

Solidification–stabilization of organic and inorganic contaminants using portland cement: a literature review

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Abstract: The treatment of hazardous wastes using cement-based solidification–stabilization (S–S) is of increasing importance as an option for remediating contaminated sites. Indeed, among the various treatment techniques, S–S is one of the most widely used methods for treating inorganic wastes. To enhance the application of S–S and to further develop this technology for site remediation, particularly for organic contaminants, it is important to have a better understanding of the mechanisms involved in the process. The primary objective of this review is to survey the current knowledge in this subject, focusing on (i) cement chemistry, (ii) the effects of inorganic (heavy metals) and organic compounds on cement hydration, and (iii) the mechanisms of immobilization of different organic and inorganic compounds. For heavy metals, cement-based S–S technology has been shown to be effective in immobilizing the contaminants, even without any additives. In applying cement-based S–S for treating organic contaminants, the use of adsorbents such as organophilic clay and activated carbon, either as a pretreatment or as additives in the cement mix, can improve contaminant immobilization in the solidified–stabilized wastes. The concept of degradative solidification–stabilization, which combines chemical degradation with conventional solidification–stabilization, seems promising, although further study is required to assess its technical and economic feasibility.

Key words: cement, contaminated soil, immobilization, organics, precipitation, adsorption.

Résumé : Le traitement des déchets dangereux utilisant la solidification–stabilisation basée sur le ciment (S–S) prend de l'importance comme option en vue de la remédiation des sols contaminés. En effet, parmi les diverses techniques de traitement, le S–S est une des méthodes les plus utilisées pour traiter les déchets inorganiques. Si on souhaite augmenter l'application du S–S et de poursuivre le développement de cette technique pour la remédiation des sites, particulièrement pour les contaminants organiques, il est important de mieux comprendre les mécanismes impliqués dans ce procédé. Le premier objectif de cette revue consiste à faire un survol des connaissances courantes sur ce sujet, en mettant l'accent sur (i) la chimie du ciment, (ii) les effets des composés inorganiques (métaux lourds) et organiques sur l'hydratation du ciment, et (iii) les mécanismes d'immobilisation des différents composés organiques et inorganiques. On a démontré que pour les métaux lourds, la technologie S–S basée sur le ciment est efficace pour immobiliser les contaminants, même

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sans additifs. Lorsqu'on applique la technologie S-S basée sur le ciment à des composés organiques, l'utilisation d'adsorbants tels que l'argile organophile et le charbon activé, que ce soit comme prétraitement ou comme additif au béton, peut améliorer l'immobilisation des contaminants dans les déchets solidifiés-stabilisés. Le concept de stabilisation-stabilisation dégradative, qui combine la dégradation chimique avec la S-S conventionnelle, semble prometteur, bien que d'autres études soient nécessaires pour évaluer sa faisabilité technique et économique.

Mots clés: ciment, sol contaminé, immobilisation, substances organiques, précipitation, adsorption.

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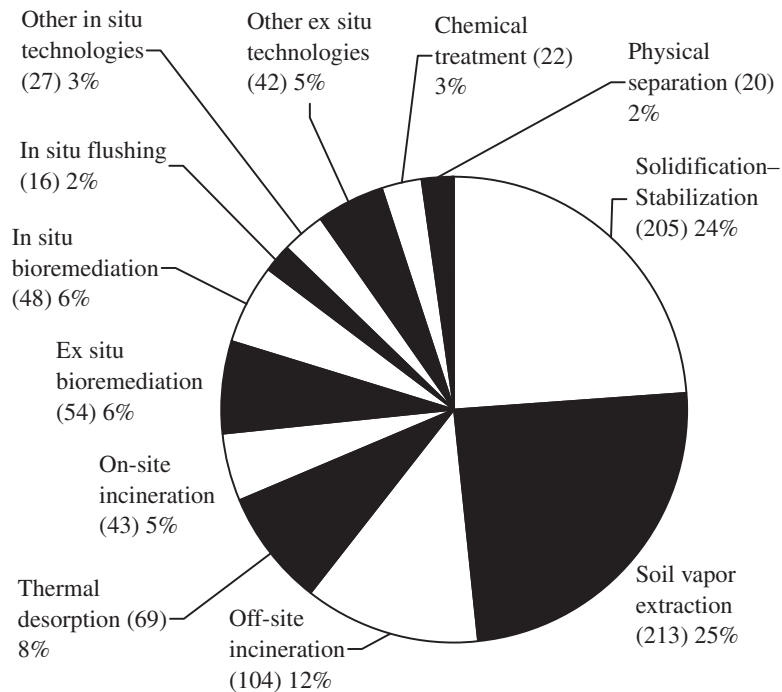
1. Introduction

Cement-based solidification-stabilization (S-S) is a chemical treatment process that aims to either bind or complex the compounds of a hazardous waste stream into a stable insoluble form (stabilization) or to entrap the waste within a solid cementitious matrix (solidification) (Wiles 1987). The US Environmental Protection Agency (EPA) has identified S-S as the best demonstrated available technology for 57 RCRA (Resource Conservation and Recovery Act)-listed hazardous wastes, and S-S technology was selected in 24% of all source control treatments at Superfund remedial action sites in the United States (see Fig. 1) (USEPA 2004). The use of cement-based S-S in Canada is still in the early stages. However, with the selection of cement-based S-S as one of the remediation technologies in major projects such as the Sydney Tar Ponds cleanup, it is likely that this technology will gain further acceptance. In light of this development, there is indeed a need for a comprehensive review of the subject, which should provide both researchers and practitioners in this field with a concise reference and source of information. The primary objective of this review is to survey the current knowledge on cement-based S-S of contaminated soil, focusing on cement chemistry, the effects of inorganic (heavy metals) and organic compounds on cement hydration, and the mechanisms of immobilization of different soil contaminants.

Compared with other remediation technologies, cement-based S-S has the following advantages (Conner and Hoeffner 1998; Shi and Spence 2004):

- Relatively low cost and ease of use and processing,
- Composition of Portland cement is consistent from source to source, eliminating some of the variables in designing the S-S process,
- Good long-term stability, both physical and chemical,
- Good impact and comprehensive strength,
- Non-toxicity of the chemical ingredients,
- High resistance to biodegradation, and
- Relatively low water permeability.

Stabilization of heavy metals is achieved by converting the metals into insoluble precipitates, or by the interaction (e.g., sorption and ion substitution) between metallic ions and cement hydration products such as ettringite and calcium silicate hydrate gel (Gougar et al. 1996). Organic compounds are generally nonpolar and hydrophobic; they do not react with the inorganic binders and may interfere with the hydration reactions of cement or pozzolanic materials and inhibit the setting of cement. Instead, organics are generally sorbed or encapsulated in the pores, and their leachability depends on their solubility in water and their diffusivity through the waste matrix. In S-S processes, immobilization of contaminants, depending on their nature, occurs by three main mechanisms:

Fig. 1. Technologies selected for source control treatment at Superfund remedial action sites (USEPA 2004).

- (1) Chemical fixation of contaminants by interactions between the hydration products of cement and the contaminants,
- (2) Physical adsorption of contaminants on the surface of cement hydration products, or
- (3) Physical encapsulation of contaminated waste or soil.

Solidification–stabilization processes can be applied using several schemes (Wiles 1987):

- In-drum processing — In this process, the S–S binders are added to the waste contained in a drum or other container. The waste–binder matrix is normally disposed of in the drum after mixing and setting.
- In-plant processing — A plant and (or) process is specifically designed for solidifying and stabilizing bulk waste materials. The process may be used to manage wastes from an internal industrial operation, or a plant may be specifically built and operated to solidify and stabilize wastes from external sources.
- Mobile plant (ex situ) processing — In this scheme, the processing equipment, which is either mobile or can be easily transported, is set up site to site.
- In-situ processing — Binders or solidifying–stabilizing materials are injected directly to a lagoon or soil subsurface to promote the solidification–stabilization of the contaminated sludge or soil.

2. Soil

To facilitate the design of S–S processes, it is important to have a thorough knowledge of the physical and chemical properties of soil, and to understand the mechanisms of interactions between soil and contaminants.

Table 1. Major minerals in igneous rocks and primary minerals in soils (Wild 1993).

Minerals	Chemical formula	Presence in soil
Quartz	SiO ₂	Most common mineral in sand and silt fractions
Orthoclase feldspar	KAlSi ₃ O ₈	Present in weakly and moderately weathered soils
Muscovite (a mica)	K(Si ₃ Al)Al ₂ O ₁₀ (OH) ₂	
Biotite (a mica)	K(Si ₃ Al)(Mg, Fe) ₃ O ₁₀ (OH) ₂	Easily weathered to form clay minerals
Pyroxenes	(Mg, Fe)SiO ₃	
Amphiboles	(Mg, Fe) ₇ (Si ₄ O ₁₁) ₂ (OH) ₂	
Olivines	(Mg, Fe) ₂ SiO ₄	

2.1. Chemical and physical properties

Soil can be defined as loose materials composed of weathered rock and other minerals, as well as partly decayed organic matter (Wild 1993). The soil components include about 50% by volume mineral particles, 25% water, 20% air, and 5% organic matter. Except for a few organic soils, the bulk of soil is derived from solid geological deposits and is mineral in character. Table 1 lists the general chemical formulae of the major minerals in soil. The mineral particles in soil vary widely in size, shape, and chemical composition. Three groupings of soil particles are in common use, namely clay (particle diameter less than 0.002 mm), silt (particle diameter between 0.002 mm and 0.02 mm), and sand (particle diameter between 0.02 mm and 2 mm). These categories can be further subdivided according to specific requirements (Townsend 1973). Because of their structure and chemical composition, humus and clay minerals, which are mainly aluminosilicates and hydrous or hydrated oxides of iron and aluminum, usually bear negative charges. These charges are formed by the dissociation of protons from the surfaces and edges of clay minerals and the acidic groups in humus, and they increase with increasing pH.

2.2. Contaminant-soil interactions

The interactions between soil particles and contaminants occur through three major mechanisms: (i) sorption, (ii) complexation, and (iii) precipitation (Yong et al. 1992). The term "sorption" is generally used to describe the process in which the solutes (ions, molecules, or compounds) partition between the liquid phase (pore water) and the soil particle interface. Physical adsorption occurs when the contaminants in the soil pore water (aqueous phase) are attracted to the soil constituents' surfaces because of the net charges on the soil particles (attractive forces). Chemical adsorption refers to the high-affinity, specific adsorption that generally occurs in the inner Helmholtz layer through covalent bonding (Yong et al. 1992). In specific adsorption, ions penetrate the coordination shell of the structural atom and bond to the structural cations by covalent bonding via the oxygen and hydroxyl groups.

Complexation occurs when a metallic cation reacts with an anion that functions as an inorganic ligand. Metallic ions that can be complexed by inorganic ligands include the transition metals and alkaline earth metals. The complexes formed between the metal ions and the inorganic ligands are much weaker than those complexes with organic ligands. As noted earlier, precipitation is a key mechanism of retaining heavy metals in soils. The concentration of solutes and the pH of both the soil and the soil pore water are important factors in controlling precipitation (Yong et al. 1992).

3. Portland cement

Portland cement is made by heating a mixture of limestone, clay, and other materials, including fly ash and shale. Nodules of clinker are formed at approximately 1450 °C after partial fusion (Kosmatka et al. 2002). The clinker is then mixed with a small amount of gypsum to delay the initial setting time, and the mixture is finely ground (more than 90% pass through a 90- μ m sieve) to make the cement. The

Table 2. Typical composition of Portland cement (Lawrence 1998).

Components	Minimum (%)	Average (%)	Maximum (%)
SiO ₂	18.4	21.02	24.5
Fe ₂ O ₃	0.16	2.85	5.78
Al ₂ O ₃	3.1	5.04	7.56
CaO	58.1	64.18	68
MgO	0.02	1.67	7.1
Na ₂ O	0	0.24	0.78
K ₂ O	0.04	0.7	1.66
SO ₃	0	2.58	5.35
Free lime	0.03	1.24	3.68
Chloride	0	0.016	0.047

Table 3. Properties of major clinker phases (Dalton et al. 2004).

Mineral phase	Properties in cement
Alite	Rapid hydration, high initial and final strength
Belite	Slow hydration, good final strength, low heat of hydration
Aluminite	Rapid hydration, high heat of hydration
Ferrite	Slow and moderate hydration, moderate heat of hydration

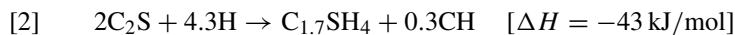
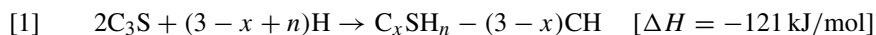
principal use of Portland cement is in concrete. Concrete, which is a major construction material, is a mixture of cement, water, and aggregates such as sand and gravel.

