilities, reactions and modes of transport of leached materials.	The most effective complexing agents are generally organic compounds. Fulvic and humic acids are two naturally occurring complexing agents of possible significance in terms of transport of heavy metals and organics.

Table 8.2: (cont) Definition and significance of factors affecting leachate generation (after Löwenbach, 1978 and reported by Lewin *et al.,* 1994)

FACTOR	DEFINITION	SIGNIFICANCE	REMARKS
Ionic strength	The ionic strength of a solution, I, is defined as $I = \frac{1}{2}\sum C_i Z_i{}^2$, where C_i is the concentration of an ion in moles per litre, Z_i is its charge and the sum is taken over all ions in the solution.	Ionic strength has a significant effect on reaction rate and therefore influences the solubility of ionic species. In general the solubility of an ionic salt is roughly proportional to $\sqrt{I}$ for dilute solvents.	The ionic strength is generally calculated rather than measured directly. The ionic strength together with the dielectric constant define in part the polarity of a medium.
Dielectric constant	The dielectric constant is defined by ε in the equation $F = QQ^{1}\sqrt[2]{\varepsilon r}$ where F is the force of attraction between two charges Q and Q^1 separated by the distance r in a uniform medium.	The dielectric constant is related to the solvating power of the eluant. It increases with addition of ionic species. Polar substances become more soluble with increasing dielectric constant, while non-polar substances become less soluble	The dielectric constant of a system is determined by both the molecular nature of the system (e.g. polarisability) and the composition of the system. The dielectric constant together with ionic strength define in part the polarity of a system.
Surface area	The surface area is somewhat difficult to define operationally but practically involves the measurement of some property that qualitatively depends on the extent of surface development and can be related (by means of theory) to absolute surface area. Suitable methods of determination include particle or pore size measurement and permeability studies.	Heterogeneous reactions of solids and liquids are often governed by surface processes that occur at a rate directly proportional to the surface area of a solid, in addition to the reagent concentration in the liquid phase. Finely divided particles have a greater solubility than large crystals. The surface energy of particles smaller than 1µm may become large enough to affect surface properties.	Different methods of surface area measurement will lead to different results. For the purpose of discussing leachate generation within a landfill, methods based on permeability studies or particle size measurement are most useful. The particle size of materials deposited in landfill usually decreases with time due to physical and chemical weathering processes.

Table 8.3: Factors that influence the leaching of PAHs and proposed testing conditions (from Comans, 2001)

Factor	Availability test	Batch compliance test
DOC concentration and composition	Aldrich humic acid at 1000mg/l specified as leachant	Leached under DOC derived from soil or waste using deionised water
pH - influence on DOC, to a plateau at pH 12-13	Specified as pH12	$5 < pH < 7.5$
L/S ratio - increase in leaching PAH, with plateau at very high ratios (500-1000) - very impractical for testing purposes and unrealistic when consider disposal or re-use scenarios	L:S 100	2 step batch test at L:S 2 and 8 (total L:S = 10)
Contact time - little change after 48 hours	48 hours	24 hours each step (total = 48 hours)
Container - losses by adsorption	Glass	Glass
Filtration - losses by adsorption; difficulty due to high humic content in availability test	Centrifugation	Centrifugation

8.3 Type of Leaching Tests

Leaching tests can be designed to address a number of contaminant release scenarios. These scenarios should be considered in relation to actual likely conditions on site and the potential for variability in these conditions, including plausible "worst-case" scenarios:

Equilibrium conditions – to assess the leaching performance when the solution is in contact with the solid under saturated, low-flow conditions. This must be performed at low L/S ratios and equilibrium is either assumed or demonstrated by steady-state conditions for key indicators, such as pH or electrical conductivity. Although it should be noted that whilst pH is often used as an indicator of steady state conditions, this doesn't always apply for all species in solution. The test measures the solubility at equilibrium and may be useful where the treated material is granular.

In many leaching scenarios equilibrium conditions can be approached for the majority of principal phases in an S/S system. This is particularly important for the identification of chemical factors controlling leaching. These include (van der Sloot *et al.,* 1997):

- influence of pH on controlling solubility;
- influence of insoluble inorganic and organic complexing agents;
- the role of redox potential; and
- re-precipitation / sorption processes.

Kinetic (diffusion) control – to assess the rate of diffusion of contaminants from pore water in the solid matrix to the leachant (e.g. ASTM C1308, 2001; NEN 7345, 1997). This type of test may be particularly valuable where the treated material is monolithic, is compacted to promote flow around rather than through the waste form (permeability around 100 times lower than the surrounding ground), or is permanently protected from infiltration by a low permeability capping or surface (e.g. blacktop).

It is important to consider that during S/S treatment the waste form may not be in equilibrium with its environment of deposition. Waste forms will invariably be subject to solid-aqueous phase reactions. These can include longer-term hydration reactions, carbonation reactions and solid-solid transformations, such as conversion of aragonite to calcite. Some of these reactions may be rapid and take place in hours/days, whereas others may take place over geological time scales (see Chapter 9 for further details).

Leaching tests generally fall into two categories – single extraction tests and dynamic tests:

- single extraction tests are carried out by placing a leachant in contact with a solid material for a specific duration without replacement of the leachant. A sample of leachate is removed throughout the test or more usually at the end of the test after solid separation and is chemically analysed to determine the elemental fraction that passes through a 0.45 μm filter; and
- dynamic tests involve continuous or intermittent renewal of the leachant to retain a high concentration difference between the solid and liquid phase. Although these tests are potentially more complex, expensive and time consuming than batch tests, they do provide data relating to the kinetics of contaminant mobilisation and the likely complex mechanisms related to leaching.

The Environment Canada Wastewater Technology Centre (1990) developed a general classification of leaching tests that is summarised in Figure 8.1.

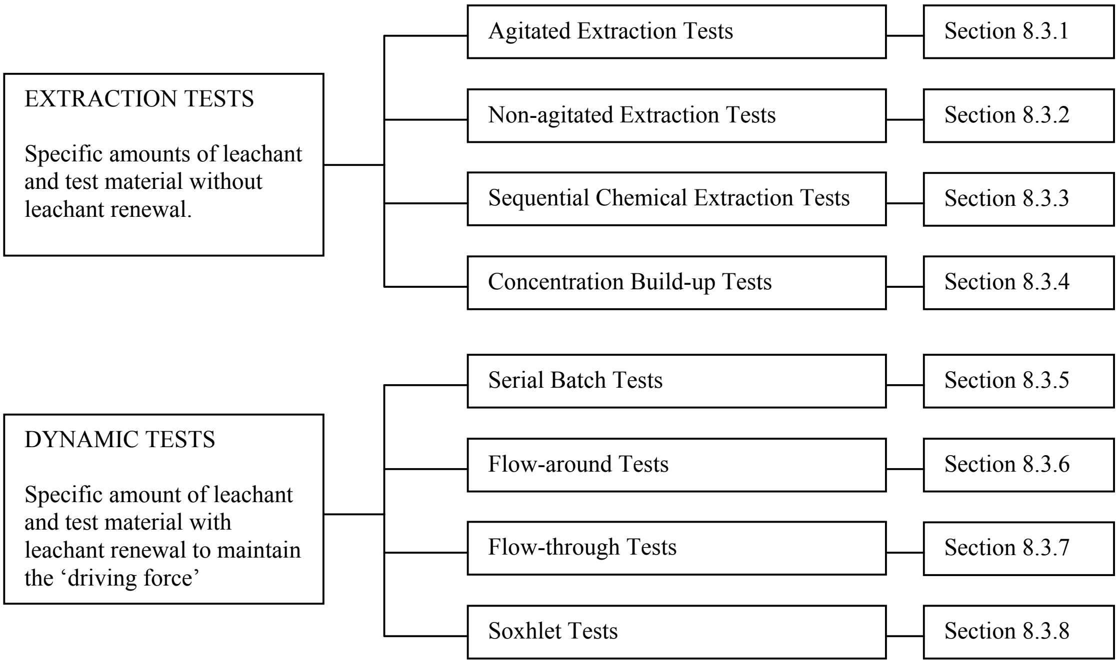


Figure 8.1: Leaching test categories (adapted from Environment Canada, 1990 and reported by Lewin *et al.,* 1994**)**

An evaluation of leaching tests was conducted by Löwenbach (1978) for the USEPA. Lewin *et al.* (1994) made significant use of this report when producing the UK National Rivers Authority Interim NRA guidance (R & D Note 301) for a UK leach test. Table 8.4 provides a summary of the advantages and disadvantages of each category of test.

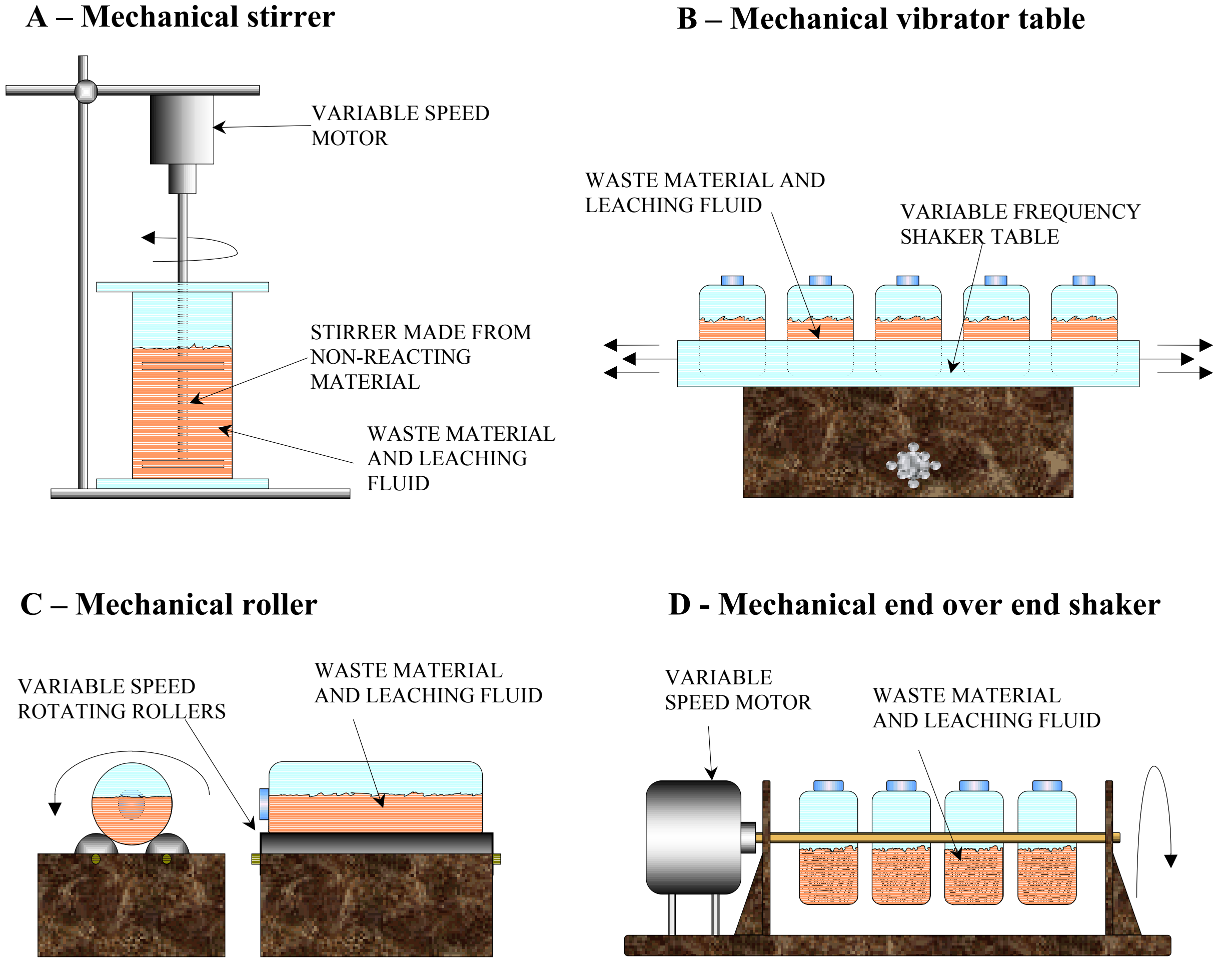
The following sections provide a review of the methods available to determine the mobility of contaminants in granular and monolithic waste-forms.

Table 8.4: Advantages and disadvantages of the principal types of leaching tests

TEST CATEGORY/ OPERATING PARAMETER	ADVANTAGES	DISADVANTAGES
Agitated extraction tests (Batch tests)	• Tests are simple to set up and perform. • Tests can be of short duration (hours) in controlled conditions and if performed at various times can highlight the mechanisms of contaminant retention. • Disturbed samples can be tested easily. • Drying material makes it easier to crush samples if desired and achieve required solid to liquid ratios. • Deionised water is an easily controllable substance that does not affect the stabilisation and solidification contaminant retention mechanism in the same way as an acid. • Once equilibrium is achieved leachate can be removed and replaced with 'fresh' leachant as many times as required. • Synthetic or real leachants, representing leachants *in-situ* can provide a more representative leaching model.	• Does not represent environmental leaching conditions and is therefore inherently qualitative. • Drying can affect the species of contaminants present and volatile organics. • Neither drying nor crushing represent environmental conditions. • Distilled water does not necessarily represent site-leaching conditions. • Synthetic or *in-situ* leachants require characterisation to obtain leaching results by subtraction. • There is no account of time dependent changes in leachant composition. Some minerals do not separate easily from the liquid fraction. • Filter medium can affect chemical determination by element release or attenuation from or onto filter membranes respectively. • Centrifugation can affect results.
Flow-around tests (Diffusion tests)	• Easy to control leachant, solution temperature. • Contaminated samples can be tested as monoliths without pre-treatment. • Diffusion mechanisms are investigated, which are important in low leachate flow conditions. • Solid and liquid separation is not necessarily required.	• Difficult to interpret the results and may not represent the diffusion conditions of a particular disposal site. Results are therefore qualitative similar to the extraction tests.
Flow-through tests (Column leach tests)	• Can represent environmental leaching conditions. • Conditions can be controlled and changed throughout the test. • Unlike the other tests the sample can be subjected to varying physical stress conditions to represent individual sites. • Monolithic samples can be tested without pre-treatment. • Leachate can be passed through samples under pressure to accelerate leaching.	• The tests are not considered suitable for regulatory purposes due to the poor reproducibility and duration. • Tests can last a number of months depending on material permeability and are difficult to set up and perform. • It is difficult to obtain representative undisturbed *in-situ* samples. • Data from this process is inherently qualitative.

8.3.1 Single batch tests

Single batch tests are also commonly known as agitated extraction tests and are used to test granular material of a specified maximum particle size. Steady state conditions are achieved as quickly as possible by mixing, stirring or shaking the material with the leachant. The test measures the chemical properties of the system at or near equilibrium. The methods of mixing samples can be very important since it determines the level of particle abrasion and contact with the leachant. Methods of mixing commonly adopted are illustrated in Figure 8.2.


A – Mechanical stirrer

B – Mechanical vibrator table

C – Mechanical roller

D - Mechanical end over end shaker

Figure 8.2: Mixing methods for extraction tests (courtesy of David Boardman)

Batch leaching tests were initially developed for assessment of the short-term impact of wastes in landfill. Development was due to the complexity, time dependence and resultant cost of column leaching methods. The first batch testing methods were probably developed in the USA by the USEPA and these tests have undergone several refinements over the last two decades. A number of countries worldwide have developed batch extraction tests to satisfy the individual requirements of a country's environmental legislation.

It is very difficult to comment on all batch tests and compare their results due to the number available. For example in the USA, the nuclear industry has one testing method whereas the USEPA has several test methods. These are outlined in the Code of Federal

Regulations (CFR). The American Standards of Testing and Materials (ASTM) has two different tests. Additionally, certain states in the USA have their own testing methods. Examples include the Minnesota Pollution Control Agency (MPCA) "Land Disposal Leach Test", the Illinois Environmental Protection Agency test (IEPA), and the IU Conversion Systems test (IUCS) which was an adaptation of the early Pennsylvanian Department of Environmental Resources test (DER) (Welsh *et al.,* 1981).

Table 8.5 illustrates the differences in conditions for some of the agitated batch tests that have been used.

8.3.2 Non-agitated extraction or static tank tests

Non-agitated tests involve placing a monolithic mass into a leachate bath and monitoring chemical changes within the batch solution. This is usually modelled by diffusion mechanisms and essentially provides data on rate limiting physical mechanisms in the leaching process from the monolithic samples rather than chemical characteristics of the material. These tests have generally been developed for application to radioactive waste, and are useful when assessing the leachability of contaminants from S/S treated monolithic materials.

8.3.3 Sequential extraction tests

Sequential extraction tests involve separation of the waste from the previous leachant and adding this solid to a fresh leachant, hence allowing further leaching to occur. In theory the sequential extraction can be unlimited and may be analogous to column leaching. Some tests are carried out with increasingly aggressive leachants. Lewin *et al.* (1994) state that the resulting fractions of this type of test are not well defined in terms of chemical speciation and do not provide quantitative data, therefore they cannot be applied to field conditions. More recent developments involving multi-variant geochemical analyses may provide a useful method for determining speciation of metals in S/S waste forms.

8.3.4 Concentration build-up tests

Concentration build-up tests involve repeatedly contacting aliquots of fresh contaminated material with the same leachate at very low cumulative liquid to solid ratios and monitoring the subsequent chemical changes. These are not commonly used tests and little literature is available to determine their application to the assessment of S/S waste-forms.

Table 8.5: Summary of agitated batch leaching tests used around the world (after Löwenbach, 1978 and Lewin *et al.,* 1994)

Test name	**Development status**	**Leaching container**	**Sample preparation**	**Sample mass**	**Leachant**	**L/S ratio**	**Agitation method**	**Duration of test**	**Method of leachate separation**
Extraction Procedure Toxicity Test (EP Tox, USEPA 1310A)	Regulatory method (U.S.EPA, 1980)	Unspecified	Non-monolithic waste: phase separation. Monolithic waste: particle size reduction.	100g	Deionised water 0.5N acetic acid (max 2.0meq$H^{=}g^{-1}$ solid)	1:20	Unspecified, continuous	24 to 48h	0.45µm filtration
ASTM D3987 shake test (1979)	Research method (ASTM, 1979)	Round, wide neck bottle	As received	700g	Distilled water (ASTM Type IV)	1:4	Shaking	48h	0.45µm filtration
IUCS modified 48 hour shake leaching test	Research method (IUCS, 1977)	3 litre Polyethylene container	As received, or for monolithic samples: circular slice from a standard proctor or 3”×6” cylinder. No phase separation	5 at 125g and 1 at 500g	Water specific for the field or type II ASTM D1193	1:4	Shaking	1,2,4,8,24 and 48h	0.45µm filtration
Minnesota Pollution Control Agency (MPCA) land disposal leach test	Research method (MPCA, 1977)	2 litre, glass separatory funnel	As received	25g	1)Buffered acetic acid pH=4.5 2)deionised distilled water	1:4	Shaken vigorously for 60 seconds and left to stand for 24h	24h	Medium porosity ashless (<0.1 ash) filtration
Leachate Extraction Procedure (LEP), Ontario	Regulatory method (MOE, 1985)	1250ml, wide neck cylindrical bottle	Phase separation by 0.45µm membrane filter	50g of dry solids	Distilled water, acetic acid (2.0meq$H^{=}g^{-1}$ solids)	1:20	End over end (10rpm)	24h	0.45µm filtration
Quebec R.s.Q., Q-2, R12.1	Regulatory method (1987)	>1 litre bottle	No phase separation. Grinding. No structural integrity	100g dry solids. 50g for volatiles	Inorganics: buffered acetic acid (0.82meq $H^{+}g^{-1}$ solids)	1:10	End over end (10 to 20 rpm)	24h	30 min decantation, 0.45µm filtration.
Waste Extraction Test (WET), California	Regulatory method (SOC, 1985)	Polyethylene or glass container	Milling 0.45µm filtration	50g	0.2M sodium citrate at pH5.0	1:10	Shaker table or rotary method	48h	Centrifugation, 0.45µm filtration
Toxicity Characteristics Leaching Procedure (TCLP, USEPA 1311)	Standard method (U.S.EPA, 1986)	Any material compatible with sample, zero headspace extractor (ZHE) for volatiles	Cutting/crushing and grinding. Solid/liquid phase separation. No structural integrity	100g (25g for ZHE	Buffered acetic acid 1)pH=4.93 2)pH=2.88	1:20	End over end (30rpm)	18h	0.6 to 0.9µm borosilicate glass fibre filter combines liquid phase with extract
TCLP variant, USEPA 1311 Pre-SPLP Test (1312)	Modified TCLP (U.S.EPA, 1989)	As USEPA 1311	As USEPA 1311	As USEPA 1311	Simulated acid rain (sulfuric/nitric acid)	As USEPA 1311	As USEPA 1311	As USEPA 1311	As USEPA 1311
Equilibrium Extraction (EE), Environment Canada.	Published research method (EC, 1990)	Inorganic: 250ml wide neck plastic sample bottle. Organic: 500ml glass	Inorganic: Grinding Organic: Pestle and mortar	Inorganics 40g Organics 80g	Distilled water	1:4	National Bureau of standards rotary extractor	7 days	0.45µm vacuum screen

Table 8.5: (cont.) Summary of agitated batch leaching tests used around the world (after Löwenbach, 1978 and Lewin *et al.,* 1994)

Test name	**Development status**	**Leaching container**	**Sample preparation**	**Sample mass**	**Leachant**	**L/S ratio**	**Agitation method**	**Duration of test**	**Method of leachate separation**
Multiple Batch Leach Testing (MBLP), Environment Canada	Published research method (Constable and Côté, 1986)	1 to 2 litre Square polyethylene or glass bottle	Remove free liquid. Reduce particle size to <9.5mm	Variable to fill 90% of bottle	Distilled water. Acidic water buffer to pH4.5. Synthetic municipal waste	1:4 or 1:20	Slow rotary tumbling	24h	0.45μm filtration
French Leach Test (AFNOR) NF X 31-210	Regulatory method used particularly relative to land-filling hazardous waste (Chateau, 2003)	Straight wall 1.5litre bottle	Remove free liquid, reduce particle size to < 4mm	100g	Demineralised water	1:10	Roller or Shaker	1:24 hr or 3:16 hr	0.45μm filtration or centrifugation
Material Characterisation Centre MCC-3	Regulatory method (radioactive wastes)	Teflon container 20ml to 1 litre	Crush monolithic waste-form into two fractions 74 to 149μm and 180 to 425μm	>1g	Choice of high purity water, silicate water, brine, repository water	1:10	Rolling and rocking	Variable: 28 days to several years	N/A
Italian CNR-IRSA	Regulatory method (1986). (Cernuschi *et al.,* 1990)	Not known	Not known	Not known	1) Acetic acid 0.5N, pH=5 2) CO_2 saturated water	1:16	Continuous stirring	24h	Not known
German leachability by water. DIN 38414-S4	German standard method. (Din-Normen, 1984)	200ml wide necked flask	Sample reduction only if particles >10mm. No grinding	100g	Deionised water	1:10	Initial gentle swirl or flask inversion only	24h	Filtrational centrifugation
CEN / BS EN 12457: Part 1	European standard compliance test	500ml glass / HDPE / PP bottle	At least 95% (by mass) particle size <4mm with or without size reduction	175g ± 5g dry mass	Distilled, demineralised, de-ionised water or equivalent, pH 5-7.5	1:2	End-over-end tumbler 5-10 rpm, roller table at ~10rpm or equivalent	24 hr ± 0.5 hr	Settling and vacuum or high pressure filtration 0.45μm
CEN / BS EN 12457: Part 2	European standard compliance test	1 litre glass / HDPE / PP bottle	At least 95% (by mass) particle size <4mm with or without size reduction	90g ± 5g dry mass	Distilled, demineralised, de-ionised water or equivalent, pH 5-7.5	1:10	End-over-end tumbler 5-10 rpm, roller table at ~10rpm or equivalent	24 hr ± 0.5 hr	Settling and vacuum or high pressure filtration 0.45μm
CEN / BS EN 12457: Part 4	European standard compliance test	1 litre glass / HDPE / PP bottle	At least 95% (by mass) particle size <10mm with or without size reduction	90g ± 5g dry mass	Distilled, demineralised, de-ionised water or equivalent, pH 5-7.5	1:10	End-over-end tumbler 5-10 rpm, roller table at ~10rpm or equivalent	24 hr ± 0.5 hr	Settling and vacuum or high pressure filtration 0.45μm

Table 8.6: Summary of serial agitated batch leaching tests used around the world (after Löwenbach, 1978 and Lewin *et al.,* 1994)

Test name	Development status	Leaching container	Sample preparation	Sample mass	Leachant	L/S ratio	Agitation method	Duration of test	Leachate separation	No. of elutions
Multiple Extraction Procedure (MEP, USEPA 1320)	Standard test method (U.S.EPA, 1986-B)	Same as EPTox	Same as EPTox	Same as EPTox	Acetic acid Synthetic acid Distilled water	1:20	Same as EPTox	Same as EPTox	Same as EPTox	10
Monofill Waste Extraction Procedure (Gaskill, *et al.,* 1986)	Technical resource document (Gaskill *et al.,* 1986)	Wide neck bottle	Particle size reduction to <9.5mm or to structural integrity	Unspecified	Distilled water or site water	1:10	Rotary tumbler	18h	Settling and filtration	4
Graded serial batch test US Army	Research method for waste and soil (Long *et al.,* 1987)	Unspecified	Unspecified	300g	Distilled water	1:2 or 3 or 6 or 12 or 24 or 48 or 96	Gentle periodic shaking 4 to 5 times a day	Until steady state conditions achieved	Vacuum filtration	>7
ASTM D4793-88 Sequential Batch Extraction	Standard method (1988) (ASTM, 1991)	2 litre wide necked bottle	Drying phase separation	100g	Reagent water (Type II D1193)	1:20	None	24h	0.45µm membrane filter	10
Waste Research Unit Leach Test (WRU) AERE Harwell (UK)	Standard method (Young and Wilson, 1982)	50ml wide neck flask	Crushing and vacuum filtration	100g	Distilled water Dilute acetic acid buffered (pH5)	One bed volume (1st 5 elutions), 10 bed volumes (> six elutions)	Mechanical flask shaker	2 to 80 hours Steady state	Vacuum filtration	5
Standard Leach (v) Test (SLT Cascade Test). The Netherlands, BEOP-31	Standard research method for combustion residues (Van der Sloot *et al.,* 1984)	1 litre polyethylene bottle	Crushing/sieving. Drying	40g	Demineralised water acidified to pH4 with nitric acid	1:20	Shake/roll	23h	Settling and 0.45µm filtration	5
NVN 2508-Cascade Test	Dutch pre-standard (1988)	1 litre polyethylene bottle	Dry sample to constant mass, crushing, sieving to <3mm	40g	Demineralised water acidified to pH4 with nitric acid	1:20 or 40 or 60 or 80 or 100	Shake/roll	23h	Settling and 0.45µm filtration	5
NVN 5432-Maximum Leachability Test	Dutch pre-standard (DPS, 1991)	Pyrex 1 litre glass beaker	Crush/grind to 565-125µm	8g	Demineralised water (pH 7 and pH4)	1:100	Magnetic stirrer	3h	Settling and 0.45µm filtration	2
Leachability by water (DIN 38414-S4)	German standard method (Din-Normen, 1984)	200ml wide neck flask	Sampling reduction only if particles>10mm. No grinding	100g	Deionised water	1:10	Initial gentle swirl or flask inversion only	24h	Filtration/ centrifugation	1-4 / 2+
Standard Leach Test Procedure R, University of Wisconsin (SLT)	Past standard (1974) (Hamm, 1977)	Square flask	Remove liquid phase by 0.45µm pressure filtration	40g (wet mass)	Synthetic landfill leachate	1:10	Rotating shaker	24h	0.45µm filtration	3
CEN / BS EN 12457: Part 3, 2002	European standard compliance test	Glass / HDPE / PP bottle. 500ml 1st step, 2 litre 2nd step.	At least 95% (by mass) <4mm particle size with or without size reduction	175g ± 5g dry mass	Distilled, demineralised, de-ionised water or equivalent, pH 5-7.5	1:2 1st step, 1:10 2nd step	End-over-end tumbler 5-10 rpm, roller table at ~10rpm or equivalent	6 ± 0.5 hr 1st step, 18 ± 0.5 hr 2nd step	Settling and vacuum or high pressure filtration 0.45µm	2

8.3.5 Serial batch tests

Serial batch tests are perhaps one of the simplest dynamic tests. The tests are performed in the same manner as the batch extraction tests highlighted in Section 8.3.1 and Figure 8.2, with the exception that after agitation of the solid and liquid for a predetermined duration, the solid and liquid are separated and the solid is added to a new leachant. An extraction profile can be established from the data, which could be used to model temporal release of leachable contaminants. There are many serial tests used around the world, some of which are described in Table 8.6.

8.3.6 Flow around tests

Flow-around tests are generally used by the nuclear industry for radioactive waste repository studies and allow leachant to flow around monolithic samples, changing the leachant continuously or intermittently. Periodically either the monolithic mass and/or the leachant is removed for chemical analysis.

A number of flow-around tests have been developed in Europe for construction materials or monolithic wastes, and CEN/TC292 Working Group 6 has prepared a review of dynamic leach tests for monolithic materials in Europe with a view to standardisation (CEN, 2001). Standard tank tests are available in Austria, France and the Netherlands for disposal or re-use purposes and work is currently underway on a European standard, likely to be based on the NEN 7345 (1997) test. Leaching is carried out using deionised water under mild agitation in three stages, exposing the monolithic material to fresh leachant consecutively for 6, 24 and 48 hours (CEN, 2000).

8.3.7 Column flow-through tests

Column flow-through leaching tests are probably the most well known dynamic test. In a column flow-through test the leachant is passed through a vertical column of waste material in up-flow or down-flow and fractions are collected and analysed. Upflow is the preferred method to reduce the effect of air trapped in the column and reduce the likelihood of by-pass flow developing. The process is similar to the infiltration of rainwater infiltration and percolation through soil or granular waste. The flow rate is often accelerated compared to natural conditions and the duration of the test is typically weeks or months to ensure that L/S ratios of up to 10 lkg^{-1} are achieved (van der Sloot *et al.,* 1997).

One of the limitations of this test is the velocity of flow of water through the sample. Forcing the leachant through the sample at higher pressures could increase this, although the relevance of such a test to environmental conditions is questionable. Tests by Griffin and Shimp (1976) overcame the low permeability and low flow through clay samples of landfill leachate by addition of sand to the clay samples. A potential improvement on this method would be to replace the sand with very small diameter Teflon beads.

8.3.8 Soxhlet testing

Soxhlet test apparatus applies a similar principle to column testing, although leachant is boiled, condensed and repeatedly re-circulated through or around the sample. The data produced is believed to provide information on the maximum amount of a contaminant that can be removed under extreme circumstances. These tests have also been used in radioactive studies. It is generally a parametric test used for modelling and can generally be viewed as a worst-case scenario test. It is therefore unlikely to provide results representative of the service environment.

8.4 Development of Standard Leach Tests

In the early 1990s the first work for the standardisation of leaching tests in Europe began, with the creation of Technical Committee TC292 and working groups to standardise tests for waste evaluation within the CEN framework. Following this, the Network on Harmonization was also established and has conducted a thorough review of leaching tests and inter-laboratory comparisons of some of these CEN tests (Van der Sloot *et al.* 1997).

CEN (1997) specifies a methodology for the determination of the leaching behaviour of waste under specified conditions and outlines the importance of performing tests in relation to a particular scenario and to the questions to be answered. It suggests a seven stage process, involving (taken from CEN, 1997):

1. Definition of the problem and the solution sought.
2. Description of the scenario.
3. Description of the waste.
4. Determination of the influence of parameters on leaching behaviour.
5. Modelling of leaching behaviour.
6. Behavioural model validation.
7. Conclusion.

However, there is little merit in having a wide range of leach tests available that have not been stringently validated in terms of repeatability and reproducibility for a range of materials. This has been recognised in Europe and the European Network on Harmonization of Leaching/Extraction Tests (NHLET, www.leaching.net) was set up under the EC Measurements and Testing Programme. The network objectives include:

- to harmonise the approaches to leaching tests and tests to be developed for soil, sediment, sludge, waste, stabilised waste and construction materials;
- exchange information derived from different scientific fields;
- facilitate the development of a generic approach to leaching and a common strategy for the use and interpretation of tests;
- to form a network of experts in relevant fields, including waste disposal and soil remediation; and
- to make recommendations for approaches to the evaluation of leaching test results and define future research needs (NHLET, 1995).

In addition, CEN and ISO technical committees are working to standardise leach tests. The standardisation process involves a comprehensive validation exercise to assess the robustness of individual tests and correlation between tests under corresponding conditions (van der Sloot *et al.*, 2001). Table 8.7 summarises the validation results for the recently published agitated batch eluate tests (BS EN 12457:2002) for a number of key test variables.

Table 8.7: Validation results for a number of key test variables from agitated batch eluate tests (after van der Sloot *et al.*, 2001)

Parameter	**Variation**	**Allowable variation**	**Comment**
Contact time	+/- 2 hours	+/- 0.5 hours	No significant influence
Liquid: Solid ratio	+/- 10%	+/- 2%	Critical for a number of components (allowable variation not likely to be significant)
Material weight	50g and 200g	100g +/- 5g	Significant effect for some components (headspace factor), mainly for smaller sample size
Temperature	10-30 °C	20 +/- 5 °C	Significant effect for some components
Mode of agitation	End-over-end tumbler Roller table Wrist shaker	Option of end over end (recommended) or roller table	Significant effect
Filter size	47-147 µm	Not specified Prescribed minimum flow rate of 30 $\mathrm{mlcm^{-2}hr^{-1}}$	Significant effect for several components; importance of recording filtration flow rate and meeting prescribed rate
Mode of size reduction	Jaw crusher Hammer mill Rotary mill	Jaw crusher	Significant effect for several components

There are a number of leaching tests that have been developed by the CEN Technical Committee on waste characterisation (TC292) that are likely to be required in the characterisation of waste for disposal to landfill. The tests are also identified as applicable to the characterisation of wastes for re-use, treatment and non-landfill disposal routes (Lewin *et al.* 2002). These tests are outlined in Environment Agency (in prep.) and summarised in Table 8.8 below.

Table 8.9 provides details of other methodologies under development/approval for the characterisation of waste, by the European Committee for Standardization (CEN), taken from: www.cenorm.be/standardization/tech_bodies/cen_bp/workpro/tc292.htm.

Table 8.8: Summary of leaching tests used for basic characterisation or compliance testing (after Lewin *et al.* 2002)

Test method	Purpose	Reference
Draft upflow percolation test	• To determine the rate of leaching of various contaminants as a function of liquid to solid ratio (i.e. relative time), particularly at the low liquid to solid ratios prevailing in landfill disposal scenarios. This approximately simulates the leaching process occurring when rainwater or other liquids infiltrate and percolate through a granular waste material that is being assessed for reuse or disposal. • Characterisation (leaching behaviour) test for granular wastes.	Draft prEN 14405, (CEN 2002b)
pH dependence test	• To determine the effect of falling or increasing pH conditions on leachability of monolithic, granular or paste-like wastes or sludges. • Two main applications are leachability predictions for waste: o After chemical mixing (e.g. admixing with acid or alkaline wastes) prior to land-filling. o After land-filling, should local pore water / leachate pH conditions change. • Characterisation (leaching behaviour) test for granular wastes.	CEN 2002c and Draft prEN 14429 (CEN 2002d)
Maximum availability leaching test	• To determine the potential (maximum) availability of leaching under worst case environmental conditions rather than natural infiltration conditions. • Characterisation (leaching behaviour) test.	NEN 7341, 1995
Diffusion test (tank test for monolithic wastes)	• To assess leachability of wastes that have been solidified for reuse or disposal. • Characterisation (leaching behaviour) test for monolithic wastes. A draft CEN/TC2 compliance test has been prepared based on emissions from the first three steps of the test.	NEN 7345, 1997
Compliance test for granular waste materials and sludges	• To assess leachability under mild extraction conditions for waste disposal or material reuse options. Two step test indicates relative timescales for release particularly when compared with availability for leaching.. • Characterisation and compliance test for granular wastes. If used as a compliance test, it must also be undertaken as part of basic characterisation.	BS EN 12457 Parts 1-4, 2002

Table 8.9: CEN / TC292 Work Programme (04/2003)

WI N°	PROJECT REFERENCE	TITLE	CURRENT STATUS
00292001	-	Characterization of waste - Sampling of liquid and granular waste materials including paste-like materials and sludges - Part 1: Framework for sampling plan preparation	Under Development
00292002	-	Characterization of waste - Sampling of liquid and granular waste materials including paste-like materials and sludges - Part 2: Selection and application of criteria for sampling under various conditions	Under Development
00292010	-	Characterization of waste - Compliance leaching test for monolithic material	Under Development
00292017	-	Characterization of waste - Sampling of liquid and granular waste materials including paste-like materials and sludges - Part 3: Sampling techniques	Under Development
00292018	-	Characterization of waste - Sampling of liquid and granular waste materials including paste-like materials and sludges - Part 4: Sample pre-treatment in the field	Under Development
00292019	-	Characterization of waste - Sampling of liquid and granular waste materials including paste-like materials and sludges - Part 5: Procedures for sample packaging, storage, preservation, transport and delivery	Under Development
00292025	prEN 13965-1	Characterization of waste - Terminology - Part 1: Material related terms and definitions	Under Approval
00292026	prEN 13965-2	Characterization of waste - Terminology - Part 2: Management related terms and definitions	Under Approval
00292030	-	Characterization of waste - Preparation of a test portion from the laboratory sample	Under Development
00292031	-	Characterization of waste - Assessment of the monolithic character	Under Development
00292033	-	Characterization of waste - Leaching behaviour test - Influence of pH on leaching with continuous pH control	Under Development
00292034	prEN 14405	Characterisation of waste - Leaching behaviour test - Up-flow percolation test	Under Approval
00292035	-	Characterization of waste - Simulation of the leaching behaviour of a waste material under specific conditions - Down-flow percolation test	Under Development
00292040	-	Characterization of waste - Dynamic leaching test for monolithic waste	Under Development
00292041	-	Sampling of liquid and granular waste materials including paste-like materials and sludges - Part 6: Examples of developing of generic/specific sampling plans	Under Development
00292045	-	Characterization of waste - Leaching behaviour tests - Influence of pH on leaching with initial acid/base addition	Under Development
00292046	-	Characterization of waste - Leaching behaviour tests - Acid and base neutralisation capacity test	Under Development

8.5 Physical Testing Methods

Materials that have been treated using S/S have been used in a wide variety of applications, many requiring specific physical tests to meet design criteria. In the majority of environmental situations it will be advantageous to define some minimum physical properties of the treated material, in addition to its ability to retain contaminants. Physical properties may be needed to inform contaminant transport modelling, confirm the monolithic nature of a waste form (and therefore diffusion as the important leaching mechanism), or to confirm structural properties (e.g. load bearing properties). Generally there are likely to be minimum parameters defined to enable handling and treatment during construction and to ensure long-term performance of the material against factors such as weathering, loading and saturation. Physical properties such as permeability can often play a key role in reducing the potential for contaminant release through leaching. It is important that tests are selected that replicate, as closely as possible, the environmental setting in which the material will be placed.

The selection of appropriate physical tests requires careful consideration of the following aspects (after CIRIA, 1995):

- the end use of the site or material (in particular where strength is an important factor);
- whether contaminants are immobilised by physical or chemical methods;
- for cementitious systems it is important to distinguish between 'setting' properties and subsequent strength development;
- the influence of heat usually generated during hydration of cementitious systems;
- the affect of different curing conditions (temperature, moisture, exposure to air at critical stages) and the variation in material properties this can result in;
- the time period over which properties such as strength and reduction in permeability may continue to develop;
- the likelihood of exposure of the waste-form to degradation mechanisms such as chemical attack, wet/dry cycles and freeze/thaw cycles and that these mechanisms are often slow and may take several to tens of years to manifest under field conditions;
- that agitation of material may drive off volatile organic compounds (VOCs) and some semi-volatiles (particularly if temperatures rise during processing);
- cementitious treatments are unlikely to result in placement of all material continuously, therefore the possible need for joints or accommodation of movement to be considered; and
- test turn-around times will often be in the order of hours or days, therefore a proposal for recovery, safe deposit or re-treatment of non-compliant material is necessary.

This section will detail the more common geotechnical tests that are commonly associated with stabilised material. Often reference will be made to British Standard testing procedures for particular parameters. However, it should be ensured prior to specifying these tests, that their use is appropriate to the particular material to be tested. This is both in terms of any modifications that will be made at the laboratory during sample preparation, such as particle size screening, or health and safety implications associated with the contamination present in the material to be tested.

There are a variety of physical tests, commonly used in civil engineering applications, that are not covered here, including site testing such as SPT testing, skip load tests or geophysical test methods. The application of these test methods is not covered by codes or guidance that relate specifically to S/S treated materials, however literature on their use in non-S/S specific applications exists in the public domain. The following sections review physical characterisation tests commonly used during the screening stage of S/S treatment, treatability trials and for compliance testing during construction.

8.5.1 Tests on materials before stabilisation

Table 8.10 shows common physical parameters and test methods that are applicable for testing carried out prior to the addition of the binder. It should be noted that some test methods are not applicable to materials after stabilisation, even if they are freshly mixed, because large errors can be caused from the allowances that have to be made for moisture contents and stabiliser content. It should also be recognised that BS 1924: 1990 details testing methodologies for materials before and after stabilisation and not necessarily contaminated soils and wastes. The implications of the presence of contaminants may have a bearing on the use of these test methods.

Details of tolerances, sampling and sample preparation are given in BS 1924: Part 1: 1990.

Table 8.10: Test procedures for material before stabilisation
(BS1924: Part 1: 1990)

Parameter	**Test procedure**
Moisture content	BS 1924: Part 2: 1990
Particle size distribution	BS 1924: Part 1: 1990
Fine and medium-grained naturally occurring materials	BS 1377: Part 2: 1990
Medium and coarse grained naturally occurring materials and slags	BS 812: Part 103.1: 1985
Waste materials and industrial by products	BS 6543: 1985
Liquid limit	BS 1924: Part 2: 1990
Plastic limit	BS 1924: Part 2: 1990
Ten Percent Fines Value	BS 812: Part 111: 1990
Sulfate Content	
Soils	BS 1377: Part 2: 1990
Aggregates	BS 812: Part 118: 1988
Slags	BS 1047: 1983 or BS 12620: 2002
Pulverised Fuel Ash	BS 3892: Part 1: 1997
Total Sulfur Content	BS 1047: 1983
Chloride Content	
Soils	BS 1377: Part 3: 1990
Slags and Aggregates	BS 812: Part 117: 1988
Total Organic Content (natural soils only)	BS 1377: Part 3: 1990

8.5.2 Tests on cement stabilised and lime stabilised materials

Table 8.11 shows common physical parameters and test methods that are applicable for testing carried out on stabilised materials either immediately after mixing to confirm acceptable mix parameters, or longer-term testing of set materials.

8.5.3 Moisture content to BS 1924: Part 2

There are a variety of test methods identified in BS 1924: Part 2: 1990 to determine moisture content of stabilised material:

Oven drying method

This is the definitive method and is based on drying the sample at 105-110°C to remove the water. This assumes that heating the material removes all 'free' water and 'chemically bound' water such as that of hydration is not removed by the test procedure. This is generally true for most materials, but problems can occur with materials that contain hydrated salts such as gypsum ($CaSO_4.2H_2O$) that lose water at temperatures below 105°C. It should also be noted that oven drying at this temperature may remove volatile compounds present, therefore the value obtained may not be the true water content.

Sand bath method

This method again relies on heating the sample. It is a rapid alternative to the oven-drying method, enabling a faster turn-around of results. It is therefore more suitable as a site test, but is less accurate than the oven drying method. It is not suitable for use with materials suspected of containing gypsum, calcareous matter or organic material e.g. unburnt coal in minestone and pulverised fuel ash (PFA).

Microwave oven method

This method is another rapid alternative to the oven drying method, but is only suitable for fine-grained materials, as containers of adequate size are not readily available to hold the mass of medium or coarse-grained materials required. Most siliceous and calcareous aggregates can be dried satisfactorily in a microwave, but flints, slag and some calcareous aggregates have a tendency to shatter. Materials such as PFA, colliery spoil (minestone) or aggregates derived from them are not suitable, as any carbonaceous matter present will ignite in the microwave. Materials with a high proportion of iron compounds may also give rise to problems. For these reasons it is necessary to carry out trials to establish whether the material being tested reacts adversely to microwave radiation.

Calcium carbide method

This method relies on the reaction of water in the aggregate with calcium carbide to evolve acetylene. The amount of acetylene released, is a measure of the moisture content of the aggregate and can be assessed by the pressure it generates in a confined space. It is a rapid method of assessing moisture content, but may not correspond exactly with results obtained using the oven drying method.

Nuclear gauge method

This method determines moisture content by placing a fast neutron source and a neutron detector on or adjacent to the material under test. The intensity of slow or moderated neutrons detected is dependent on the hydrogen content of the material under test and hence indirectly to the moisture content. This test method is identified for on-site testing only.

Table 8.11: Test procedures for stabilised materials (BS1924: Part 2: 1990)

Parameter	**Test procedure**
Moisture content	BS 1924: Part 2: 1990
Effect of stabilizer on plasticity properties	BS 1924: Part 2: 1990
Degree of pulverisation	BS 1924: Part 2: 1990
Bulk density	BS 1924: Part 2: 1990
Specific gravity	BS 1924: Part 2: 1990
Compaction related tests	
Dry density/moisture content relation	BS 1924: Part 2: 1990
Moisture condition value	BS 1924: Part 2: 1990
In-situ density tests	BS 1924: Part 2: 1990
Strength and durability tests	
Compressive strength	BS 1924: Part 2:, 1990
Effect of immersion in water on compressive strength	BS 1924: Part 2: 1990
Tensile splitting strength	BS 1924: Part 2: 1990
California bearing ratio (Laboratory method) including soaked CBR test	BS 1924: Part 2: 1990
Plate loading test / California bearing ratio (*In-situ* method)	BS 1377: Part 7 / 9: 1990
Frost heave	BS 1924: Part 2: 1990
Chemical tests	
Cement content	BS 1924: Part 2: 1990
Lime content	BS 1924: Part 2: 1990
In-situ pH	BS 1924: Part 2: 1990
Initial consumption of lime	BS 1924: Part 2: 1990
Permeability	BS 1377: Part 5 / 6: 1990

8.5.4 Particle size distribution

BS 1924: Part 1, 1990 identifies three different methods for determining the particle size distribution of a material, depending on its origin. These methods are broadly similar and unlikely to give results that are significantly different. It should be noted that the methods are only appropriate for materials before stabilisation, as the allowances for moisture content and binder content that have to be applied can lead to large errors, even for freshly mixed materials.

Sherwood (1992) identifies that a well-graded material is required for cement stabilisation of a material for reuse as capping, as uniformly graded materials involve the use of uneconomic additions of cement and may be difficult to compact. A well-graded material can be defined by a grading envelope, or a limit can be defined for the uniformity coefficient.

The uniformity coefficient is defined as the ratio of the particle diameters D_{60} and D_{10} on the particle size distribution curve. These are defined as:

D_{10} is the particle diameter at which 10% of the soil by weight is finer
D_{60} is the particle diameter at which 60% of the soil by weight is finer

Sherwood (1992) suggests a minimum value of 5 for granular materials for cement stabilisation for re-use as capping.

8.5.5 Atterberg limits / plasticity properties to BS 1924: Part 2

After lime (and to a lesser extent cement) is added to materials containing clay minerals, there is a marked change in plasticity properties. This is discussed in further detail in Section 3.2.2.1. The procedure given in BS 1924: Part 2 determines the liquid limit and plastic limit of the material, from which the plasticity index can be calculated. When using lime to stabilise a material, a lower bound limit of plasticity index is often applied to ensure sufficient clay fraction for the lime to react with.

The sample preparation details provided in the British Standard assume that the test is being carried out to determine the effect of addition of binder on the material. The sample preparation procedure is not applicable for field-mixed material. In order to use this procedure for field mixed material, appropriate modifications would need to be made to the procedures as detailed in the sample preparation notes of BS 1924: Part 2, 1990.

8.5.6 Ten percent fines value

The ten percent fines value is used to measure the mechanical strength of the individual particles of medium or coarse-grained materials. It can be used before stabilisation to determine whether the strength of the individual particles will decrease when soaked in water, before assessing any loss of strength of the treated material as a whole.

8.5.7 Sulfate content

The test given in BS 1377 for total sulfate content (or acid soluble sulfate) provides a measure of the amount of sulfate in the soil at the time of testing, expressed as % SO_3.

In their natural state, sulfates occur as SO_4^{2-} and consequently some limits are expressed as % SO_4^{2-}. To convert to % SO_4^{2-}, results expressed as % SO_3 should be multiplied by 1.2.

There are a variety of limits for total sulfate content that have been identified for cement or lime stabilised material (Buxton Lime Industries, 1990, Sherwood, 1992). However, the Highways Agency (2000) recommends that the limit be ultimately defined by the amount of swell measured during the soaked CBR test.

In addition to the sulfate in the material itself, consideration of the potential for sulfates to migrate from the surrounding ground and groundwater may also be required. In this situation determination of water-soluble sulfate is generally used, with results expressed in terms of SO_3 or SO_4 grams per litre. Highways Agency (2000) sets a limit of 1.9 gl^{-1}

SO_3 for material containing water-soluble sulfate within 500mm of cementitious materials.

