

THE BINDING CHEMISTRY AND LEACHING MECHANISMS OF HAZARDOUS SUBSTANCES IN CEMENTITIOUS SOLIDIFICATION/STABILIZATION SYSTEMS*

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Summary

The chemistry of binding and the mechanisms of leaching of hazardous substances, particularly priority (heavy) metal pollutants, in cementitious stabilization/solidification (S/S) systems are discussed in terms of their bulk and surface states. Particular attention is given to the nature of the surface species and their surface and solution chemistries. Key to understanding the binding and leaching processes in cement is the characterization of the chemical and physical states involved. The available characterization techniques will be outlined and their application to model doped samples will be demonstrated. Recent efforts in the surface bulk, and morphological characterization of model S/S hazardous metal-portland cement systems will be presented with the results summarized in physical and chemical concepts. The ultimate aim of the work is to provide information to provide the understanding necessary for the design of new or improved stabilization and solidification systems and for information needed to mathematically model the leaching.

Introduction

With the implementation of the Resource Conservation and Recovery Act of 1976, stabilization and solidification [1] of those hazardous substances not eliminated by resource recovery, incineration, and source reduction became a necessity. Hazardous wastes converted to or produced as aqueous solutions or suspensions are being isolated from the environment by incorporation into cement based waste containment where the waste is physically contained and/or chemically bound. Stabilization is the process by which industrial wastes are treated in ways to prevent dissolution of the toxic components into the environment. This could imply chemical bonding or physical entrapment and the term should be modified with the appropriate adjective if the details of the mechanisms are known. Unfortunately this is too often not known and this generic term must be used. The term fixation is defined by Tittlebaum et al.

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[2] and refers to the stabilization process that is known to involve chemical bonding or specific interactions between the waste and the binding agent. Recent review articles [3,4] summarize the technology of stabilization/solidification but there is inadequate treatment of the chemical aspects involved. This article is an attempt to delineate the several chemistry and characterization problems involved. It will summarize some of the recent results from the author's laboratory and will serve to focus attention on the problem from its chemical nature.

The chemistry of cement especially with regard to the mechanism of hydration is still a very active and controversial area. This is in part due to the complexity of the system and the inadequacy of our analytical tools. Add to this the rich chemical nature of hazardous wastes and the mutual chemical and physical interactions that may occur in the solidified system and one is faced with an extremely challenging problem that will require a highly coordinated characterization effort to reach reasonable solutions.

The enormous challenge to delineate the chemical binding in hazardous substances contained in cement is illustrated in Fig. 1. Even the most mundane question "where is the hazardous substance located" is difficult to answer and has not been adequately addressed. Figure 1 also illustrates the complexity of

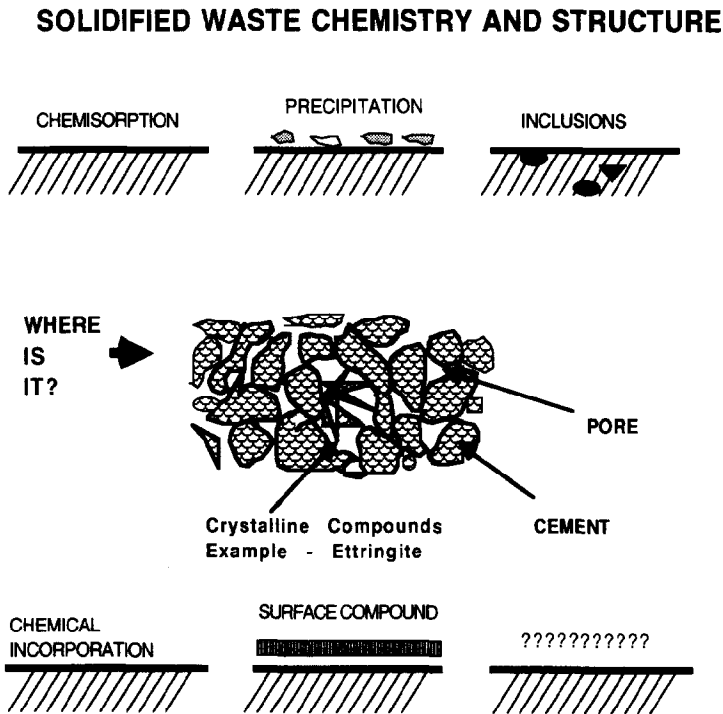


Fig. 1. Illustration of the various possibilities for the location of hazardous substances.

the problem by sketching the several types of interactions that may occur in the solidified system. The waste component may chemisorb, precipitate, or form a surface compound to any of several cement component surfaces, or it may form inclusions or be chemically incorporated into the cement components. Each situation requires a special set of characterization tools to address the problem. In practice the simultaneous occurrence of several of these situations is quite likely.

Hazardous Wastes

Hazardous wastes can be classified into two broad groups: organic and inorganic. The first form, which may range from biological organisms to chemicals expelled from industrial processes, is beyond the scope of this work and will not be further considered. The inorganic contaminants, which may range from radioactive wastes to incineration residue, can be made less hazardous in some cases by conversion to other compounds but the toxicity of their elemental forms in many cases means that they must be disposed of by concentration and storage. In this review we focus on the inorganic nonnuclear wastes that require stabilization and solidification. The Environmental Protection Agency (EPA) has identified priority metallic pollutants in this class and these are Pb, Cr, Zn, Hg, Cd, Se, Ag, As, and Ba.

Since most of these are commonly found as ions (cations or anions), their interactions with the cement and aqueous systems are expected to be rich in chemistry. The aqueous chemistry of the priority pollutants in alkaline solutions must be considered as well as the interaction with the cement components through adsorption, precipitation, or solid solution.

Characterization approaches

The characterization problem is brought into perspective in Fig. 2, where the "black box" containment system is seen to require a large number of characterization tools to provide insight into the nature of the surface and bulk chemistry that is involved. Each characterization method has its own set of limitations that restricts achieving a complete answer to most questions concerning complex heterogeneous systems such as cement. If one then includes the waste chemistry and the coupled chemistries between the waste and the cement, as well as the binding and the leaching chemistry, then a large group of carefully selected characterization tools is needed. Only a very cursory introduction to the characterization tools will be given (interested readers are encouraged to examine the reviews and monographs that are referenced).