3.1. Composition of Portland cement

The clinker has a typical composition of 67% CaO (C), 22% SiO₂ (S), 5% Al₂O₃ (A), 3% Fe₂O₃ (F), and 3% other components. It normally contains four major phases: alite (50–70% Ca₃SiO₅ or “C₃S”), belite (15–30% Ca₂SiO₄ or “C₂S”), aluminite (5–10% Ca₃Al₂O₆ or “C₃A”), and ferrite (5–15% Ca₄Al₂Fe₂O₁₀ or “C₄AF”) (Taylor 1997). A typical composition of Portland cement is given in Table 2, representing an average of compositions taken from different countries. Although the four phases perform different functions in the final product, the most important phases are alite and belite, which are the most abundant in the clinker and contribute significantly to the compressive strength. The properties of different phases in cement are given in Table 3.

3.2. Hydration of Portland cement

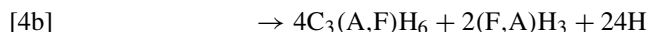
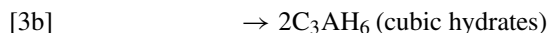
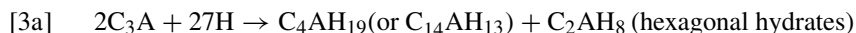
The cementing action of Portland cement mainly derives from the hydration reactions of alite (C₃S) and belite (C₂S) with water. In a typical modern Portland cement, about two-thirds of hydration is achieved in 28 days (Glasser 1997). The hydration of C₃S usually controls the setting and early strength development of Portland cement pastes, mortars, and concretes. The hydration reactions can be represented as (Gartner et al. 2002)



where H denotes H₂O, in accordance with the abbreviated notation commonly used in cement chemistry (see also section 3.1 for the definition of other symbols). The same notation is also used in eqs. [3] and

[4] and in section 3.7. The immediate contact period between cement and water is referred to as the pre-induction period, in which rapid dissolution of ionic species occurs and produces the hydrates. The alkali sulfates present in the cement dissolve completely within seconds, contributing K^+ , Na^+ , and SO_4^{2-} ions. Calcium sulfate dissolves until saturation and forms Ca^{2+} and SO_4^{2-} ions. C_3S undergoes hydration and a thin layer of calcium silicate hydrate, usually written as “C-S-H”, precipitates at the cement grain surface (Odler 2000). The formation of C-S-H, which is an apparently amorphous phase of variable composition (Gartner et al. 2002), has important implications on the mechanisms of fixation during solidification (Mollah et al. 1995; Hills et al. 1996) and is principally responsible for strength development (Cartledge et al. 1990).

The hydration of C_3A and C_4AF can be represented as follows (Lea 1970; Gartner et al. 2002)



C_3A is the most reactive among all the phases in Portland cement, and is known to have a strong influence on the early hydration and rheology of Portland cement and concrete. Initially C_3A forms the metastable hexagonal hydrates (C_4AH_{19} and C_2AH_8) in the presence of water, which are then slowly converted to stable cubic hydrates (C_3AH_6) (Ramachandran 1973; Milestone 1976). In the presence of gypsum, or calcium sulfate ($CaSO_4$), however, C_3A can be hydrated to form ettringite according to the following reaction (Gartner et al. 2002)



where \bar{S} denotes SO_3 . The formation of ettringite slows the hydration of C_3A by forming a precipitate on the particle surface, and may also cause a volume increase, leading to structure disruption and increase in permeability and concomitant loss in strength (Pollard et al. 1991; Perraki et al. 2003). The hydration of C_4AF is very similar to that of C_3A .

Two models, the gel or osmotic model and the crystalline model, have been proposed to explain the observed phenomena associated with cement hydration and subsequent setting (Mollah et al. 1995). As shown schematically in Fig. 2, according to the gel model, a membrane of C-S-H gel is formed on the surface of a cement particle upon hydration, whereas the crystal model assumes that charged calcium and silicate ions are formed upon contact with water, and concentrated as a thin layer on the cement grain surface, which retards further release of calcium and silicate ions. The initial hydration is followed by nucleation and growth of calcium hydroxide and C-S-H precipitation on the cement grain surface. Sheets of tobermorite are then formed gradually through the formation and aggregation of ettringite. The overall rate of cement hydration is dependent on the hydration of individual components, and it may be accelerated by increasing the fineness of grinding, by increasing the temperature of hydration, or by increasing the water-to-solid ratio (Lea 1970).

3.3. Pore structure in cement

Hardened cement paste is a composite material whose properties ultimately depend on the properties and composition of the components, water-to-solid ratio, etc. It contains a wide range of pore sizes, with effective diameters ranging over several orders of magnitude. Large pores and micro structures are usually present; however, since they do not form a continuous network, their influence on permeability is not large. Total porosity, which is often determined based on water loss upon heating, affects every major

Fig. 2. Schematic models for the hydration and setting of Portland cement. (a) Gel model (b) crystal model (After Mollah et al. 1995).

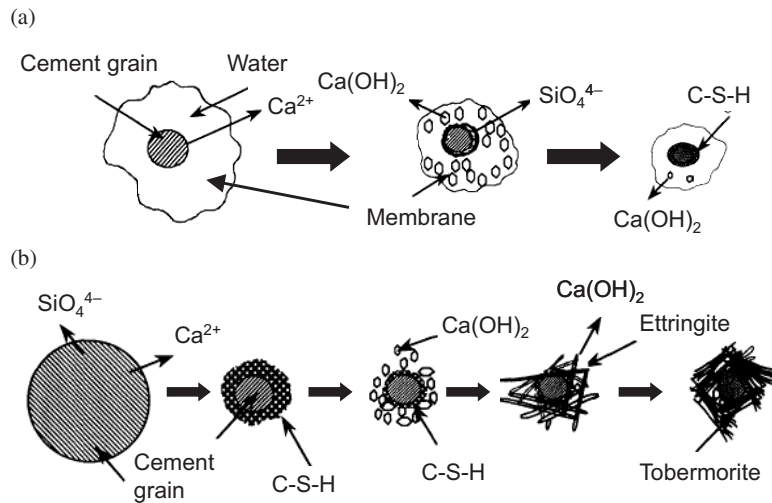


Table 4. Pore characteristics in hardened Portland cement paste (Gartner et al. 2002).

Designation	Diameter	Description	Origins
Macropores	10 000–50 nm	Large capillaries, interfacial pores	Remnants of water filled space
Mesopores	50–10 nm	Medium capillaries	Remnants of water filled space
Micropores	2.5–0.5 nm or < 0.5 nm	Internal spaces	Intrinsic part of C-S-H

Table 5. Specific surface areas of different hydrated cements (Lea 1970).

Cement	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Specific surface area (m ² /g)
A	45	26	13	7	219
B	49	28	5	13	200
C	28	58	2	6	227
D	61	12	10	8	193

property of hardened cement paste. In addition to porosity, pore size distribution is also an important parameter, but it is difficult to determine. The characteristics of various pore structures are summarized in Table 4.

In general, organic compounds have a strong effect on the microstructure of the cement paste. The structure and nature of the organic molecules are responsible for the microstructure characteristic. For example, the presence of 1-chloronaphthalene in the cement paste increases its porosity and decreases its mechanical strength, while the effect of 2-chlorophenol is less significant (Cioffi et al. 2001). On the other hand, as shown in Table 5, the specific surface area of hydrated cement does not vary much with the proportion of the clinker components.

3.4. Influence of additives on cement hydration

Most of the development work on stabilization of hazardous contaminants was done before 1990. Portland cement-based processes remain the most common, and many different additives, including activated carbon, organophilic clays, phosphates, rubber particulates, silica fume, slag, and fly ash, are being used to improve performance and reduce cost with specific waste streams (Conner and Hoeffner 1998).

3.4.1. Inorganic additives

The effects of soluble inorganic salt on hydration of C_3S have been studied thoroughly by Kantro (1975). The efficiency of hydration acceleration of different cations are found to be $Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+} \sim Li^+ > K^+ > Rb^+ \sim Cs^+ > Na^+ > NR_4^+ > H_2O$ where NR_4^+ denotes quaternary ammonium ion and H_2O denotes the absence of additive. In most cases, an accelerated rate of hydration, i.e., shortened setting time, would increase the rate of early strength development. The results indicate that (i) calcium has the highest efficiency and (ii) the efficiency mainly depends on the charge and size of the ion, with small, highly charged ions being the most effective. For the highly soluble salts of calcium at the same equivalent concentration, the order of effectiveness of anions is $Br^- \sim Cl^- > SCN^- > I^- > NO_3^- > ClO_4^- > H_2O$, which shows a similar trend as that of cations in terms of ion size. The salts of Zn, Sn, Pb, soluble phosphates, and fluorides retard the hydration process, and inorganic salts that form complexes with calcium also act as retarders.

3.4.2. Organic additives

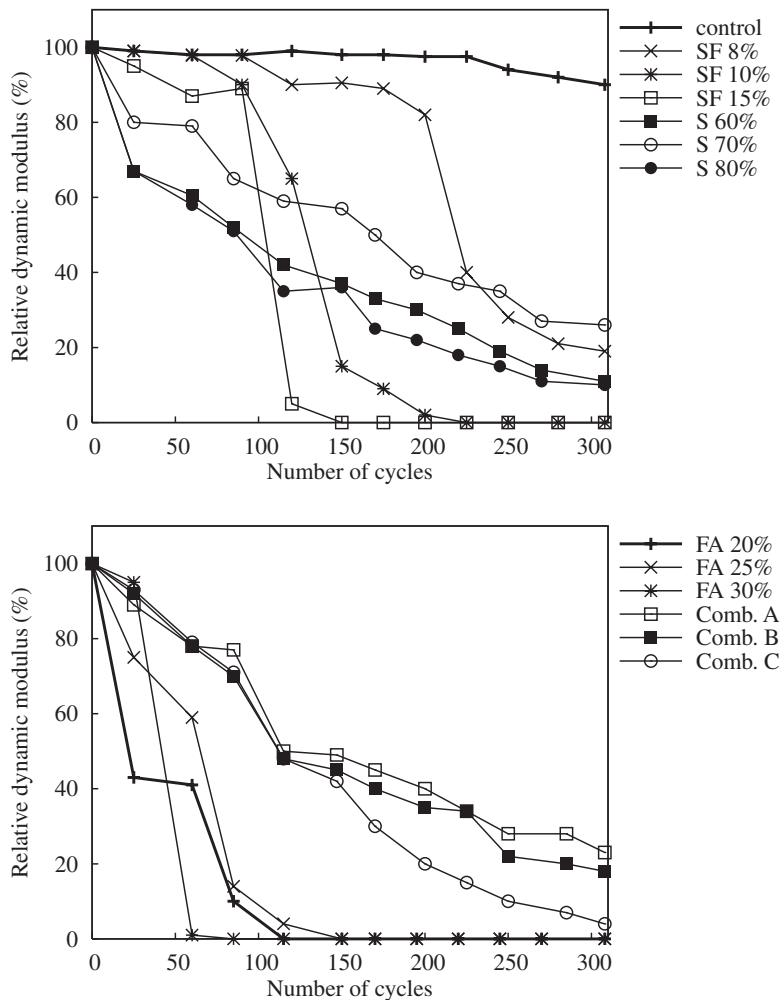
Almost all organic compounds are retarders in cement setting, and many organic acids that strongly chelate calcium also have strong retarding capability. Organic compounds retard the cement setting process by forming a protective layer around the cement grain, thus hindering the formation of calcium hydroxide (Chandra and Foldin 1987; Edmeades and Hewlett 1998; Montgomery et al. 1991a; Sora et al. 2002). Organic alcohols such as methanol and phenol not only retard the hydration process, but also form amorphous structures after drying, resulting in detrimental effects on the compressive strength of the cement (Sora et al. 2002). It is reported that phenol retards the initial and final setting times of cement by hindering the normal hydration reactions and by preventing the formation of calcium hydroxide during the initial period of setting and hardening (Vipulanandan and Krishnan 1993). 3-Chlorophenol interferes with the hydration of cement by stabilizing ettringite formation and delaying its conversion to monosulfate (Pollard et al. 1991). In general, the mechanisms of retardation by organic compounds include: (i) formation of insoluble calcium compounds, (ii) adsorption, and (iii) complexation.

3.5. Influence of additives on freeze–thaw and wet–dry cycling resistance

The durability of concrete under cold and high-salinity conditions has been of great concern to civil engineers. For example, the freezing of water in moist concrete produces osmotic and hydraulic pressures in the cement paste and the aggregate, mainly due to a 9% expansion of the water in the concrete (Neville and Brooks 1987). As these pressures increase, micro-cracks begin to form and rupture occurs when the pressure exceeds the tensile strength of the paste or aggregate. Wet–dry cycling can also contribute to the deterioration of concrete, particularly with high-salinity brackish waters. During wet–dry cycling, salts are incorporated into the mix through the naturally occurring voids in the concrete. These salts then attack the bonds in the concrete, causing the mix to develop cracks and eventually fail.

