

STATE OF PRACTICE REPORT UK STABILISATION/SOLIDIFICATION TREATMENT AND REMEDIATION - PART V: LONG-TERM PERFORMANCE AND ENVIRONMENTAL IMPACT

ASR Perera^a, A Al-Tabbaa^a, JM Reid^b and D Johnson^c

^aDepartment of Engineering, University of Cambridge, Cambridge, UK

^bViridis, Berkshire, UK, ^cS/S Remediation Consultancy, Nottingham, UK

INTRODUCTION

Treatment techniques such as stabilisation/solidification (S/S) are becoming increasingly important in the waste and contaminated land sectors with increasing awareness of the environmental impact arising from these activities and resulting materials. The application of S/S, for the immobilisation of contaminants by the addition of cement-based additives has been widely practised for many years, and has been generally used successfully, although some contaminants are known to pose problems in treatment (Conner, 1990). However, most of this success is based on results of treatability studies, which are normally conducted over short time periods, typically up to 28 days after treatment. As a result, concerns regarding the long-term effectiveness of the technique have regularly been raised in recent years (Conner, 1990; Borns, 1997; Glasser, 1997; Loxham et al., 1997). These concerns are due to (i) the uncertainties in test methods, (ii) observed deficiencies in the process application, (iii) observed lack of chemical binding in crushed samples of treated waste, suggesting that contaminants could leach out under certain conditions and (iv) uncertainties of performance arising from anticipated behavioural degradation of the material over time.

Degradation, however, ranges between two extremes: complete release of the contaminant in a relatively short time period and a gradual release over a long period of time. It is highly likely that degradation of S/S materials is possible as nothing lasts forever. Degradation with complete release of the contaminant in a relatively short time period is clearly not acceptable and such catastrophic failure is unlikely. However, a gradual release of some contaminants over a long period of time is more likely, and where the level of contaminant release at any time does not represent a significant risk it will satisfy remediation objectives.

These uncertainties can best be quantified by obtaining real-time long-term data. However, despite the widespread use of S/S techniques, evidence of validation in the long-term is still very limited and there is still no direct evidence of time-related material performance in the field (Kirk, 1996). Validation of the long-term effectiveness of any contaminated ground and waste treatment methodology is essential for its success and in the assessment of its sustainability.

In addition to the provision of data on long-term behaviour, prediction of this behaviour at the design

stage is vital and hence the need for the formulation of predictive methods; experimentally this means the development of methods for predicting the ageing of immobilised materials. Very limited work is available on such methods at present.

Hence, this report outlines the range of degradation mechanisms which could take place over time and which could lead to concerns over the long-term performance of S/S materials. Mechanisms directly related to S/S materials are presented first. This is then followed by degradation mechanisms of related materials. These are materials with similarities to S/S materials because they contain the same binders, they contain the same parent material being treated and/or they have similar consistency of the end product. These include concrete, soils and rocks and stabilised uncontaminated soils for ground improvement purposes. The report then describes a range of methods by which the long-term performance could be assessed, outlining real-time case studies of long-term behaviour work and studies on accelerated tests and accelerated ageing.

ENVIRONMENTAL IMPACT OF S/S MATERIALS

The main concern about the long-term behaviour of S/S treated material is based on the environmental impact that would occur should a treated material fail in terms of its requirements in the future. The time frame could be as short as the onset of the treatment application if the treatment was not performed in accordance with treatability studies, in other words from errors arising due to lack of care. But generally, barring external factors whose influence should be minimised, failure will be based on the dominant deterioration mechanism(s) prevailing at the service exposure (location) and pH conditions of the system. The time involved would then depend on the mechanism and rate, and also on the treated material itself and could vary from a few months to several years. Conner (1990) suggests that the resulting environmental impact will be closely related to the disposal site or situation. These would include all landfills and re-use scenarios of both treated contaminated ground and waste. The environmental impact due to deterioration of the material could arise in the form of vapour and particulate emissions, generation of leachates and/or compromise of the physical integrity of the material. The impact itself will be based on the pathway and receptor, and any other indirect consequences that may arise. Pathways of interest would

include air, groundwater and surface waters, and receptors would include humans, aquatic life and vegetation.

Hence criteria to be met by treated S/S material are now generally based on the probabilistic risk associated with the receptors including groundwater. For landfills the European Landfill Directive (Council Directive 1999/31/EC, 1999), adopted in the UK as The Landfill (England and Wales) Regulations, will set out acceptance criteria based on the type of landfill, as landfills are engineered to accept material with certain classified levels of contamination. In other management cases the assessment will normally be on a site-specific basis. The guidelines and models available to carry out risk assessment were outlined in an earlier report (Perera et al., 2004).

Although it is hoped that the treated material would maintain its stability by meeting the set criteria and hence maintain an acceptable level of environmental exposure, it is necessary to ensure that proper mitigating measures have been considered to cope in cases of failure of the system.

Although this report mainly refers to environmental impact based on failure of the S/S material, it should be noted that in most cases the impact on the environment occurs at a much earlier time. This could be as early as when the decision is made to conduct S/S treatment and the waste is being transported for treatment or mixed in the ground. Evans et al. (2001) suggested that the impact could include fugitive vapour and particulate emissions, generation of leachate/bleed water, runoff of liquid from equipment washing, noise, impact on local groundwater flow regime and impact on groundwater chemistry. Another impact as a result of S/S treatment would be the potential volume change that might occur as a result of the addition of binders to treat a given volume of waste or contaminated soil.

DEGRADATION MECHANISMS

(i) Degradation Mechanisms of S/S Treated Materials

General overview

Several degradation mechanisms exist that could affect the long-term performance of a S/S material once it is disposed of or utilised. Hence, it is vital to identify and understand these potentially destructive mechanisms, which may be physical, chemical or biological in action. These could be broadly classified as intrinsic or extrinsic actions. Intrinsic actions are as a result of poor workmanship, poor design, reactions between waste components and binders, and reactions between different waste components. Extrinsic actions, which include physical and chemical weathering, mechanical damage, biological attack and attack by aggressive water, are as a result of the final exposed environment.

The reasons for poor design and workmanship need to be understood and overcome at the beginning of the work schedule. Otherwise this would directly or indirectly lead to the failure of the system. Directly this would mean delayed setting, reduced strength or non-uniform strength due to inadequate mixing, higher porosity, higher leaching etc. Indirectly failure would result in higher leaching of contaminants due to higher porosity, improper mixing, improper fixation etc.

Poor design could be overcome by conducting treatability studies encompassing the binders and contaminants involved in the study and the quantity of water used. Although these are conducted over a short time scale, if performed properly they are sufficient to understand the initial behaviour of the mixes and eliminate the adversities that could occur by ad-hoc use of a design. When involving cement, Board et al. (2000a) stated that a key factor controlling the physical characteristic of a hardened cement paste is the water:cement (w/c) ratio, as the initial starting w/c ratio controls the eventual porosity and strength of the hardened cement. Means et al. (1995) considered that a w/c ratio of greater than 0.48 is detrimental to the final porosity and strength of S/S material. However, this is not as straightforward as it appears as nowadays other binders are also being used alone or alongside cement in the mix and hence the suitable water:binder (w/b) ratio will vary accordingly.

Poor workmanship can be overcome by conducting trial mixes adopting similar conditions to what the actual mixes would undergo and understanding where the problem exists. Some probable reasons could include the mixing technique, where the service conditions are different to trial mixing conditions, improper mixing due to insufficient water and lack of care on the part of the workers. The adoption of suitable quality control procedures will greatly reduce the potential for poor workmanship.

Binder-contaminant interactions

The purpose of mixing contaminants with binders is to stabilise and/or solidify the contaminants by immobilising them with the binders. Generally the main consequence of the presence of contaminants is to alter the properties of the fresh or hardened binders. This is mainly in the form of delayed setting and hydration, and results in lower strengths in relation to the uncontaminated binders. Akther et al. (1997) stated that the presence of inorganic and organic contaminants often has a deleterious effect on the hydration of Portland cement. However, provided these effects are within controllable/acceptable limits, the fact that contaminants are immobilised within the binders by various mechanisms as they undergo hydration and their leaching potential being reduced, provide the means of treatment which is required for the final service environment. It should however be stated that not all interactions are destructive and some contaminants actually enhance the properties, especially strength, of binders.

As mentioned above, when considering S/S materials, attention has to be given to the contaminant

immobilisation potential of the binders. This understanding is important, as changes that occur to S/S materials (with regard to both the binder and the contaminants) over time will influence the contaminant solubility properties and release rates, and also the physical integrity of the material. Although there is a lack of knowledge in this area, it is agreed that an understanding is required of the binder characteristic variations over time due to interaction with contaminants and also due to cement replacement and extended materials. The contaminant properties may also change (Conner, 1990) and the altered contaminants may then have a different effect on the binder system.

