



RESEARCH & DEVELOPMENT

Stabilization of Heavy Metals in Portland Cement, Silica Fume/Portland Cement and Masonry Cement Matrices

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ABSTRACT

The effects of heavy metals on the physical and chemical properties of portland-cement based pastes were studied using different types of cement, four metal oxides, and four soluble metal salts. Type I (high calcium aluminate content) and Type V (low calcium aluminate content) portland cements were used to study the effects of their chemical differences on paste properties and metal stabilization. Fresh pastes were tested for workability, initial setting times, and heats of hydration. Hardened pastes were tested for strength and leachability by both TCLP (Toxic Characteristic Leaching Procedure) and column leaching with acetic acid.

The cement matrix was an excellent stabilization matrix, better than could be projected from pH considerations alone.

The investigation also involved examining Type I portland cement paste treated with three metals together—chromium, cadmium and lead, added at very high (1% by mass of cement) and intermediate (1000 ppm by mass of cement) levels. The leaching solutions were acetic acid, “synthetic acid rain” (pH 3 sulfuric/nitric acid), and deionized water. A Type N masonry cement matrix was also investigated. The leachabilities were very low throughout the pH range of 6-11 for lead and chromium. At very high pH values, the leachabilities of lead and chromium were significantly higher. Cadmium leachability was negligible above pH 10, but became rapid and highly significant below pH 9. At pH values below 6, which generally corresponded to the extraction of nearly all calcium present, all metals were rendered highly leachable. For all the metals, the leachability in masonry cement-stabilized matrix was higher than with Type I during the intermediate leaching steps.

A series of tests involved testing of a contaminated soil matrix, both dry and contaminated with aged SAE 10 W oil (without additives). Cement was used at 8% by weight of total mix. The results of leachability vs pH generally were consistent with those obtained in the multiple metals leaching studies; as long as calcium silicate hydrate was present, metals solubility was very low, irrespective of pH.

In an attempt to address the early high pH leaching of lead and chromium, a series of experiments was run with silica fume, in an amount calculated to react with all calcium hydroxide generated from hydration of the calcium silicates. The reasoning was based on the fact that if calcium hydroxide was all used up, it could not displace the larger heavy metal cations from either calcium silicate hydrate or sulfoaluminate or sulfoferrite hydrates. The results indicated that leachabilities of lead and chromium were reduced at pH values greater than 11.0, and also at the low pH values obtained after multiple sequential batch leaches. Since ettringite is known to be much less soluble than calcium monosulfoaluminate hydrate, it was also thought that a system in which extra sulfate is present might yield even lower leachabilities for those metals which were substituted in the ettringite lattice. (This reasoning may not apply to anionically substituted metals, because the extra sulfate may tend to displace them from the ettringite lattice). The results indicated that at very high pH values, the leachability of chromium was reduced with the lower excess gypsum level, and at low pH values, less than about 5.0, with both high gypsum levels. At intermediate pH values, chromium leachability was minimum for the unaltered matrix. Excess sulfate reduced lead leachability also at the low and high pH levels, but increased it at intermediate pH values.

Arsenic is a metalloid whose stabilization has presented difficulties in solidification/stabilization systems because of solubility. Because the stabilization of arsenic (III) is more difficult than that of arsenic (V), an oxidizing agent is often added to the system to ensure that arsenic is not reduced to the trivalent state. Three separate regimens were evaluated: Ferrous sulfate was used to produce a very insoluble iron arsenate precipitate; this system was evaluated for arsenic (III), arsenic (V), and arsenic (III) which had been treated with hydrogen peroxide to oxidize it to As(V). The neat soil cement matrix and one in which ethylenediamine tetraacetic acid had been added as a chelating agent were also tested. Whereas arsenic stabilization was not as effective as that for cadmium, chromium and lead, the optimum system functioned admirably to reduce As leachability. The intermediate pH levels around 9.5 proved the most difficult for As stabilization, unlike the other metals, which were generally least soluble in this pH range.