Although soil–cement mixtures are different from concrete (ACI 1990), the factors involved in freeze–thaw and wet–dry cycling that cause deterioration of concrete may also be found in hardened soil cement, since their effects mainly depend on the microstructure and permeability of the hardened material. In particular, resistance to freezing and thawing depends on factors such as permeability, degree of saturation, amount of freezable water, and rate of freezing. Many researchers have proposed

Fig. 3. Relative dynamic moduli of elasticity of different mixes. SF: silica fume, FA: fly ash, S: slag. Comb. A: 50% cement, 10% SF, 25% S, 15% FA; Comb. B: 50% cement, 5% SF, 35% S, 10% FA; Comb. C: 50% cement, 7.5% SF, 30% S, 12.5% FA (After Toutanji et al. 2004).

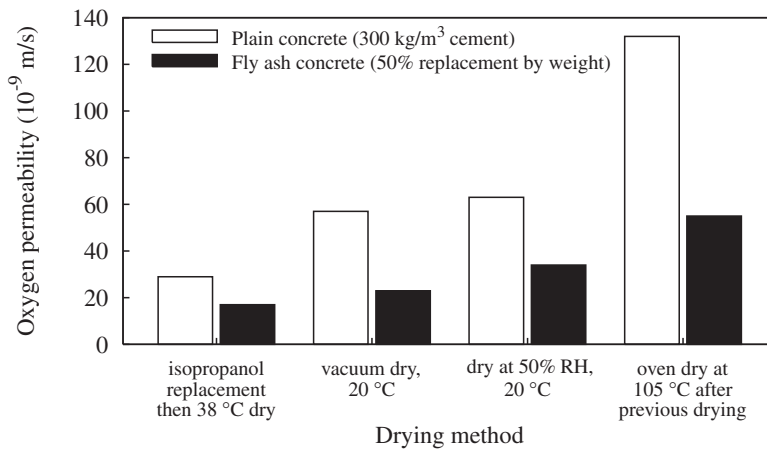


the use of various additives to alleviate these concerns caused by freeze–thaw and wet–dry cycling. For example, it has been found that freeze–thaw resistance can be increased with the use of small-particle additives, low water/cement ratio, the right amount of cement content, and proper curing conditions (Toutanji et al. 2004).

3.5.1. Inorganic additives

Toutanji et al. (2004) have studied the effects of silica fume and fly ash on freeze–thaw resistance. Using the relative dynamic modulus, P_c , as a measure of durability, their results show that the control sample, i.e., without additives, has a higher resistance to freeze–thaw exposure than mixes with supplementary cementitious materials. Note that P_c is defined as $P_c = 100(\eta_1/\eta_0)^2$, where η_0 and η_1 are the fundamental transverse frequencies without cycling and after c cycles of freezing and thawing, respectively. As shown in Fig. 3, addition of up to 8% silica fume shows similar durability as that of the control sample, but durability decreases drastically beyond 8%. Addition of silica fume increases early

Fig. 4. Effect of drying method on oxygen permeability in plain and fly ash concrete (After Day and Konecny 1989).



strength while reducing permeability (Duval and Kardi 1998). Because of their small size, silica fumes can improve packing by filling the spaces between the cement particles. In addition, they also react with calcium hydroxide during cement hydration, which may reduce bleeding and porosity. Similar results were observed with slag and fly ash. The mixtures of silica fume, slag, and fly ash show a slightly better performance, indicating the formation of a more stabilized mixture.

The effect of pozzolan on the permeability of oxygen in concrete is shown in Fig. 4. The term “pozzolan” is used to describe a range of materials that react with lime, set, and develop strength in the presence of water (Neville 1996). Note that, regardless of the drying method, fly ash concrete (50% replacement by weight of cement) has lower oxygen permeability than a comparable plain concrete of the same age (30 days) (Day and Konecny 1989). This result thus supports the notion that concrete porosity is reduced by the presence of pozzolan.

Toutanji et al. (2004) also showed that, when subject to wet–dry cycling using salt water, addition of silica fume, slag, and fly ash increased the compressive strength of concrete compared to the control sample. More specifically, the presence of 20% and 30% fly ash increased the strength against wet–dry exposure by about 16% and 30%, respectively. Similar results were also observed with slag, silica fume, and mixtures of fly ash, slag, and silica fume. Diamond (1986) reported that, in the presence of calcium chloride, the depth of penetration of chloride ion into pozzolanic cement concrete is about 15% lower than that into plain concrete. These results suggest that pozzolanic materials such as slag and fly ash may be used in cement to improve its performance in seawater environment.

Costa et al. (1992) reported that oxygen permeability, diffusion coefficient, and the compressive strength of concrete are highly dependent of the type of cement, water/cement ratio, cement content, and curing time. They proposed a general relationship for calculating the coefficient of permeability or diffusion, y

$$[6] \quad y = Ax^{-B}$$

where x is the compressive strength and A and B are constants.

3.5.2. Organic additives

Organic additives such as surfactants are used in cement as air-entraining admixtures (AEA). Surfactants are added to cement to create fine air bubbles (<1 mm diameter) during mixing (Külaots et al. 2003). These bubbles impart freeze–thaw resistance by providing void volume to accommodate the

expansion of residual water during freezing. In addition, since the hydrocarbon chain of the surfactant molecule orients towards the air bubble, the charged sheath of surfactants surrounding each bubble leads to mutual repulsion, thus preventing bubble coalescence. The presence of surfactants also improves dispersion by reducing interparticulate attractions between cement grains and preventing the particles from agglomerating, thus reducing the amount of hydration water for a required workability (Andersen 1986).

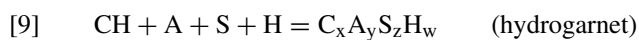
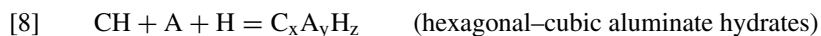
Sarda et al. (2003) demonstrated the formation of macroporous calcium phosphate bone cement using sodium dodecylsulfate (SDS), an anionic surfactant, as air-entraining agent. The amount of air entrapped depends on both the liquid/cement ratio and the surfactant concentration. The cement porosity increased with increasing liquid/cement ratio and SDS concentration up to a threshold value of 17.3 mM, beyond which no further increase was observed. It was also shown that the SDS concentration did not change the setting time, but the compressive strength decreased with increasing porosity.

3.6. Effects of alkali on the mechanical properties and durability of concrete

The literature review by Jawed and Skalny (1978) shows that alkali can reduce the ultimate strength of concrete and cause a quick setting, an increase in expansion of concrete in the presence of water, and shrinkage under drying conditions. However, from the review and the experimental studies by Smaoui et al. (2005), it is clear there is no general trend regarding the effects of alkali on expansion, shrinkage, and freeze–thaw durability of concrete.

3.7. Hydration of pozzolanic materials

Pozzolanic materials are used either separately or as an admixture with cement for S–S purposes. These substances contain SiO_2 , Al_2O_3 , Fe_2O_3 , and a small amount of CaO . Pozzolanic substances alone are not cementitious, but they may become so when reacting with calcium hydroxide and water. The use of blended Portland–pozzolan cements generally results in improved durability, sulfate resistance, and obvious economic benefits (Pollard et al. 1991). The following reactions have been proposed for the hydration of pozzolan (Pollard et al. 1991):



Pozzolanic reactions are similar to the hydration reactions of Portland cement, but they take place more slowly.

3.8. Durability

Durability reflects the structural performances over time, and it depends on both the properties of the hardened cement paste and the environmental conditions. Pure water can decompose cement compounds and dissolve the lime from them; continued leaching eventually leaves only a residue of incoherent hydrated silica, iron oxide, and alumina (Lea 1970). This action is very slow with pure water, but it can be significant under acidic condition, such as in the presence of carbon dioxide, organic or inorganic acids. Leaching rate of lime is high when the cement matrix is porous or when the water is continuously renewed. Chloride ion can affect durability by increasing the rate of leaching of portlandite, thus increasing the porosity of the cement matrix. Cement that contains natural pozzolans, fly ashes, or silica fume has been shown to be able to reduce the depth of penetration of chloride (Massazza 1998).

4. Standard testing methods

This section describes a suite of commonly used standard test methods for characterizing the properties of a soil–cement specimen, including freeze–thaw resistance, compressive strength, and leaching behaviour. In designing a cement-based S–S treatment for contaminated soil, these tests are mainly used in treatability studies to compare the laboratory performance of different cement mixes. However, it must be emphasized that there are no regulations requiring any particular test, and the set of parameters to be tested is usually selected by the technology vendor based on various factors such as soil characteristics, location of the contaminated site, method of treatment implementation, and the subsequent use of the remediated site. For example, if the cement monolith is to be buried below the frost line, then testing for freeze–thaw resistance may not be necessary.

4.1. Freeze–thaw resistance

The American Society for Testing and Materials (ASTM) D560 test method determines the resistance of compacted soil–cement mixtures to repeated cycles of freezing and thawing (ASTM 2006a). Two different test methods may be used, depending on soil gradation:

- Test Method A — Used when all the soil sample passes through a No. 4 (4.75-mm) sieve.
- Test Method B — Used when part of the soil sample is retained on a No. 4 sieve. This method is used on those materials that have 30% or less retained on a 3/4 in. (19.0 mm) sieve.

The two methods differ in the preparation procedure and composition of the compacted specimen. For both methods, the test consists of alternately freezing a cylindrical specimen (4 in. diameter) at -10°F (-23°C) for 24 h and thawing at 70°F (21°C) for 23 h. The test is continued for 12 cycles, and data collected during these cycles, i.e., mass and dimension measurements, allow the calculation of volume and water content changes and soil–cement losses.

4.2. Compressive strength

The compressive strength of a material reflects its resistance to mechanical stresses and is a useful performance indicator for cement solidified–stabilized materials. The unconfined compressive strength (UCS) can be measured using two common procedures: (i) UCS of cohesive soils (ASTM 2006b) and (ii) UCS of cylindrical cement specimens (ASTM 2006c). In ASTM standard D2166 (ASTM 2006b), the test is usually performed under controlled-strain condition, where the specimen, which is not supported laterally (unconfined), is subjected to an axial load having a vertical strain rate of 0.5 to 2% per minute. The stress–strain curve is then used to determine the UCS, which is defined as the peak stress at failure. For cement-like materials, ASTM standard D1633 (ASTM 2006c) provides an alternative test procedure. In ASTM standard D1633, a cylindrical sample is loaded axially under controlled-stress condition, and the stress recorded at sample failure is taken as the UCS. Two cylinder height-to-diameter ratios can be used: 1.15 (Method A) and 2.0 (Method B). Method A tends to yield a higher UCS than Method B, and comparisons in UCS should only be made for samples tested using the same method.

4.3. Permeability (hydraulic conductivity)

The permeability, also referred to as hydraulic conductivity, of a solidified–stabilized material is an important parameter, as it provides a measure of how easy water can pass through the material. More importantly, when considered in conjunction with leaching test results (see section 4.5), it allows assessment of a solidified–stabilized material with respect to its ability to retain contaminants. Permeability can be measured in the laboratory using two methods: (i) constant-head and (ii) falling-head (USEPA 1986). In the constant-head method, water is allowed to flow through the sample under a constant liquid

Table 6. Different leaching procedures (modified from USEPA (1989)).

Test method	Leaching medium	Liquid/solid ratio by weight	Maximum particle size	Number of extractions	Time of extraction
TCLP	Acetic acid (pH \approx 5 and 3)	20:1	9.5 mm	1	18 h
SPLP	Sulfuric/nitric acids (pH \approx 4.2 and 5)	20:1	9.5 mm	1	18 h
Semi-dynamic leaching test (ANS 16.1)	Water	$V_L/S^a = 10$ cm	Intact sample	10	Fixed time intervals
EP Tox (extraction procedure toxicity test)	0.4 mol/L acetic acid (pH = 5)	16:1	9.5 mm	1	24 h
Cal WET (California waste extraction test)	0.2 mol/L sodium citrate (pH = 5)	10:1	2.0 mm	1	48 h
Multiple extraction procedure (MEP)	Same as EP Tox, then synthetic acid rain (sulfuric acid:nitric acid in 60:40 wt% mixture)	20:1	9.5 mm	9 (or more)	24 h per extraction
Modified waste extraction procedure (MWEP)	Distilled/ deionized water	10:1 per extraction	9.5 mm or monolith	4	18 h per extraction
Equilibrium leach test	Distilled water	4:1	150 μ m	1	7 days
Acid neutralization capacity	HNO ₃ solution of increasing strength	3:1	150 μ m	1	48 h per extraction
Sequential extraction tests	0.04 mol/L acetic acid	50:1	9.5 mm	15	24 h per extraction
Sequential chemical extraction	Five leaching solutions increasing in acidity	Varies from 16:1 to 40:1	150 μ m	5	Varies from 2 to 24 h

^aRatio of leachant volume (V_L) to specimen surface area (S).

pressure (head) on both sides of the sample. The permeability can then be related to system parameters such as pressure gradient and water flow rate using Darcy's law, after the flow rate at the outlet (usually maintained at atmospheric pressure) has reached a constant value. The constant-head method is suitable for samples with high permeability ($>10^{-6}$ cm/s) (USEPA 1989).