Thus, the overall S/S system chemistry involved could be complex and is made even more complicated when the system has to be considered within its dynamic disposal environment, which would also have an influence on the immobilisation potential of the contaminants. Hence as a first step to develop this understanding, it is necessary to first consider the chemical features, which control the chemical immobilisation potential of binders and in particular cements due to contaminant-binder interactions. Glasser (1993) set out the chemical immobilisation potential of cements as:

- a) Absorption of ion into, and adsorption on, high surface area CSH.
- b) Precipitation of insoluble hydroxides, owing to high alkalinity.
- c) Lattice incorporation into crystalline components of set cements.
- d) Development of hydrous silicates, basic calcium-containing salts, etc. which become solubility-limiting phases.

The chemical features of cement matrices which promote or inhibit these immobilisation processes include internal pH, internal redox potential, sorption potential, precipitation and crystallochemical incorporation (Glasser, 1993).

Internal pH control

pH control is normally considered with respect to contaminant (metal) fixation. This is because it is widely accepted that in cement-based materials containment relies heavily on the pH (Conner, 1990). Although this is mainly true for metals, it has also been shown to affect the leachability of other inorganic and organic species (Conner, 1990). The relationship of pH with metal fixation is based on the metal's solubility. Ideally it is desirable to have a high pH in the system, in the presence of diffusion and leaching, as most metals have minimum solubility in the range of pH 7.5 – 11. Cement-based materials in a closed system would generally yield a high pH of above 11, due to the coexistence of Ca(OH)_2 and CSH, and would also buffer the pH. Hence when diffusion and leaching occur, although the pH would reduce, it would generally drop to within the desirable minimum solubility range. However, other factors could have an influence on the pH of the system, which might alter the benefits offered. These factors are given by Glasser (1993) as:

- a) Presence of additional components known to be in cements, such as alkalis, alumina and iron oxides.
- b) Content of supplementary cementitious materials, such as fly ash, slag etc., whose reactions would remove Ca(OH)_2 and change the bulk Ca:Si ratio of the system.
- c) Environmentally conditioned reactions leading to degradation of cement performance.

The third factor is directly related to long-term, but the first two may also have effects which develop over time.

Internal redox potential (E_h)

A change in the internal redox potential would lead to a variation in the speciation and solubility of contaminants. The most favourable conditions for immobilisation of contaminants are perceived to lie in achieving a low E_h , as the multivalent metals can be chemically reduced in high pH environments to lower-valent, less soluble species (Glasser, 1993). Even some metals, such as Ag, Cu, Cd and Zn, with only one valence state are reported to be strongly influenced by redox processes (Dragun, 1988). Cement is beneficial as a binder in this respect as it generally has a low E_h in addition to its high pH. But due to various influences from the incorporated material and the external environment, E_h could change over time and this change could influence the immobilisation potential. However, as illustrated by Conner (1990) the benefits of low E_h are not always true especially where some contaminants when reduced may become toxic or more soluble. Hence this implies that some benefit may actually be achieved, depending on the contaminants present in the treated waste, with E_h increasing over time.

Sorption potential

This has an important role in the immobilisation of contaminants, as they are adsorbed or chemisorbed onto other materials in the system. The potential for sorption is directly related to large specific area, which in turn is a function of particle size, shape and porosity (Conner, 1990), and in CSH also to the high density of irregular hydrogen bonding (Glasser, 1993). The sorption will depend on various factors such as the pH of the system, concentration and type of species, and in cement-based systems on the surface charge of CSH, which changes with its composition. The sorption potential would also increase in S/S materials containing sorptive materials such as clays or zeolites. However, this process could be reversed/changed, more so in adsorption than chemisorption, due to various influences including changes to the factors influencing sorption. This would mean that over time contaminants held could be released due to changes in the system affecting the performance of the S/S materials with time.

Precipitation

Precipitation of metals present in contaminants would most commonly occur in the form of hydroxide precipitation. Other forms of significance in which metals would precipitate are carbonates, sulphides, silicates, sulfates and complexes. Coprecipitation with other metal species is also a possibility which should not be ignored. The problem posed by this is that the reactions are difficult to characterise (Glasser, 1993). Although some are stable, changes to the system composition over time might create competition between species and as a result

some metals will be released into solution compromising the immobilisation potential. However, precipitation of certain species may occur only after some time when the desired pH is reached and this might actually improve the immobilisation of that species with time.

Crystallochemical incorporation

Depending on the formulation of the cement-based binder system, different crystalline phases will be present at different curing durations. This would also vary based on the disposal environment. These crystalline phases would incorporate contaminants into their matrix, generally on a preferential basis. This would hence immobilise these contaminants, but only as long as the relevant phase exists. However, as the phase balance changes with time the contaminants which have not consequently been taken up by other phases will be released compromising the performance of the S/S materials.

In addition to the above mechanisms macro-encapsulation of contaminants could also occur (Conner, 1990). This is where contaminants are physically entrapped in the discontinuous pores within the larger structural matrix of the solidified material. Hence the immobilisation is mainly dependent on the physical integrity of the S/S material. Deterioration of the material with time would enable the contaminants held to leach out.

Binder-contaminant interference

The above section considered the chemical features which promote or inhibit the immobilisation of contaminants within cement which could develop over time. Although these mechanisms exist to capture the contaminants, the presence of the contaminants, as mentioned earlier, could alter the normal behaviour of the binders. These binder-contaminant effects due to individual contaminant elements and compounds, which could arise in the short-term or long-term, are not well understood. Further, the problem is made more complex when the effect is also concentration dependent, when several contaminants are present, as sometimes their effects are additive or synergistic, and when the contaminants change form after reacting with other compounds.

Numerous studies have been conducted to understand these various effects, but they are few in comparison to the possible combinations that could exist in relation to the contaminant variables mentioned above and binder types in use. Further, most of the studies have been limited to short-term investigations. Conner (1990) conducted a comprehensive review on the effects certain individual compounds have on the setting and curing behaviour of cement-based S/S materials. It considered individual inorganic and organic contaminant compounds. An example of these is summarised in Table 1. The general consensus is that although both organic and inorganic contaminants have been treated by S/S, organic contaminants are more difficult to treat than inorganic ones.

The consequences of interference could be insufficient development of strength, changes in porosity and permeability and reduction in durability, which could lead to the S/S material being considered to have failed under the stipulated physical and chemical parameters. However, not all interferences should be considered as having negative effects. For example it was shown in a study by Bhatti and West (1996), that although lead markedly decreased the early strength (3 day) as a consequence of it retarding the cement hydration, it did not affect the 90-day strength. However, although zinc also showed similar characteristics (Tashiro et al., 1977; Ortega et al., 1989), it was found to increase the permeability of the hardened cement product, probably by promoting ettringite formulation (Poon et al., 1985; Poon et al., 1986).

It is also important to bear in mind that a number of other cementitious and non-cementitious agents are used in S/S. The behaviour of these agents may be significantly different from that of cement.

(ii) Degradation Mechanisms of Concrete

When considering the durability of concrete, emphasis is generally placed on compressive strength. This is usually achieved by specifying the minimum cement content and maximum water:cement (w/c) ratio. However, it is stated (Eglinton, 1998) that it is the development of cements with increased chemical resistance and the quality of the concrete which are primarily important in resisting damage. It is further stated that quality need not necessarily be related to strength. Thus, whilst strength will be a factor affecting durability other factors such as permeability, porosity and transport mechanisms will also play a key role. However, it must be stated that some of the above factors are interrelated and also that the materials utilised in the mix have a direct influence on these properties.

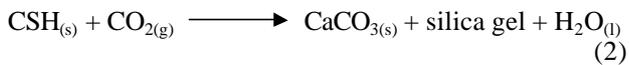
The principal forms of attack on concrete have been categorised in Hills et al. (2004), under the two headings of primary and secondary degradation mechanisms. These are briefly outlined below. The mechanisms themselves are also described by others e.g. Neville (1997), Taylor (1997) and Lea (1998).

Primary degradation mechanisms:

Carbonation:

This is simply the process where carbon dioxide reacts with the hydrated products of cement-based materials. It is a naturally occurring, essentially slow post-hydration, process, which in the presence of moisture utilises the carbon dioxide concentrations in the atmosphere ranging from 0.03-0.04%. It mainly involves the chief hydration products calcium silicate hydrate (CSH) and calcium hydroxide ($\text{Ca}(\text{OH})_2$), which are converted to calcium carbonate (CaCO_3). The pH of the pore fluid will also reduce due to carbonation. Papadakis et al. (1992) and Shah and Hookham (1998) amongst others suggest that the pH value would reduce to 8.3 in regions where all the available alkali hydroxide has reacted. These reactions involving cement and carbon dioxide are well

documented (Reardon et al., 1989; Dewaele et al., 1991; Sarott et al., 1992) with the principal reactions being as shown in equations (1) and (2). This process is controlled by the diffusion of CO₂ into the cementitious material generally over a long time.