KEYWORDS

solidification, stabilization, hazardous waste, trace metals, chromium, cadmium, lead, arsenic, portland cement, contaminated soils, leaching, TCLP

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EXECUTIVE SUMMARY

The research presented in this report was undertaken with the goal of establishing the mechanisms by which portland cement and portland cement-based stabilizing reagents immobilize certain regulated trace metals in inorganic form in solidification/stabilization (S/S) systems. The metals studied included lead (Pb), chromium (Cr), cadmium (Cd), arsenic (As), and mercury (Hg). Solidification and stabilization of metal salts and oxides were first studied. The addition of metals as oxides or metal salt solutions decreased the workability of Type I cement pastes; for metals that caused set retardation (particularly lead), the effect was more pronounced for the oxide form than for the salt. The addition of chromium (III) salts in solution accelerated both setting time and strength development, whereas both variables were retarded with lead addition. As judged by compressive strength development, although these metals influence early hydration reactions, ultimate cement hydration is as complete as in control samples. When added as oxides or salt solutions, the metals studied (lead, cadmium, chromium, and mercury) were well stabilized. The stabilization of cadmium and chromium was particularly good; some high pH leachability of lead was observed.

Inasmuch as metals usually occur in wastes in the form of hydroxide sludges, or are rapidly converted to that form by portland cement, the balance of the S/S studies used the metals in that form. Initially, the metals were studied individually in paste matrices. Sequential batch leaching using nominally 0.1 M acetic acid was carried out on mature pastes. Stabilization was very effective; metals mobility as

a function of decreasing pH (increasing acidity) was in general far less than would be predicted by the solubility of the corresponding metal hydroxide. It was first apparent in this phase of the study that the stabilization of particularly lead, but also cadmium and chromium, was far better than would be anticipated from pH considerations alone. Lead was slightly better stabilized with low C₃A cement (Type V) than with Type I cement.

In the next phase, three metals (lead, cadmium and chromium) were added together to paste at the 0.1% and 1% levels by mass, and the batch leachability determined, using as leachants 0.1 M acetic acid, distilled water, and synthetic acid rain. With the exception of the early high-pH leachability of lead, very little of any of the metals were dissolved by increments of the latter two leachants. The effectiveness of stabilization of the other metals was in most cases orders of magnitude better than would be projected from the respective hydroxide solubilities. Lead showed the greatest improvement in stabilization, followed by chromium, and then cadmium. Even for cadmium, the insolubilization was better than would be predicted. Combinations of the three metals were shown to be slightly better stabilized in a cement matrix than were the individual metals.

The next phase of the study focused on stabilization in a soil matrix, both dry and oil-contaminated. Type I cement was added to two soils (a dolomitic soil and a siliceous soil) at the 8% addition rate; the systems were hydrated, and after 28 days of hydration, leaching tests were begun. Stabilization of the metals (especially chromium) in a soil matrix was at least as good as in cement paste, after accounting for differences in the cement con-

tent. Generally, dolomitic soils stabilized the metals better than did the siliceous soil—in part because of pH effects. For the oily waste, appropriate emulsifiers avoided early phase separation, and the leaching results with added oil were essentially comparable to those without oil.

Attempts to suppress the initial high-pH leachability of lead and chromium were the next phase of the study. Additional gypsum was added to the cement to create the potential for more ettringite on hydration of the cement. Under certain conditions, particularly at high pH, the additional gypsum suppressed metals leachability. An additional series of tests employing silica fume was carried out to discover if removing the calcium hydroxide from hydration products would inhibit calcium ion replacement of the metals in hydration products. This would avoid resolubilization. Silica fume was very effective under certain circumstances, particularly for lead at high pH, and for all metals at low pH after almost all calcium had been leached out. There will undoubtedly be applications especially for lead stabilization where the use of added silica fume, or a less expensive alternate such as Class F fly ash, may be appropriate. However, the materials should optimally be cured for a long enough period that the silica fume or fly ash has time to react with the calcium hydroxide generated from cement hydration. If only a short curing time can be allowed, it may be preferable to consider the use of alkali silicate solutions as the source of reactive silica to tie up calcium hydroxide.

The next phase of the study involved the stabilization of arsenic in siliceous soils. Arsenic is generally more difficult to stabilize than lead, cadmium or chromium, at least in part because it forms oxyanions in aqueous systems, not hydroxides. Further complexity is derived from the various oxidation states in which the metalloid can be found. Our study showed that it is beneficial to oxidize arsenic to the higher oxidation state (arsenate) before attempting stabilization. Effective stabilization can be achieved by the use of ferrous salts, together with a relatively high binder-to-waste ratio. At a higher binder-to-waste ratio than that studied here, perhaps about 0.4, better stabilization would be expected. The use of iron salts, at an iron/arsenic ratio of at least 6, may result in significant increases in the volume of the stabilized waste. For long term stabilization, it may be necessary to increase both the binder-to-waste and iron-to-arsenic ratios. Further work is needed to address the large volume increase caused by high requirements in water-cement ratio with ferrous sulfate. A common retarder

such as citric acid or a superplasticizer could be used, or perhaps a non-sulfate ferrous compound could be substituted. Much of the water demand experienced may result from precipitation of gypsum on addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. One issue of concern with arsenic stabilization is the fact that arsenic shows a maximum solubility around pH 9.5. This is the pH at which the solubility of lead and chromium is near a minimum. When wastes contain arsenic and either lead or chromium, it is necessary to be especially careful in the design of the S/S composition.