Total sulfur content

In addition to the existing sulfate concentration of a material, the oxidation of sulfides can further increase concentrations of sulfate present. As oxidation of sulfides can occur during construction, it is important to also consider sulfates that can be converted from sulfides. Determination of total sulfur content in BS 1047 (1983) gives a measure of the sulfates already present in the soil as well as those converted from oxidation of sulfides, expressed as % S. This value can then be converted to % SO_3 to allow comparison of results, using the following formula:

$$S\ \% \times 80/32 = SO_3\ \%$$

8.5.8 Total organic content to BS 1377: Part 3

There are certain deleterious organic compounds that can interfere with the hydration process of cement and lime stabilised materials. Determination of the total organic content (TOC) of a material is likely to give a poor indication of the presence of these organic compounds, because it is the type of organic compound present rather than the total amount of organic matter that is the crucial factor (Sherwood, 1992).

Whilst testing TOC is unlikely to give an accurate indication of the severity of interference, some specifications require an upper limit. In this situation it should be noted that testing in accordance with BS 1377: Part 3 (1990) can only be carried out on natural soils and cannot be used for any other materials.

Historically a test was available to detect the presence of organic matter able to interfere with the hydration of Portland Cements. However, this test method has since been omitted as the high alkalinity of most cements currently available are not suitable to enable the test to be undertaken.

8.5.9 Degree of pulverisation to BS 1924: Part 2

This test provides information on how well the binder and water have mixed with the material being treated. It is generally used on site on samples of mixed material. It is based on the mass of material retained on a 5mm sieve, before and after individual lumps of material are broken down. It is determined from the formula:

$$P = 100\ (m1-m2)/(m1-m3)$$

Where m1 is the total mass of the sample (g), m2 is the mass of the unbroken material retained on the 5mm sieve (g) and m3 is the mass of the material finally retained on the sieve after lumps have been broken down (g).

8.5.10 Bulk density and specific gravity

These parameters can be used together with moisture content to calculate S/S product porosity and degree of saturation. These properties are related to durability and leachability, although the relationship is not simple. They can also be used to assess the homogeneity of the S/S material. Bulk density can also be used together with mass change factor to calculate volume increase due to treatment (Perera *et al.*, in prep.).

In-situ density tests

There are a variety of tests available to determine *in-situ* density, depending on the type of material to be tested, the circumstances in which the test is being made and the equipment available. Some of these test methods are similar to the test methods of BS1377 and use corresponding apparatus.

Nuclear moisture/density gauges to BS 1924: Part 2

This method can be used either by the back scatter method or by direct transmission. Either of these methods can be used on newly treated or set S/S treated material, as long as the probe can be inserted for the back scatter method. The depth of testing is limited to the length of the probe, which is often around 0.5m.

Sand replacement method to BS 1924: Part 2

This method involves digging a hole in the material to enable the density of the material removed and the moisture content to be determined. The hole is then filled with sand of known mass to determine the volume removed.

Core-cutter method to BS 1924: Part 2

This method is applicable to unhardened fine-grained materials, free of stones that are sufficiently soft that the cutter can penetrate the material.

Immersion in water method/water displacement method to BS 1924: Part 2

This method can be used with a variety of shapes or sizes of material where one dimension is not significantly smaller than the other two. It is generally appropriate for use with compacted material following stabilisation.

The possibility that immersion may mobilise contaminants, should be considered, as these may interfere with the hydration and/or stability of the soil/binder mixture.

8.5.11 Compaction related tests

The dry density of a material depends on the degree of compaction and the moisture content. There are two methods identified in BS 1924 Part 2 that investigate these parameters for freshly mixed materials. BS1924 Part 1 identifies the procedure for mixing materials with either cement or lime.

Dry density / moisture content relationship to BS 1924: Part 2

The optimum moisture content is that at which the dry density reaches a maximum value. It should be noted however that the moisture content of a free draining material may have little affect on the compaction achieved, therefore determining the optimum moisture content may be meaningless.

There are three methods of compacting the sample identified:

- light compaction using a 2.5 kg rammer;
- heavy compaction using a 4.5 kg rammer; and
- vibratory compaction (intended for granular (non-cohesive) materials). This method is identified as the definitive method for highly permeable materials.

It should be noted that materials containing more than 15% retained on a 37.5 mm sieve are too coarse to be tested by this method.

Moisture condition value

The moisture condition value determines the compactive effort necessary to almost fully compact a sample under test. The penetration of the rammer is measured and the MCV value is based on the number of blows corresponding to a change in penetration of 5mm. Testing would usually be carried out on treated material at pre-determined intervals after mixing.

8.5.12 Strength and durability tests

Compressive strength of cubic or cylindrical specimens to BS 1924: Part 2

The cylindrical method is not suitable for use with coarse-grained materials as the size of the mould required would be very heavy to handle when filled with compacted material. In the case of cement-stabilised materials, specimens should be completed within 2 hours of mixing. Lime stabilised materials may benefit by being allowed to cure or mellow before proceeding with the preparation of test specimens.

Effect of immersion in water on compressive strength to BS 1924: Part 2

Sulfates present in materials stabilised with cement or lime may affect the long-term durability of the cement or lime-stabilised material. The effect on the durability may be addressed by the test described in BS 1924: Part 2 for determining the effect of the immersion in water on the compressive strength of stabilised materials. (BS 1924: Part 1: 1990)

Tensile splitting strength

This method uses cubic specimens of stabilized material that are placed in a rig in such a way that they split into two halves. The force required to split the cubes is a function of the tensile strength of the material.

Laboratory determination of California Bearing Ratio (CBR)

This method measures the forces required to cause a cylindrical plunger of specified size to penetrate the specimen at a specified rate. Due to the restriction in mould size and plunger, the test is only appropriate to the part of the material up to a maximum size of 20mm.

The Highways Agency (2000) requires the following preparation for CBR testing of materials being stabilised for reuse as capping:

- for lime stabilisation, samples are left to mellow before compacting. There is then 3 days curing followed by 4 days soaking and then the test is carried out; and
- for cement stabilisation, samples are cured for 3 days and soaked for 4 days and then tested.

Plate loading test

This method is as that described in BS 1377-7. There are no particular technical considerations identified in relation to S/S material.

Frost heave and frost shattering

The frost heave test is carried out in accordance with the procedure identified in BS 812-124. However, BS1924: Part 2: 1990, identifies that stabilised materials with high compressive strengths (in excess of 2.5 MNm^{-2} at the time of the test) are very likely to have frost-heave values within acceptable limits. The British Standard states it is therefore not necessary to test these materials, unless only a small amount of cement is being added to improve frost heave characteristics or for lime stabilised cohesive materials where the lime may increase the susceptibility to frost heave properties.

There are standard test procedures defined by ASTM that determine the material losses, changes in moisture content and volume changes (swell and shrinkage) produced by repeated freezing and thawing of specimens. The samples are compacted into a mould immediately after treatment to maximum density at optimum moisture content. The method used will depend on the grading of the material being tested and assumes that the samples are physically, chemically and biologically representative, hence it does not address problems resulting from samples that are not homogeneous.

The two standard test methods that may be used with S/S treated materials are:

- ASTM D560-96 Standard test for freezing and thawing compacted soil-cement mixtures;
    - Method A (Carried out on material passing 4.75mm sieve, when 100% passing 4.75mm sieve);
    - Method B (Carried out on material passing the 19mm sieve, when <100% passing 4.75mm sieve);
- ASTM D4842-90 (2001) Standard test method for determining resistance of solid wastes to freezing and thawing.

Repeated wetting and drying testing
Section 9.4.5 discusses the durability issues of cyclic wetting and drying. The following standard test methods may be appropriate for use with S/S treated materials:

- ASTM D559-96 Standard test methods for wetting and drying compacted soil-cement mixtures;
    - Method A (Carried out on material passing 4.75mm sieve, when 100% passing 4.75mm sieve);
    - Method B (Carried out on material passing the 19mm sieve, when <100% passes 4.75mm sieve);
- ASTM D4843-88 (1999) Standard test method for wetting and drying test of solid wastes.

These procedures determine the material losses, water content changes and volume changes (swell and shrinkage) produced by repeated wetting and drying of the material samples. The method used will depend on the grading of the material being tested and assumes that the samples are physically, chemically and biologically representative, hence it does not address problems resulting from samples that are not homogeneous.

Durability tests (freeze - thaw and wet - dry) have been applied in the UK to assess the relative performance of selected binder formulations during treatability studies following a screening exercise using unconfined compressive strength (UCS) and the TCLP leach test on 7 and 28 day core samples (Al-Tabbaa and Evans, 1998). The ASTM durability tests were carried out on 28-day core samples of four mixes selected from the screening exercise. Permeability and compressibility tests were also carried out to further determine the physical characteristics of the selected mixes. UCS tests were then carried out on the samples following the wet-dry durability test. All samples passed the wet - dry test, but all failed the freeze - thaw test by fracturing before the twelve cycles were complete.

Following the treatability study, site trials were carried out using the four mixes plus an additional three to test potential improved freeze - thaw and permeability performance. Durability tests were also carried out on core samples from the site trial involving *in-situ* mixing. For the site trial the freeze - thaw test was modified to allow a gradual reduction in freezing temperature with 3 successive sets of 6 cycles at $0^{o}C$, $-10^{o}C$ and $-20^{o}C$ (Al-Tabbaa *et al.*, 1998). The results of the tests were similar to the wet - dry tests from the treatability studies, with less than 2% mass loss. The freeze - thaw tests produced similar mass loss during the first two cycles, but the third cycle at $-20^{o}C$ had more detrimental impact with mass loss over 20% for the original 4 mixes, around 10% with modified (lower) soil:grout ratios and around 1% for the mix with increased cement (8% as opposed to 2.5-3%) content.

8.5.13 Chemical tests

Cement content of cement stabilised materials to BS 1924: Part 2
This method compares the calcium contents of the stabilised material, the material in an unstabilised condition and the cement used. This test is not applicable to materials containing a large or variable amount of calcium or to materials stabilised with both lime and cement.

Lime content of lime stabilised materials to BS 1924: Part 2
This method compares the calcium contents of the stabilised material, the material in an unstabilised condition and the lime used. This test is not applicable to materials containing a large or variable amount of calcium or to materials stabilised with both lime and cement. In such cases it may be possible to determine the lime content by chemical means.

***In-situ* pH of lime or cement stabilised material to BS 1924: Part 2**
The pH of lime or cement stabilised materials will generally remain at values in excess of 12 whilst any unreacted lime or cement remains. Even then high pH values are still likely to prevail. On long term exposure to air the hydration products may, under adverse conditions, react with carbon dioxide causing a large decrease in pH and possible loss in strength. The determination of pH in this test on an exposed surface of stabilised material is used as a guide to the degree of carbonation.

It should be noted however, that pH values less than 12 could be obtained if the lime content is reduced through pozzolanic reactions with clay present in the soil or if PFA/slag are combined with the binder.

Initial consumption of lime to BS 1924: Part 2
This method gives an indication of the quantity of lime that needs to be added to achieve an improvement in plasticity qualities.

8.5.14 Permeability

The term permeability is used to express the coefficient of permeability or hydraulic conductivity, describing the rate at which water can flow through a permeable medium in ms^{-1}. It is an important parameter as it is a measure of the ability of a material to transmit fluids through its structure. Stabilised/solidified materials often rely on a reduction of the ingress and egress of water in and out of a monolithic mass of material to reduce leaching potential. Determining the likely permeability of the treated material is therefore especially important in regards to determining the potential for the transport of leachate bearing contaminants to move through the treated material into underlying strata and eventually into groundwater. Equally, this applies to the potential release of gases into the atmosphere or for the ingress of gases such as carbon dioxide into the waste form. The permeability measurement can also be used in models to predict contaminant transport through the ground.

The permeability of stabilised materials is likely to be affected by the particle size distribution, the water:solid ratio of the waste form, the degree of compaction, the development of hydration products, uniformity of material and in the case of cohesive material, the effect of cracks on the overall permeability of the material. It is therefore important to consider these implications when deciding on the test procedure to use. Test methods include:

- BS 1377: Part 5 1990. Constant head method. The coefficient of permeability is determined by applying a hydraulic pressure gradient in a sample of saturated soil and measuring the consequent rate of flow. The coefficient of permeability is expressed as a velocity. The test is suitable for soils with a permeability of between 10^{-2} and 10^{-5} ms^{-1}
- BS 1377: Part 6 1990. Permeability in a hydraulic consolidation cell or a tri-axial cell. Suitable for soils of low and intermediate permeability
- BS EN 12697: Part 19 (Draft). Permeability of hot mix asphalt

8.6 Mineralogical and Microstructural Tests

A number of tests suitable for characterising microstructural development are available for use with S/S waste forms. They may include the use of petrographic methods whereby resin-impregnated polished blocks or thin sections of material are examined with plain and polarized light using a polarizing microscope, or where samples are investigated using high-energy electron beams in a vacuum environment.

A considerable number of techniques can be used to investigate S/S waste, however they often take time and can be expensive to perform. Furthermore, they require specialists to prepare samples and undertake the work. Table 8.12 lists some of the tests available and their likely output.

Table 8.12: Example of mineralogical and microstructural investigative techniques

Technique	Application	Output
Petrographic analysis	Uses thin sections or polished blocks with polarising microscope	Data on mineralogy, morphology; especially useful for identifying weathering/alteration reactions
X-ray absorption spectroscopy	Mono-chromatic x-rays are used to excite photo electrons from the sample surface.	Useful in studying the chemistry of metals and metal oxides.
X-ray photoelectron spectroscopy (XPS)	Mono-energetic x-rays are used to excite a sample surface.	The binding energy of electrons can be used to determine the chemical environment of a particular element.
Fourier transform infra-red spectroscopy (FTIR)	Samples are ground and pelletised. The frequencies of adsorption of infrared light and the intensity of the adsorption by the sample are measured.	The infrared spectrum of a sample is dependent on its chemistry and the technique can be used for quantitative analysis.
Scanning electron microscopy (SEM)/Energy dispersive analysis of X-rays (EDAX)	A sample is placed in a vacuum and the sample surface interacts with an electron beam. Electrons and x-rays emitted are collected and analysed.	Data on morphology and mineralogy can be obtained from electron images. X-rays can be used for quantitative chemical analysis (EDAX).
Differential thermal analysis (DTA)	Samples are placed in a small furnace and heated. The endothermic or exothermic reactions are measured. Changes in sample weight upon heating (Thermogravimetric analysis or TGA) can also be obtained.	The thermal response of samples can be used to quantify sample chemistry.
Mercury intrusion porosimetry (MIP)	Mercury is forced into a sample under high pressure. The rate of mercury intrusion is measured.	Data on sample total porosity/pore size distribution are obtained.
Nitrogen sorptometry (BET)	The surface of a powdered sample is placed in nitrogen. The histerisis between the nitrogen gas sorption and de-sorption curves at liquid nitrogen temperatures is measured,	Data such as sample surface area and pore structure can be obtained.
X-ray adsorption spectroscopy (XAS)	High energy element specific x-rays are used to probe the structure of elements in a sample.	Data obtained is useful in determining the speciation of the trace elements (<10ppm) in a sample
Transmission electron microscopy (TEM)	Ultra thin samples are examined using a high energy transmission electron beam.	Fine detailed crystallographic data can be obtained and used, e.g. to examine where pollutants are encapsulated in mineral phases.
X-ray Diffractometry	Powdered samples are irradiated by monochromatic x-rays and the diffraction pattern obtained is recorded and analysed.	The diffraction pattern of different minerals are characteristic and can be used for qualitative and semi-quantitative analysis.

8.7 Summary

A range of chemical and physical tests exists to characterise materials presented for S/S and for the treated products. The following summarises the main points from this chapter:

- appropriate analysis of the S/S waste form during treatability studies can be used to validate whether S/S is a suitable remediation technology for a site, its proposed after use, and to make predictions about the lifetime of the waste form.
- leaching tests are used to determine the concentration of contaminant(s) that are present in the S/S waste form and their likely mobility. The conditions of these tests can be modified to assess significant parameters that will affect leaching behaviour in the environment of deposition of the waste-form and evaluate performance of the waste form if environmental conditions vary.
- as a result of the testing it should be possible to validate the remedial options chosen and to determine if the selected treatment complies with regulatory requirements.
- most leach tests are not designed to evaluate leaching of organic contaminants, and DOC or TOC are used as indicators of organic content for waste acceptance criteria for landfill.
- physical tests involve the measurement of properties such as strength, durability and permeability. Minimum criteria for physical parameters are likely to be specified for the treated product based on the end-use of the material.
- physical parameters such as permeability are likely to influence leaching characteristics and should be used together with leach test results to develop an understanding of the performance of the material.
- criteria used to evaluate the results of leaching tests will be end use specific. Treated waste will need to meet acceptance criteria for landfill and site-specific remedial targets should be set for the treatment of contaminated soil where the treated material remains on-site.

REFERENCES

Al-Tabbaa, A. and Evans, C.W. (1998) Pilot In-*situ* Auger Mixing Treatment of a Contaminated Site. Part 1: Treatability Study. *Proc. Instn. Civ. Engrs. Geotech. Engng*. 131, pp. 52-59.

Al-Tabbaa, A., Evans, C.W. and Wallace, C.J. (1998) Pilot In-*situ* Auger Mixing Treatment of a Contaminated Site. Part 2: Site Trial. *Proc. Instn. Civ. Engrs. Geotech. Engng*. 131, pp. 89-95.

Association Française de Normalisation (AFNOR) (1992) *Leaching of Waste* NF X31-210.

American Society of Testing for Materials (1991). *Standard Test Method for Sequential Batch Extraction of Waste with Water*. American Society of Testing for Materials ASTM D4793-88.

American Society of Testing for Materials (1996) *Standard Test Methods for Freezing and Thawing Compacted Soil-Cement Mixtures*. American Society of Testing for Materials ASTM D560-96.

American Society of Testing for Materials (1996) *Standard Test Methods for Wetting and Drying Compacted Soil-Cement Mixtures*. American Society of Testing for Materials ASTM D559-96.

American Society of Testing for Materials (1999) *Standard Test Method for Shake Extraction of Solid Waste with Water*. American Society of Testing for Materials ASTM D3987-85.

American Society of Testing for Materials (1999) *Standard Test Method for Wetting and Drying Test of Solid Wastes*. American Society of Testing for Materials ASTM D4843-88.

American Society of Testing for Materials (2001) *Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste-forms.* American Society of Testing for Materials ASTM C1308-95.

American Society of Testing for Materials (2001) *Standard Test Method for Determining the Resistance of Solid Wastes to Freezing and Thawing*. American Society of Testing for Materials ASTM D4842-90.

Buxton Lime Industries (1990) *Lime Stabilisation Manual* (2nd Edition). Buxton Lime Industries Ltd.

Bordas, F. and Bourg, A. (2001) Effect of Solid/Liquid Ratio on the Remobilization of Cu, Pb, Cd and Zn from Polluted River Sediment. *Water, Air and Soil Pollution* 128, pp. 391-400.

British Standards Institution BS EN 12457. (2002). *Characterisation of Waste. Leaching. Compliance Test for Leaching of Granular Waste Materials and Sludges*. British Standards Institution, London.

Part 1: One stage batch test at a liquid to solid ratio of 2 lkg^{-1} for materials with a high solid content and with particle size below 4mm (without or with size reduction)
Part 2: One stage batch test at a liquid to solid ratio of 10 lkg^{-1} for materials with particle size below 4mm (without or with size reduction)
Part 3: Two stage batch test at a liquid to solid ratio of 2 lkg^{-1} and 8 lkg^{-1} for materials with a high solid content and with a particle size below 4mm (without or with size reduction)
Part 4: One stage batch test at a liquid to solid ratio of 10 lkg^{-1} for materials with particle size below 10mm (without or with size reduction)

British Standards Institution BS EN 12620. (2002) *Aggregates for Concrete*. British Standards Institution, London.

British Standards Institution BS 10175 (2001) *Code of Practice for the Site Investigation of Contaminated Land*. British Standards Institution, London.

British Standards Institution EN 12390: Part 2. (2000) *Testing Hardened Concrete - Part 2: Making and Curing Specimens for Strength Tests*. British Standards Institution, London.

British Standards Institution EN 12697: Part 19. (2000) *Test Methods for Hot Mix Asphalt. Permeability of Specimen* (Consultation draft). British Standards Institution, London.

British Standards Institution BS1377 (1990) *Methods of Test for Soils for Civil Engineering Purposes*. British Standards Institution, London.

British Standards Institution BS 1924: Part 1 (1990*) Stabilised Materials for Civil Engineering Purposes – Part 1: General Requirements, Sampling, Sample Preparation and Tests on Materials before Stabilisation*. British Standards Institution, London.

British Standards Institution BS 1924: Part 2 (1990) *Stabilised Materials for Civil Engineering Purposes: Methods of Test for Cement-Stabilised and Lime–Stabilised Materials*. British Standards Institution, London.

British Standards Institution BS 1047 (1983) *Specification for Air-cooled Blast Furnace Slag Aggregate for use in Construction*. British Standards Institution, London.

British Standards Institution BS 812 (1975) *Testing Aggregates*. British Standards Institution, London.

Comité Européen de Normalisation (1997). *Characterisation of Waste - Methodology for the Determination of Leaching Behaviour of Waste under Specified Conditions.* ENV 12920 (CEN/TC292/WG6). [Published by BSI as Draft for Development in 1998]

Comité Européen de Normalisation (2000) *Characterisation of Waste – Leaching - Compliance Test for Leaching of Monolithic Waste of Regular Shape*. CEN/TC292/WG2 Doc 128.

Comité Européen de Normalisation (2001) *Revised document of document N239 of CEN/TC292/WG6 "State of the art review from a standardization point of view on a dynamic leaching test for monolithic waste materials"*. CEN/TC292/WG6 N242.

Comité Européen de Normalisation (2002a) *Sampling of Liquid and Granular Waste Materials Including Paste-like Materials and Sludges, Part 1: Framework for the Preparation of a Sampling Plan*. CEN/TC292/WG1

Comité Européen de Normalisation (2002b) Draft prEN 14405. *Leaching Behaviour Test – Upflow Percolation Test*. CEN TC292/WG6.

Comité Européen de Normalisation (2002c) *Characterisation of Waste – Leaching Behaviour Tests – Influence of pH on Leaching with Continuous pH Control*. CEN TC292/WG6.

Comité Européen de Normalisation (2002d) prEN 14429. *Characterisation of Waste – Leaching Behaviour Tests – Influence of pH on Leaching with Initial Acid/base Addition*. CEN TC292/WG6.

Cernuschi, S., Giugliano, M. and Paoli, I.D.E. (1990) Italian CNR-IRSA. *Waste Management and Research* 8, pp.419-427.

Chateau, L. (2003) Personal communication. ADEME.

Chin, Y-P., Weber, W.J.Jr. and Eadie, B.J. (1990) Estimating the Effects of Dispersed Organic Polymers on the Sorption of Contaminants by Natural Solids. 2. Sorption in the Presence of Humic and Other Natural Macromolecules. *Environmental Science and Technology* 24, pp.837-842.

Construction Industry Research and Information Association (1995*) Remedial Treatment for Contaminated Lad Volume 3: Site Investigation and Assessment*. CIRIA SP103.

Comans, R.N.J., Filius, J., van Zomeren, A. and van der Sloot, H.A. (2000) *Karakterisering organische stof. Haalbaarheidsstudie naar genormalise erde methoden voor de bepaling van de beschik baarheid en rol van organische stof in grond, afval- en bouwstoffen m.b.t.verhoging van de uitloging van slecht water-oplosbare verontreinigingen*. Report ECN-C--00-060 (in Dutch).

Comans, R.N.J. (Ed.) (2001) *Development of Standard Leaching Tests for Organic Pollutants in Soils, Sediments and Granular Waste Materials*. Final Report EU Project SMT-4-CT97-2160. ECN-C--01-121.

Comans, R.N.J. and Roskam, G.D. (2002) Leaching Procedure for the Availability of Polycyclic Aromatic Hydrocarbons (PAHs) in Contaminated Soil and Waste Materials. In: P. Quevauviller (Ed.) *Methodologies for Soil and Sediment Fractionation Studies -*

Single and Sequential Extraction Procedures, pp. 123-141. Royal Society of Chemistry, Cambridge.

Constable, T.W. and Côté, P.L. (1986*) Development and Application of a Multiple Batch Leaching Procedure*. Environment Canada Report EPS 3/AT/1.

Din-Normen. (1984) *Determination of Leachability by Water* (S4). German Standard Methods for the Examination of Water, Waste Water and Sludge and Sediments (Group S). DIN 38414-S4.

Dutch Pre-Standard. (1991) *Waste Materials, Construction Materials and Stabilised Waste Products. Part 1-Determination of Maximum Leachability*. NVN5432.

Environment Agency (*in prep.*) *Guidance on Sampling and Testing of Wastes to Meet Landfill Waste Acceptance Procedures*, External Consultation Document, Version 4.3a, December 2003.

Environment Canada. (1990) *Compendium of Waste Leaching Tests*. Report EPS 3/HA/7. Environment Canada, Waste Water Technology Centre.

Gaskill, A.Jr., Allen, C.C., and Tinesdale, R.S. (1986) *A Procedure for Estimating Monofilled Solid Waste Leachate Composition*, (Second Edition), USEPA-SW924.

Griffin, R.A. and Shimp, N.F. (1976) Effect of pH on Exchange-Adsorption or Precipitation of Lead from Landfill Leachates by Clay Minerals. *Environmental Science and Technology* 10, pp.1256-1261.

Highways Agency. (2000) *Treatment of Fill and Capping Materials using either Lime or Cement or Both*. HA74/00.

Hamm, R.K. (1977) *Development of a Standard Leaching Test – Second Progress Report*. University of Wisconsin, USA.

IUCS. (1977) *Shake Test for Evaluation of the Leaching Potential for Land Disposal of Waste Materials*. I.U. Conversion Systems Incorporated. Philadelphia, Pennsylvania, USA.

Lewin, K., Bradshaw, K., Blakey, N.C., Turrell, J., Hennings, S.M. and Flavin, R.J. (1994) *Leaching Tests for Assessment of Contaminated Land* – Interim NRA Guidance. R and D Note 301. National Rivers Authority, Bristol, UK.

Lewin, K., Turrell, J. and Young, C.P. (2002) Landfill Waste Acceptance Criteria Sampling and Testing. In: *Proc. Waste 2002 Integrated Waste Management and Pollution Control: Research, Policy and Practice*. 24-26 September 2002, Stratford on Avon, UK, pp. 553-562.

Long, D.E., Howle. M.J., Weatherhead, D.C. and Richas, G.K. (1987) *Migration of Hazardous Substances Through Soil, Part IV. Development of a Serial Batch Extraction Method and Application to the Accelerated Testing of Seven Industrial Wastes*. United States Army, Dugway Proving Ground, Report No: DRG-FR-87-015.

Löwenbach, W. (1978) *Compilation and Evaluation of Leaching Test Methods*. United States Environmental Protection Agency. Report EPA-600/2-78-095.

Ministry of the Environment (1985) Ministry of the Environment Regulation 309/Leachate Extraction Procedure. Government of Ontario.

Minnesota Pollution Control Agency. (1977) *Land Disposal Leach Test*. MPCA Division of Solid Wastes.

NEN 7341. (1995) *Leaching Characteristics of Solid (Earth and Stoney) Building and Waste Material. Leaching Tests. Determination of the Availability of Inorganic Components for Leaching*. Netherlands Normalisation Institute

NEN 7345 (1997). *Leaching Characteristics of Soil and Stoney Building and Waste Materials - Leaching Tests - Determination of Leaching Behaviour of Inorganic Components From Building and Monolithic Waste Materials with the Diffusion Test*. Netherlands Normalisation Institute

NHLET (1995) European Network for Harmonization of Leaching / Extraction Tests. www.leaching.net. Newsletter, March 1995, No. 1.

Perera, A. S. R., Al-Tabbaa, A., Reid, J. M. and Stegemann, J. A. (in prep) State of Practice Report UK Stabilisation/Solidification Treatment and Remediation. Part IV: Testing and Performance Criteria.

Sansom, M.R. (2000) *In-situ Stabilisation of Chemical Waste*. CIRIA Project Report 37.

SOC. (1985) *Criteria for Identification of Hazardous and Extremely Hazardous Wastes*. State of California Code Title 22 Article 11 1800.M5 – 1800.28

Sherwood, P. T. (1992) *Stabilized Capping Layers using either Lime or Cement or Lime and Cement*. Contractor Report 151. Transport Research Laboratory. ISSN 0266-7045.

United States Army Corps of Engineers (1995) *Treatability Studies for Solidification/Stabilization of Contaminated Material*. USACE Technical Letter No. 1110-1-158. U.S. Army Corps of Engineers, Washington D.C.

United States Environmental Protection Agency. *Method 1310A. Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test. Test Methods for Evaluating Solid Wastes Physical/Chemical Methods*. USEPA Report Number: SW-846. United States Environmental Protection Agency.

United States Environmental Protection Agency. *Method 1311. Toxicity Characteristics Leaching Procedure. Test Methods for Evaluating Solid Wastes Physical/Chemical Methods*. USEPA Report Number: SW-846. United States Environmental Protection Agency.

United States Environmental Protection Agency. *Method 1312. Synthetic Precipitation Leaching Procedure. Test Method for Evaluating Solid Waste*. USEPA Report Number SW-846. United States Environmental Protection Agency.

United States Environmental Protection Agency. *Method 1320. Multiple Extraction Procedure. Test Method for Evaluating Solid Waste*. USEPA Report Number SW-846. United States Environmental Protection Agency.

United States Environmental Protection Agency (1999) Waste Leachability: The Need for Review of Current Agency Procedures. *EPA Science Advisory Board Environmental Engineering Committee Commentary* EPA-SAB-EEC-COM-99-002, February 26, 1999.

van der Sloot, H.A., Piepers, O. and Kok, A. (1984) *A Standard Leaching Test for Combustion Residues*. Bureau Energie Onderzoek, Netherlands Projecten BEOP-31

van der Sloot, H. A., Heasman, L. and Quevauviller, Ph. (1997) *Harmonisation of Leaching Extraction Tests.* Studies in Environmental Science 70. Elsevier, Amsterdam.

van der Sloot, H.A., Hjelmar, O., Bjerre Hansen, J., Woitke, P., Lepom, P., Leschber, R., Bartet, B. and Debrucker, N. (2001) *Validation of CEN/TC 292 Leaching Tests and Eluate Analysis Methods PrEN 12457-1 to 4, ENV 13370 and ENV 12506 in Co-operation with CEN/TC 308*. ECN-C--01-117, Final Report.

Wahlström, M., Laine-Ylijoki, J., Pihlajaniemi, M. and Ojala, M. (2000) Leaching of PCBs and Chlorophenls from Contaminated Soil and Waste - Influence of Leaching Test Characteristics. In: Woolley, G.R., Goumans, J.J.J.M. and Wainwright, P.J. (Eds.). *Waste Materials in Construction. Proceedings of the International Conference on the Science and Engineering of Recycling for Environmental Protection*, Harrogate, England, 31 May, 1-2 June 2000, pp.462-474. Pergamon.

Welsh, S. K., Gagnon, J. E. and Elanabarawy, M. T. (1981) Comparison of Three Acid Extraction-Leaching Test Protocols. In: Conway R. A. and Malloy, B. C. (Eds.*), Hazardous Solid Waste Testing: First Conference*, American Society for Testing and Materials STP 760, pp.28-39

Yong, R.N., Mohamed, A.M.O. and Warkentin, B.P. (1992) *Principles of Contaminant Transport in Soils.* Elsevier, Amsterdam.

Young, P.J. and Wilson, D.C. (1982) *Testing of Hazardous Wastes to Assess Their Suitability for Landfill Disposal.* AERE Harwell, Environmental and Medical Sciences Division. Aere-R 10737.

9 THE LONG-TERM BEHAVIOUR OF CEMENT-BASED STABILISED/SOLIDIFIED WASTE FORMS

9.1 Introduction

Many of the major phases within a S/S waste form are thermodynamically unstable (Klich *et al.,* 1999) and the fact that waste forms will change with time is widely accepted in the scientific community. Accordingly, it must be acknowledged that retained contaminants will be liberated from the waste form in due course and that disposal and re-use schemes should be designed for controlled release at a rate that can be attenuated rather than to attempt indefinite isolation.

There is an increasing body of literature on the modelling of the long-term behaviour of a variety of wastes, including S/S treated wastes, which is described in Chapter 10. Some predictive modelling approaches can use the results of leaching tests, and the durability of S/S waste materials could be based on a measure of the estimated long-term leaching of hazardous components from the S/S materials exposed to external influences (Felix *et al.,* 2000).

However, this approach does not examine the processes leading to the degradation of the waste forms, the chemical and physical changes that are likely to lead to increased (or decreased) leaching of hazardous components, or the impact of external influences on the leaching characteristics of S/S waste materials (Felix *et al.,* 2000). There is little published literature on these aspects of the long-term behaviour of S/S treated waste forms, and it is necessary to look to other materials undergoing exposure to the environment for information on likely performance in the field.

This chapter examines the degradation mechanisms that affect the durability of concrete and the weathering processes of rock and soil. The implications for the durability of S/S waste forms are discussed and a number of generic disposal and re-use scenarios are presented.

9.2 Deterioration of Concrete

About 22 million cubic metres of concrete are placed in the UK each year and the vast majority suffers no durability problems during a design life that may extend from 25 to 100 years. In the UK's temperate climate, problems encountered largely result from poor workmanship and inadequate specification (Price, 2002).

Although failure of concrete structures has been extremely rare, extensive research, into the ways in which the durability of concrete can be compromised, has been carried out over the last 100 years. Much of this knowledge has been incorporated in the development of standards, codes of practice, guidance documents and working practices over the past 20 years (EN 206-1: 2000; Basheer *et al.,* 2001; Walker*,* 2002; BS 8500-1: 2002; BS 8500-2: 2002). Good concrete durability is dependent on specifying the nature and proportions of the aggregate, cement and mix water; and controlling the mixing, placing, compacting and curing process (Kropp, 1995; Ali and Dunster, 1998).

The results of intrinsic reactions involving materials may be controlled at the design stage. The effects of extrinsic factors involving aggressive agents might not always be foreseen and will have a greater impact if they penetrate into the concrete mass via the pore network.

9.2.1 Porosity and Permeability

The porosity and permeability of concrete are fundamental to their performance in the environment. The size and shape of the pore network within concrete control the specific surface area and hence the area available for reaction with aggressive agents. The extent of penetration of these will depend on the permeability of the concrete (Ollivier *et al.,* 1995). The permeability, in turn, is a function of the size, distribution and connectivity of the pores.

Permeability greatly influences the supply of deleterious species to the interior of the concrete and thereby controls the degradation of the concrete. The permeability can be expressed in terms of transport coefficients for diffusion, permeation and capillary suction for ions, liquids and gases. These coefficients have been discussed by Kropp (1995), Buenfeld (1997) and Baroghel-Bouny and de Larrard (2000). Buenfeld (1997) states that the service life or durability of the concrete is generally inversely related to the relevant transport coefficients.

The most rapid diffusion in concrete matrices is through the pore network as a direct pathway (Glasser, 2001). The pores within the concrete matrix vary considerably in size and shape with mix design and with time, because the cement in the concrete continues to hydrate for months and even years.

The pores of concrete can be subdivided into:

- nanoscale pores (10^{-9} m), involve C-S-H gel and impede the movement of water (Glasser, 2001);
- micropores (1×10^{-9} m to 5×10^{-8} m), and are involved in drying shrinkage and creep (Basheer *et al.,* 2001); and
- macropores ($> 5 \times 10^{-8}$ m), are detrimental to both strength and permeability (Basheer *et al.,* 2001).

Because aggregates are generally of low permeability, (e.g. granite, dolerite, limestone) the permeability of concrete is controlled by the cement paste and the aggregate-paste interface (Scrivener and Nemati, 1996). Typical coefficients of permeability of hardened cement pastes are 10^{-13} ms^{-1} for a water/cement ratio of 0.4 and 10^{-5} ms^{-1} for a water/cement ratio of 0.7 (Mehta, 1986).

9.2.2 Strength

Strength is a key parameter in concrete mix design. Higher strength concrete generally has lower permeability and porosity and is therefore more durable. However, in concrete mix design, there has to be a compromise between ultimate strength and durability of the concrete and its workability when it is being placed. The compressive strength of the concrete is controlled by the capillary porosity, and its measurement represents an average value over the volume tested. In contrast, durability is controlled by properties of the concrete in the near surface zone (Hilsdorf, 1995). Yuasa *et al.* (2000) indicate that the compressive strength of concrete near the surface of test specimens was lower than the interior due to an increase in the total pore volume. This variation was attributed to inadequate curing and early drying of the surface layers, to a depth of 5 cm in concrete with a water/cement ratio of 0.4 to 0.6.

9.2.3 Key factors that influence the permeability and strength of concrete

There are a variety of parameters that influence concrete permeability and the transport characteristics for a particular attacking agent. These are summarised in Table 9.1.

Crack development in the hardened concrete can result in the development of secondary permeability and preferential pathways into the concrete mass. There are a number of processes which cause cracking; some involving the surface layers of the concrete and some the interior (Table 9.2). The outer layer is taken as being 1-2 mm thick in high quality concrete or as much as 50 mm in lower grade concrete.

Plastic shrinkage and thermal cracking occur early in the life of the concrete, the former as the result of the concrete drying too quickly, and the latter resulting from the heat of hydration generating thermal gradients within the concrete. Thermal cracking can also result from the differing coefficients of thermal expansion between the different constituents of the concrete when the concrete is affected by external sources of heat.

The processes which cause cracking of concrete are the principal causes of failure in concrete structures, as they result in loss of strength and flaking of the concrete surface as well as accelerating the attack of external aggressive agents through the increased permeability. (St. John *et al.,* 1998).

9.2.4 Degradation processes in concrete

The factors controlling the durability of concrete (and S/S waste forms) include both intrinsic and extrinsic factors:

Intrinsic factors	**Extrinsic factors**
Poor workmanship	Temperature
Poor design	Pressure
Mineralogy/chemistry	Moisture conditions
Structure/fabric/texture	Environmental chemistry (e.g. pH, E_h)

Together these factors influence the significance of key degradation mechanisms. Primary degradation mechanisms; resulting from the design of the concrete and the nature of the materials used are:

- carbonation;
- sulfate attack;
- chloride penetration; and
- alkali-aggregate reaction.

Table 9.1: Effect of key design factors on the performance of concrete and their relevance to S/S waste forms

Key Design Factors	Effect on Permeability	Effect on Strength	Performance Constraints	Relevance to S/S waste forms
Water:cement ratio	Higher water content leads to higher permeability, potential for 'bleeding'	Higher water content and higher permeability result in lower strength because of increased pore size and lower density	Water required for hydration reactions, excess water required for workability. Low density porous areas can occur adjacent to aggregate particles	Cement content generally lower than in structural concrete. Workability not usually a design constraint
Curing time	Increased curing time results in decreased permeability	Increased curing time results in increased strength	Adequate curing prevents surface drying and incomplete hydration, which result in more porous surface zones. Good surface finishing, compaction and consolidation also important	Waste forms generally buried after mixing or mixed *in-situ*, tend to be protected from excessive surface drying, curing conditions more difficult to control. Higher curing temperature reduces the leachability of heavy metals in the short term. Variety of contaminants may extend curing time or retard hydration.
Curing temperature	High ambient temperatures and excess heat of hydration with large volumes result in drying out and increased permeability	High ambient temperatures and excess heat of hydration with large volumes result in drying out and decreased strength		Waste forms have lower volumes, lower binder contents, are buried in the ground and are less affected by either elevated climatic temperatures or excess heat of hydration
Aggregate size	Well graded aggregate important in minimising the permeability/porosity	Increased maximum size of aggregate decreases strength as a result of micro-cracking at cement/aggregate interface. Strength increased by well graded aggregate as a result of reduced pore volume.	Increased proportion of fines reduces workability of concrete and commonly requires addition of plasticisers	Waste materials can be considered as the aggregate component, the grading and overall grain size are difficult to control.
PFA, ggbs and silica fume	Increased proportion of these pozzolans reduces the permeability	Increased proportion of pozzolans lowers heat generated during hydration and reduces thermal cracking	Use of these materials limited to 30% by volume because of workability. Addition of pozzolans also reduces alkali-silica reaction, and sulphate attack	Pozzolans are commonly used in the mix designs for S/S waste forms to reduce moisture content and increase cementitious solids. They are also important in controlling the redox of the S/S system and assist in the adsorption of organics.

Table 9.2: The causes of cracking and their relationship to the outer layer and interior of a concrete (after St. John *et al.,* 1998)

Outer Layer	Shrinkage	Plastic settlement and bleeding
		Plastic Shrinkage
		Drying shrinkage
		Carbonation
	Expansion	Surface cracks over an expanding core
		Corrosion of reinforcement
		Freeze/that attack
		Recrystallisation of salts
		Thermal gradients from the environment
Interior of Concrete	Shrinkage	Plastic settlement and bleeding
		Drying shrinkage
		Heat of hydration expansion and contraction
		Shrinkable aggregates
	Expansion	Alkali-aggregate reaction
		Hard burnt lime, magnesia
		Reformation of ettringite *in-situ*

Secondary degradation mechanisms; resulting from the environment in which the concrete is placed include:

- freeze/thaw;
- wetting and drying;
- biological attack;
- loading; and
- fire damage.

A useful summary of these degradation mechanisms is given by Paul (1994) in a study of the performance of building materials in contaminated ground. These degradation mechanisms may be equally applicable to S/S waste forms and are described in detail below.

9.2.4.1 Primary degradation mechanisms

Carbonation

Carbonation is a natural phenomenon that occurs when cement-bound systems are exposed to the atmosphere. The process is of particular interest to concrete technologists because the steel reinforcement is protected from corrosion by the high pH of the concrete. Carbonation reduces the pH and can result in steel corrosion, expansion and cracking (Building Research Establishment, 1995).

When carbon dioxide diffuses into concrete in the presence of water it reacts with calcium hydroxide and the C-S-H gel phases to form calcium carbonate, as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$

$$H_2CO_3 + C\text{-}S\text{-}H \rightarrow CaCO_3 + SiO_2 + H_2O$$

Once all the available alkali hydroxide in the region has reacted, the pH of the pore solution is reduced to 8.3 (Shah and Hookham, 1998).

There is an optimum moisture content at which carbonation will occur, for example concrete exposed to rain shows lower carbonation rates than concrete sheltered from rain (Basheer *et al.,* 2001). Shah and Hookham (1998) state that an environment with 50 - 70% humidity is the most conducive to carbonation. Roy *et al.* (1999) showed, in concrete tested at high CO_2 levels, that the depth of carbonation, after a specific time period, increased between 52 and 75% humidity, decreased between 75 and 84% humidity and increased again to 92% (see also Table 9.3). The carbonation reaction is hindered if CO_2 has to diffuse through water filled pores and enhanced if the pores are partially filled thus increasing the area of the gas/liquid interface. (Gervais *et al.*, 2004).

It has been suggested that the rate of carbonation can be predicted from Fick's first law, however this is in doubt because of the variability of cementitious material (Shah and Hookham, 1998). It is established, however, that the mean carbonation depth of concrete decreases as compressive strength increases (Baroghel-Bouny and de Larrard, 2000) because of the inverse relationship between strength and permeability/porosity.

Table 9.3: Influence of ambient relative humidity on some deterioration processes in concrete (after Paul, 1994)

Ambient relative humidity	**Relative severity of deterioration process**		
	Carbonation	**Frost attack**	**Chemical attack**
Very low (<40%)	Slight	Insignificant	Insignificant
Low (40-60%)	High[1]	Insignificant	Insignificant
Medium (60-80%)	Medium[2]	Insignificant	Insignificant
High (80-98%)	Slight	Medium	Slight
Saturated (>98%)	Insignificant	High	High

[1] For 40%-50% relative humidity, carbonation is medium

[2] For 60-70% relative humidty, carbonation is high

Carbonation is a relatively slow process except in the high temperatures that occur, for example, in the Middle East or in the high humidity of tropical countries such as Hong Kong. In respect of the former, carbonation to depths of several mms may occur in as many days (Walker, 2002). In a temperate climate, carbonation proceeds at a rate of between 0.05 mm and 1.0 mm per year (Shah and Hookham, 1998), dependant on the design of the concrete. Higher rates of carbonation have been recorded with blast furnace slag cements (Osborne, 1999) despite their lower permeability, possibly as a result of the lack of portlandite to neutralise the carbonic acid.

The precipitation of the calcium carbonate in the pore spaces results in a decrease in the permeability and an increase in strength. Because carbonation proceeds as a reaction front, the initial carbonation of the concrete surface blocks the capillary pores in the surface zone and reduces penetration of CO_2 to deeper levels with the concrete mass. However, in the long term, carbonation results in the dissolution of CH and the decalcification of the C-S-H gel and an overall decrease in strength (Gervais *et al.,* 2004).

Carbonation can also occur as the direct result of attack by acidic groundwater. Most natural waters have a pH between 4 and 9.5. A pH of less than 5 is usually due to the presence of humic acid, which is only mildly aggressive because calcium humate is almost insoluble in water and forms a protective layer on the concrete (St. John *et al.,* 1998). When natural waters contain dissolved carbon dioxide, two attacking species are generated, carbonic acid (H_2CO_3) and calcium bicarbonate ($Ca(HCO_3)_2$). These react with calcium hydroxide in the cement paste to form calcium carbonate, leaving gelatinous hydrated silica, and soluble aluminium and iron hydroxides.

In summary, in temperate climates, carbonation rates increase as a result of:

- air voids in excess of 3% by volume;
- capillary porosity in excess of 7% by volume;
- microcrack density greater than 100 per metre;
- a dry bulk density of less than 2200 kg/m^3;
- a water:cement ratio greater than 0.6;
- a cement content of less than 14% by weight;
- increased proportions of ggbs in the cement;
- an environmental relative humidity in the range 52% - 72%; and
- the presence of acidic groundwater.

Sulfate attack

Sulfates can be derived from the groundwater, the contaminants on site, natural sulfates e.g. as gypsum, from the oxidation of pyrite, seawater and sea spray, sulfur oxidising bacteria, (for example in sewage works), or contaminated aggregates.

Sulfates in solution have the ability to attack concrete causing expansion and disintegration. The sulfates react with calcium hydroxide and calcium aluminate hydrate in the cement paste. The products of the reactions, gypsum and Aft (ettringite), have a considerably greater volume than the compounds they replace, and this leads to expansion and disruption of the concrete (Building Research Establishment, 2001).

$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + 2NaOH$

$3C\text{-}S\text{-}H + MgSO_4.7H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2 + SiO_2.nH_2O$

Sulfate attack is controlled by diffusion in saturated pores and by capillary suction in dry conditions (Hilsdorf, 1995). For a given concentration of sulfate, the rate and amount of deterioration increases with:

- the amount of C_3A in the cement paste;
- a lower cement content;
- a higher water/cement ratio;
- porous and permeable concretes;

- high concentrations of CH in the cement matrix; and
- acid conditions.

Two types of damage can occur: interaction with AFm may form AFt, which may cause cracking; and sulfates, particularly magnesium sulfate, can react with the CH and C-S-H and after long exposure may cause loss of strength and cracking (Shah and Hookham, 1998).

Ettringite occupies more than twice the volume of the hydrated aluminates it replaces and the expansive forces accompanying its formation in the cement matrix can exceed the tensile strength of the concrete (Fookes, 1997). This delayed ettringite formation (DEF) has tended to increase in recent years as the cement clinkers have had increased sulfur contents, due the use of sulfur rich wastes and fuels in cement kilns (Collepardi, 2000).

$$3CaO.Al_2O_3.12H_2O + 3(CaSO_4.2H_2O) + 14\ H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$$

$$3CaO.Al_2O_3.CaSO_4.12H_2O+SO_4^{2-}+2Ca(OH)_2+20H_2O \rightarrow$$
$$3CaO.Al_2O_3.3CaSO_4.32H_2O+4OH^-$$

At temperatures of around 6ºC and under conditions of high humidity, sulfate solutions can attack concrete to produce thaumasite. Thaumasite formation has more serious consequences than the formation of ettringite, and the hardened cement can become completely disintegrated by softening (Figures 9.2 and 9.3). The thaumasite formation decomposes C-S-H in the cement and destroys the fabric of the cement paste (Taylor, 1998).

Sulfate resisting cements may not provide protection against this form of sulfate attack and thaumasite formation is a possibility under high humidity/low temperature conditions (St. John *et al.,* 1998; Building Research Establishment, 2001; Marsh, 2002).

$$CaCO_3 + CaSO_4.2H_2O + C\text{-}S\text{-}H \rightarrow CaCO_3.CaSO_4.CaSiO_3.15H_2O$$

Sulfate attack may also result from bacterial action controlled by the environmental conditions (see Section 9.3.3).

Figure 9.1: Thaumasite formation on the surface of a concrete core (Photograph **courtesy of Geomaterials Research Services Ltd)**

Figure 9.2: Disintegration of a column that has been subjected to thaumasite attack (Photograph courtesy of BRE)

Chloride penetration

The most important effects of chloride ions, associated with normal exposure of concrete, are corrosion of reinforcement, causing expansion of the reinforcement and subsequent cracking of the concrete (Basheer *et al.,* 2001). The high pH of the cement inhibits corrosion and chloride penetration only becomes a problem when the pH is lowered for example through carbonation. However, interactions between chloride ions and hydration products of the cement, may contribute to the development of frost damage through the expansive precipitation of chloride salts which typically occurs in wet/drying environments.