SOLIDIFIED WASTE CHARACTERIZATION

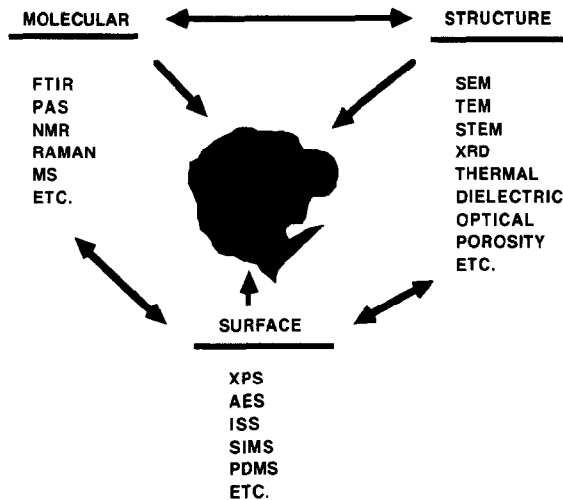


Fig. 2. Illustration showing the range of characterization techniques needed to study the binding chemistry and leaching mechanisms of stabilized and solidified hazardous substances.

Physical characterization

Physical characterization involves determining the macroscopic, microscopic, and morphological structure of the material. Optical microscopy can be a valuable approach and has reached a high degree of sophistication with literally thousands of compounds being identified by their visual characteristics [5]. However, identification of the hydrated materials present in cement is very difficult. Electron microscopy by SEM, STEM, TEM, HRTEM [6] can provide very valuable insight into the structure and morphology. Particularly valuable is analytical electron microscopy provided by the SEM and STEM using X-ray analysis [7].

Pore structure analysis has been used for years in heterogeneous catalysis and mercury porosimetry [8] has been highly developed to provide details of pore structure. The method is based on the behavior of nonwetting liquids in capillaries. The interfacial tension σ , opposes the entrance of the liquid into the pore, which can be overcome by external pressure. For a cylindrical pore the force opposing the entrance is acting along the circumference and equals $-2\pi r\sigma \cos\theta$. The opposing external force is $\pi r^2 P$. At equilibrium the two forces equal and the radius is given by: $r = - (2\sigma \cos\theta) / P$ which reduces to $r = 7,500 /$

Using the surface tension for Hg to be 0.48 N/m and an average wetting angle, θ , of 140° .

Molecular characterization

Molecular characterization is being provided by FTIR [9], which examines vibrational aspects and provides insight into molecular structure. Solid State NMR [10] is providing structural detail around selected nuclei such as Si and Al that is ideal for cement characterization.

Bulk characterization

X-ray diffraction (XRD) [11] provides the best structural look at the solid system. However, it is limited in that it sees effectively only the crystalline components. Since some of the material is expected to be amorphous, XRD cannot be used to describe the complete system. Composition can be supplied by X-ray fluorescence [12], electron probe techniques such as EDAX and WDAX [7] and UV fluorescence [13].

Surface characterization

Surface characterization is a rather recent but absolutely necessary component of S/S research. Since the waste has a rather large chance of being found on the surface of the cement particles it is very important to examine directly the surface chemistry involved. Several techniques have become rather standard methods. These are XPS [14], AES [15], ISS [16], and SIMS [17]. X-ray photon spectroscopy (XPS) measures the binding energies of electrons ejected from the surface region of a material and provides elemental identification and chemistry (mainly oxidation states) by the shifts in the binding energies. Auger electron spectroscopy (AES) measures the surface composition by the characteristic kinetic energies of ejected Auger electrons. Since an electron beam that can be focussed and scanned across the sample is used to eject the Auger electrons, lateral resolution down to a few hundred ångströms is possible. Ion scattering spectroscopy (ISS) measures the energy of scattered ions from the surface and through comparison of this to the impinging ion beam energy the very outer atomic layer can be identified and depth profiling provides atomic depth information over a few monolayers. Secondary ion mass spectroscopy (SIMS) has the greatest surface sensitivity and can provide surface composition by mass analyzing the ions ejected from a surface by a primary ion beam. Many other techniques listed in Fig. 2 provide complimentary information.

Cement chemistry

Portland cement clinker is a mixture of four principal compounds, C_3S (Ca_3SiO_5) 50–70 percent by weight; C_2S (Ca_2SiO_4) 20–30 wt.%; C_3A

($\text{Ca}_3\text{Al}_2\text{O}_6$) 5–12 wt.%, and C_4AF ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$) 5–12 wt.%. Their hydration chemistries and the dehydration of their hydration products, as well as the carbonation of hydroxide components, are the cement chemistries of concern [18]. In addition there are additional components such as gypsum that have been added to alter the hydration chemistry of certain components. Gypsum has been added to slow the rapid setting caused by the C_3A . It dissolves, however, rapidly into the solution during initial contact of the clinker with water and becomes immediately available to react with the waste components present. Quickly on mixing with water the solution contains hydroxides and sulfates of calcium sodium, and potassium. After 10 to 20 hours, the sulfate has been almost completely removed from solution by formation of calcium sulfoaluminate. The solution is then mainly that of KOH , NaOH , and saturated $\text{Ca}(\text{OH})_2$.

The hydration of portland cement is illustrated in Fig. 3. The main chemical that is considered in hydrated cement is colloidal calcium silicate gel known as C-S-H. This is a poorly crystalline porous solid. The mechanism of formation of C-S-H from tricalcium silicate and dicalcium silicate is an active area of research in cement chemistry that has strong implications in the S/S processes.

It appears that the C-S-H gel product is formed at the cement particle surfaces. The proposed surface coating has been observed to retard the setting of cement [19,20] in the presence of heavy metal wastes. It can be thought of as a membrane as proposed by Double et al. [21,22] and by Birchall et al. [23,24]. This provides an important direction in studying the hydration mechanism and the interfacial zone of importance in metal waste interaction with cement.

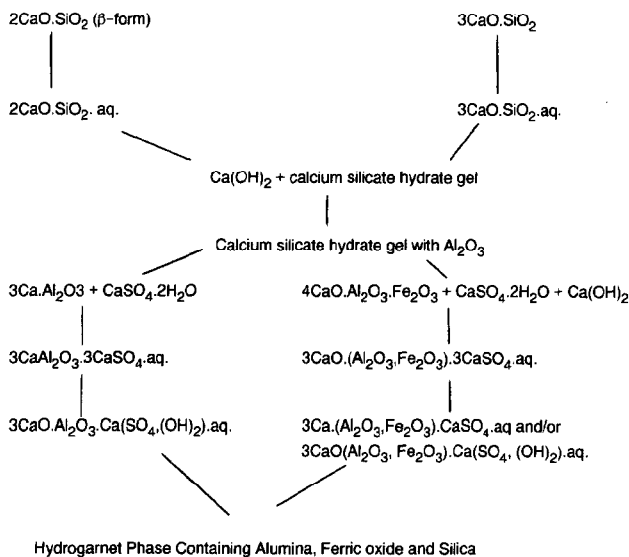


Fig. 3. The hydration of portland cement.