The limited work devoted to issues of S/S durability has concluded that carbonation, or the attack of acidic waters from the decomposition of organic matter, or acid rain may cause disintegration of cement forms or paste. Acids such as CO_2 may cause degradation of calcium hydroxide and calcium silicate hydrate to calcium carbonate and silica gel, and the similar degradation of ettringite, perhaps via the intermediate thaumasite. However, the amount of acidic material required to bring about this transformation is very large. If an adequate amount of cement is used, and if the material is cured, durability of S/S systems for centuries is by no means unrealistic.

The report concludes with an X-ray diffraction study of certain residues from the batch leaching tests. The results from these studies are consistent with the mechanisms of stabilization suggested in the report. Suggestions are offered for further work, to include:

- Further glimpses into the mechanism
- Optimization of the levels of silica fume
- Studies for arsenic stabilization on the replacement of ferrous sulfate with reduced iron compounds of lower water demand
- Investigations of the comparative stabilization efficiencies of Type I and Type V cements for Cr, As, and Cd
- Scanning electron microscope/energy-dispersive X-ray analysis studies of individual phases in hydrated systems to verify the observed apparent association of lead with alumina and chromium with silica.

This work demonstrates the effectiveness of portland cement systems in stabilizing wastes. It provides confirmation that this stabilization involves far more than simple pH control, and suggests some possible mechanistic explanations for the effectiveness. It studies certain additives designed to enhance some particular stabilization mechanism, and suggests modifications to further improve the immobility of metals.

The following table may be appropriate to sum-

marize the results obtained in this study. It is arranged on the basis of a "good/better/best" method for stabilizing the metals studied. It must be emphasized that the table is based only on the results of the present study. Other methods not included in this study may be equal or superior to those outlined below as "best."

Solidification/Stabilization of Hazardous Wastes

Solidification/Stabilization (S/S) has been identified as Best Demonstrated Available Technology (BDAT) for a wide range of non-wastewater hazardous

| Metal | Good | Better | Best |
|----------|--|--|---|
| Lead | Type I cement | Type I cement with silica fume | Type V with silica fume and a little extra gypsum |
| Cadmium | Cement with silica fume | Higher cement factor, no silica fume | Still more cement for long term durability |
| Chromium | Portland cement | Portland cement with a silica fume | Same, but with oxidation inhibitor to avoid hexavalent chromium |
| Arsenic | Portland cement with added FeSO ₄ | Portland cement with preoxidation with H ₂ O ₂ and added FeSO ₄ | Same, but with higher cement factor and higher Fe/As ratio |
| Mercury | Portland cement | Higher cement factor | Even more cement to ensure strongly reduced porosity |

INTRODUCTION

Industrial and manufacturing processes produce by-products—sludges, liquids, dusts, and other waste materials—which, in the past, were simply disposed of in any convenient manner. Today, efforts to use, recycle, or reduce waste streams are ecologically and economically essential. For wastes, particularly those classified as toxic or otherwise hazardous, special treatment is required. Additionally, there is now the problem of the remaining contaminated soil where such materials have been previously stored, spilled, or discarded. The U.S. EPA prioritizes the management of hazardous waste by listing, in order of decreasing desirability, four approaches to its management. These are reduction/elimination of the source, closed-loop recycling, off-site recycling, and treatment/disposal of the remaining wastes. This last management choice includes solidification/stabilization processes. For inorganic wastes, the intrinsic hazard generally is associated with heavy metals content.

wastes, and portland cement is the material most widely used for the purpose of S/S. In large part this is due to its ability to immobilize or "fix" a wide range of heavy metals. Thus the terms "immobilization" or "fixation" are also used in reference to S/S technology. Although often used interchangeably, by definition "solidification" refers to a process in which cement or other materials are added to a waste in order to produce a solid, thus tying up free water to improve the handling characteristics of a waste or making it suitable for landfill disposal. "Stabilization" refers to converting the waste into a chemically more stable form which results in a decrease in the mobility of contaminants. Aqueous wastes must be solidified as well as stabilized, but many solids may also require stabilization prior to storage or landfill disposal. In every case, the objective is for conditioned waste, which would otherwise allow the release of its hazardous constituents to the environment, to become more resistant to decomposition, chemical attack, or leaching.