Chlorides of Na, K and Ca are generally regarded as being non-aggressive towards mass concrete. Concrete brine containers in salt mines have remained serviceable for 20 years in spite of being heated to 100^oC (Biczok, 1972). Paul (1994) reported on the work of Smolczyk (1969) where two Portland cements and one PC/slag cement (75% slag) were stored in saturated NaCl, 1 and 3 molar $CaCl_2$, 3 molar $MgCl_2$ and 3 molar NH_4Cl solutions. Samples stored in the saturated solution of NaCl and weak $CaCl_2$ showed no loss of strength after two years. Portland cement samples in the other solutions underwent severe cracking and spalling and were totally destroyed after 16 weeks. The use of slag increased the chemical resistance of the concrete with samples containing slag only showing loss of strength in NH_4Cl solution. The formation of oxychloride was thought to be responsible for the disintegration of the samples together with the reaction of magnesium chlorides and ammonium chlorides with portlandite in the hardened cement.

British Standard BS 8110: Part 1 gives limits to the chlorides that can be incorporated into the concrete mix, but does not quantify the allowable limits for chlorides in groundwater or from salt spray or de-icing salts. However, Paul (1994) gives a classification of chloride conditions in groundwater according to the degree of attack. (Table 9.4).

Table 9.4: Classification of chloride conditions in groundwater (from Paul, 1994 after Bartholomew, 1979)

Degree of attack	Chloride Limit (ppm) Temperate Climate	 Tropical climate
Negligible	0 –2,000	Not applicable
Moderate	2,000 – 10,000	0-2,000
High	>10,000	2,000 – 10,000
Very high	Not applicable	>>20,000

Alkali-aggregate reactions

Alkali-aggregate reactions are expansive reaction between Na and K in the pore solution of the concrete and minerals in the aggregate. The cement itself is the principal source of the alkalis, but any source of sodium or potassium can contribute to the reaction if they are available in the pore solution of the concrete, creating the necessary hydroxyl ion concentrations (St. John *et al.*, 1998).

There is a large amount of literature on the problems of alkali aggregate reaction, (Building Research Establishment, 1988; British Cement Association, 1987) most recently covered in the codes of practice published by the Concrete Society (1995). Guidance on these matters can be obtained from BRE Digest 1 (Building Research Establishment, 2001).

The most important type of reaction is alkali-silica reaction (ASR): the reaction between alkalis and varieties of glassy or poorly crystalline silica minerals such as opal, chalcedony, cristobolite and tridymite to produce expansive alkali-silica gels. The alkali-silica gels absorb pore fluid and swell, exerting pressure on the surrounding materials, causing extensive cracking (Figure 9.3).

Figure 9.3: Cracking associated with ASR, River Exe Bridges, Exeter, Devon. (Photograph courtesy of Paula Carey)

The reaction can only proceed if there is sufficient moisture; not less than 85% humidity in the pore structure of the concrete, high alkalinity (Na_2O + 0.658 K_2O is greater than

0.6%) in the pore fluid surrounding the reacting particle and if reactive silica is present in sufficient quantity. The reactions are also controlled by the diffusion coefficient for alkali ions in the cement matrix and the capillary suction of water (Hilsdorf, 1995). BS 8500-2, allows 0.02% expansion in a mortar bar test. At this value or above aggregates are considered as reactive.

Reaction can also take place between the alkalis in the cement and siliceous rocks or carbonates in the aggregates. A variety of rocks including cherts, phyllites, greywackes, quartzites or granites, that contain chalcedony, cryptocrystalline or strained quartz, can react with the alkalis in the cement and produce an expansive, silica gel. These reactions tend to be less rapidly expansive than those of alkali-silica reaction. In the case of carbonate rocks such as argillaceous dolomitic limestones or argillacaeous calcitic dolostones, expansion results from the uptake of water by dry clay minerals and can vary from slow to rapid (Oberholster *et al.,* 1984).

9.2.4.2 Secondary degradation processes

Freeze/thaw and wetting/drying

The following mechanisms have been proposed to explain the damaging effects of freeze/thaw (Basheer *et al.,* 2001):

- freezing in the capillaries generating hydraulic pressure;
- diffusion of gel water into capillaries followed by freezing;
- localised shrinkage and swelling and thermal strains; and
- osmotic pressures resulting from partial freezing in capillaries of solutions with local salt concentration.

The pore size, porosity and the amount of freezable water in the capillary pores are critically important in determining the extent of damage (Pigeon and Regourd, 1986). The critical saturation of the pores can be achieved through capillary suction. The most straightforward protection measure, if applicable, is burial below the depth of penetration of frost. Frost damage may also be prevented by air entrainment. The air bubbles formed are typically 0.05 mm in diameter. They do not affect the permeability because the bubbles are discrete, but they do reduce the strength of the concrete. (Pigeon and Lachance, 1981). Frost attack on concrete, like other deterioration processes, requires a high relative humidity for deterioration to be severe (Table 9.3).

Cyclic wetting and drying, as a result of fluctuating water table or penetration of rainfall or floodwater, may cause cracking as a result of the expansion of constituents in the concrete and cyclic solution and precipitation of mobile salts (e.g. chlorides and sulfates, see Section 9.3.1 and Table 9.5). Again, protection may be straightforward through exclusion of water by barriers or keeping the permeability of the concrete low.

Biological attack

There are several studies on the effects of microbial activity on concrete, particularly with regard to the performance of concrete in sewers (Monteny *et al.,* 2000; Mansfield *et al.,* 1991; Sand and Bock, 1988). In anaerobic conditions, sulfate-reducing bacteria, e.g. *Desulfovibrio,* reduce sulfate compounds to H_2S, which may then oxidise in the sewer atmosphere to form elemental sulfur. The sulfur then becomes available for oxidising bacteria, e.g. *Thiobacilli* sp. which converts the sulfur into sulfuric acid, causing corrosion of the concrete by formation of gypsum and ettringite and dissolution of the cement paste. Corrosion rates of up to 10 mm/yr have been observed in concrete pipes in the Hamburg sewer system (Sand and Bock, 1984). The microbes that cause microbial influenced degradation (MID) are ubiquitous in the environment and can produce either organic or inorganic acids that attack the concrete matrix (Rogers *et al.,* 2003). The micro-organisms continuously release acid on micro scale (Rogers *et al.,* 1996).

Loading

The tendency of hardened concrete to creep under load is related to the percentage of cement in the mix as well as the quality of the aggregate. A high proportion of strong angular aggregate limits both the short-term drying shrinkage and long–term creep (McNally, 1998). Up to 40% of the short-term, strength (28-day strength) the amount of creep is proportional to the applied load. Above 40%, micro-cracking contributes to creep and the creep-stress relationship becomes non-linear. At 70-80% of the short-term strength, sustained loading will eventually result in failure. (Neville and Brooks, 1987).

The process of creep is not fully understood at the micro-scale, but might involve plastic deformation of the gel phase and/or micro-cracking associated with the aggregate cement interface. However, approximately 75% of the long-term creep occurs within 1 year.

Fire Damage

Fire damage also causes cracking as a result of drying and shrinkage of the cement paste hydrates, together with the differential expansion of successive layers within the concrete. Cracking and spalling also occurs as the result of internal pressure as moisture in the concrete is converted to superheated steam (Concrete Society, 2000).

9.3 The Deterioration of Rock or Soil

Weathering is the process by which rocks are broken down *in-situ* by the action of extrinsic agencies, such as wind, rain, temperature changes, plants and bacteria.

Weathering processes can be divided into three types:

- physical weathering;
- chemical weathering; and
- biological weathering.

Weathering can cause rock to become more porous, individual mineral grains to be weakened and bonding between mineral grains to be lost. New minerals may be deposited within pores, at grain boundaries and along fractures. The rock will lose its strength, become more deformable and its permeability may change depending on the nature of the rock, the presence and type of weathering products and the stage of weathering. Changes in permeability with weathering depend upon three main factors: the growth of voids, loss of integrity of the framework of relict minerals, with the development and subsequent leaching of weathering products and the development and healing of fractures. A progressive increase in mass permeability due to the development of fractures and pores during early stages of weathering may be reversed at later stages as fractures become filled with weathering products (Anon, 1995; BS 5930: 1999).

Present day weathering profiles within rock can be seen in many historic buildings, where dimension stone has been subjected to sub-aerial weathering for, in the order of, 500-1000 years (Figure 9.4). Deterioration of building stone is particularly marked where the stone has been subjected to atmospheric pollution in the form of SO_2, NO_x and freeze-thaw action. Schaffer (1932), and more recently Lai Gauri and Bandyopadhyay (1999), give an extensive review of the weathering agents acting on building stone.

9.3.1 Physical weathering

Physical weathering involves the disaggregation of rock, without mineralogical change, induced by cyclic stresses. These stresses are the result of heating and cooling, freeze/thaw and wetting/drying (Fookes *et al.,* 1988) and are very similar to the processes described above for concrete.

Figure 9.4: Surface degradation of building stone, the London monument.
(Photograph courtesy of Paula Carey)

Pressure exerted by crystal growth is the reason that both freeze/thaw and salt crystallisation can be particularly deleterious to rock materials even over short periods. Water penetrating into cracks and pore spaces can freeze and expand by about 9% at 0ºC, exerting forces across the existing cracks or initiating cracks from the ice-filled pore spaces. Similarly, salts may be carried by percolating water into pore spaces and exert pressures, which may exceed the tensile strength of the host material (Price, 1995; Fookes *et al.,* 1988). Sources of salts include, de-icing salts, sulfates and chlorides within groundwater, or salts carried by sea spray or atmospheric dust. Salt corrosion or salt fretting is particularly common in low latitudes such as in the Middle East and is visible along the upper fringe of the capillary water transport front.

Ollier (1984) suggested that ordered water molecular pressure variation could explain disintegration as a result of wetting and drying. Ordered water molecules grow within the rock fabric and exert expansive forces on the host materials. Substantial volume changes can also be caused by absorption of water. The presence of clay minerals makes a rock or soil particularly vulnerable to slaking or the flaking of layers of rock, as the result of shrinkage and swelling with wetting and drying. Even non-swelling clay minerals are important, as there is a loss of cohesion between particles during weathering with a release of residual stresses (Moon and Beattie, 1995). Zeolite minerals also undergo swelling and shrinkage, which can disrupt the rock structure (Senderov and Khitarov, 1970). Table 9.5 gives the approximate values of the forces imposed by physical weathering processes.

Table 9.5: Typical forces exerted by physical weathering processes

Process	**Force**	**Reference**
Freezing to –20°C	200 MPa	Ollier, 1984
Crystallisation of salts	2-20 MPa	Ollier, 1984
Hydration of salts	100 MPa	Ollier, 1984
Clay expansion	2 MPa	Tucker and Poor, 1978

9.3.2 Chemical weathering

Chemical weathering largely depends on the presence of water. The susceptibility of rock to chemical weathering increases with reducing grain size, increased porosity and higher permeability (Anon, 1995) and is much more effective in hot and wet climates.

Chemical weathering results in:

- breakdown of the parent material structure with release of ions or molecules;
- removal in solution of some of the released constituents; and
- reconstitution of the residue with components from the atmosphere to form new minerals that are stable or metastable under the prevailing conditions.

On an engineering timescale, the most relevant chemical processes are oxidation/reduction, hydrolysis and carbonate solution.

9.3.2.1. Oxidation/reduction

Oxidation is an important process in the weathering of rocks and soils (Oyama and Chigira, 1999). Oxygen diffuses into the rock or soil and oxidises minerals. For example, the oxidation of pyrite (FeS) can generate sulfuric acid, which dissolves the surrounding materials, particularly carbonates. Evaporation of the pore water can then cause the expansive precipitation of gypsum. The rate of weathering through oxidation is controlled by diffusion in the same way as carbonation of concrete and can be approximated by Fick's law with recorded oxidation rates of between 5 and 0.3 cm/yr (Oyama and Chigira, 1999).

9.3.2.2. Hydrolysis

Most silicate minerals are susceptible to hydrolysis (Anon, 1995). It affects the more weakly bonded metal cations; Ca^{2+}, Mg^{2+}, Fe^{2+}, Na^{+}, K^{+}. These are the first cations to be removed by weathering. The degree of initial weathering of silicate minerals depends on the number and accessibility of these cations. This process is responsible for the complete structural breakdown of minerals rich in magnesium and ferrous ions such as the orthosilicates and inosilicates. More superficial alteration occurs with phyllosilicates and considerable structural weakening occurs with tektosilicates, such as feldspar, that contain these cations (Paton, 1978).

Hydrolysis is promoted by a low pH because the process is dependent on the concentration of hydrogen ions. However, in the immediate vicinity of the solid face the release of Na^{+}, K^{+} and Ca^{2+} ions causes a high pH, which drops off rapidly away from the face as the hydroxides produced are removed by the passing water. Amorphous silica is more soluble in this high pH environment and small amounts of both Si and Al can go into solution. Si can travel some distance as H_4SiO_4 but the majority of Si and Al is reprecipitated, as the pH drops away from the interface.

The extent to which the products of hydrolysis are subject to leaching depends on their ability to form stable ions in aqueous solutions. This in turn is determined by the ratio between ionic size and valency (Paton, 1978). Elements belonging to groups I and II of the periodic table (including Ca, Na, K, Mg and Fe), are relatively more mobile than elements from group IV (including Al, Si). Leaching is particularly intense under alternate wetting and drying conditions typical of tropical environments and can lead to the complete loss of cations and alteration of silicate minerals to clay minerals.

9.3.2.3. Solution of carbonates

The solution of calcium carbonate in mildly acidic rainwater is an important weathering process, which is responsible for the formation of the karstic geomorphology of limestone terrains. Solution occurs along preferential pathways such as joints and fractures and leads to the formation of solution hollows, caverns and pinnacled rock head which can have enormous engineering consequences (Fookes and Hawkins, 1988)

The degree of solution depends on the quantity of water passing over the surface of the rock, the solubility of the species being dissolved and the pH of the water (Price, 1995). The solution of carbonates in rocks bound by calcareous cement can result in decalcification of rocks and soils (Figure 9.5) and significant loss of strength (Hawkins and McDonald, 1992).

Figure 9.5: Surface decalcification of building stone, Bari, Italy.
(Photograph courtesy of Brian Bone)

9.3.3 Biological weathering

Biological activity is a significant factor in weathering processes. Such activity can include physical disruption by plant roots or animal burrowing or chemical activity associated with plant roots or micro-organisms. One gramme of soil can contain between 10^6 and 10^9 bacteria (Berthelin *et al.*, 2000). Micro-organisms cause weathering of minerals through:

- dissolution and release of metal ions by acids and complexing compounds produced by heterotrophic and autotropic micro-organisms,
- oxidation and reduction of mineral elements (Fe, Mn, S) promoting dissolution of sulfide minerals by oxidation or of oxyhydroxides by reduction, and
- change in pH and E_h by uptake or release of different compounds or ions (NH_4^+, Na^+, etc).

During degradation of organic matter, bacteria and fungi can produce carbonic, aliphatic or aromatic acids, which can then be involved in the solution of minerals. Oxalic and citric acids formed by micro-organisms dissolve minerals by formation of stable soluble organo-metallic compounds (Berthelin *et al.*, 2000). For example, lead solubilisation by soil-fungi - transformation of insoluble Pb compounds into lead oxalate (Sayer *et al.,* 1999) - indicates that microbial processes are important in determining the availability of lead in soils.

9.3.4 Rates of weathering

There is a lack of literature on the weathering of rocks and soils within the ground in temperate climates, other than references to frost susceptibility. This is partly because the processes operating are very slow and so their effects are difficult to measure and also because there is no reason to exhume the materials to examine them. The sub-aerial weathering of building stone, however, has been studied extensively and has been accelerating as the result of increasing atmospheric pollution (Department of the Environment, 1989).

The propensity for a rock material to weather or degrade is also dependent on its intrinsic properties, including the stability of the minerals present under current environmental conditions. Similarly, S/S waste forms are mineralogically metastable under the ambient conditions of service (Klich *et al.,* 1999) and the minerals should gradually react to form an assemblage stable at prevailing temperatures, pressures, E_h and pH conditions in the environment of disposal.

In temperate climates, such as the UK, weathering processes are extremely slow but, as illustrated by studies of historic building stone, can be significant over several hundred years (Mottershead, 2000). Rates of 'natural weathering' have been calculated for Carboniferous Limestone from Yorkshire, Eire and South Wales by estimating the surface degradation since the start of the Holocene period (10,000 – 12000 years ago). These rates vary from 3 to 75 μm yr^{-1} (Department of the Environment, 1989) (Table 9.6).

Building stone has been used in construction for 1000s of years, along with lime-based mortars, with obvious success. However, there have been notable failures where unsuitable stone has been used in unsuitable environments. For example, a magnesium limestone from Chesterfield had been used very successfully in the relatively unpolluted atmosphere of York, but disintegrated rapidly when used in the highly polluted atmosphere of London (Bishop, 1998).

In tropical climates, where temperature and rainfall conditions are extreme, weathering rates are much greater and lead to the formation of deep weathering profiles at rates in excess of 11.5 mm yr^{-1} (Fookes *et al.,* 1988). On exposure, e.g. when rock is quarried as a building stone, extensive weathering can occur in the short term and cause deterioration of engineering structures within decades or even months (Emerick, 1995).

Table 9.6: The variation in rates of weathering recorded in different climatic conditions and different rock types.

Rock type	Situation	Process	Timescale	Calculated weathering rate mm/yr	Reference
Limestone	Austrian alps covered by acid soil	Solution	1000 years	0.028	Bauer, 1962
Limestone	Yorkshire, South Wales and Eire	Solution	12,000 years	0.0003 –0.0075	DoE, 1989
Limestone	Australia, temperate surface exposure	Solution	13 years	2.2 – 11.5	Sweeting, 1960
Shale	Great Pyramids	Physical weathering	1000 years	0.2	Emery, 1960
Sandstone	Spitzbergen, Glacial Surface	Physical weathering	10,000 years	0.34 – 0.5	Rapp, 1960
Clay	Lias Clay Gloucestershire temperate surface exposure	Oxidation	1000s years	10	Chandler, 1972

9.4 Implications for the Durability of S/S Waste Forms

Certain trace metals have been fixed in cementitious materials for thousands of years in a variety of geochemical settings, (Dole, 1985). Means *et al.* (1995) show ancient grouts, from Cyprus and Greece, have held their trace element fingerprints for 2300-3500 years albeit in a drier climate than in the UK. The Pantheon in Rome is an example of a concrete structure that has lasted for at least 1500 years (Murdock and Blackledge, 1968), and C-S-H gels have been shown to be stable in geological environments for 1000s of years (McConnell, 1955).

Environmental performance of treated waste should be considered in terms of at least 100 years (van der Sloot, 2000), but most waste forms will not be accessible for either direct inspection, or maintenance. Prediction of long-term performance must therefore rely on comparison with natural or historical analogues (see Sections 9.2 and 9.3 above) and/or modelling approaches (see Chapter 10).

Because of difficulties involved in characterising the waste materials, and the use of smaller quantities of binder, the waste forms cannot be designed to such tight specifications as high quality concrete. The waste or soil presented for treatment may incorporate chemical and mineralogical phases that would not be permitted for use with concrete and the curing conditions may be more difficult to control.

Van der Sloot (2000) predicted the release of a variety of heavy metals, stabilised in a 1 m^3 monolith, after 100 years (Table 9.7). The results make no allowance for ambient temperature or wet/dry periods, as they refer to a cube of material saturated with water. If these corrections are taken into account the release of Mo, for example, at 100 years reduces from 72 to 19 mg/m^2 as a result of the reduced contact time with the water. However, Garrabrants *et al.* (2002) proposed that intermittent wetting could lead to underestimates of cumulative release from cement-based waste forms. Intermittent wetting increases the degree of carbonation because carbon dioxide can diffuse into the pore spaces and transfer into the liquid phase more readily, lowering the pH of the pore solution (Gervais *et al.,* 2004). Therefore, metals such as Cd, that are more soluble at lower pHs, are released. In contrast, Pb and Zn form less soluble species at the lower pH and leaching with intermittent wetting decreases (Sanchez *et al.*, 2002; Chapter 4).

Table 9.7: Predicted release of a variety of heavy metals stabilised in a monolith (after van der Sloot, 2000)

Element	Release predicted mg/m^2 in 100 years, 20^oC, saturated
S	7900
Zn	29
V	92
Mo	72
Pb	138
Cr	209
Ba	2004

Like many other workers (see Chapter 10), van der Sloot (2000) used short term leaching behaviour to model the longer-term performance of the materials without consideration of the processes of degradation that might be occurring within the waste forms. Felix *et al*., (2000) considered the physical processes leading to enhanced leaching and Valls and Vazquez (2000) and Bodenan *et al.* (2000) also considered carbonation of the waste as an important consideration in determining its long-term leaching potential. Mostbauer *et al.* (2003) developed a combined weathering and upflow percolation leaching procedure and compared the results of their laboratory tests against lysimeter data. At the same liquid to solid ratio the results showed good to excellent correlation between artificially weathered inorganic waste and leachate data from the naturally-weathered waste placed in the lysimeters.

BUWAL (1987) concluded that reduced permeability was the most important factor in heavy metal immobilisation in cement stabilised APC residues. S/S waste forms will tend to have higher permeability and lower density than even low specification concrete (Table 9.8). The surface of the waste form produced *in-situ* is likely to be very variable as there is no surface finishing or form work similar to that associated with most concrete. The nature of the surface of the S/S waste is liable to have an important effect on its durability. If low permeability cannot be achieved, cementitious materials need to be protected from aggressive environments. Table 9.9 gives a classification of chemically aggressive conditions for concrete modified from ENV 206 (2000).

Table 9.8: Typical S/S regulatory limits (in comparison to concrete)

	28 day UCS MPa	**Permeability ms^{-1}**
Ardeer	0.200	$< 1 \times 10^{-7}$
Sealosafe	>0.700	$< 1 \times 10^{-7}$
USA waste acceptance criteria	>0.350	$< 1 \times 10^{-9}$
Concrete specifications: BS 8500-2: 2002	32.5 – 62.5	$(10^{-5} - 10^{-13})$

Other studies suggest that the long-term stability of S/S waste is largely dependent on geochemical rather than physical factors (AGW, 1991 in Ludwig *et al.,* 2000). Matrix components are important as they control leachate composition and provide surfaces for contaminant binding.

Table 9.9: Chemical attack of concrete by water and soils containing aggressive agents: assessment of the degree of attack (modified from ENV 206 and King, 1977)

	Weak	**Moderate**	**Strong**
Water			
pH	6.5 to 5.5	5.5 to 4.5	4.5 to 4.0
Aggressive (mg CO_2 /l)	15 to 40	40 to 100	>100
Ammonium (mg NH^{4+}/l)	15 to 30	30 to 60	60 to 100
Magnesium (mg Mg^{2+}/l)	300 to 1000	1000 to 3000	>3000
Sulphate (mg SO_4^{2-}/l)	200 to 600	600 to 3000	>3000
Soil			
Degree of acidity	200 ml/kg (20ºC Baumann-Gully)		
Sulphate (mg SO_4^{2-}/l) air dry soil	2000 to 6000	6000 to 12000	12000 to 24000
Redox potential mV at pH 7	>400 (>430 in clay soil)	400 to 100	<100

The efficacy of S/S waste forms to encapsulate metallic (and other) pollutants is not solely attributable to the mineralogy of the cement-bound matrices. 'Textural' features such as specific geometric surface area; pore characteristics, compaction, and the amount of entrained air will also significantly influence the performance and durability of a treated waste form.

From the consideration of degradation of concrete and soil or rock, a number of factors that control their degradation can be identified and applied to the re-use or disposal scenario developed for a waste form. Table 9.10 summarises the principal degradation mechanisms described in this chapter and the effects that these mechanisms may have on S/S waste forms.

Table 9.10: Summary of degradation mechanisms and their effects on waste forms

Degradation mechanism	Contributing factors	Case study/ applications	Effect on waste form
Carbonation	High permeability, acidic groundwater, high water/solids ratio, high humidity	Weathering of thermal residues: Landfill (Johnson *et al.*, 1998) Superfund (Klich *et al.,*1999)	Physical and chemical release of sorbed metals through dissolution of CaOH and C-S-H. Reduction in strength
Oxidation	High permeability and flow of water	Landfill after methane production phase (Bozkurt *et al.,* 2000)	Change in solubility of inorganic and organic species
Hydrolysis	High permeability and flow of water		Weathering of soil minerals changing soil/binder interactions
Solution of soluble salts	High quantities of soluble salts		Increase in porosity/perm., reduction in strength
Alkali/aggregate reaction	High alkalis or crypto-crystalline silica within the waste	Superfund sites (Klich *et al.,*1999)	Cracking of waste – increasing possibility of other forms of attack. Reduction in strength
Organic acid attack	Contact with degrading organic matter from soil or organic waste in landfill	Shimaoka and Hanashima (1996), recognised neutralisation of leachate	Physical and chemical release of sorbed metals through dissolution of CH and C-S-H
Sulfate attack	High permeability, pyrite or gypsum in soil. Non sulfate resisting cement	Superfund sites (Klich *et al.,*1999) Formation of ettringite and thaumasite	Cracking of waste – increasing possibility of other forms of attack Reduction in strength
Chloride attack	Saline ground water, typical of hot climates. Ferrous components in waste.		Cracking through salt precipitation and/or expansion of ferrous components in waste Reduction in strength.
Freeze/thaw	S/S waste form buried too shallowly (above 450 mm in the UK)	Identified in waste forms stored at the surface (Klich *et al.,*1999; Reid and Clarke, 2001)	Cracking of waste – increasing possibility of other forms of attack Reduction in strength
Wet/dry	S/S waste form not adequately protected from infiltration or exposed to fluctuating groundwater		Cracking of waste – increasing possibility of other forms of attack. Redox changes, reduction in strength Increased carbonation through partially saturated pores.
Biological attack	Contact with organic and inorganic acids produced by micro-organisms	Knight *et al.,* (2000) attack on waste binder in laboratory	Physical and chemical release of sorbed metals through dissolution of CH and C-S-H

9.4.1 Carbonation

Gradual carbonation will occur if a S/S waste form is exposed to carbon dioxide and moisture in the unsaturated or saturated zone. It will result in a reduction in the pH of the material, which may have consequences for the solubility of some of the amphoteric heavy metals or for metals with a minimum solubility above a pH of 8 (see Chapter 4). In the UK's temperate climate, carbonation occurs on the outer surface of the waste form (and along preferential pathways). The consequent formation of calcium carbonate reduces the surface permeability and slows the rate of carbonation in the interior of the material**.** In extreme cases, it is possible for S/S material to be exposed to elevated levels of carbon dioxide gas, for example from a nearby landfill site. In the process of carbonation, portlandite and C-S-H will gradually be removed (Basheer *et al.,* 2001). Portlandite plays little role in the S/S process other than through physical encapsulation of the contaminants and through buffering the pH (see Section 4.2.5.1). C-S-H holds the contaminants through sorption, substitution and encapsulation and its reaction will release these contaminants into the pore water (Section 4.2.4).

Van Zomeren *et al.* (2003a) reported a pH change in the top 2cm in cores of cement-stabilised hazardous waste deposited at the VBM Sustainable landfill, The Netherlands. Between 1 week and 4 months after emplacement the pH dropped from about 12-12.4 to about 11, compared to pH 11.9 below 2cm.

The carbonation process can be accelerated and used specifically to achieve S/S. This process involves placing the soil or waste with a hydraulic binder and water in a CO_2 rich atmosphere before hydration of the binder. A carbonate product is formed within 15 to 20 minutes of mixing, and has been shown to be very effective in the S/S of principally heavy metals such as Zn, Ni and Cu, which might otherwise cause retardation of cementitious systems. (Lange, *et al.,* 1997; Sweeney, *et al.,* 1998; Whitehead, *et al*., 2003).

9.4.2 Chemical weathering: oxidation, hydrolysis and solution of soluble salts

Weathering of industrial wastes, particularly bottom ashes and slags, is an important component of their management prior to S/S treatment or utilisation. If left in stockpiles open to the atmosphere, such solids undergo hydrolysis, hydration, and carbonation as well as oxidation/reduction, which lead to the formation of new more stable phases and changes in volume, pore cementation, grain size and pore distribution (Meima and Comans, 1997; Zevenberger, *et al.,*1996).

Oxidation/reduction reactions are important in the release of contaminants from wastes in two ways. Firstly, the solubility and toxicity of contaminants depend on their oxidation state, influencing both the extent of any release and the potential environmental impact. Secondly, the stability of mineral phases capable of immobilizing metal ions through precipitation and/or sorption phenomena is dependent on the oxidation/reduction potential. Immobilisation of contaminants is favoured by low E_h as these gives increased sorption onto C-S-H gels and lower solubility of some contaminant compounds (Section 4.2.3; Glasser, 1993). Over a short time-scale H_2 and elemental metals (Al, Fe, or Zn) and Fe^{2+} can act as reducing agents: O_2, and H_2O can act as oxidising agents (Sabbas *et al.,* 2003). The oxidation of iron in the waste can lead to the formation of iron oxides, goethite and hydrous ferric oxides. These phases can be fine grained and able to sorb heavy metals which might be released through other degradation processes (Sabbas *et al*., 2003).

The oxidation reaction of sulfides in the waste or the soil can generate sulfuric acid that may attack the landfill containment system and the waste form. Excavation and replacement of soils during civil engineering works aerates the soil and can result in the development of oxidising conditions where they did not exist before the works (Floyd *et al.,* 2003; Longworth, 2003). The oxidation of pyrite has caused problems in the lime stabilisation of road sub-bases with swelling caused by gypsum formation and has also be linked to the formation of thaumasite in foundations for motorway bridge abutments (Building Research Establishment, 2001; Hobbs and Taylor, 2000).

9.4.3 Alkali – aggregate reactions

Dependent on the type of waste, there is considerable potential for S/S waste forms to contain potentially reactive silica in the form of glass and sufficient quantities of alkalis for expansive alkali-silica reactions to occur. Expansion will cause cracking increasing the surface area for attack and increasing the flow of infiltrating fluids. The lower density and lower cement content of S/S waste forms may restrict the impact of such expansive reactions particularly in granular waste forms.

9.4.4 Acid attack

The influence of acids on the integrity of cementitious systems has been studied by several researchers, and the morphological and physical properties of S/S waste forms subject to acid attack have been studied by Cheng and Bishop (1996a, 1996b). They were able to confirm the increased porosity and decreased density of samples of a Type 1 portland cement – synthetic metal sludge material that had been leached in acetic acid solutions (Cheng and Bishop, 1996b). Cheng and Bishop (1996a) identified outer leached layers and a well-defined leaching boundary with the unleached core, represented by a remineralisation zone and change in pH from <6 to >12 across the 100 μm wide leaching boundary. Although the waste form was a porous structure the rate of acid attack was very slow; a 0.7 mm leached zone developed after the leaching equivalent of tens to hundreds of years.

9.4.5 Sulfate attack

Within S/S waste forms, the effects of sulfate-induced expansion and the consequent reduction in UCS might not be a problem if dimensional stability is maintained, particularly if the waste form is granular. Ettringite is capable of extensive substitution and contaminants released from portlandite or C-S-H during DEF may be incorporated into the ettringite structure (Section 4.2.5.2). However, for monolithic wastes, expansion may cause cracking and allow further leaching and softening associated with thaumasite attack will reduce the UCS. The reaction of the portlandite and calcium aluminate hydrates in the binder will cause release of contaminants held by physical encapsulation and substitution.

9.4.6 Chloride attack

S/S waste forms are unlikely to contain steel reinforcements but may contain fragments of metals, which could corrode through chloride attack and cause expansive cracking. Waste forms may be subjected to high concentrations of a variety of chlorides either from the waste being stabilised or from the groundwater in the environment of disposal/storage. The formation of oxychlorides and magnesium or ammonium chlorides that can react with portlandite in the binder of the waste form is quite possible.

9.4.7 Wetting and drying and freeze/thaw

Felix *et al.* (2000) considered that freeze/thaw, (wind) erosion (as defined by the NEN 2875 durability test) and wetting and drying were the main degradation mechanisms that caused changes in leaching behaviour with time. These degradation mechanisms may therefore be important in controlling the durability of S/S waste forms at shallow depth, such as those reused in road sub-base (Section 9.5.4) and embankments (Section 9.5.5).

9.4.8 Biological attack

The action of bacteria will be limited within S/S waste forms because of the high pH of the systems. However, Rogers *et al.* (1996) reported microbially-influenced degradation of cement-based waste forms. Micro-organisms, ubiquitous to disposal or re-use environments, will generate mineral or organic acids that can attack the surface of the waste form. Bacteria commonly known to attack concrete structures include:

- sulfur-oxidising bacteria (genus *Thiobacillus*) - oxidise reduced, inorganic sulfur, assimilate carbon dioxide as a carbon source and produce sulphuric acid;
- nitrifying bacteria (genus *Nitrosomonas* and *Nitrobacter*) - oxidise inorganic nitrogen compounds (ammonium and nitrate respectively) and produce nitric acid; and
- heterotrophic bacteria - a diverse and ubiquitous group of bacteria that can produce organic acids through assimilation of organic matter.

Rogers *et al.* (1996) suggest that growth of biofilms on waste form surfaces can produce local acid conditions to below pH 2. Experimental work by Rogers *et al.* (2003) showed that aggressive micro-organisms (*T. thiooxidans*) can form a biofilm on cement-solidified wastes and, through the generation of sulfates, dissolves portlandite, decalcifies C-S-H and precipitates gypsum. Contaminants will be released through reduction in the physical encapsulation and reduced sorption and substitution.

9.4.9 Time frame for leaching contaminants from S/S waste forms

Whatever the stabilisation technique, or the engineering of its long-term storage environment, it is unlikely that any containment system will be completely effective in the long-term. The treated material will break down gradually and allow the slow release of contaminants within the design life of the S/S waste form.

Many of the major phases within a treated waste form are thermodynamically unstable and retained heavy metal species may be liberated from the waste form during transformation to more stable forms. Thus, the waste form should be designed so that any failure is gradual and rates of release are minimised. The determination of the potential rate of release of contaminants is problematical because of the variability and general lack of characterisation of S/S systems in terms of:

- the binder/contaminant interactions;
- the permeability/porosity variations with time;
- the quality of workmanship; and
- the nature of the environment of service.

Table 9.11 summarises research where the time frame of interest for the durability of S/S waste forms and other analogues is known or predicted.

The presence of deleterious materials within the wastes will have an effect on the equilibrium between solid and aqueous phases in a waste form. These may include, for example, alkalis, or cement replacement/extending materials that react with portlandite, and these will affect the buffering capability of binder system against aggressive agents with time (Macphee *et al.,* 1989).

To date, there are too few durability studies involving S/S products to show what happens to a waste form in the longer term. By using predictive tools (Chapter 10), it is possible to show that, providing the conditions of service of a waste form are maintained, effective immobilisation of contaminants can be achieved. However, because of intrinsic and extrinsic processes, a slow change in environmental conditions is inevitable and the potential for release of contaminants into the environment will increase. This is likely to be gradual and take place over timescales involving hundreds to thousands of years.

Table 9.11: Summary of references relating to durability timescales

Timescale (years)	**Concrete**	**Rock**	**S/S waste form**	**Other**
0-10	Walker (2000)	Bishop (1998) Emerick (1995) Fookes *et al.,*(1988)	Reid and Clarke (2001) Board *et al.,* (2000) Baur *et al.,* (2001) Ludwig *et al.,* (2000)	
10-50	Hobbs and Taylor (2000)	Sweeting (1960)		Brouwer *et al.* (2003
50-100			Kilch, (1997) Kosson *et al.,* (1996) van der Sloot (2000)	
100-1000		Mottershead (2000)	van Zomeran *et al.,* (2003)	
>1000	Means *et al*. (1995) Murdock and Blackledge (1968)	McConnell (1955) Fookes *et al.*(1988) Emery (1960) Chandler (1972) DoE (1989)	Bozkurt *et al.,* (2000)	Astrup *et al.*, (2001, 2003) Hall *et al.,* (2003) Dole (1985)

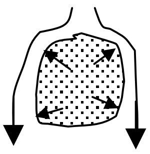
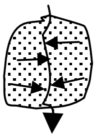
9.5 The Performance of S/S Waste Forums in Re-use and Disposal Scenarios

A treated S/S waste form may be exposed to variable environmental conditions and its performance will be dependent on a number of internal and external factors associated with the properties of the material and their interaction with the environment. A framework for evaluating the leaching performance of waste is described in ENV 12920 (CEN, 1997). This is based on understanding the characteristics of the waste form and its behaviour in its environmental setting, whether contained in a landfill site, re-used on site or as a manufactured product. The framework involves:

- definition of the problem and solution sought;
- description of the scenario;
- description of the waste;
- determination of the influence of parameters on leaching behaviour;
- modelling of leaching behaviour; and
- behavioural model validation.

This approach integrates laboratory testing and modelling with a particular disposal or re-use scenario developed from knowledge of both the waste and surrounding environment (Hjelmar, 2003). Broadly, leaching behaviour can be defined by percolation or diffusion controlled scenarios (Kosson *et al.,* 1996, 2002), differentiated by the mode of water contact with the waste form (Table 9.12). One of the aims of S/S is to change the process of release of contaminants from percolation dominated to a diffusion dominated regime (Rietra *et al.,* 2001).

Table 9.12: Summary of percolation versus diffusion regimes

Liquid/Solid contact	**Waste form characteristics**	**Type of flow of leachate**	**Leaching process**	**Controls**
High Liquid/Surface area (in $l\ m^{-2}$) Non-equilibrium (kinetic controlled release)	Low permeability, monolithic or compacted granular waste forms	Rapid flow over surface 	Diffusion through solid	diffusion coefficients of contaminant; tortuousity of pathway; pH of leachant
Low Liquid/Solid (in $l\ kg^{-1}$) Equilibrium (liquid-solid equilibrium at local pH)	Granular materials	Flow through waste form 	Percolation / advection	contaminant solubility and availability; pH of leachant

At the time of disposal, S/S waste forms will display their maximum alkalinity. As they are exposed to progressive leaching the buffering capacity of the material will decrease at a rate dependent on the acid neutralisation capacity (ANC) of the waste form, the pH of the infiltrating fluid and the rate of infiltration (Astrup *et al.*, 2001). Buffering within cementitious systems is initially provided by the dissolution of portlandite and C-S-H. Figure 9.6 shows the acid neutralising capacity of ground PC; the plateaux represent periods of acid addition when buffering is effective and the steep zones on the graph represent changes in the mineral phase providing the buffering (Glass and Buenfeld, 1999). Over time, carbonation may lead to a decrease in pH to below 9 and calcite will become the dominant buffer to acid attack without loss of buffering capacity (Astrup *et al.*, 2001). The buffering capacity of the waste form is of key importance where immobilisation is dependent on pH control.

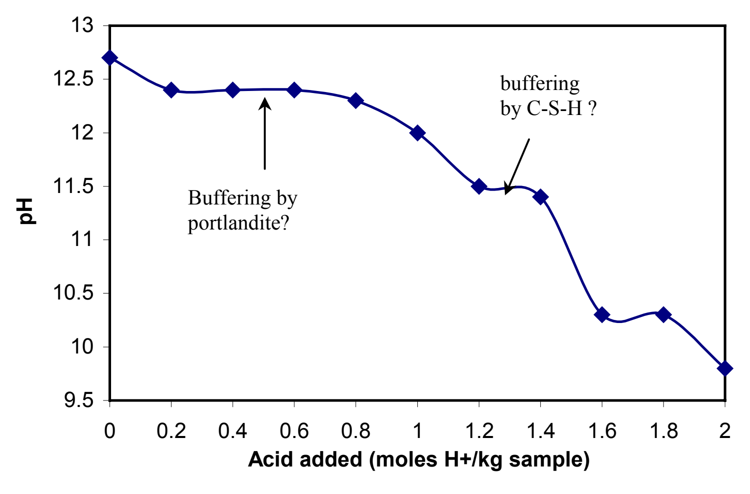


Figure 9.6: Steady state pH as a function of the quantity of acid added to samples of ground PC concrete (after Glass and Buenfeld, 1999)

There is significant active research in accelerated ageing testing (for example, see Astrup and Christensen, 2003, Eighmy *et al.*, 2003, Mostbauer *et al.*, 2003, Polettini and Pomi, 2003) using a variety of methods, including Arrhenius ageing (elevated temperature), freeze-thaw/wet-dry, cyclic loading and solution-carbonation techniques. The research ranges from laboratory based (Astrup and Christensen, 2003, Polettini and Pomi, 2003) to a comparison of physical and/or chemical performance in the laboratory and field (Eighmy *et al.*, 2003, Mostbauer *et al.*, 2003). Such tools may well be developed to become standard leaching performance tools in the future.

The specific environmental conditions influence and change the leaching behaviour and contaminant release from waste materials during utilisation or final land disposal. Research has been published on S/S treated waste forms in a number of environments of deposition that include:

1. Disposal in a non-hazardous waste cell or hazardous waste cell.

2. Co-disposal with biodegradable wastes.
3. Disposal via *in-situ* remediation or utilisation as engineering fill.
4. Reuse as sub-grade or capping layer beneath road/pavement.
5. Embankments.
6. Above-ground storage.

These six scenarios are discussed below:

9.5.1 Disposal in non-hazardous waste cells or in hazardous waste cells

With the implementation of the Landfill Directive in the UK, the use of S/S as a pre-treatment for a variety of waste streams is likely to increase. The S/S treatment may allow the wastes to be classified as non-hazardous or permit stable, non-reactive hazardous wastes to be landfilled in separate cells at a non-hazardous landfill site (see Section 7.5). Figure 9.7 shows the key processes that may influence leaching behaviour in a hazardous or non-hazardous waste landfill cell containing S/S waste forms.

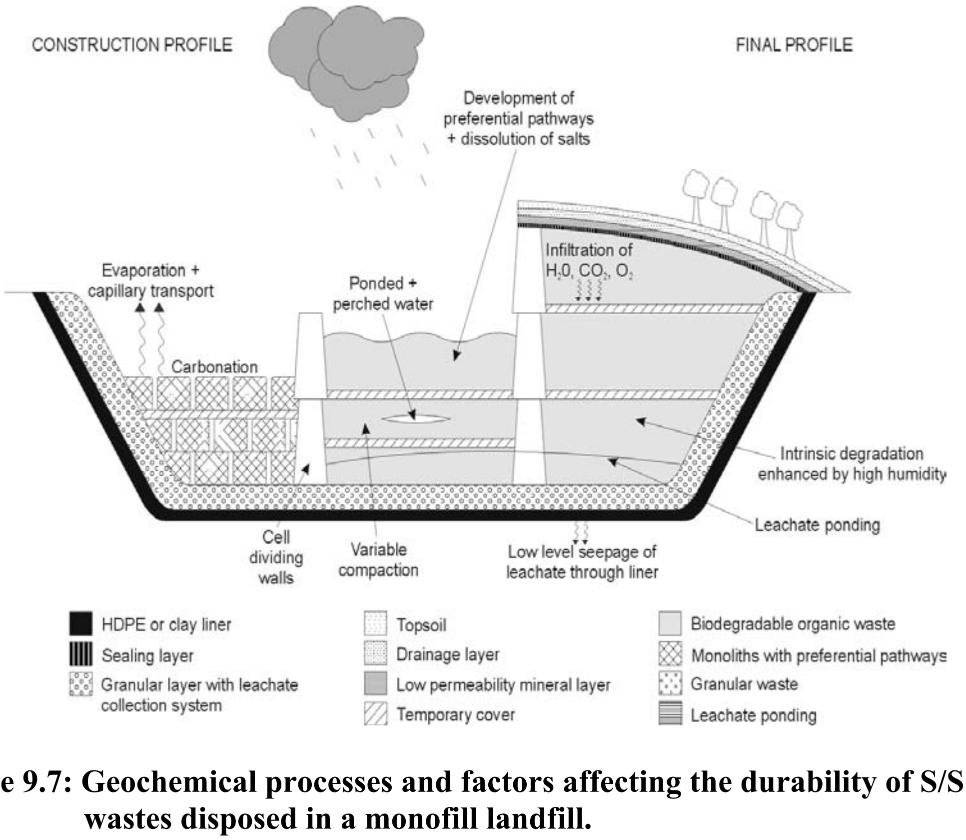


Figure 9.7: Geochemical processes and factors affecting the durability of S/S wastes disposed in a monofill landfill.

The degradation processes that are operating in the, largely inorganic, waste forms are chiefly the result of intrinsic chemical reactions and the infiltration of rainwater and air. Current landfill design and operation is such that water infiltration is minimised using temporary and final low permeability covers. This results in low liquid to solid ratios (L/S in $\mathrm{l\ kg^{-1}}$), even during the operational phase as a consequence of waste thickness. The cumulative L/S will increase very slowly with time, and Bone *et al.* (2003) estimated L/S of less than 0.3 for a number of mixed hazardous waste landfills in northern Europe after operating for up to 12 years. Vestskoven landfill, Denmark was filled with MSWI bottom ash and fly ash between 1973 and 1976 and Hjelmar and Hansen (2004) present 30 years of leachate monitoring results. The landfill was covered with soil only, and a L/S of 0.98 was attained over this monitoring period. This unique data set confirms the slow increase of L/S in a landfill scenario, even without modern capping standards.

During operation, residual moisture in the residues is displaced by compaction and precipitation may percolate through the wastes. On final closure, the cover system ensures that infiltration is reduced but not eliminated. Because of the low L/S ratios, the solubility or availability of species controls contaminant release (Kosson *et al.,* 1996).

Climate and vegetation have an influence on the landfill water balance (Lerner, 1997). The vegetation developed on the cover system will be specific to the soil and climate of the particular site and should be taken into account when considering the leachate generation (Berger and Dunger, 2001; Sabbas *et al.,* 2003).

Collection and analysis of leachates from the landfill record the degradation of the waste forms and allow the development of an understanding of how infiltration interacts with the waste form. Baur *et al.* (2001) and Ludwig *et al.* (2000) reported on the monitoring of a lysimeter field study in which 0.5 m cubes of cement stabilised APC residues were placed in a 1.5 m deep lysimeter and covered with geotextile, gravel and humus layers. They concluded that the materials developed preferential pathways, which allowed rainfall to percolate through the wastes in 2-3 days with little interaction with the waste form. The flow rate was primarily controlled by the permeability of the cover. However, rainfall was only a minor component (13-43%) of the drainage discharge from the lysimeter. The remainder consisted of water that had a residence time in the lysimeter of between 2 months and several years and had a relatively constant composition. This residence time was long enough to allow the water to interact and equilibrate with the solids in the landfill. However, true thermodynamic equilibrium was not attained and the system was in a metastable state as the processes that transform the solids act on a time scale of hundreds of years.

Johnson *et al.* (1998) also observed circum-neutral pH leachate from an ash landfill in Switzerland, and attributed this to carbonation along preferential flow paths indicating little interaction with the ash matrix. Occasional spikes of high pH were attributed to flushing highly alkaline porewater from the matrix during high rainfall events. The proportion of by-pass to matrix flow reached a maximum limit of around 60%; somewhat higher that that reported from the lysimeter tests above.

Van der Sloot *et al.* (2003) compared leachate from lysimeters and field data with eluate from upflow column tests and implied, from cumulative contaminant release, that preferential flow is important and that only around 30% of the waste is involved in the leaching process. Van Zomeran *et al.* (2003a) observed that leachate production, through a variety of cement stabilised wastes, comprised only 4-15% of total precipitation and that the stabilised waste needed to be saturated before net leachate production took place (see also Meij and te Winkel, 2000). They implied that only prolonged or rather intense rainfall led to leachate production. Both van Zomeran et al. (2003a) and Meij and te Winkel (2000) state that evaporation from the landfill, prior to capping, is important down to a depth of 3.5 m, reducing the impact of precipitation and decreasing the amount of pore water that can reach equilibrium with the waste.

Baur *et al.* (2001) and Ludwig *et al.* (2000) confirmed that the solubility of the minerals in the S/S wastes limit the concentrations of the main constituents, and modelled the dissolution of C-S-H, ettringite and K-feldspar in a high pH environment to account for the chemistry of the leachate. They stated that leaching and weathering are likely to change the solubility controlling phases as well as the pH, with calcite, aluminium hydroxides, iron hydroxides, aluminium silicates and quartz becoming important. Their tank-leaching of cores from the lysimeter, when it was dismantled after 7 years, allowed a prediction that Na and K in the waste will be washed out in 80 years, followed by a drop in the pH to 12.5 when the leachate will be buffered by dissolution of C-S-H and portlandite (Baur *et al.,* 2001).

Carbonation was an important process both within the waste and in the leachate. Carbon dioxide uptake from the atmosphere will also occur in the leachate collection and storage system reducing the pH of the leachate to near neutral (Kosson *et al.,* 1996; van Zomeran *et al.,* 2003a). Van Zomeran *et al.* (2003a) also suggested that a 1 m thick layer of slightly contaminated soil at the base of the landfill would not only protect the leachate collection system but provide buffering of the alkaline percolate water for at least 55-115 years.

Mixed hazardous waste leachate is characterised by high total dissolved solids (several 10s of g l^{-1}) mainly composed of highly mobile chlorides and sulfates (Bone *et al.*, 2003). The EC waste acceptance criteria for hazardous waste landfill and stabilised hazardous wastes deposited in a non-hazardous waste cell permit total dissolved solids (TDS) of 100 and 60 gl^{-1} respectively (at L/S10). It is not clear whether carbonation and the wash-out of soluble salts are beneficial (pore sealing) or detrimental (increased porosity and loss of strength) processes, particularly where highly mobile salts form a significant proportion of the waste form. Little information is available on the effect of solution weathering on the stability of high-TDS wastes in landfills. However, research has been carried out on bottom ash from MSW incinerators using a pre-wash step to remove soluble salts prior to carbonation with or without phosphate addition to immobilise Pb (Hjelmar *et al.*, 2000, 2001).