For materials with permeability lower than 10^{-6} cm/s, the falling-head method provides a more accurate alternative. In this method, the head of the inflowing water is allowed to drop while keeping the outlet pressure constant. The transient flow behaviour, i.e., the change in head within a certain time, is then used to determine the permeability. Typical permeabilities of solidified-stabilized materials range from 10^{-4} to 10^{-8} cm/s, which are comparable to that of clay and much lower than sand (10^{-2} cm/s). In addition, it is also recommended that the permeability of solidified-stabilized wastes should be at least two orders of magnitude below that of the surrounding materials (USEPA 1989).

4.4. Leaching

4.4.1. Toxicity characteristic leaching procedure

Toxicity characteristic leaching procedure (TCLP; SW-846, Method 1311, USEPA 1992) is a single-extraction batch test. The waste S-S specimens are crushed to a particle size smaller than 9.5 mm. Two

choices of buffered acidic extraction fluids (acetic acid and sodium acetate solution) are offered under TCLP, depending on the alkalinity and the buffering capacity of the wastes. Extraction fluid # 1 has a pH of 4.93 ± 0.05 and extraction fluid # 2 has a pH of 2.88 ± 0.05 . The extraction fluid is added to a zero head space extractor (ZHE) at a liquid-to-solid ratio of 20:1, and the sample is agitated with a National Bureau of Standards (NBS) rotary tumbler for 18 h. The liquid solution is filtered through a 0.6 to 0.8 μm borosilicate glass filter under 50 psi (1 psi = 6.895 kPa) pressure for analysis. Other leaching procedures are given in Table 6 (USEPA 1989).

4.4.2. Synthetic precipitation leaching procedure

The synthetic precipitation leaching procedure (SPLP; SW-846, Method 1312, USEPA 1994) is very similar to TCLP, except that the samples are leached with different extraction fluids. For waste materials located east of the Mississippi River, an aqueous solution of sulfuric and nitric acids with a pH of 4.20 ± 0.05 is used. For materials from west of the Mississippi River, a similar solution, with a pH of 5.00 ± 0.05 , should be used. If the waste materials contain cyanide, however, then water should be used for extraction since leaching of cyanide-containing samples with acid solutions may result in the formation of hydrogen cyanide gas.

The toxicity characteristic leaching procedure was developed based on the “mismanagement scenario” that the wastes are co-disposed with municipal solid wastes (MSW) in a landfill. On the other hand, SPLP was intended to simulate the effect of acid rain on land-disposed wastes, hence the difference in the extraction fluids. The applicability of TCLP or SPLP to cement stabilized–solidified materials is still a subject of debate; however, it has been argued, in the case of treatment of mineral processing wastes, that SPLP is more appropriate for monodisposal situations, since it is unlikely that such wastes will be in contact with the organic acids normally produced by the waste decomposition in a MSW landfill (USEPA 1995).

4.4.3. Semi-dynamic leaching test

In addition to TCLP and SPLP, semi-dynamic leaching tests (ANS 1986) can also be used to determine the leaching behaviour of contaminants out of a cement solidified material. Unlike TCLP or SPLP, where the samples are crushed into small particles, an intact sample is used in the semi-dynamic leaching test. Several specimen geometries (cylinder, parallelepiped, or sphere) and dimensions can be used, but the cylindrical shape is preferred. The procedure specifies the leachant replacement intervals, and the cumulative fraction (CFR) of a substance released during the test is measured. Assuming a constant effective diffusion coefficient, D_e , the CFR can be expressed as (Dutr   et al. 1998)

$$[11] \quad \text{CFR} = \frac{2}{\sqrt{\pi}} \frac{S}{V} \sqrt{D_e t}$$

where t is leach time, S is the specimen surface area, and V is the volume of specimen. The value of D_e can therefore be determined by plotting CFR against \sqrt{t} .

In addition to the standard test methods described above, other test procedures, particularly for contaminant leaching, have also been developed for cement-based S–S treated wastes (Sanchez et al. 2000; van der Sloot and Dijkstra 2004; Barna et al. 2005). A database of test data from the literature (“MONO-LITH”) has also been developed, with an objective of developing models to examine correlations within the data set and predict properties of cement-based S–S materials (Perera et al. 2005).

5. Solidification–stabilization of organic contaminants

Although S–S treatment of inorganic contaminants has been practiced for many years, and there are many studies on the application of S–S technology in the remediation of inorganic contaminants, studies on the use of S–S with organic contaminants are comparatively less extensive (Al-Tabbaa and Rose

Table 7. Solidification–stabilization of organic compounds studied by different researchers.

Organic compound	Modifying agent or system	Reference
Phenol	–	Vipulanandan and Krishnan 1990
Phenol	–	Vipulanandan 1995
Dioxins, pentachlorophenol (PCP), creosote	–	Bates et al. 2002
2-chloroaniline	–	Sora et al. 2002
Organic halogens (AOX) and polychlorinated biphenyl (PCB)	–	Yilmaz et al. 2003
3-chlorophenol	Organophilic clay	Montgomery et al. 1991 <i>b</i>
2-chlorophenol, 2,4- dichlorophenol	Organophilic clay	Lo 1996
Methylene blue	Natural and organophilic bentonite clay	Al-Tabbaa and Rose 1996
Benzene, toluene, ethylbenzene, o-xylene	Bentonite clay	Gitipour et al. 1997
Phenol	Activated carbon	Hebatpuria et al. 1999 <i>b</i>
Phenol	Activated carbon	Arafat et al. 1999
2-chlorophenol, 1-chloronaphthalene	Organophilic bentonite	Cioffi et al. 2001
Phenol, 2-chlorophenol	Activated carbon, H ₂ O ₂	Rho et al. 2001
Carbon tetrachloride	Fe(II)	Hwang and Batchelor 2002
Phenol, aniline, methyl ethyl ketone (MEK), chlorobenzene, 2-chlorophenol	Activated carbon	Gong and Bishop 2003
2-chloroaniline	Organophilic clays	Botta et al. 2004
Polycyclic aromatic hydrocarbons (PAH)	Carbon black	Bednarik et al. 2004
PAH	Organophilic clays, activated carbon	Mulder et al. 2005

1996; Lo 1996; Gitipour et al. 1997; Hwang and Batchelor 2002; Bates et al. 2002; Sora et al. 2002; Yilmaz et al. 2003; Botta et al. 2004). The suitability of S–S treatment for organic contaminants has been reviewed by Pollard et al. (1991), and a recent extensive review of this technology by Bone et al. (2004) is also available. Table 7 summarizes the different studies of S–S treatment of organic compounds. Cement-based S–S treatment of organic contaminants can be classified into three categories: (i) direct immobilization of organic contaminants, (ii) immobilization of organic contaminants after adsorption, and (iii) immobilization of organic contaminants using oxidizing and reducing agents.

5.1. Direct immobilization of organic contaminants

As mentioned in section 3, organic compounds tend to have a detrimental effect on the properties of cementitious materials (Pollard et al. 1991), and they may be leached out after the curing process (Vipulanandan 1995; Sora et al. 2002). Sora et al. (2002) showed the inadequacy of cement structure to immobilize 2-monochloroaniline (2-MCA). They studied the hydration and structure of cement in the presence of methanol and 2-MCA and the leaching efficiency of 2-MCA from the dried structure after 28 days. The result showed that a maximum of about 75% of 2-MCA was released in the leachate solution, which indicates that the treatment is not suitable for that compound without using any adsorbent. Bates et al. (2002) reported the results of S–S treatment of various organic contaminants, including dioxins,

Table 8. Selected results of the ACW treatability study (Bates et al. 2002).

Parameter	Units	Untreated	Treated \$39/ton ^a	Treated \$62/ton ^a	Target
PCP					
Total	mg/kg	200	–	–	–
SPLP (pH) ^b	μg/L	8200 (7.0)	120 (11.8)	12 (11.8)	200
Dioxins					
Total	μg/kg	50	–	–	–
SPLP (pH)	pg/L	320 (7.0)	12 (11.8)	14 (11.8)	30
PAHs					
Total	mg/kg	29	–	–	–
SPLP (pH)	μg/L	2.8 (7.0)	<2.8 (11.8)	<2.8 (11.8)	10
Physical properties ^c					
UCS ^d	psi	–	1435	1240	>100
Permeability	cm/s	–	1.1 × 10 ⁻⁶	4.1 × 10 ⁻⁷	<1.0 × 10 ⁻⁶

^aCost (US dollar) of reagent only per ton of untreated soil using different composition.

^bSynthetic precipitation leaching procedure.

^c28 day cure time.

^dUnconfined compressive strength.

pentachlorophenol (PCP), and creosote, using cement formulations containing activated carbon or other proprietary reagents at the American Creosote site (ACW site) in Jackson, Tennessee. As shown in Table 8, the case study results show that the method is successful in reducing the concentration of organics to a target level in the leachate. In a site trial conducted at West Drayton, UK, soil contaminated with both inorganic and organic substances, including lead, copper, mineral oils, and other hydrocarbons, was successfully treated using cement mixed with a specially developed modified bentonite clay for the immobilization of PAHs. On a different site at the same location, soil contaminated with high levels of hydrocarbons was treated on a commercial scale using cement containing organophilic clay additives (Al-Tabbaa and Perera 2005).

Yilmaz et al. (2003) reported a Portland cement-based S–S treatment of adsorbable organic halogens (AOX) and polychlorinated biphenyl (PCB) contaminated soil. As shown in Table 9, they found that the S–S process reduced the mobility of AOX by 85%, but the efficiency did not increase significantly when the cement concentration was increased from 30% to 50%. Analysis of PCB in the TCLP leachates of the treated S–S waste samples shows an efficiency of approximately 65% in 20% cement concentration, and the efficiency increases about 10% at 35% cement concentration. By comparing two S–S treatments using cement and thermosetting polyester polymer, Vipulanandan and Krishnan (1990) showed that polyester polymer performed better than cement. Most of the polyester polymer solidified specimens showed no measurable amount of phenol in the leachate after the extraction procedure test.

5.2. Immobilization of organic contaminants after adsorption

As indicated by the cases cited in the preceding section, the efficiency of S–S treatment of organic contaminants may be improved using adsorbents for the organic components. These adsorbents can be incorporated as additives in the cement mix, or they can be used as a pretreatment prior to conventional cement-based solidification. Several materials have been investigated for use as adsorbents for organics in solidification–stabilization treatment. These include metal oxide, clays, natural materials (zeolites, fly ash, organic polymers, etc.), and activated carbon.

Table 9. S–S treatment of contaminated soil and sludge: AOX and PCB concentrations in TCLP leachates at different cement ratio (Yilmaz et al. 2003).

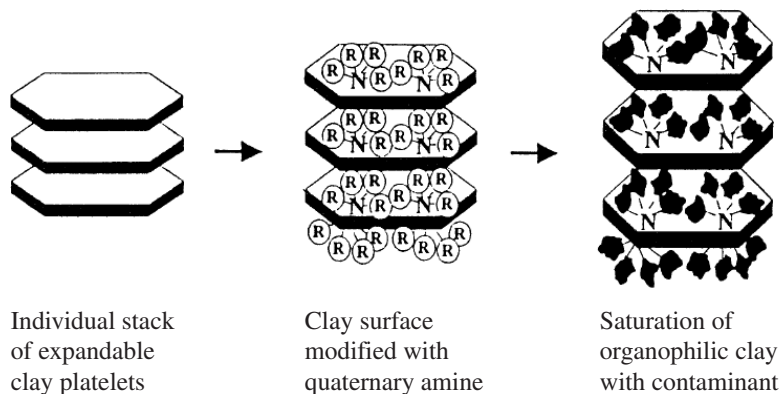
Types of waste and treatments	Leachate concentrations of treated S–S waste (mg/L)	
	Aggregate size 1–2 mm	Aggregate size > 2 mm
Sludge containing AOX ^a		
30% cement	3.37 (0.19) ^b	3.22 (0.14)
50% cement	3.11 (0.08)	3.20 (0.09)
PCB oil-contaminated soil ^c		
20% cement	0.03 (0.001)	0.018 (0.0009)
35% cement	0.022 (0.0006)	0.011 (0.0003)

^aAOX TCLP leachate concentration of untreated sludge was 20 mg/L.

