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ORIGINAL CONTRIBUTION

ETTRINGITE AND C–S–H PORTLAND CEMENT PHASES FOR WASTE ION IMMOBILIZATION: A REVIEW

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ABSTRACT. The formation, structure and chemistry of the ettringite and C–S–H phases of Portland cement have been reviewed as they relate to waste ion immobilization. The purpose of this review was to investigate the use of Portland cement as a host for priority metallic pollutants (Cr, Pb, Ba, Se, Zn, Ag, Hg, As and Cd) as identified by the Environmental Protection Agency and as a host for radioactive waste ions (various isotopes of Am, C, Cs, I, Np, Pu, Ra, Sr, Tc, Th, Sn, U) as identified in 40 CFR 191. Ettringite acts as host to a number of these ions in both the columnar and channel sections of the crystal structure. Substitutions have been made at the calcium, aluminum, hydroxide and sulfate sites. C–S–H also hosts a number of the waste species in both ionic and salt form. Immobilization mechanisms for C–S–H include sorption, phase mixing and substitution. The following ions have not apparently been reported as specifically immobilized by one of these phases: Ag, Am, Np, Pu, Ra, Tc, Th and Sn; however, some of these ions are immobilized by Portland cement. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Cementitious, or cement-based, waste forms are commonly used worldwide for disposal of radioactive, hazardous and mixed wastes. The U.K., for example, routinely 'encapsulates' intermediate level radioactive waste into cement forms at its nuclear fuel reprocessing facility.[1] In the U.S.A., an independent panel of scientists and engineers commissioned by the NRC in 1977 concluded that cementitious solidification technologies ought to be given serious consideration for wastes similar to those processed by France and the U.K.[2] The U.S. Environmental Protection Agency also recognizes cementitious solidification as the 'best demonstrated available technology' (BDAT) for land disposal of most toxic elements.[2,3]

There are two main reasons for converting raw wastes into more formal waste forms which immobilize radioisotopes. One is to allow for safer transport of the waste to a repository using the existing transportation systems. The other is to reduce the probability of total 'system failure' should the repository itself fail. In both cases, the key is the immobilization of the waste ions in the waste form and the subsequent prevention of waste ion migration to the 'biosphere'.

The most commonly used medium in this solidification/stabilization (s/s) process is Portland cement. A great deal of testing has been done on Portland cement waste forms to determine their viability in terms of waste ion compatibility, waste loading potential and performance in leach tests. Beyond this, however, it is important to understand the mechanisms by which waste ions become immobilized in a particular host in order to pair the most compatible waste and host. In a collection of papers from the *Chemistry and Microstructure of Solidified Waste Forms Symposium*,[4] editor Roger D. Spence comments that 'despite common usage worldwide, the fundamental chemistry and microstructure of these waste forms is not well known, although some fundamental knowledge does exist.' This paper provides a review of the 'fundamental knowledge' and of some recent studies on the chemistry of Portland cement as it relates to waste ion immobilization.

PORTLAND CEMENT

Composition

Portland cement is manufactured by heating a mixture of quartz, limestone and clay, or other similar materials. At an approximate temperature of 1450°C, partial fusion occurs among these components forming

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an assemblage of crystalline and amorphous phases called clinker. The Portland cement clinker is subsequently ground with gypsum to a fine powder which is cement.[5]

The four main crystalline clinker phases which form are called alite, belite, aluminate phase and ferrite phase. Alite is tricalcium silicate (Ca_3SiO_5) and constitutes 50–70% of Portland cement clinkers. Belite constitutes 15–30% of clinkers and has the dicalcium silicate formula and structure (Ca_3SiO_4). The aluminate phase (tricalcium aluminate, $Ca_3Al_2O_6$) and the ferrite phase (tetracalcium aluminoferrite, Ca_2AlFeO_5) constitute 5–10% and 5–15%, respectively.[5]

Cement powder (anhydrous cement) created from the co-grinding of clinkers and gypsum is mixed with water and hydrate phases are formed. The hydration process in cement chemistry is generally more complex than the simple conversions of anhydrous compounds into the corresponding hydrates. Entirely new compounds are formed during this exothermic process, and the phases change in structure and composition as the cement ages. The rate of these changes is adjusted by the use of gypsum in order to maximize the strength and durability of the cement.

Waste Ion Incorporation

If waste ions are mixed with anhydrous cement and water, there is a possibility of ion incorporation during the hydration process. Several types of waste ion interactions that may occur in the cement structure are illustrated in Fig. 1. Cocke and Mollah,[6] suggest a waste ion may 'chemisorb, precipitate, form a surface compound to any of several cement component surfaces, form inclusions or be chemically incorporated into the cement structures, or have simultaneous occurrence of several of these situations'.

Ion immobilization in Portland cement allows for its use as a waste form for heavy metals and radioactive wastes, among others. The heavy metal ions of concern are identified by the Environmental Protection Agency as priority metallic pollutants. They are chromium (hexavalent), lead, barium, selenium, zinc, silver, mercury, arsenic and cadmium.[6] A list of radionuclides for consideration is provided in 40 Code of Federal Regulations, Part 191, entitled 'Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Wastes'. These ions are shown in Table 1 along with the legal release limits for radioactive waste containment requirements.