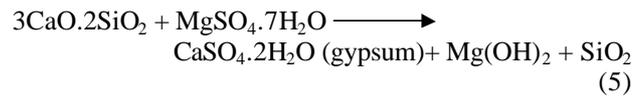
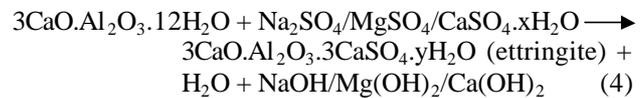
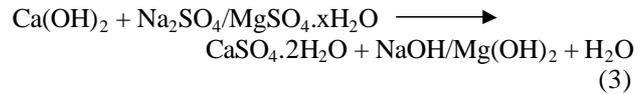
The rate at which carbonation will occur depends on the influence of many factors. These include diffusivity of CO₂ and its concentration, moisture content in the material, relative humidity of the surrounding atmosphere, permeability of the material which depends on the water to cement (w/c) ratio and the level of compaction, the binder(s) used, the degree of hydration (Neville, 1997) and also temperature (Walker, 2002). Other environments also exist in which carbonation could take place. These are in natural waters whose pH is generally about 5.7 and ground water, which could be more acidic and could have a pH as low as 3.8 (Eglinton, 1998).

Carbonation by itself does not cause deterioration of the material but can have important effects on the microstructure (Neville, 1997). These include volume changes, which cause cracking and increased permeability, and softening of the cement paste, all of which potentially lower the strength. In contrast higher strengths are obtained by the lowering of permeability due to precipitation of CaCO₃ in the pore spaces. Which effect prevails will depend on the circumstances of each situation. The lowering of the pH of pore fluids leads to the depassivation of any reinforcement (i.e. corrosion of reinforcement) present in concrete (Lea, 1998). This has led to the common belief that carbonation is deleterious to concrete products, which in this context is only relevant to S/S materials if used within reinforced concrete. However, carbonation as a result of the reduction in pH of the pore fluids could make any present heavy metals more soluble and this could lead to unacceptable levels of contaminant leaching into the environment.

Sulfate attack:

This is the process where naturally occurring sulfates or sulfates present in the binder material (e.g. gypsum), which are in solution, chemically react with compounds present in set cement-based material. Although all soluble sulfates have a deleterious effect on Portland cement (PC), the mechanism and severity of attack will vary according to the base present (Eglinton, 1998). Generally it is the sulfates of sodium and magnesium which are considered as the active salts for sulfate attack (Neville, 1997). Calcium sulfate is also considered as it may also exist initially, or be formed as the secondary step of the reaction of sodium or magnesium sulfate and contribute to the attack. The principal reactions are shown in equations (3) to (5). Magnesium sulfate has a more far-reaching action than the other sulfates and can additionally decompose the hydrated calcium silicates (Neville, 1997; Eglinton, 1998) and this is shown by

equation (5). This reaction can proceed further over a long period of time to form a hydrated magnesium silicate which appears to have no binding power and it can also cause the destruction of CSH (Neville, 1997; Eglinton, 1998).



This process is controlled by diffusion in saturated pore conditions and by capillary suction in dry pore conditions (Hilsdorf, 1995). The rate and amount of deterioration due to sulfate attack will depend on factors such as concentration and type of sulfate, amount of calcium hydroxide and calcium aluminate, cement content, water/cement ratio, porosity and permeability, and acidic conditions.

Sulfate attack will cause expansion, cracking or spalling or softening and disintegration. The expansion which is as a result of the increase in the solid volume is caused by the conversion of calcium hydroxide to gypsum (Eglinton, 1998) and then also by the conversion of the hydrated calcium aluminate with gypsum to calcium sulfoaluminate (Eglinton, 1998; Shah and Hookham 1998). The softening and disintegration is specifically due to the attack by magnesium sulfate as mentioned earlier and leads to strength loss and cracking.

The thaumasite form of sulfate attack could occur with the production of the non-binding calcium carbonate silicate sulfate hydrate (thaumasite). This formation is a possibility in the presence of sulfate and carbonate when there is high humidity and low temperature conditions (St. John et al., 1998; BRE, 2001; Marsh, 2002).

Portland cement is susceptible to sulfate attack and over time cements such as sulfate-resisting Portland, pozzolanic and Portland blastfurnace cements have been produced to minimise the attack. These have been achieved mainly with the change in composition of the cementitious material. Although these cements have a higher resistance, they are not immune to sulfate attack in all situations and at all concentrations of sulfate in solution (Eglinton, 1998). However, it should also be noted that sulfates are frequently associated with acidic ground conditions and hence even when sulfates may not affect S/S materials directly, acids might.

Guidance on concrete in aggressive ground is given in BRE Special Digest 1 (BRE, 2001). Guidance on protecting S/S materials from sulfate attack in earthworks applications is given in the Highways Advice Note 74/00 (DMRB 4.1.6) and limiting values for sulfur compounds in earthworks applications are given in the Specification

for Highway Works (MCHW 1). The presence of reduced sulfur compounds, such as pyrite, as well as soluble sulfates has to be taken into account (Reid et al., 2001). Providing the existing guidance is adhered to and appropriate testing undertaken, sulfate attack should not be a problem for S/S materials.

Chloride attack:

Primarily, although not important from the point of view of S/S material, chloride attack is the process which causes corrosion of reinforcement in concrete. Other processes include the interaction of chloride ions with hydration products. Chlorides may be present in concrete either because they have been incorporated in the mixture, due to use of contaminated material, seawater or brackish water, or because of chloride ion ingress from outside, due to exposure to de-icing salts, seawater or brackish groundwater. It is the ingress of chloride ions which is usually expected to contribute to the problem of chloride attack (Neville, 1997). The penetration of chloride ions occurs by transport of water containing chloride, by the diffusion of ions in the water and by absorption (Neville, 1997). The factors that influence the ingress of chloride ions include cycles of wetting and drying, concentration of the chloride ions and other ions, permeability and porosity, and the pH of the pore water.

Chloride attack as mentioned earlier causes corrosion of the reinforcement and the expansion produced by rust causes the surrounding material to crack and spall (Taylor, 1997). Also the interaction between chloride ions and hydrated products is thought to contribute to frost damage through the expansive precipitation of chloride salts (Hills et al., 2004).

A study by Page et al. (1986) showed that the binding and diffusivity of chloride ions play an important role in controlling chloride-induced corrosion. The main forms of binding of chloride ions are by reaction with the tricalcium aluminate and tetracalcium aluminoferrite, which result in the formation of calcium chloroaluminate and calcium chloroferrite respectively (Neville, 1997). Hence this implies that materials with higher quantities of tricalcium aluminate will reduce chloride attack but unfortunately these then could be susceptible to sulfate attack.

Alkali-Aggregate reaction:

This is the process where hydroxyl ions in the pore solution react with minerals in the aggregate. The most important reaction is the alkali-silicate reaction (ASR). The alkaline hydroxides are derived from sodium and potassium alkalis in the pore solution where cement is the main source for the alkalis and the reactive forms of silica include opal, chalcedony and tridymite. The ASR occurs only in the presence of water and calcium ions, and results in an alkali-silicate gel being formed in planes of weakness, in the aggregate pores or on the aggregate surface (Taylor, 1997; Neville, 1997). The gel formation is similar to that of a pozzolanic reaction, but as this happens in an environment poor in calcium ions in relation to the rate of gel formation, the gels persist for long periods without being converted to CSH, unlike in what takes place in a pozzolanic reaction (Taylor, 1997).

The factors that influence the rate at which the reaction proceeds include presence of water and calcium ions, presence of other ions, humidity, pH, permeability, availability of alkali and silicate, size of the siliceous particles (Diamond and Thaulow, 1974) and temperature. Depending on these factors the process could take from a few months to as long as a few years. The gel absorbs water and swells, but as the gel is confined it exerts pressure on the surrounding material and as a result causes expansion, cracking and disruption of the hydrated cement paste (Neville, 1997).

The best approach to prevent ASR is to remove the main variables which cause the reaction to take place. The types of aggregate that are susceptible to ASR are well known and are listed in standards and guidance documents, and should be avoided for S/S materials. Also, drying out the S/S material and eliminating calcium ions, alkalis and silica may help. In practice it is possible to dry out the material and to maintain its dryness thereafter, which has been suggested as the only means of stopping ASR (Neville, 1997) and/or lowering the pH. The other variables are made available from the material itself hence it is not practically possible eliminate them. However, it is possible to reduce the consequences of ASR by reducing contributing materials such as silica, with the exception of microsilica which may be good at reducing ASR. Also reducing the permeability reduces the movement of the aggressive agents, and pozzolanas and ground granulated blastfurnace slag help to reduce permeability.

Secondary degradation mechanisms:

Damage due to freeze/thaw cycles:

This is the process where water in the pores freezes as the temperature drops and then thaws with subsequent increase in temperature. In service this is a cyclic process and it intensifies the damage caused to the material. As it is related to the freezing of water in pores, water is essential for the mechanism to proceed. Hence this action takes place mainly within the hardened cement paste and not in the larger voids, as these are usually air-filled (Powers, 1956). Various theories exist for frost damage. Earlier theories associated damage directly with the volume expansion that occurs on freezing, which is based on the fact that the space available is insufficient to accommodate this additional volume (Taylor, 1997; Eglinton, 1998). The damage was also attributed to the development of pressure due to the growth of ice lenses parallel to the surface caused by the migration of water from capillaries (Taylor, 1997). Some such as Powers (1945) attributed the damage to the development of water pressure within the capillaries as ice crystals grow. Osmotic pressure arising also causes water to move within capillaries and this too aids in frost damage.