This may be a dominant feature that relates the solid surface directly to the interfacial chemistry of the solution. A colloidal gel membrane is formed by precipitation at high local levels of supersaturation between calcium in solution and the hydrolyzed silicate-rich surfaces of the cement particles. A protective C-S-H gel coating initially retards the hydration giving an induction period. However, the membrane is ruptured by osmotic processes allowing a secondary growth of silicate hydrates during the acceleration stage of hydration. The Thomas and Double model [22] explains the sequence of the hydration reaction and accounts for the mechanism of transport of the silicate material during precipitation of the C-S-H gel. The significance of this is that the surface composition and chemistry of the interface is an important area to be studied.

The extremely rich ion chemistry must be considered in the system. The metal ions can exchange with the ions in the clinker. They can precipitate with the anions that are a part of the clinker or gypsum. They can become included in the C-S-H. They can chemisorb at ionic or charge sites at the surfaces. Any chemisorption phenomena will depend on the surface structure of the C-H-S in a very basic environment.

Chemical surface structure

The surface structure of the hydration products and the C-H-S in a basic solution is one of a deprotonated hydroxylated surface that is depicted in Fig. 4E. The interactions of metal ions with hydrous oxide surfaces have been extensively studied. Quantitative predictions of the extent of the pH dependent reversible adsorption have been considered [25–31].

Adsorption

The surfaces an adsorbate sees under various conditions are illustrated in Fig. 4. Figure 4A shows an oxide surface that has been created in vacuum. Exposure of this surface to water results in the adsorption of water molecules (Fig. 4B) and these can dissociatively chemisorb to produce surface hydroxyls that have both acidic and basic properties (Fig. 4C). In acid solution the basic hydroxyls are removed from the surface producing Lewis acid sites that may have a full positive or partial positive charge. These are marked L in Fig. 4D. The acidic hydroxyls can add additional protons producing Brønsted acid sites with positive charges. In acidic solutions the surface can pick up positive charge which restricts cation adsorption. In basic solutions the surface hydroxyls that can give up protons are deprotonated producing negative oxide sites (Lewis base sites). The basic hydroxyls remain on the surface but a net negative charge can develop that restricts anion adsorption and promotes cation adsorption.

A very successful approach has been the surface complexation model [25,26] that treats specific adsorption as the interaction of the metal ion with the oxide

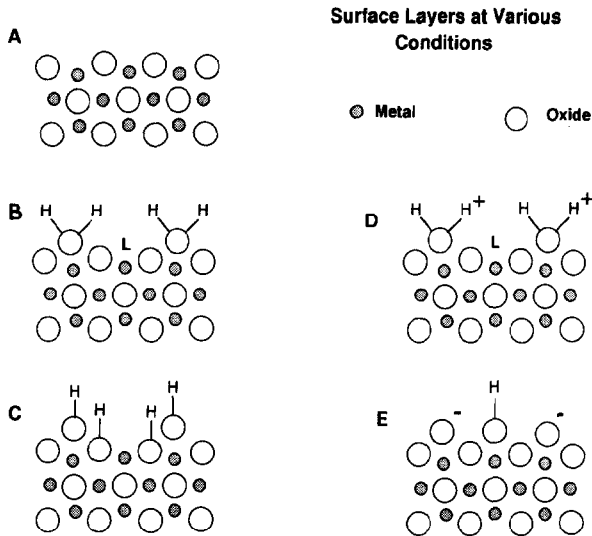


Fig. 4. Cross sectional views of the surface regions of an oxide under various conditions: (A) oxide surface formed in vacuum, (B) oxide surface with molecularly adsorbed water, (C) oxide surface with dissociatively adsorbed water, (D) oxide surface in acid solution, (E) oxide surface in basic solution. L is a Lewis acid site.

surface in analogy to the complexation of metal ions by ligands in solution. The hydroxyl groups on a surface have the coordination properties of oxygen donor ligands. Protons and metal cations compete for the oxygen coordination sites on the surface. The major reaction with the silicate surface is competitive adsorption between the cations, such as H^+ , Na^+ , K^+ , and Ca^+ , and since at the high pH values protons are in extremely low concentration the latter ions are competing for surface sites with the hazardous ions. In principle a set of equilibrium constants can be written that permits the estimation of the surface speciation, however, the complexity and lack of information on the composition and its rapidly changing nature in cement make this approach difficult. The complexation of metal ions by oxide surfaces occurs over a very narrow pH range and at high pH values the adsorption of metal ions is 100 percent. In addition to adsorption, the direct precipitation of oxides, oxyhydroxides, and hydroxides will occur on the surface along with the expected adsorption reactions.

Precipitation

Corey [32] has discussed adsorption vs. precipitation and summarized the processes:

- (1) Crystal growth occurs if the adsorbate is a component of the cement adsorbent.

- (2) Crystal growth and/or diffusion into the solid phase occur if the adsorbate is not a component of the adsorbent but can form a solid solution with it.
- (3) Formation of a stable surface compound can take place if the adsorbate is not capable of forming a three-dimensional solid solution with the adsorbent.
- (4) Stabilization of metastable polynuclear ions occurs by adsorption onto oppositely charged surfaces of the adsorbent.
- (5) Heterogeneous nucleation of a new solid phase may involve a new phase composed of the adsorbate and a component from the solution (hydroxides, carbonates etc.).
- (6) Heterogeneous nucleation of a new solid phase may occur, where the new phase is composed of the adsorbate and a component of the adsorbent resulting in dissolution of the adsorbent and redeposition as a different compound.

It is clear that all these processes are potentially active in the cement stabilization and solidification process.

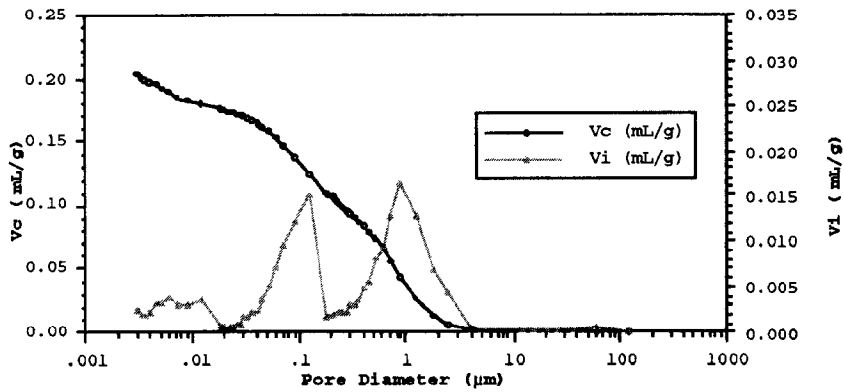
Pore structure

Hardened cement is a very porous material with a trimodal pore distribution. The Hg porosimetry data for lead and chromium doped systems as well as for their leached analogs are shown in Fig. 5. The system formed by the smallest pores, gel pores, are approximately $0.01 \mu\text{m}$ in diameter. These are likely associated with inner layer spacing. The next larger pores averaging about $0.1 \mu\text{m}$ in diameter are due to the original water filled space in porous cement gel and are called capillary pores. The volume of these pores is directly proportional to the water/cement ratio. The largest pores are formed by air void. The pore system has continuity as demonstrated by permeability.