It should be noted that, although this list of radionuclides was taken from a source specifically addressing high-level and transuranic wastes, the ions present in low-level radioactive wastes are also represented in this table.

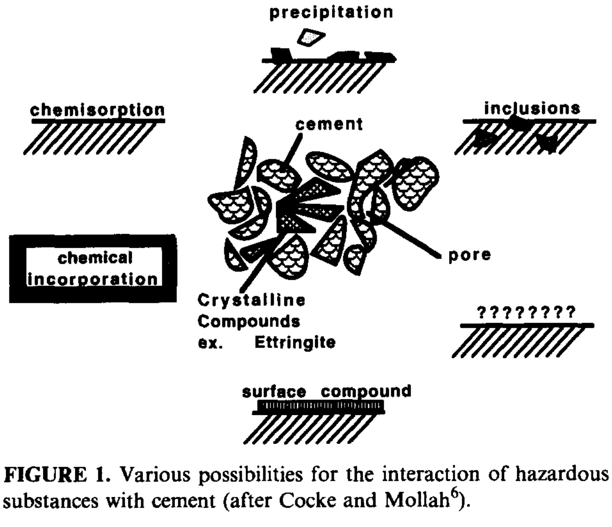


FIGURE 1. Various possibilities for the interaction of hazardous substances with cement (after Cocke and Mollah[6]).

TABLE 1
Radioactive Waste Nuclides and their Release Limits for Containment Requirements*[7]

Radionuclides	Release limit per 1000 MTHM† or other unit of waste (Curies)
Americium-241 or -243	100
Carbon-14	100
Cesium-135 or -137	1000
Iodine-129	100
Neptunium-237	100
Plutonium-238, -239, -240, or -242	100
Radium-226	100
Strontium-90	100
Technetium-99	10,000
Thorium-230 or -232	10
Tin-126	1000
Uranium-233, -234, -235, -236, or -238	100

*Cumulative releases to the accessible environment for 10,000 years after disposal,
†MTHM, metric tons of heavy metal.

ETTRINGITE

Ettringite is the prototype of the AFt phases of hydrated cement which have the general formula (tricalcium)-*A*luminate *F*errite · *t*ri (sulfate, -hydroxide, etc.) · (hydrate). The AFt designation was first suggested by Smolczyk in a 1961 publication in order to distinguish the high sulfate hydrate phases from the low sulfate phases, which are collectively termed AFm (*A*luminate *F*errite · *m*ono).[8] Ettringite occurs as a natural mineral along with others of similar structure and composition fitting into the ettringite group of minerals.

Formation

Ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) appears as a hydrate phase of Portland cement in the first stage

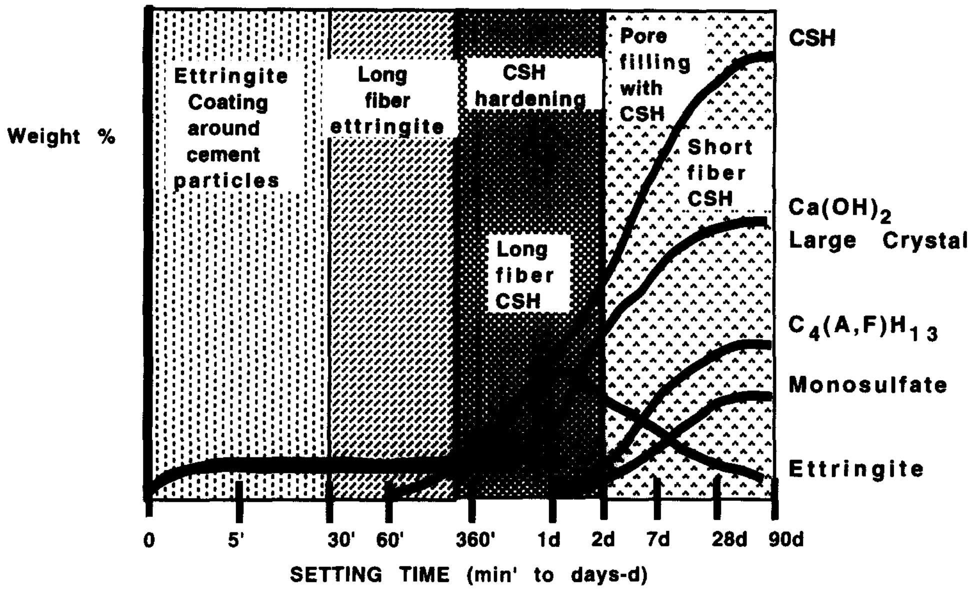


FIGURE 2. The hydration of Portland cement (after Cocke and Mollah[6]).

of hydration. The setting of cement can be divided into four overlapping stages as shown in Fig. 2.

In stage one, the aluminate phase reacts with water in the presence of calcium sulfate to form ettringite

$$3CaO \cdot Al_2O_3 + 3CaSO_4 + 32H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (6)$$

It can also form through a reaction of the ferrite hydrate phase. Taylor[5] observes that the ettringite produced in this first hydration stage tends to be in the form of stubby, prismatic crystals close to the aluminate surface while also forming away from these surfaces. As is indicated in Fig. 2, ettringite is formed within minutes of the start of cement hydration. Its concentration increases to a maximum at about 1 day and then begins to decrease and may even approach zero. As the ettringite disappears, a mono-sulfate (AFm) hydrate phase takes its place due to the lower sulfate concentration in the pore solutions. While Greene[9] has described some past controversy over which sulfate phase is formed first in cement hydration, it is now generally accepted that the high sulfate ettringite phase is the initial component. Midgley and Rosaman[10] support this theory by describing a study of three Portland cements in which the initial hydrate precipitate is of nearly pure ettringite composition.