The factors that influence the damage include amount of freezable water, exposure conditions, pore size and porosity in addition to permeability, rate of absorption and degree of saturation. The damage due to frost action is generally first observed as a flaking of the surface which then gradually moves inwards, although deep

fissures/cracks may occur, especially in poor concrete (Taylor, 1997; Eglinton, 1998). The worst conditions for frost action occur when the surface area exposed to the weather is large and remains wet for long periods (Eglinton, 1998).

The basic requirement for resisting frost damage is for the material to be of low permeability and absorption. It also needs the material to be of good quality. Other forms of protection are burial of material below the depth of frost penetration and air entrainment. In the UK, it is generally agreed that the depth is 1 metre owing to the insulation properties of soil.

Damage due to wet/dry cycles:

This is the process where the material is subjected to wet and dry exposure conditions. This may occur as a result of fluctuating water table, or penetration of rainwater or floodwater. Here too the effect is more pronounced when the process is cyclic. Damage is in the form of cracking caused by the expansion of constituents in the material. The expansion is caused by the absorption of water by the cement gels and other absorbing material in the cement-based material resulting in the water molecules acting against the cohesive forces to force the particles further apart. Further, the movement of water into the material reduces the surface tension of the gel and this allows a smaller expansion to occur (Powers, 1959).

This action could be remedied by having a low permeability, high quality material and by preventing exposure to water.

Shrinkage:

This is the process whereby the material reduces in volume. It could happen due to various reasons and at different stages in the life of a material in which the water moves out of the pores. Some of the types of shrinkage are considered below.

Plastic shrinkage: shrinkage due to water loss caused by evaporation or suction by adjacent dry material such as soil (L'Hermite, 1960) when the material is still in the plastic state. This begins at the surface.

Drying shrinkage: shrinkage due to withdrawal of water from set material exposed to unsaturated air. The removal of absorbed water is the significant component in relation to the removal of free water. Part of this movement is reversible when exposed to water, but there is a component which will not be recovered. This could occur over a long period of time (Neville, 1997).

Carbonation shrinkage: shrinkage due to the breakdown of hydroxyl ions or removal of combined water, in the presence of carbon dioxide, from solid areas in the hydrated cement and replacing them with carbonate ions in spaces free from stress (Neville, 1997; Lawrence, 1998). This temporarily increases the compressibility of the material allowing shrinkage to occur.

In the above types, the amount of shrinkage will depend on the amount of water available for withdrawal and the duration over which it happens, and other factors such as

temperature, humidity, exposure conditions, permeability, porosity and material shape and size. However, for carbonation shrinkage the issues with water are not directly significant. The magnitude of drying shrinkage is independent of the rate of drying, except under extreme ranges (Neville, 1997). A situation of extreme ranges is when the material is transferred directly from water to be exposed to a very low humidity environment.

The problem associated with shrinkage is that it leads to the development of cracks and under extreme conditions, as mentioned above, can lead to more pronounced fracture as it does not allow relief of stress by creep (Neville, 1997).

Shrinkage could be minimised by controlling the w/c ratio, which would also control the strength and hence the cracking, and by controlling the other factors mentioned earlier. Use of expansive cements to compensate for shrinkage could also be adopted, but these do not prevent the development of shrinkage. Also including aggregates in the material reduces shrinkage, but the amount of reduction will depend on the type and amount of aggregates in the material. Prolonged curing only delays the advent of shrinkage and in fact well-cured concrete is said to shrink faster (Neville, 1962).

Settlement:

This is the process where the material settles under its own weight or external load. This is generally applicable to fresh concrete and it is the differential settlement that is of main concern. Differential settlement can occur as a result of some obstruction such as large particles of aggregate. The settlement in fresh concrete, termed 'plastic' settlement, generally leads to cracking on the surface. This can be overcome by the use of a dry mix, good compaction and by not allowing a rapid build-up of the material (Neville, 1997) used in the S/S process.

Radiation damage:

This is mainly due to a rise in temperature as the absorbed energy of radiation is converted to heat. The greatest amount of heat is generated in the part of the concrete closest to the source of radiation. The failure mechanism then proceeds as for fire damage. Another aspect of concern with regard to this damage is that harmful radiation can affect the microstructure of cement at the molecular level (such as breakage of Si-O bonds), in the same way that radiation affects human tissue.

Fire damage:

This is the process by which materials exposed to high temperatures break down due to the stresses developed. As temperature increases, starting initially from the surface, the material starts to expand, but at temperatures greater than about 300°C the cement starts to contract due to water loss. However, aggregates continue to expand. These two opposing actions progressively weaken the material due to the build up of the resultant stresses. This results in loss of strength, spalling and cracking. A further consequence is that a material that has withstood a fire if subjected to wetting or moist air after cooling may expand and crack due to rehydration of calcium

oxides (as a result of the fire) to calcium hydroxide (Taylor, 1997; Eglinton, 1998). Further, extensive carbonation is also said to occur in fire-damaged material when left exposed for a few years (Taylor, 1997).

The duration of exposure to heat plays a vital role in resisting damage. This is because when subjected to longer exposure the damage could originate at a lower temperature and also the damage may progress more into the material.

The aggregates themselves will behave differently upon heating. For example, blastfurnace slag is shown to be highly resistant to fire exposure (Eglinton, 1998).

(iii) Degradation Mechanisms of Stabilised Uncontaminated Soils

Various binders, especially cement and lime, have been used for the improvement of uncontaminated soils. This is usually quantified in terms of increased strength and reduced settlement potential. Hence, changes in mechanical, physical or chemical characteristics of such improved soils in the long-term could have correlations to those of S/S materials when the same binders are used and similar material consistencies are produced.

Most of the factors relating to binders were outlined in the earlier section under concrete.

Although several studies have been carried out on soil-cement mixes it seems that only two aspects of real-time long-term change have been considered namely strength increase with time and possible strength decrease with time due to deterioration. Kujala et al. (1985) and references cited in Terashi (2003) are amongst many who reported long-term strength increase of soil-cement mixes. On the other hand only a few such as Shihata and Baghdadi (2001), Kitazume et al. (2003) and Hayashi et al. (2003) reported the possibility of long-term deterioration. The deterioration mentioned by these references seems to be mainly related to the surrounding environment and caused by the leaching of calcium from the treated material to the untreated material (surrounding soil environment usually). This phenomenon occurs as a result of the free lime initially present in the mix and thereafter due to the degradation of the main cementing products. The aggressiveness of the permeant and its pH is expected to influence the timing of these processes.

Kitazume et al. (2003) conducted laboratory studies and showed generally that the deterioration, when measured in terms of penetration resistance, begins at the boundaries and then progresses inwards over time. A similar trend is seen in the calcium dissolution. Hence the deterioration was seen to be dependant on the surrounding environment, although the exposure environments had varying rates of influence, with some showing negligible influence. Hayashi et al. (2003) conducted field investigations on 17-year old deep mixed columns and reported that although leaching of calcium took place from the treated columns to the untreated surrounding soils, the extent and magnitude of strength reduction at the outer edges of the columns was very

small. However, the strength in the central portion increased with time, confirming that it is the outer region which is generally prone to deterioration. Some numerical analysis has also been undertaken by Nishida et al. (2003) as part of their study on the 17-year soil cement column. Here they show that the related changes in Ca/Si mole ratio, or void ratio, to calcium leaching can be expressed by numerical analysis using ion migration and calcium leaching models.

In a similar manner, Sherwood (1993) outlined the chief factors that affect the strength of lime and cement stabilised soils. These were the chemical and physical composition of the soil and the subsequent external environment. The latter is mainly influenced by temperature and moisture conditions of the surroundings. He categorised the soil constituents as inert, beneficial and deleterious based on the chemical effect they will have on the stabilised soils. He included organic matter, sulfates, sulfides and carbon dioxide under deleterious constituents. The physical composition was considered based on how it affected the degree of compaction achieved, moisture content required, ease of mixing the soil with the stabiliser and the stabiliser content required to give the desired strength.

The majority of the work in the UK involving lime has been related to road networks. Biczysko (1996) reported on the long-term performance of lime stabilised road subgrade constructed in the early 1980s. This long-term investigation was able to confirm the durability and effective service of the lime stabilised subgrade. Longer term proof of performance is available in other countries (Greaves, 1996). In this respect Kelley (1977) reviewed the use of the soil stabilisation process at numerous sites in the USA between 1940 and 1960, and found that these sites performed well over a 25-30 year period with minimal maintenance.

(iv) Degradation Mechanisms of Rock and Soil

Unlike concrete, there is principally only one main degradation mechanism in rock and soil and this is weathering. Weathering in this case could be described as the process by which the material is broken down due to external factors such as rain, frost, wind, temperature, plants and organisms. Based on this explanation weathering could be considered under three categories, viz. physical, chemical and biological. In addition to external factors, the degree to which weathering would occur is also dependent on the material's intrinsic properties, including the stability of the minerals present under the current environmental conditions (Hills et al., 2004).