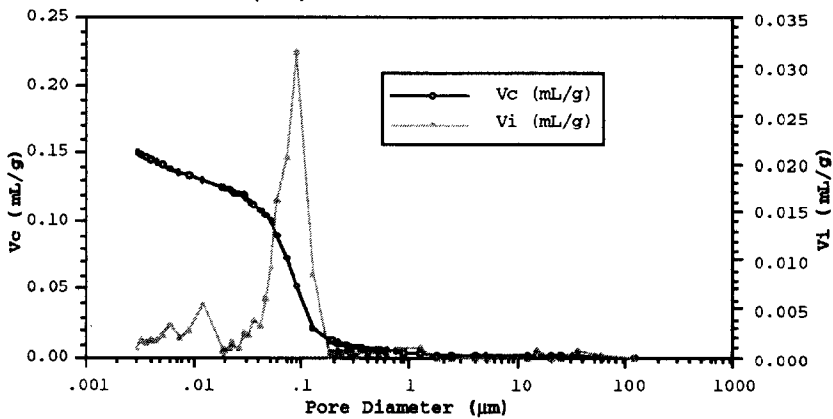
Aqueous chemistry of metals

The prediction of the speciation of the metals in the cement is dependent on the solution chemistry of the metal ion in very basic solutions containing sulfate. Here the solution chemistry of Pb(II) and Cr(III) ions will be used to illustrate the approach.

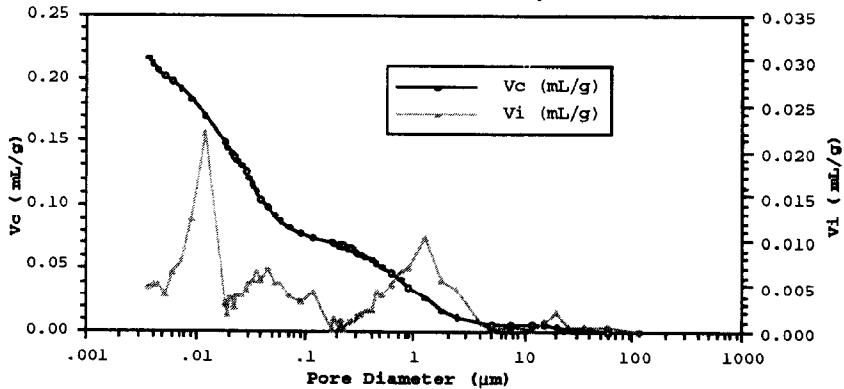
A lead ion in basic solution forms $\text{Pb}(\text{OH})_2$ in a dilute hydroxide solution and the plumbite ion, PbO_2^- in a concentrated hydroxide solution. Given the anionic nature of the plumbite, it is unlikely to adsorb to the negative oxygen sites on the silicate. This is supported by the observation that anions adsorb best at low pH while cations adsorb best at high pH [33]. It can be argued that the lead may be deposited as a precipitate. The simultaneous presence of sulfate and lead ions is expected to produce lead sulfate which is similar to barium sulfate but because of its greater density it is deposited more readily. The mechanism by which a precipitate can quickly cover the hydrating clinker particles

(A) Lead Doped

(a.) Plain Cement

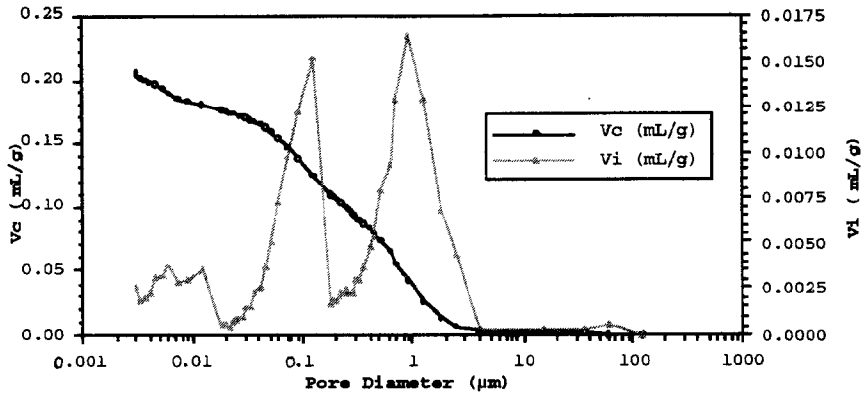


(b.) 10% Lead Nitrate added, unleached

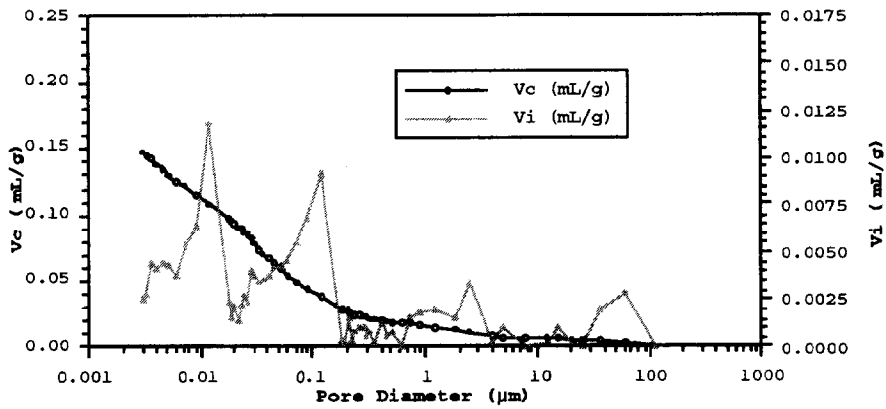


(c.) 10% Lead Nitrate added, leached 5 hrs.