Structure

Ettringite, like other AFt phases, forms hexagonal prismatic or acicular crystals. The crystals have two distinct structural components

Columns

$$\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}^{+6} \quad (11)$$

and

Channels

$$\{(SO_4)_3 \cdot 2H_2O\}^{-6} \quad (12)$$

Figure 3 illustrates the structure of ettringite. The columns consist of $Al(OH)_6$ octahedra alternating with triangular groups of edge-sharing CaO_8 polyhedra. Column alignment is along the *c*-axis of a trigonal–hexagonal unit cell. The eight oxygens in the polyhedra come from Ca coordination with four OH^- ions shared with the $Al(OH)_6$ octahedra and from coordination with four H_2O molecules. The hydrogen atoms on the water molecules form the cylindrical surface of the columns. The channels contain four sites per formula unit of the column structure which

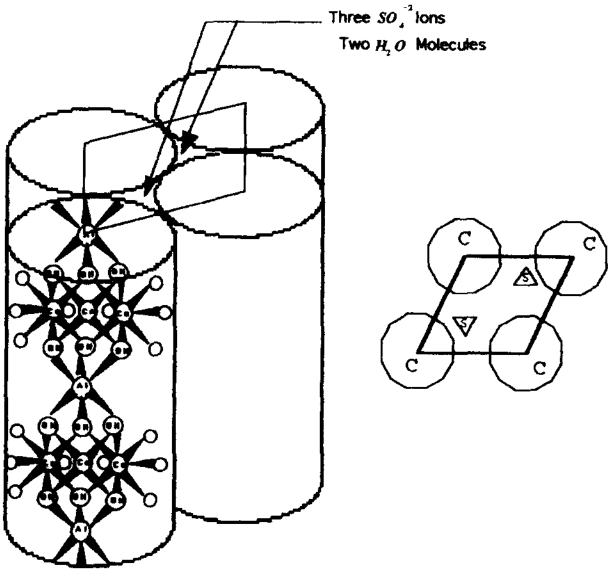


FIGURE 3. Ettringite structure where 'C' indicates the column structures and 'S' indicates the sulfate oxyanion tetrahedra (after Taylor[13] and Kumarathasan *et al.*[12]).

TABLE 2
Structures of the Ettringite Group of Natural Minerals[13]

Charlesite subgroup	
Bentorite	$Ca_6Cr_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
Charlesite	$Ca_6(Al,Si)_2(SO_4)_2[B(OH)_4](OH,O)_{12} \cdot 26H_2O$
Sturmanite	$Ca_6Fe_2(SO_4)_2[B(OH)_4](OH)_{12} \cdot 26H_2O$
Ettringite subgroup	
Ettringite, syn	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
Thaumasite subgroup	
Jouravskite	$Ca_6Mn_2(OH)_{12}(SO_4)_2(SO_3)_2 \cdot 24H_2O$
Thaumasite	$Ca_6Si_2(OH)_{12}(SO_4)_2(CO_3)_2 \cdot 24H_2O$

contains six calcium atoms. Three of these sites are occupied by SO_4^{-2} and one by two H_2O molecules.[5]

Waste Ion Immobilization

The ettringite structure is a very 'forgiving' one. It can withstand modest deviations in composition without a change in structure. This compositional change occurs on the crystal chemical level in the form of ionic substitution. The ions available for substitution in the ettringite structure are Ca^{+2}, Al^{+3}, SO_4^{-2} and OH^-. Examination of the ettringite group of minerals provides naturally occurring evidence of compositional change at these sites. When compared with ettringite $\{Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O\}$, the thaumasite mineral formula $\{Ca_6Si_2(OH)_{12}(SO_4)_2(CO_3)_2 \cdot 24H_2O\}$,[12] for example, shows aluminum replaced by the tetravalent cation, Si^{+4}, along with sulfates' partial replacement by another divalent anion, CO_3^{-2}. Thaumasite and ettringite are not completely miscible, but Taylor[5] suggests limited solid solutions probably occur. It is interesting to note the maintenance of charge balance accomplished by the substitutions described while the stoichiometry has been sacrificed. In fact, the stoichiometries of ettringites produced in cement and in nature usually exhibit an excess or deficiency of several components.[11]

Table 2 provides a complete list of the ettringite group of minerals. Study of these structures provides information on some natural and, therefore, stable ionic substitutions possible in the structure of ettringite.