Weathering reactions only occur where materials are exposed to the atmosphere for prolonged periods. In most cases, S/S materials will be designed to be protected from the elements, and hence should not be subjected to the processes that affect rocks and soils. These processes would only be relevant if the materials were not designed properly or were exposed in the long-term in an uncontrolled fashion.

Physical weathering:

This is also termed mechanical weathering or disintegration and is the process of breakdown of rocks without a considerable change to their mineralogy due to the action of temperature, impact from raindrops and abrasion from mineral particles carried by the wind. Hence the net effect is particle size reduction, increased surface area and unchanged chemical composition. The various processes involved can be categorised as mechanical unloading/loading, thermal loading, wetting and drying, crystallisation and pneumatic loading (Blyth and de Freitas, 1984).

Mechanical unloading, as a result of erosion at the surface, will allow the rock to expand and will cause breakdown due to tension cracks, spalling and fracturing. Mechanical loading, as a result of impact and abrasion of windborne particles and raindrops, will cause breakdown by erosion, fragmentation and pitting. Freezing/thawing, due to frost action, will cause flaking, fissuring and cracking. Wetting/drying, will cause swelling and shrinkage and will lead to flaking and cracking. Heating/cooling will cause damage such as cracking and fissuring due to expansion and contraction. Crystallisation will cause damage due to expansion of pores and fissures and is most severe when salt crystal growth occurs within a confined pore space.

Chemical weathering:

This is also termed decomposition and is the process of breakdown of minerals into new compounds due to the action of chemical agents such as acid in the air, rain and river water (Blyth and de Freitas, 1984). Water is an essential factor for decomposition of materials. There are several processes involved in chemical weathering including solution, carbonation, oxidation, reduction, hydration, hydrolysis and leaching. The rate of these processes depends on the availability of water and hence is greater in wet than in dry climates.

Chemical weathering is observed most readily in its solvent action on some rocks such as limestone where calcium bicarbonate is formed due to the action of carbon dioxide in the presence of water dissolving the limestone and forming depressions. In rocks, it often results in a deep weathering profile within the mass due to the chemical processes associated with deep percolating water.

Biological weathering:

This describes mechanical and chemical changes in the material that could be directly related to the activities of animals and plants. This is considered less significant in relation to the other two, but is noticeable in aggregates. Degradation could occur in several forms. Animals burrowing into the ground and moving rock fragments and sediment, aid in the disintegration of rocks and rock fragments. Fungi and Lichens, which are acid producing micro-organisms that live on rocks and dissolve nutrients (phosphorus, calcium), assist in the breakdown and weathering of rocks. Organic products derived from plants through the action of micro-organisms aid in causing chemical decay in rock. Plant roots hasten the mechanical breakdown as they penetrate into cracks and

wedge apart the material. The damage could be minimised by attempting to keep the area of concern free of vegetation and animals.

METHODS OF ASSESSING PERFORMANCE OVER TIME

There is a need for observing and understanding the behaviour of S/S materials over time in order to assess their durability and long-term performance. This is in addition to the need to predict this behaviour so that it can be taken into account at the design stage of S/S systems. There is currently concern about the lack of evidence of validation work in the long-term both in the laboratory and in the field. Although several attempts have been made at predicting the behaviour of S/S materials, there is still considerable lack of information on the long-term behaviour. Hence there is a need for formulation and verification of predictive techniques. This could be achieved experimentally, by using accelerated tests or developing techniques for predicting the ageing of S/S material, and/or numerically by using existing tools such as neural network analysis and risk assessment tools or by developing new tools or models.

Although many degradation mechanisms have been outlined, assessment of the durability of S/S materials is generally based on a few selected properties of the material that would be affected as a result of one or a combination of those mechanisms. The studies on real-time, accelerated tests and ageing, and predictive modelling have generally concentrated on these few selected properties. The most common of these is measuring the release of contaminants in the leachate either directly or by adopting a test procedure as outlined in Perera et al. (2004) and others (WTC, 1990; Lewin et al., 1994; van der Sloot et al., 1997). The other properties of common interest would be strength (generally, the unconfined compressive strength), permeability, weathering (freeze/thaw and wet/dry) and leachate pH. However, all these tests have not been collectively adopted in many research and commercial projects, and in some instances, different properties have been determined.

It must be stated that predicting the behaviour of S/S materials, such as the rate of release of contaminants, is not straightforward. This is mainly due to the variability of the material in question, its behavioural developments over time, and the lack of comprehensive knowledge on the binder-to-binder, binder-to-contaminant and contaminant-to-contaminant interactions. The use of composite binder systems and a plethora of contaminants, which are of varying concentrations, increase the scale of the problem further. The lack of sufficient information available on the characterisation of material and service environment especially in commercial projects is also a problem when attempting to predict the long-term behaviour of S/S materials.

However, some work has been undertaken in attempting to model various behavioural modes using existing models or modified versions of models, and some of these have shown promise. Having said that most models

have considered only one or a few factors of degradation or interaction mechanisms. As none of these models has considered all the most dominant mechanisms collectively, their usefulness is limited and they are not robust. Some of these models, which are not restricted to work carried out in the UK, have been outlined in Hills et al. (2004) (Table 2). Therefore, although modelling using various techniques is useful to predict the behaviour of S/S materials based on selected properties or degradation mechanism, it still requires to be developed further prior to being accepted as a predictive tool for assessing the performance of S/S materials over time.

Another factor which hinders the process of modelling is the lack of availability of real-time data. This is required for the verification of any predictive model used. Databases of real-time data are being developed but only slowly (Atkins et al., 1992), as developing these is considered less attractive than the prospect of carrying out rapid computer-based calculations of modelling.

Real-time validation based on material properties is essential, as this is the only exact method of knowing the performance of a material over time. It also provides information for the back analysis of modelling work. However, even here the reliability of the information will depend on various factors. These include proper documentation of source material and characterisation, consistent use of a set test method regime and its procedure over all time durations of testing, consistent extraction and sample preparation procedures in the case of extracted samples and consistent curing conditions in the case of laboratory samples. Another factor that should be considered is that comparison of laboratory and field data should be performed with caution as the variability in the field is expected to be much greater than in a laboratory, which is generally under controlled conditions.

Real-Time Case Studies of Long-Term Performance

Although essential, the biggest drawback with real-time performance work is that it is a site-specific justification system and thus its success or failure is only known on a real-time basis. If it is a failure then it is a problem which needs to be rectified even though some damage would already have been caused as a result of the failure. If it is a success, which is again based on the results achieving levels of acceptance after a fair number of years of monitoring, then it could be applied with a fair degree of confidence to treat other but only very similar materials. This cautiousness is needed because of the uncertainties regarding the various interactions that could take place within materials and over time.

Several studies have been conducted to observe the behaviour of S/S materials over time. These cover studies on treatment of contaminated soil and waste. In this report only studies on S/S treated materials which include tests exceeding one year after treatment have been considered.

Artificial fishing reefs site, New York, USA

A project to investigate the environmental consequences of utilising stabilised waste blocks as construction material for artificial fishing reefs was carried out in New York, USA (Hockley and van der Sloot, 1991). A Portland cement and lime mix was used as the binder to treat a coal combustion waste, which was formed into blocks and then placed at a 40m depth in seawater. A block was retrieved after 8 years and analysed for strength, and chemical and mineralogical profiling including SEM, EDAX and XRD. Other investigations were undertaken on blocks retrieved after 18 months (van der Sloot et al., 1985) and 4 years of exposure (Woodhead et al., 1984; Parker et al., 1985; Roethel and Oakley, 1985; van der Sloot et al., 1985; Woodhead and Jacobson, 1985). Further, some blocks were placed in fresh water and analysed after 1 year's exposure (Flynn et al., 1985). It was concluded that the strength was unaffected and that the precipitation and dissolution processes moved as a sharp boundary penetrating about 10-20mm in 8 years with the leaching of minor elements being restricted to this region. It was also concluded that precipitation of non-reactive sea salts in the pores near the surface restricted diffusion (pore refinement) and that this may have minimised any degradation of the block matrix as the block exposed to freshwater for 1 year showed marked surface softening.

Douglasville, USA

A contaminated site in Douglasville, USA, was treated ex-situ using a mobile field blending unit (de Percin and Sawyer, 1991). The site was contaminated at different locations with primarily different levels of lead, oil and grease, and minor concentrations of volatile and semi-volatile organics. Six locations were selected for treatment. The soil from the designated locations was excavated, screened and treated by mixing with Portland cement and a proprietary additive (Chloronan). The additive was added to neutralise the effect of the organics on the hydration of cement. The blended mixtures were placed in moulds for curing for 48-96 hours prior to being de-moulded and replaced into the excavation holes which had been modified by adding a liner and some clean soil. The blocks were also covered with additional clean soil. Cores were taken from the same blocks after 28 days, 9 months and 18 months, and samples analysed for properties such as bulk density, moisture content, UCS, freeze-thaw and wet-dry durability, permeability and TCLP leachate. Microstructural examination using SEM, optical microscopy and XRD were also undertaken. The investigation concluded that (i) there was little or no observed deterioration of the test blocks, (ii) while the heavy metals remained immobilised, the organic concentrations decreased with time, and (iii) the curing process was still continuing after 18 months.