^bMean (standard deviation); duplicate samples.

^cInitial, untreated TCLP leachate concentration PCB contaminated soil was 0.087 mg/L.

Fig. 5. Structure of modified clay platelets. N: nitrogen, R: alkyl group (After Boldt-Leppin et al. 1996).



5.2.1. Natural or organophilic clay

Most of the current research efforts in this area focus on organophilic clays, which are formed by exchanging the naturally occurring cations, such as Na⁺, K⁺, Ca²⁺, and Mg²⁺, in bentonite or montmorillonite clays with organic cations, usually from quaternary ammonium salts (QAS) bearing long alkyl chains. The quaternary alkylammonium ions are substituted between the clay platelets, resulting in increased spacing and enhanced adsorption of organic contaminants, including benzene, ethylbenzene, toluene, xylene (BTEX), phenols, and chlorinated phenols, due to the hydrophobicity of the alkyl chains (Boyd et al. 1988a, 1988b; Smith et al. 1990; Montgomery et al. 1991b; Xu and Boyd 1994; Sheng et al. 1996; Lo et al. 1997; Jaynes and Vance 1999; Sora et al. 2005). Figure 5 depicts pictorially the changes in the inter-platelet spacing and the process of organic modification. In general, when the alkyl group is large and nonpolar (e.g., C₁₆H₃₃), the modified clay exhibits greatly improved sorption capacity when compared to unmodified clays.

Organophilic clays seem to be the most promising option as an adsorbent for organic hazardous waste (Lo 1996; Zhu et al. 2000). The effectiveness of organophilic bentonite clays in removing BTEX was studied by Gitipour et al. (1997), who showed that (i) modified clay was about 51% more efficient than unmodified clay in removing BTEX from aqueous streams and (ii) solidified samples prepared with Portland cement and modified clay improved the immobility of BTEX by 55%. Figure 6 illustrates the effect of organophilic clay on the immobilization of phenol and phenolic compounds (see Table 10

Fig. 6. TCLP leaching test results for different solidified samples with varying amount of organophilic clays (After Lo 1996). The sample compositions are given in Table 10.

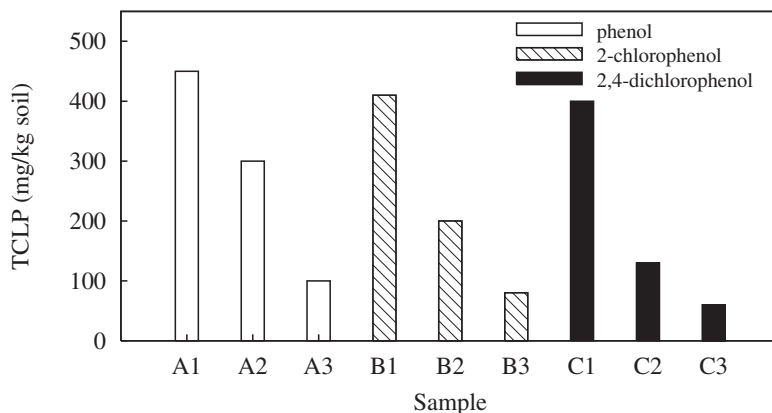


Table 10. Composition of mix development samples (Lo 1996).

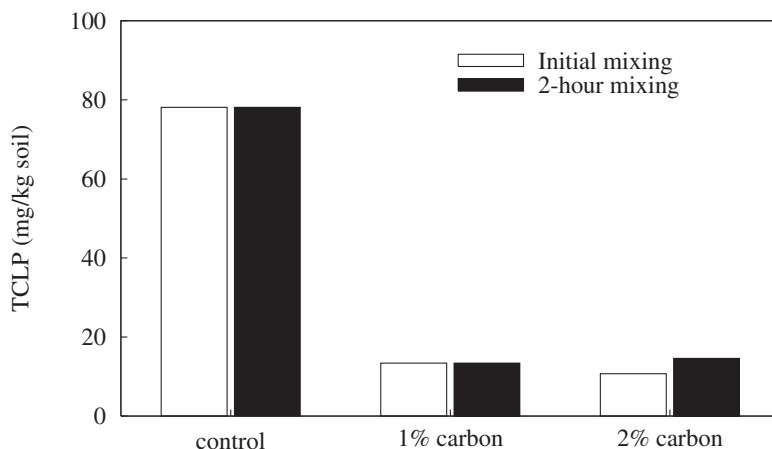
Sample	Contaminant	Soil (% wt)	Cement (% wt)	Organophilic clay (% wt)
A1	Phenol	92	8	0
A2	Phenol	86	8	6
A3	Phenol	82	8	10
B1	2-Chlorophenol	92	8	0
B2	2-Chlorophenol	86	8	6
B3	2-Chlorophenol	82	8	10
C1	2,4-Dichlorophenol	92	8	0
C2	2,4-Dichlorophenol	86	8	6
C3	2,4-Dichlorophenol	82	8	10

for sample compositions). The results show that, depending on the relative amounts of contaminated soil and cement, more than 90% of the phenol compounds can be immobilized with 10% organophilic clay. Note that the effectiveness of organophilic clays in immobilizing organic contaminants is inversely related to the water solubility of the contaminant, due to the fact that organic molecules adsorb on the organophilic clay surface through hydrophobic attraction, which is more favorable when the compound is more hydrophobic (less water soluble).

As discussed earlier, Sora et al. (2002) reported the inability of cement matrix to retain 2-MCA without any pre-adsorption. Botta et al. (2004) also showed that immobilization of 2-MCA in cement matrix could be improved greatly when organophilic clay was used as an adsorbent. In their study, an analysis of the cement microstructure indicated that porosity increased with increasing clay/cement ratio, and an optimal proportion of clay would result in better organics immobilization. In addition, organic amino compounds, which are weakly basic, can also adsorb on the acidic sites of the clay surface, in which case the system pH will be an important parameter.

The United States Environmental Protection Agency (USEPA) (1990) reported a S-S study on polychlorinated biphenyl (PCB)-contaminated soil using a proprietary additive called HWT-20. The results showed that, for low PCB-contaminated soils (83 mg/kg), the leachate PCB concentrations were below the detection limit (0.1 $\mu\text{g/L}$), whereas for high PCB-contaminated soils (5628 mg/kg), the leachate PCB concentrations were as high as 98 $\mu\text{g/L}$. On the other hand, the immobilization of 1-chloronaphthalene and 2-chlorophenol by S-S treatment in the presence of organophilic bentonite clay

Fig. 7. Effect of regenerated activated carbon on TCLP leachate analysis of phenol (1000 mg/L) from 7-day cured solidification–stabilized soil samples. Initial mixing: all components were mixed initially. Two-hour mixing: the cement was added two hours after the addition of reactivated carbon (After Hebatpuria et al. 1999b).



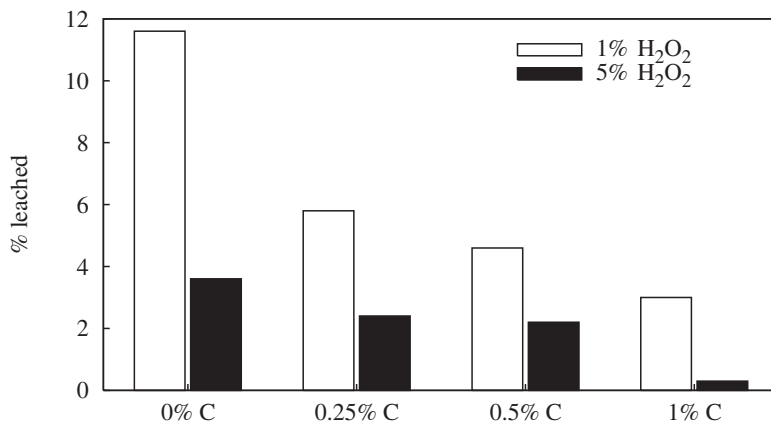
has shown to be highly effective (Cioffi et al. 2001). Immobilization of different oils in cement matrix after absorption with clay, silicate, and natural solids has also been reported by Lin and Mackenzie (1983).

5.2.2. Activated carbon

Activated carbon is commonly used in water and wastewater treatment for capturing organics and trapping many heavy metals. However, the use of activated carbon in S–S treatment has not been widely reported (Hebatpuria et al. 1999a, 1999b; Arafat et al. 1999; Rho et al. 2001). Although the use of activated carbon in S–S technology will increase the treatment cost, it may be an attractive option if cost-effective activated carbon could be used. Hebatpuria et al. (1999b) mentioned that the cost of thermally reactivated carbon might be less than one-fourth that of virgin carbon. Unlike the food industries, which prefer virgin carbon because of the potential for cross contamination, S–S technology may benefit from the reduced cost of regenerated activated carbon as a pretreatment adsorbent.

The effectiveness of using regenerated activated carbon in S–S treatment of contaminated sand is shown in Fig. 7. With the addition of 2 wt% reactivated carbon, the leaching of phenol was drastically reduced to about 11% of the original amount. Indeed, in the control samples (without activated carbon), leaching of phenol was as high as 87% of the original organic content, indicating that S–S treatment was not effective for immobilizing phenol in the absence of reactivated carbon. Figure 7 also compares the effect of two mixing sequences of activated carbon and cement on leaching of phenol. In one set of experiments, the reactivated carbon, phenol-contaminated sand, and cement were mixed together, while in the other set, cement was added 2 hours after the addition of reactivated carbon to the phenol contaminated sand. The leaching test results showed no significant difference in the amount of phenol that leached out, which suggests that the adsorption of phenol on reactivated carbon is much faster than the hydration of cement and complexation reactions of calcium with phenol. More specifically, it is known that adsorption of organic compounds, including phenol, on activated carbon is pH sensitive (Snoeyink et al. 1969). In the first set of experiments, $\text{Ca}(\text{OH})_2$ precipitation on the carbon surface could, in principle, reduce phenol adsorption by increasing the system pH (≈ 12). Thus, the observation that the leachate phenol concentration was not affected by the mixing sequence indicates that phenol adsorption is much faster than the cement hydration reaction.

Fig. 8. Effect of hydrogen peroxide and activated carbon on the leaching of phenol from cement solidified samples. Initial phenol concentration in contaminated samples is 5000 mg/L (After Rho et al. 2001).



5.3. Immobilization of organic contaminants using oxidizing and reducing agents

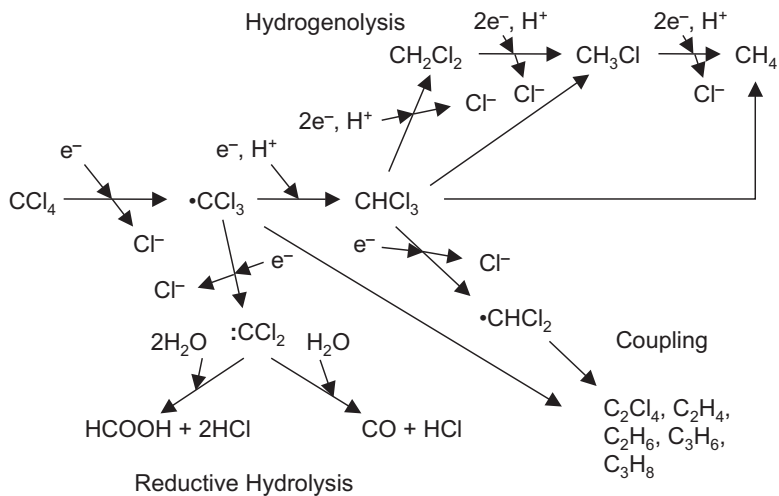
A key aspect of the preceding discussion is that immobilization of organic compounds by cement matrix, with or without adsorbent, is mainly a result of physical entrapment. Thus, for better long-term effectiveness, a more desirable process would be to transform the organic wastes to less hazardous hydrocarbons. Rho et al. (2001) has reported the immobilization and decomposition of phenol and phenolic compound inside a cement matrix in the presence of hydrogen peroxide and activated carbon. Their results, which are summarized in Fig. 8, show that with 5000 mg/L initial phenol concentration a small percentage (6%) of phenol was leached when using 0.25% carbon and 1% H₂O₂. The leached amount was further reduced to 3% when 1% carbon was used. Figure 8 also shows a considerable reduction in the leached amounts for all carbon loadings when 5% H₂O₂ was used. In the absence of any carbon, increasing the H₂O₂ concentration from 1% to 5% reduced the leached amount from 11.6% to 3.6%; with 1% carbon, the leached amounts were 7.5%, 3%, and 0.3% for 0%, 1%, and 5% H₂O₂, respectively. These results indicate that hydrogen peroxide is an oxidizing agent for phenol and demonstrates the importance of H₂O₂ addition.