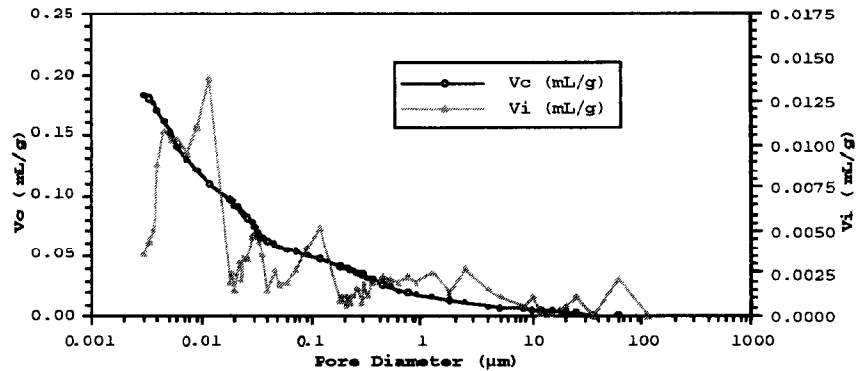
Fig. 5(A). Mercury intrusion porosimetry results for the Pb doped and leached samples.

(B) Chromium Doped

(a.) Plain Cement



(b.) 10% Chromium (III) Nitrate added, unleached



(c.) 10% Chromium (III) Nitrate added, leached 5 hrs

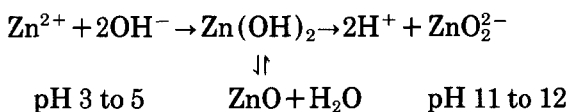
Fig. 5(B). Mercury intrusion porosimetry results for the Cr doped and leached samples.

with a membrane precipitate is not clear. One then may be forced to look at adsorption once again and wonder whether there are any cationic species that are generated in the process that can adsorb on the negative surface. At high pH values Pb(II) may form cluster ions containing up to six Pb atoms such as $[\text{Pb}_6\text{O}(\text{OH})_6]^{4+}$. In the cement environment, these hydroxy-cations may adsorb to the silicate surface and/or precipitate as sulfates forming a membrane that slows the hydration process.

Barium is expected to produce barium sulfate in cement.

Mercury, Hg^{2+} , precipitates as red or yellow (depending on particle size) HgO in alkalihydroxide solutions and is expected in the cement environment. $\text{Hg}(\text{OH})_2$ is not known to exist in cement.

Zinc hydroxide, a typical ampholyte, functions both as an acid and a base. The equilibria appear as:



Considering water in the equilibria, $\text{Zn}(\text{H}_2\text{O})_2(\text{OH})_4^{2-}$, the hydroxy complex, is present in strongly basic solution. Its anionic properties preclude its adsorption in basic solution. From these solutions, the crystalline zincates can be formed.

The most stable aqueous solutions of Cr are the Cr(III) and Cr(IV) systems. The oxide, being amphoteric, forms chromites in concentrated alkaline solutions. The $\text{Cr}(\text{OH})_3$ which forms at intermediate pH values dissolves at high pH to form $\text{Cr}(\text{OH})_4^-$ like ions which again are unlikely to adsorb to the silicate surface. Precipitation or the formation of solid solutions may need to be considered here.

Coupled chemistries

It is not unexpected that the addition of chemically active inorganic species to the hydrating cement will affect the cement chemistry. As well the very strong alkaline environment with large buffering capacity will dominate the chemistry of the inorganic species. In addition, the presence of chemically active interfaces will influence and be influenced by the added inorganic species. Some of these coupled chemistries will be illustrated below. The retardation of the setting of cement by lead and zinc, the enhancement of surface carbonates, the redistribution of cations such as K^+ , and the structural effects will be discussed.

Recent results

Recent results from surface analysis techniques and physical structure techniques have brought us insight into the chemical binding and mutual influ-

ences between hazardous metal substances and portland cement. The XPS technique has been used to examine Pb, Cr [34,35], Hg [36], Zn, Cd [37], and Ba [38] doped portland cement. The strong differences between Pb and Cr have been investigated further using mercury porosimetry and modelling [39]. In addition the leaching of these samples is studied by similar approaches and the results are being correlated with the FTIR studies of Ortego and coworkers [40,41]. The essence of this work can be illustrated by considering several key questions:

- (a) Where are the metals located?
- (b) What is the chemical nature (speciation) of the metals in the cement?
- (c) What are the mutual influences of the metals and cement on each other?

Location

The location of the metals is best illustrated by comparing Pb and Cr [34]. We have made a comparative study using XPS, ISS, EDS, and SEM. A significant finding of this research is the preferential deposition of lead at the surface of the cementitious material. This observation, combined with the fact that lead salts such as carbonates, silicates, etc. are extremely insoluble and have low surface energies, serve to give credence to the proposed surface sites for Pb ions [42,43] and strongly supports the coating of clinker particles discussed above by Pb species. Since portland cement contains C_3S 50–70 wt.%, C_2S 20–30 wt.%, C_3A 5–12 wt.% and C_4AF 5–12 wt.% [43,44], one needs to explore the interaction of the metal dopants with each of these to further investigate the mechanism. C_3A is known to react very rapidly with water followed by the precipitation of calcium aluminate hydrates with considerable evolution of heat [42]. However, C_3S and β - C_2S are also involved in initial setting and provide most of the strength in the first days. C_3S and β - C_2S are metastable phases and have substantial negative free energy of hydration. However, the rates of hydration are slower than for C_3A indicating a substantial activation energy of hydration [42], which is determined by the nature of the chemical interaction between the water and the surfaces of C_3S and β - C_2S particles. It is generally believed that these have open structures that readily allow water interaction. In addition, CaO is believed to provide favored sites for water attack. Since Pb ions drastically retard setting [45] and ultimate strength, it must be intimately involved in blocking these hydration mechanisms. Since the hydration of the C_3A and β - C_2S occurs at dramatically different rates and by different mechanisms the Pb ions apparently interfere with both. This would support Pb species creating a barrier to water interaction. Figure 6 shows a comparison of the XPS signals from 10 wt.% Pb and Cr in portland cement.