All crystal chemical substitutions in the minerals occur at the aluminum and sulfate sites. The aluminum site, in general, accommodates a variety of trivalent and tetravalent cations in a spectrum of proportions. In fact, as first shown by McIntire and Shaw in 1925, solid solution in the $\mathbf{Fe^{+3}}$–$\mathbf{Al^{+3}}$ series is almost continuous.[8] This was later confirmed by Malquori and Cirilli in 1940 and again in 1943 by Cirilli.[8] Taylor[5] suggests a probable gap in the solution at 70–80 mole % $\mathbf{Fe^{+3}}$. Bensted and Varma[15] confirmed some of the mineral substitutions by replacing Al_2O_3 with various sesquioxides of the first transitions. Also attempted in this study was a replacement of alumina with $\mathbf{B_2O_3}$. In addition to those substitutions seen in the minerals, Bonen and Sarkar[16] report $\mathbf{Ni^{+3}}$ and $\mathbf{Co^{+3}}$ replacing aluminum and Bensted and Varma[17] make reference to an analogue of ettringite with $\mathbf{Ti^{+3}}$ in the aluminum site.

Additional sulfate substitutions have also been reported. In 1956, Serb-Serbina described a Cl-bearing ettringite in which $\mathbf{CaCl_2}$ replaces $CaSO_4$. This substituted ettringite was later produced and studied by Schwiete and Ludwig, who also succeeded in preparing an AFt-phase with **CaS** instead of $CaSO_4$.[8] Solid solutions involving sulfate-substitution by $\mathbf{OH^-}$ and $\mathbf{CrO_4^{-2}}$ have been reported by Midgley and Rosaman[8] and Bensted and Varma,[17] respectively. More recently, Kumarathasan *et al.*[12] performed a rather extensive study on oxyanion substituted ettringites. They reported experimental evidence to support replacement of sulfate by $\mathbf{AsO_4^{-3}}$, $\mathbf{CrO_4^{-2}}$, $\mathbf{SeO_4^{-2}}$ and $\mathbf{VO_4^-}$. They also speculated about other ions that would be likely to substitute, such as $\mathbf{MnO_4^-}$, $\mathbf{WO_4^{-2}}$, $\mathbf{SeO_3^{-2}}$, $\mathbf{TeO_4^{-2}}$, $\mathbf{PO_4^{-3}}$, $\mathbf{SbO_4^{-3}}$, $\mathbf{BiO_4^{-3}}$. Included in the paper by Kumarathasan *et al.* is a review of previously reported oxyanion substitutions. The contents of that review not discussed in this paragraph are included in Table 3 which summarizes reported ettringite substitutions. McCarthy *et al.*[11] later reported $\mathbf{BrO_3^-}$, $\mathbf{NO_3^{-3}}$ and $\mathbf{MoO_4^-}$ will replace SO_4^{-2}.

Although no calcium-site substitutions occur in the ettringite minerals, a number of reports suggest a variety of divalent cations will replace Ca^{+2}. An ettringite analogue with $\mathbf{Sr^{+2}}$ replacing Ca^{+2} is reported by Bensted and Varma,[18] and Glasser[19] suggests that $\mathbf{Ba^{+2}}$ and $\mathbf{Pb^{+2}}$, among others, will generally replace calcium in cement hydrate phases. Bonen and Sarkar[16] report the ettringite phase accommodating $\mathbf{Cd^{+2}}$, $\mathbf{Co^{+2}}$, $\mathbf{Ni^{+2}}$, and $\mathbf{Zn^{+2}}$ at the M^{+2} site in the crystal structure.

Poon *et al.*[20] provided some support to the studies by Bonen and Sarkar in which ettringite immobilized **Zn**, while they also provided evidence of **Hg** immobilization. Based on S.E.M. and leach studies, they concluded the degree of chemical fixation as opposed to physical entrapment in a cement was greater for zinc than for mercury. Both metals, however, were present in leachate in dramatically increased concentrations after 5 days of leaching which coincided with the disappearance of the AFt phase in 5-day micrographs of the cement. The authors concluded that, although there was no direct evidence of metal fixation by the ettringite phase, its disappearance marked the 'beginning of the breakdown of the structures' responsible for such fixation.

Except for the replacement of hydroxyl by oxygen in the minerals thaumasite and charlesite, there does not seem to be any notable substitution at this site. Glasser[19] does suggest a potential for cement pastes to substitute $\mathbf{F^{-1}}$, $\mathbf{Cl^{-1}}$, $\mathbf{Br^{-1}}$ and $\mathbf{I^{-1}}$ for hydroxyl; however,

TABLE 3
Reported Waste Ion Substitutions in Ettringite Minerals and Synthetics

$(Ca^{+2})^{VIII}$ site	$(Al^{+3})^{VI}$ site	(SO_4^{+2}) site	(OH^{-1}) site
Sr^{+2}	Cr^{+3}	$B(OH)_4^{-1}$	O^{-2}
Ba^{+2}	Si^{+4}	CO_3^{-2}	
Pb^{+2}	Fe^{+3}	Cl^{-1}	
Cd^{+2}	Mn^{+3}	OH^{-1}	
Co^{+2}	Ni^{+3}	CrO_4^{-2}	
Ni^{+2}	Co^{+3}	AsO_4^{-3}	
Zn^{+2}	Ti^{+3}	SeO_4^{-2}	
		VO_4^{-3}	
		BrO_3^{-1}	
		NO_3^{-1}	
		MoO_4^{-2}	
		ClO_3^{-1}*	
		SO_3^{-2}*	
		IO_3^{-1}*	

*From Kumarathasan *et al.*,[12] table II.

it is the authors' opinion that this would more likely occur in the more abundant $Ca(OH)_2$ phase.