Degradative solidification–stabilization (DS–S) is a novel remediation technology that combines chemical degradation with conventional solidification–stabilization. Hwang and Batchelor (2000) showed that cement slurries containing Fe(II) could effectively transform tetrachloroethylene to nonchlorinated products such as ethylene and ethane. For chlorinated alkanes such as carbon tetrachloride (CT), several degradation pathways have been proposed, as depicted in Fig. 9. However, in the Fe(II)–cement system, reductive hydrolysis was not likely because nearly all the CT was initially transformed to chloroform, and products from coupling reactions were not detected (Hwang and Batchelor 2002). Thus, dechlorination of CT in this system proceeded primarily via a hydrogenolysis pathway, resulting in a reaction product that still contains chlorinated compounds, including chloroform, methylene chloride, and a minor amount of methane. In addition, it was found that the degradation reactions in the Fe(II)–cement system were strongly dependent on pH, with an optimal value of approximately 13 (Hwang and Batchelor 2002).

6. Inorganic contaminants

Cement-based S–S has been used extensively with inorganic solid wastes that contain heavy metals such as As, Cd, Cr, Cu, Ni, Pb, and Zn (Bhatty et al. 1999), and numerous experimental and modeling studies can be found in the literature (see, for example, Islam et al. 2004a, 2004b; Catalan et al. 2002;

Fig. 9. Reaction pathways for the transformation of carbon tetrachloride (After Hwang and Batchelor 2002).



Stegemann and Buenfeld 2002, 2003; and references therein.) These processes are usually categorized based on the type of additives through which solidification is achieved (Sharma and Lewis 1994):

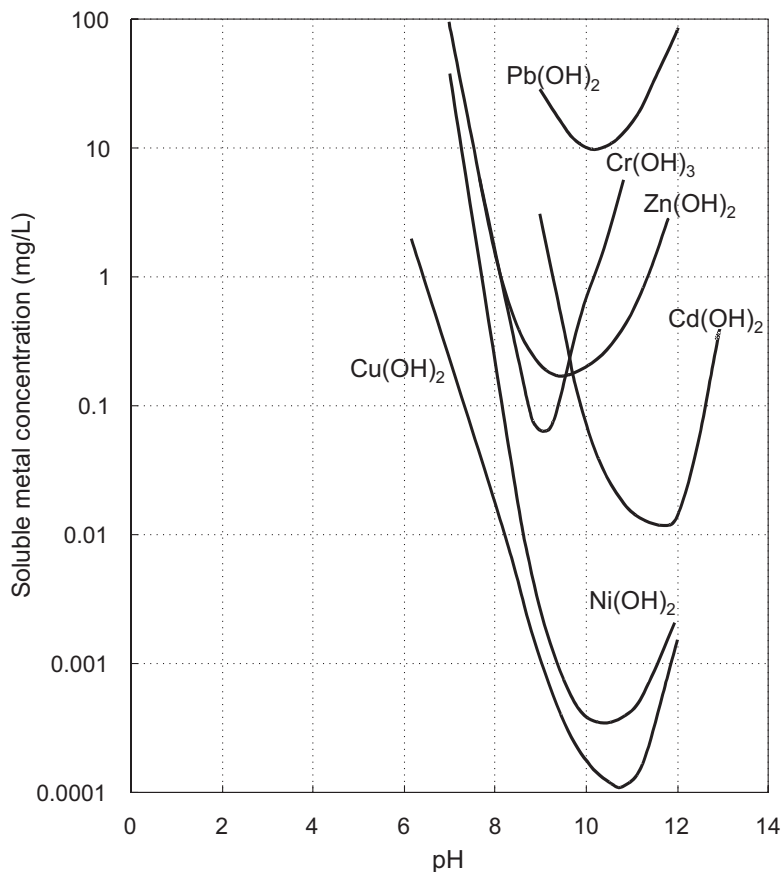
- Cement based
- Pozzolan based
- Thermoplastic method
- Organic polymerization method
- Encapsulation method
- Organophilic-clay based

Each technique has certain advantages and disadvantages. Cement-based and pozzolan-based techniques are preferred over the others mainly because of their low material and equipment cost while having good solidification characteristics at the same time. Some metals such as arsenic(III), chromium(VI), and mercury are not suitable for use with this type of treatment since they do not form highly insoluble hydroxides (Mulligan et al. 2001). The formation of insoluble hydroxides is an important aspect of cement-based S-S technology. As shown in Fig. 10, the solubility of Cd, Cr, Cu, Pb, Ni, and Zn hydroxides decreases with increasing pH up to a value of about 10 (Cullinane et al. 1986; Shi and Spence 2004). Above this pH, the solubility increases with pH as the metal cations form soluble complex anions with excess hydroxide ions. Indeed, the variation of metal hydroxide solubility with pH is an important factor for the S-S process because the pore solution of hydrated cement paste is highly alkaline (pH ≈ 13) (Mollah et al. 1995).

6.1. Arsenic

Arsenic (As) is known to be a toxic element and a carcinogen to humans (Mollah et al. 1998); even trace amounts of arsenic can be harmful to human health (Karim 2000). In recent years, arsenic has caused great public concern due to the increased awareness of the health risks associated with consumption of arsenic-containing water. The USEPA reduced the maximum concentration level (MCL) of arsenic in drinking water from 50 to 10 μg/L in January 2001 (Federal Register 2001). In nature,

Fig. 10. Calculated solubilities of metal hydroxides at different pH (After Cullinane et al. 1986; Shi and Spence 2004).



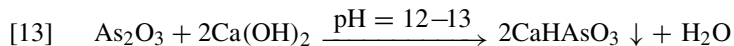
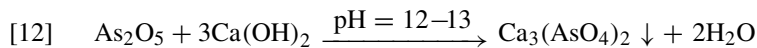
arsenics are present in two valence states, As(III) and As(V) (Boyle and Jonasson 1973), with As(III) being both mobile and toxic (Boyle and Jonasson 1973; Pansar-Kallio and Manninen 1997). Indeed, As(III) is 25–60 times more toxic than As(V) (Dutr e and Vandecasteele 1995a; Corwin et al. 1999). Large quantities of arsenic trioxide (As(III)), As_2O_3 , are available worldwide as a concentrated byproduct from various metal (Cu, Au, Ni, Pb, Zn) extraction and refining operations, mainly copper extraction and refining (Dutr e and Vandecasteele 1998; Leist et al. 2000). Another source of As is the waste fly ash from the metallurgical industry. It was also used extensively for agricultural applications such as herbicides and insecticides (Leist et al. 2000).

Several researchers have shown that arsenic can be immobilized using S–S technology. To improve the immobilization efficiency of arsenic, many researchers have used other additives with Portland cement (see Table 11). In general, the primary purposes for using additives are: (i) oxidation of As(III) to As(V), because As(V) can form low leachable compound, and (ii) formation of stable complex with calcium or iron. Many researchers have shown that, in the presence of lime, As immobilization is mainly due to the formation of Ca–As precipitates. For example, the formation of $Ca_3(AsO_4)_2$ and $CaHAsO_3$ precipitates are the main mechanism of immobilization of As in contaminated soils that have been treated with cement, lime, and pozzolanic material (Dutr e and Vandecasteele 1995a, 1998; Dutr e et al. 1999; Vandecasteele et al. 2002). In the presence of lime at high pH (12–13), the precipitation reactions

Table 11. Additives used with Portland cement in solidification–stabilization processes.

Additive	Reference
Cement	Buchler et al. 1996; Dutré et al. 1998; Leist et al. 2003; Seco et al. 2003; Halim et al. 2004
Gypsum + lime + fly ash	Ghosh and Subbarao 1998.
Cement + lime + fly ash + H ₂ O ₂	Dutr�e et al. 1999
Pozzolan + lime; lime + kaolinite	Moon et al. 2004
Cement + lime	Dutr�e and Vandecasteele 1995 <i>b</i> , 1998; Dutr�e et al. 1998; Leist et al. 2003; Vandecasteele et al. 2002
Cement + lime + H ₂ O ₂	Vandecasteele et al. 2002
Cement + H ₂ O ₂	Fuessle and Taylor 2004 <i>a</i>
Cement + iron	Miller et al. 2000; Leist et al. 2003; Jing et al. 2003; Fuessle and Taylor 2000
Cement + lime + iron	Voigt et al. 1996
Cement + Iron + H ₂ O ₂	Palfy et al. 1999
Cement + fly ash	Akhter et al. 1997; Shih and Lin 2003
Cement + organophilic clay	Buchler et al. 1996

can be written as

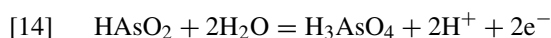


Bothe and Brown (1999) suggested that lime addition reduces As mobility in contaminated slurries due to the formation of low-solubility Ca–As precipitates such as Ca₄(OH)₂(AsO₄)₂·4H₂O and Ca₅(AsO₄)₃(OH).

The effectiveness of both As(III) and As(V) immobilization can be enhanced by increasing the Ca/As molar ratio. More specifically, Moon et al. (2004) found a significant increase in As(III) immobilization at Ca/As molar ratios greater than 1:1, and similar observation was made for As(V) at Ca/As molar ratios greater than or equal to 2.5:1. A different compound, NaCaAsO₄·7.5H₂O, was reported when As(V) was reacted with cement-lime-kaolinite or cement-fly ash (Moon et al. 2004; Akhter et al. 1997).

The efficiency of arsenic immobilization can also be improved with iron salt (Voigt et al. 1996; Miller et al. 2000; Fuessle and Taylor 2004*a*, 2004*b*; Jing et al. 2003). Fuessle and Taylor (2000) suggested that Fe(II) is generally preferable for arsenic S–S because it is effective over a wide range of mixing ratios and over the long term. The use of Fe(III) is not recommended for arsenate S–S since fresh cement mix adsorbs ferric ion and does not allow adequate S–S until after a long cure time. Furthermore, the ferric hydroxy – arsenic complex is a larger molecule than the ferrous arsenic compound, which makes encapsulation by the cement matrix more difficult. Miller et al. (2000) showed that leaching was reduced when the soil was pretreated with FeSO₄, then with Portland cement (7 days after), rather than mixing Portland cement and FeSO₄ together.

Since it is well known that As(V) can be immobilized more easily than As(III) with cement, many researchers have attempted the oxidation of As(III) to As(V) using H₂O₂ before S–S treatment for better performance (Dutr e et al. 1999; Palfy et al. 1999; Vandecasteele et al. 2002; Fuessle and Taylor 2000). The oxidation reaction in aqueous solution can be written as



In the presence of hydrogen peroxide, the reaction is

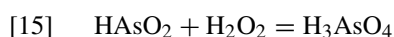
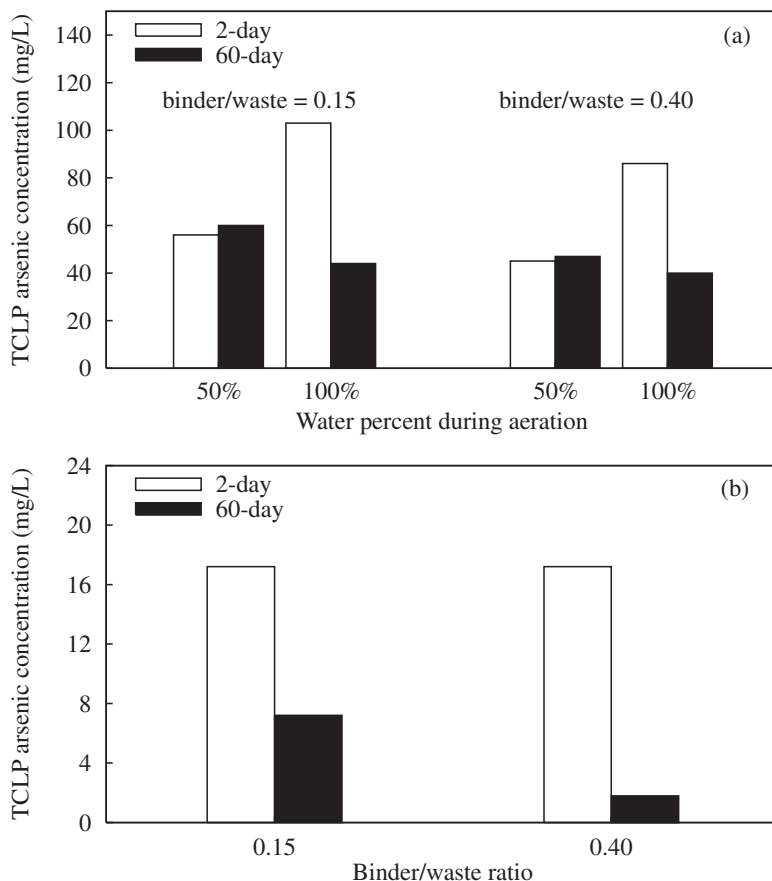


Fig. 11. TCLP results for arsenite stabilization. (a) Pretreatment by air oxidation and (b) pretreatment by 1/2 stoichiometric amount of H₂O₂ (After Fuessle and Taylor 2004a).