Since XPS probes only the outer 15 Å of the surface, it is clear that the Pb is located on the outer surface of the cement particles while the Cr is below the surface. Since XPS and ISS show that the lead is located mainly at the surface it would suggest that a lead compound is coating the clinker components re-

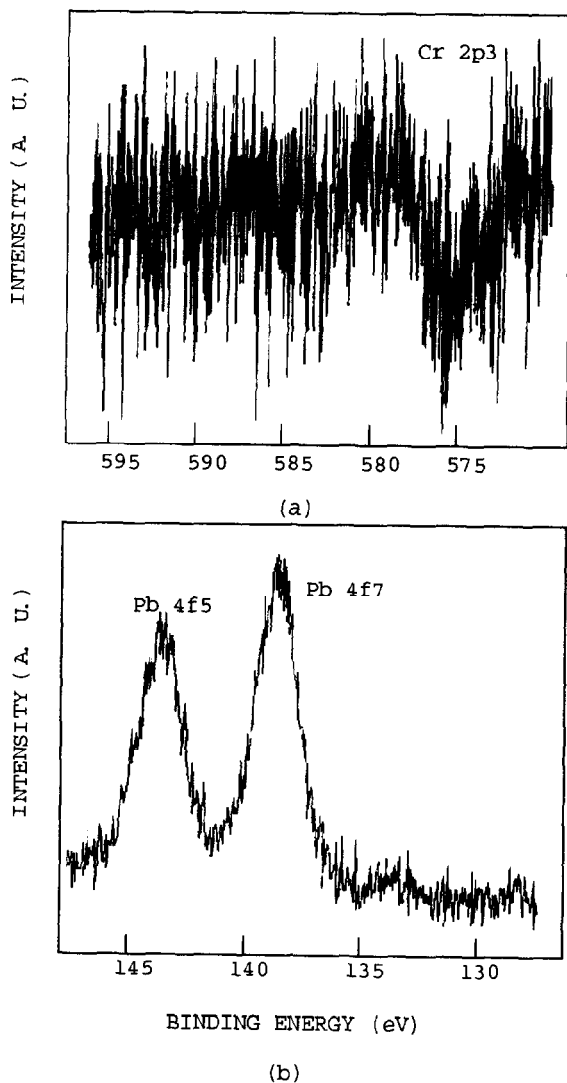


Fig. 6. XPS spectra of the chromium (a) and lead (b) doped cement surfaces.

possible for initial setting thus passivating their surfaces to hydration. This observation combined with the fact that lead salts, such as carbonates, sulfates, etc. are extremely insoluble and have low surface energies [43], suggests that lead ions selectively coat the outer portions of the cement components but are not selective about which components are coated. The shift in Si 2P binding energy for the Pb doped system as compared to that for the Cr and standard undoped cement is shown in Fig. 7 and suggests that Pb is associated with the C_3S and $\beta-C_2S$ components.

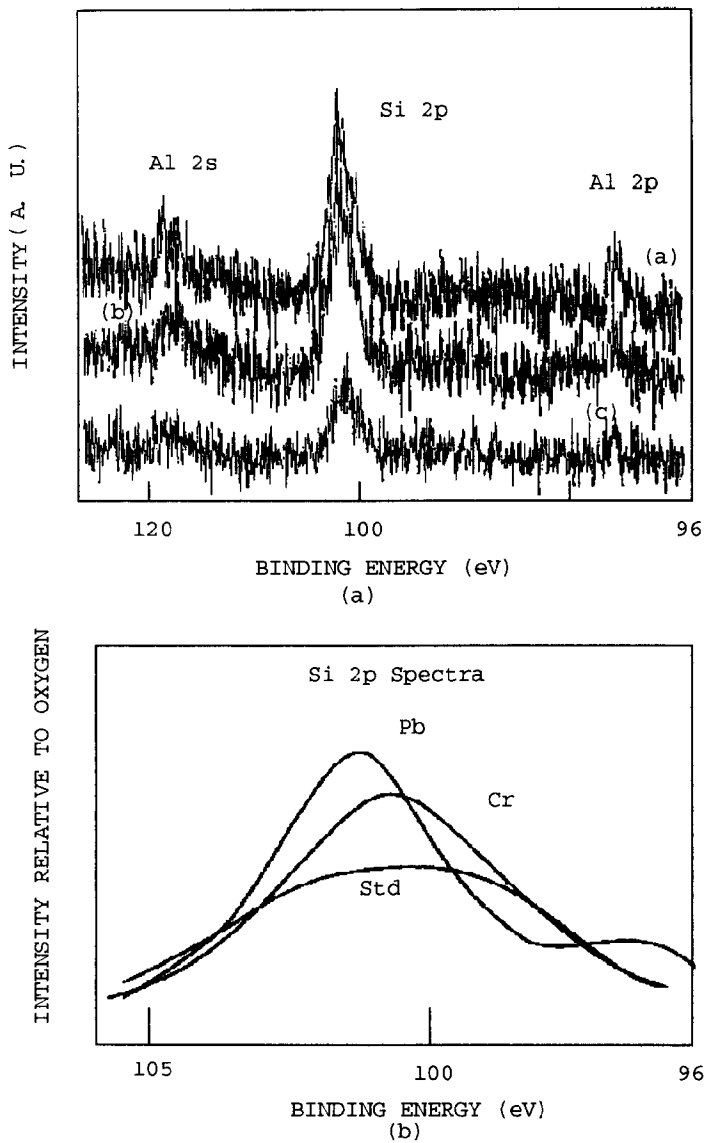


Fig. 7. XPS spectra. (a) The Al and Si 2p lines for (a) Pb doped, (b) Cr doped and (c) undoped standard cement sample: (b) XPS Si 2p spectra standardized to oxygen for Cr, Pb, and standard cement.

The peak position for the Si 2p indicates enhanced polymerization over that of the Cr doped and the standard. The situation is different for the chromium doped samples in which no chromium is detected on the surface. Apparently, size and charge differences allow Cr to be incorporated throughout the solid material during hydration.

Also XPS shows that lead and chromium are present in their original oxidation states the Pb^{2+} and Cr^{3+} , respectively. Their binding energies are consistent with silicate, carbonate, or hydroxide compounds and not with their oxides.

The appearance of potassium at the surface of the doped samples and its absence from the surface of the standard (Fig. 8) suggests that the doping is causing a redistribution of the potassium.

Apparently the K^+ is moving into solution to charge compensate the NO_3^- anions as the Pb^{2+} and Cr^{3+} are deposited in the solid state. Potassium is then deposited at the surface as the liquid is lost to evaporation and chemical reaction with clinker components. In addition the enhanced presence of carbonate in the doped samples is suggested.

A highly recognizable trait in the lead doped samples is the presence of a flakey material encapsulating the cementitious grains observed by SEM. The low intensity lead peaks observed in the EDS supports XPS data for the preferential surface binding of lead. The reasoning is based on the fact that EDS has penetration greater than $1\ \mu\text{m}$ and in essence is not a pure surface probe. Hence, the technique will have a very poor sensitivity for surface species.

The overall Ca/Si ratio of the Pb doped cement obtained by EDS was slightly lower than that of the standard. This result was due to the Si K_α peak intensities increasing above those of the standard. These reduced Ca/Si ratios support the findings of Thomas et al. [45] and our XPS results showing increased Si at the surface of the Pb doped sample.