Table 3 provides a summary of documented substitutions into the ettringite structure as researched by the authors. These have all been reported or referenced in the preceding text.

Size limits for each ion substitution site in the ettringite structures were estimated using Shannon and Prewitt ionic radii. For the Ca^{+2} and Al^{+3} ions' sites, the size limits are simply represented by the range of radii for the substituted ions for each site listed in Table 3. For the sulfate and hydroxide ions' sites, size limits were estimated by summing the ionic radii for the elemental components of the polyatomic ions listed in Table 3. The size ranges for each site are as follows: Ca^{+2} site 0.90Å to 1.42Å; Al^{+3} site 0.42Å to 0.76Å; SO_4^{-2} site 0.62Å to 3.71Å; and OH^{-1} site 0.62Å to 1.38Å.

CALCIUM SILICATE HYDRATE GEL (C–S–H)

Calcium silicate hydrate gel is the principal hydration product of Portland cement. It comprises approximately 50 mol% of most cement pastes, which makes it quantitatively the most important cement hydrate.[21] In cement chemists' notation this hydrate phase is generally referred to as C–S–H, where C represents CaO, S represents SiO_2, and H represents H_2O. The dashes indicate unspecified composition in any amorphous or poorly crystalline calcium silicate hydrate. This notation will be used throughout the remainder of the paper.

Formation

The calcium silicate hydrate formed during hydration reactions of the alite and belite clinker phases of Portland cement is a particular variety of C–S–H with specified composition. Its formation is represented in the following equations

$$\begin{gathered} 2(3CaO \cdot SiO_2) + 6H_2O \rightarrow \\ 3CaO \cdot 2SiO_2 \cdot 3H_2O\ (\text{C–S–H}) + 3Ca(OH)_2 \\ 2(2CaO \cdot SiO_2) + 4H_2O \rightarrow \\ 3CaO \cdot 2SiO_2 \cdot 3H_2O\ (\text{C–S–H}) + Ca(OH)_2 \qquad (6) \end{gathered}$$

These reactions begin to occur slowly in stage 1 of Portland cement hydration (Fig. 2) and then rapidly accelerate in stage 3. The C–S–H formed *in situ* from the larger anhydrous grains of clinker is called 'inner product' gel. 'Outer product' gel is formed in the water-filled space of the cement.[5] Cocke and Mollah[6] discuss two models for cement setting both of which suggest that inner product C–S–H, forming on cement particle surfaces, initially retards the hydration process. This effect is eventually overcome, however, as indicated by the rapid formation of C–S–H in hydration stages 3 and 4 (Fig. 2).

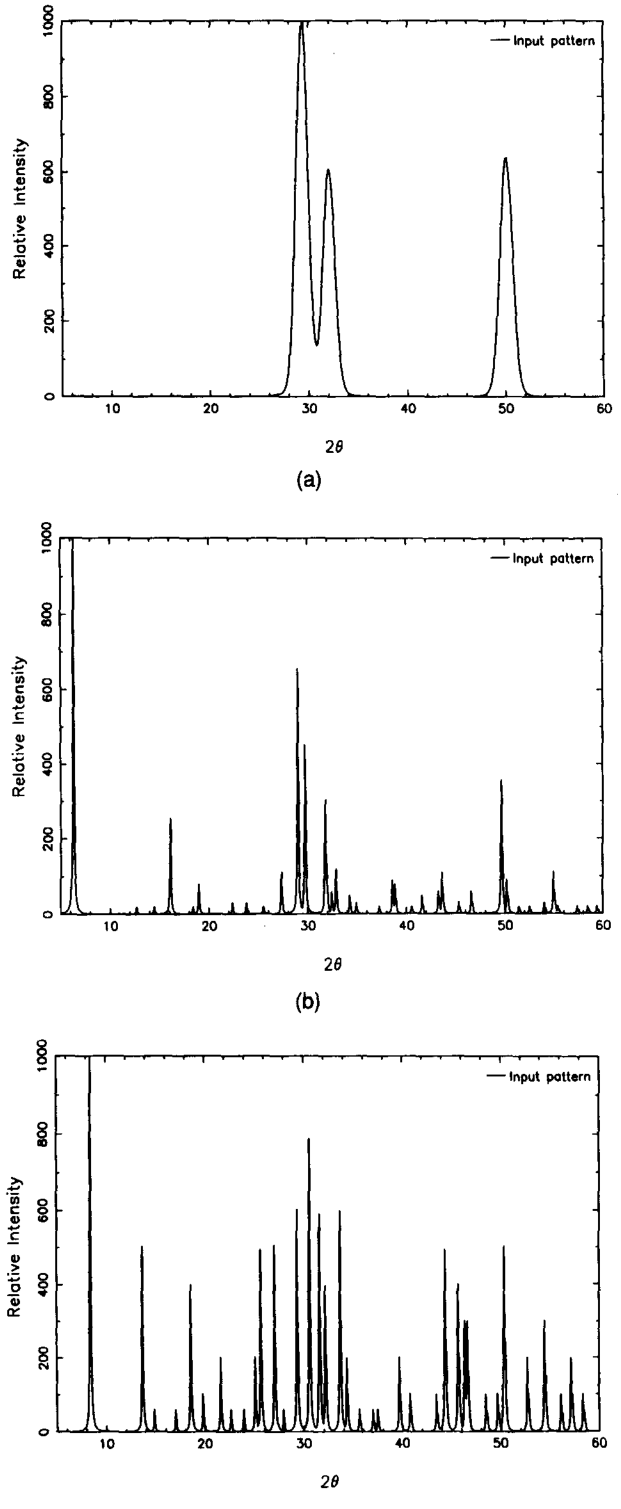
NMR studies show that during hydration, SiO_4 groups in the clinker phases change to dimer (Si_2O_7), some of which eventually react to form larger species collectively termed 'polymer'.[5] This polymer consists of single chains or rings (mostly pentamer and octamer), but not more complex species such as double chains or clusters. The average chain length increases with the age of the cement, but dimer still makes up approximately 40% of the chains after 20–30 years.[5]