Oxidation reactions with H₂O₂ are often slow in acidic solutions but fast in basic solutions. Hydrogen peroxide also reacts with calcium hydroxide to form crystals of calcium peroxide, which loses the crystal water and again forms calcium hydroxide

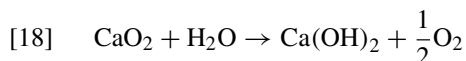
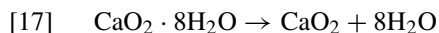
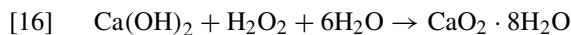
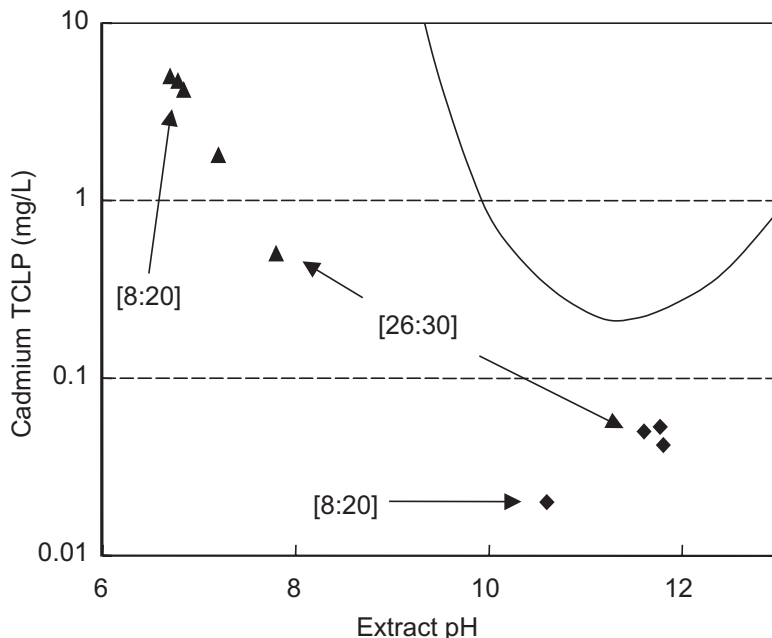


Figure 11 shows that the immobilization efficiency of As is improved when arsenite is oxidized to arsenate by H₂O₂ prior to S-S. Buchler et al. (1996) reported that addition of organophilic clay to Portland cement reduced arsenic leachability by a factor of 5–6 compared to cement alone.

6.2. Cadmium

A natural source of cadmium (Cd) comes from volcanic activities, which can release Cd into the atmosphere, spreading it over a wide area (Mulligan et al. 2001). In the past 20 years, cadmium has become a concern due to its extensive use in industrial applications such as steel plating, pigment

Fig. 12. Cadmium solubility and TCLP data. Diamond: cadmium (2 days); triangle: cadmium (370 days); solid line: cadmium solubility (After Fuessle and Taylor 2004b).



stabilization, and nickel-cadmium batteries. Excessive accumulation of cadmium is associated with various toxic effects in human, including renal dysfunction and osteomalacia (Burgatsacaze et al. 1996). Cadmium is more mobile at lower pH (4.5–5.5) and less mobile above pH 7.5.

Fuessle and Taylor (2004b) have studied the effect of aging of cement matrix on the leaching characteristic of cadmium. They found low Cd concentration in TCLP extracts when the curing time of the cement matrix was short, and the concentration increased when the curing time was more than 1 year (see Fig. 12). This phenomenon may be attributed to pH variation. As shown in Fig. 12, cadmium hydroxide has the lowest solubility at about pH 11. With the short aging time, the extract pH was between 10 and 12 for two mix designs, suggesting a low solubility for cadmium hydroxide. The importance of pH has also been reported by other researchers (Halim et al. 2003, 2004; Coz et al. 2004). In particular, high cadmium concentrations were found in the leachate when the leachate pH was below 5, which is consistent with the study described above. In addition, based on an analysis of the cementitious structure, it was also found that Cd(OH)₂ precipitates are not homogeneously distributed in the C-S-H matrix. Rather, they are concentrated within the cement pores or adsorbed on the C-S-H matrix, with up to 30% concentrated at various other locations. Shokes and Moller (1999) have also reported that colloidal iron can reduce the mobility of cadmium.

6.3. Chromium

The effects of chromium (Cr) on different Portland cement phases and the solidification of Cr in cementitious matrices have been studied by various researchers (Stephan et al. 1999a; Omotoso et al. 1996; Vallejo et al. 1999; Park 2000; Trezza and Ferraiuelo 2003; Fatta et al. 2004; Halim et al. 2004; Polettoni et al. 2004). The solidification of chromium can be related to the formation of Ca–Cr aluminates and the formation of phases such as Ca₄Al₆O₁₂CrO₄ and Ca₆Al₄Cr₂O₅ (Stephan et al. 1999b). Some authors consider that the ettringite phase is also involved in this mechanism by the substitution of Al by Cr(III) and (or) SO₄²⁻ by CrO₄²⁻, since modified Cr-ettringite, 3CaO·Al₂O₃·3CaCrO₄·32H₂O,

was observed in the XDR study by Macias et al. (1997). Trezza and Ferraiuolo (2003) studied the properties of limestone-blended (20%) cement in the presence of Cr(VI) and showed that (i) hydration was retarded and the compressive strength was reduced, especially at early ages, and (ii) leaching test result was similar to that of ordinary Portland cement at neutral pH, but Portland cement performed better at acidic pH (3). Vallejo et al. (1999) have reported the stabilization of Cr(III) with 20% Portland cement and 3% Depocrete SM/2 (a type of cement that cures very rapidly) as a stabilizer.

6.4. Copper

Copper (Cu) is found naturally in sandstones and in minerals such as malachite and chalcopyrite. Increased levels of copper in soil are due to uses in fertilizers, pesticide sprays, building materials, rayon manufacture, agricultural and municipal wastes, and industrial emissions. Polettini et al. (2004) reported the immobilization of copper in cement using an agglomeration agent, sodium methasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$). In their study, two phases, copper hydroxide ($\text{Cu}(\text{OH})_2$) and atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$), were identified as candidates for controlling copper solubility in leachate solution. Copper hydroxide was the controlling phase at pH values higher than 7, while atacamite became the solubility-controlling solid under acidic conditions. They showed that the predominant immobilization mechanism for copper was related to the precipitation and dissolution phenomena and was strongly dependent on the pH of the leachate solution. Copper can also be effectively immobilized using cement based, lime based (Yukselen and Alpaslan 2001; Fatta et al. 2004), and natural zeolite like clinoptilolite (Balkan and Kocasoy 2004) based solidification–stabilization treatment. Zain et al. (2004) have shown that the waste copper slag from blasting operation can be safely solidified and stabilized in a cement-based system.

6.5. Nickel

There are many studies on the S–S treatment of nickel (Ni) with Portland cement (Roy et al. 1992, 1993; Fatta et al. 2004; Fuessle and Taylor 2004b), cement–fly ash (Roy et al. 1993), and cement–zeolite mixture (Shanableh and Kharabsheh 1996; Balkan and Kocasoy 2004). Roy et al. (1992) observed that hydration of Portland cement was retarded by Ni-containing sludge, but the hydration products are the same as those formed without Ni. They suggested that physical encapsulation of metal hydroxide by the cement is the principal mechanism of stabilization.

6.6. Lead

Lead (Pb) is found naturally in soils, most commonly in the form of ore galena (PbS) and in smaller quantities in cerussite (PbCO_3), anglesite (PbSO_4), and crocoite (PbCrO_4). Sources of lead contaminants include lead–zinc smelters, piping, insecticides, paints, and batteries. Lead concentration in leachate after solidification–stabilization by Portland cement has been found to be dependent primarily on the leachate pH (Yukselen and Alpaslan 2001; Alpaslan and Yukselen 2002; Halim et al. 2003; Fuessle and Taylor 2004b). In particular, Pb concentration in leachate decreases with increasing pH. It becomes undetectable when the pH is between 9 and 11 due to the formation of insoluble hydroxide, but is again detectable at pH 12 due to the formation of amphoteric Pb hydroxide complexes. It was suggested that the mechanism of Pb immobilization involves not only a physical encapsulation mechanism, but also the formation of a new phase with Al and Si-rich species. Using X-ray analysis, Halim et al. (2004) found that Pb was evenly distributed throughout the C–S–H of cementitious matrix, which supports the notion that Pb immobilization is not only due to physical encapsulation.

6.7. Zinc

Sources of zinc (Zn) in soil include brass and bronze alloys, galvanized products, cosmetics, pharmaceuticals, batteries, metal coatings, glass, paint, and zinc-based alloys. Zinc is commonly found in waste as zinc chloride, zinc oxide, zinc sulfate, and zinc sulfide. Zinc hydrolyzes at pH 7.0–7.5, forming

Table 12. Superfund remedial actions: number of projects completed by technology (USEPA 2004).

Technology	Number of projects	
	Complete	Not complete
Ex situ source control		
Solidification–stabilization	105	52
Incineration (off-site)	88	16
Thermal desorption	52	17
Bioremediation	27	27
Incineration (on-site)	40	3
In situ source control		
Soil vapour extraction	73	140
Bioremediation	9	39
Solidification–Stabilization	33	15
Flushing	3	13
Chemical treatment	1	11
In situ groundwater		
Air sparging	6	52
Bioremediation	5	39
Chemical treatment	5	16
Permeable reactive barrier	0	17
Multiphase extraction	3	11
Groundwater pump and treat		
Pump and treat	63	680

Zn(OH)₂ at pH above 8 (Mulligan et al. 2001). Under anoxic conditions, ZnS can form ZnOH⁺, ZnCO₃, and ZnCl⁺. In a study using cement and binder, Coz et al. (2004) showed that zinc concentration in the leachate under a wide range of pH was very similar to that calculated based on the solubility of the hydroxide ions. In addition, the hydroxy complexes Zn(OH)₄²⁻ and Zn(OH)₅²⁻ can also be present in a strong alkaline solution (Li et al. 2001), although their anionic properties preclude their adsorption onto the negative surface of C-S-H. However, zinc may form hydrated complexes such as CaZn₂(OH)₆·H₂O (Mollah et al. 1992) and hemimorphite [Zn₄Si₂O₇(OH)₂·H₂O] (Ziegler et al. 2001a; 2001b), which may interact with and adsorb onto C-S-H.

7. Case studies

The status and achievement of S–S technology can be found in a recent report published by the USEPA (USEPA 2004), which provides information up to March 2003. Bone et al. (2004) mentioned in their review that a number of organizations in the United Kingdom are also working on the application of S–S in contaminated site remediation. Table 12 lists the number of Superfund remediation projects, categorized according to the technology employed. Note that ex situ S–S treatment is used for a significant number of sites. Ex situ source control projects usually involve the excavation of contaminated soil and the application of an aggressive treatment technology in a controlled environment. This type of remediation typically requires a shorter time to complete. In situ treatments are those that are applied to the contaminated media in place, without excavation. These projects usually require longer treatment times because they take place in a less controlled environment, which may limit the treatment rate. However, in some cases, such as large scale in situ auger-mixed S–S projects, the treatment can be done relatively quickly.

Table 13. Superfund remedial actions using S–S treatment for different contaminated sites (USEPA 2004).

Group of the contaminants	Number of sites
Polycyclic aromatic hydrocarbons (PAH)	16
Nonhalogenated semivolatile organics (exclude PAH)	18
Benzene-toluene-ethylbenzene-xylene (BTEX)	12
Nonhalogenated volatile organics (exclude BTEX)	13
Organic pesticides and herbicides	14
Halogenated semivolatile organic compounds (not pesticides and herbicides)	7
Halogenated volatile organic compounds	14
Polychlorinated biphenyls (PCB)	35
Metalloids and metals	174
<i>Total</i>	303

Table 13 summarizes nine major groups of contaminants treated by S–S technology in different sites in the US. Note that S–S technology has been used mostly for inorganic contaminants (58% out of 303 sites), but it has also been applied to a considerable number of sites (42%) with different organic contaminants. For example, as cited in section 5, Bates et al. (2002) reported a successful S–S treatment of organic contaminants using cement mixed with activated carbon at the American Creosote Superfund Site in Jackson, Tennessee.