S/S technology is used to treat a variety of wastes under a number of Federal And State regulatory programs. Two notable programs are the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as "Superfund," and the Resource Conservation and Recovery Act (RCRA). The Superfund program is a federal program administered by the U.S. EPA to clean up the nation's worst abandoned hazardous waste sites. By the end of Federal Fiscal Year 1995, S/S treatment technology had been included in 30% of all Superfund source-control remedies. RCRA is the federal program that regulates the disposal of waste, including hazardous waste. The RCRA program requires treatment of some hazardous wastes prior to land disposal. Such wastes must be treated at least as well as the Best Demonstrated Available Technology (BDAT) designated for the waste can achieve. S/S treatment has been designated by the U. S. EPA as BDAT for a wide variety listed RCRA hazardous wastes.

S/S Processes

Weitzman [1990] lists six major categories of S/S processes, as follows:

- Cement based binders, including portland cement and cement kiln dust (CKD)
- Lime-based binders, including lime, lime kiln dust, and lime-fly ash mixtures
- Absorbents, including clays and sawdust
- Thermoplastic materials, including asphalt
- Thermosetting polymers
- Vitrification

Of the above, the first two categories are perhaps best suited to condition inorganic hazardous wastes containing RCRA and other heavy metals. Vitrification and polymer encapsulation techniques can also immobilize metals. These techniques are, however, significantly more expensive than portland cement-based S/S. Lime (calcium hydroxide) does not form a solid matrix with water, but it does provide the pH conditions for precipitation of many heavy metals as metal hydroxides, and it can provide the high acid buffering capacity required for maintaining long term alkalinity. The presence of fly ash in such mixtures may permit a pozzolanic reaction that can increase strength and develop a matrix. Portland cement, however, has many additional advantages. Cements are unique among S/S binders in that they provide a strong chemical binding as well as physical encapsulation. The hydration of cement provides the high pH for precipitation of metal hydroxides, the high surface area calcium sili-

cate hydrate (C-S-H) reaction product for immobilization of many hazardous constituents and matrix strength development, and the formation of metals-substituted calcium aluminate or sulfoaluminate hydrates.

A number of investigations, pertinent to the subject of the present study, on the stabilization of metal-containing wastes using solidification/stabilization (S/S) techniques have been carried out in the past. Conner, Cotton and Lear [1992], Bishop [1988], and Zamorani and Serrini [1992] have investigated the mechanism of metal fixation in S/S systems using portland cement. Bishop [1988] has also studied leaching characteristics of selected S/S systems. Other S/S studies have been conducted on synthesized heavy metal sludges using calorimetry, NMR (Nuclear Magnetic Resonance), and SEM (Scanning Electron Microscopy) techniques to understand the metal fixation mechanism [Butler et al., 1987; Tittlebaum and Yang, 1988; Akhtar et al., 1989; and Komarneni et al., 1988]. Bhatti [1987] studied heavy metal fixation in tricalcium silicate (C₃S)-water systems and proposed a general mechanism of partial substitution or replacement by metal in the calcium silicate hydrate gel (C-S-H) phase. Ivey et al. [1992] studied the characterization of the alite phase in cement with trace metal contamination, especially chromium. Jones, Bricka, and Cullinane [1992] studied interference of S/S by copper, lead, and zinc nitrate and other agents using cement and other binders but always in the presence of a mixed metal (cadmium, chromium, mercury, and nickel) hydroxide sludge.

During the solidification process, much water is incorporated into the hydration products. This property is often used to treat a waste containing free water prior to land disposal. RCRA regulations prohibit land disposal of wastes containing free water. RCRA policy requires attainment of a compressive strength of 50 psi in treated waste to demonstrate that the free water was treated chemically rather than merely sorbed using adsorbents. Such portland cement-based binders may also contain fly ash, slag, silica fume, natural pozzolans, or even CKD for special applications. Wilk [1995] has reviewed the use of portland cement in S/S technology and the heavy metals in wastes which are amenable to cement-based stabilization, either alone or in conjunction with various additives. The potential cement market, especially for Superfund sites and RCRA wastes, is very large. The Portland Cement Association [1993] has estimated, based on the assumptions that Superfund cleanups will continue for 16 years, Department of Defense (DOD) clean-

ups for 20 years, and Department of Energy (DOE) cleanups for 25 years, that approximately 25% of the estimated 17,850 sites will select S/S as a remediation technology; this translates into an S/S potential for portland cement of from 72 to 118 million tons over the next 20 years. This estimate is based on the current rate of selection of Superfund site remediation methods (presently more than 25%), and extended to these other programs.