Sabbas *et al.* (2003) summarised the time-scales for key geochemical processes relevant to landfilled incinerator residues. They defined ‘short term’ as the period within which landfill operation and active aftercare are required to meet adequate environmental protection levels. ‘Long-term’ represents the timeframe within which the environmental safety of the landfill no longer relies on the active protection systems, but is based on the controlled release of contaminants in an environmentally acceptable rate (Figure 9.8).

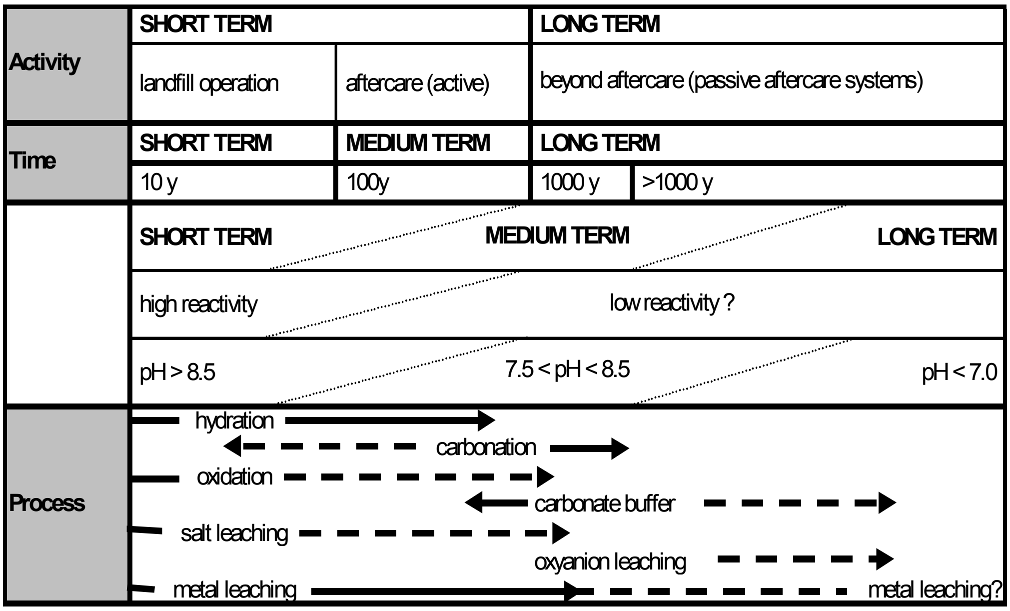


Figure 9.8: Classification of time scales relevant to landfilling (after Sabbas *et al.*, 2003)

Leaching within hazardous waste landfills or non-hazardous waste cells containing stabilised wastes will be dominated by percolation or diffusion-controlled contaminant flux, depending on the nature of the waste forms (granular or monolithic), permeability of surrounding waste and rate of infiltration. In a landfill scenario, the dominant flow mechanism may vary spatially due to development of preferential flow paths.

Even through granular waste, leachate quality is reported to be influenced by carbonation along preferential flow paths (e.g. Johnson *et al.*, 1998). This, in part explains the discrepancy between high pH eluates from leach tests and circum-neutral pH of leachates from full-scale landfills, however buffering may also be taking place due to percolation through non-alkaline wastes and/or air ingress and carbonation within the leachate collection system.

Van Zomeren *et al.* (2003a, 2003b) report results from laboratory and field-scale leaching of cement-stabilised hazardous wastes deposited at the VBM landfill, The Netherlands. To date, the leaching data shows good correlation between leached concentration and pH from field and laboratory data, and supports the identification of solubility-controlling mineral phases for heavy metals using PHREEQC (Van Zomeren *et al.*, 2003a). Van der Sloot *et al.* (2003) observed good correlation between laboratory characterisation data and field leachate quality from mixed wastes, supporting the view that characterisation testing and geochemical modelling can be used effectively to predict long-term leaching behaviour.

Our understanding of the processes that control leaching from stabilised wastes in a landfill has advanced as a consequence of studies such as the above, particularly where laboratory and field-scale testing is combined.

Design considerations for landfill sites including S/S waste forms include:

- minimise the permeability of the waste form, through compaction of granular wastes or design of low permeability monoliths;
- consider using a layer of uncontaminated soil in the base of the cells to assist in the neutralisation of percolating water;
- establish a good vegetation cover on the landfill cover system to help reduce infiltration; and
- restrict access of air to reduce the rate of carbonation and, in particular, to leachate collection system to minimise excessive scaling and blockage.

9.5.2 Co-disposal with biodegradable wastes

The USEPA are required under the Resource Conservation and Recovery Act (RCRA) to classify wastes as either hazardous or non-hazardous and a plausible mismanagement scenario was defined to aid assessment. For industrial wastes the "worst case" mismanagement scenario was defined as co-disposal in a MSW landfill (see Figure 9.9 for a generic scenario). This approach has resulted in the development of the Toxicity Characteristic Leaching Procedure (TCLP, see Table 8.5) for hazardous waste classification based on the co-disposal scenario, even although co-disposal with MSW is not a management option for many industrial wastes.

Under the Landfill Directive co-disposal of hazardous waste with MSW is no longer permissible in the UK from July 2004, but S/S wastes may have been disposed with biodegradable wastes in the past and this practice may continue outside the European Community. Leachate quality from co-disposal landfills will be dominated by biological processes, rather than the chemical processes dominant in the scenario above. Biodegradation of the organic material will result in more acidic leachate infiltrating through the waste forms. Differential compaction of the different waste types will result in variations in permeability, which might result in perched water tables within the landfill and significant variations in saturation levels. Knight *et al.* (2000) considered that the landfilling of cement-based solidified wastes together with organic wastes was unwise. Micro-organisms can produce strong mineral acids and the surface region of a porous S/S waste may provide all the nutrients necessary for their growth. This continuous and proximal source of acid may cause accelerated matrix dissolution and metal release. Figure 9.9 shows the key processes acting on S/S waste in a co-disposal landfill site.

Shimaoka and Hanashima (1996) constructed a large semi-aerobic landfill lysimeter in which they placed bottom ash from a stoker incinerator, shredded municipal waste and composted domestic waste in a ratio of 70:15:15. The lysimeter was 1.2m in diameter and 9.25m in height, with an open leachate collection pipe at its base. Six kinds of cement-solidified fly ash, in samples 50mm in diameter and 100 mm in length, were buried up to 7.2m in depth. Samples of the six waste types were retrieved from each level between six months and three years. The pH of the leachate changed from strongly alkaline to a pH of 7 or 8 within six months. The total organic carbon and total nitrogen contents of the leachate also reduced over the three years.

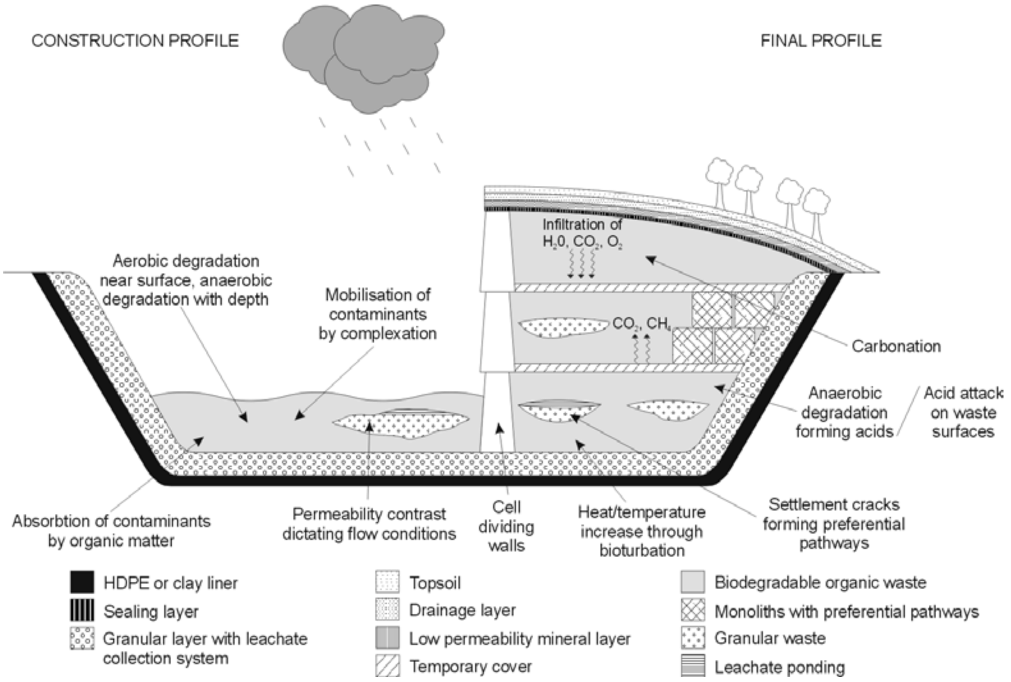


Figure 9.9: Key processes operating in a co-disposal landfill scenario

The cement-solidified fly ash did not show a conspicuous reduction in strength and some samples showed an increase in strength due to compaction and carbonation. However, Pb from the fly ash was released into the leachate from two of the six waste types after 60 days and significant concentrations of Cd were also released into the leachate after 80 days of storage. The reduction in the pH of the leachate and the consequent release of heavy metals is explained by the anaerobic decomposition of the organic matter within the lysimeter.

In contrast, Bozkurt *et al.* (2000) modelled the long-term behaviour of organic matter within a landfill site and showed that the binding capacity of humic substances is sufficient to bind all toxic metals (Cd, Cr, Pb, Zn and Hg) likely to be released. Sulfides and ferric oxides in the waste had the potential to bind two and three times the total amounts of toxic metals found in the waste, respectively. These authors modelled that the higher mobilisation rates of heavy metals due to lowering of the pH of the landfilled wastes would not be expected for many thousands of years.

Christensen and Tjell (1984) considered the phases of degradation within municipal compost in a landfill site in terms of three phases of degradation of the waste: an initial aerobic phase followed by an anaerobic phase with the final humic phase reached after as much as 100 years. During the first two phases, only 0.1% of toxic metals were leached. Even within the humic phase, the acid neutralisation capacity of the waste material was thought to be sufficient to buffer infiltrating acid rainwater (pH 4) for in excess of 3000 years in a 10m deep landfill.

Together with work by Garcia *et al.* (1990) and Kertmann *et al.* (1993) the acid neutralisation capacity of organic wastes suggests that co-disposal with bio-degradable wastes is not necessarily an unsustainable approach. However, the local development of acidic conditions on surfaces of S/S waste forms will result in the waste forms degrading more quickly in a co-disposal landfill. Contaminant partitioning between the waste form, other wastes and the leachate will depend largely on the nature of organic matter present.

9.5.3 Disposal via *in-situ* remediation or utilisation as engineering fill

Treatment of soils *in-situ* or re-use on site as engineering fill after *ex-situ* treatment is a well-known route for the recovery of contaminated soil. The key processes affecting this scenario will be similar to the first scenario, but the waste form will be in direct contact with untreated ground, i.e. without an engineered containment system. The waste form may be exposed to direct infiltration before a low permeability capping layer or cover system is in place or, in the long-term, as a result of deterioration of the cover system. If the waste is of low permeability a perched water table may form and its surface may be exposed to prolonged standing water. Fluctuations in the water table may also result in the material being periodically immersed in groundwater. Figure 9.10 illustrates the key processes that affect the durability of a S/S waste form constructed using *in-situ* auger mixing.

The contaminated soils may contain clay minerals that could be susceptible to swelling and shrinkage, or the cement paste/soil structure may have porosity of the critical dimensions to make the material susceptible to freeze/thaw damage or cyclic wetting/drying damage. Significant evaporation from the surface may cause capillary movement of soluble salts and formation of a duricrust (Bell, 2000).

The sites visited by Jones *et al.* (2001) as part of a study mission to the USA (see Chapter 6) all included some form of protection to the waste form. Such protection was provided by the redevelopment itself, e.g. office buildings, shopping malls or car parks/goods yards, with restrictions placed on the deeds. Other schemes involved the construction of an engineered capping system utilising natural and synthetic layers. The *ex-situ* remediation schemes all required clean backfill to about 0.2 to 0.3 m above the water table to ensure that the treated soil did not leach directly to groundwater. Post-completion monitoring of these sites was determined on a site specific basis, which varied from a 30 year programme monitoring leachate, to no monitoring at sites where Licensed Site Professionals had performed a risk assessment and certified that the remediation project was completed in a satisfactory manner.

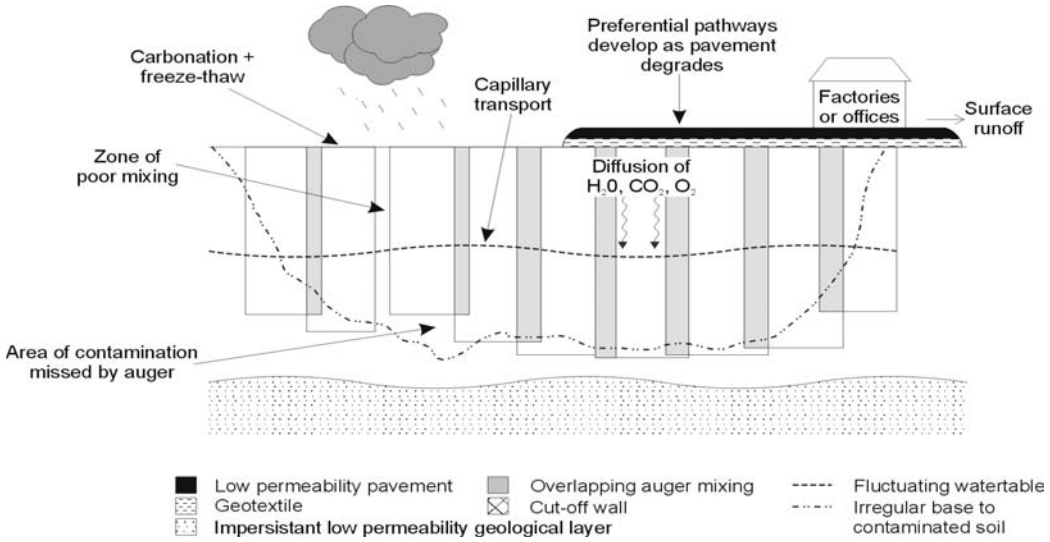


Figure 9.10: Key processes operating in *in-situ* remediation scenarios

Although the use of S/S treated material, either *in-situ* or *ex-situ*, is a relatively common activity in the UK and elsewhere, there is little information available on the long-term performance of the material. Barker *et al.* (1996) and Sansom (2000) report on an *in-situ* stabilisation project at Ardeer, Scotland (see Section 6.3.3 for a summary). The remedial criteria set for the project included a limit for acid neutralisation capacity (ANC) and monitoring of groundwater quality around the monolith.

Contaminated soil at a former Ministry of Defence site at West Drayton, England has been stabilised using *in-situ* auger mixing, and studied to evaluate the time-related performance of the monolithic material retrieved by coring 4.5 years after emplacement (STARNET, 2002). The soil, cohesive made ground over sand and gravel, contained mixed metal and hydrocarbon contaminants and was treated using seven different cement-based binders during a site trial in 1995. Coring was carried out after 55 days and 4.5 years and the properties of the material compared for single columns and overlap areas. The results are summarised in Table 9.13.

Table 9.13: Changes in properties of Stabilised soil over 4.5 years at West Drayton (after STARNET, 2002)

Parameter	Single column	Overlap
UCS	UCS increased from 1.0-1.5 to 3.0-6.5 MPa	UCS halved
Permeability (ms^{-1})	Remained around target level (1 x 10^{-9} ms^{-1})	Increased by 30-50%
Wet-dry and modified freeze-thaw durability test	Passed wet-dry with minimal deterioration; variable performance with freeze-thaw	Slight improvement in durability tests
TCLP leach test	pH reduced from 9.5-11.0 to 6.3-7.3; leachability well below target levels, slight increase at 4.5 years	pH slightly higher than single column; similar contaminant leaching

EPRI (2003) on behalf of the USEPA, carried out an evaluation of the effectiveness of *in-situ* S/S of soils containing PAHs, VOCs and cyanide at a gas-manufacturing site in Georgia, USA. The site was remediated in 1992, using 2.4 m diameter hollow stem augers. A mixture of 10% binding agent was used for most of the site, although a mix of 25% was used adjacent to a river so that the stabilised soil would act as a barrier wall. An HDPE cover was placed over the treated soils in turn covered by 2 m of clean backfill.

A visual inspection and sample collection via five drill-cores was undertaken 10 years after the remediation. The core samples were tested for geotechnical characteristics, solid phase geochemistry, solidified media contaminant analysis, and leachability. The data was then used in contaminant transport modelling to predict the leaching potential of the site.

A comparison of test data during remediation, the acceptance criteria and the tests after ten years is given in Table 9.14

All the samples had gained strength over the 10 years and the large variability in test results was attributed to fracturing during drilling and large debris such as bricks in the samples. As can be seen in Table 9.14, the permeability of the samples was also variable, with some samples showing a higher permeability after 10 years, to the extent that some samples had permeability marginally greater than the acceptance criteria. No explanation of this change in permeability is provided in the report.

In the leachability study of the ten year old samples, naphthalene was the only constituent detected in the leachate above the Federal maximum contaminant levels (MCL) for Georgia. Cyanide levels were below the MCL level of 200 mg/l.

Table 9.14: Comparison of test data from the Georgia gas-manufacturing site (after EPRI 2003)

Test		10% Binder	25% binder
Permeability	Acceptance Criteria	1 x 10^{-7} m/s	1 x 10^{-8} m/s
	Bench scale Pre-remediation trial	1 to 4 x 10^{-9} m/s	
	Post remediation quality control study	3.7 x 10^{-9} m/s	6.8 x 10^{-9} m/s
	After 10 years	1.6 x 10^{-7} to 2.8 x 10^{-10} m/s (average 2.7 x 10^{-9})	1.6 x 10^{-8} to 1.8 x 10^{-9} m/s
Uniaxial Compressive Strength	Acceptance criteria	0.41 MPa	
	Bench scale pre-remediation trial	1.68 MPa	
	Post-remediation Quality Control	1.14 MPa	
	After 10 years	1.77 to 6.20 MPa (average 3.10)	3.16 to 4.39 MPa (average 3.81)

Remedial Options Assessment Modelling (ROAM) was used to predict the leaching potential of the S/S site to a monitoring well immediately down-gradient of the site. The study concluded that the most leachable component, naphthalene, would not exceed 1 mg/l at 10,000 years and would not be detectable in the surrounding groundwater system. This hypothesis was confirmed (at least in the short term) by monitoring results, where all the constituents measured were below detection limits.

FTIR and XRD analysis of the samples revealed a strong carbonate vibration band, assigned to vaterite, which was interpreted as a product of *in-situ* carbonation of the cement.

In conclusion, the re-use of treated contaminated soil or sludge on-site should be subject to detailed investigation and treatability studies, and the remediation designed to:

- ensure uniform mixing of the soil and binder;
- protect the waste form from infiltration using a low permeability cover system or suitable end-use;
- minimise the occurrence of wetting and drying cycles by reducing infiltration (see above) and/or exposure to fluctuating groundwater;
- place treated material below the depth of penetration of frost or provide adequate protection;
- minimise the occurrence of significant capillary rise; and
- implement a maintenance and monitoring plan, where appropriate, to verify long-term performance.

9.5.4 Reuse as sub-base or capping layer beneath road/pavement

S/S waste forms used as sub-base or as capping layers beneath roads or pavement areas such as car parks or goods yards are likely to be granular in nature and placed in relatively thin layers. Unless covered by a low permeability wearing course, these layers will be subjected to a degree of unsaturated flow via downward percolation of rainwater possibly contaminated with pollution from traffic, from cracks in the road pavement, surface drains and rainfall on embankment shoulders (Reid and Clarke, 2001). Because of their granular nature, there will be large surface areas of the waste form exposed to potentially aggressive water containing contaminants, e.g. from vehicle emissions and tyre wear. Such contaminants include acid gases (e.g. NO_x), heavy metals, PAHs and water rich in dissolved CO_2 (Hvitred-Jacobson and Yousef, 1991). The material may also be within the zone of freeze-thaw activity. Figure 9.11 shows a conceptual model for the processes that might operate in the use of S/S waste beneath pavement materials.

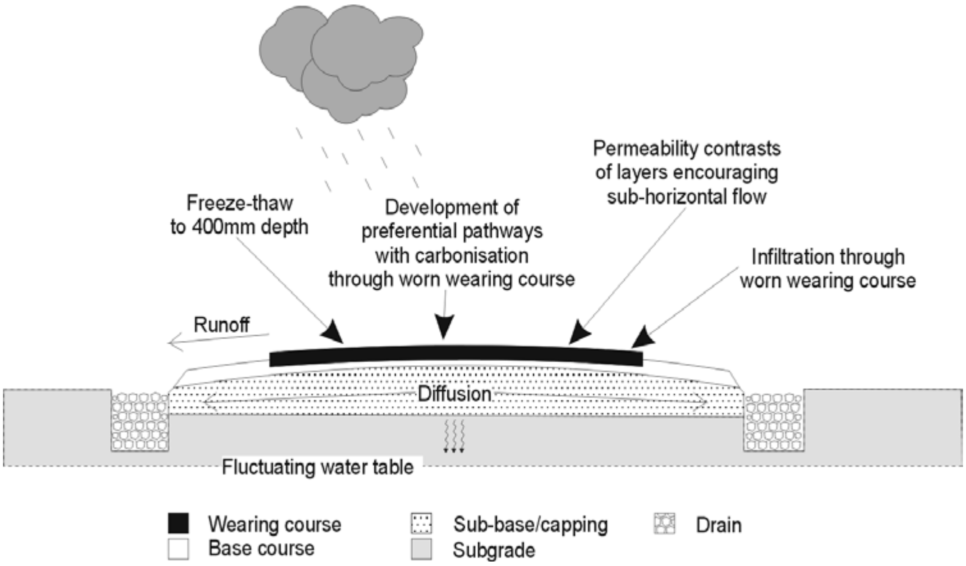


Figure 9.11: Key processes operating where S/S wastes have been utilised in road construction.

Industrial by-products such as steel slags, PFA, or MSWI bottom ash have been used extensively as materials for road construction in Europe with and without binders. In Germany, 97% of steel slags produced have been used as aggregates for road construction, earthworks, armourstones or hydraulic structures (Motz and Geisler, 2001). A number of authors have reported on the behaviour of such materials e.g. Hill *et al.* (2001), Schreurs *et al.* (2000), Baldwin *et al.* (1997) and Dawson *et al.* (1995).

The Transportation Research Laboratory (TRL) has evaluated S/S treated contaminated materials for the Highways Agency with a view to reusing the materials in road construction. Two soil/slag mixtures, two metal-working slags, a contaminated soil and

PFA were stabilised using cement and a proprietary agent, for a CIRIA project (Jardine and Johnson, 2000). The treated wastes were placed under "worst case" conditions - as exposed ground slabs in excavations lined with a polyethylene membrane. Percolating leachate was collected in a sump separated from the surface water drainage.

The materials were sampled at 1216 days (3 years and 4 months) after they were placed and cores tested for strength, permeability, porosity and leaching. In addition, one material was crushed and tested as an aggregate and water samples were taken from the leachate sump and surface water sump (Board *et al.,* 2000).

All the slabs showed some obvious signs of surface weathering and carbonation to a depth of 10 mm. Some of the materials were still gaining strength after 1216 days. During leach testing, Cd, Cu, Hg, Ni and Zn were immobilised below Environment Quality Standards (EQS). However, Al, Cr and Pb, total phenols and total polyaromatic hydrocarbons (PAHs) exceeded EQS values. Concentrations of other elements varied throughout the period with some values exceeding those of untreated waste. Comparison of the eluate data with dilution factors determined by Baldwin *et al.* (1997) suggested that the majority of the materials would pose no threat to water resources and required no environmental restrictions to the re-use of the materials in road construction.

Kosson *et al.,* (1996) suggested that waste materials used in road construction would be subjected to a dominantly diffusion controlled regime because of the impermeable cover layer of concrete or asphalt and adjacent high permeability road drains, with flow limited to the boundary or external surfaces of the material. The controlling factors in the degradation of the waste form in this scenario will be the temperature, the fraction of time the material is wetted and the degree of water saturation, particularly if there is a fluctuating water table. These authors provide two cumulative release nomographs one for Cl and one for Pb. The Pb nomograph is shown in Figure 9. 16.

The nomographs plot contaminant availability on the x axis against diffusion coefficient on the y axis, calibrated with lines of constant cumulative release over a 100 year interval. The validity of the approach was tested against a field study of a service road in Rotterdam, where a 40 cm thick layer of compacted bottom ash, overlain by a clinker surface. The road base and underlying soil were cored after 10 years of service. Preliminary estimates of the cumulative release of Pb over the 10 year period were 0.1 – 0.4 g Pb/m^2 compared with the calculated value of 0.38 g Pb/m^2. The released Pb was found to have accumulated in the top few centimetres of the underlying soil.

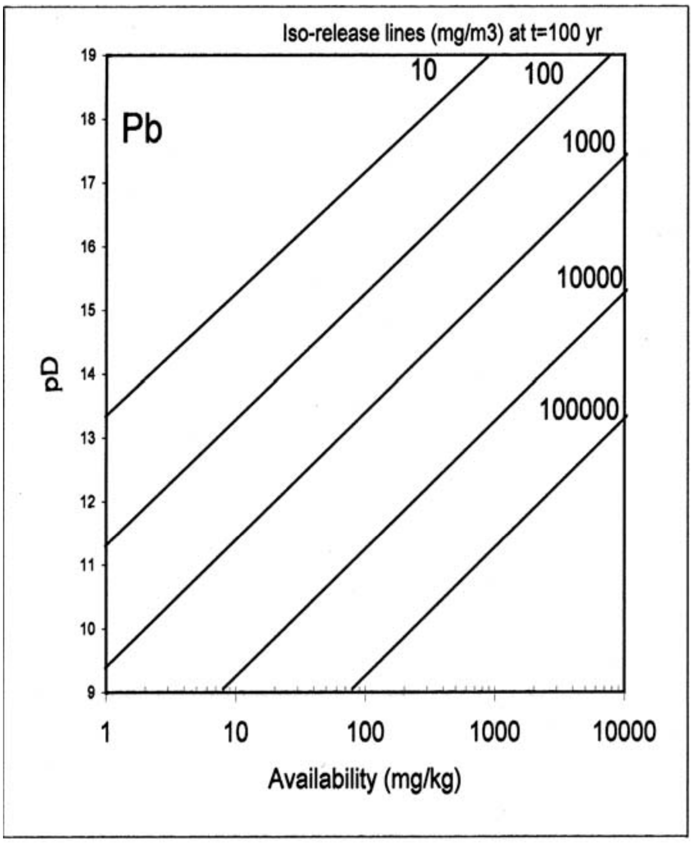


Figure 9.12: Example cumulative release nomograph for Pb release during a 100 year interval (after Kosson *et al.,* 1996)

A number of other studies have looked at long-term performance of concrete pavement (Eighmy *et al.*, 2003) and fly-ash (PFA) road base (Brouwer *et al.*, 2003). Eighmy *et al.* (2003) compared the physical properties of a slab of naturally weathered, 10 year old highway pavement that had undergone early loss of strength with cores of material subject to the same mix design that were exposed to various accelerated tests. The tests involved elevated temperature (60^oC), freeze-thaw and cyclic loading. The overall results showed good correlation between the field slab and the cores subjected to accelerated ageing. Some secondary chemical reactions (e.g. ettringite formation, microcracking) observed in the field were successfully reproduced during accelerated testing. The study has demonstrated that accelerated ageing tests have the potential to predict long-term physical performance of Portland cement concrete exposed to natural weathering, and that temperature may be a useful experimental variable. However, further work is needed to enable shorter testing periods and to assess both physical and chemical leaching performance using contaminated materials as aggregate.

Brouwer *et al.* (2003) evaluated the leaching mechanism from cement-stabilised PFA road base constructed under an 18 year old asphalt road. The road was in poor condition and the base largely disintegrated. Cores of the old road base were taken and sawn into slices to establish leaching profiles with depth. The profiles for pH, electrical conductivity and most contaminants were very similar - little variability through an "unaltered" zone and a sharp decline in the bottom 25mm. The data indicates that leaching is controlled by local pH and not by independent diffusion coefficients of each component, similar in concept to the "shrinking core model" discussed in Chapter 10.

An interesting aspect of this work is that the wide variation in diffusion coefficients for different contaminants derived from laboratory diffusion tests (e.g. the NEN 7345) do not correspond to the relatively uniform concentration profiles identified by Brouwer *et al.* (2003). Although diffusion tests are carried out under saturated conditions and at 20°C, extrapolation of the data underestimated the actual leaching determined from the field samples.

Road base material is placed compacted as a granular fill, but will often behave as a monolith due to a combination of:

- low permeability cover material (concrete or asphalt wearing course); and
- permeable pathways (drains) adjacent to S/S material.

Initially, for a well-constructed road, the dominant contaminant transport mechanism will be diffusive, along the edges and base of the S/S material. Preferential pathways will develop through the S/S material as the road surface deteriorates, leading to combined advective and diffusive mass transport. In the extreme case, where the sub-base becomes exposed, infiltration will increase significantly and advective flow may dominate.

Cement and lime stabilisation of road capping has been undertaken in the UK for the past 30 years (Building Research Establishment, 2001) and is covered by the Specifications for Highway Works Amendment (Highways Agency, 2001) and Part 6 of the Design Manual for Roads and Bridges (Highways Agency, 2000). However, there is little available information on its long-term performance. The principle requirements for aggregates used in road capping, sub-base or base course are stiffness rather than strength. Work by Nunes (1997) showed that the stiffness of stabilised aggregates was controlled by the particle size of the coarse fraction whereas the strength was controlled by the efficiency of the binder. Treated alternative materials exhibit stiffness well in excess of those of conventional unbound granular materials and therefore the layers within the road structure do not need to be as thick. However, the alternative materials are prone to cracking and a strain absorbing layer should be provided to prevent the upward propagation of cracks (Hill *et al.,* 2001).

S/S waste forms used in road construction as fill, capping, sub-base or base materials, will have to meet the Specifications for Highways Works (Highways Agency, 2001). For capping materials, the waste form would have to achieve a CBR of 15%, conforming to Class 6E or 7F material before stabilization to produce Class 9A and 9B materials. For sub-base and base materials, the waste form would be equivalent to CBM 1, 2, 3 or 4 with an average 7-day compressive strength of between 4.5 and 15 MPa depending on the grading of the material. If used within 450 mm of the road surface the waste form would also have to be frost resistant. Because of the influence of moisture content on CBR, road drainage is designed to keep the materials above the water table.

9.5.5. Embankments

Embankments are common structures associated with road building, either constructed to support a raised section of road or adjacent to a road (or other form of development) for visual/noise screening. S/S may be used to improve the strength characteristics of the material used in the core of the embankment, as such material is usually derived from cut sections along the road corridor. Materials used in road embankments will need to meet the Specifications for Highway Works (Highways Agency, 2001). Figure 9.13 shows the key processes that influence the durability of a granular waste form in the core of an embankment, in this case without a road.

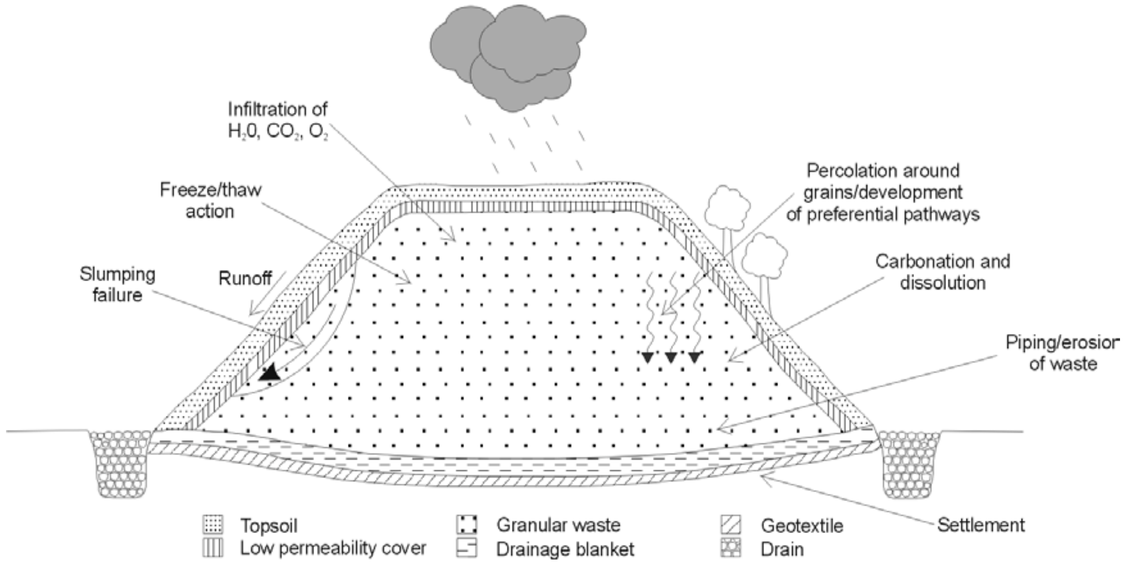


Figure 9.13: Key processes acting on granular waste forms in an embankment

Mildly contaminated silts treated with lime and PFA were used successfully as a lightweight fill within the A13 improvement scheme in Essex (Nettleton *et al.*, 1996). The lime and PFA were used to improve the physical properties of the silt as contamination levels were not particularly high. 100,000 m^3 of material were treated with a 2:1 ratio of silt to PFA plus 3% lime by weight of silt to yield 150,000 m^3 of lightweight fill. This was placed in 1995 with a long-term commitment to monitor the embankment for leachate quality and degradation of the material.

Samples were taken from the embankment when it was excavated in 1998 and testing carried out to compare the material performance in comparison to the original material tested in 1995. These tests included shear box tests and leach testing using the NRA test (Lewin *et al.*, 1994). After three years, the material had retained its engineering properties including bulk and dry density and apparent cohesion. The pH of both the soil and leachate had dropped from 10.7 and 11.75 respectively in 1995 to 8.2 and 7.2 in 1998 (Table 9.11). Commensurate with the reduction in pH there was a large increase in the solubility of sulfate. There was little change in the solubility of other contaminants. Reid and Clarke (2001) concluded that formerly unacceptable material had been rendered suitable for general earthworks and was unlikely to cause significant pollution.

Material from the A13 site was also lime stabilised at TRL to monitor long-term mechanical and environmental stability. Samples of the silt/PFA material were mixed with 5% sewage sludge to increase the levels of contamination and 5% lime. Environmental performance was tested using a flow-through dynamic leaching test as well as the NRA test and geotechnical performance was examined via shear strength. Some of the material was compacted into a pilot scale, outdoor, test bed, consisting of a concrete tank 200 mm deep lined with an impermeable rubber membrane and fitted with drainage and a leachate collection system. The surface of the material was left open to the atmosphere and samples of the drainage taken at regular intervals over 15 months. Again, the material maintained its shear strength over the period of testing and the average pH of the soil decreased from 12.5 to 10.6 after a year. The pH of the leachate decreased from 12.2 to 7.5 with a marked reduction in the concentration of Ca. The surface soil pH dropped to just less than 9 with a gradual increase to 11.5 at the base, indicating leaching of the lime and/or progressive carbonation.

Table 9.11: Summary of soil and leachate chemistry from the A13 embankment, Essex (from Reid and Clarke, 2001)

	Soil (1995) (mg/kg)	**Soil (1998) (mg/kg)**	**Leachate (1995) (µg/l)**	**Leachate (1998) (µg/l)**
pH	10.7	8.2	11.75	7.6
Arsenic	31	36	2	25
Lead	170	99	28	<20
Sulfate	9,017	2,661	36,000	525,000
Total organic carbon	61,100	18,000	26,000	21,700

Depending on the degree of compaction, granular waste forms within the embankment may act as monolithic material with diffusion processes dominating in the core and percolation/advection processes dominating at the surface. Less well compacted materials will be dominated by percolation processes if not well protected from infiltration. Excess water may also cause engineering failures such as rotational failures or piping. Ponding of water in the base of the embankment may also occur as a result of settlement or if the base is not well drained.

9.5.6 Above ground storage

An unlikely method of long-term storage is that of monolithic or granular waste forms stored above ground, covered only by a geosynthetic liner. However, waste forms may be stored in this manner before removal to landfill or other utilisation, This method of storage should therefore be considered as it may have a major effect on the long-term durability of the waste at its final disposal scenario. Figure 9.14 shows the key processes acting on S/S material in this scenario.

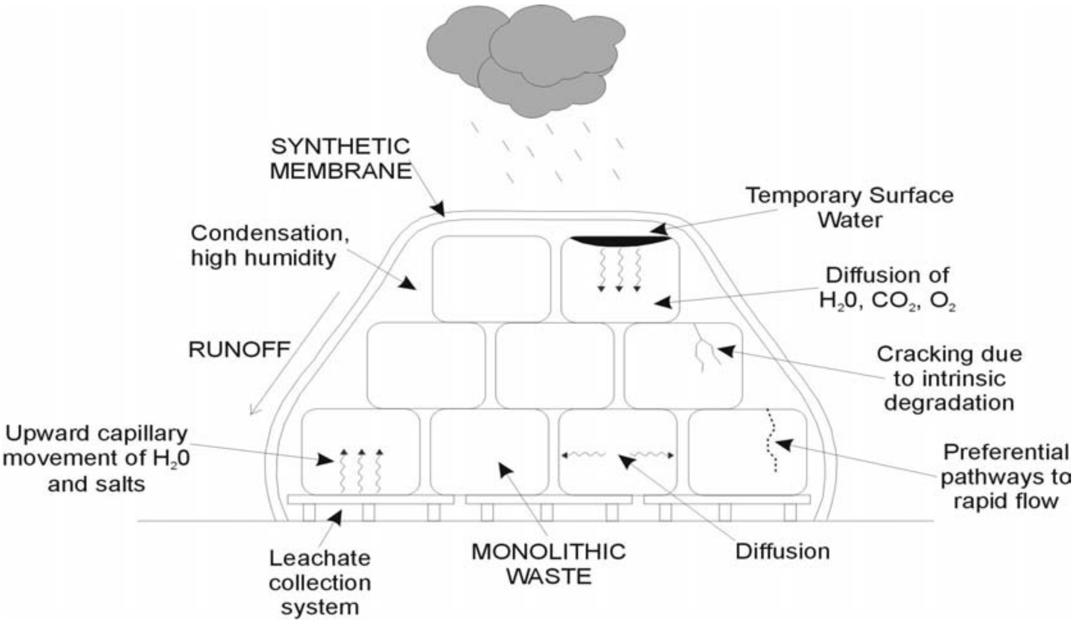


Figure 9.14: Key processes operating when S/S wastes are stored above ground

One of the oldest solidified waste forms systematically examined is that produced in the USEPA Superfund Innovative Technology Evaluation Programme. Two proprietary systems: Soliditech and Chemfix were used to stabilise and solidify Pb contaminated soil, and filter cake and oily sludge with principal contaminants As, Ba, Cd and Pb. The material was stored above ground and in the laboratory. In the field, the waste was stored on pallets and covered by polythene sheeting to prevent direct rainfall (Badamchian *et al.,* 1995, Klich, 1997, Klich *et al.,* 1999).

The waste was examined using petrographic methods, compressive strength determinations (UCS) and leach testing (TCLP) after a storage period of six years. All samples were heterogeneous with large voids and pockets of untreated waste. After six years, no increase in the leachable metals was recorded, but the filter cake and oily sludge wastes, stored outside, were extensively cracked, probably as a result of the poor mixing, carbonation and ettringite formation, both of which were recognised in thin section.

The UCS of the laboratory stored samples of Soliditech treated waste had increased, but there was a significant decrease of strength in the field-stored samples (Badamchian *et al.,* 1995). However, the UCS of the materials remained above the EPAs recommended level of 345 kPa (50 psi).

Klich *et al.* (1999) also studied a variety of wastes stabilised with PC, stored above ground, in the laboratory and in a landfill site. Carbonation was the most common form of environmental attack; altering and softening the paste and decomposing it to calcite, highly porous silica-gel and water. The precipitation of calcite caused microcracking and changes in porosity/permeability (Klich, 1997). Materials also showed evidence of freeze/thaw cracking with vertical cracks and a network of micro-fractures parallel to and concentrated along exposed surfaces. During the natural freeze/thaw cycles, portlandite had migrated along the capillaries and been deposited as large crystalline platy masses in the pores and cracks. Pyrite was observed within the cement of treated waste and both ettringite and thaumasite were recognised in the waste forms. Alkali silica gel and microcrystalline gypsum were also observed indicating that some of the cracking was the result of sulfate attack and alkali-aggregate reaction.

There were no significant increases in the leachability of metals after six years, although there was evidence that the metals had migrated from the waste aggregates into the porous cement paste. Pb, Ti and Sn had either substituted for Ca in the cement hydrates, precipitated as complex Pb-Ti-Sn oxides within the micropores or been adsorbed onto the amorphous cement micromass. Zinc was observed disseminated in the cement micromass in haloes around waste aggregates and Cu had migrated to form $CuSO_4.H_2O$. Because there was no significant increase in the leachability of metals in these wastes it suggests that the metals were quite tightly held within the cement paste and the process had increased the stability of the wastes.

The overall extent of degradation of the treated wastes after six years was considered as only slight to moderate but the recognition of freeze/thaw, carbonation, alkali-aggregate reaction, and sulfate attack suggested that these treated wastes would disintegrate completely in 50 - 100 years. (Klich, 1997).

Stockpiled waste forms will perform in a similar way to materials used in embankments except that temporary covers such as polythene may cause high temperature and humidity, and accelerate degradation processes such as carbonation and hydrolysis. Temporary storage environments should be designed to minimise humidity, ensure that any leachate could be collected, and to prevent capillary movement of water and salts. With both granular and monolithic waste forms there is a possibility that ponding of water will occur. Leaching of contaminants will be controlled by advection occurring along boundaries between monoliths or through preferential pathways developed due to intrinsic degradation and cracking, and by diffusion through the monolithic blocks.

9.6 Summary

In view of the timescales required to assess the durability of S/S waste forms or field test predictive modelling approaches, it may be appropriate, when developing a conceptual understanding of the waste form in its environment of deposition to consider information from the degradation of concrete or rock. From this a number of factors that control their degradation can be identified and applied to the re-use or disposal scenario developed for a waste form.

A number of re-use and disposal scenarios have been discussed, with reference to research and field applications, to highlight key processes that influence the long-term leaching behaviour of S/S waste forms. It is clear that contaminant transport mechanisms are complex and still poorly understood for most scenarios. However, a number of general features may be applied to the design of S/S waste forms:

- ensure the material to be treated is adequately characterised and treatability studies are carried out to select an appropriate and durable binder;
- understand the processes that may affect the durability of the waste form and evaluate the leaching behaviour of the treated material under suitable testing conditions;
- minimise the porosity and permeability of the waste form;
- ensure that the waste does not contain significant quantities of materials that may be deleterious to the long-term durability of the treated waste, e.g. reactive silica;
- place the waste form below the limit of freeze/thaw action or provide appropriate insulation;
- where possible, place the waste form above the water table;
- take adequate measures to minimise infiltration;
- ensure good workmanship and quality control through the S/S process and follow a high quality testing regime;
- develop and implement a maintenance plan to ensure in-service conditions are controlled; and
- develop and implement a monitoring plan to verify that environmental pollution or harm is not being caused by the release of contaminants from the waste form.

REFERENCES

AGW. (1991) *Immobilisierung von Rauchgasreinigungsrũckständen aus Kehrichtverbrennungsanlagen, Schlussbericht zum Projekt*. IMRA, April 1991. Projektleitung AGW, Zũrich, Switzerland.

Ali, A. and Dunster, A. (1998) *Durability of Reinforced Concrete: Effects of Concrete Composition and Curing on Carbonation under Different Exposure Conditions*. BRE Report 360, Building Research Establishment.

Anon. (1995) The Description and Classification of Weathered Rocks for Engineering Purposes. Geological Society Engineering Group Working Party Report. *Quarterly Journal of Engineering Geology* 28, pp.207-242.

Astrup, T., Hansen, J.B., Hjelmar, O. and Christensen, T.H. (2001) Long-Term Development in APC Ash Landfills with Respect to pH. In*: Proceedings Ninth International Waste Management and Landfill Symposium*, 1-5 October, 2001, S. Margherita di Pula, Cagliari, Italy. CISA, Environmental Sanitary Engineering Centre, Italy.

Astrup, T. and Christensen, T.H. (2003) Estimating Long-Term Leaching of Heavy Metals from MSWI APC Residues. In*: Proceedings Ninth International Waste Management and Landfill Symposium*, 6-10 October, 2003, S. Margherita di Pula, Cagliari, Sardinia, Italy.

Badamchian, B., Brock, C.L., Klich, I. And Hubbard, J. (1995) Evaluation of Long-Term Effectiveness of Solidified and Stabilized Wastes. *Proceedings of Superfund XVI*, pp. 599-608.

Baldwin, G., Addis, R., Clark, J. and Rosevear, A. (1997) *Use of Industrial By-Products in Road Construction - Water Quality Effects.* CIRIA Report 167. Construction Industry Research and Information Association. London.

Barker, P., Wyllie, P.J.M., and Esnault, A. (1996) Investigation, Planning and Execution of the Remediation of the Ardeer Landfill, Scotland. In: *Polluted and Marginal Land – 96: Re-use of Contaminated Land and Landfills.* Preprints of Conference held at Brunel University, London, July, pp. 153 – 166.

Baroghel-Bouny, V. and de Larrard, F. (2000) In Place Durability Assessment for the Next Millennium – Long Term Study. In: Malhotra, V.M. (Ed*.) Durability of Concrete. Proceedings of the Fifth International Conference*. Volume 1. Barcelona, Spain.

Bartholomew, R. F. (1979) The Protection of Concrete Piles in Aggressive Ground Conditions: an International Appreciation. In: *Proceedings of the Conference on Recent Developments in the Design and Construction of Piles*. London, Institute of Civil Engineers, pp. 131-141.

Basheer, L., Kropp, J., Cleland, D.J. (2001) Assessment of the Durability of Concrete From its Permeation Properties: A Review. *Construction and Building Materials* 15, pp.93-103.

Bauer, F (1962) Karstformen in den Oesterreichischen Kalkhochalpen. *2nd International Congress on Speleology*, pp. 299-329

Baur, I., Ludwig, C., and Johnson, C.A. (2001) The Leaching Behaviour of Cement Stabilised APC Residues: A Comparison of Field and Laboratory Investigations. *Environmental Science and Technology* 35, pp. 2817-2822.

British Cement Association (1987) *The Diagnosis of Alkali-silica Reaction*. British Cement Association, Slough. Working Party Report No. 30.

Bell, F.G. (2000) *Engineering Properties of Soils and Rocks*. 4th Edition. Blackwell Science.

Berger, K. and Dunger, V. (2001) Vergleichende Simulationsrechnungen mittels der Deponie- und Wasserhaushaltsmodelle HELP und BOWALHALD. *DGZF-Seminar "Simulation zu Halden-/Deponie-wasserhaushalt"* Dresden.

Berthelin, J., Leyval, C. and Mustin, C. (2000) Illustrations of the Occurrence and Diversity of Mineral-Microbe Interactions Involved in the Weathering of Minerals. In: Cotter-Howells, J.D., Campbell, L.S., Valsami-Jones, E. and Batchelder, M. (Eds). *Environmental Mineralology: Microbial Interactions, anthropogenic influences, contaminated land and waste management*. Mineralological Society Series, 9. Mineralogical Society, London.

Biczok, I. (1972) *Concrete Corrosion, Concrete Protection*. Budapest, Hungarian Academy of Science.

Bishop, C. (1998) Personal Communication.

Board, M.J., Reid, J.M., Fox, D.S.J. and Grant, D.I. (2000) *The Effects of Age on Cement Stabilised/solidified Contaminated Materials.* TRL Report 451. Transport Research Laboratory, Crowthorne

Bodenan, F., Azaroual, M. and Piantone, P. (2000) Forecasting the Long-term Behaviour of Municipal Solid Waste Incinerator Bottom Ash: Rapid Combined Tests. In: *WASCON 2000 Fourth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials*. Harrogate, UK.

Bone, B.D., Knox, K., Picken, A. and Robinson, H.D. (2003) Leachate Quality from UK Landfills After Implementation of the LFD: Hazardous Wastes. In: *Proceedings Ninth International Waste Management and Landfill Symposium*, 6-10 October, 2003, S. Margherita di Pula, Cagliari, Sardinia, Italy.

Bozkurt, S., Moreno, I and Neretnieks, I. (2000) Long Term Processes in Waste Deposits. *The Science of the Total Environment* 250, pp.101-121.

Brouwer, J.P., Frénay, J.W., Jansen, E.W. and van der Bruggen, P.W. (2003) Leaching from an 18 Year Old Cement-Stabilised Fly-Ash Roadbase. In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

Building Research Establishment B.R.E. (1988) *Alkali Aggregate Reactions in Concrete.* Digest 330. Building Research Establishment.

Building Research Establishment (1995) *Carbonation of Concrete and Its Effect on Durability.* Digest 405. Building Research Establishment.

Building Research Establishment (2001) *Concrete in Aggressive Ground*. Special Digest 1, Building Research Establishment.

British Standards Institution BS 5390: 1981. *Code of Practice for Site Investigations*. British Standards Institution, London.

British Standards Institution BS 5390: 1999. *Code of Practice for Site Investigations*. British Standards Institution, London.

British Standards Institution BS 8110-1: 1997. *Structural use of concrete. Code of practice for design and construction*. British Standards Institution, London.

British Standards Institution BS 8500-1: 2002 *Concrete. Complementary British Standard to BS EN 206-1. Method of Specifying and Guidance for the Specifier*. British Standards Institution, London.