Structure

Four morphological types of C–S–H gel have been identified. Type I, prominent at early stages of hydration, is a material consisting of fibers that grow up to 2 μm long. Type II is generally also an early hydration product described as forming honeycombs or reticular networks. Types III and IV are both fairly massive and seem to appear only in older pastes.[5]

C–S–H is an essentially amorphous material, which makes its characterization rather difficult. As early as 1952, an hypothesis suggesting a layer structure for C–S–H was proposed on the basis of X-ray diffraction evidence.[22] In a more recent publication, Taylor[22] compares his 1986 model of a layer structure for C–S–H to the Richardson–Groves model. While the models differ on whether the focus should be on the nature and proportions of ions present or how those ions are arranged, the concept of a highly disordered layer structure is consistent in both.

The proposed layer structure seems to have many similarities to 1.4-nm tobermorite and jennite. In particular, Taylor[5] suggests C–S–H(I) and C–S–H(II) as having structures intermediate between C–S–H gel and tobermorite and jennite, respectively. The computer-simulated X-ray powder diffraction pattern of OPC C–S–H is shown in Fig. 4(a) as generated by the SIMUL program using data from the ICDD Powder Diffraction File. (The SIMUL program[23] was developed by The Pennsylvania State University under the ZEOPAK consortium.) It shows characteristic C–S–H peaks at 0.27–0.34 nm and a peak at 0.182 nm. These features can be seen in sharper peak form in the patterns for either 1.4 nm tobermorite or jennite (see Figs 4(b) and (c)).



(a)

(b)

(c)

FIGURE 4. (a) Computer-simulated XRD powder diffraction pattern of OPC C–S–H. (b) Computer-simulated XRD powder diffraction pattern of 1.4 nm-tobermorite. (c) Computer-simulated XRD powder diffraction pattern of jennite.

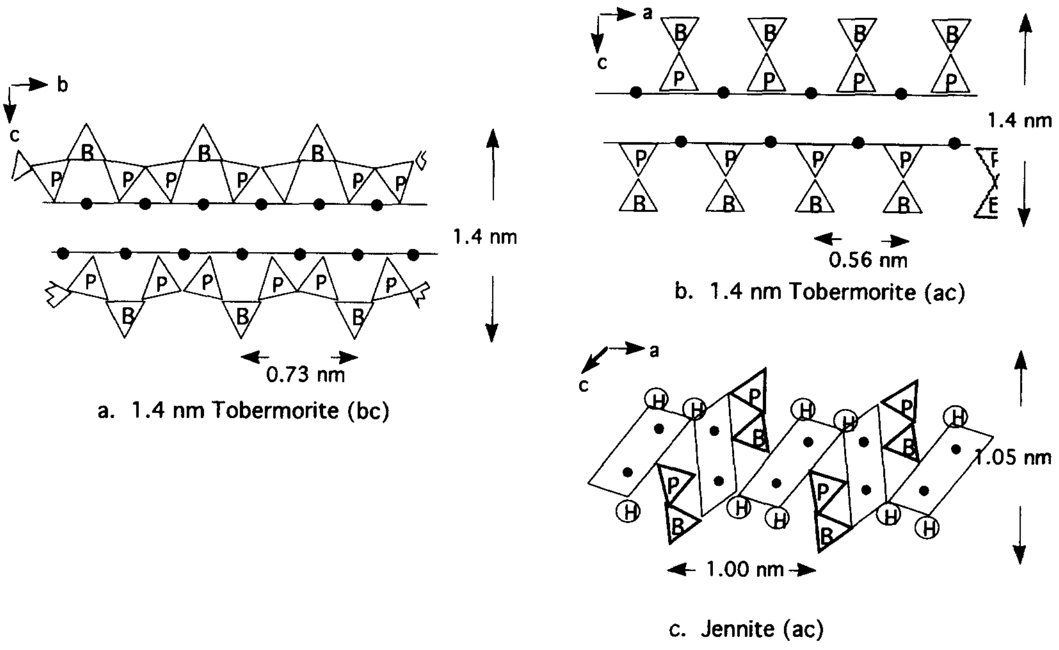
To understand the proposed layer structure for C–S–H, it is helpful to examine the structures of 1.4-nm tobermorite and jennite. The basic structure of both materials is one of alternating layers of Ca–O and silica tetrahedra. This pattern of layers can be seen in Figs 5(a) and (b) which illustrate the structure of 1.4-nm tobermorite. Also shown, in Fig. 5(c), is the jennite structure, 'somewhat resembling that of 1.4-nm tobermorite but with alternate chains replaced by rows of OH groups'.[5]

The Si–O chains in these structures are distinct in their arrangement. They consist of groups of three silica tetrahedra called *dreirketten*, which means 'three-chain'.[5,24] Two of the three tetrahedra are called paired tetrahedra and are labelled with 'Ps' in Fig. 5. They have silicon atoms which lie in the same row. The bridging tetrahedron is the third (labelled with a 'B'), having its silicon atom in a row above or below the row of 'paired' silicons. According to Taylor,[5] this arrangement of silica tetrahedra arises from coordination requirements of the calcium ion and is common in calcium silicates.