It is therefore clear that the future market for portland cement in S/S activities is bright. However, there are a few real or perceived drawbacks to the use of portland cement for stabilization that need to be addressed. The very high pH of hydrating portland cement can to some extent solubilize certain amphoteric metal hydroxides, such as lead and chromium (III). Arsenic does not form a hydroxide, and must be rendered insoluble by another means. The durability of the waste form is important, especially with respect to carbonation by atmospheric or water-borne carbon dioxide, but also with respect to groundwater or surface water with the potential to alter the pH of the wasteform system. The purposes of this study were (1) to quantify the physical properties of cement pastes and soil matrices containing selected heavy metals, (2) to characterize the leaching characteristics of these metals when subjected to various leachants, (3) to observe the effect, if any, of oil contamination on the effectiveness of stabilization, (4) to address the special problems of arsenic stabilization, and (5) to assess the long-term durability of cement-stabilized systems to the aggressive action of acidic groundwater or surface water, or of aqueous or gaseous carbon dioxide.

CHAPTER 1

Effects of Salts and Oxides on Paste Properties and Acetic Acid Leachability

The work reported in this section was introductory to the sequential leaching studies discussed later in the report. In this chapter, investigations on several engineering properties of cement-based solidification/stabilization (S/S) systems incorporating trace metals at different levels are reported. Both soluble and insoluble forms of metal compounds commonly found in wastes are tested in the studies. The effects of cement composition on metal stabilization and physical properties of pastes are examined. The critical properties of the pastes studied are workability, initial setting, compressive strength, and durability. In keeping with the subsequent work, some leachability characteristics of the solidified pastes at varying ages are also investigated using the U.S. EPA Toxic Characteristic Leaching Procedure (TCLP) solution, 0.1N acetic acid, as leachant.

MATERIALS AND METHODS

Analytical grade soluble salts and oxides of a number of RCRA (Resource Conservation and Recovery Act) metals were used in preparing the cement pastes. Two chemically different types of portland cements, ASTM Type I [high tricalcium silicate (C_3S), high tricalcium aluminate (C_3A)] and ASTM Type V [low C_3S , low C_3A], were used in preparing the pastes to study the effect of the compositional differences on metal stabilization and physical properties. Type I portland cement is commonly used for general construction cement, whereas Type V cement is intended chiefly for applications requiring high sulfate resistance, particularly where soils or groundwater have high sulfate content. Their oxide analyses and the calculated potential compound composition are shown in Tables 1-1 and 1-2. Values in Table 1-2 are calculated by the method described in ASTM Standard Specification for Portland Cement (C150).

Four RCRA metals, lead (Pb), cadmium (Cd), chromium (Cr), and mercury (Hg), were selected for preparing three sets of cement pastes.

Set 1 - using soluble metal compounds. In this case, the water-soluble compounds lead (II) nitrate [$Pb(NO_3)_2$], cadmium chloride hydrate ($CdCl_2 \cdot 2.5H_2O$), chromium (III) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$), and mercury (II) chloride ($HgCl_2$) were dissolved in deionized water and used as mix water in preparing individual pastes, separate for each metal. At the concentration levels, the anions will have minimal effects in the presence of sulfate in cement.

Set 2 - using insoluble metal oxides. In this case, relatively insoluble lead (II) oxide (PbO), cadmium oxide (CdO), chromium (III) oxide (Cr_2O_3), and mercury (II) oxide (HgO) were blended dry with cements and mixed with deionized water to prepare pastes with metal loading equivalent to that of Phase 1 on a final paste basis.

Set 3 - same metals as oxides at higher concentration levels. The same four metals were used here but at higher levels.

High concentration levels for both soluble metal salts and oxides were purposely selected to simulate adverse practical situations. The highest metal concentrations in liquid and solid wastes were chosen as similar to the highest levels cited by Conner [1990].