Laboratory study, Baton Rouge, Los Angeles, USA

A long-term laboratory research study was carried out in Los Angeles, USA to observe the behaviour of a Portland cement-electroplating sludge wasteform in the presence of copper nitrate (Roy and Cartledge, 1997). The amount

of copper nitrate present was varied to include 2, 5 and 8% in the mix. The electroplating sludge contained Ni, Cr, Cd and Hg. The microchemistry and microstructural studies of these materials were conducted over a period of 8 years. This was achieved by adopting XRD, SEM, energy dispersive x-ray spectroscopy, thermal analysis and Fourier transform infrared spectroscopy (FTIR). The samples were stored in polyethylene bottles and most testing was conducted at 4 months, 4 years and 8 years. The study concluded that at a given copper nitrate loading there was very little visible change in the microstructure over time whilst subtle changes occurred in the microchemistry. This was mainly in the form of the emergence of $\text{CuO}\cdot 3\text{H}_2\text{O}$ and depletion of calcium hydroxide.

Laboratory experiments, Los Angeles, USA

Another laboratory experiment was carried out in Los Angeles, USA to examine the behaviour over time of two arsenic salts treated using different binders (Akhter et al., 1997). The waste was treated using several binders comprising Portland cement (PC), PC without gypsum, fly ash (FA), silica fume, sodium silicate, bentonite, organoclay, white cement, PC with air entraining agent and high alumina refractory cements (Lumnite and Refcon). The wastes were NaAsO_2 and $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$. The treated samples were placed in vials, sealed and kept at room temperature prior to testing at 28 days, 1 year and 3 years after mixing. The analysis comprised of TCLP leachability, magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR), XRD and derivative thermogravimetry (DTG). The main finding of the research was that PC-FA mixtures showed substantial respeciation during long curing times and that the matrix changes correlated with increased leachability. This indicated that such changes in the matrix over time had serious consequences for predictive leach modelling. In addition, it was vital to undertake long-term studies to understand the behaviour of matrices that were likely to undergo respeciation and resulting leachability changes over long curing periods.

A13: Thames Avenue, UK

TRL carried out a long-term investigation of S/S material at the A13 Thames Avenue to Wennington: Contract 2, where the opportunity arose to investigate the site after 3 years of treatment (Reid and Clark, 2001). This project considered the applicability of adopting a lightly contaminated silt as a lightweight fill after treatment. The treated material was used in embankments over soft ground on the edge of Rainham Marshes. The description of the original project was given by Nettleton et al. (1996). The treatment, carried out with the aim of modifying the silt to produce an acceptable general fill, was achieved by mixing the silt with pfa in a 2:1 ratio and adding 3% lime. Samples of undisturbed blocks of the lime-modified material were obtained after 3 years and geotechnical and leaching tests were carried out to compare against the results during construction. Geotechnical tests showed no significant changes from the values obtained during construction, and the material remained within the specification limits. In the leaching

tests, the only significant change was that the pH of the leachate dropped from nearly 12 at the time of construction to 7.6 three years later. The pH of the soil showed a similar drop, from 10.7 to 8.2. This supported the results obtained from a test bed at TRL (see 'Laboratory and test bed study, Berkshire', below), that carbonation can occur over a period of a few years in service conditions. Concentrations of contaminants in the leachate were very low in both sets of tests, and did not present any threat to the environment. Based on the results it was concluded that the treatment at this low level of lime was solidification rather than stabilisation, and that treatment with similar levels of lime or other cementitious agents of certain contaminated materials could be a satisfactory method of utilising these as general fill.

Experimental landfill cell, Sarnia, Ontario, Canada

A study was undertaken to observe the variability of field solidified waste (Stegemann et al., 1997). It involved the treatment of an electric arc furnace dust using a pre-prepared binder comprising blastfurnace slag, hydrated lime, silica fume, and sodium metasilicate. The mixing was performed either using a mobile treatment system or manually, and the treated materials were placed in a landfill cell. The collected samples were tested for various physical and chemical properties at several durations. The results of the UCS tests conducted at 56 days, 7 and 19 months indicated a doubling in strength from 56 days to 7 months followed by a decrease in strength of about 20% at 19 months. Although the strength values were satisfactory they never achieved the 56 day UCS of the design mix carried out in the laboratory. The variation in UCS over time indicated the variability of the treated material with time although the majority of the study was based on depicting the variability rather than time effect.

Wombwell site, Barnsley, UK

A two-phase project was conducted, with the initial involvement of CIRIA and then TRL, to assess the suitability of a S/S treated system (Sansom and Jardine, 1997; Jardine and Johnson, 2000; Board et al., 2000a). The first study was carried out over the initial 18 months after placing the material and the second after 40 months. The study used 6 different contaminated soils and industrial waste by-products, which were treated with the Geodur S/S system. This system used cement as the binder together with a proprietary additive (TracelokTM) and limestone aggregate. The mixing was performed using a concrete batching plant and the treated materials were transferred to a site in Wombwell, Barnsley where they were spread and compacted into ground slabs, and thereafter left exposed to natural weathering and leaching. Samples were also placed in moulds at the time of mixing for determination of crushing strength, bulk density, leachability, permeability, porosity and long-term durability and chemical compatibility after 1, 7 and 28 days, and 1 year. Cores were taken from the slabs initially at 3, 6 and 15 months (first phase) and again at 40 months (second phase) for testing as above. Part of the slab containing made ground was crushed and compacted

after 1 year and left in place to test its suitability as an aggregate. Leachate collected at the base of the slab and collected surface run-off was also analysed. On strength, it was concluded that the different rates of gain of compressive strength over time for different materials were due to time dependant effects of the various contaminants, even though in this case all materials reached significant levels of strength after 28 days. The strength of all the materials increased with time, and there was no indication of any physical breakdown or loss of strength in the long term. Leaching tests showed that cadmium, mercury, nickel, zinc, hydrocarbons and PCBs were effectively immobilised by the S/S treatment. However aluminium, lead, chromium, phenols and PAHs were leached from one or more of the materials at concentrations greater than the Environmental Quality Standards. Using the scheme proposed in the CIRIA Report 167 (Baldwin et al., 1997), four of the six treated materials fell into Group 1 (no restrictions on use based on potential to affect water quality) and two fell into Group 2 (may require some restrictions on use based on potential to affect water quality). Samples of drainage water from the site were of high quality, suggesting little leaching of contaminants was actually taking place. On the aspect of the reuse potential, it was concluded that the resulting made ground S/S material achieved the physical specifications required for a material to be reused in several road construction applications (Board et al., 2000b). In addition, the other treated materials were considered to be transformed into viable, relatively strong and durable construction materials (Jardine and Johnson, 2000).

West Drayton, Middlesex, UK

An in-situ trial treatment was carried out on a contaminated site in West Drayton, near Heathrow Airport (Al-Tabbaa and Evans, 1998; Al-Tabbaa et al., 1998). The site was an old chemical works site contaminated with a mixture of heavy metals and organic compounds with concentrations of up to 3000mg/kg of lead and copper, 2000mg/kg of mineral oil and 9000mg/kg of total petroleum hydrocarbons. The treatment of the 14m³ of soil was carried out using a soil mixing auger which applied seven different cement-based grouts, that also contained pfa, lime and/or bentonite. Samples of the treated ground were cored initially at 2 months after treatment and then again at 4.5 years for testing at 2, 14 and 28 months and 5 years respectively (Al-Tabbaa and Evans, 1998; Al-Tabbaa et al., 1998; Al-Tabbaa and Evans, 2000; Al-Tabbaa and Boes, 2002). After the initial coring at 2 months, samples were cured in the laboratory for testing at 14 and 28 months. The testing regime was based on a set design criteria and consisted of unconfined compressive strength (UCS), freeze-thaw and wet-dry durability, permeability, leachability, using both NRA and TCLP leaching tests, and leachate pH. In addition microstructural examination using SEM and XRD were also carried out. It was concluded that in terms of the imposed design criteria, the properties tested showed that the treatment was generally still effective after 5 years, with continued hydration and no serious signs of deterioration with age (Al-Tabbaa and Boes, 2002).