It is important to note the differences in Ca/Si ratios between C–S–H and these crystalline materials. The average ratio for C–S–H in Portland cement (OPC) is 1.75, which is higher than 0.8 for 1.4-nm tobermorite and 1.5 for jennite. Taylor[5,22] suggests this difference can be explained by the absence of some of the bridging tetrahedra in the C–S–H structure. These missing tetrahedra would also help explain C–S–H chain lengths fitting the formula $3n–1$ for the number of tetrahedra per chain (where n = number of tetrahedra). The 1.4-nm tobermorite and jennite chains are longer and have $3n$ tetrahedra per chain. These described characteristics all point to the amorphous qualities of C–S–H.[24]

Waste Ion Immobilization

In 1952, it was proposed by Kalousek that all **Al**$^{+3}$, **Fe**$^{+3}$ and **SO**$^{-4}$ ions present in cement eventually enter C–S–H. By 1965, Kalousek provided some evidence for the immobilization of the sulfate ion by showing that concentrations of crystalline sulfate compounds were too low to account for the total sulfate concentration. Copeland, Bodor, Chang and Weise also provided some support to Kalousek's theory by suggesting possible immobilization mechanisms for **Al**$^{+3}$ and **Fe**$^{+3}$ in 1967. Based on evidence including X-ray data Copeland *et al.* concluded that **Al**$^{+3}$ enters C–S–H by joining with an **H**$^{+1}$ to replace Si^{+4} or by joining with another **Al**$^{+3}$ to replace 3Ca^{+2}. It was also concluded that 2Fe^{+3} replaced 1Ca^{+2} and 1Si^{+4}.[25]



a. 1.4 nm Tobermorite (bc)

b. 1.4 nm Tobermorite (ac)

c. Jennite (ac)

FIGURE 5. (a) and (b) Structure of a single layer of 1.4-nm tobermorite in bc- and ac-projections, respectively. In (b), the chains are seen end on. (c) Suggested structure for a single layer of jennite, in ac-projection; the chains are seen end on and the Ca–O sheets edge on, parallel to their corrugations, and circled 'Hs' denote hydroxyl groups. In (a), (b) and (c), full circles denote calcium atoms, P and B denote paired and bridging tetrahedral, respectively (after Taylor[5]).

Despite the early work of these scientists, the actual mode of immobilization for most ions is largely unknown and is, therefore, a very active area of investigation. Due to the amorphous nature of C–S–H, crystal chemical substitution of waste ions is unlikely. Both Taylor[22] and Richardson and Groves[26] have suggested models for the C–S–H structure as gel in hardened paste, as previously mentioned in this paper. The models are closely similar and, in fact, complement each other. The Richardson–Groves model is shown below to help describe reports of waste ion immobilization by C–S–H

$$\mathrm{Ca}_x\mathrm{H}_{(6n-2x)}(\mathrm{Si}_{1-a}\mathrm{R}_a^{[\mathrm{IV}]})_{(3n-1)}\mathrm{O}_{(9n-2)}\cdot \mathrm{A}^{c+}{}_{a(3n-1)/c}\cdot z\mathrm{Ca(OH)_2}\cdot m\mathrm{H_2O}$$

where $x = 0.5(6n-w)$
and $z = 0.5\{w+n(y-2)\}$
and for $0 < y < 2$; $n(2-y) < w < 2n$
$2 < y < 4$; $0 < w < 2n$
$4 < y < 6$; $0 < w < n(6-y)$
and $0 < a < n-1/3n-1$

where $\mathrm{R}^{[\mathrm{IV}]}$ is a trivalent cation in tetrahedral coordination; A^{c+} is an interlayer ion which charge balances the R^{+3} substitution for Si^{+4}.[26]

According to Richardson and Groves,[26] $\mathrm{R}^{[\mathrm{IV}]}$ is usually **Al^{+3}** or **Fe^{+3}**, and A^{c+} is either a monovalent alkali cation or Ca^{+2}. They also suggest that other species detected by X-ray analyses in a substituted C–S–H, such as **OH^{-1}**, **$\mathrm{SO_4}^{-2}$** and **$\mathrm{CO_3}^{-2}$**, can be accounted for by considering intimate mixing with other hydration phases of cement.