EXPERIMENTAL

Total metal levels in the final solidified paste for Phases 1 and 2 were 7,300 mg/kg for lead, 5,800 mg/kg for cadmium and chromium, and 140 mg/kg for mercury. Metal levels in Phase 3 were 38,000 mg/kg for lead, 12,600 mg/kg for cadmium, 14,900 mg/kg

Table 1-1. Oxide Analysis of Cements

| Cements | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | Na ₂ O | K ₂ O | TiO ₂ | LOI |
|---------|------------------|--------------------------------|--------------------------------|-------|------|-----------------|-------------------|------------------|------------------|------|
| Type I | 20.89 | 4.72 | 2.25 | 63.57 | 2.77 | 3.10 | 0.010 | 0.62 | 0.18 | 1.31 |
| Type V | 23.03 | 3.77 | 4.25 | 63.06 | 2.31 | 2.23 | 0.04 | 0.62 | 0.22 | 0.69 |

Table 1-2. Bogue Potential Compound Composition (wt %)

| Cements | C ₃ S | C ₂ S | C ₃ A | C ₄ AF |
|---------|------------------|------------------|------------------|-------------------|
| Type I | 55 | 19 | 9 | 7 |
| Type V | 42 | 34 | 4 | 13 |

kg for chromium, and 330 mg/kg for mercury. A different way to express values for Phase 3 is as concentrations of oxides by mass of cement; these were: lead oxide (PbO) 5%, cadmium oxide (CdO) 2%, chromium oxide (Cr₂O₃) 3%, and mercuric oxide (HgO) 0.05%.

Paste mixing was done in a standard Hobart “mortar” mixer [ASTM C 305-94, 4.73 L nominal capacity]. The required amount of mix-water (deionized water) was placed in the mixer bowl. The mixer was turned on at low speed (speed 1) while a vibrating feeder delivered cement to the mix-water within one minute. The paste was then mixed for two (2) minutes at speed 1. Following a rest period of three (3) minutes (during which the paste adhering to the sides was scraped down, and any cement stuck to the bottom was scraped loose, turned, and remixed), final mixing for two (2) minutes was done at speed 2. The water-to-cement ratio (w/c) chosen for all the pastes was 0.4, to avoid bleeding while maintaining reasonable workability.

Paste temperatures were recorded immediately after mixing. The fresh cement pastes were tested for their workabilities by an updated version of the mini-slump cone method [Kantro, 1980]. This test, in a very simple way, is a composite measure of the flow properties of paste at ten minutes after the cement and water are mixed. Masons and concrete workers consider the slump as one of the most important indicators of the workability of their material. For neat cement pastes, the greater the water-to-cement ratio (w/c), the larger is the resulting pat area. Initial setting times of the pastes were determined by a modification of the Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle (ASTM C 191). This method measures penetration by a 1 mm needle into cement paste contained in a 100 mL open plastic cup. Initial set in

this modified test occurs when penetration depth is 10 mm. Separate calorimetry tests on the pastes were done by injection-mixing inside a conduction calorimeter cell and the output curves were recorded. From experience in these laboratories over several years using these tests, it is estimated the experimental error for paste temperatures is ± 1°C, for initial set ±12 min, for mini-slump area ±1.0 cm², for initial calorimeter peak ±0.2 mV, and for induction time ±30 min.

In order to test the paste for compressive strength, 25.4 mm (one-inch) paste cubes were prepared in stainless steel molds. Molds were lightly coated with form oil and placed on a small vibrating table. The pastes were loaded in the vibrating molds and each cube cavity was filled to about 90% of its volume. A flat laboratory spatula was then used with an up-and-down motion, first on the sides and then in the corners of the mold, and finally working across the molds-first in one direction and then across the mold perpendicular to the first pass. In the meantime, the molds were continuously vibrated to remove air bubbles while consolidating the paste. The molds were then overfilled with paste (about 10% excess to compensate for paste shrinkage), and the spatula again used sparingly with the same motion to obtain a bubble-free paste. Thereafter, the molds were stored in the moist-room at 100% relative humidity and 23°C.

The cubes were demolded on the third day using a wide and stiff spatula to remove excess hardened paste and leave a smooth top surface, level with the top of the molds. After demolding, the cubes were kept in the moist-room for curing. Compressive strength tests were conducted after 3-, 28-, and 90-day curing. The measurements were made on three replicate samples and the mean value reported.

Toxicity Characteristic Leaching Procedure (TCLP) and column leaching (CL) tests were conducted on 28-day and 90-day old samples using the specified TCLP leachant (approximately 0.1N acetic acid). Column leaching was conducted for each metal through beds of 100 g hardened paste containing each heavy metal, ground to -9.5 mm (-3/8 in.), and placed in a 50 mm (2 in.) wide

and 400 mm (16 in.) long cylindrical column. Acetic acid was filtered through the bed at a constant rate close to 15 ml/hr. Leachates for each paste were collected at 24, 48, and 72 hours, and analyzed for their respective metal. The acid additions represent 0.4, 0.8, and 1.2 equivalent/Kg of paste at 24, 48, and 72 hours respectively.