Thomas et al. (45) did not include an EDS analysis of the Al in the doped cement samples. In this work, the peak areas of the Al K_α peaks from the noncavity areas of Pb doped sample were about the same as those from the standard. However, the Al peak intensities from the cavity regions of the Pb doped sample were nearly twice as large.

In the case of the Cr doped sample, the Al intensities did not differ from that of the standard. Also, the Ca and Si peak intensities did not vary greatly from those of the standard. Hence, no inferences of preferential components association could be drawn, but to say that Cr was more widely dispersed in the bulk, as supported by the XPS data.

The presence of cavities and "needleshaped" crystals in the Pb doped sample would suggest a possible mechanism for the role of Pb in the setting of cement. To initiate the growth of "needleshaped" crystals in the cavity regions, a supersaturated solution must be present. An EDS analysis of the crystals did not reveal the presence of the Pb L_α peak to the S K_α peak at 2.3 keV, the elemental composition of the crystals would consist of Ca, Si, Al, and S, with the S being derived from the sulfate ions in gypsum. The elemental composition would be similar to a calcium sulfoaluminosilicate compound suggested by Thomas et al. [45]. Based on this assumption, the Pb species coat some of the calcium silicate phases in the clinker, preventing its hydration, and at the same time,

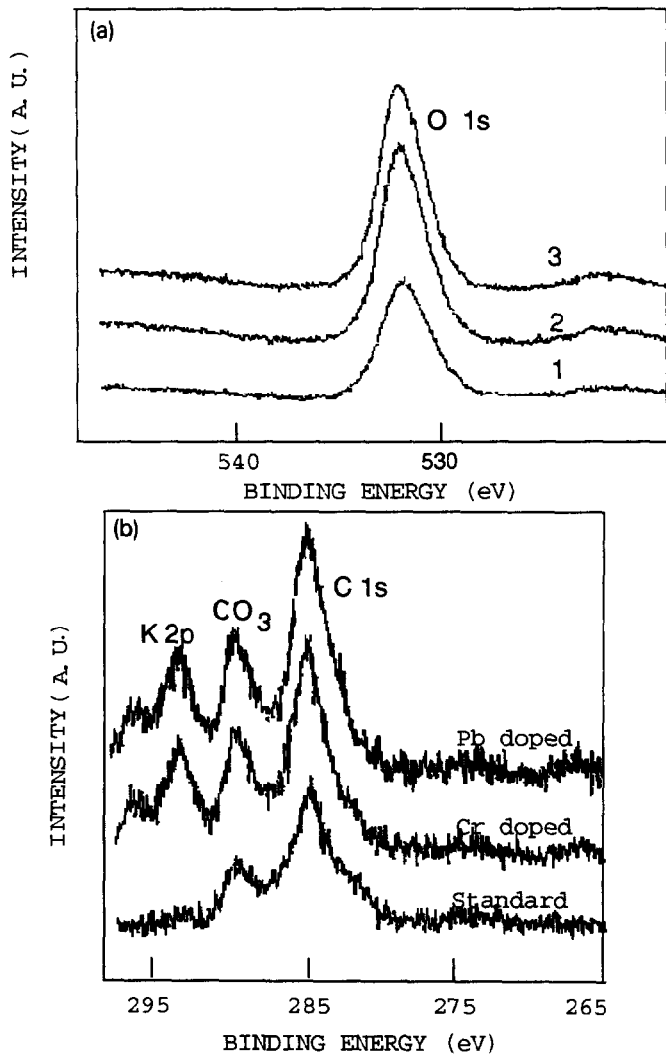


Fig. 8(a) XPS spectra of oxygen 1s line for (1) cement standard (2) chromium doped and (3) lead doped samples, (b) XPS spectra showing surface carbon, carbonate and potassium lines for the lead doped, chromium doped and standard cement. The latter does not show any surface potassium.

allowing a supersaturated solution to be trapped in localized pockets, where the longer setting time promotes crystal development. From these findings we have developed a model for the retardation of the cement setting as shown in Fig. 9.

The hydration is slowed by the lead precipitate coating and allows the outer silicate to be in contact with water longer relative to the inner silicate of the

MODEL FOR LEAD RETARDATION OF CEMENT SETTING

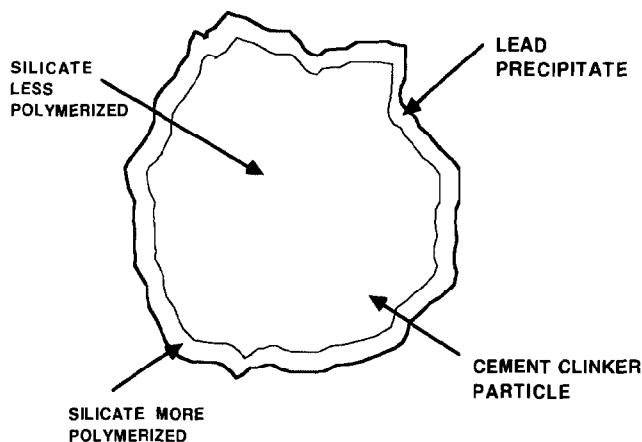


Fig. 9. Sketch of a lead coated clinker particle with the coating enriched in more polymerized silicate.

clinker particle. Results of XPS shown in Fig. 7 show the lead enhances the degree of polymerization of the silicate at the surface. By FTIR the inner silicate is shown to be less polymerized than for the undoped cement.

The other metals have been observed at the outer surface to varying degrees and in various chemical states. Mercury and barium in portland cement have been relatively well characterized by us and will be used here to illustrate the approach.

Chemical nature

The chemical nature of the metal in the cement is illustrated by the Hg [35] and Ba [37] cases. In both these systems the chemical nature of the metal species has been delineated. The XPS spectrum of the Hg doped sample is shown in Fig. 10.

Here the Hg oxidation state is identified as Hg(II). The Hg is present as highly dispersed HgO. The color changes from yellow to red on heating the sample at about 40°C. This is commonly observed for HgO in small crystallite form.

From XPS, Ba was found to be present as BaSO₄ and BaCO₃. The presence of BaSO₄ is supported by FTIR studies as well [39,40]. Figure 11 shows the FTIR spectrum of barium sulfate.