British Standards Institution BS 8500-2: 2002 *Concrete. Complementary British Standard to BS EN 206-1. Specification for Constituent Materials and Concrete*. British Standards Institution, London.

Buenfeld, N. (1997) Measuring and Modelling Transport Phenomena in Concrete for Life Prediction of Structures. In: Glanville, J. and Neville, A. (Eds.) *Durability of Concrete*. Spon.

BUWAL, (1987) Behandlung und Verfestigung von Rũckständen aus Kehrichtverbrennungsanlagen. *Schriftenreihe Umweltschutz* 62, pp.141.

Chandler, R.J. (1972) Lias Clay Weathering Processes and their Effect on Shear Strength. *Geotechnique* 22, pp. 403-431.

Cheng, K.Y. and Bishop, P.L. (1996a) Property Changes of Cement-Based Waste Forms During Leaching. In: Gilliam, T.M. and Wiles, C.C. (Eds.) *Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes*. ASTM STP 1240, 3rd Volume, pp. 73-79. American Society for Testing and Materials.

Cheng, K.Y. and Bishop, P.L. (1996b) Morphology and pH Changes in Leached Solidified / Stabilized Waste Forms. In: Gilliam, T.M. and Wiles, C.C. (Eds.) *Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes*. ASTM STP 1240, 3rd Volume, pp. 375-387. American Society for Testing and Materials.

Christensen, T.H. and Tjell, J.C. (1984) Leaching from Land Disposed Municipal Compost: 4 Heavy Metals. *Waste Management Research* 2, pp.347-357.

Construction Industry Research and Information Association (1997) *On site curing - Influence on the durability of concrete: A review.* CIRIA Report C568, London.

Collepardi, M., (2000) Ordinary and Long-term Durability of Reinforced Concrete Structures. In: Malhotra, V.M. (Ed*.) Durability of Concrete. Proceedings of the Fifth International Conference*. Volume 1. Barcelona, Spain.

Comité Européen de Normalisation ENV 12920 (1997) *Basic Characterisation of Leaching Behaviour in Specified Conditions* (published as a British Standards Draft for Development in 1998).

Comité Européen de Normalisation EN 206-1 (2000*) Concrete Performance, Production Placing and Compliance Criteria. Part 1: Specification, Performance, Production and Conformity*.

Concrete Society (1995) *Alkali-silica Reaction. Minimising the Risk of Damage to Concrete. Guidance Notes and Model Specification Clauses.* Concrete Society Technical Report. No. 30.

Concrete Society (2000) *Diagnosis of Deterioration in Concrete Structures.* Concrete Society Technical Report. No. 54.

Dawson, A.R., Elliot, R.C., Rowe, G.M. and Williams, J. (1995) *An assessment of the suitability of some industrial by-products for use in pavement bases in the United Kingdom*. Transport Research Record No. 1486, pp. 114-23.

Dole, L.R., (1985) Overview of the Applications of Cement-Based Immobilisation Technologies at US-DOE facilities. In: Post, R.G., (Ed.) *Waste Management '85 Symposium* Arizona pp. 455-463

Department of the Environment (1989) *The Effects of Acid Deposition on Buildings and Building Materials in the United Kingdom. Building Effects Review Group Report.* HMSO

Eighmy, T.T., Spear, J.C.M., Cook, R., Gress, D.L., Coviello, A., van Dam, T., Peterson, K.R., Hover, K., Pinto, R., Hobbs, S., Kosson, D.S., Sanchez, F., Korhonen, C. and Simon, M. (2003) Use of Accelerated Aging to Predict Future Behaviour of Recycled Materials in Portland Cement Concrete: Physical Properties. In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

Emerick, K. (1995). The Survey and Recording of Historic Monuments. *Quarterly Journal of Engineering Geology* 28, pp. 201-205.

Emery, K.O (1960) Weathering of the Great Pyramid. *Journal of Sedimentary Petrology*.30 pp.140-143.

EPRI, (2003) Evaluation of the effectiveness of in situ S/S at the Columbia, Georgia, Manufactured gas plant site. EPRI Palo Alto CA 1009095.

Felix, F., Fraaij, A.L.A. and Hendriks, Ch.F. (2000) Assessment of the Leaching due to Degradation Factors of Stabilised/Solidified Waste Materials. In: *WASCON 2000 Fourth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials*. Harrogate, UK.

Floyd, M., Czerewko, M.A., Cripps, J.C. and Spears, D.A. (2003) Pyrite Oxidation in Lower Lias Clay at Concrete Highway Structures Affected by Thaumasite, Gloucestershire, UK. *Cement and Concrete Composites* 25, pp 1015-1024.

Fookes, P. G. (1997) Aggregates: A Review of Prediction and Performance. In: Glanville, J and Neville, A (Eds.) *Durability of Concrete*. Spon.

Fookes, P.G., Gourlay, C. and Ohikere, C. (1988) Rock Weathering in Engineering Time. *Quarterly Journal of Engineering Geology* 21, pp.33-57.

Fookes, P.G. and Hawkins, A.B. (1988) Limestone Weathering: its Engineering Significance and a Proposed Classification System. *Quarterly Journal of Engineering Geology* 21, pp. 7-31.

Garcia, C., Herandez, T., and Costa, I. (1990). The Influence of Composting and Maturation Processes on the Heavy Metal Extractability from Some Organic Wastes. Biological Wastes*,* 31, pp. 291-301.

Garrabrants, A.C., Snachez, F., Gervais, C., Moszkowicz, P. and Kosson, D.S. (2002) The Effect of Storage in an Inert Atmosphere on the Release of Inorganic Constituents During Intermittent Wetting of a Cement-Based Material. *Journal of Hazardous Materials* 91, pp. 159-185.

Gervais, C., Garrabrants, A.C., Sanchez, F., Barna, R., Moszkowicz, P. and Kosson, D.S. (2004) The effects of carbonation and drying during intermittent leaching on the release of inorganic consitutents from a cement-based matrix. *Cement and Concrete Research*, 34, pp. 119-131.

Glass, G.K. and Buenfeld, N.R. (1999). Differential Acid Neutralisation Analysis. *Cement and Concrete Research* 29, pp. 1681-1684.

Glasser, F.P. (1993) Chemistry of Cement-Solidified Waste Forms. In: Spence R.D. (Ed.) *Chemistry and Microstructure of Solidified Waste Forms*, Lewis Publishers. Ann Arbor,

Glasser, F.P. (2001) Concrete Durability and the Role of Porosity. Network News No 3 EPSRC Engineering Network for the Application of NMR Techniques to Improve Concrete Performance

Hall, D.H., Drury, D., Smith, J., Potter, H. and Gronow, J. (2003) Predicting the Groundwater Impact of Modern Landfills: Major Developments of the Approach to Landfill Risk Assessment in the UK (LANDSIM 2.5). In: *Proceedings Ninth International Waste Management and Landfill Symposium*, 6-10 October, 2003, S. Margherita di Pula, Cagliari, Sardinia, Italy.

Hawkins, A.B. and McDonald, C. (1992) Decalcification and Residual Shear Strength Reduction in Fuller's Earth Clay. *Geotechnique* 42, pp.453-464.

Highways Agency (2000) *Treatment of Fill and Capping Materials using either Lime or Cement or Both. Design Manual for Roads and Bridges*, Volume 1, Section 1, part 6, HA 74/00.

Highways Agency (2001) *Specification for Highway Works* Volume 1 Series 600 Earthworks Amendment May 2001 pp 15-17, 28-29.

Hill, A.R., Dawson, A.R., and Mundy, M. (2001) Utilisation of aggregate materials in road construction and bulk fill. *Resources, Conservation and Recycling.* 32, pp. 305-320.

Hilsdorf, H.K. (1995) Concrete Compressive Strength, Transport Characteristics and Durability. In: Kropp, J and Hilsdorf, H.K. (Eds.) *Performance Criteria for Concrete Durability*. RILEM Report 12. Spon.

Hjelmar, O. (2003) Environmental Performance of Waste Materials. In: Dhir, R.K., Newlands, M.D., and Halliday, J.E. (Eds) *Recycling and Reuse of Waste Materials. Proceedings of the International Symposium*, University of Dundee. Thomas Telford. pp 653-668.

Hjelmar, O. and Hansen, J.B. (2004) Towards Final Storage Quality in Landfilling: an Example. In: *Proceedings of Waste 2004. Integrated Waste Management and Pollution Control: Policy and Practice, Research and Solutions*. 28-30 September 2004. The Waste Conference Ltd., Coventry, UK.

Hjelmar, O., Birch, H. and Hansen, J.B. (2000) Further Development of a Process for treatment of APC Residues from MSW Incinerators. In: Woolley, G.R., Goumans, J.J.J.M. and Wainwright, P.J. (editors). *Waste Materials in Construction*, 872-883. Elsevier Science Ltd.

Hjelmar, O., Birch, H. and Hansen, J.B. (2001) Treatment of APC Residues from MSW Incineration: Development and Optimisation of a Treatment process in Pilot Scale. In:

Proceedings of Sardinia 2001. Eighth International Waste Management and Landfill Symposium. 1-5 October 2001, Margherita de Pula, Cagliari, CISA, Italy.

Hobbs, D.W and Taylor, M.G. (2000) Nature of the Thaumasite Sulfate Attack Mechanism in Field Concrete. *Cement and Concrete Research,* 30, pp.529-533
Hvitred-Jacobson, T and Yousef, Y.A. (1991) Highway runoff quality, environmental impacts and control. In: Hamilton, R.S. and Harrison, R.M. (eds) *Highway Pollutants*. Elsevier, London, pp. 165-208.

Jardine, F.M. and Johnson, S.T. (2000) *Demonstration of the Geodur Solidification/stabilisation System.* CIRIA Project Report 41. London.

Johnson, C.A., Richner, G.A., Vitvar, T., Schittli, N and Eberhard, M. (1998) Hydrological and Geochemical Factors Affecting Leachate Composition in Municipal Solid Waste Incinerator Bottom Ash Part I: The Hydrology of Landfill Lostorf, Switzerland*. Journal of Contaminant Hydrology* 33, pp 361-376.

Kertman, S.V., Kertman, G.M. and Chibrikova, Zh. S. (1993) Peat as a Heavy Metal Sorbent. *Journal of Applied Geochemistry* 66, 465-466.

King R.A.(1977) *A review of soil corrosiveness with particular reference to reinforced earth.* Transport and Road Research Laboratory Supplementary Report 316. Crowthorne, TRRL.

Klich, I., (1997) *Permanence of Metal Containment in Solidified and Stabilized Wastes*. Unpublished Ph.D. Thesis University of Texas A and M.

Klich, I., Batchelor, B., Wilding, L.P., and Drees, L.R. (1999) Mineralogical Alterations that Affect the Durability and Metals Containment of Aged Solidified and Stabilized Wastes. *Cement and Concrete Research* 29, pp.1433-1440.

Knight, J., Cheesman, C. and Rogers, R. (2000) Microbial Influenced Degradation of Solidified Waste Binder. *Waste Management* 22, pp. 187-193.

Kosson, D.S., Sloot, H.A. van der, and Eighmy, T.T. (1996) An Approach for Estimation of Contaminant Release During Utilisation and Disposal of Municipal Waste Combustion Residues. *Journal of Hazardous Materials* 47, pp. 43-75.

Kosson, D.S., van der Sloot, H.A., Sanchez, F. and Garrabrabts, A.C. (2002) An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environmental Engineering Science* 19(3), pp 159-184.

Kropp, J. (1995) Relations Between Transport Characteristics and Durability. In Kropp, J and Hilsdorf, H.K. (Eds.) *Performance Criteria for Concrete Durability.* RILEM report 12. Spon

Lai Gauri, K. and Bandyopadhyay, J.K. (1999) *Carbonate Stone: Chemical Behaviour, Durability and Conservation*. Wiley, New York.

Lange, L.C., Hills, C.D. and Poole, A.B. (1997) Effect of Carbonation on Properties of Blended and Non-blended Cement Solidified Waste Forms. *Journal of Hazardous Materials* 52, pp.193-212
Lerner, D.N. (1997) Groundwater Recharge. In: Saether, O.M., and de Caritat, P. (Eds) *Geochemical Processes, Weathering and Groundwater Recharge in Catchments,* Balkema, Rotterdam.

Lewin, K., Bradshaw, K., Blakey, N.C., Turrell, J., Hennings, S.M., and Flavin, R.J. (1994) *Leaching Tests for Assessment of Contaminated Land* – Interim NRA Guidance. R and D Note 301. National Rivers Authority, Bristol, UK.

Longworth, T.I. (2003) Contribution of Construction Activity to Aggressive Ground Conditions Causing the Thaumasite Form of Sulfate Attack to Concrete in Pyritic Ground. *Cement and Concrete Composites* 25, pp. 1005-1013.

Ludwig, C., Johnson, C.A., Käppeli,M., Ulrich, A. and Riediker, S. (2000) Hydrological and Geochemical Factors Controlling the Leaching of Cemented MSWI APC Residues: A Lysimeter Field Study. *Journal of Contaminant Hydrology* 42, pp. 253-272.

McConnell, J.D.C. (1955) The Hydration of Larnite (B-Ca_2SiO_4) and Bredigite (A1-Ca_2SiO_4) and the Properties of the Resulting Gelatinous Plombierite. *Mineral Magazine* 30, pp. 672-680.

Macphee, D.E., Atkins, M. and Glasser, F.P. (1989) *Scientific Basis for Nuclear Waste Management VII*. Materials Research Society, Pittsburgh, pp. 475-480.

Mansfield, F., Shih, H., Postyn, A., Devinny, J., Islander, R. and Chen, C.L. (1991) Corrosion Monitoring and Control in Concrete Sewer Pipes. *Corrosion* 47, pp. 369-376.

Marsh , B. (2002) *Update on Thaumasite Sulfate Attack of Concrete*. Building Research Establishment.

Means, J.L., Smith, L.A., Netiring, K.W., Brauning, S.E., Gavasker, A.R., Sass, B.M., Wiles, C.C. and Mashni, C.I. (1995*) The Application of Solidification/ Stabilisation to Waste Material*. CRC Press.

Mehta, P.K. (1986) *Concrete Structures, Properties and Materials.* Prentice-Hall.

Meij, R. and te Winkel, B.H. (2000) Seven Years Experiences with Lysimeter Leaching of PFA. In: *WASCON 2000 Fourth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials*. Harrogate, UK.

Meima, J.A., and Comans, R.N.J. (1997) Geochemical Modelling of Weathering Reactions in Municicial Solid Waste Incinerator Bottom Ash. *Environmental Science and Technology* 31, pp. 1269-1276.

Monteny, J., Vincke, E., Beeldens, A., De Belie, N., Taerwe, L., Van Gemert, D., and Verstraete, W. (2000) Chemical, Microbiological, and Insitu Test Methods for Biogenic Sulfuric Acid Corrosion of Concrete. *Cement and Concrete Research* 30, pp.623-634.

Moon, V.G. and Beattie, A.G. (1995) Textural and Microstructural Influences on the Durability of Waikato Coal Measures Mudrocks. *Quarterly Journal of Engineering Geology* 28, pp.303-312.

Mostbauer, P., Riegler, H. and Lechner, P. (2003) Artificial Weathering of Inorganic Waste - Evaluation of laboratory Weathering and Leaching Methods. In*: Proceedings Ninth International Waste Management and Landfill Symposium*, 6-10 October, 2003, S. Margherita di Pula, Cagliari, Sardinia, Italy.

Mottershead, D.N., (2000) Weathering of Coastal Defensive Structures in South-West England: A 500 Year Stone Durability Trial. *Earth Surface Processes and Landforms* 25, pp. 143-1159.

Motz, H. and Geiseler, J. (2001) Products of steel slags an opportunity to save natural resources. *Waste Management* 21, pp. 285-293.

Murdock, L.J. and Blackledge, G.F. (1968). *Concrete Materials and Practice.* Arnold.

Nettleton, A, Robertson, I and Smith, J.H. (1996) Treatment of silt using lime and pfa to form embankment fill for the new A13. In: Rogers, C.D.F., Glendinning, S. and Dixon, N. *Lime stabilisation*. London: Thomas Telford, pp 159-175.

Nunes, M.C.M. (1997) *Enabling the use of alternative materials in road construction*. Unpublished Ph.D. thesis. Department of Civil Engineering, University of Nottingham.

Oberholster, R.E., van Aardt, J.H.P. and Brandt, M.P. (1984) Durability of Cementitious Systems. In Barnes, P. (Ed). *Structure and Performance of Cements.* Spon

Ollier, C.D. (1984) *Weathering.* Longman.

Ollivier, J.P, Massat, M and Parrott, L. (1995) Parameters Influencing Transport Characteristics. In: Kropp, J and Hilsdorf, H.K. (Eds.*) Performance Criteria for Concrete Durability*. RILEM Report 12. Spon

Osborne, G. J. (1999) Durability of Portland Blast-furnace Slag Cement Concrete. *Cement and Concrete Composites* 21, pp.11-21.

Oyama, T. and Chigira, M. (1999) Weathering Rate of Mudstone and Tuff on Old Unlined Tunnel Walls. *Engineering Geology* 55, pp.15-27.

Paton, T.R. (1978) *The Formation of Soil Material*. Allen and Unwin.

Paul, V. (1994) *Performance of Buildings in Contaminated Land.* Building Research Estblishment. Report No. BR 255.

Pigeon, M. and Lachance, M. (1981) Critical Air Void Spacing Factors for Concrete Submitted to Slow Freeze-thaw Cycles. *Journal of the American Concrete Institute* 78 (4), pp.282-291.

Pigeon, M. and Regourd, M. (1986) The Effects of Freeze-Thaw Cycles on the Microstructure of Hydration Products. *Durability of Building Materials* 4(1), pp.1-19.

Polettini, A. and Pomi, R. (2003) The influence of accelerated ageing on leaching behaviour of incinerator bottom ash. In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

Price, D.G. (1995) Weathering and Weathering Processes. *Quarterly Journal of Engineering Geology* 28, pp.243-252

Price, W. (2002) Advances in Concrete Durability. Conference Presentation, Concrete Durability: Recent Advances. SCI Construction Materials Group, London.

Rapp, A. (1960) Recent Development of Mountain Slopes in Käekevagge and Surroundings, Northern Scandinavia. *Georg. Annur.* 42, pp.65-200.

Reid, J.M. and Clarke, G.T. (2001) *The Processing of Contaminated Land in Highway Works.* TRL Report 489.

Rietra, R.P.J.J., van der Sloot, H.A., van Zomeren, A and Bleijerveld, R. (2001) Integration of Laboratory Scale Testing and Pilot Scale Monitoring of a Stabilised Waste Landfill to Reach Sustainable Landfill Conditions. In: *Proceedings of Sardinia 2001: Eighth International Waste Management and Landfill Symposium*, S. Margherita di Pula, Cagliari, Sardinia, Italy 1st –5th October, 2001, pp. 243-250.

Rogers, R.D., Hamilton, M.A., Veeh, R.H. and McConnell, J.W. Jr. (1996) Microbially Influenced Degradation of Cement-Solidified Low-Level Radioactive Waste Forms. In: Gilliam, T.M. and Wiles, C.C. (Eds.) *Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes*. ASTM STP 1240, 3rd Volume, pp. 73-79. American Society for Testing and Materials.

Rogers, R.D., Knight, J.J., Cheeseman, C.R., Wolfram, J.H., Idachaba, M., Nyavor, K. and Egiebor, N.O. (2003) Development of test methods for assessing microbial influenced degradation of cement-solidified radioactive and industrial waste. *Cement and Concrete Research* 33, pp. 2069-2076.

Roy, S.K., Poh, K.B. and Northwood, D.O. (1999) Durability of Concrete – Accelerated Carbonation and Weathering Studies. *Building and Environment* 34, pp. 597-606.

Sabbas, T., Polettini, A., Pomi, R., Astrup, T.,. Hjelmar, O., Mostbauer, P., Cappai, G., Magel, G., Salhofer, S., Speiser, C., Heuss-Assbichler, S., Klein, R. and Lechner, P. (2003) Management of municipal solid waste incineration residues. *Waste Management* 23, pp. 61–88.

Sanchez, F., Gervais, C., Garrabrants, A.C., Barna, R. and Kosson, D.S. (2002) Leaching of inorganic contaminants from cement-based waste materials as a result of carbonation during intermittent wetting. *Waste Management* 22, pp.249-260.

Sand, W. and Bock, E. (1984) Concrete Corrosion in the Hamberg Sewer System. *Environmental Technology Letters* 5, pp.517.

Sand, W. and Bock, E. (1988) Biogenic Sulphuric Acid Attack in Sewerage Systems. In: Houghton, D.R., Smith, R.N., and Eggins, H.O.W., (Eds.) *Seventh International Biodeterioration Symposium*, Cambridge, England, pp 113-117.

Sansom, M.R. (2000) *In-situ Stabilisation of Chemical Waste*. Construction Industry Research and Information Association Report 37. CIRIA, London. ISBN 0 86017 837 4.

Sayer, J.A., Cotter-Howells, J.D.S., Watson, C., Hillier, S and Gadd, G.M. (1999) Lead Mineral Transformation by Fungi. *Current Biology* 9, pp.691-694.

Schaffer, R.J. (1932) *The Weathering of Natural Building Stones.* Special Report No. 18, Department of Scientific and Industrial Research. London: HMSO.

Schreurs, J.P.G.M., van der Sloot, H.A. and Hendriks, Ch. (2000) Verification of laboratory-field leaching behaviour of coal fly ash and MSWI bottom ash as a road base material. *Waste Management*, 20, pp. 193-201.

Scrivener, K.L. and Nemati, K.M. (1996) The Percolation of Pore Space in the Cement Paste/aggregate Interfacial Zone of Concrete. *Concrete and Cement Research* 26, pp.35-40

Senderov, E.E. and Khitarov, N.I. (1970) *Zeolites: Their Synthesis and Conditions of Formation In Nature.* Nauka, Moscow.

Shah, V.N. and Hookham, C.J. (1998) Long-term Aging of Light Water Reactor Concrete Containments. *Nuclear Engineering and Design* 185, pp.51-81.

Shimaoka, T., and Hanashima, M. (1996) Behaviour of Stabilized Fly Ashes in Solid Waste Landfills. *Waste Management* 16 pp.545-554.

Smolczyk, H. G. (1969) Concrete in Chloride Solutions. In*: Proceedings of the RILEM International Symposium on the Durability of Concrete*, Prague, Preliminary Report, Part

II. International Union of Testing and Research Laboratories for Materials and Structures. Prague, Academia. pp. C113-C125.

STARNET (2002) Time-Related Performance of Soil-Mixed S/S Contaminated Site. *STARNET News*, Issue 1, January 2002, p. 4. Stabilisation/solidification Treatment and Remediation NETwork, www-starnet.eng.cam.ac.uk.

St. John, D.A., Poole, A.B. and Sims, I. (1998) *Concrete Petrography*. Arnold.

Sweeney, R.E.H., Hills C.D. and Buenfeld, N.R. (1998) Investigation into Carbonation of Stabilised/Solidified Synthetic Waste. *Environmental Technology* 19, pp. 893-902.

Sweeting, M.M. (1960) The Caves of the Buchan Area, Victoria. *Zeitschrift fur Geomorphologie* 2, 81-91.

Taylor, H.F.W. (1998) *Cement Chemistry*. 2nd Edition. Thomas Telford, London.

Tucker, R.L. and Poor, A.R. (1978) Field Study of Moisture Effects on Slab Movements. Proceedings of the American Society of Civil Engineers, *Journal of Geotechnical Engineering* 104 (GT4), pp. 403-14.

Valls, S. and Vazquez, E. (2000) Durability Study of a Sewerage Sludge-Cement-Sand System and its Environmental Impact. In: *WASCON 2000 Fourth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials*. Harrogate, UK.

van der Sloot, H.A. (2000) Comparison of the Characteristic Leaching Behaviour of Cements Using Standard (EN 196-1) Cement Mortar and an Assessment of Their Long-term Environmental Behaviour in Construction Products During Service Life and Recycling. *Cement and Concrete Research* 30, pp. 1079-1096.

van der Sloot, H.A., van Zomeren, A., Dijkstra, J.J., Hoede, D., Jacobs, J. and Scharff, H. (2003) Prediction of Long Term Leachate Quality and Chemical Speciation for a Predominantly Inorganic Waste Landfill. In: *Proceedings Ninth International Waste Management and Landfill Symposium*, 6-10 October, 2003, S. Margherita di Pula, Cagliari, CISA, Italy.

van Zomeren A., van der Sloot, H.A. and Hoede, D. (2003a) Laboratory, Pilot and Field Studies on Stabilized Waste Produced at the VBM Site for Recipe development, Quality Control and Support of Regulation. In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

van Zomeren A., van Wetten, H., Dijkstra, J.J. van der Sloot, H.A. and Bleijerveld, R. (2003b) Long Term Prediction of Release From a Stabilised Waste Monofill and Identification of Controlling Factors. In: *Proceedings Ninth International Waste*

Management and Landfill Symposium, 6-10 October, 2003, S. Margherita di Pula, Cagliari, CISA, Italy.

Walker, M., (Ed.) (2002) *Guide to the Construction of Reinforced Concrete in the Arabian Peninsula.* CIRIA Publication C577, Concrete Society Special Publication CS136.

Whitehead, K., Hills, C.D., MacLeod, C.L., and Carey P.J. (2003) A Field Application of ACT for the Remediation of an ex-Pyrotechnics Site: Monitoring Data and Microstructural Studies, In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

Yuasa, N., Kasai, Y and Matsui, I., (2000). Inhomogeneous Distribution of Compressive Strength from Surface Layer to Interior of Concrete in Structures. In: Malhotra, V.M. (Ed.) Durability of Concrete. Proceedings of the Fifth International Conference. Volume 1. Barcelona, Spain.

Zevenbergen, C., Van Reeuwijk, L.P., Bradley, J.P., Blomen, P. and Comans, R.N.J. (1996) Mechanism and Conditions of Clay Formation During Natural Weathering of MSWI Bottom Ash. *Clays and Clay Minerals* 44, pp. 546-552.

10 OVERVIEW OF MODELLING TECHNIQUES AND THEIR APPLICATION TO S/S WASTE FORMS

10.1 Introduction

In recent years there has been increasing interest in developing and applying modelling tools to predict thermodynamic and kinetic constraints upon waste forms in their likely environment of service. The data required to predict performance of S/S materials is specific to each site and is dependent upon both intrinsic (chemistry of the waste, the type/proportion of binders used) and extrinsic (environment of service/environmental loads etc.) factors. These data are not readily available in the literature and can normally only be obtained from a thorough understanding of the waste to be treated and the environment of deposition or use.

Modelling methods offer a means by which both spatial and temporal predictions may be made beyond the limits imposed by observation alone. For example, the rate at which waste interacts with its surroundings may be accelerated by the use of an experimental model, or calculated, using a numerical model. In each case, a conceptual model must first be developed, which describes the processes operating in the system. The importance of conceptual model development cannot be over-emphasised.

In many cases, modelling will be required to predict the fate and transport of contaminants, particularly in aqueous systems. Groundwater transport codes abound and vary in complexity from 1, 2 or 3 spatial dimensions, with or without the ability to simulate solute transport. The majority of codes focus on solving the advection-dispersion equations, and may utilise source term data from thermodynamic or kinetic models. The mathematical simulation of flow in porous media is described at length in the literature and readers are referred to standard texts such as Fetter (2000) or Freeze and Cherry (1979). Transport codes are not discussed further in this chapter.

The amount of data in the literature on the prediction of the behaviour of S/S waste forms with time and under different scenarios is limited. However, considerable effort was expended in the 1980s and 1990s on modelling the performance of cement-based barrier systems for the containment of nuclear waste (e.g. Sumerling, 1991).

Atkinson and Hearne (1984) assessed the long-term durability of concrete in shallow and deep nuclear repositories. Sulfate attack and leaching of portlandite were identified as the most likely processes causing degradation in the repository environments. Carbonation, the action of micro-organisms, crystallisation and environmental cycling were considered to be of little importance for either disposal scenario. Later work by the same authors (Atkinson and Hearne, 1989) concluded that the durability of concrete in radioactive waste repositories is likely to be limited by sulphate penetration from saturated groundwater leading to eventual disruption.

Atkinson (1984) applied empirical formulae to examine the effect of permeability of waste forms and their barrier systems on the release of radionuclides, and concluded that in shallow repositories (above the water table) the release is sensitive to the permeability of the surrounding geology/containment systems. Atkinson *et al.* (1987) modelled the free energy of formation of C-S-H gels as a function of composition and used this to validate experimental data obtained.

Reactions with CO_2, $CaSO_4$ and dissolution by water were used as examples of the predictive potential of the model. They demonstrated that in the disposal scenario considered (slow dissolution of cements by percolating groundwater) the alkaline reserve is likely to persist for some hundreds of thousands of years and is governed by the dissolution of portlandite and C-S-H phases. Reactions of the aluminate hydrates with external sulphate ions and of calcium (in both portlandite and C-S-H) with carbonate, were not anticipated to compromise the stable chemical environment until very late ages.

Glasser *et al.* (1985) examined the chemical environment of cements and used two chemical models to evaluate the long-term performance of cementitious barriers.

Parrott and Lawrence (1991) reviewed the durability of cementitious, engineered barriers and identified a series of key chemical processes controlling mobility of radionuclides, including chemical degradation and leaching. Robinson *et al.* (1988) utilised a source-term model for predicting the behaviour of long-lived nuclides and concluded that the major processes involved sorption, elemental solubility limits, chain decay and transport due to groundwater flow. From this work it was predicted that some nuclides might be present in sufficient quantities to reach their solubility limit even when the assumed sorption coefficients of the cementitious system are large.

Considerable interest in numerical modelling has paralleled the availability of powerful, low cost computing and the waste and remediation industries have access to a number of potential tools, including commercially available programs, to aid the prediction of waste behaviour. Mathematical models of interest operate on many scales:

- quantum mechanical predictions focus on atomistic modelling and are dominantly applied by the nuclear sector of the industry. Typically, such models are concerned with identifying compounds, which may contain particularly toxic elements and in determining their structure and stability (Minervini and Grimes, 1999; Zacate *et al.,* 2000). Such approaches are not discussed further;

- equilibrium thermodynamic models are mainly used as predictive tools to describe, for example, the precipitation-dissolution reactions in solution (e.g. Parkhurst *et al.,* 1980) or the crystallisation-melting processes of a molten waste (e.g. Davies *et al.,* 1994). The chemical interactions between waste, binder, host rock and groundwater may be investigated by this approach and at present, this is the most active area of chemical model development, mainly through the application of geochemical codes; and

- chemical kinetic modelling is concerned with rates of reaction in waste systems. Often, reactions are relatively rapid in comparison to rates of mass transfer (for example water movement) so kinetic constraints need not be considered. In some situations however, reaction rates may be sufficiently slow to maintain disequilibrium conditions for a considerable period (e.g. the diffusion of contaminants from a monolithic waste form).

Modelling approaches can range from simple to 3-D representations of complex systems. The subject of modelling approaches has been reviewed extensively (e.g.

Mangold and Tsang, 1990, Moszkowicz *et al.*, 1998) in the literature, with numerous dedicated web sites and discussion groups.

Breysse and Gerard (1997) and Sugiyama *et al.* (2001) used thermodynamic and kinetic studies to predict the longevity of cement-based systems. However, they concluded that the rates of evolution of specific phases in waste forms might not always be possible to predict using thermodynamic models. When considering service life of waste forms the speciation of particular contaminants is important and must be considered if realistic forecasts are to be produced. Nevertheless, intrinsic and extrinsic processes acting upon waste forms will also have a considerable effect on phase development within S/S wastes with time.

10.2 Thermodynamic Modelling

Thermodynamic models rely largely on the numerical minimisation of the total Gibbs free energy of a system. The procedure is conceptually simple, but numerically intensive. The system chemistry is represented by a matrix of simultaneous equations and an estimate of its free energy is calculated. By varying parameters in the matrix, a second estimate of free energy is made and compared to the first. The comparison indicates in which direction the free energy must change in order to find the lowest value and the process is repeated iteratively until the minimum free energy is found. By definition, a system must be at equilibrium when its free energy reaches a minimum value.

For a known assemblage of distinct phases (solids, liquids and gases) the prediction of their final equilibrium condition may be made to improve our understanding of the chemistry of the system and/or aid prediction of long-term behaviour. Typically, input parameters would include the composition of the phases (mineralogy, groundwater chemistry, cement chemistry and waste composition, along with temperature, redox potential, pH *etc.*) and for some codes, the absolute quantities to be simulated. Predictions of these same quantities after reaction to reach chemical equilibrium may be supplemented by other calculated parameters such as the activity of aqueous species, the fugacity of gases and saturation state of solutions with respect to solid or gaseous solutes. Codes such as PHREEQC (Parkhurst and Appelo, 1999), MTDATA (Davies *et al.,* 2002), EQ3/6 (Wollery, 1992), MINTEQA2 (Allison *et al.*, 1991) and Geochemist's Workbench (Bethke, 2002) are all highly suited to studies of waste chemistry and the choice of model is often based on local expertise, and availability, in the user's organisation.

Astrup *et al.* (2001) examined the long-term behaviour of MSWI ash and semi-dry APC residues in a landfill environment subject to advective ground water flow using thermodynamic calculations (MINTEQA2). They concluded that these wastes were likely to maintain their pH>8 for 100,000 years (L/S ratios >2000 l/kg).

Rakotoarisoa and Tiruta-Barna (2003) used the Geochemist's Workbench code to calculate major element speciation in leachate and predict the solubility-controlling phases in coal fly ash. The model predictions of equilibrium leachate quality showed good correlation with laboratory leaching test data over a wide pH range.

The most widely used thermodynamic model over the last 2 decades is the U.S. Geological Survey-developed PHREEQ family of programs. The now obsolete PHREEQE program (Parkhurst *et al.*, 1980) has been used to model the degradation of cementitious barriers in radioactive waste repositories due to the interaction with groundwater (e.g. Haworth *et al.,* 1989, Tyrer, 1994). Haworth *et al.* (1989) used a model for predicting the degradation of cement employing PHREEQE (Parkhurst *et al.*, 1980) and CHEQMATE (Haworth *et al.,* 1988). They estimated that the degradation of cementitious barriers (considered to be in the order of 10^7 years) would involve very slow processes.

PHREEQC was a completely new program that added many new functions not available in PHREEQE, such as ion-exchange equilibria and advective transport (Parkhurst, 1995). Version 2 adds further functionality including kinetically controlled reactions, solid-solution equilibria, and diffusion or dispersion in 1D transport (Parkhurst and Appelo, 1999).

Astrup and Christensen (2003) used PHREEQC (version 2) to model solubility-controlling phases for Pb, Cd and Cr in MSWI residues by evaluating leachate data from pH-static tests. The results, when combined with data on the development of pH with time (see Astrup *et al.,* 2001), were used to develop leaching curves for the heavy metals and assess time-dependent leaching behaviour.

Van Zomeren *et al.* (2003a) used PHREEQC (version 2) to assess the consistency of geochemical processes in cement stabilised wastes operating at laboratory (leach tests) and field scales. They identified the likely mineral phases that control the solubility of some heavy metals and modelled long-term leaching curves. Good correlations were found between modelled and measured concentrations for Pb, Zn, Ni and Cu.

Dijkstra *et al.* (2003) report that the time-dependent leaching behaviour of both major and minor elements in MSWI bottom ash can be successfully predicted by taking account of precipitation/dissolution and sorption processes. However, non-equilibrium processes can be inferred from abrupt changes in modelling curves in comparison to gradual changes from column tests. Further modelling and experimental work is required to differentiate between diffusion-control and preferential flow as the dominant non-equilibrium process.

Thermodynamic modelling (as with other models) predicts results that reflect the quality of the data available. Paucity of data, particularly relating to complex phases such as non-ideal solid solutions, or kinetic constraints on reactions, may limit the utility of models in specific systems. One particular pit-fall is in applying a model in conditions where it is not strictly valid. For example, calculations in high ionic strengths such as brines, require a specific mathematical treatment of ion activity correction, available in some, but not all codes

In conclusion, a robust model with a reliable thermodynamic database will provide a very useful guide to the chemical evolution of a system in order to understand the system chemistry and extrapolate predictions beyond real-time laboratory testing or field data. Time spent performing calculations can be cost-effective and helps avoid unnecessary experiment and observation. Calculations are not however an alternative to measurements; it has often been said that the greatest use of thermodynamic calculations is in selecting which experiments not to perform!

10.3 Kinetic Modelling

An approach to determine the declining source term for non-volatile substances has been modified within LandSim2.5, the contaminant transport model widely used by the waste industry for groundwater risk assessment (Environment Agency, 2003). The change in concentration of each non-volatile species through time is based upon the following equation:

$$C_{(t)} = C_{(0)} * \exp(-K * L/S)$$

where:

$C_{(t)}$	is the concentration of the species in leachate at any time t (mg/l);
$C_{(0)}$	is the initial concentration of the species in leachate (mg/l), usually determined when liquid:solid ratio L/S = 0.05 l/kg; and
K (kappa)	is a species and waste-specific constant (kg/l).

Kappa is related to the rate of release of a non-volatile substance from the solid (waste) to the aqueous (leachate) phase within the landfill. The concentration of a contaminant with a high value of kappa (e.g. chloride) will decline more rapidly with time than that of a species with a low value of kappa (e.g. arsenic). Kappa values are experimentally derived from column leaching tests (CEN, 2002) and therefore attempt to simulate the physical and chemical processes occurring during the breakdown and flushing of the waste mass.

Leaching from monolithic wastes will not be controlled by the solubility of the species, but by diffusion from the solid matrix. Thermodynamic equilibrium is therefore not attained and different, less conservative approaches are available to model diffusion-controlled cumulative release. Such approaches range from consideration of simple bulk diffusion from a homogeneous matrix (American Nuclear Society, 1981) to complex models that consider dissolution/precipitation (e.g. Batchelor, 1990, Hinsenveld, 1992) or sorption/desorption and matrix heterogeneity (Sanchez *et al.*, 2001).

Matte *et al.* (2000) used local geochemistry models (NIST and DIFFU-Ca) to predict degradation in waste forms following the square route of time *via* diffusion of dissolved species and predicted a 15 mm outer leached layer for 300 years of exposure.

Barna *et al.* (2000a) examined the diffusion of contaminants from MSW APC residues blended with cement using a combination of modelling and the results of leaching tests. They concluded that a good correlation was obtained when modelling release up to 500 hrs for alkaline species and 1000 hrs for Ca and Cl. However, when the concentration of leachate fell to 1000 times lower than the initial concentration, predictions deviated from the experimental results. Nevertheless, in other related work (Barna *et al.*, 2000b) the authors concluded that source-term modelling is satisfactory for predicting the long-term leaching behaviour of S/S APC residues.

Redmond *et al.* (2002) modelled the hydration behaviour of solidifying APC and utilised predictions of the diffusion coefficient and capillary porosity of waste forms in a simplified macroscopic leaching model on the kinetics of leaching. The model showed that changes in microstructure would affect the kinetics of the release of different chemical species.

10.3.1 Bulk diffusion based on Fick's second law

Kosson *et al.* (2002) describe a Fickian diffusion model based on Fick's second law that will result in an overestimate of actual release in most cases. A number of assumptions are made to simplify the modelling approach, including:

- the species (e.g. contaminant) of interest is present at uniform concentration throughout a homogeneous, porous matrix;
- mass transfer occurs in response to concentration gradients in the pore water; and
- extrinsic factors (e.g. pH, carbonation, redox changes) are not significant.

Release is controlled by the initial concentration (C_o) and observed diffusion coefficient of the species of interest. The cumulative amount leached follows a square root of time relationship.

A one-dimensional solution is provided by Crank (1975), whereby the species of interest is at zero concentration at the liquid-solid interface (i.e. a high liquid to solid surface area scenario where contact liquid is sufficiently renewed) and is not depleted over the time frame of interest. This assumption reflects a maximum concentration gradient for mass transport that may not be reflected in field scenarios. In most cases this will result in conservative predictions of actual release rates.

Two testing protocols are presented (Kosson *et al.*, 2002) to reflect these assumed conditions for diffusion-controlled leaching from monolithic and compacted granular materials. These protocols are analogous to the NEN tank tests for monoliths (NEN, 1994) and compacted granular wastes (NEN, 1997) respectively, which form the basis for tests under development by CEN Technical Committee 292.

Other modelling approaches (e.g. as described by Garrabrants, 2001, Tiruta-Barna *et al.*, 2001) may provide a more accurate representation of field conditions, for example by taking account of intermittent wetting, carbonation or changes in field pH.

10.3.2 Shrinking core model

One limitation of the bulk diffusion model is that the nature of the leachant is not considered to have a significant effect on mass transport. The shrinking core model has been used to describe acid attack on concrete (Neville, 1981), and calcium leaching from cement in a neutral leachant (Buil *et al.,* 1992). Hinsenveld (1992) developed the model to represent leaching of substances from cement-stabilised wastes. Hinsenveld and Bishop (1996) illustrate the influence of acid strength on the leaching of Pb from a cement-stabilised sludge and conclude that acid strength, rather than bulk concentration, is the dominant influence on diffusive leaching.

The model assumes that the reaction is controlled by the diffusion of acid through the outer leached layer and the acid neutralising capacity available at a sharp interface with the unleached core. Leaching progresses as the interface slowly moves into the unleached core. Like bulk diffusion, leaching is related to a square root of time function.

Leaching is controlled by the dissolution of portlandite, and associated metal hydroxides, as acid penetrates. However, contaminants more strongly fixed in the matrix (C-S-H gel) will be kinetically released over a longer period of time (Hinsenveld and Bishop, 1996). The relative importance of these processes (local solubility or diffusion) with regard to metal leaching from a stabilised waste form will depend on the partitioning of metals between hydroxide precipitation and incorporation in the C-S-H gel. Acidity of the leachant is the driving force, rather than bulk concentration of the contaminant, and the parabolic leach rate (square root of time) at constant acid strength is a consequence of movement of the reaction interface.

Brouwer *et al.* (2003) reported findings from a study of the leaching profiles within an 18 year-old cement-pfa road sub base (see Section 9.5.4). The leaching profiles showed a 25mm thick leached zone at the base of the layer and largely unaltered material of consistent properties above. The leached zone shows a sharp drop in pH of 2-3 pH units to the base of the layer and this drop is reflected in the concentration of contaminants and Ca, but not Na and K. It was concluded that mass transport is a function of solubility (and contact time) under local pH conditions. Results from diffusion tests (NEN, 1994) on "unaltered" cores from the road base were compared to actual leaching (in gm^{-2}). The diffusion tests are designed to give conservative results in most circumstances due to the high liquid to surface area ratio, fully saturated conditions and temperature of 20^oC. The test results underestimated the actual leached mass for many contaminants, reinforcing the importance of pH. However, this observation must be qualified as the "unaltered" core material had already been exposed to a degree of leaching, resulting in an unknown underestimate of mass transport from the diffusion test.

10.4 Summary

A considerable amount of work has been carried out on the performance of cement-based barrier systems specifically designed to mitigate the impact of radionuclides in both deep and shallow repositories. With respect to S/S waste forms the complex interaction of a variety of contaminants with different binder systems requires special attention and the results of modelling should be verified through targeted field investigations and long-term monitoring.

A number of modelling approaches are available to characterise the interaction of waste forms and the environment. These include kinetic and thermodynamic models and methods to simulate mass transfer in waste forms. The chemical evolution of waste forms, the stability of their constituent phases and their interactions within the waste-groundwater-rock system can all be simulated using appropriate models.

Waste encapsulation or stabilisation materials may be examined by chemical thermodynamic modelling to predict their chemical evolution over time. Inclusion of kinetic considerations allows robust predictions of leaching rates to be undertaken and these in turn, combined with mass transfer predictions can provide the source term for contaminant transport calculations.

The role of modelling techniques in this field is important for evaluating:

- the dominant geochemical processes that control porewater chemistry;
- the long-term leaching performance of S/S waste forms: and
- the fate and transport of contaminants released from S/S waste forms.

Once the source term is determined, a range of transport codes are available to assess the ultimate fate and impact of released contaminants. Van der Lee and de Windt (2001) reviewed the use of geochemical modelling and reported much progress in predicting the fate of contaminants. They discussed the differences between static models and hydrodynamic models and showed the latter could account for variable processes. These reactive transport models could be used to model extrinsic systems and show the important reaction pathways. The authors recommend the use of the sequential iterative approach to modelling because of its advantages, namely, it can be readily used as a base model for contaminant transport and geochemistry, provides a stable platform for modelling and can account for spatial heterogeneity in data.

A close correlation between modelling of contaminant interactions and their release and results obtained during verification in the laboratory has been achieved by a number of researchers. Comparison of laboratory and field data has increased our understanding of leaching processes, and modelling studies have predicted long-term performance of waste forms in the order of thousands of years.

The main conclusions are:

- a number of models exist to predict the behaviour of engineered barrier systems and S/S waste forms;
- models can be used to simulate the chemical evolution of S/S waste, the transport of contaminants under leaching conditions and the interactions of waste forms in a geological setting;
- the stability of cementitious barriers and pozzolanic APC residue monofill have been modelled and acceptable (theoretical) buffering capacity in the order of thousands to hundreds of thousands of years has been predicted; and
- modelling tools are becoming increasingly available for assessing the environmental impact of treated materials in the environment. When tested in the laboratory, the results of modelling can be used to formulate risk management plans long into the future.

The use of thermodynamic modelling techniques to investigate the stability of cementitious materials has one main drawback in that many systems to be modelled are not in equilibrium. Furthermore, there is a fundamental lack of data pertaining to groundwater-rock-cement systems and the tools to adequately deal with data of this kind are not fully developed. To be able to address this, the following are required:

- equilibrium thermodynamic models that can model non-equilibrium systems through the use of kinetic constraints. Although some models do this at present there are a number of modelling tools that do not;

- the ability to model non-ideal solid solutions. For example, in cements, C-S-H and hydrogarnet are non-ideal systems, and although we have the ability to model them, the data collection and generation are at an early stage of development;

- models that work with high ionic strength solutions. Once solution strengths exceed, for example, 0.3 molal strengths, existing models become increasingly inaccurate due to the activity correction calculations required. This is largely overcome by more complex formulisms such as the PITZER approach although few determinations of the required virial coefficients have been published; and

- models utilising advanced formulations. However, the fundamental data required are still lacking or proprietary in nature and thus, not publicly available.

The coupling of chemistry and transport, through for example, feedback-loop architecture to enable an assessment of precipitation/dissolution influence on transport through changes in porosity/ permeability in porous solids would also be useful. To the authors' knowledge, there is only one modelling system available at the present time which utilises this approach (Quintessa, 2003) and this is an area of active investigation.

REFERENCES

Allison, J.D., Brown, D.S. and Novo-Gradac, K.J. (1991) *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: version 3.0 user's manual.* USEPA Report EPA/600/3-91/021, March 1991.

American Nuclear Society (1981) *Measurement of the leachability of solidified low-level radioactive wastes*. Working Group A.N.S. 16.1.

Astrup, T., Hansen, J.B., Hjelmar, O. and Christiansen, T.H. (2001) Long-term development in APC ash landfills with respect to pH. In: *Proceedings of Sardinia 2001, 8th International Waste Management and Landfill Symposium*, Cagliari, Italy, 1–5 October. CISA, Environmental Sanitary Engineering Centre, Italy.

Astrup, T. and Christensen, T.H. (2003) Estimating long-term leaching of heavy metals from MSWI APC residues. In: *Proceedings of Sardinia 2003. Ninth International Waste Management and Landfill Symposium*. 6-10 October 2003, Margherita di Pula, Cagliari, Italy.

Atkinson, A. (1984) *The influence of wasteform permeability on the release of radionuclides from a repository*. UKAEA; AERE; Materials Development Division, DOE/RW/83.157;AERE-R11077.

Atkinson, A. and Hearne, J.A. (1984) *An assessment of the long-term durability of concrete barriers exposed to sulphate-bearing groundwaters*. UKAEA; AERE: Materials Development Division. Nirex, AERE-R11465.

Atkinson, A., Hearne, J. A. and Knights, C. F. (1987) *Aqueous chemistry and thermodynamic modelling of CaO-SiO2-H2O Gels*. UKAEA; AERE; Materials Development Division, DOE/RW/87.048; AERE-R12548; HL87/1304.

Atkinson, A. and Hearne, J.A. (1989) *Mechansitic model for the durability of concrete barriers exposed to sulphate-bearing groundwaters*. UKAEA; AERE: Materials Development Division. Nirex Report NSS/R196.

Barna, R., Rethy,Z., Perrodin,Y., Moszkowicz, P. and Tiruta-Barna,L. (2000a) Environmental behaviour of a construction made of a mixture of hydraulic binders and air pollution control residues from municipal solid waste incineration. Part 1. physico-chemical characterisation and modelling of source term. *Waste Management* 20, pp. 741-750.

Barna, R., Rethy,Z., Perrodin,Y., Moszkowicz, P. and Tiruta-Barna,L. (2000b) Environmental behaviour of a construction made of a mixture of hydraulic binders and air pollution control residues from municipal solid waste incineration. Part 2 simulation tests and validation of the source term modelling. *Waste Management* 20, pp. 751-759.

Batchelor, B. (1990) Leach models: theory and application. *Journal of Hazardous Materials* 24 (2-3), pp. 255-266.

Bethke. C. (2002) *The Geochemist's Workbench, Release 4 A Users Guide to Rxn, Act2, React and GTPlot.* University of Illinois Press.

Breysse, D. and Gerard, B. (1997) Modelling of permeability in cement-based materials: Part 1-uncracked medium. *Cement and Concrete Research* 27, (5) pp. 761.