Taylor[22] interprets NMR and other evidence as indicating most of the **Al** present in C–S–H of Portland cement pastes occurring in regions of AFm or other structures intermixed with C–S–H on the micrometer to single-layer scale. Substantially all the **Fe^{+3}** and **Mg^{+2}** are also present in these admixed regions. The **$\mathrm{SO_4}^{-2}$** may be present in admixed regions or sorbed. **Alkali cations** are thought to substitute in interlayer sites, which corresponds to the A^{c+} position in the Richardson–Groves model. According to Taylor, the incorporation of other phases by C–S–H gel, as suggested by Richardson and Groves,[26] may occur because of the opposite charges on the phase layers.[22]

In a recent study on thermodynamic modelling of blended cements, Atkins *et al.*[21] studied the interactions between cement and the nuclides **I**, **Ni**, **Sn** and U. All but **Sn** are immobilized by sorption onto C–S–H. Iodine was sorbed as **I^{-1}** at an uptake value of 19% with a Ca/Si ratio of 1.7. X-ray diffraction showed that nickel was present as **$\mathrm{Ni(OH)_2}$** gel, intermixed with the C–S–H phase. Uranium is immobilized by sorption and co-precipitation (mostly as **uranyl silicate hydrate–urophane**), showing strong retention characteristics of C–S–H.

Bonen and Sarkar[16] have characterized various heavy metals as to their mode of immobilization in cement-based materials. Based on the work of Komarneni *et al.*, they concluded that **Ni** and **Co** substituted at the C–S–H surface, probably for Ca^{+2}, instead of a crystalline substitution as previously

TABLE 4
Species Reported as Immobilized by Calcium Silicate Hydrate Gel (C–S–H)

Li, Na, K, Rb, Cs
Mg, Ni, Co, Hg, Zn, Cd
Al, Fe, Cr
Pb, U
Cl, I
OH^{-1}, CO_3^{-2}, SO_4^{-2}

thought. They also interpreted investigations of **Cr**-bearing pastes by Ivey *et al.* as suggesting that **Cr** may substitute for Si in poorly crystalline C–S–H. While Bonen and Sarkar found no substitution for **Cd**, **Pb** or **Zn**, these elements were still immobilized by their precipitation as hydroxides and carbonates. **Mercury** did not have any chemical reaction with the cement phases, but rather was physically encapsulated as **HgO**.

Cadmium and **lead** were also studied by Cartledge *et al.*[27] in an effort to show immobilization mechanisms using Portland cement fixing agents. Cadmium was successfully solidified/stabilized in the form of **$Cd(OH)_2$** incorporated into the layer structure of C–S–H. **Lead** salts, however, remained on the surface of cement particles and were easily removed from the cement during TCLP leaching tests.

Chlorine's interaction with C–S–H was the topic of a 1990 study by Beaudoin *et al.*[28] Experimental evidence suggests that **Cl** can reside both in interlayer positions and on the surface of the C–S–H sheets where it is alcohol insoluble but water soluble. **Chlorine** is also thought to act as a crystal lattice substitute based on significant changes that were observed in the transition temperature at which β-wollastonite forms for high C/S ratio C–S–H preparations. In this mode of sorption, **chlorine** is water insoluble or 'tightly held'.

Studies on tobermorite- and jennite-type structures may also provide some insight into the potential chemistry of C–S–H because of their similar structures. For example, a synthetic calcium silicate hydrate, essentially identical with the naturally occurring mineral 1.1-nm tobermorite, was studied by Shrivastava and Glasser[29] for its ion-exchange properties. **Cobalt** is found to substitute for Ca and small amounts of **Cs** are thought to go with **Al** when it substitutes for Si. Preliminary results also indicate that **Mg** and **Cu** exchange Ca, but not **Sr**. Another example is provided by a study of natural 1.4-nm tobermorite and synthetic jennite by Komarneni *et al.*[30] In general, the 1.4-nm tobermorite and synthetic jennite had low cation exchange capacities suggesting that most exchange was on the surfaces as opposed to interlayer exchange, which occurs in substituted tobermorites and jennites.

Table 4 provides a summary of documented waste ion immobilization by C–S–H as researched by the authors. The waste species are listed mostly in elemental form but may actually be incorporated into the C–S–H structure as a monatomic ion, a polyatomic oxyanion, or a salt. This should not be viewed as a complete list.

SUMMARY

This paper has reviewed the formation, structure and chemistry of the ettringite and C–S–H phases of Portland cement as they relate to waste ion immobilization. Ettringite acts as host to a number of waste ions through crystal chemical substitution both in the column and channel sections of its structure. A summary of these substitutions is provided in Table 3. Semi-crystalline C–S–H gel isolates ions and salts of the waste species through a variety of mechanisms, including sorption, admixing of other phases, and substitution at interlayer sites. Table 4 summarizes the documented ion incorporation by C–S–H.

A comparison of Tables 3 and 4 with the lists of heavy metal and radioactive waste ions provided in the introduction shows that the following elements have apparently not been reported as immobilized: silver, americium, neptunium, plutonium, radium, technetium, thorium and tin. This is not to say, however, that these species are not immobilized by cement, but rather that they have not been proven to be isolated by either of the hydrate phases under consideration. Indeed, numerous studies have revealed strong immobilization potential for such wastes by cement.

In the authors' view, cement is a suitable waste form for heavy metal and radioactive waste ions. Understanding the exact mechanisms of immobilization of these ions in cement will serve to improve its usefulness. It is, therefore, suggested as an area for further study.

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