The presence of both these metals as common compounds show clearly that the normal chemical forces are working and that in the pores, Hg and Ba are precipitated as the very insoluble precipitates. The barium carbonate comes from the reaction of carbon dioxide with the excess (exceeding the sulfate con-

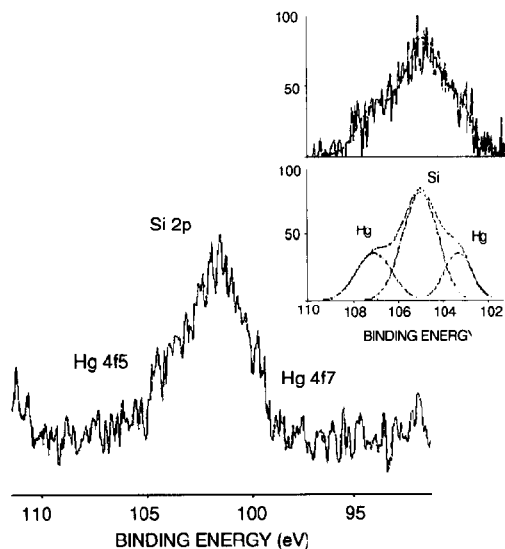


Fig. 10. XPS spectra of Hg doped cement showing the Si 2p region flanked by the Hg doublet for the $4f_{7/2}$ and $4f_{5/2}$. The insert shows the decomposed peaks.

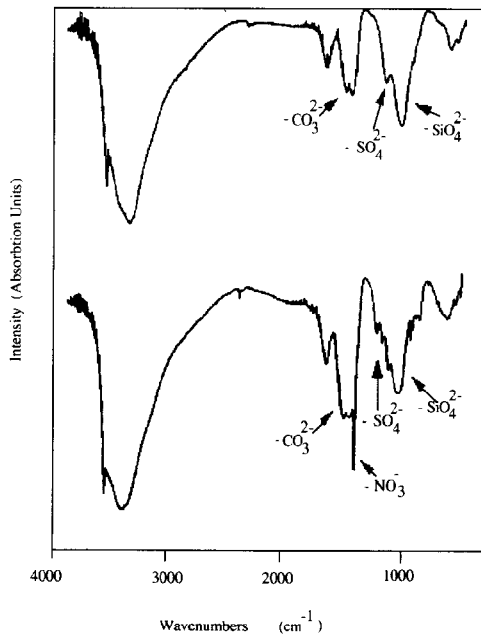


Fig. 11. FTIR spectra of undoped portland cement (top) and Ba doped portland cement (bottom).

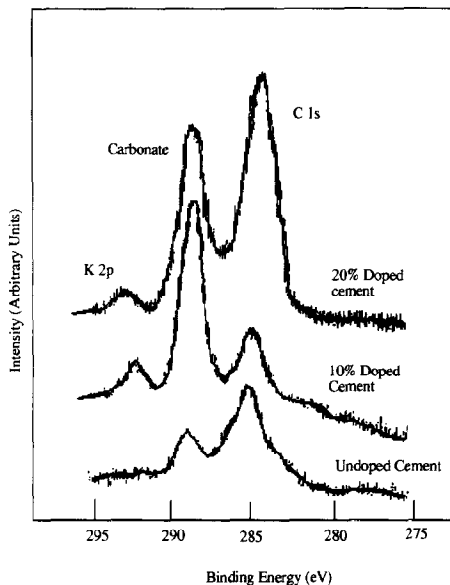


Fig. 12. XPS spectra of barium doped cement (upper two spectra) and undoped cement (lower spectrum).

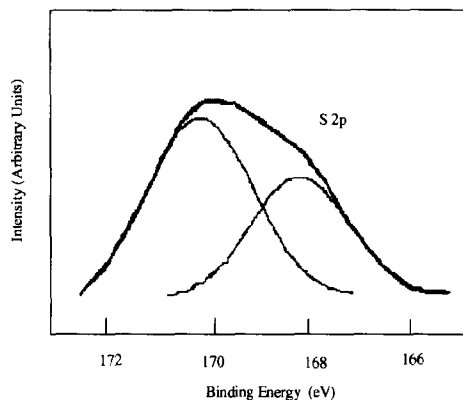


Fig. 13. XPS spectra of sulfur 2p in Ba doped portland cement. The two separate peaks are for sulfate associated with Ba (168 eV) and aluminosilicate (170 eV).

centration) Ba that is present as the hydroxide. With both Hg and Ba the surface is exceptionally rich in carbonate. In fact the carbonate is associated with the metals. For the Hg case, calcium carbonate was found, by observation with analytical electron microscopy, to be preferentially located around the HgO particles. The presence of potassium on the surface in addition to the carbonate is illustrated in Fig. 12. It shows that the Ba produces additional carbonate at the surface.

Figure 13 clearly shows that two types of sulfate are present at the surface; one is associated with the Ba and the other associated with the sulfoaluminate. This agrees with the FTIR results in so far as both techniques see BaSO_4 . The FTIR results fail to conform the presence of BaCO_3 but this may be due to the FTIR probing deeper than the XPS.

Physical changes

The addition of metal ions to the Portland cement results in significant physical changes. The mercury intrusion porosimetry results shown in Fig. 5 indicate that Pb and Cr have different effects. The addition of Pb causes the disappearance of the $1\ \mu\text{m}$ pores with increased amounts of $0.1\ \mu\text{m}$ pores. Chromium addition has a quite different effect. It causes a wide variety of pore diameters to appear with the small $0.01\ \mu\text{m}$ diameter pores dominating. Clearly the chromium gets more involved in the formation of the silicate structures than does the Pb. In fact, the Pb addition appears to only change the relative amounts of pores in the structure, while the Cr addition effects the pore formation mechanisms. These observations basically agree with the results discussed for the location of the metals. Leaching in both cases causes substantial changes in the cement pore structure indicative of the actual dissolution of the cement, as is suggested by the loss in strength caused by leaching.

Leach testing

The ultimate goal is the design of the best stabilization/solidification system from both the physical and chemical immobilization. The achievement of this goal will be hastened by understanding the physical and chemical aspects of the system. Understanding the way hazardous substances are bound in the S/S medium can provide the key to designing improved systems. In addition the information can be useful for understanding the leaching mechanism which will be in many cases the reverse of the deposition under different pH conditions. In acidic solutions the chemistry of metal ions requires their deposited form to dissolve. The chemistry is as complex as the deposition processes discussed above. Similar approaches are being used in our laboratory to examine the surface chemistry involved in the process. The modeling process needs the chemical information that will be forthcoming from such studies. Standard techniques for measuring leaching provides only an observed diffusivity that does not separate the chemical and physical factors. The observed diffusivity that can be calculated from modeling has been shown to depend on the true effective diffusivity and the coefficients that describe the chemistry involved

[46]. The modeling of the leaching which should separate the influences of the physical and chemical aspects will ultimately provide reliable projections and design parameters that will ensure long term protection of the environment.

Conclusion

The ideas put forward in this work and the experimental results found point toward substantial future progress. The application of the best surface and bulk characterization techniques to the chemical and physical aspects of stabilization and solidification will be required if the the complex systems are to be mastered to the extent needed for design improvements.

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