Brouwer, J.P., Frénay, J.W., Jansen, E.W. and van der Bruggen, P.W. (2003) Leaching from an 18 year old cement-stabilised fly-ash roadbase. In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

Buil, M., Revertegat, E. and Oliver, J. (1992) A model of the Attack of Pure Water Undersaturated Lime Solutions on Cement. In: Gilliam, T.M. and Wiles, C.C. (Eds.) *Stabilization and Solidificationof Hazardous, Radioactive and Mixed Wastes*. ASTM STP 1123, pp. 227-241.

Comité Européen de Normalisation (2002) Draft prEN 14405. *Leaching Behaviour Test – Upflow Percolation Test*. CEN TC292/WG6.

Crank, J. (1975) *The Mathematics of Diffusion*. Oxford University Press, London.

Davies A., Wood, B., Barry, T., Dinsdale A. and Gisby, J. (1994) The thermodynamics of mineral-melt equilibria in the system CaO-MgO-Al_2O_3-SiO_2. *J. Mineral. Mag.* 58A, pp. 213-214.

Davies R.H., Dinsdale A.T., Gisby, J.A., Robinson, J.A.J. and Martin, S.M. (2002). MTDATA - thermodynamics and phase equilibrium software from the National Physics Laboratory. *CALPHAD* 26(2), pp. 229-271. Paper available from*:* *http://www.npl.co.uk/npl/cmmt/mtdata/mtdata.html*

Dijkstra, J.J., Meeussen, J.C.L., van der Sloot, H.A. and Comans, R.N.J. (2003) Modelling speciation and transport in MSWI bottom ash. In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

ENV 12920 (1998) *Characterisation of Waste. Methodology for the Determination of the Leaching Behaviour of Waste under Specified Conditions*. Published by British Standards Institution as a Draft for Development.

Environment Agency (2003) *The Development of LandSim 2.5*. National Groundwater and Contaminated Land Report GW/03/09 (available from www.landsim.com).

Fetter, C.W. (2000) *Applied Hydrogeology*. Prentice Hall College Div; Book and CD edition.

Freeze, R.A and Cherry., J.A. (1979) *Groundwater*. Prentice Hall; 1st Edition.

Garrabrants, A.C. (2001) Assessment of Inorganic Constituent Release from a Portland Cement-based Matrix as a Result of Intermittent Wetting, Drying and Carbonation.

Dept. Chemical and Biochemical Engineering. Rutgers, The State University of New Jersey, New Brunswick, NJ.

Glasser, F. P., Angus, M. J., McCulloch, C. E., MacPhee, D. and Rahman, A. A. (1985). The Chemical Environment in Cements. *Materials Research Society Symposium Proceedings* 44, pp. 849 – 858.

Haworth, A., Sharland, S. M., Tasker, P.W. and Tweed, C. J. (1988*) A guide to the coupled chemical equilibria and migration code CHEQMATE*. NSS Report NSS-R113.

Haworth, A., Sharland, S. M. and Tweed, C. J. (1989) Modelling of the Degradation of Cement in a Nuclear Waste Repository. In: Lutze, W. and Ewing, R.C. (Eds.) *Scientific Basis for Nuclear Waste Management XII*, pp. 447-454, Materials Research Society, Pittsburgh.

Hinsenveld, M. (1992) *A Shrinking Core Model as a Fundamental Representation of Leaching Mechanisms in Cement Stabilized Waste.* Unpublished PhD thesis, University of Cincinnati, OH.

Hinsenveld, M. and Bishop, P.L. (1996) Use of the Shrinking Core/Exposure Model to Describe the leachability from Cement Stabilized Wastes.In: Gilliam, T.M. and Wiles, C.C. (Eds.) *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes* 3rd Volume. ASTM STP 1240. American Society for Testing and Materials.

Kosson, D.S., van der Sloot, H.A., Sanchez, F. and Garrabrants, A.C. (2002) An intergrated framework for evaluating leaching in waste management and utilisation of secondary materials. *Environmental Engineering Science* 19, pp. 159-203.

Matte, V., Moranville, M., Adenot, F. Richet, C. and Tourrenti, J.M. (2000) Simulated Microstructure and Transport Properties of Ultra-High Performance Cement-based Materials. *Cement and Concrete Research* 30, pp 1947-1954.

Mangold., D.C and Tsang., C.F. (1990) *A summary of subsurface hydrological and hydrochemical models*. Lawrence Berkley Laboratory Publ.

Minervini, L. and Grimes, R.W. (1999) Defect clustering in wüstite. *Journal of Physical Chemistry and Solids* 60, pp. 235-245.

Moszkowicz, P., Sanchez, F., Barna, R. & Mehu, J. (1998) Pollutants leaching behaviour from solidified wastes: a selection of adapted models. *Talanta* 46, pp 375-383.

NEN (1994) *Leaching characteristrics of soil, construction materials and wastes - leaching tests - determination of the release of inorganic constituents from construction materials, monolithic wastes and stabilized wastes.* Netherlands Normalisation Institute, Delft, The Netherlands.

NEN (1997) *Leaching characteristics of soil, construction materials and wastes - leaching tests - compacted granular leach test of inorganic constituents*. Netherlands Normalisation Institute, Delft, The Netherlands.

Neville, A.M. (1981) *Properties of concrete*. Longman, New York.

Parkhurst, D.L. (1995) *User's Guide to PHREEQC-a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations*. U.S. Geological Survey Water-Resources Investigations Report 95-4227, 143 p.

Parkhurst, D.L. and Appelo, C.A.J. (1999) *User's Guide to PHREEQC (version 2)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312p. Program available at: http://wwwbrr.cr.usgs.gov/projects/GWC coupled/phreeqc/

Parkhurst, D.L., Thorstenson, D.C., and Plummer, L.N. (1980) *PHREEQE--a computer program for geochemical calculations*. U.S. Geological Survey Water-Resources Investigations Report 80-96, 195 p. (Revised and reprinted, 1990) *Note this original reference relates to a now obsolete code replaced by PHREEQC. Readers are referred to the U.S. Geological Survey web site, where a full set of references, current versions of the code and thermodynamic data may be obtained: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/*

Parrott, L. J. and Lawrence C. D. (1991) *Review of durability of cementitious engineered barriers in repository environments*. DOE/HMIP/RR/92.020.

Quintessa. (2003). RAIDEN Commercial, in house code used by Quintessa Ltd. See: http://www.quintessa.org/

Rakotoarisoa, Z. and Tiruta-Barna, L. (2003) Coal fly ash leaching behaviour and geochemical modelling. In: Ortiz de Urbana, G. and Goumans, J.J. (Eds.) *Proceedings of WASCON 2003, Waste Materials in Construction*, June 4th – 6th, San Sebastian, Spain. CD version.

Redmond, S., Bentz, D.P. and Pimienta, P. (2002) Effects of the incorporation of municipal solid waste incinerator fly ash in cement pastes and mortars. II: modeling. *Cement and Concrete Research* 32, pp. 565-576.

Robinson, P.C., Hodgkinson, D.P., Tasker, P.W., Lever, D.A., Windsor, M.E., Grime P.W. and Herbert, A.W. (1988) *A solubility-limited source term model for the geological disposal of cemented intermediate-level waste*. UKAEA Report AERE-R11854 and DOE/RW/88.015

Sanchez, F., Massry, I.W., Eighmy, T.T. and Kosson, D.S. (2001) Multi-regime transport model for leaching of heterogeneous porous materials. *Waste Management,* 23, pp. 219-224

Sugiyama, D., Fujita, T. and Nakanishi, K. (2001) Environment (1) - Thermodynamic modelling for the dissolution and precipitation of calcium silicate hydrates. Denryoku Chuo Kenkyusho Hokoku Kenkyu Hokoku Series, *Chemical Alteration of Cement Materials in a Radioactive Waste Repository*, No. 01007, Komae Research Laboratory.

Sumerling,T.J. (1991) *Dry run 3: a trial of methodology for the probabilistic risk assessment of underground disposal of radioactive waste that accounts for long-term environmental change: overview.* UK DoE Report TR-DR3-10.

Tiruta-Barna, L.R., Barna, R. and Moszkowicz (2001) Modeling of solid/liquid/gas mass transfer for environmental evaluation of cement-based solidified waste. *Environ. Science and Technol.* 35, pp. 149-156.

Tyrer, M. (1994) *Modelling the interaction of blended cements with natural groundwater*. Her Majesty's Inspectorate of Pollution Technical Report TR/WSA/53 (PECD 7-9-483).

van der Lee, J. and de Windt, L. (2001) Present state and future directions of modelling of geochemistry in hydrogeological systems. *Journal of Contaminant Hydrology* 47, pp. 265-282.

van der Sloot, H.A., van Zomeren, A., Rietra, R.P.J.J., Hoede, D. & Scharff, H. (2001) Integration of lab-scale testing, lysimeter studies and pilot scale monitoring of a predominantly inorganic waste landfill to reach sustainable landfill conditions. In: *Proceedings of Sardinia 2001. Eighth International Waste Management and Landfill Symposium*. 1-5 October 2001, Margherita de Pula, Cagliari, Italy.

van der Sloot, H.A. (2003) Horizontal standardization and harmonization of leaching test methods for waste, secondary raw materials, construction materials and (contaminated) soil. In: Ortiz de Urbana, G. and Goumans, J.J. (Eds.) *Proceedings of WASCON 2003, Waste Materials in Construction*, June 4th – 6th, San Sebastian, Spain. CD version.

van Zomeren A., van der Sloot, H.A. and Hoede, D. (2003a) Laboratory, pilot and field studies on stabilized waste produced at the VBM site for recipe development, quality control and support of regulation. In: Ortiz de Urbina, G. and Goumans, J.J.J.M. (Eds.) *Proceedings of WASCON 2003 Waste Materials in Construction*. 4-6 June, 2003, San Sebastian, Spain.

van Zomeren, A., Van Wetten, H., Dijkstra, J.J., van der Sloot, H.A. and Bleijerveld, R. (2003b). Long term prediction of release from a stabilised waste monofill and identification of controlling factors. In: *Proceedings of Sardinia 2003, 9th International Waste Management and Landfill Symposium*. 6th –10th October, S.. Margherita di Pula, Sardinia, Italy.

Wollery T.J. (1992) *EQ3NR a computer program for geochemical aqueous speciation-solubility calculations: theoretical manual, users guide and related documentation (Version 7.0)* Lawrence Livermore National Laboratory Report UCRL-MA-110662 Part IV.

Zacate, M.O., Minervini, L., Bradfield, D.J. and Grimes, R.W. (2000) Defect cluster formation in M_2O_3 doped cubic ZrO_2. *Solid State Ionics* 128, pp.243-254.

11 SUMMARY

11.1 Introduction

Stabilisation/solidification technology is utilised widely outside of the UK as a treatment or remediation option. Indeed, in countries such as France and the United States, S/S is used to treat substantial volumes of contaminated materials each year.

S/S is a technology based on the principle that contaminants can be rendered immobile in a product that is chemically and physically stable over long time-scales. The S/S waste forms will gradually release contaminants into the environment but, when adequately designed and constructed, at a rate that causes minimal environmental impact. In some cases, regular monitoring of contaminants in groundwater within the vicinity of the waste form is required to ensure that concentrations remain within environmental quality targets.

In practice, the application of S/S to hazardous waste and contaminated soil is supported by a significant body of scientific evidence gathered from numerous laboratory investigations and the widespread application of S/S in the field, extending over several decades.

The increased use of process-based technologies in the UK has an important role in achieving government objectives for sustainable development and brownfield regeneration, in particular by:

- improving recovery of waste and a reducing the quantity of waste taken to landfill;
- minimising vehicle movements; and
- reducing the need to import engineering fill.

The main cost considerations in the application of S/S include:

- availability of binding agents;
- need for additional treatment steps;
- site access and space requirements; and
- cost of alternative remediation technologies.

In the USA, for example, the cost of landfill in the State of Massachusetts was approximately £240 per ton (British Cement Association, 2001), and this places alternative remediation options such as S/S at an advantage. In the UK, the landfill tax escalator, requirement for pre-treatment and restrictions on use of landfill resulting from the Landfill Directive are expected to have a similar impact.

The following discusses the main findings of this report and their importance in the context of the application of S/S within the UK.

11.2 Basic Principles

The specific nature of contaminated materials, in respect of substrate and speciation of contaminants has an obvious influence on the impact they may have on the environment. Other factors, including temperature, pH, moisture content and redox environment can also influence the mobility of contaminants. Thus, careful consideration of soil properties and the nature of contamination are important when predicting the outcome of remediation by S/S.

A wide range of binder-materials suitable for use during S/S is available. Binding agents commonly include lime and cement (the hydraulic binders) and bitumen (an organic binder). The hydraulic binders can be blended with other material which include PFA, ggbs and silica fume to optimise the treated product and meet design criteria. In addition, the chemical environment within the bound S/S system can be adjusted by adding specific materials. In this way difficult contaminants can be targeted and remedial targets achieved.

The application of hydraulic binders can result in a product in which contaminants are both physically and chemically encapsulated. The interaction of soils themselves with cementitious binders during S/S invariably improves the encapsulation of contaminants and the engineering properties of the treated waste form. When bitumen is used, soil particles (and contaminants) are physically encapsulated in the binder emulsion but do not take part in any chemical reactions.

11.3 Fixation

Inorganic and organic contaminants are commonly found together in contaminated soil or hazardous waste. In media where the contaminants are dominantly inorganic in nature, S/S is a well established and a reliable treatment technique. However, the speciation of heavy metals may mean that additional pre-treatment steps are necessary.

Inorganic contaminants may be strongly bound to soil-like matrices by sorption processes. Addition of binders to soil or waste is likely to cause changes in speciation (and potentially mobility) of inorganic contaminants, but as the S/S products have low permeabilities and a high pH, mobile contaminants can become fixed in the treated product. Metals are immobilised in solidified waste forms through a number of mechanisms, which include pH control, sorption, precipitation and physical encapsulation. Nevertheless, chemical fixation is the most important factor for long-term stability and, as the binder system can be tailored to the contaminants to be treated, it is possible to design S/S for optimised waste form performance.

The interference effects from some inorganic or combinations of inorganic contaminants can adversely affect setting and hardening reactions and the ultimate performance of S/S waste form. Knowledge of the nature of contaminants, supported by adequate bench testing will ensure the best choice of binder-system and eliminate any threat to performance from interference effects.

Where organic contaminants are present in significant quantities they may present difficulties during treatment. Many organic compounds are mobilised at the high pH associated with hydraulic binders because they form organic complexes. In addition, soil organic matter can be soluble at high pH and organic compounds may undergo complex reactions, sorption, and degradation reactions during solidification.

Organic compounds may also interfere with the hydration reactions that take place in cement or lime-based systems, resulting in unsatisfactory physical characteristics and unacceptably high leachate concentrations. Nevertheless, organic contaminants can successfully be treated by S/S. When leaching of organic contaminants is deemed to be a problem a number of sorbents suitable for use with S/S systems may be used in a pre-treatment step or as a component of the binder system itself. These include activated carbon, shredded car tyres and modified bentonite.

To ensure that S/S is used effectively there must be an effective interaction between the contaminants and the binding agent (either chemically, physically or both). In addition, extrinsic factors such as temperature and humidity and waste-borne compounds, that may cause interference, should be controlled. A large body of historical data and objective guidance, especially in the USA, exists to help vendors successfully apply S/S.

11.4 Construction

If the simple procedures recommended for use in the accompanying guidance are followed the chances of failure of S/S are low. One of the most important steps to be employed during S/S is the treatability trial. Here, the most appropriate mix can be determined and tested and problem materials can be addressed. The presence of dust or volatile emissions, physical and chemical uniformity, and the extent of volume increase during processing can also be identified. Treatability trials should include testing methods that enable an assessment of leaching performance against key influences and a range of tests have been developed by CEN to be applicable to a range of materials, including contaminated soil. The disposal or re-use scenario should be identified, and test boundaries (e.g. pH or L/S range) should be set having regard to most likely and extreme field conditions. In doing this, the vendor is able to demonstrate that full-scale operations are based on optimised systems that meet remedial targets.

Once the mix design(s) have been chosen, the plant and process options for field implementation can be selected. It should be emphasised, however, that the application of S/S utilises well-established civil engineering techniques that may involve *in-situ* or *ex-situ* process operations. The proper application of S/S in the field is another critical factor in the successful implementation of S/S.

With respect to the treatment of wastes, it is important to emphasis that S/S is an accepted technology in the U.S, Europe and elsewhere prior to disposal in landfill. The UK does have a history of treatment of wastes prior to landfill. Between the 1970-1990s a small number of plants were in operation, however, unlike elsewhere (e.g. USA), the criteria for judging success were defined on a local basis. Up to 500 kt/yr. of contaminated material was treated using cement-based systems in the UK in the 1980s.

11.5 Long-Term Performance Considerations

Our understanding of the management of risk in the longer term is currently dependent upon predictive studies that are augmented by field-based data from deposited materials. Although S/S has been widely applied over the past 20-30 years there are few reliable studies yielding data showing performance with time. However, confidence in long-term performance is essential if risk-based management tools, such as S/S are to be routinely employed.

Weathering/degradation of S/S materials may be similar to that affecting concrete or rock, particularly if the exposure environment is near–surface. The mechanisms may include carbonation, sulfate attack and freeze/thaw. However, with specific reference to the degradation processes known in rocks and soils, physical weathering (heat/cool, freeze/thaw, wet/dry, and crystal growth) and chemical weathering (hydrolysis, oxidation and solution) are the anticipated primary mechanisms that will influence waste form performance.

Models to predict field performance of S/S waste forms are still under development and generally focus on the dominant leaching mechanism. There is increasing confidence in the use of models to predict the performance of waste forms with time. However, the chemical complexity of contaminated soil and waste and the very large number of site-specific factors complicate the use of modelling techniques. Nevertheless, there are studies reporting predicted service lives of thousands of years for S/S waste forms, and a growing number of studies that show good correlation between field and laboratory leaching performance.

11.6 Conclusion

It will be seen from the preceding review that the remediation of contaminated soil and treatment of hazardous waste using S/S is widely practised and regulated in a number of countries around the world. This review when used together with the accompanying guidance document should provide the basis for a sound understanding of S/S technology and what steps are necessary to ensure the technology is used as an appropriate risk management strategy in the future.

REFERENCES

BCA. (2001) *Cement Based Stabilisation and Solidification for the Remediation of Contaminated Land*. British Cement Association Publication 46.050

APPENDIX 1:
DEPARTMENT OF THE ENVIRONMENT INDUSTRY PROFILES

Airports
Animal and animal products processing works
Asbestos manufacturing works
Ceramics, cement and asphalt manufacturing works
Chemical works: coatings (paints and printing inks) manufacturing works
Chemical works: cosmetics and toiletries manufacturing works
Chemical works: disinfectants manufacturing works
Chemical works: explosives, propellants and pyrotechnics manufacturing works
Chemical works: fertiliser manufacturing works
Chemical works: fine chemicals manufacturing works
Chemical works: inorganic chemicals manufacturing works
Chemical works: linoleum, vinyl and bitumen-based floor covering manufacturing works
Chemical works: mastics, sealants, adhesives and roofing felt manufacturing works
Chemical works: organic chemicals manufacturing works
Chemical works: pesticides manufacturing works
Chemical works: pharmaceuticals manufacturing works
Chemical works: rubber processing works (including works manufacturing tyres or other rubber products)
Chemical works: soap and detergent manufacturing works
Dockyards and dockland
Engineering works: mechanical engineering and ordnance works
Engineering works: railway engineering works
Engineering works: shipbuilding, repair and shipbreaking (including naval shipyards)
Engineering works: vehicle manufacturing works
Gas works, coke works and other coal carbonisation plants
Metal manufacturing, refining and finishing works: electroplating and other metal finishing works
Metal manufacturing, refining and finishing works: iron and steelworks
Metal manufacturing, refining and finishing works: lead works
Metal manufacturing, refining and finishing works: non-ferrous metal works (excluding lead works)
Metal manufacturing, refining and finishing works: precious metal recovery works
Oil refineries and bulk storage of crude oil and petroleum products
Power stations (excluding nuclear power stations)
Pulp and paper manufacturing works
Railway land
Road vehicle fuelling, service and repair: garages and filling stations
Road vehicle fuelling, service and repair: transport and haulage centres
Sewage works and sewage farms
Textile works and dye works
Timber products manufacturing works
Timber treatment works
Waste recycling, treatment and disposal sites: drum and tank cleaning and recycling plants
Waste recycling, treatment and disposal sites: hazardous waste treatment plants

Waste recycling, treatment and disposal sites: landfills and other waste treatment or waste disposal sites
Waste recycling, treatment and disposal sites: metal recycling sites
Waste recycling, treatment and disposal sites: solvent recovery works
Profiles of miscellaneous industries incorporating:
  Charcoal works
  Dry cleaners
Fibreglass and fibreglass resins manufacturing works
Glass manufacturing works
Photographic processing industry
Printing and bookbinding works

APPENDIX 2:
SOIL/WASTE/WASTE FORM PROPERTIES FOR EVALUATION

(after Perera et al., 2002)

Property	**Before treatment**	**During S/S**	**After S/S**
Bound water	x	x	x
Bulk density (as is)	x	x	x
Bulk density (dry)	x	x	x
Bulk density (saturated)	x	x	x
Chloride permeability	x		x
California Bearing Ratio (CBR)	-	-	x
Flexural strength			x
Flow table spread diameter	-	x	-
Hydration heat	x	x	-
Hydraulic conductivity	x		x
Intrinsic permeability	x		x
Modulus of elasticity			x
Moisture content	x	x	x
Oxygen permeability	x		x
Penetration resistance			x
Porosity	x	x	x
Shrinkage/expansion	x		x
Slump	x	x	
Soundness			x
Specific gravity	x	x	x
Tensile strength			x
Unconfined compressive strength	x		x
Water absorption	x		x
Initial setting time	x	-	-
Final setting time	x	-	-
Leach testing & analysis of waste	x		
Leach testing & analysis of S/S treated material			x
Other chemical tests	x		x
Microstructural examination	x		x

APPENDIX 3: EXAMPLE HEALTH AND SAFETY CONSIDERATIONS OF COMMON S/S BINDERS

Consideration	**Potential risks**
Cement, hydrated lime and milk of lime	• Contact with the eyes can cause painful irritation and may cause serious damage unless immediate treatment is given • Burns in the presence of moisture due to generation of strong alkaline solution • Prolonged or repeated contact with skin may result in more severe irritation or dermatitis • Inhalation can irritate the respiratory tract in high concentration. Prolonged repeated inhalation of high dust/mist concentrations may cause ulceration and perforation of the nasal septum and pneumonitis • Ingestion of large doses may irritate the gastrointestinal tract • Reacts vigorously with strong acids
Quicklime	• As above for cement • Substance reacts violently with water and generates heat. Risk of igniting combustible materials when wetted. • Ingestion may cause corrosion of the gastrointestinal tract
Pulverised fuel ash and furnace bottom ash	• Exposure to airborne dust may cause irritation to the eyes and respiratory system • When damp, PFA and FBA are moderately alkaline, prolonged skin contact with these materials may result in abrasion and irritation

APPENDIX 4: SUBSTANCES AFFECTING CEMENT REACTIONS
(after Conner 1990)

Substance or factor	Inhibition	Property Alteration
Fine particulates	X	X
Clay	X	
Silt	X	
Ion exchange materials	X	
Metal lattice substitution	X	
Gelling agents	X	X
Organics, general	X	X
Acids, acid chlorides		X
Alcohols, glycols	X	X
Aldehydes, Ketones		X
Carbonyls	X	
Carboxylates	X	
Chlorinated Hydrocarbons	X	X
Grease	X	X
Heterocyclics		X
Hydrocarbons general		X
Lignins	X	
Oil	X	X
Starches	X	
Sulfonates	X	
Sugars	X	
Tannins	X	
Organics, specific		
EDTA		X
p-Bromophenol		X
Phenols	X	X
Trichloroethene		X

Substance or factor	Inhibition	Property Alteration
Inorganics general		
Acids		X
Bases		X
Borates	X	
Chlorides (at high concentrations)	X	X
Copper compounds	X	
Heavy metal salts	X	X
Lead compounds	X	
Magnesium compounds	X	X
Phosphates	X	
Salts, general	X	X
Silicas	X	
Sodium compounds	X	
Sulphates	X	X
Sulphides	X	
Tin compounds	X	
Zinc compounds	X	
Inorganics, specific		
Calcium chloride	X	
Copper hydroxide	X	
Copper nitrate		X
Gypsum, hydrate	X	
Lead hydroxide	X	
Lead nitrate	X	X
Sodium arsenate	X	
Sodium borate	X	
Sodium hydroxide		X
Sodium iodate	X	
Sodium sulphate		X
Sulphur	X	
Zinc nitrate		X
Zinc oxide / hydroxide	X	

APPENDIX 5: EXAMPLE ADDITIVES USED IN CEMENT-BASED S/S (after Conner, 1997)

	Additive	Effect
pH control and buffering: pH adjustment, removal of interfering substances from solution, destruction of gels and film formers	Lime, sodium hydroxide, sodium carbonate	Neutralises acids, raises pH
	Sodium bicarbonate, magnesium oxide	Buffer
	Ferrous sulphate, sulphuric acid	Lowers pH / alkalinity
Reduction: alteration of valence state of metals	Ferrous sulphate, sodium metabisulphite	Reducing agent in acid conditions
	Sodium hydrosulphite	Reducing agent in alkaline conditions
	Blast furnace slag, metallic iron	Reducing agent
Oxidation: Alteration of valence state of metals; destruction/conversion of interfering substances	Potassium permanganate, sodium persulphate, potassium persulphate	Powerful, non-selective oxidising agent; alteration of biological status
	Sodium hypochlorite, calcium hypochlorite	Non-selective oxidising agent; alteration of biological status
	Hydrogen peroxide	Mild, non-selective oxidising agent; alteration of biological status
Speciation, Re-speciation: Alteration of the species of the constituents of concern to fix metals and other ions	Carbonates	With lead, forms carbonates, basic carbonates
	Iron and aluminium compounds	Various
	Phosphoric acid and salts	With lead, forms phosphate compounds that have low solubility through a wide pH range
	Sodium silicate	Forms low-solubility, silicate species with a variety of metals in solution; anti-inhibitor
	Sodium sulfide, calcium polysulphide, organic sulphur compounds – thiocarbamates, sulphur + alkali	Forms metal sulphides, except with chromium (organic sulfur compounds are safer than inorganic sulphides)
	Xanthates	Form low solubility starch or cellulose xanthate substrates with metals attached
	Sodium chloride (silver fixant), sodium sulphate (barium fixant)	Fixant
	Ferrous sulphate	Removes sulphide ion from solution

	Additive	Effect
Precipitation and flocculation: Aggregation of fine particles and film-formers; dispersion of oils, greases and fine particulates away from reacting surfaces	Ferrous sulfate	Co-precipitating agent
	Proprietary organic flocculants, surfactants	Flocculants and dispersants
	Alcohols, amides	Wetting agent
	Carboxylic acids, aldehydes and ketones, sulfonates	Dispersants
	Amines, Iron salts, magnesium salts, silica	Flocculants
Sorption, bulking, structural modification: Removal of interfering substances from reacting surfaces; immobilisation of organic species; free water reduction; viscosity control; improvement of microstructure	Activated carbon (especially VOCs), organoclays, rubber particulate (especially SVOCs), PFA, rice hull ash (especially VOCs)	Sorbent for some organics
	Activated carbon, PFA, natural clays, expanded minerals, diatomaceous earth	Sorbent for some metals
	Wood chips, ground corn cob	Sorbent
	PFA, GGBS, silica fume	Pozzolanic reaction with alkalis
	Rice hull ash	Reacts with alkalis to form soluble silicates
	Natural clays,	Viscosity control
	GGBS,	Reducing agent
	Silica fume, GGBS, superplasticisers	Structural modification
	PFA, natural clays, expanded minerals, diatomaceous earth, GGBS, silica fume, wood chips, ground corn cob, cement kiln dust (pozzolanic)	Bulking agent
Acceleration / Anti-inhibition: Counter the effects of set retarders in waste; accelerate the normal set time of cement based systems	Calcium chloride, calcium aluminate, calcium sulfate, glycols, sugar, amines, organic acid salts, triethanolamine, calcium formate, phosphates, cement kiln dust (in some cases)	Accelerates set
	Lime	Supplies additional calcium for reaction; reacts with certain interfering organics; anti-inhibitor; controls biological status
	Sodium silicate	Reacts with interfering metals; anti-inhibitor; causes acceleration of initial set; fixes metals
	Iron compounds	Counters effects of tin, lead arsenates, sulfides by reaction

	Additive	**Effect**
	Bentonite	Sorbs oils, organics; anti-inhibitor
Retardation: Retardation of setting to allow for better processing control	Sugar (at low concentrations), sugar derivatives, zinc hydroxide, copper hydroxide, lead hydroxide, calcium chloride >4%, magnesium salts, tin salts, phosphates, lignosulfonic acid salts and derivatives, hydroxy carboxylic acids, polyhydroxy compounds	Retards setting
Free water control: control (usually reduction) of the free water content of the system	Slag, PFA, cement kiln dust	Bulking agent, pozzolan
	Concrete water reducing additives	Reduce water requirement where applicable
Miscellaneous	Biocides	Counter biological activity
	Organic polymers	Fill pores, improve microstructure, improve durability
	Air entrainment additives, wood resins	Improve durability

APPENDIX 6: PREVIOUS APPLICATIONS OF S/S TREATMENT

(after USEPA 1989a, Al-Tabbaa and Perera *in prep.*)

The following table provides details of S/S treatments that have been carried out worldwide. The details have been obtained from publications, conference proceedings and supplied by vendors. Their inclusion does not necessarily validate the performance of the binder system used.

Site/Contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pre-treatment	Binder	Binder(s) added %	Process type	Disposal location	Volume increase %	Scale of operation
Treatment of electric arc furnace dust, UK	EAF dust containing boron, cadmium, chromium, lead and mercury	63 tonnes (~35m^3)	EAF dust	N	Blast furnace slag, hydrated lime (dolomitic), silica fume (~66:26:8) activated by sodium silicate	53-62% waste 36-44% dry binder 0.5-3.1% silicate and 14-38% water	Mobile batch plant	Not available	Not available	Field trial
Eurosoilstab, Dartford, UK	Up to 55% organic content	Not available	Soft alluvial soil	N	Cement and ggbs	Not available	Not available	Not available	Not available	Bench-scale
Treatment of river dredgings and sewage sludge, TRL, UK	Heavy metals and organic contamination	Not available	Very soft organic silty clay	PFA	Quicklime	1:2 PFA: dredgings 5% quicklime by weight	Not available	Not available	Not available	Bench-scale and site trial
A13 Thames Ave to Wennington , UK highway scheme	Lightly contaminated – exact details not available	150,000 m^3	Silt dredgings	PFA	Lime	1:2 PFA: silt 3% lime	Not available	On site	Not available	Full-scale
Ardeer site, Scotland, UK Bachy Soletanche	Heavy metals	10,000 m^3	Granular material	N	Cement based grout with lime and PFA	Not available	*In-situ* multiple overlapping augers	On site	Negligible	Full-scale
Former paint factory West Drayton, London, UK May Gurney /Envirotreat	High levels of hydrocarbons	4,000 m^3	Soil	N	Cement, modified clays and modified reactive bentonite	5.0 % total binder (w/v)	*In-situ* auger	On site	Negligible	Full-scale
Former industrial site, Chineham, Basingstoke, UK Envirotreat/Laing Homes	Heavy metals (<1-18%) Hydrocarbons (<1-8% plus free product)	1,200 m^3	Soil & free product	N	Cement, modified clays and modified reactive bentonite	4.0 % total binder (w/v)	*Ex-situ* excavator mixing	On site	Minimal	Full-scale
Liquid waste settlement lagoon,	Heavy metals (Zn ≤24,360 ppm	4,750 m^3	Sludge - settlement	N	Cement, modified clays and	8.5 % total binder (w/v)	*Ex-situ* specialist excavator	On site	No net change	Full-scale

Site/Contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pre-treatment	Binder	Binder(s) added %	Process type	Disposal location	Volume increase %	Scale of operation
Ipswich, UK Envirotreat/Cranes Fluid Systems	Cu ≤1,000 ppm) Hydrocarbons (TPH ≤154,000 ppm & toluene)		lagoon residue		modified reactive bentonite		attachment			
Marina (dredging) Mylor, Falmouth, UK Envirotreat	Tributyl tin (0.44-0.68 ppm)	2270 m^3	Dredged sediment	N	Cement, modified clays and modified reactive bentonite	5.5 % total binder (w/v)	*Ex-situ* excavator mixing	On site	N/A	Full-scale
Pumpherston site, Edinburgh, UK Bachy Soletanche	Heavy hydrocarbons consisting of paraffin, wax and tar.	10,500m^3	Up to 40% pure tar.	N	Cement based grout	Not available	*In-situ* multiple overlapping augers	On site	~ 20% by volume	Full-scale
Leytonstone Site, London, UK	Arsenic, cadmium, lead, mercury, copper, nickel, zinc and boron	Not available	Soil	N	Cement	5%	*In-situ* direct mixing	On site	Not available	Full-scale
Winterton Holme Water Treatment Works Site, UK	Not available	4,000 m^3	Water treatment sludge	N	Proprietary product	Not available	On site	Off site	Not available	Full-scale
Nantieux Landfill site. INERTEC	Arsenic and other metals	98,500 tons	Solid waste	Y	Proprietary product	Not available	*Ex-situ*	On site	Not available	Full-scale
Brest, INERTEC	Hydrocarbons	23,500 m^3	Sludge waste	Y	Proprietary product	Not available	*In-situ*	On site	Not available	Full-scale
Le Havres, INERTEC	Hydrocarbons	15,000m^3	Sludge waste	Y	Proprietary product	Not available	*In-situ*	On site	Not available	Full-scale
Independent, Nail, SC, Region IV	Zn, Cr, Cd, Ni	6,600 yd^3 (~5,000m^3)	Solid/soils	N	Portland Cement	20%	Batch plant	On-site	Small	Full-scale (delisting in progress)
Midwest, US Plating Company, Envirite	Cu, Cr, Ni	16,000 yd^3 (~12,200m^3)	Sludge	N	Portland Cement	20%	*In-situ*	On-site	Negligible	Full-scale
Unnamed, ENRECO	Pb/soil 2-100 ppm	7,000 yd^3 (~5,300m^3)	Soild/soils	N	Portland Cement & proprietary product	Cement 15-20% proprietary product 5%	*In-situ*	Landfill	>20% by mass >30-35% by volume	Full-scale
Marathon Steel, Phoenix, AZ, Silicat, Tech	Pb, Cd	150,000 yd^3 (~115000m^3)	Dry – landfill	N	Portland Cement & proprietary silicate	Cement, varied 7-15%	Concrete batch plant	Landfill	Not available	Full-scale
Alaska Refinery HAZCON	Oil/oil sludges	2,300 yd^3 (~1,800m^3)	Sludges, variable	Y	Portland Cement and proprietary product	Varied 50+%	Concrete batch plant	On-site	>35%	Full-scale
Unnamed, Kentucky,	Vinyl chloride Ethylene dichloride	180,000 yd^3 (~138,000m^3	Sludges, variable	Y	Portland Cement and proprietary	Varied 25+%	*In-situ*	On-site (2 secure cells	>7-9%	Full-scale

Site/Contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pre-treatment	Binder	Binder(s) added %	Process type	Disposal location	Volume increase %	Scale of operation
ENRECO		)			product			built on site)		
N. E. Refinery ENRECO	Oil sludges, Pb, Cr, As	100,000 yd^3 (~76,000m^3)	Sludges, variable	N	Kiln dust (high CaO content)	Varied 15-30%	*In-situ*	On-site	Varied, ~20% av.	Full-scale
Velsicol Chemical Memphis Env. Centre	Pesticides and organics (resins etc) up to 45% organic	20,000,000 gallons (~75,700m^3)	Sludges, variable	N	Portland Cement and kiln dust proprietary product	Cement, varied 5-15%	*In-situ*	On-site	Varied, 10% or less	Full-scale
Amoco Wood River, Chemfix	Oil/solids Cd, Cr, Pb	90,000,000 gallons (~340,000m^3)	Sludges	Y	Proprietary product	Not available	Continuous flow (proprietary process)	On-site	Average 15%	Full-scale (site delisted 1985)
Pepper Steel & Alloy, Miami, FL VFL Technology Corporation	Oil saturated soil Pb – 1000ppm PCBs – 200ppm As – 1-200ppm	62,000 yd^3 (~47400m^3)	Soils	Y	Pozzolanic and proprietary product	~30%	Continuous feed (proprietary design)	On-site	~1%	Full-scale
Vickery, Ohio Chemical Waste Management	Waste acid PCBs (<500ppm) dioxins	~235,000 yd^3 (~180,000m^3)	Sludges (viscous)	Y	Lime and kiln dust	~15% CaO ~5% kiln dust	*In-situ*	On-site (TSCA cells)	~9%	Full-scale
Wood Treating, Savannah, GA Geo-Con, Inc	Creosote wastes	12,000 yd^3 (~9,200m^3)	Sludges	Y	Kiln dust	20%	*In-situ*	On-site lined cells	~14%	Full-scale
Wyandotte, MI Treatment Plant Chem Met	Various/combined	20M gallon (~75,700m^3) per year	Various	N	Lime	Not available	Continuous	Off-site – secure landfill	Not available	In-plant process
Chem Refinery, TX HAZCON	Combined metal, sulfur, oil sludges etc.	445 yd^3 (~340m^3)	Sludges (synthetic oil sludges)	N	Portland Cement and proprietary product	Not available	Continuous flow	On-site – secure landfill	Estimated 10%	Full-scale
Chicago Waste Hauling, American Colloid	Metals: Cr, Pb, Ba, Hg, Ag	55 gallon (~0.2m^3) (bench trial)	Various	Not available	Proprietary product	10-40%	Batch mix (pug mill)	Not available	Variable	Bench-scale
API sep. sludge, Puerto Rico, HAZCON	API separator sludges	100 yd^3 (~75m^3)	Sludges	N	Portland Cement and proprietary product	50% Cement ~4% Proprietary	Concrete batch plant	Offsite secure landfill	~4-5%	Full-scale
Metalplating, WI, Geo-con, Inc	Al – 9500ppm Ni – 750ppm Cr – 220ppm Cu – 2000ppm	3,000 yd^3 (~2300m^3)	Sludges	N	Lime	10-25%	*In-situ*	On-site landfill	>4-10%	Full-scale
James River Site Virginia	Kepone contaminated sediments	Not available	Wet oil sludges	N	Cement-base, thermoplastic, polymer	Various	Various	Not available	Not available	Bench-scale only
Massachusetts,	Oil/gasoline	Variable	Wet Soil	Y	Bitumen	Variable	Batch	Used as road	Not available	Bench-scale (pilot

Site/Contractor	Contaminant (concentration)	Treatment volume	Physical form	Chemical pre-treatment	Binder	Binder(s) added %	Process type	Disposal location	Volume increase %	Scale of operation
American Reclamation Corporation	contaminated soils							patch/paving materials		in progress)
Saco Tannery Waste Pits, Maine/VFL Tech. Corporation	Cr > 50,000ppm Pb > 1,000ppm and organics	Varied	Sludge	Not available	Fly ash, quicklime	30% fly ash 10% quicklime	*In-situ*	On-site	>15%	Pilot scale
Sand Springs Petrochemical, Complex, OK/Arco	Sulfuric acid and organics	Not available	Sludge	Not available	Fly ash, quicklime	Varied	Batch	On-site	Not available	Not available
John's Sludge Pit, KS/Terracon Consultants, Inc.	Pb, Cr, acid	Not available	Sludge	Not available	Cement kiln dust and fly ash	Varied	Batch	Not available	Variable	Bench-scale
Hialea, FL Geo-con, Inc.	PCBs 0.800ppm	300 yd^3 (7,000 yd^3/ 5350m^3 total)	Wet soil	N	Proprietary product	15%	*In-situ*	On-site	Small	Pilot scale
Douglasville, PA HAZCON	Zn – 30-50ppb Pb – 24,000ppm PCBs - 50-80ppm Phenol – 100ug/l Oil & grease	250,000 yd^3 (~191100m^3) total on site	Various soil/sludges	N	Portland Cement and proprietary product	Not available	Batch	Not available	Not available	Pilot scale
Portable equipment, Clackanas, OR, CHEMFIX	PB, Cu, PCBs	40 yd^3 (~30m^3)	Soil	N	Cement, silicate	Not available	Batch	Not available	Not available	Pilot scale
Imperial Oil, Morgenville, NJ, Solidtech	PCBs	60 yd^3 (~45m^3)	Soil	N	Cement, proprietary product	Not available	Batch	Not available	Not available	Pilot scale

APPENDIX 7: MIX DESIGN AND ENGINEERING IMPLICATIONS

ATTRIBUTE	POSSIBLE IMPLICATIONS	POSSIBLE MITIGATION ACTION(S)	REFERENCE (incl. section of this document)
PHYSICAL PROPERTIES OF SOIL			
Particle size	Oversized particles can cause damage to mixing plant. Poor grading or irregular shaped particles may influence final properties e.g. air voids, permeability etc.	Screening before treatment to remove oversized particles Crushing/processing to provide acceptable/improved PSD Liaise with plant contractor to determine appropriate plant Assess influence during bench trial.	2.2.1.1
	The addition of small quantities of binder to uniformly graded materials may not result in the increase in strength otherwise expected, as the binder is acting as a filler.	Process material to improve grading. Increase binder content to act as filler	TRL151 (6.2.4)
	Sands and silts with little or no clay or organic matter are likely to transport contaminants more quickly.	Increase binder content to reduce permeability	2.2.1.1
Cohesion and plasticity	Material with a high silt content may be difficult to handle due to the sensitivity of moisture content.	Control drainage Treat with lime Combine with other materials	2.2.1.1, 2.2.1.2
	Cohesive material can result in poor mixing due to clods. This precludes the use of *ex-situ* (pugmill) S/S treatment.	Pre-treat with lime	2.2.1.1, 2.2.1.2

ATTRIBUTE	POSSIBLE IMPLICATIONS	POSSIBLE MITIGATION ACTION(S)	REFERENCE (incl. section of this document)
Moisture content	Moisture content affects the density that can be achieved during compaction and hence the strength of the material. High moisture content may limit bearing capacity for plant. High or low moisture contents may result in poor workability and a stratified product. High moisture content may lead to increased permeability Moisture content may influence the quantity of bleed water, which may be contaminated. Low moisture contents can result in insufficient water being available for full hydration of the lime or cement	Selection of low ground bearing plant or use of support platform during mixing Add water / Dewater to improve moisture content Addition of lime / sorbent to reduce moisture content Design around long-term strength restrictions. Increase compaction to reduce permeability	2.2.1.3 TRL151
Compressibility and bearing capacity	Any settlement that may occur, is likely to be dictated by the compressibility/strength and depth of the S/S material The bearing capacity of the S/S material is likely to depend primarily on the compacted dry density of the material and the strength gain associated with the addition of lime and/or cement.	Assess compaction characteristics, compressibility and strength development during treatability trials. Increase binder content to increase strength	2.2.1.4
Permeability	Generally soils with higher coefficients of permeability will transport water-borne contaminants faster If sulphates are present in the groundwater, soils with higher coefficients of permeability are likely to be more susceptible to attack	Compact final product to minimise air voids Increase binder content to fill voids Hydration products resulting from the addition of lime and/or cement will help fill voids and decrease permeability.	2.2.1.5
CHEMICAL PROPERTIES OF SOIL			
Soil organic matter	Reduced bearing capacity for plant or final use	Selection of low ground bearing plant Use of support platform during mixing	2.2.2.1
	High organic content can cause retarded mix setting and impeded hydration	Assess during treatability trials Isolated pockets of peat/organic matter/plant debris could	Lime Stabilisation Manual 3.5.3

ATTRIBUTE	POSSIBLE IMPLICATIONS	POSSIBLE MITIGATION ACTION(S)	REFERENCE (incl. section of this document)
		be separated/excavated prior to treatment. Increase binder content to overcome detrimental effects of organic matter, (may only be effective at low concentrations)	
Mineralogy	The clay minerals present, the quantity of them and their charge, will influence the transportation of contaminants within the soil.		Lime Stabilisation Manual 2.1
	Lime stabilisation requires a reactive clay content of over 10%. This generally equates with a plasticity index of >10, although preliminary tests should be carried out on materials with PI<20.	More economic designs can be achieved where the soil reacts well following lime stabilisation. If the reactive clay content is low, consider using cement rather than lime stabilisation.	
Sulfate	Retarded mix setting In the presence of excess water, lime/cement may react with sulphates to produce ettringite and/or thaumasite. This can cause take in of a considerable proportion of water, leading to cracking & heave of the S/S material. There is also likely to be associated loss in strength.	Design reduced porosity/permeability S/S waste form Carry out swell tests to evaluate effect.	TRL151 3.5.4.
Sulfide	If oxidation can take place, sulphides can be transformed to sulphates, forming acidic conditions. Acidic conditions can further release metals present in a soluble form.	Reduce time S/S materials are exposed to oxidising environment Ensure well-compacted S/S material to reduce oxidation See also implications of sulphate	TRL151 3.5.5
pH	Stabilisation of very acidic materials can cause rapid heat evolution following the addition of the binder/neutralising agent.	Staged addition of the neutralising agent to control heat evolution. Use of calcium carbonate, agricultural lime can neutralise acidity without causing generation of significant heat	LSM Bates, 2003
	Low pH materials can be deleterious to cement setting, leading to the requirement for excessive binder contents.	Pre-treatment of the material with an alkaline material, to neutralise pH prior to addition of cement.	

ATTRIBUTE	POSSIBLE IMPLICATIONS	POSSIBLE MITIGATION ACTION(S)	REFERENCE (incl. section of this document)
	Major changes in pH by the addition of lime or cement can cause mobilisation e.g. Amphoteric metals	Increase binder to optimise minimum permeability Choose appropriate binder system for speciation of contaminants at high pH.	
Contaminants	Interference effects	Pre-treatment to remove or treat problematic contaminant Change or modify binder type to avoid interference Use of additives to manage the effect	
EXTERNAL ENVIRONMENT			
Temperature	The reaction between lime and clays is very temperature dependant. Temperatures below 7ºC have been identified to be detrimental to the curing of lime stabilised material and can cause retardation of the hydration process. The effect of temperature on cement-stabilized soils is considered to be less critical, and a limit of 3ºC is commonly used. Frost heave causes expansion in susceptible materials and is influenced by the strength of a material and its permeability. Frost shattering can occur up to 300mm from the surface where excess moisture is present in the voids. Initially lime stabilisation can cause a slight increase in porosity and may increase susceptibility to frost heave.	Restrict the temperatures/time of year in which S/S treatment takes place Avoid placing treated material adjacent to frozen ground Assess susceptibility of S/S material to frost heave through laboratory testing (note this will not identify susceptibility of frost shattering). Provide sufficient cover to prevent frost penetration. The strength gain associated with the addition of lime and/or cement will reduce the susceptibility to frost heave. The production of hydration products following the addition of lime and/or cement, fills the voids between particles, reducing permeability and hence reducing frost heave susceptibility. The addition of cement to lime modified soil will reduce the susceptibility to frost attack.	Lime Stabilisation Manual 1.4.3 DtP spec identifies suitable cover. TRL151 6.3.1, 6.3.2.
	Hot, dry conditions can cause material to dry out, which will reduce the moisture content and could affect properties such as workability, curing, permeability and strength.	Assess susceptibility of material to the affect of moisture content during treatability trials Restrict the temperatures in which S/S treatment takes place for materials sensitive to a reduction in moisture content	
pH	If treated material is to be placed in a new environment,		

ATTRIBUTE	POSSIBLE IMPLICATIONS	POSSIBLE MITIGATION ACTION(S)	REFERENCE (incl. section of this document)
	groundwater could alter the pH conditions of the treated material.		
Moisture	An increase/decrease in moisture content can cause some clays to swell/shrink respectively. An increase in moisture content can be decrease the strength of stabilized material	The addition of lime and/or cement is likely to reduce the effect of these implications, although it may not eliminate the problems. Assess during treatability trials. Provide drainage to limit moisture content increase. Increase degree of compaction to reduce take-up of moisture on S/S material (may require modification of moisture content during compaction, closer to OMC).	TRL151 6.2.2, 6.3.3 Lime Stabilisation Manual

APPENDIX 8: EXAMPLE ENVIRONMENTAL CONSIDERATIONS OF S/S TREATMENT

Consideration	**Details**
Contaminated materials before treatment	Run-off from stockpiles may contaminate surrounding ground, water courses and/or ponds Fine dry materials may generate dust in windy conditions, which may contain contaminants
Processing of natural and contaminated materials	Moving, crushing, mixing, drilling and/or deposition of materials may generate dust, which may contain contaminants Processing may cause release of volatile contaminants Potential for increased release of contaminants into groundwater during in-situ mixing or excavation of material due to disturbance Treatment plant may generate unacceptable noise levels Potential impact on vegetation and wildlife
Transportation of materials	Movement of contaminated materials into non-contaminated areas by plant, vehicles or personnel Dust and leachate containment during the movement of contaminated materials around the site and off-site
Accidental spillage during fuelling of plant	Contamination of ground, surface water and/or groundwater Risk of fire
Accidental release of cement or lime into the environment	Harmful to aquatic organisms in high concentrations (generally greater than 100mg/l) and prolonged contact times Soluble in water (at low concentrations) to form alkaline solution Low mobility in most ground conditions Non bio-degradable No potential for bioaccumulation in the food chain High concentrations (>~100mg/l of calcium hydroxide) may have a sterilising effect in sewage works

APPENDIX 9:TYPICAL COSHH ASSESSMENT SCENARIOS

MATERIAL	TYPICAL EXPOSURE	PERSONS AFFECTED	TYPICAL CONTROL MEASURES
Binder	Possible exposure during delivery, depending on nature of storage	Workforce	Provision of respirator*, goggles and gloves. Good hygiene practice to be observed.
	Inhalation or skin contact during mixing of binder with excavated material or adding to *in-situ* treatment plant. Intermittent exposure	Mixing plant operator, workforce	Provision of dust masks, goggles, gloves and/or wetting of materials to prevent dust generation. Good hygiene practice to be observed.
Oils	Occasional exposure during plant maintenance	Workforce	Provision of gloves, use of barrier cream, good hygiene practice to be observed. Flammable – no smoking or naked light.
Gases – VOCs, SVOCs or others	Inhalation of gases given off from contaminated material during processing due to ground disturbance or temperature increase	Workforce, visitors, supervising staff	Gas monitoring in confined spaces, e.g. excavation. Extraction hoods to be used on plant during processing if applicable. Appropriate PPE.
Gas Oil	Skin contact and inhalation hazard during refuelling. Occasional exposure.	Workforce	Good hygiene to be observed. Use of barrier cream and rubber gloves. No smoking or naked light.
Ready mixed or site mixed concrete	Skin contact during placing. Occasional exposure.	Workforce	Protect hands, arms, feet and legs. Good hygiene practice to be observed.
Contaminants existing on site	Inhalation, skin contact or ingestion of contaminants present in pre-treated or treated material	Workforce	Provision of respirator*, gloves, goggles, overalls, boots. Good hygiene practice to be observed.