RESULTS AND OBSERVATIONS

Fresh Pastes

Data on the initial setting time, workability (mini-slump), and temperatures of pastes prepared from Type I and V cements using both soluble salts and metal oxides are presented in Table 1-3. Changes in the initial setting and mini-slump area are all compared to those of the control, a neat cement paste prepared under identical conditions without the addition of any metal salts.

All additions of metal (i.e. both in the form of water-soluble salts and insoluble oxides) to Type I cement pastes in this study reduced the mini-slump area (that is, decreased workability). For Type V cement, soluble cadmium and chromium salts de-

creased the mini-slump area while both forms of lead increased the area.

Data from hydration conduction calorimetry on the induction times and the intensity of initial peaks for pastes made with Type I and V cements and both soluble metal salts and metal oxides are given in Table 1-4. (In calorimetry, as explained in detail later in the report, induction times represent the length of time between the first and second peaks of hydration heat release; peak intensity [measured in millivolts (mv)] is related to the amount of heat released by these individual components of hydration reactions.) Induction time decreased, compared to the controls, for pastes made with soluble metal salts except for the pastes made with either type of cement and lead nitrate. Pastes containing cadmium or lead oxide had longer induction times. Type I and V cement pastes made with oxides of chromium and mercury had the same induction times as the control, within experimental error.

In general most Type V pastes with either soluble or insoluble compound additions exhibit lower paste temperatures, similar or longer setting and induction times, and similar or larger mini-slump areas compared to Type I pastes made with the same compounds and concentrations. One significant

Table 1-3. Initial Setting Times, Temperatures, and Slump Areas for the Type I and Type V Cement Pastes Containing Heavy Metals as Solutions and Oxides

| Metals (mg/kg) in solidified waste | Solutions | | | Oxides | | |
|--|--------------------------|------------------|----------------------------------|--------------------------|------------------|----------------------------------|
| | Initial set (hrs:min) | Paste temp °C | Slump area (cm ²) | Initial set (hrs:min) | Paste temp °C | Slump area (cm ²) |
| Type I Cement | | | | | | |
| Pb (7 300) | 16:30 | 29.1 | 17.38 | 13:0 | 28.6 | 22 |
| Pb (38 000) | - | - | - | >38:00 | 31.2 | 26.25 |
| Cd (5 800) | 3:30 | 30.2 | 17.44 | 10:0 | 28.6 | 17.19 |
| Cd (12 600) | - | - | - | 13:30 | 29.0 | 17.94 |
| Cr (5 800) | 0:52 | 36.8 | 16.56 | 3:35 | 27.7 | 21.81 |
| Cr (14 900) | - | - | - | 3:25 | 27.5 | 22.44 |
| Hg (140) | 3:15 | 27.6 | 23.25 | 3:20 | 27.4 | 22.75 |
| Hg (330) | - | - | - | 3:00 | 29.8 | 21.88 |
| Control | 3:40 | 26.4 | 25.5 | 3:40 | 26.4 | 25.5 |
| Type V Cement | | | | | | |
| Pb (7 300) | 20:00 | 24.2 | 46.69 | - | - | - |
| Pb (38 000) | - | - | - | 53:00 | 22.5 | 49 |
| Cd (5 800) | 4:55 | 26.1 | 24.81 | - | - | - |
| Cd (12 600) | - | - | - | >11:00 | 24.5 | 37.94 |
| Cr (5 800) | 1:00 | 36.5 | 14.31 | - | - | - |
| Cr (14 900) | - | - | - | 3:25 | 25.8 | 31.56 |
| Hg (140) | 3:20 | 24.9 | 34.94 | - | - | - |
| Hg (330) | - | - | - | 3:20 | 25.0 | 36.19 |
| Control | 3:10 | 24.5 | 35.63 | 3:10 | 24.5 | 35.63 |