Imperial College field site, South East England

An industrial waste was S/S treated ex-situ and placed at a site in SE England to investigate the impact of exposure to the environment (Fitch and Cheeseman, 2003). The waste was a filter cake obtained from a metal-plating company and comprised of Zn, Fe, Cu, Ni and Pb, with Zn and Fe concentrations of up to 310,000 and 135,000 mg/kg respectively. The treatment was performed using a Portland cement and pfa mix as the binder, and the batches were mixed in a planetary mixer. The blended material was placed in steel cylindrical moulds leaving approximately 2cm at the top allowing rainwater to pond. The surface of the treated waste was covered for 28 days prior to exposure to the environment. The samples in the steel moulds were examined after an exposure of 10 years in which time the S/S material was expected to have experienced extended periods of surface saturation, freeze/thaw cycles and wet/dry periods during seasonal changes. The results showed that the surface had degraded severely, with the top 2-3cm having soil like texture, and also colonised by algae, insects and other organisms, and the core of the sample had negligible strength. The surface fractured segments were examined by XRD and cores from 15 and 50cm depth (termed as 'bulk') were analysed for chemical composition, acid neutralisation capacity (ANC) combined with leachate analysis and leachate pH, and XRD. The major conclusions of the examination were that the surface region was severely degraded and extensively carbonated, had reduced ANC in relation to the bulk samples and had plate-like deposits of calcium hydroxide together with calcium carbonate. The metal concentrations were in general significantly reduced in this surface region and bulk samples appeared to be amorphous with calcite being the only crystalline phase detected and they also retained high ANC. It was also concluded that deriving conclusions on the performance and behaviour of S/S materials by post-disposal analysis was problematic.

Laboratory and test bed study, Berkshire, UK

TRL conducted a project to establish the long-term mechanical and environmental stability of a treated fine-grained contaminated material (Reid and Clark, 2001). The waste material consisted of lightly contaminated silt from the A13 improvement scheme combined with pfa and heavily contaminated sewage sludge. The latter was added to increase the contaminant loading of the waste material. The treatment was carried out using lime in order that the resulting material could be classified as suitable for general earthwork fills in highway works. The research programme consisted of three main parts: trial mixes, laboratory leaching tests, and an experimental test bed. The trial mixes showed that a mixture of 2:1 dredgings: pfa with 5% sewage sludge could yield a material with acceptable engineering properties for general fill when mixed with 5% lime. Specialised flow-through laboratory leaching tests were then carried out on this mixture. The concentrations of most metals in the leachate were very low. However, concentrations of copper, nickel and phenol were higher in the leachate

from the treated material than from the untreated material. This was ascribed to the reaction of lime with organic matter, resulting in the breaking of the metal-organic bonds of these metals (McKinley et al., 1999). The strength however did not appear to be affected by the leaching.

The test bed was constructed at TRL using the same mixture to observe the behaviour of the materials under field conditions. However the exposure conditions represented a more severe environment than service conditions as the material in service would be covered with other layers of highway construction, whereas the test bed was left open to the atmosphere. During the construction of the test bed, samples were collected and cured in the laboratory in order to compare with results from the test bed. Tests were conducted at regular intervals over a 1 year period for moisture content, dry density and shear strength. CBR and moisture condition value (MCV) were measured at the start and end of the test period. The pH, conductivity and concentrations of selected species in the drainage from the test bed were also measured over a 15 month period.

At the end of a year, the shear strength, CBR and MCV of the test bed material were higher than at the start, despite the severe exposure conditions, and the strength was similar to the samples kept in the laboratory. The chemistry of the drainage water showed similar patterns to that from the laboratory leaching tests with one important exception: the pH rapidly decreased to between 10 and 11, and after a year decreased to about 8. This was accompanied by a rapid drop in calcium concentration. In the laboratory tests, the pH remained above 12 at all times and the calcium concentration was about 500 mg/l. The laboratory leaching tests were carried out under fully saturated conditions, whereas the test bed was open to the atmosphere. The pH of the test bed material decreased from above 12 to about 10 over the 15 month period. This suggested that carbonation reactions were taking place over the timescale of the test. This study concluded that the geotechnical properties of the treated material appeared to show no significant deterioration over time with the main change between the two scenarios being the drop in pH in both the material and the drainage water. The effect of treatment with lime at this specified dosage was considered to be solidification rather than stabilisation.

Studies on Accelerated Ageing

Another approach available for observing the long-term performance, in addition to predictive modelling and real-time behaviour, is to subject S/S materials to accelerated processes. This could be achieved in two modes: conducting accelerated tests on real-time cured materials or subjecting the S/S materials to accelerated ageing processes. Accelerated tests are designed to treat the material harshly and to observe their behaviour based on exposure conditions. These include tests such as some leaching tests and, freeze/thaw and wet/dry weathering tests. However, these may not be satisfactory as they only indicate the performance of a material at its current

maturing stage, but subjected to harsh conditions and hence may perform differently at an advanced age.

Thus, what is more appropriate for this purpose are methods which will accelerate the ageing of S/S materials. The ideal situation would be where the acceleration method enables holistic prediction based on both physical and chemical characteristics of a wide range of mix designs, which takes into account even the exposure conditions. Unfortunately this is a difficult requirement and the methods considered here, as possible accelerated methods, may not satisfy the ideal scenario in their attempt to predict the long-term behaviour of S/S materials.

The acceleration methods considered are basically achieved by accelerating the curing of the S/S material and are expected to accelerate the whole intrinsic system. Hence this method is expected to be a plausible process to predict and characterise long-term treatment effectiveness. However, the curing conditions may not take into consideration the varying exposure conditions that naturally cured material will undergo. The accelerated curing conditions considered here include studies using elevated temperature, chemical additives and carbonation. Generally some form of modelling is also undertaken to produce a mathematical model of the observed behaviour and to predict the performance in the much longer term.

The effect of curing cement-based materials at elevated temperatures has been reported by many researchers (Conner, 1990; Kindness et al., 1994; Patel et al., 1995; Sabir, 1995; Odler, 1998; Porbaha et al., 2000). It is generally agreed that when cement is considered on its own the hydration rate increases with increasing temperature, especially at lower degrees of hydration. Thus at shorter hydration times the strength of the material increases significantly with increasing temperature due to the faster rate of hydration. In contrast, at longer hydration times and especially at higher curing temperatures, the attained strength may lie below that of the material cured at lower temperature, mainly due to the higher porosity and/or coarser pore structure (Cao and Detwiler, 1995). Further variations from the norm include the general effects, which would alter with the addition of other elements to cement (Sherwood, 1993; Porbaha et al., 2000). There is also uncertainty regarding the optimum elevated temperature for curing as macrocracks may develop at higher temperatures (Conner, 1990; Glasser, 1997). This optimum temperature may vary depending on the material constituents (i.e. mix design).

Certain chemicals that behave as accelerators for cement-based materials can also be used to accelerate the hydration and achieve a significant increase in the rate of early strength development. There are many substances which perform this task, including alkali hydroxides, silicates, fluorosilicates, organic compounds, formates, nitrates, thiosulfates and chlorides of calcium and aluminium, potassium carbonate and sodium chloride (Fuessle and Taylor, 1999). Of these calcium chloride (CaCl_2) is proven to be the most widely adopted to

accelerate the hydration process and the development of strength in cements because of its availability, low cost and predictable performance (Ramachandran, 1984). Although the accelerating effect of CaCl_2 can be seen in most constituents of cement it is mainly related to the C_3S phase. This is because CaCl_2 decreases the dormant period in the hydration of C_3S (Ramachandran, 1976). Various researchers have stipulated the rate and mechanism of the hydration (Kurczyk and Schwiete, 1960; Skalny and Odler, 1967; Ramachandran, 1976 and 1984). The effects seen include changes to the morphology (but not of C_2S), porosity, surface area, chemical composition and early strength development. However, there is concern regarding the chemical's inability to continue to act as an accelerator after the initial mechanisms have progressed. Also, this additive causes corrosion of steelwork in reinforced concrete and would therefore be expected to affect any steel structure close to soil containing the material. Therefore, it may not be advisable to use this in the field, but could be limited to controlled research environments. In addition these salts would be considered as contaminants and hence in the presence of existing contaminants it would lead to confusion and difficulty in separating the effect of the original contaminants from the added salts.

Accelerated carbonation has been considered as a means of accelerating the carbonation process of cement. This process involves the transformation of the hydration products to mainly CaCO_3 at a faster rate than would occur naturally. However, other forms will also occur as a result of reactions involving other compounds. The mechanisms and components involved were described in an earlier section. Variation on curing can be achieved by changing variables such as pressure and humidity. However, whilst the mechanism of breakdown of the hydration products is clear, there is uncertainty regarding the strength development. Some researchers (Lange et al., 1996; Maries, 1998) indicated strength gain whilst others (Hannawayya, 1984) and initial studies of Sweeney et al. (1998) showed the 28 day strength of the accelerated samples to be lower than that of the normal cured samples.

Other options are to combine some of the above methods of accelerated curing with variables such as pressure and humidity as a means of accelerated ageing. Al-Tabbaa et al. (2003a&b) considered the combination of elevated temperature and accelerated carbonation as part of an on-going research programme.

Some examples of studies, which have been conducted using the curing techniques described above, are given below.