* Depending on the type, a respirator can protect against organic solvents, mists etc.

Effect of phosphate treatment on the solubility of lead in contaminated soil

R. Stanforth · J. Qiu

Abstract Lead-contaminated soil was used for treatment testing with phosphate-based additives. Reactions controlling leached lead concentrations from soil before and after phosphate treatment were evaluated. The concentration of lead from untreated soil is controlled by a desorption reaction from hydrous metal oxides. Phosphate addition reduced lead solubility in the acidic pH range, but not in the alkaline range. The addition of chloride further reduced lead solubility. The phosphate-treated soil released lower concentrations of lead in simulated digestion tests.

Keywords Lead solubility · Treatment · Phosphate · Pyromorphite

Introduction

Lead is one of the more common contaminants in contaminated soil. In a study of Superfund sites in the USA, lead was the second most common contaminant (Devitt and others 1987), and it is second on the list of the top 20 hazardous substances for 1999 prepared by the US Environmental Protection Agency (EPA) and Agency for Toxic Substances and Disease Registry (ATSDR 1999). Classification of soils or waste as hazardous is based on the presumed threat to groundwater, as modeled by the Toxcity Characteristic Leaching Procedure (TCLP) test used to classify soils or wastes as hazardous. In addition, there is increased concern about the impact of lead in soil on children, as increasing evidence suggests impacts on children at increasingly lower concentrations (Needleman and others 1990; Goyer 1993; Bellinger and others 1994). An impact of lead on both learning ability and social behavior of children has been postulated. Generally, the major source of lead for children is considered to be household dust and soil (Cotter-Howells and Thorton 1991; Thorton and others 1994; Lanphear and others 1998), although one study identified drinking water as a major source (Moffat 1989). Speciation of the lead is also recognized as an important influence on the bioavailability of lead (or other metals). Cotter-Howells and Thorton (1991) suggest that chloropyromorphite (a lead phosphate) is less bioavailable than other forms of lead, and there have been suggestions that lead sulfide is also less bioavailable (Renner 1995).

Treatment of hazardous wastes or soil can be done using a phosphate-based additive. Lead reacts with phosphate to form a series of very low solubility compounds, including simple lead phosphate, pyromorphite ($Pb_5(PO_4)_3OH$) and chloropyromorphite ($Pb_5(PO_4)_3Cl$). Nriagu (1973, 1974) discussed the theoretical conversion of lead in soil to lead phosphate and pointed out the importance of lead phosphates in controlling lead solubility in the environment, as did Lindsay a few years later (1979). Nriagu showed that chloropyromorphite was the least soluble of the lead phosphates in the acid to neutral pH range, and could potentially reduce soluble lead concentrations by three orders of magnitude compared to pyromorphite. Nagel and others (1983) applied the concept of stabilizing lead with phosphate to the treatment of hazardous foundry wastes using sodium phosphate, while Etzel (1988) suggested the use of the fertilizer component triple superphosphate (TSP – a form of calcium dihydrogen phosphate) a few years later. More recently, Ma and others have shown that apatite and similar calcium phosphates can reduce the solubility of lead in soil by forming lead phosphates (Ma and others 1993, 1995; Ruby and others 1994; Laperche and others 1996; Ma 1996; Berti and Cunningham 1997; Eighmy and others 1997). Zhang and others (1998) and Zhang and Ryan (1999a, 1999b) have shown that hydroxyapatite will convert soil-bound lead, lead carbonate or lead sulfide to a pyromorphite. At pH less than 4, they found that the reaction was quite rapid, but at higher pH values, the reaction rate was considerably slower, and was presumably controlled by the rate at which the apatite released

Received: 18 July 2000 / Accepted: 16 October 2000

R. Stanforth · J. Qiu (✉)
Chemical and Environmental Engineering Department,
National University of Singapore,
10 Kent Ridge Crescent,
119260-Singapore
E-mail: cheqiuj@nus.edu.sg
Tel.: +65-8742186
Fax: +65-7791936

DOI. 10.1007/s002540100262

phosphate (Zhang and others 1998; Zhang and Ryan 1999a, 1999b). They identified the product as chloropyromorphite by X-ray diffraction.

The practical application of phosphate stabilization technology for hazardous waste treatment has been developed by several groups (O'Hara and Surgi 1988; Stanforth 1991; Forrester 1993; Pal and Yost 1993; Ryan and others 1996; Stanforth and Knopp 1997). Such application requires that the lead be immobilized relatively quickly so that it will not leach in the EPA TCLP test and the waste is no longer considered hazardous. Hazardous waste treatment technologies using phosphate to stabilize lead have generally used TSP, phosphoric acid or a "water soluble" phosphate, since these provide a much higher concentration of dissolved phosphate in the soil or waste than does hydroxyapatite. In treatability studies for lead contaminated soils, hydroxyapatite or rock phosphate was not effective at reducing the TCLP leachable lead to below the hazardous waste levels (previously 5 mg/L, currently 0.75 mg/L), presumably due to the low dissolved P concentration engendered by the hydroxyapatite (unpublished results).

While these soluble phosphates reduce dissolution of lead from contaminated soil in TCLP tests, there has been little investigation of the chemistry of the reaction, particularly using the soluble phosphates at the high doses needed for treating hazardous waste or soil. Furthermore, there has been relatively little work on the solubility of the treated soil at either very acid or alkaline pH values. The acid pH values are of concern since ingested soil is subjected to the acid conditions of the stomach, while many waste solidification processes involve the high pH values associated with cements or liquid silicates (i.e., 11.5 to 12.5). As Cartledge and others have shown (1990), lead in treated soil is soluble at these high pH values. Sauve and others (1998) found that the lead solubility did not follow a simple solubility curve in phosphate treated soil, probably due to organic matter present in the soil. The authors found that the free Pb^{2+} concentration (as measured by anodic stripping voltammetry) in soil solutions was several orders of magnitude lower than the total dissolved lead concentration measured by graphite furnace atomic absorption spectrophotometry under acid conditions.

In this study, the solubility of lead from a contaminated soil and waste over a wide pH range was investigated, and the form of lead in the soil controlling leachable lead was identified. The contaminated soils and waste were then treated with phosphate and subjected to leaching tests to investigate the lead solubility from both the untreated and treated materials over a wide range of pH values. The reduction in the solubility of the lead as shown in pC–pH diagrams was used as a means of showing the chemical stabilization of lead and of identifying the reaction products. The treatment process was expanded to include halide salts to determine whether a halide pyromorphite (e.g., chloropyromorphite) could be formed during treatment and their impact on the metal solubility. Finally, the untreated and treated samples were subjected to simulated digestion tests to evaluate the reduction in bioavailable lead during treatment.

Methods

Two samples of lead-contaminated material were tested. One is a soil from a rifle range, and the other an industrial waste. The rifle range soil originates from the backstop at a rifle range. The backstop has eroded, and the soil has been redeposited in a nearby low-lying area. The soil is predominantly sand coated with aluminum and iron hydrous oxides, and between 0.1 and 1% lead. (The backstop contains up to 10% lead in the soil, excluding the bullets themselves.) The industrial waste is an electric arc furnace dust from steel manufacturing, and contains about 1.8% lead and 23% zinc. Compositional analysis of the soil and waste are given in Table 1.

The soil/waste was subjected to a modified TCLP test (US EPA 1986). The soil was mixed with a leaching solution at a 1:20 solid to liquid ratio, then tumbled overnight on a rotating shaker. Leaching solutions of varying pH values were prepared using nitric acid or sodium hydroxide. In some cases, calcium hydroxide solutions were used rather than sodium hydroxide solutions for some alkaline pH solutions. While the 1:20 solid:liquid ratio was maintained for all samples (unless noted otherwise), the amount of solid and liquid was varied from the TCLP protocol to reduce the amount of soil used and leachate generated. Either 5 g soil was used with 100 mL solution in a 125-mL plastic bottle, or 2 g solid and 40 mL solution in a 40-mL Oak Ridge type polycarbonate centrifuge tube. After 18 h tumbling, the samples were removed and filtered through a 0.45-μm pore size filter, using Whatman Company Autovials. The filtrates were then acidified and analyzed for lead and other metals using a Perkin Elmer Optima 3000 ICP spectrometer. Low levels of lead (<0.05 mg/L) were analyzed using a Perkin Elmer atomic absorption spectrophotometer, equipped with a graphite furnace. Phosphate was analyzed using the ascorbic acid–molybdenum blue colorimetric method (APHA 1985).

The soils were treated with varying doses of phosphate, using sodium phosphate solutions of varying P concentration at pH 7 (equimolar sodium dihydrogen phosphate and disodium hydrogen phosphate). Dosages were based on the molar ratio of phosphate to lead. The treatment solution was mixed with the soil and allowed to react for at least 24 h before testing. For some samples, commercial

Table 1
Compositional analysis of rifle range soil and electric arc furnace (*EAF*) dust samples

Parameter	Parameter concentration	
	Rifle range soil	EAF dust
Aluminum	3.02%	1.03%
Iron	3.67%	32.0%
Lead	5,150 mg/kg	1.84%
Zinc	91 mg/kg	24.8%
Copper	433 mg/kg	0.02%
Non-digestibles[a]	90%	Not tested

[a] Weight of non-digested material after hot nitric acid digestion, presumably mostly silicates

calcium dihydrogen phosphate (triple superphosphate fertilizer) was used as a treatment additive.

The effects of other cations and anions on the phosphate treatment process were evaluated by using a sample of soil treated with an 8:1 Pb:P molar ratio. Chloride salts were used for sodium, calcium, and magnesium, while the sodium salts were used for fluoride, chloride, and sulfate.

The reaction kinetics between soil lead and the added phosphate was evaluated by allowing reaction times of between 10 min and 28 days prior to the 18-h leaching test. Some samples were also incubated at 50 °C for 1 day and 1 week to evaluate the effect of temperature.

For the lead desorption studies, goethite (α-FeOOH) was prepared using the method of Atkinson and others (1968). The goethite had a surface area of 56 m^2/g. Lead was adsorbed on the goethite at a pH value of 7, using initial lead concentrations of between 0.00625 and 0.141 g Pb/g FeOOH. Lead nitrate was used as the source of lead. The slurry was shaken overnight, then filtered and dried. The leaded goethite was subjected to a similar series of leaching tests as the rifle range soil, except that the solid:liquid ratio was lowered to 1:200 from 1:20 to model the amount of iron and lead in the rifle range soil leaching tests.

Simulated digestion tests

Recently, a test has been developed modeling the solubilization of lead during digestion (Ruby and others 1992, 1996). This test, the Physiologically Based Extraction Test (PBET), subjects the sample to acidic leaching conditions followed by neutral conditions to simulate the intestinal pH, with appropriate digestive reagents in the leaching solution. The dissolved lead concentration is then measured. The PBET test was modified slightly by using a reciprocal shaker for agitation rather than bubbled nitrogen. The effect of temperature on the PBET results was also investigated, and it was found that, for the soil being tested, temperature had no effect on the PBET results – performing the test at room temperatures gave the same results as performing the test at 37 °C as called for in the test protocol. However, all the PBET results reported in this study were obtained at 37 °C.

Reproducibility

The reproducibility of the modified TCLP test was monitored by analyzing replicate leaching samples in one batch at two different pH values, pH 0 and pH 3. The results indicate that there is some variability in the leach test results for lead. At pH 0 the relative standard deviation for lead is 5.0%. At pH 3 the variability is somewhat higher (17.5%).

Some variation also occurred between samples analyzed on different days. The average difference between the replicates was 3.2% (difference/mean) for leaching results on the soil in the acidic pH range. Duplicate PBET tests samples gave an average difference of 5.8%.

A problem was encountered with the leaching tests run at neutral and mildly alkaline pH values. The lead concentrations for replicate runs show considerable variation. In this pH range, colloids are generated from the soil which pass through the filter used in the analysis, and give rise to variable results. It was found that the problem was much greater when sodium was present; the use of calcium hydroxide for pH adjustment minimized the release of the colloidal material. The problem was further minimized by pretreating the soils to remove the finer colloids; however, there may be still some colloids present in the samples in the pH range 7–9.

Results and discussion

Identification of the form of lead present in the soil

The solubility of lead from the untreated soil is shown on a pC–pH diagram in Fig. 1. (No corrections have been made for activities – the measured concentrations are plotted.) The results fall into three sections. At very low pH values (<2) essentially all the lead is removed from the soil, and the measured concentration is close to the calculated value for the test assuming complete dissolution of the lead from the soil. Between pH 2 and 5 or 5.5 the lead concentrations slowly decrease with increasing pH. Above pH 5.5 the lead follows the general pattern of an amphoteric metal hydroxide/oxide or carbonate. The concentration decreases rapidly with increasing pH between pH 5 and 7, then the concentrations increase with increasing pH throughout the alkaline region. Between pH 5.5 and 7, the measured line follows the theoretical solubility curve for lead hydroxide fairly closely, as shown in Fig. 1. The slope of the pH

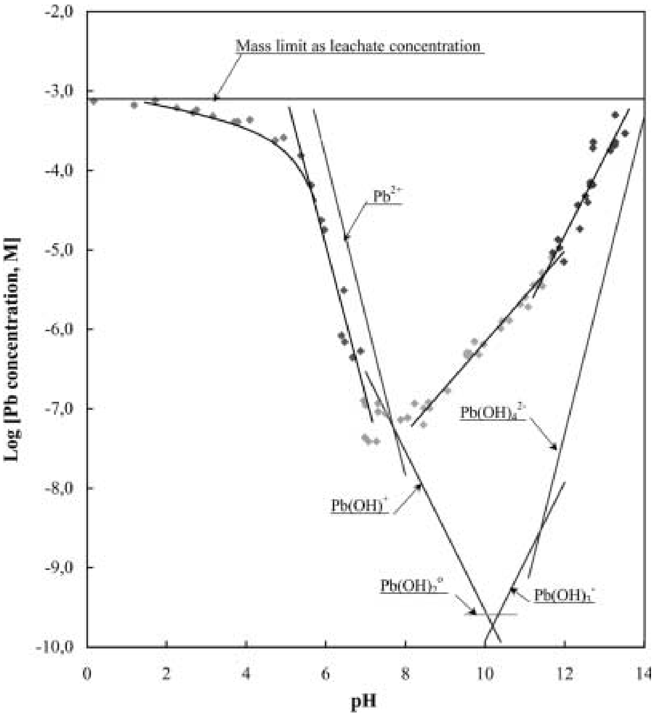


Fig. 1
Leachable lead concentrations from contaminated soil versus pH. Also shown are the maximum possible concentration, based on the amount of lead present in the soil, and the theoretical solubility of lead hydroxide

versus concentration results in this region is –1.89, which is close to the theoretical slope of –2. However, in the alkaline region, the lead is far more soluble than would be predicted based on the solubility of lead hydroxide. The results in this region fall along two straight-line segments; one with a slope of 0.57 (pH of 7.5 to 11.5) and the second with a slope of 0.98 (pH>11.5).

The predicted solubility for lead hydroxide shown in Fig. 1 is based on the solubility and complexation constants given by Nriagu (1973), Smith and Martell (1976), and Lindsay (1979). The solubility constant is based on the free energy of the dissolution reaction. Other authors, however, give the solubility constant for lead oxide as that of the hydroxide or else do not give a solubility product for lead hydroxide, notably Stumm and Morgan (1996) and Morel and Hering (1993). Furthermore, the lead oxide K_{sp} appears to be the constant used by several texts when plotting the solubility of lead hydroxide (Wentz 1995; Sawyer and others 1994).

To provide a reference solubility diagram for lead precipitated as an oxide/hydroxide from solution, the pH of a lead solution was raised to the alkaline region to precipitate an alkaline solid. The solid was then subjected to the varying pH leaching tests described above. The results (Fig. 2) show that the solubility of the solid is quite similar to that of the oxide, and much more soluble than the predicted solubility of the hydroxide. X-ray diffraction analysis of the solid indicated an amorphous solid of no strong crystal structure. Since one would expect a hydroxide to precipitate first, rather than the oxide, the results suggest that the hydroxide solubility calculated from the free energy values may not describe the hydrous lead oxide that precipitates from solution.

Lead carbonate has a similar solubility in the mildly acidic region as lead hydroxide. Thus, it is possible that the lead in the soil is actually in the form of lead carbonate rather than lead hydroxide. This possibility was tested by treating the samples to convert any carbonates present to the hydroxide, then leaching the treated soil and comparing the concentrations. Carbonates were removed in two ways on separate samples: first, one sample was heated to above the temperature where lead carbonate decomposes [315 °C for $PbCO_3$ and 400 °C for $Pb_2CO_3(OH)_2$]. The sample was heated to 450 °C and the leaching pattern compared with that of a soil heated to 175 °C. Lead hydroxide decomposes to lead oxide at around 150 °C. [All decomposition temperatures are taken from the CRC handbook of chemistry and physics (Weast 1968)]. A second set of carbonate-free samples were prepared by slurrying the soil in a pH 6 solution, then purging the slurry with nitrogen gas. At pH 6 the lead was fairly soluble. Any carbonate released from the soil should be stripped from solution, and more lead carbonate will dissolve. The sample was purged with nitrogen for 24 h, following which the solids were removed and subjected to leaching tests. In addition, the final pH and lead concentrations of the slurry were measured. For both treatment processes, the results of the leaching tests after carbonate removal were very similar to the untreated soil and to the soil heated at 175 °C (Fig. 3), indicating that lead leaching is not controlled by lead carbonate.

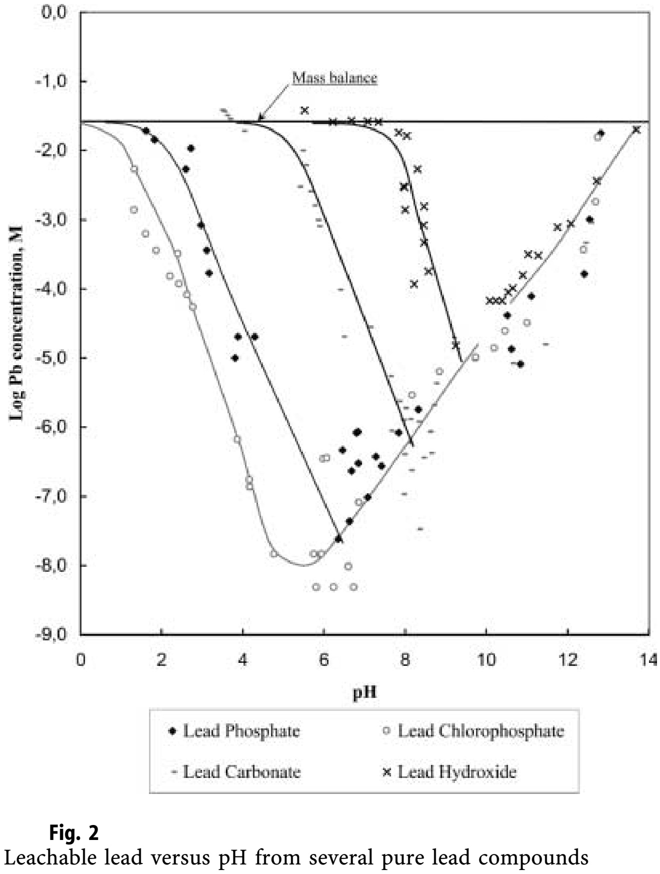


Fig. 2
Leachable lead versus pH from several pure lead compounds

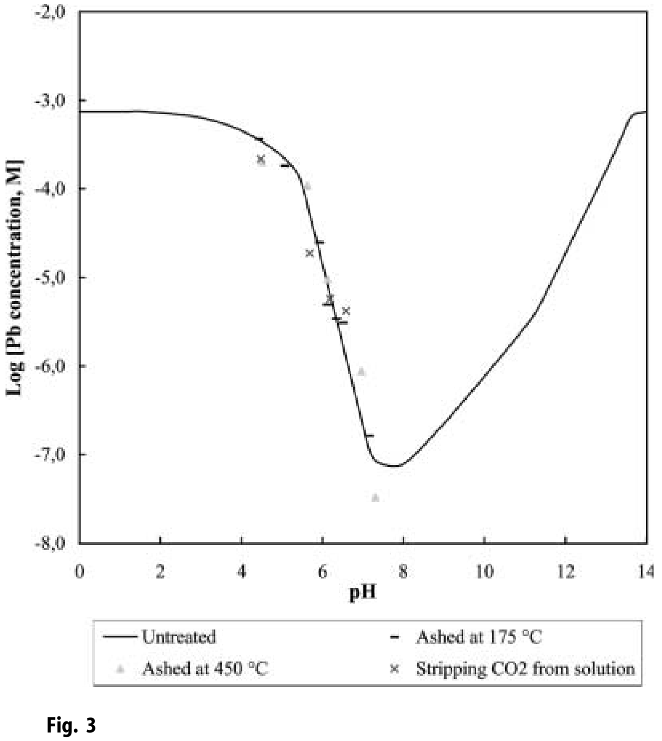


Fig. 3
Effect of carbonate removal from the contaminated soil on the leaching profile of lead

The solubility diagrams developed thus far have approached the final concentration from the undersaturated side, i.e., contaminated soil has been placed in the leaching solution and the lead concentration allowed to increase toward the final value. As May and others (1979) point out, a better demonstration of equilibrium is to approach the equilibrium concentration from both the undersaturated and supersaturated sides. Therefore, some samples were spiked with lead nitrate to well over the saturation concentration at the pH of the solution, and the final lead concentration was monitored. The spike concentrations gave increases in lead concentration of 10 and 50 mg/L. The results are shown in Fig. 4. The results fall on the solubility line (within the reproducibility of the experiment) for the untreated soil, indicating that the lead concentrations measured are close to the equilibrium values for those pH values. This is true both for the acid side of the pH plot and the alkaline side. The results on the alkaline side suggest that the measured concentrations are the result of a fairly stable complex, and not a transient one, since one would not expect the same transient complex to be formed from both undersaturated and oversaturated solutions.

When several different samples of varying lead concentrations were tested, it was found that the concentration of lead released from the soil was dependent on the lead concentration in the soil (Fig. 5). Furthermore, the equilibrium lead concentration varied with the solid:solution ratio [i.e., the amount of solid per liter of leaching solution (Table 2)]. Both of these behaviors are inconsistent with a solubility control of the lead concentration. An alternative explanation is that the dissolved lead concentrations are controlled by a desorption process. To test this hypothesis, lead was adsorbed on a hydrous iron oxide (goethite, α-FeOOH), then desorbed at various pH values using the same leaching test as was used for the soil. The lead concentrations on the goethite and the amount of goethite used was adjusted to have approximately the same amount of lead in the desorption test as was present in the soil leaching tests. The results (Fig. 6) are quite similar in shape to the "solubility" diagrams for lead from the soil. Furthermore, the concentration of lead desorbed depends on the amount of lead adsorbed on the goethite (Fig. 6), similar to the effect of lead concentration on the concentrations of lead leached from the soil. It appears, therefore, that the lead solubility is controlled by a desorption reaction from a hydrous metal oxide, rather than by a dissolution reaction. With this in mind, the lead leaching results in the acidic pH range were plotted as if they were the result of a lead adsorption study, with the percent of

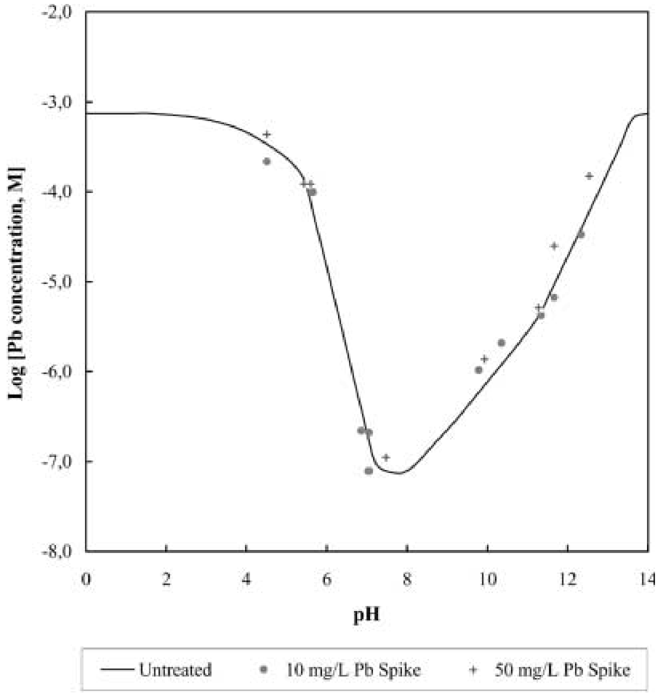


Fig. 4
Comparison of the solubility of lead in contaminated soil and $Pb(OH)_2$ unsaturated and supersaturated conditions

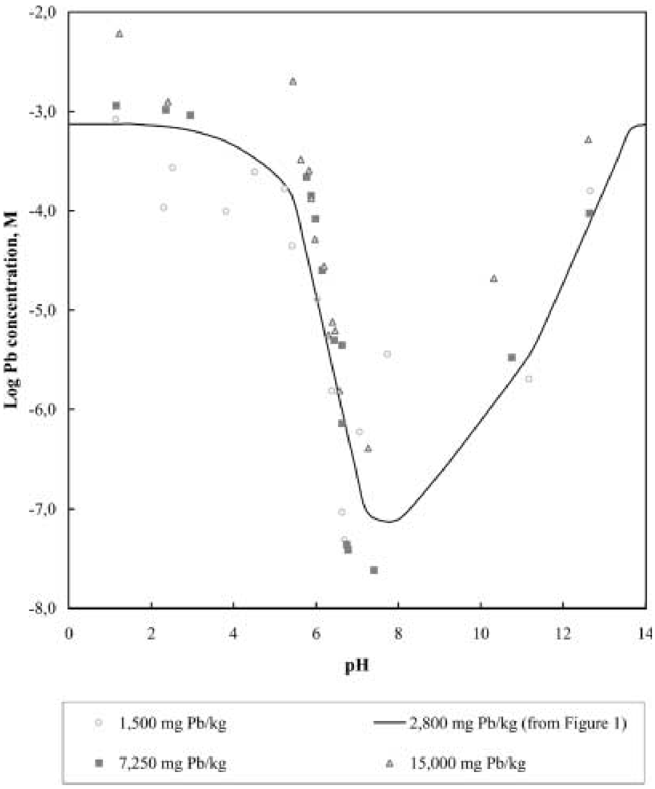


Fig. 5
Effect of the compositional level of lead in the contaminated soil on leachable lead profiles

Table 2
Effect of solid:liquid ratio on leachate lead concentrations

Solid:liquid ratio (g/mL)	Leachate concentration	
	pH	Lead concentration (mg/L)
1:20 (5 g soil/100 mL solution)	6.47	0.082
1:10 (10 g soil/100 mL solution)	6.95	0.117
1:5 (20 g soil/100 mL solution)	6.53	0.197

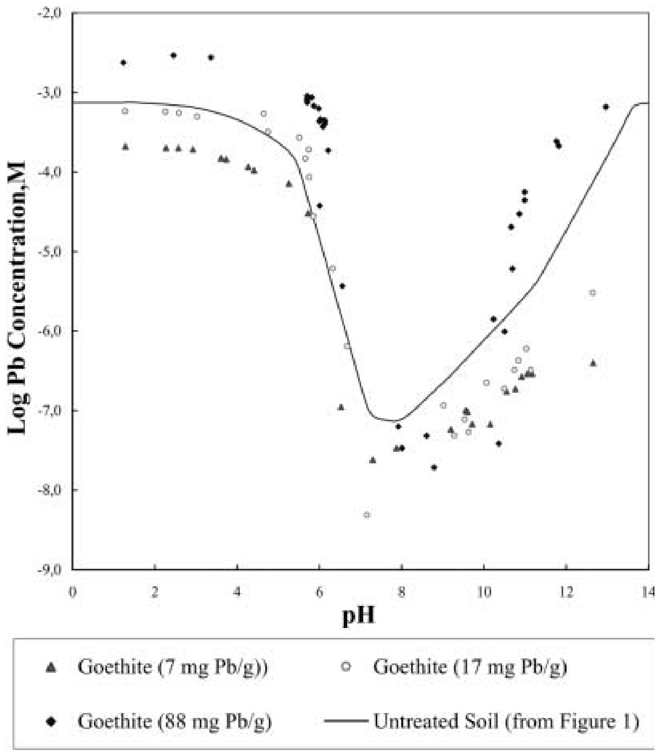


Fig. 6
Desorption of lead from goethite with pH at varying levels of adsorbed lead

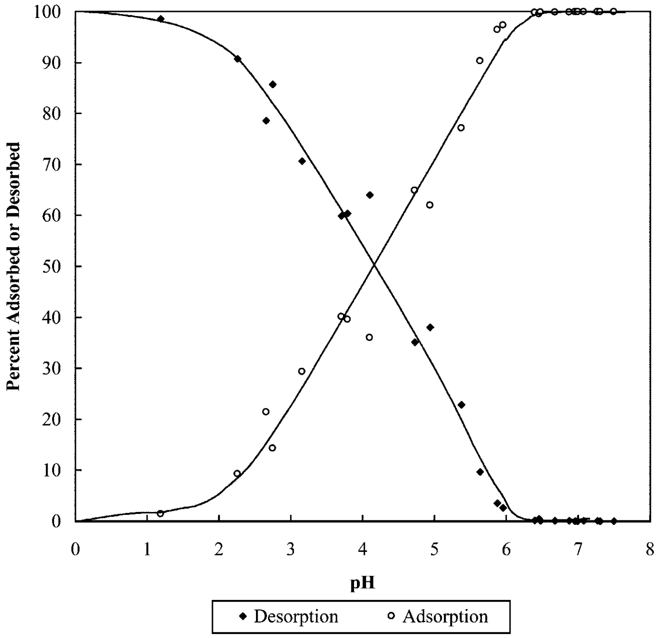


Fig. 7
Percent lead leached from the contaminated soil with pH, plotted both as adsorption and desorption curves

the initial lead concentration remaining in solution plotted versus pH. The initial lead concentrations were calculated from the compositional lead concentration and the solid:liquid ratio. The results shown in Fig. 7 are quite similar to an adsorption profile for lead on hydrous iron oxide (e.g., Kinniburgh and Jackson 1981) and support the conclusion that the lead is adsorbed on metal oxides in the soil rather than precipitated as a discrete solid.

Phosphate treatment

Effect of phosphate dose

The addition of phosphate reduced the leachability of lead from the soil, particularly in the mildly acidic pH range. Increasing the phosphate dose from a 0.5:1 to 6:1 P:Pb molar ratio resulted in increasingly lower lead solubility in the acid pH range (Fig. 8). The results for 4:1 and 6:1 P:Pb ratios were similar, suggesting that further increases in the phosphate dose would have diminishing reductions in lead leaching potential. Lindsay (1979) lists several lead phosphates that could exist in soil, with most having similar solubilities. Comparing the results of the phosphate treated samples with the theoretical solubilities in the acid pH range, it is not clear which form of lead phosphate is being formed (Fig. 9). Both $Pb_3(PO_4)_2$ or pyromorphite ($Pb_5(PO_4)_3OH$) have similar solubilities to those of the lead phosphate formed in the treated soil. However, the test results are not sufficiently precise to allow selection between the different lead phosphate compounds. What is clear, however, is that the lead solubilities for the phosphate-treated soil are very similar to the theoretical solubilities for several of the lead phosphates.

Tests on the phosphate treated soil were carried at alkaline as well as acidic pH values. Results are shown in Fig. 10. The solubility increases in the alkaline region so that at pH values 12 and above, the solubility is similar to that of the

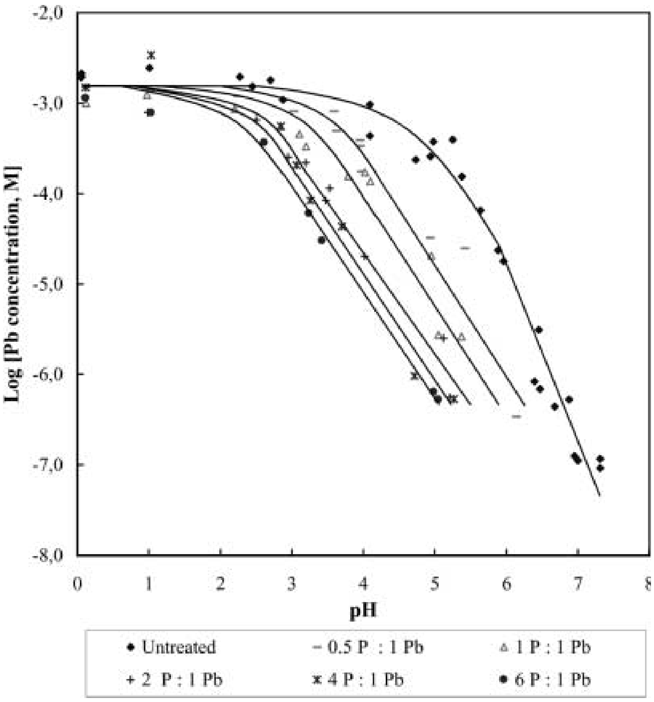


Fig. 8
Effect of phosphate treatment on the solubility of lead in contaminated soil at different molar ratios of phosphate to lead

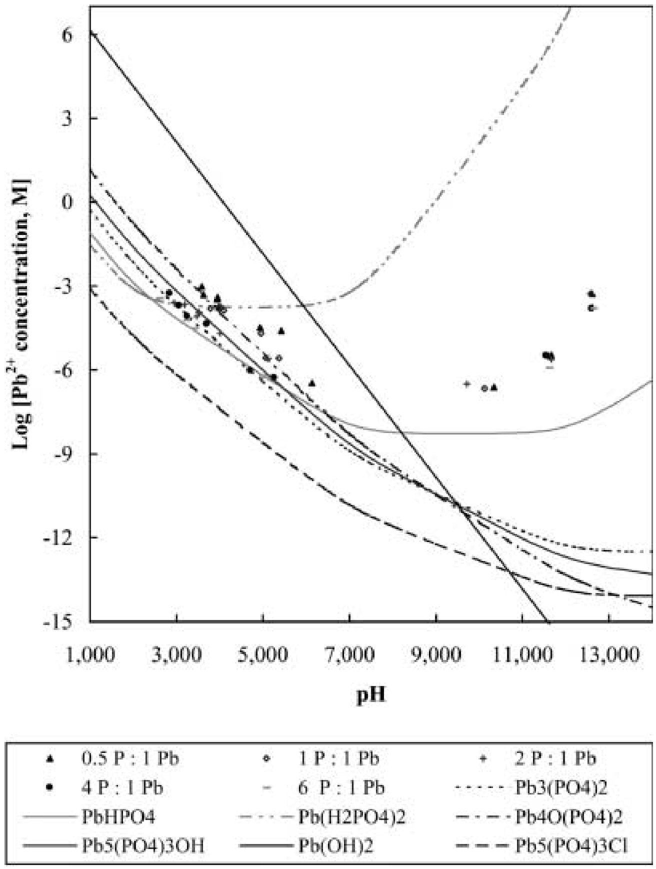


Fig. 9
Comparison of the solubility of lead in phosphate treated soils with the theoretical solubility of various lead phosphate compounds

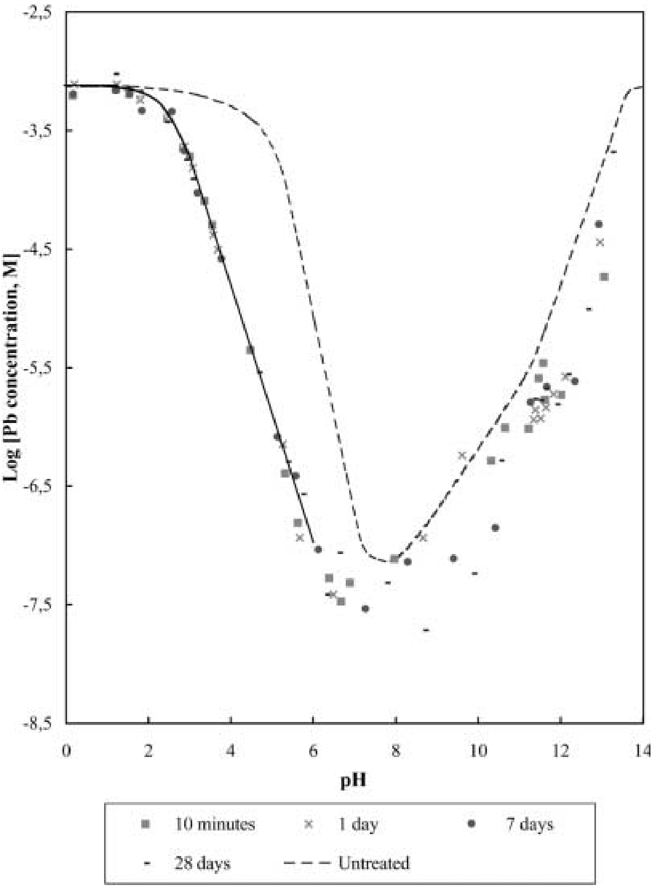


Fig. 10
Influence of reaction time on phosphate stabilization of lead

untreated waste. Even in the mildly alkaline region, the solubility is just slightly lower than that of the untreated waste. The greatest decrease in solubility occurs in the pH range of around 5, where the lead phosphate has a solubility roughly three orders of magnitude lower than lead hydroxide in the untreated soil. Coincidentally, the TCLP test uses a leaching solution with a target pH of 5.

Effect of reaction time and temperature

The effect of reaction times between 10 min and 28 days on lead solubility after phosphate treatment is shown in Fig. 10. Reaction time had no effect on the reduction in lead solubility – the reaction was essentially complete after 10 min (of course, the reaction can still occur during the 18-h leach period, so the shortest time measured was really 18 h and 10 min). There was also no effect of incubation temperature – the results for samples incubated at 50 °C were the same as those incubated at room temperature (approximately 25 °C in the laboratory; results not shown). Thus, the conversion of the lead from the form in the soil to the phosphate form is very rapid.

Effect of other ions

The potential effects of other ions on the stabilization of lead were also investigated. Chloropyromorphite ($Pb_5(PO_4)_3Cl$) has a much lower solubility than any of the other lead phosphates (Nriagu 1973). There are also some claims that sulfate can reduce the solubility of lead phosphate (Pal and Yost 1993). Therefore, the ability of several ions, both anions and cations, to further reduce the solubility of lead was determined by adding the appropriate ions to the soil along with phosphate and measuring the lead solubility of the treated soil at a pH value of 2.7–2.9. The pH was chosen as a range where the lead phosphate had a moderate solubility, so that the enhanced treatment effects of the other ions could be easily measured. The results are given in Table 3. Of the ions added, chloride had the greatest impact, reducing the solubility by about half, while the other ions had smaller effects. Fluoride had a moderate effect, while sulfate had little effect. Presum-

Table 3
Effect of different ions on the solubility of lead phosphate under acidic conditions

Additive	Leachate concentration	
	pH	Lead concentration (mg/L)
TSP	2.70	97.6
TSP+NaF	2.96	61.8
TSP+NaCl	2.77	42.0
TSP+Na_2SO_4	2.76	78.8
TSP+$MgCl_2$	2.73	41.4
TSP+$CaCl_2$	2.67	38.8

ably these effects are related to the solubility of the lead phosphate compounds formed. The influence of the additional ions was further tested by measuring lead solubility over the pH range of 1 to 6 (Fig. 11). These results show more clearly that chloride reduces lead solubility by a measurable amount (roughly half a log unit), while fluoride and sulfate had no measurable effect on the lead solubility. The solubility of lead chlorophosphate was further investigated over a wider pH range, from 1 to 14 (Fig. 12). On the alkaline side, the presence of chloride does not have much effect on lead solubility, while there is a small but measurable effect on the acid side. The solubility of the lead chlorophosphate in the soil is much greater than the theoretical solubility of chloropyromorphite, suggesting that either the chlorophosphate formed is not chloropyromorphite or the K_{sp} value used by Nriagu (1973) and Lindsay (1979) for chloropyromorphite is too low. As with the phosphate compound, longer reaction times (up to 28 days) and higher incubation temperatures did not change the solubility profile for the chlorophosphate.
The use of calcium rather than sodium phosphate resulted in similar lead leaching patterns, indicating that the use of either sodium or calcium did not affect the final results, with the exception of the mobilization of colloidal material by sodium, as discussed earlier.

Simulated digestion tests

The bioavailability of lead in the untreated and phosphate treated soil was evaluated by using a PBET test. The results are presented in Table 4. A large portion of the total lead is extracted in the PBET test from the untreated waste in both the acid and neutral (stomach and intestinal) phases of the test. The high concentration in the neutral phase indicates that the digestive enzymes used in the extraction medium are complexing the lead, since the concentrations are much higher than were found in the leaching studies at the same pH values. Addition of phosphate and phosphate plus chloride lowered the concentration of lead in the PBET test by a factor of around three, demonstrating that the formation of lead phosphate or lead chlorophosphate reduces the bioavailability of lead in the soils.

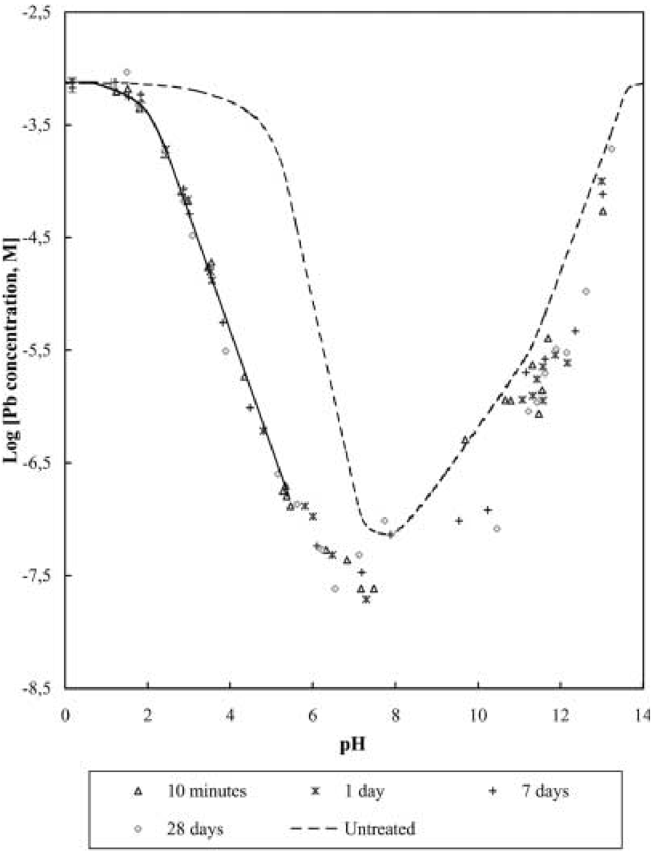


Fig. 12
Solubility of lead chlorophosphate in treated soil over the pH range 1 to 14

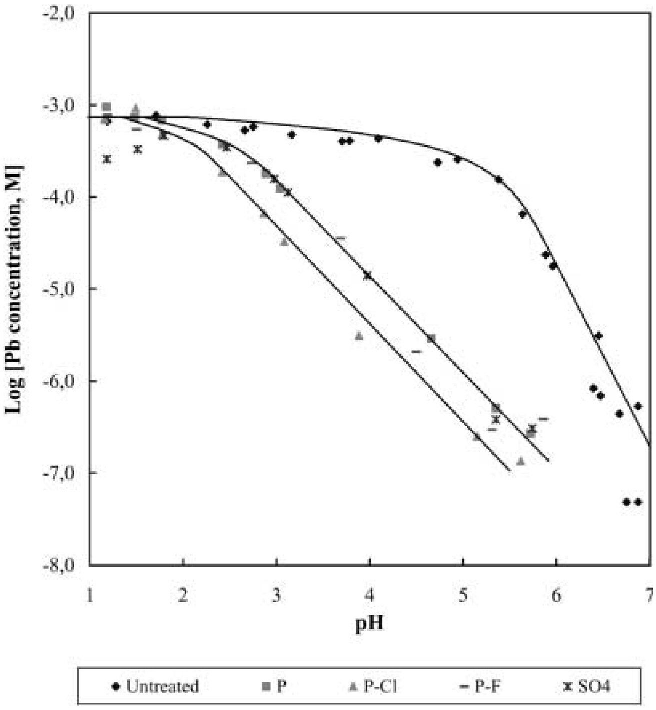


Fig. 11
Effect of different anions on phosphate stabilization of lead

Table 4
Effect of phosphate and phosphate plus chloride on lead solubility in simulated digestion (PBET) tests

Sample	Simulated digestion test results			
	Stomach		Intestines	
	pH	Pb (mg/L)	pH	Pb (mg/L)
Contaminated soil				
Untreated soil	2.54	17.1	7.23	12.4
+ phosphate	2.55	5.25	7.14	4.74
+ phosphate and chloride	2.57	4.70	7.231	3.63
EAF dust				
Untreated	4.63	54	8.06	5.9
+ 5% TSP	3.65	18.1	8.30	0.31

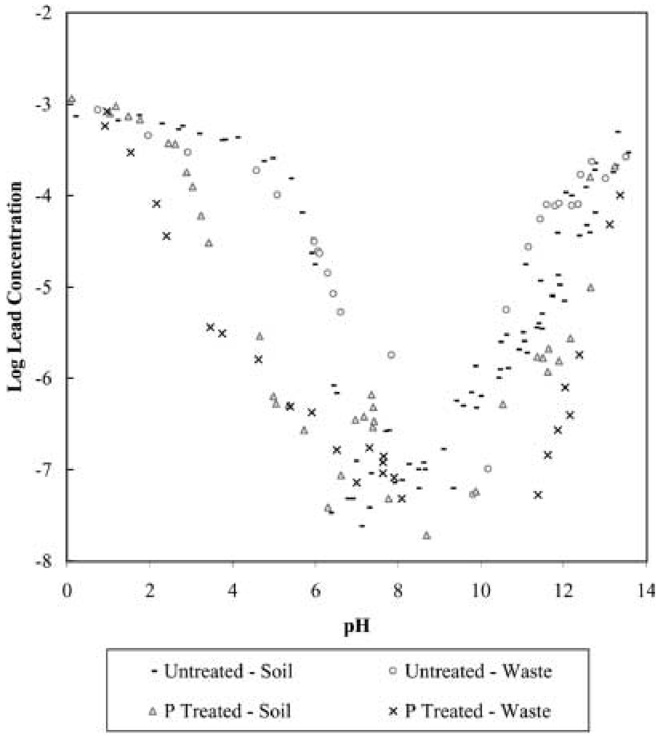


Fig. 13
Solubility of lead with pH from steel mill waste and from contaminated soil with and without phosphate treatment

Electric arc furnace dust results

For comparison with the rifle range soil, a sample of electric arc furnace (EAF) dust from a steel plant (K061) was also subjected to the leaching tests. The results, presented in Fig. 13, are quite similar to those of the rifle range soil. The electric arc furnace dust contains a very high iron content, and the similarity in the leaching profiles for the rifle range soil and the EAF dust suggests that desorption also controls the leached concentrations of lead from the EAF dust.

Phosphate treatment of the EAF dust resulted in reduced metal leaching from the dust (Fig. 13). The solubility of lead from the phosphate treated dust is very similar to lead solubility from the treated soil, indicating that a similar phosphate compound is formed in both materials during phosphate treatment. Likewise, PBET soluble lead was reduced by the addition of phosphate (Table 4), again indicating similar treatment chemistry in the soil and waste.

Conclusions

Lead solubility in a heavily contaminated rifle range soil appears to be controlled by desorption reactions from hydrous metal oxides rather than by dissolution of a separate lead solid. The pC–pH diagram of lead concentrations resulting from the desorption reaction looks like a solubility diagram of an amphoteric metal compound, although lead was much more soluble under alkaline pH conditions than predicted for lead carbonate or hydroxide. Addition of soluble phosphate, in the form of TSP or a sodium phosphate solution, greatly reduced lead solubility. Lead solubility after phosphate treatment under acidic conditions was in the general range expected for lead phosphates, but the precise compound formed could not be identified from the solubility profiles. Addition of chloride further reduced lead solubility, but not to the extent predicted based on the solubility product of chloropyromorphite.

Lead solubility from an electric arc furnace dust leached at various pH values is similar to the solubility from the contaminated soil both before and after treatment, suggesting that similar chemistries are controlling lead solubility in both solids.

Acknowledgements This research was supported by a grant and a research scholarship from the National University of Singapore, and the support is gratefully acknowledged.