8. Canadian regulations

The legislations, regulations, and guidelines related to contaminated site remediation in Canada can be considered at two levels: federal and provincial. There are no laws on the federal level that specifically address the designation and remediation of contaminated sites. However, several federal legislations, particularly the *Canadian Environmental Protection Act, 1999* and the *Fisheries Act*, would find general applicability in site remediation projects. On the provincial level, each jurisdiction adopts a slightly different approach to managing contaminated sites. The provinces establish their own sets of regulations and guidelines for various aspects of contaminated site management, including site identification or designation and the approaches used throughout the remediation process. In addition, it is important to note that Canada is a party to the Stockholm Convention on Persistent Organic Pollutants (PoPs), which is a global treaty aiming at reducing or eliminating the release of many PoPs such as PCB into the environment.

8.1. Federal legislations

The major legislations applicable to contaminated site remediation include (AMEC 2004)

- (1) Canadian Environmental Assessment Act
- (2) Fisheries Act
- (3) Canadian Environmental Protection Act, 1999 (CEPA)
- (4) Navigable Waters Protection Act
- (5) Transportation of Dangerous Goods Act, 1992

A number of regulations under the CEPA can potentially be applied to contaminated site remediation. For example, section 4 of the Disposal at Sea Regulations specifies the concentration levels for five

Table 14. Concentration levels of five substances specified in the disposal at sea regulations of the Canadian Environmental Protection Act, 1999.

Substances	Concentration
Cadmium	0.6 mg/kg
Mercury	0.75 mg/kg
Total PAHs	2.5 mg/kg
Total PCBs	0.1 mg/kg
Persistent plastics and synthetic materials	4% by volume

substances above which an assessment of the waste matters is required (see Table 14). Section 7 of the Federal Mobile PCB Treatment and Destruction Regulations specify that all gas released into the environment from any thermal and chemical treatment technology must meet the following standards:

- (1) Particulate matter less than 50 mg per normal cubic meter of gas released
- (2) Hydrogen chloride less than 75 mg per normal cubic meter of gas released
- (3) 2,3,7,8-substituted polychlorinated dibenzo-para-dioxins and 2,3,7,8-substituted polychlorinated dibenzofurans less than 12 ng per normal cubic meter

Cement-based S-S technology, although not a thermal treatment, may conceivably be categorized as a chemical treatment, particularly if the cement slurry is formulated to chemically modify the organic contaminants (See section 5.3). In such cases, any gas released during the treatment process may be subject to these emission regulations.

The *Fisheries Act* prohibits the discharge of “deleterious substances” into water frequented by fish and requires that any adverse effects be remedied if such deposits occur (Mitchell and Seward 2001). However, under the *Fisheries Act*, there are no regulations or guidelines that define the water quality standards for site remediation purposes (AMEC 2004). Instead, these standards are found in guidelines developed by the Canadian Council of Ministers of the Environment (CCME) and individual provinces. Other federal legislations affect site remediation in other, less direct, manner. For instance, the *Canadian Environmental Assessment Act* provides the definition of a “project” and details how an environmental assessment may be triggered. The *Transportation of Dangerous Goods Act* applies whenever there is movement of chemicals or contaminated waste materials (e.g., to off-site treatment plants).

8.2. Provincial legislations and guidelines

Each province has set up its own legislations, regulations, and guidelines for managing contaminated sites. The major provincial environmental legislations and guidelines applicable to contaminated site remediation are summarized in Table 15. In addition to these provincial legislations and the major federal legislations discussed above, other legislations, guidelines, and policies, both federal and provincial, may also be applicable. For example, in Nova Scotia, compliance with the *Dangerous Goods Transportation Act*, the *Occupational Health and Safety Act*, and the Municipal Solid Waste Landfill Guidelines is required. A more extensive summary of applicable provincial legislations can be found in the Environmental Guide for Federal Real Properties Managers (TBS 1999).

8.2.1. Site identification and designation

The authority and procedure for identifying and designating a site as contaminated varies among the provinces. In Alberta, British Columbia (BC), Manitoba, Yukon, and Nova Scotia, legislations specifically provide for the designation of contaminated sites, either by a manager, or director, or by the

Table 15. Major provincial legislations and guidelines related to contaminated site remediation (Mitchell and Seward 2001).

Province	Legislations
Alberta	Environmental Protection and Enhancement Act Guideline for the Designation of Contaminated Sites under the Environmental Protection and Enhancement Act
British Columbia	Waste Management Act Contaminated Sites Regulation Special Waste Regulation
Manitoba	Environment Act Dangerous Goods Handling and Transportation Act Contaminated Sites Remediation Act Contaminated Sites Remediation Regulations Guidelines for the Designation of Contaminated Sites in Manitoba Guideline for Environmental Site Investigations in Manitoba
Saskatchewan	Environmental Management and Protection Act, 2002 Environmental Spill Control Regulations Hazardous Substances and Waste Dangerous Goods Regulations Mineral Industry Environmental Protection Regulations, 1996 Municipal Refuse Management Regulations
Ontario	Environmental Protection Act Guideline for Use at Contaminated Sites
Québec	Environment Quality Act Soil Protection and Contaminated Sites Rehabilitation Policy
Northwest Territories and Nunavut	Environmental Protection Act Spill Contingency Planning and Reporting Regulations Environmental Guideline for Contaminated Site Remediation
Yukon	Environment Act, 1991 Contaminated Sites Regulation Spills Regulations
New Brunswick	Clean Environment Act Guideline for the Management of Contaminated Sites –Version 2
Newfoundland and Labrador	Environmental Protection Act Storage and Handling of Gasoline and Associated Products Regulations, 2003 Air Pollution Control Regulations, 2004 Guidance Document for the Management of Impacted Sites
Nova Scotia	Environment Act Guidelines for Management of Contaminated Sites in Nova Scotia
Prince Edward Island	Environmental Protection Act Petroleum Contaminated Sites Remediation Guidelines

Minister. Their decision regarding site designation is made after following certain guidelines or criteria, and is often based on information obtained through site investigation. In Alberta, for example, the Guideline for the Designation of Contaminated Sites under the *Environmental Protection and Enhancement Act* details the core and supplemental criteria for determination of contaminated sites. However, it is important to note that, except for Manitoba (*Contaminated Sites Remediation Act*), site designation is mostly discretionary.

In other provinces, there are no specific legislations for site designation, but the authority is often vested in the director or Minister, as in the case of Ontario and Saskatchewan. In Québec, the *Envi-*

Environment Quality Act also does not define contaminated sites and does not provide for site designation. Similar to Québec, the *Environmental Protection Act* of the Northwest Territories contains no provisions for definition and designation of contaminated sites. However, the Environmental Guideline for Contaminated Site Remediation (NWT 2003) does provide a definition of contaminated sites as “areas of land, water, groundwater, or sediments that have levels of contaminants exceeding the remediation criteria.” In the Yukon, a site may be designated as contaminated by the Minister under the *Environment Act, 1991*, but the Minister must follow the process and a number of criteria outlined in the Contaminated Sites Regulations, and the decision is discretionary.

8.2.2. Remediation standards

There are two general approaches to establishing objectives in contaminated site remediation: (i) guideline-based or criteria-based and (ii) risk-based. The guideline-based approach uses specific concentration values for each contaminant set in the guidelines and regulations, which are usually established to cover a wide range of scenarios. In most cases, these guideline values are used to trigger further, more detailed, site investigation. With the risk-based approach, each site is assessed separately for the risk posed to both human and the ecological system by the contaminants. Factors such as the type and concentration of the contaminants, and the possible receptors and exposure pathways are considered, and proper concentration limits for individual contaminants are then established specifically for the site. In many cases, risk-based standards do not necessarily require the complete removal and destruction of the contaminants.

The provinces establish their guideline values using one of the following three approaches (Punt 2002):

- (1) Adopting the Canadian Council of Ministers of the Environment (CCME) Environmental Quality Guidelines (EQGs) (Manitoba, Newfoundland and Labrador, Northwest Territories, and Nunavut)
- (2) Establishing own values based on the soil, water, and sediment categories set by the CCME (BC, Alberta, Saskatchewan, Ontario, Québec, and Yukon)
- (3) Establishing guideline values based on the surface–subsurface and potable–nonpotable categories (Ontario, New Brunswick, Nova Scotia, and Prince Edward Island)

The CCME EQGs include the Canadian Soil Quality Guidelines (CSoQGs) and the Canadian Water Quality Guidelines (CWQGs). The CSoQGs for various contaminants are categorized based on proposed land-uses: (i) agricultural, (ii) residential and (or) parkland, (iii) commercial, and (iv) industrial. The CWQGs are subdivided into four sets of guidelines:

- (1) Canadian Water Quality Guidelines for the Protection of Aquatic Life
- (2) Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses
- (3) Guidelines for Canadian Drinking Water Quality
- (4) Guidelines for Canadian Recreational Water

In addition to soil and water quality, the EQGs also contain guidelines for sediments and tissue residue. A summary of these guidelines can be found at the CCME web site (CCME 2002). The CSoQGs for selected contaminants are summarized in Table 16.

Among those provinces that adopt their own criteria values based on the CCME EQGs, there is no general trend as to whether the values are higher or lower than the CCME values. British Columbia and the Yukon have both generic and matrix numerical soil standards. The coverage of the contaminants also varies among the provinces. For example, Ontario, Québec, and BC have guideline based values for a wide range of substances, whereas the Yukon has a list of soil values focused on heavy metals and a few organics.

Table 16. Canadian soil quality guidelines for selected contaminants (CCME 2002).

Contaminant	Land-use categories			
	Agriculture (mg/kg)	Residential/parkland (mg/kg)	Commercial (mg/kg)	Industrial (mg/kg)
Arsenic (inorganic)	12	12	12	12
Cadmium	1.4	10	22	22
Chromium (total)	64	64	87	87
Copper (total)	63	63	91	91
Lead	70	140	260	600
Nickel	50	50	50	50
Zinc	200	200	360	360
Benzene	0.05	0.5	5	5
Ethylbenzene	0.1	1.2	20	20
Naphthalene	0.1	0.6	22	22
Phenol	3.8	3.8	3.8	3.8
PCBs	0.5	1.3	33	33
Toluene	0.1	0.8	0.8	0.8
Trichloroethylene	0.1	3	31	31
Xylene	0.1	1	17	20

9. Concluding remarks

In this review, we have summarized the results of various reports and research literature on the immobilization of organic and inorganic contaminants using cement-based solidification–stabilization technology. More specifically, we have focused on the mechanisms of cement setting and immobilization of contaminants in the presence of other additives. The major conclusions can be summarized as follows:

- (1) Inorganic and organic compounds may interfere with the hydration of cement, hence affecting the pore structure and the final strength. The interference mechanisms of these compounds include adsorption, complexation, precipitation, and nucleation. Inorganic compounds generally shorten the setting time and increase the rate of early strength development. The efficiency of immobilizing these compounds depends mainly on the ion charge and size; small, highly charged ions can be immobilized more effectively. Organic compounds may act as retarders in cement hydration process.
- (2) Immobilization of organic contaminants can be classified into three categories: (i) direct immobilization of organic contaminants, (ii) immobilization of organic contaminants after adsorption, and (iii) immobilization of organic contaminants using oxidizing and reducing agents.
- (3) Heavy metals can be stabilized in the cement matrix by forming insoluble metal hydroxides, whose solubility is highly pH dependent (reaching a minimum at $\text{pH } 10 \pm 1$). Leachate pH is therefore an important factor in determining the leaching behaviour of heavy metals in S–S treatment. Oxidizing agent can improve the immobilization of arsenic, as As(III) is oxidized to As(V), which forms low leachable compounds. Metallic contaminants can also be immobilized through sorption into C–S–H or ion substitution in ettringite.
- (4) In the S–S treatment of organic compounds using cement alone, the contaminants are physically trapped within the pores in the cement matrix and are not reacting with the polar inorganic components of the cement constituents. Use of adsorbents such as organophilic clays and activated

carbon, either as a pretreatment or as additives in the cement mix, can more effectively immobilize organic compounds in the cement matrix.

- (5) Use of oxidizing agents with S–S treatment is a novel remediation technology, which decomposes and (or) transforms the organic wastes encapsulated in the cement matrix.
- (6) Each provincial jurisdiction adopts a slightly different approach to managing contaminated sites, and each has established its own set of regulations and guidelines for various aspects of contaminated site management, including site identification or designation, and the approaches used throughout the remediation process.
- (7) Guideline or criteria values for various contaminants are established in all provinces, but they are used mainly to trigger further investigation within the site management scheme. Most provinces have adopted the risk-based approach, in which each contaminated site is evaluated, and the risk posed to human health and the ecological system is assessed, separately to develop site specific criteria. The selection of remediation options can be more flexible under the risk-based approach, which does not necessarily require the complete destruction or removal of contaminants.

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