Research at University of Cincinnati, USA

Kirk (1996) reported on accelerated ageing studies conducted at the University of Cincinnati, USA, adopting mainly heat, and pressure. Specially constructed environmental chambers were used to carry out the ageing process using high temperatures and pressures. The S/S material comprised of sludges, containing lead nitrate, sodium arsenite and cadmium nitrate at high pH,

as the waste and Portland cement, lime/fly ash or kiln dust as the binders. Waste concentrations and sludge-binder ratio were varied to obtain different experimental sets of specimens. The accelerated ageing procedure was based on the Arrhenius model (Brown and LeMay, 1988), which assumes a log linear relation between temperature and lifetime, and used it to determine the temperatures required to represent 50 and 100 year aged-material. The equation for the Arrhenius model adopted is given below.

$$\frac{t_s}{t_a} = \exp \left[\left(\frac{E_a}{k} \right) \left(\frac{1}{T_s} - \frac{1}{T_a} \right) \right]$$

Where t_s is the service time, t_a is the accelerated time, E_a is the activation energy, k is the Boltzman's constant, T_s is the service temperature and T_a is the accelerated temperature.

The UCS results of the aged samples showed a significant decline. A 45% and 80% decline in strength was reported for the 50 and 100 year aged samples respectively in comparison to the strength of the 295 day normal cured sample. Also the permeability had a three to four fold increase in the aged material. However, the leaching test results indicated the heavy metals to be efficiently immobilised.

Research at Bradley University, USA

Fuessle and Taylor (1999) conducted studies at Bradley University, USA, to investigate the accelerated ageing of stabilised hazardous wastes, by adopting heating and chemical accelerators to cure S/S treated materials. The studies were conducted using an arc furnace dust waste and a Portland cement and fly ash binder. The mix design matrix was based on varying the binder/waste ratio. The waste/solid ratio was made up after conducting preliminary studies to identify the important parameters. The investigation included the testing of naturally cured samples and material subjected to various durations and methods of fully and partially accelerated exposure.

Except for the real-time samples, the other results were reported based on the leachate pH and column leach test for cadmium and lead for two of the mixes. The column leaching tests were adopted into the study as it was believed that such dynamic tests provided the time rate of metal release from S/S material and these were set up to be comparable to the TCLP leaching test. It was reported that the samples exposed to temperatures ranging from 40°C to 120°C with 100% humidity, and at 40°C tested with column leaching for various durations did not yield TCLP leach results consistent with the respective naturally cured samples. The results of the chemical accelerator solutions of calcium chloride and calcium nitrite used for 4 days of curing and subjected to column leaching tests indicated that the leaching rates correlated with trends in long-term treatment effectiveness. Simple regression was used in this study to derive trends for mixes and between mixes.

Research at University of Cambridge, UK

Chitambira (2004), at the University of Cambridge, investigated the feasibility of accelerating the ageing of S/S treated contaminated and uncontaminated soils with the use of elevated temperatures. The materials investigated were based on the West Drayton site trial work, described in an earlier section. Model contaminated soils, which comprised of five heavy metals and paraffin oil as contaminants, mixed with combinations of PC, pfa, lime and/or bentonite as binders were tested. The study also considered model soils contaminated with one organic compound (paraffin oil) and one inorganic compound (lead nitrate) as contaminants, in isolation and combined. This was carried out in order to study the effect of two individual contaminants and the effect of the presence of one compound on the behaviour of the other. Uncontaminated soils were also tested for comparison in order to highlight the effect of the contaminants present. The elevated temperatures adopted were 45°C and 60°C and the treated materials were cured for 1, 2 and 3 months. Some samples were subjected to longer curing periods of up to 2 years. The control samples were cured in the laboratory at 21°C. The laboratory results were compared with the results obtained from the site trial.

All the samples were wrapped throughout the curing period to minimise moisture loss and thereby minimise cracking of samples at elevated temperatures due to the higher rate of drying. Following the different curing temperatures and durations, the samples were tested for UCS, permeability, NRA and TCLP leachability and leachate pH, and their microstructure analysed using SEM and XRD.

The Arrhenius equation, used in what is known as the 'Maturity concept' in concrete studies (Carino and Lew, 2001) and referred to in an earlier section, was used to facilitate the prediction of the development in the UCS as a function of time and curing temperatures. The results showed that the different soil-binder mixes responded differently to higher temperatures and different curing periods. Generally an increase in strength with an increase in curing temperature and curing period was observed, but a decrease in strength was also seen which is referred to as the 'cross-over' effect in concrete behaviour (Carino and Lew, 2001). The leachability of the heavy metals and the leachate pH values generally reduced with time and elevated temperature. Numerical modelling performed on selected materials using the Maturity method with the Arrhenius equation showed very promising results in which better correlations were obtained as the similarity between the compared materials increased (Al-Tabbaa et al., 2003a; 2003b).

Studies were also conducted by the first author (Perera, 2005), as part of an on-going research projects, to accelerate the ageing using carbon dioxide (accelerated carbonation) and elevated temperatures. The study investigated the behaviour of the same S/S treated contaminated soils relating to the West Drayton site mentioned in an earlier section. In addition the behaviour of the binder spiked with the same contaminants was also

investigated. Different curing exposure conditions were utilised on selected materials such as carbonation alone, heating alone at 45°C, carbonation followed by a period of heating, exposure to carbonation at different humidities and simultaneous carbonation and heating (45°C and 60°C) at two relative humidity levels (90% and 70%). The samples were subjected to curing durations of 1, 2 and 3 months, and up to 6 months for a limited number of mixes. The behaviour of the materials was then observed by testing them for their UCS, NRA and TCLP leachability and leachate pH, carbonation depth, relative quantitative carbonation by thermo-gravimetric methods and microstructure using SEM and XRD.

The results so far have shown that different mixes behave differently at the different exposure conditions and curing periods and in some cases the same mix behaved differently under different exposure conditions. The UCS results generally showed an increase with increase in temperature but tended to reduce in some cases with exposure to carbonation at high relative humidity levels. The latter however contrasted with some results in the same study that showed an increase in strength with lower relative humidity levels. Leaching results generally showed an improvement, i.e. reduced leachability of the heavy metals, and leachate pH showed reduction both with exposure to CO₂ and heat, and also with duration. However, samples which reached low leachate pH values mainly as a result of carbonation tended to mobilise some metals which were not leaching out at the higher pH values. This is possible when considering the solubility curves of these metals with varying pH. The degree of carbonation and carbonation penetration varied based on the mixture, exposure condition and duration. The treatment by elevated temperature prior to exposure to carbon dioxide tended to achieve a greater degree of carbonation and carbonation depth for some mixes when compared to the similar samples which were exposed to carbonation alone.

CONCLUSIONS

A number of potential degradation mechanisms for S/S materials have been assessed. These include binder-contaminant interactions, carbonation, sulfate and chloride attack, alkali silica reaction, freeze-thaw and wetting-drying cycles and long-term weathering reactions. Many of these mechanisms can be avoided by using existing design methods for concrete and other materials, and by ensuring good quality control during construction. The biggest areas of uncertainty are binder-contaminant interactions and the long-term performances of the binders, particularly where relatively low concentrations of binder are used. A number of case studies are presented where these issues are addressed. Further, studies on accelerated ageing are described. Overall this is an area where further research is required to understand more clearly the chemistry of binder-contaminant reactions in the long-term and to calibrate laboratory studies with high quality field data.

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Table 1. Selected compounds that affect solidification (adapted from Connor, 1990)

Compounds	Effect	Mechanism Affected
Fine Particulates	I,P	P
Grease	I,P	P
Oil	I,P	P
Ethylene Glycol	P	I
Phenol	P-	I
Trichloroethylene	P-	I
Acids	P-	I
Bases	P-	I
Iron Compounds	A	F,M
Lead Compounds	R	M
Magnesium Compounds	R	M
Salts (General)	P-,A,R	I
Sulfates	R,P	I
Calcium Chloride	A,R	M
Copper Nitrate	P+	I
Gypsum Hydrate	R	I
Lead Nitrate	P-,P+	I
Sodium Hydroxide	P+,P-	I

Key

Effect :

I = setting/curing inhibition (long-term)

A = setting/curing acceleration

R = setting/curing retardation (short-term)

P = alteration of properties of cured product

P- = alteration of properties of cured product (negative effect)

P+ = alteration of properties of cured product (positive effect)

The first symbol represents effect at low concentrations and the second at high concentrations.

Mechanism :

P = coats particles

I = interferes with reactions

F = flocculent

M = disrupts matrix

Table 2. Examples of modelling studies (adapted from Hills et al., 2004)

Model	Investigation	Author(s)
Thermodynamic modelling and kinetic studies	Predict the longevity of cement-based systems	Breyse and Gerard (1997) Sugiyama et al. (2001)
Use of geochemical modelling	Predicting the fate of contaminants	Van der Lee and De Windt (2001)
Use of geochemistry models (NIST and DIFFU-Ca)	Degradation in waste forms	Matte et al. (2000)
Using a cement hydration model extended to describe pore water composition and the effects of cement grain coating	Predicting the strength and leaching resistance of solidified products and developing solidification recipes based on cement	Van Eijk and Brouwers (2001)
Neural network	Predicting leaching pH	Stegemann and Buenfeld (2002)
Developed a mathematical model with the main parameters being the effective alkalinity of the treated waste and alkalinity depletion rate (based on a S/S treated Natrojarosite waste)	Predicting the time to breakthrough of the pH front	Catalan et al. (2002)