References

APHA (1985) Standard methods for the examination of water and wastewater, 16th edn. American Public Health Association, Washington, DC, pp 448–450

Atkinson JR, Posner AM, Quirk JP (1968) Crystal nucleation in Fe(III) solutions and hydroxide gels. J Inorg Nucl Chem 30:2371–2381

ATSDR (1999) Top 20 hazardous substances: ASTDR/EPA list for 1999. Agency for Toxic Substances and Disease Registry. US Dept Health and Human Services. http://atsdr.cdc.gov:8080/cxcx3.html

Bellinger D, Leviton A, Allred E, Rabinowitz M (1994) Pre- and post-natal lead exposure and behavior problems in school-aged children. Environ Res 66:12–30

Berti WR, Cunningham SC (1997) In-place inactivation of Pb in Pb-contaminated soils. Environ Sci Technol 31:1359–1364

Cartledge FK, Butler LG, Chalasani D, Eaton HC, Frey FP, Herrera E, Tittlebaum ME, Yang SL (1990) Immobilization mechanisms in solidification/stabilization of Cd and Pb salts using Portland cement fixing agents. Environ Sci Technol 24:867–873

Cotter-Howells J, Thornton I (1991) Sources and pathways of environmental lead to children in a Derbyshire mining village. Environ Geochem Health 13:127–135

Devitt DA, Evans RB, Jury WA, Starks TR, Eklund B, Gnolson A, van Ee AJ (1987) Soil gas sensing for detection and mapping of volatile organics. National Water Well Association, Dublin, Ohio

Eighmy TT, Crannell BS, Butler LG, Cartledge FE, Emery EF, Oblas D, Krzanowski JE, Eusden JD Jr, Shaw EL, Francis CA (1997) Heavy metal stabilization in municipal solid waste combustion dry scrubber residue using soluble phosphate. Environ Sci Technol 31:3330–3338

Etzel JM (1988) Industrial pretreatment technologies for heavy metal removal and treatment of heavy metal sludges to render them nonhazardous. In: Wastewater Toxics Management Seminar, Virginia Water Pollution Control Association, 3 Nov 1998, Richmond, VA

Forrester KE (1993) Immobilization of lead in bottom ash. US Patent No 5,245,114

Goyer RA (1993) Lead toxicity: current concerns. Environ Health Perspect 100:177–187

Kinniburgh DG, Jackson ML (1981) Cation adsorption by hydrous metal oxides and clays. In: Anderson MA, Rubin AJ (eds) Adsorption of inorganics at solid–liquid interfaces. Ann Arbor Science Publishers, pp 91–160

Lanphear BP, Matte TD, Rogers J, Clickner RP, Dietz B, Bornschein RL, Succop P, Mahaffey KR, Dixon S, Galke W, Rabinowitz M, Farfel M, Rohde C, Schwartz J, Ashley P, Jacobs DE (1998) The contribution of lead-contaminated house dust and residential soil to children's blood lead levels. Environ Res 79:51–68

Laperche V, Traina SJ, Gaddam P, Logan TL (1996) Chemical and mineralogical characterizations of Pb in a contaminated soil: reactions with synthetic apatite. Environ Sci Technol 30:3321–3226

Lindsay W (1979) Chemical equilibria in soils. Wiley, New York, pp 328–342

Ma QY (1996) Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite. J Environ Qual 25:1420–1429

Ma QY, Traina SJ, Logan TJ (1993) In situ lead immobilization by apatite. Environ Sci Technol 27:1803–1810

Ma QY, Logan TJ, Traina SJ (1995) Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ Sci Technol 29:1118–1126

May HM, Helmke PA, Jackson ML (1979) Gibbsite solubility and thermodynamic properties of hydroxy-aluminum ions in aqueous solution at 25 °C. Geochim Cosmochim Acta 43:861–868

Moffat WE (1989) Blood lead determinants in a population living in a former lead mining area in southern Scotland. Environ Geochem Health 11:3–9

Morel FMM, Hering JG (1993) Principles and applications of aquatic chemistry. Wiley, New York

Nagle DL, Stanforth R, Duranceau PE, Kunes TP (1983) Treatment of hazardous melting furnace dust and sludge. Trans Am Foundrymen's Soc 89:715–720

Needleman HL, Schell A, Bellinger D, Leviton A, Allred E (1990) The long-term effects of exposure to low doses of lead in childhood. New Eng J Med 322:83–88

Nriagu J (1973) Lead orthophosphates-II. Stability of chloropyromorphite at 25 °C. Geochim Cosmochim Acta 37:367–377

Nriagu J (1974) Lead orthophosphates-IV. Formation and stability in the environment. Geochim Cosmochim Acta 38:887–893

O'Hara MJ, Surgi MR (1988) Immobilization of lead and cadmium in solid residues from the combustion of refuse using lime and phosphate. US Patent No 4,737,356

Pal D, Yost K (1993) Fixation and stabilization of lead in contaminated soil and solid waste. US Patent No 5,193,936

Renner R (1995) When is lead a health risk? Environ Sci Technol 29:256A–261A

Ruby MV, Davis A, Kempton JH, Drexler J, Bergstrom PD (1992) Lead bioavailability: dissolution kinetics under simulated gastric conditions. Environ Sci Technol 26:1242–1247

Ruby MV, Davis A, Nicholson A (1994) In situ formation of lead phosphates in soils as a method to immobilize lead. Environ Sci Technol 28:646–654

Ruby MV, Davis A, Schoof R, Eberle S, Sellstone CM (1996) Estimation of lead and arsenic bioavailability using a physiologically based extraction test. Environ Sci Technol 30:422–430

Ryan JA, Logan TJ, Ma QY, Traina SJ (1996) Method for in-situ immobilization of lead in contaminated soils, wastes and sediments using solid calcium phosphate materials. US Patent No 5,512,702

Sauve S, McBride M, Hendershot W (1998) Lead phosphate solubility in water and soil suspensions. Environ Sci Technol 32:388–393

Sawyer CN, McCarty PL, Parkin GF (1994) Chemistry for environmental engineering. McGraw Hill, New York

Smith RM, Martell AE (1976) Critical stability constants. Vol 4: Inorganic complexes, Plenum Press, New York

Stanforth R (1991) Method for reduction of heavy metal leaching from hazardous waste under acidic and nonacidic conditions. US Patent No 5,037,479

Stanforth R, Knopp PV (1997) Method of nonhazardous removal of paint containing heavy metals and coating preparation for performing the same. US Patent No 5,637,355

Stumm W, Morgan JJ (1996) Aquatic chemistry, 3rd edn. Wiley, New York

Thornton I, Watt JM, Davies DJA, Hunt A, Cotter-Howells J, Johnson DL (1994) Lead contamination of UK dusts and soils and implications for childhood exposure. Environ Geochem Health 16:113–122

US Environmental Protection Agency (1986) Test methods for the evaluation of solid wastes, SW-846. US EPA, Cincinnati

Weast RC (ed) (1968) CRC handbook of chemistry and physics, 48th edn. Chemical Rubber Co, Cleveland

Wentz CA (1995) Hazardous waste management. McGraw Hill, New York

Zhang PC, Ryan JA (1999a) Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite. Environ Sci Technol 33:618–624

Zhang PC, Ryan JA (1999b) Transformation of Pb(II) from cerrusite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH. Environ Sci Technol 33:625–630

Zhang PC, Ryan JA, Yang J (1998) In vitro Pb solubility in the presence of hydroxapatite. Environ Sci Technol 32:2763–2769

ELSEVIER

Chemosphere 56 (2004) 481–491

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Low-grade MgO used to stabilize heavy metals in highly contaminated soils

M.A. García [a], J.M. Chimenos [a,*], A.I. Fernández [a],
L. Miralles [b], M. Segarra [a], F. Espiell [a]

[a] Department of Chemical Engineering and Metallurgy, University of Barcelona,
Martí i Franqués, 108028 Barcelona, Spain
[b] Department of Geochemistry, Petrology and Geophysical Prospecting, University of Barcelona,
Martí i Franquès s/n, 108028 Barcelona, Spain

Received 10 July 2003; received in revised form 24 March 2004; accepted 21 April 2004

Abstract

Low-grade MgO may be an economically feasible alternative in the stabilization of heavy metals from heavily contaminated soils. The use of MgO is described acting as a buffering agent within the pH 9–11 range, minimizing heavy metals solubility and avoiding the redissolution that occurs when lime is used. The effectiveness of LG-MgO has been studied as stabilizer agent of heavily polluted soils mainly contaminated by the flue-dust of the pyrite roasting. The use of LG-MgO as a reactive medium ensures that significant rates of metal fixation, greater than 80%, are achieved. The heavy metals leachate from the stabilized soil samples show a concentration lower than the limit set to classify the waste as non-special residue. Regardless of the quantity of stabilizer employed (greater than 10%), LG-MgO provides an alkali reservoir that allows guaranteeing long-term stabilization without varying the pH conditions.

Keywords: Heavy metals; Contaminated soils; Magnesium oxide; Stabilization; Landfill

1. Introduction

Heavily polluted soils contaminated with heavy metals may be harmful to living human and other organisms due both to the relatively high toxicity of these metals, even at low concentrations, and to their abundance in the hydrological cycle (Alpaslan and Ali Yukselen, 2002). Soils contaminated with heavy metals have increased markedly in the last 75 years owing not only to the increased consumer use of materials containing these metals but also to technological developments. The main sources of metallic and non-metallic contamination are disposal of industrial waste, mining and smelting operations, fertilizers, and fly ash from incineration and combustion processes (Majid and Argue, 2001).

Remediation of metal contaminated soils is currently an important worldwide issue, of concern to many communities and municipalities. Many technologies are employed to restore contaminated soils, including thermal, biological, and physical–chemical treatments (Holden et al., 1989). Removing or extracting pollutants from soil matrix is an energy-intensive and time-consuming process, while immobilization technologies are a much more cost-effective solution (Alpaslan and Ali Yukselen, 2002). The majority of these immobilization

---

* Corresponding author. Tel.: +34-9340-37244; fax: +34-9340-35438.

E-mail address: chimenos@material.qui.ub.es (J.M. Chimenos).

0045-6535/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2004.04.005

processes include sorption, ion exchange, precipitation, and encapsulation mechanisms. The stabilization/solidification treatment process by means of chemical additives that limit the solubility of contaminants is the most cost-effective and promising option for soils contaminated by heavy metals. Recently, the potential of phosphate and phosphate and carbonate mixtures as stabilizer has been tested for in situ immobilization of heavy metal contaminated soil, mainly lead and cadmium (Ma et al., 1993; Hettiarachchi et al., 2000; Wang et al., 2001; Hamon et al., 2002). However, most of the stabilizer materials used for the removal and attenuation of heavy metals are either very selective or only effective within a narrow pH range, i.e. hydroxyapatite has a high capacity to remove lead in situ when the solution's pH is low enough (5–6) (Ma et al., 1993), but the presence of other metals in the solution inhibits Pb immobilization (Ma, 1994). The attenuation of heavy metals availability will depend on factors such as solid–solution equilibrium, or the solubility product (K_{sp}) of the solid phase (Hamon et al., 2002). The leaching of metals is pH-dependent, and the solubility of heavy metal hydroxides such as lead, cadmium, zinc, and nickel, among others, is minimal within pH range 9–11 (Chimenos et al., 2000).

Heavily contaminated soils are considered as hazardous wastes that are highly harmful to the environmental system. In these cases, the ex situ treatment of waste prior to its landfill disposal is recommended and, according to remediation technologies described above, the stabilization/solidification process is the most frequently employed procedure for heavy metals immobilization. On the other hand, the use of lime, Portland cement, or a mixture of both is the most cost-effective waste treatment, e.g. electric arc furnace dust (Smith, 1993). The use of different types of dolomitic limes with varying amounts of MgO equivalents is described as acting as a buffering agent within the pH 9–11 range, minimizing heavy metals solubility and avoiding the redissolution that occurs by using only lime or limestone (Smith, 1996).

There are many advantages in using MgO as raw material: magnesium oxide has minimal environmental impact, low solubility, and high alkalinity, reaching a maximum pH of 10, which helps to neutralize acids and precipitate metals (Teringo, 1987). However, due to the high cost of pure MgO, which is 8–10 times more expensive than the same grade of lime, it could only be a feasible alternative if low-grade MgO (LG-MgO) is used.

The present study aims to assess the effectiveness of LG-MgO as a stabilizer used to remove heavy metals from heavily contaminated soils. The data shown could be of significance in both in situ and ex situ treatment of contaminated soils with heavy metals; currently, there is no known publication describing the use of MgO as a stabilizer material for heavy metal stabilization. In agreement with the definition given by Conner (1990) the term stabilization is used to refer to a treatment with a stabilizer that has a buffering capacity and forces the system pH towards values in which the solubility of some heavy metals is minimized. Waste stabilization by pH control involves the solubility and precipitation of heavy metals.

2. Method and materials

2.1. Experimental procedure

The bulk chemical characterization of the polluted soil was determined after performing total acid digestion ($HClO_4/HNO_3$, HNO_3/HF) of the samples, carried out in a microwave. The leachates were further analyzed with inductive coupled argon plasma atomic emission spectrometry (ICP-AES) to determine the heavy metals and non-metallic species metals (Pb, Zn, Cu, Cr, Ni, V, As and Cd). The pH values were determined from a solid to liquid ratio 1:10 water leaching test.

Some representative samples were measured by means of X-ray diffraction (XRD) in order to determine the different mineralogical phases and by scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS) to identify the presence of the trace metals in particular solid phases.

The effectiveness of the stabilizer reactants was evaluated by means of DIN 38414-S4 (1984) leaching test procedure, used in Catalonian Regulations (Spain) to classify solid waste. The limit parameters stated by the Catàleg de Residus de Catalunya (1995) are shown in Table 1. Three waste quality standards are established: inert solids where all analyzed parameters are lower than the values described in column A, non-special waste where some values exceeded those in column A, and special waste where some parameter exceeded the values in column B. The leaching test procedure is based on the leaching of water-soluble substances released under continued exposure to nominally clean water percolation, predicting the short-term behavior. The DIN 38414-S4 leaching test experiments consisted of batch water leaching at liquid/solid ratio of 10 (i.e. amount of sample equivalent to 100 g of dry polluted soil per liter of deionised water). The experiments were performed in 2 l closed polyethylene reaction vessels with continuous stirring (3–5 rpm) at room temperature. After 24 h of equilibration, the final pH was recorded and the resulting suspensions were filtered through 0.45 μm membrane filters. Clear filtrates were divided into two samples. One sample was acidified with concentrated HNO_3 for the analysis of heavy and other metals in the leachate (Pb, Zn, Cu, Mn, Sn, Cr, Ni, V, Al, Fe, As, Se, Sb, Ca and Cd) by ICP-AES. By ion chromato-

Table 1
Catalonia Regulatory limits according to DIN 38414-S4 leaching test procedure and results obtained from the leachate of low-grade MgO

Catalonia Regulatory limits			
Parameter	Inert (A)	Non-special (B)	LG-MgO
pH	$5.5 < X < 12$	$4 < X < 13$	10.80
Cond. ($mS\,cm^{-1}$)	6.0	50.0	2.10
Pb ($mg\,l^{-1}$)	0.5	1.0	<0.10
Zn ($mg\,l^{-1}$)	2.0	5.0	0.07
Cu ($mg\,l^{-1}$)	2.0	5.0	<0.02
Cr ($mg\,l^{-1}$)	0.5	2.0	<0.04
Cd ($mg\,l^{-1}$)	0.1	0.2	<0.02
As ($mg\,l^{-1}$)	0.1	0.5	<0.10
Ni ($mg\,l^{-1}$)	0.5	1.0	<0.05
Al ($mg\,l^{-1}$)	–	–	<0.10
Si ($mg\,l^{-1}$)	–	–	<0.20
Ca ($mg\,l^{-1}$)	–	–	565.50
Fe ($mg\,l^{-1}$)	–	–	<0.02
Ba ($mg\,l^{-1}$)	–	–	0.03
Mn ($mg\,l^{-1}$)	–	–	<0.01
Sn ($mg\,l^{-1}$)	–	–	<0.20
SO_4^{2-} ($mg\,l^{-1}$)	500	1500	1323.76

graphy, sulphate concentration was analyzed on second sample, leaving it untreated.

Two different batches of experiments were performed at the same time. Different LG-MgO and lime ratios (5%, 10%, 15% and 20% in dry basis) are used to stabilize the contaminated soil in order to determine the best percentages of the stabilizer agent. This allows the determination of the optimal conditions to establish a stabilizer reservoir, which assures long-term stabilization. The results obtained in the stabilization using LG-MgO were compared with those obtained using the same amount of lime as stabilizer agent.

2.2. Characterization of the contaminated soil and sampling

The contaminated soil is an industrial site of about 125 000 m^2 located in the coastal of a city close to Barcelona (Spain). Early in the 20th century, a factory was located there and copper sulphate and phosphorous-based fertilizers were produced, mainly superphosphate.

Normal superphosphates are prepared by reacting ground phosphate rock with 65–75% of sulphuric acid. The sulphuric acid used in this type of manufacture is mainly extracted from pyrite minerals. In this case, most of these pyrites came from the south of Spain which contained enough copper (3% or 4%). The process starts with the roasting of pyrites as a source of sulphur dioxide, which is later oxidized to sulphur trioxide by means of a catalytic contact process with vanadium peroxide. The gas produced in the burning of sulphur ores holds a considerable quantity of flue-dust in mechanical suspension, which was removed before this gas was subjected to further treatment. The principal content of such dust is ferric oxide, zinc oxide, copper oxide, arsenious, sulphuric acids, and small quantities of different metals occurring in the raw ore. Moreover, this burning process also generates other minor contaminant streams: the ash collected in the precipitation chambers on leaving the kilns and sludge. The former contains a significant amount of arsenic, antimony, and selenium, all of which are trioxides, while the sludge are composed mainly of lead sulphate and small quantities of sulphates of barium and of tin.

During the production of fertilizers, the wastes were disposed in the area of interest for this work. Because of the long-term deposition of these wastes in the system, they were exposed to atmospheric conditionings and mixed with water, i.e., rainwater. Therefore, the pH dropped to low values since large amounts of dissolved metals and acid were released. As a consequence of that, both the soil and the groundwater were heavily contaminated with heavy metals which were finally poured into the sea.

The soil on which the wastes were deposited is formed by heterometric clean sands and gravels, mainly constituted by silica matrix, i.e., feldspars and quartz, with scant presence of slimes. Most of the polluted soil area is fully covered by a variable thickness of the deposited roasting pyrite and other wastes.

Samples were taken from the site at two separate times. In the first series (88 samples), soil samples were taken at different depths by means of prospecting pits and drilling-mills in order to assess the affected areas and contaminant distribution. Table 2 describes the analytical results obtained for most contaminant elements, divided into three different layers according to depth: upper layer (0–100 cm), middle layer (100–300 cm) and bottom layer (300–600 cm). The values in Table 2 corroborate the high heavy metal content in the polluted soil. These metals are heterogeneously distributed according to the wide range of concentration analyzed in the same layer. These results show that there are heavily polluted delimited sites located close to old fertilizer production facilities. Another effect is the decrease of metals and non-metals content with depth, in those places where the top layer is the most polluted layer while this bottom layer still presents a high species concentration. These results confirm two things: (a) the main focus of contamination is the uncontrolled deposition of pyrite roasting wastes on the soil, and (b) the pollutant mobilization mechanism is water percolation.

The different mineralogical phases present in the representative sample of the highest degree of soil pollution were identified by means of X-ray analysis (Fig. 1). In this diffractogram, different ferric oxides are identified such as

Table 2
Chemical composition of polluted soil as a function of depth

	Upper layer (0–100 cm)	Middle layer (100–300 cm)	Bottom layer (300–600 cm)
pH	1.6–7.9	1.6–8.8	5.7–12.3
V (mg kg l^{-1})	<5–1944	<5–684	<5–340
Cu (mg kg^{-1})	10–152 505	<10–4766	<10–687
Zn (mg kg^{-1})	21–8642	<10–3092	<10–2123
Pb (mg kg^{-1})	12–44 259	<10–4587	<10–340
Ni (mg kg^{-1})	<10–2087	<10–1304	<10–119
As (mg kg^{-1})	5–3630	<5–1145	<5–377
Cd (mg kg^{-1})	<10–391	<10–737	<10–134
Cr total (mg kg^{-1})	<10–112	<10–19	<10–16

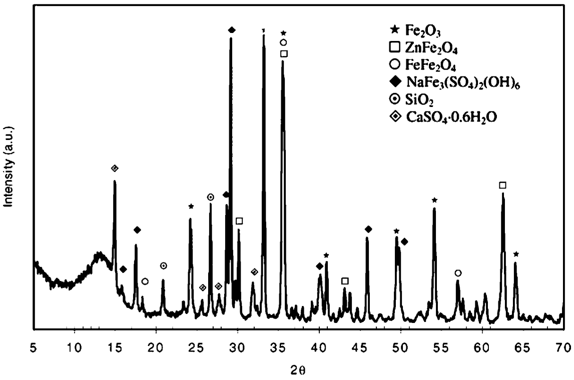


Fig. 1. XRD pattern of a representative sample from the polluted soil top layer (0–5 cm).

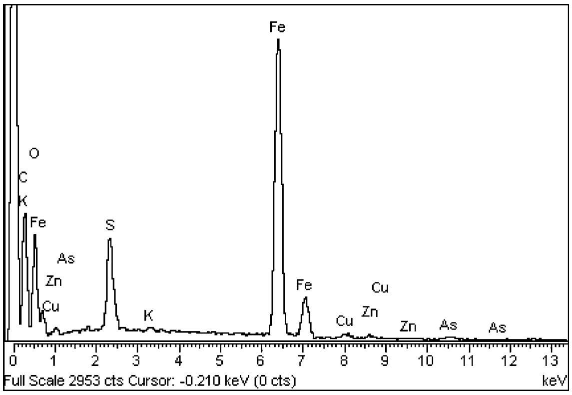


Fig. 2. Energy dispersive spectrum (EDS–SEM) of a representative sample from the polluted soil top layer (0–5 cm).

hematite (Fe_2O_3; PDI 33-0664), magnetite (Fe_3O_4; PDI 19-0629) or zinc iron oxide ($ZnFe_2O_4$; PDI 1-1109), and natrojarosite ($NaFe_3(SO_4)_2(OH)_6$; PDI 11-0302) and calcium sulphates ($CaSO_4 \cdot 0.6H_2O$; PDI 43-0605). These substances/oxides are typically generated in the pyrite roasting. The presence of heavy metals and metalloids traces is also determined in representative samples of the upper layer by means of EDS coupled to SEM. Fig. 2 shows the presence of some heavy metals and metalloids such as arsenic, zinc and copper, as well as iron, oxygen and sulphur, which are widely distributed in the sample. Likewise, the presence of other metals as lead, chromium, cadmium, and selenium are also detected by SEM–EDS analysis of different sites of the sample.

According to the results obtained above, a second series of samples were taken from the upper layer, which was characterized as the most polluted layer, to carry out the stabilization experiments. Two different stabilizer reactants LG-MgO and lime were used in order to stabilize the heavy metals.

2.3. Characterization by sequential extraction procedure

The buffer function of soil for toxicants can be characterized by the relation of the soluble fraction to elements that is immobile either because of sorption on soil colloids or the precipitation process (Welp and Brümmer, 1999). On the other hand, it is known that the availability of these heavy metals depends greatly on the characteristics of the medium, on the kind and strength of the bond, and on the properties of the solution in contact with the soil sample (Petit and Rucandio, 1999). Thus, the use of the sequential extraction procedure for speciation of trace metals described by Tessier et al. (1979) will allow us to determine the availability, mobilization, and transport of trace of metals and metalloids. According to this extraction procedure, five fractions were considered: species associated with the exchangeable phase which is likely to affect sorption–desorption processes, species associated with the acid soluble phase (e.g. carbonates), species adsorbed into solid particles (e.g. iron and manganese oxides), species associated to oxidizable organic matter and, finally, a residual fraction with mineral matter remaining unattacked. Since the first and the second fractions are considered as feasible to be leached leachate in natural conditions, they were evaluated by the leaching test procedure established by the regulatory environmental agencies to assess the solid waste potential toxicity.

Table 3 shows the trace metals and metalloids leachate concentration according to sequential extraction. These results correspond to a representative sample of the top layer (0–5 cm) of the most polluted site area. In the same way, Fig. 3 represents the percentage of trace metals and metalloids associated with each aforementioned fraction. It can be observed that the trace metals and metalloids are mainly distributed into the iron oxide particles and final residual unattackable fraction. This means that most of the species are difficult to leach and therefore and not available in natural conditions. However, in the case of pyrite roasting wastes, the unattackable fraction corresponds to the hard burned or sinterized compounds, mainly iron oxides. On the other hand, the content of trace metals in the organic fraction, i.e., vanadium and nickel, is mainly due to the presence of unburned fuel adsorbed onto the polluted soil.

According to the results, and taking into account that the DIN 38414-S4 leaching test procedure uses water as leaching media, only a small fraction of metals and metalloids will be released, corresponding to the first exchangeable water fraction.

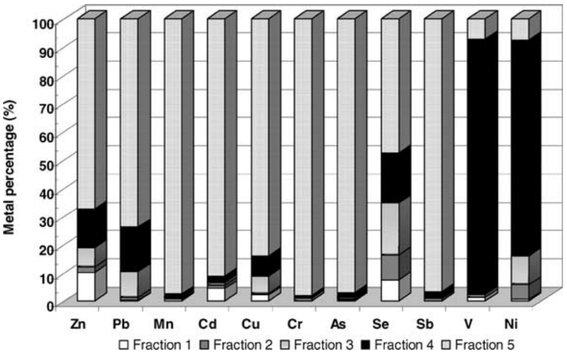


Fig. 3. Metal percentage associated to different soil fraction according to sequential extraction procedure. Fraction 1: exchangeable water phase; fraction 2: acid soluble phase; fraction 3: metals adsorbed into solid particles; fraction 4: oxidizable organic matter phase; fraction 5: residual unattacked fraction.

Table 4
Chemical composition of LG-MgO and used as stabilizer

	LG-MgO
MgO (%)	42.9
CaO (%)	4.5
Fe_2O_3 (%)	1.6
SO_3 (%)	2.0
SiO_2 (%)	2.0
Al_2O_3 (%)	0.8
d_{100} (μm)	100
d_{50} (μm)	10
d_{10} (μm)	3
LOI (1100 °C)	47.0

LOI: loss of ignition; d_x: accumulated fraction lower than particle size.

2.4. Characterization of stabilizer reactants

The LG-MgO used in this study, *Inertimag*®, is produced and sold by Magnesitas Navarras, S.A. It is a by-product of the calcination of natural magnesite in a rotary kiln at 1100 °C. In these operating conditions, the MgO obtained is termed “hard-burned” and shows a narrow range of reactivity. The flue-dust collected in the cyclones and fabric filters is stockpiled, tempered with water, and then weathered for a long period, resulting in the carbonation of the lime content. The product has an equilibrium pH of 10.5, controlled by the solubility of magnesium hydroxide. Table 4 shows the chemical composition of the LG-MgO used in this study. The MgO content ranges from 45% to 60% depending on the magnesite grade used as a raw material. The loss of ignition at 1100 °C depends on the moisture, the thermal

Table 3
Trace metals (mg kg^{-1}) associated to different soil fraction according to sequential extraction procedure

	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Zn	192.5	38.2	132.0	260.7	1288.0
Pb	6.0	39.9	283.5	488.0	2300.0
Mn	6.0	5.3	5.1	13.3	1159.5
Cd	0.7	0.2	0.2	0.4	15.3
Cu	82.2	16.4	226.7	258.6	3060.0
Cr	<0.01	0.05	2.4	2.2	228.4
As	2.3	1.5	2.0	8.2	462.2
Se	0.3	0.4	0.8	0.7	2.0
Sb	<0.01	0.7	0.1	1.6	69.6
V	0.5	<0.01	0.3	31.8	2.6
Ni	1.0	10.2	19.6	147.0	14.6

Fraction 1: exchangeable water phase; fraction 2: acid soluble phase; fraction 3: metals adsorbed into solid particles; fraction 4: oxidizable organic matter phase; fraction 5: residual unattacked fraction.

decomposition of carbonated lime and the presence of unburned dolomite and/or magnesite. Iron, aluminum, and silica do not interfere in the stabilization treatment and remain inert in the precipitated compound. Brucite ($Mg(OH)_2$; PDI 7-0239), magnesite ($MgCO_3$; PDI 8-0479), dolomite ($CaMg(CO_3)_2$; PDI 36-0426), calcite ($CaCO_3$; PDI 5-0586) and quartz (SiO_2; PDI 33-1161) were identified by means of XRD as major mineralogical phases present in LG-MgO used in this study. Finally, the cost of this stabilizer agent, *Inertimag*®, supplied by Magnesitas Navarras, S.A., is around to $40 per ton, which is cheaper than the cost of lime commonly used as alkali stabilizer agent ($48–57 per ton).

On the other hand, lime with calcium oxide purity greater than 99% (analytical grade reagent) was utilized as stabilizer agent to compare the results obtained in the soil stabilization process.

3. Results and discussion

The results obtained from the leaching test of the LG-MgO used as stabilizer reactant are also shown in Table 1. The concentrations of heavy metals and metalloids analyzed are very low and are clearly under the limits established for inert solids. As a consequence, the concentration of the heavy metals and metalloids analyzed in the stabilization experiments do not come from the reactant LG-MgO; therefore, they are released from the polluted soil.

First of all, a leaching test procedure for the non-stabilized polluted soil samples is performed in order to classify the waste and establish the initial values for a later remediation. According to the results obtained, 75% of polluted soil samples are classified as special waste (Fig. 4), since some of the analyzed values exceed the limits established in column B (Table 1). Zinc, lead and copper are the main contaminant metals released from polluted soil. So, in all the polluted soil samples classified as special residue, the zinc concentration exceeds the limit of column B, whereas 33% and 25% of the samples show, respectively, a lead and copper concentration greater than the limits established in column B.

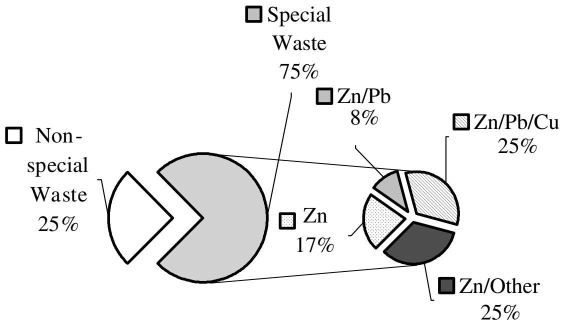


Fig. 4. Classification of non-stabilized polluted soil samples according to the limit parameters stated by the Catàleg de Residus de Catalunya (1995).

Heavy metals and metalloids analyzed from leachate obtained from three representative upper layer soil samples stabilized with LG-MgO are shown in Table 5. These samples were stabilized with different ratios of LG-MgO. The first column values are obtained from the leachate of the non-stabilized polluted soil, whereas the rest of the columns correspond to stabilized soil with different LG-MgO ratios. It can be observed that the pH of the non-stabilized polluted soil is extremely low. This fact may be attributed to the leaching of the products generated during the pyrite roasting process, e.g. jorosite and other iron sulphates, In accordance with this fact, the concentration of the sulphates is very high (values marked in bold in Table 5) and the measured values are clearly above the limit described in column B to classify the polluted soil as special waste. Likewise, the leachate also shows a high concentration of dissolved heavy metals, mainly zinc, copper, lead, arsenic and cadmium.

On the other hand, the contaminated soil stabilized with LG-MgO shows a pH close to 9.2 which is controlled by the solubility of the magnesium hydroxide. This fact is corroborated when using a greater amount of LG-MgO, e.g. 20%, the obtained pHs are again close to 9.2 and, therefore, independent of the quantity of stabilizer added. The measured pH values are always in the pH range where the metal and non-metal (hydr)-oxides show minimum solubility. Moreover, the leachate (Table 5) from the stabilized soil samples show a concentration lower than the detection limit of the analytical technique. In all cases, the metal and metalloids concentration are lower than the limit set in column A (Table 1) to classify the waste as inert. Only the leaching of sulphates from the stabilized soil samples shows a concentration greater than the non-stabilized soil. This fact is due to the high solubility of magnesium sulphate ($\approx 250\ g\,l^{-1}$) and the leaching of sulphates contained in the LG-MgO. The concentration of most of the measured heavy metals decreases as a function of percentage of the LG-MgO added to stabilize the contaminated soil. The profiles obtained are similar to the example shown in Fig. 5, concentration of lead in the leachate against percentage of LG-MgO and pH, for sample S2.

Fig. 6 summarizes the percentage decrease range of heavy metals and metalloids obtained from all upper layer polluted soil samples stabilized using different percentages of LG-MgO. In the figure, the minimum and maximum remediation percentage and the mean percentage for each metal and non-metal were represented. To calculate the percentage range, only the parameters whose analyzed concentrations from non-stabilized polluted soils were greater than the lowest standard solution used in the calibration of the analytical technique used

Table 5
Results obtained in the leachate (DIN 38414-S4) of the non-stabilized and stabilized polluted soil with LG-MgO

Parameters	S1				S2				S3			
LG-MgO (%)	0	5	10	15	0	10	15	20	0	10	15	20
pH	**2.7**[a]	9.3	9.4	9.4	**1.7**[a]	7.6	8.9	9.2	**3.6**[a]	9.1	9.6	9.6
Cond. (mS cm^{-1})	1.9	1.9	1.8	2.0	4.9	3.8	4.0	3.7	1.8	1.9	1.9	2.2
Zn (mg l^{-1})	**114.98**[a]	0.02	0.04	0.05	**292.19**[a]	0.33	0.25	0.12	**102.44**[a]	0.17	0.07	0.05
Pb (mg l^{-1})	0.08	0.10	0.08	0.08	**2.48**[a]	0.48	0.36	0.08	**2.94**[a]	0.10	0.03	0.01
Mn (mg l^{-1})	2.59	<0.01	<0.01	0.04	10.16	0.50	0.28	0.02	3.50	0.01	0.01	<0.01
Cd (mg l^{-1})	**0.36**[a]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	**0.25**[a]	<0.01	<0.01	<0.01
Cu (mg l^{-1})	**163.66**[a]	0.02	0.02	0.03	**155.49**[a]	0.19	0.16	0.10	**41.98**	0.09	0.04	0.06
Cr (mg l^{-1})	0.04	<0.01	<0.01	<0.01	*0.53*[b]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
As (mg l^{-1})	*0.13*[b]	0.01	0.01	0.01	*0.26*[b]	0.09	0.07	0.02	0.07	0.16	0.08	0.05
Mo (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Se (mg l^{-1})	<0.01	0.02	0.01	0.01	0.06	0.06	0.06	0.07	0.01	0.01	0.01	0.01
Sb (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	0.18	0.03	0.02	0.03	0.03	0.06	0.05	0.06
V (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	0.08	0.01	<0.01	<0.01	<0.01	0.01	0.01	0.01
Ni (mg l^{-1})	0.17	<0.01	0.01	0.01	*0.95*[b]	0.05	<0.01	<0.01	0.13	0.02	0.02	0.01
Hg (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cl$^-$ (mg l^{-1})	50.9	51.1	49.2	48.6	24.8	41.5	43.4	41.9	16.0	24.2	22.0	28.7
NO$_3^-$ (mg l^{-1})	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	2.1	2.0	<1.0	1.7	<1.0	<1.0
SO$_4^{2-}$ (mg l^{-1})	*697*[b]	*1151*[b]	*1230*[b]	**1682**[a]	**2158**[a]	**2708**[a]	**2852**[a]	**2656**[a]	*1052*[b]	*1175*[b]	*1162*[b]	*1349*[b]

[a] Values greater than limits established in column B (Table 1).

[b] Values greater than limits established in column A (Table 1).

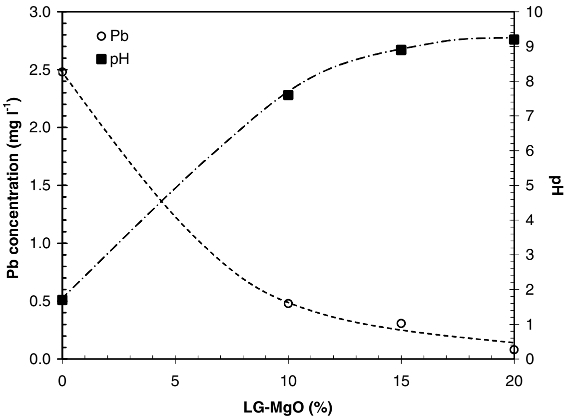


Fig. 5. Lead concentration in the DIN 38414-S4 leached as a function of pH and percentage of LG-MgO stabilizer agent added (sample S2).

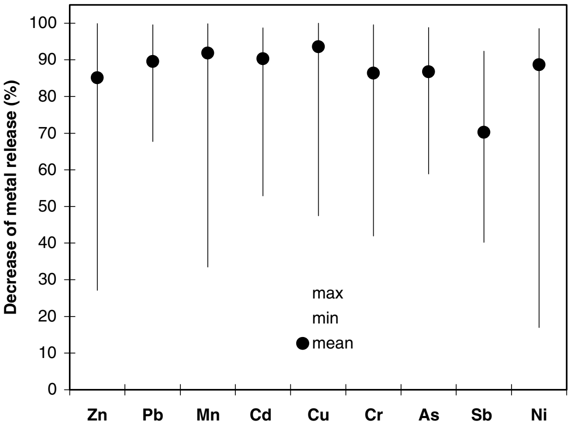


Fig. 6. Decrease of the metals release from the polluted soil samples stabilized with LG-MgO.

(ICP-AES) were considered. In the same way, percentages decreasing less than the quantizing error haves not been considered. It can be observed in Fig. 6 that the maximum release remediation for all metals analyzed is very close to 100%. On the other hand, the minimum remediation is a function of species concentration in the leachate obtained from the non-stabilized soil samples. So, the decrease of metals whose concentrations are very close to theoretical equilibrium solubility, such as metal hydroxide, is very small and of the same magnitude order as the quantizing error. In spite of that, the mean decreases of metals and metalloids release, as can be observed in Fig. 6, are in most cases close to 90%. Thus, according to the leaching of species, all polluted soil samples stabilized with a percentage of LG-MgO greater than 10% can be classified as inert (Table 1). However, for some heavy metals and metalloids, the pH-dependent species are those corresponding to lower oxidation states, i.e. As(III), Cr(III) or Sb(III), whereas the higher oxidation states, as As(V), Cr(VI) or Sb(V) are suitable to form anionic species which are non-pH-dependent. In these cases, its reduction becomes necessary previously to stabilization using alkali stabilizer agents.

Table 6 shows the results obtained in the stabilization with lime of the same contaminated soil samples studied above. The percentage of lime used in this experimental series is the same as that used in the stabilization with LG-MgO. In this case, the pH is controlled by the solubility of portlandite–$Ca(OH)_2$. However, the use of small percentages of lime shows an oversaturation of portlandite with pHs greater than 12.5. As a consequence, at these pH values, some metal hydroxides may redissolve from the polluted soil to form their corresponding soluble hydroxides complex. This fact is clearly observed in the leaching of lead (Fig. 7), which insoluble hydroxide, $Pb(OH)_2$, at pHs higher than 12 forms the corresponding soluble plumbite species, PbO_2H^-. So, the concentration of lead in the leachate increases with the percentage of lime added and therefore always shows concentrations greater than those obtained from non-stabilized polluted soil samples. This behavior is also observed in other metals like zinc or copper, in which the concentration increases in direct proportion to the percentage of lime added. However, in theses cases, the metal concentration of the leachate obtained from the stabilized soil with lime is always lower than those obtained from non-stabilized soil, and the concentration values are low enough to be within the limits established that classify a waste as non-special.

On the other hand, the sulphate concentration in the leachate of most of the samples analyzed decreases inversely with the amount of lime added. However, this results are not as good as expected from the equilibrium solubility of gypsum–$CaSO_4 \cdot 2H_2O$, showing in some stabilized samples, concentrations greater than the limits described in Table 4 (column B) for a non-special residues.

As a consequence of the results obtained, and according to the limits described in Table 1, all polluted soil samples stabilized with lime must be classified as special waste, showing an important release of heavy metals.

4. Conclusions

The mobility of metals and metalloids associated with an exchangeable water or acid soluble phase of the soil and metals adsorbed into solid particles is hindered by the neoformed solid phases and precipitation–dissolution reactions. These attenuation mechanisms depend on factors such as solid–solution equilibrium, or the

Table 6
Results obtained in the leachate (DIN 38414-S4) of the non-stabilized and stabilized polluted soil with lime

Parameters	S1				S2				S3			
Lime (%)	0	5	10	15	0	10	15	20	0	10	15	20
pH	**2.7**[a]	12.0	12.1	12.2	1.7	12.4	**13.1**[a]	**13.1**[a]	3.6	12.6	**13.2**[a]	**13.2**[a]
Cond. (mS cm^{-1})	1.9	8.2	9.2	9.5	4.9	6.6	9.5	9.6	1.8	7.0	8.6	8.1
Zn (mg l^{-1})	**114.98**[a]	**2.54**[a]	**2.65**[a]	**3.56**[a]	**292.19**[a]	*1.30*[b]	*2.00*[b]	*2.45*[b]	**102.44**[a]	*1.57*[b]	**2.53**[a]	**2.64**[a]
Pb (mg l^{-1})	0.08	**1.91**[a]	**2.01**[a]	**3.19**[a]	**2.48**[a]	**6.23**[a]	**13.71**[a]	**15.77**[a]	**2.94**[a]	**14.73**[a]	**14.99**[a]	**15.31**[a]
Mn (mg l^{-1})	2.59	<0.01	<0.01	<0.01	10.16	0.01	0.01	0.01	3.50	<0.01	<0.01	<0.01
Cd (mg l^{-1})	**0.36**[a]	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	**0.25**[a]	<0.01	<0.01	<0.01
Cu (mg l^{-1})	**163.66**[a]	0.98	0.86	1	**155.49**[a]	0.21	0.18	0.24	**41.98**[a]	0.11	0.11	0.20
Cr (mg l^{-1})	0.04	<0.01	<0.01	<0.01	0.53	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
As (mg l^{-1})	**0.13**[a]	0.07	0.07	0.02	*0.26*[b]	*0.11*[b]	*0.13*[b]	0.09	0.07	<0.01	<0.01	<0.01
Mo (mg l^{-1})	<0.01	0.02	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Se (mg l^{-1})	<0.01	0.02	0.02	0.02	0.06	0.18	0.24	0.24	0.01	<0.01	<0.01	<0.01
Sb (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	0.18	0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01
V (mg l^{-1})	<0.01	0.01	<0.01	<0.01	0.08	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni (mg l^{-1})	0.17	0.02	0.03	0.03	0.95	0.02	0.04	0.03	0.13	0.03	0.03	0.03
Hg (mg l^{-1})	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cl^- (mg l^{-1})	50.9	34.9	38.1	10.4	24.7	54.5	53.3	52.2	15.9	34.2	26.3	29.1
NO_3^- (mg l^{-1})	<1.0	<1.0	<1.0	<1.0	<1.0	7.0	7.2	7.3	<1.0	5.0	1.0	1.8
SO_4^{2-} (mg l^{-1})	*697*[b]	*533*[b]	449	153	**2158**[a]	**1226**[a]	**1247**[a]	**1142**[a]	*1052*[b]	*870*[b]	*873*[b]	*711*[b]

[a] Values greater than limits established in column B (Table 1).

[b] Values greater than limits established in column A (Table 1).

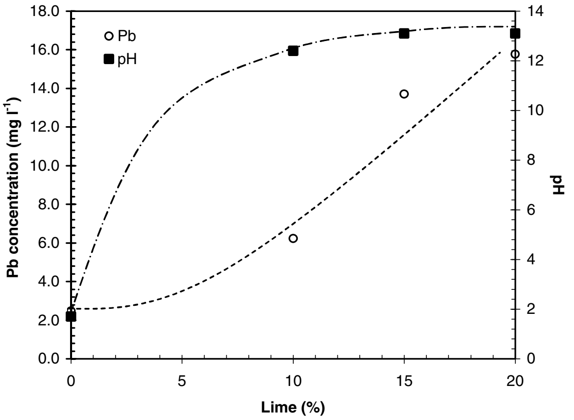


Fig. 7. Lead concentration in the DIN 38414-S4 leached as a function of pH and percentage of lime stabilizer agent added (sample S2).

solubility product (K_{sp}) of the solid phase. In this way, metals and lower oxidation states of metalloids are pH-dependent, and the solubility of most of metal and metalloid (hydr)oxides such as lead, cadmium, zinc and nickel is minimal within pH range 9–11.

The use of low-grade MgO (LG-MgO) acting as a buffering stabilizer agent within the pH 9–11 range may be an economically feasible alternative in the stabilization of heavy metals from heavily contaminated soils. The effectiveness of LG-MgO has been studied in this work as a stabilizer agent of heavily polluted soil contaminated by the uncontrolled deposition of waste generated during the production of inorganic fertilizers, mainly flue-dust from pyrite roasting.

The contaminated soil stabilized with LG-MgO shows, independently of the quantity of stabilizer employed, a pH close to 9.2, which is controlled by the solubility of the magnesium hydroxide. As a consequence, the leachates from the stabilized soil samples show a concentration lower than the limit set to classify the waste as inert, according to Catàleg de Residus de Catalunya (1995). The use of LG-MgO as a reactive medium for the treatment of soils contaminated by heavy metals ensures that significant rates of reduction of metals and metalloids are achieved, greater than 80%, particularly in cases in which there is initially a high concentration where the release remediation is very close to 100%.

The use of a percentage close to 10% of LG-MgO as stabilizer agent, prior to landfill the stabilized polluted soil, has been demonstrated to be enough to diminish the heavy metals and metalloids release and classify the waste as non-special residue. Using greater amounts of LG-MgO an alkali reservoir is provided, that guarantees long-term stabilization without varying the pH conditions and avoiding the redissolution that occurs using lime as stabilizer agent. Only the leaching of sulphates from the stabilized soil samples shows a concentration greater than the limits site to classify the waste as non-special residue using both LG-MgO and lime as stabilizer agents.

According to the results obtained in this work, low-grade MgO was found to be suitable and economically feasible for use as heavy metal stabilizer agent prior to landfill. Similarly, it is possible use LG-MgO for the in situ remediation of soft heavy metal polluted soils.

Acknowledgements

The authors would like to thank the Junta de Residus, Generalitat de Catalunya, the Waste Agency of the Ministry of the Environment of Catalonia (Spain), and Magnesitas Navarras S.A. for their cooperation in financing and supporting this work. The authors also thank Mrs. S. Arosa and Mrs. R. Hernando for their assistance with chemical analysis and data management.

References

Alpaslan, B., Ali Yukselen, M., 2002. Remediation of lead contaminated soils by stabilization/solidification. Water Air Soil Pollut. 133, 253–263.

Catàleg de Residus de Catalunya, 1995. Generalitat de Catalunya Departament de Medi Ambient. Junta de Residus, Barcelona (in Catalan).

Chimenos, J.M., Fernández, A.I., Segarra, M., Fernández, M.A., Espiell, F., 2000. Utilización de Magnesia para la estabilización de tierras contaminadas. Revista Técnica Residuos 55, 69–72 (in Spanish).

Conner, J.R., 1990. Chemical Fixation and Solidification of Hazardous Wastes. Van Nostrand Reinhold, New York.

DIN 38414-S4, 1984. German Standard Procedure for Water, Wastewater and Sludge Analysis, Sludge and Sediments (Group S). Determination of Water Leachability. Benthe-Vertrieb Gmbh, Berlin and Köln, Germany.

Hamon, R.E., McLaughlin, M.J., Cozens, G., 2002. Mechanisms of attenuation of metal availability in in situ remediation treatments. Environ. Sci. Technol. 36, 3991–3996.

Hettiarachchi, G.M., Pierzynski, G.M., Ransom, M.D., 2000. In situ stabilization of soil lead using phosphorus and manganese oxide. Environ. Sci. Technol. 34, 4614–4619.

Holden, T., Newton, J., Sylvestri, P., Diaz, M., Baker, C., Hermann, J.G., Guzman, D., 1989. How to Select Hazardous Waste Treatment Technologies for Soils and Sludges. Noyes Data Corp., Park Ridge, NJ.

Ma, Q.Y., Traina, S.J., Logan, T.J., Ryan, J.A., 1993. In situ lead immobilization by apatite. Environ. Sci. Technol. 27, 1803–1810.

Ma, Q.Y., 1994. Effects of aqueous Al, Cd, Cu, Fe(II), Ni and Zn on Pb immobilization by hydroxyapatite. Environ. Sci. Technol. 28, 1219–1228.

Majid, A., Argue, S., 2001. Remediation of heavy metal contaminated solid waste using agglomeration techniques. Miner. Eng. 14, 1513–1525.

Petit, M.D., Rucandio, M.I., 1999. Sequential extractions for determination of cadmium distribution in coal fly ash, soil and sediment samples. Anal. Chim. Acta 401, 283291.

Smith, C., 1993. Method and mixture for treating electric arc furnace dust. US Patent 5,242,122.

Smith, C., 1996. Buffering of cementations hazardous waste compositions containing electric arc furnace dust. US Patent 5,569,152.

Teringo III, J., 1987. Magnesium hydroxide reduces sludge/improves filtering. Pollut. Eng. 19, 78–83.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–851.

Wang, Y.M., Chen, T.C., Yeh, K.J., Shue, M.F., 2001. Stabilization of an elevated heavy metal contaminated site. J. Hazard Mater. B 88, 63–74.

Welp, G., Brümmer, G.W., 1999. Adsorption and solubility of ten metals in soil samples of different composition. J. Plant Nutr. Soil Sci. 162, 155–161.