Table 1-4. Conduction Calorimetry Initial Peak Intensity and Induction Time for Type I and Type V Cement Pastes Using Solutions and Oxides of Heavy Metals

| Metals (mg/kg) in solidified waste | Solutions | | Oxides | |
|--|----------------------|-----------------------------|----------------------|-----------------------------|
| | Initial peak (mv) | Induction time (hrs:min) | Initial peak (mv) | Induction time (hrs:min) |
| Type I Cement | | | | |
| Pb (7 300) | 2.44 | 36:20 | - | - |
| Pb (38 000) | - | - | 1.78 | 108:00 |
| Cd (5 800) | 2.42 | 6:12 | - | - |
| Cd (12 600) | - | - | 1.98 | 19:00 |
| Cr (5 800) | 5.73 | 2:47 | - | - |
| Cr (14 900) | - | - | 1.90 | 9:24 |
| Hg (140) | 1.89 | 4:40 | - | - |
| Hg (330) | - | - | 1.93 | 9:19 |
| Control | 1.80 | 8:51 | 1.80 | 8:51 |
| Type V Cement | | | | |
| Pb (7 300) | 1.26 | 28:23 | - | - |
| Pb (38 000) | - | - | 0.49 | 78:00 |
| Cd (5 800) | 1.54 | 7:22 | - | - |
| Cd (12 600) | - | - | 0.92 | 23:16 |
| Cr (5 800) | 4.57 | 3:42 | - | - |
| Cr (14 900) | - | - | 1.02 | 9:18 |
| Hg (140) | 1.06 | 5:42 | - | - |
| Hg (330) | - | - | 1.02 | 9:23 |
| Control | 1.10 | 9:25 | 1.10 | 9:25 |

exception is the induction time of pastes made with either lead nitrate or lead oxide.

The average temperature for Type I cement pastes is 12°C higher than the starting mix water, compared to 5°C higher for Type V. This is because Type V is a low heat cement due to lower C₃S and C₃A contents compared to the Type I. Many initial set times were close to the control set time for both cements. However, accelerated set was observed for pastes made with soluble chromium, and retarded set was observed in pastes with cadmium oxide and both lead compounds for both cements.

Mini-slump tests. The mini-slump data for metal compounds of Phase 1 (soluble salts) and Phase 2 (metal oxides) with Type I cement are shown in Figure 1-1. Results are expressed as the area of the nearly circular pat of cement paste after the confining truncated cone is removed. All metal-containing pastes have lower areas than the control, a neat paste. The reduction is quite similar for all the metals in spite of the different amounts present; for example, lead is present at fifty times the concentration of mercury. Mini-slump areas for Phase 3 (metal oxides at higher levels) using Type I cement (Figure 1-2) indicate nearly identical reduction of mini-slump areas

relative to the control when compared to the data of Phases 1 and 2, except for lead oxide. The mini-slump area for the paste containing 38,000 mg/kg of lead was larger than those both of the control paste and of the paste with 7,300 mg/kg made with PbO.

Similar experiments were performed using Type V cements. Compared to the Type I cement, substantially different mini-slump areas were observed (Figure 1-3) using soluble salts. Paste made with lead nitrate solution had greater flow, mercury paste had the same flow as the control paste, and both these mini-slump areas were significantly different from those for the same soluble metals with Type I cement.

Conduction calorimetry tests. Induction time is the time from the first peak to the second peak on the calorimetry curves. The first conduction calorimetry peak is due to a combination of exothermic wetting and early reactions, primarily of the calcium aluminate phase; this peak usually occurs within the first few minutes after the mixing of water and cement. A dormant period, usually of 1.5 to 3 hours, occurs before heat output begins to increase; it normally continues to rise to the maximum of the 2nd peak for roughly 4 to 10 hours. The main or 2nd

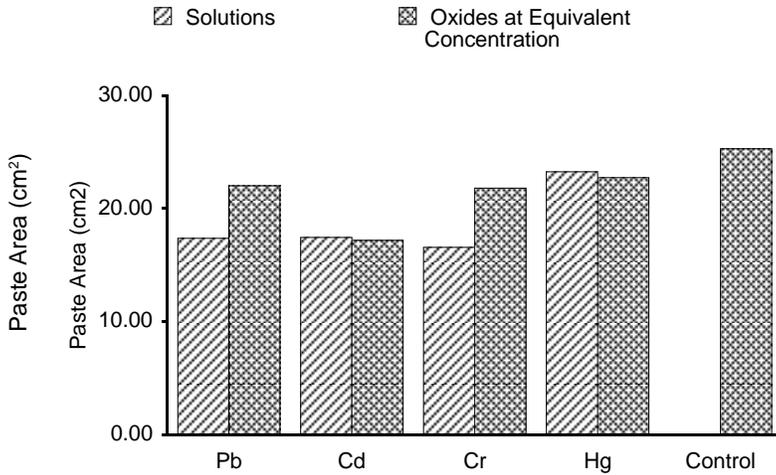


Figure 1-1. Minislump areas for Type I cements at equivalent metal levels from solutions and oxides.

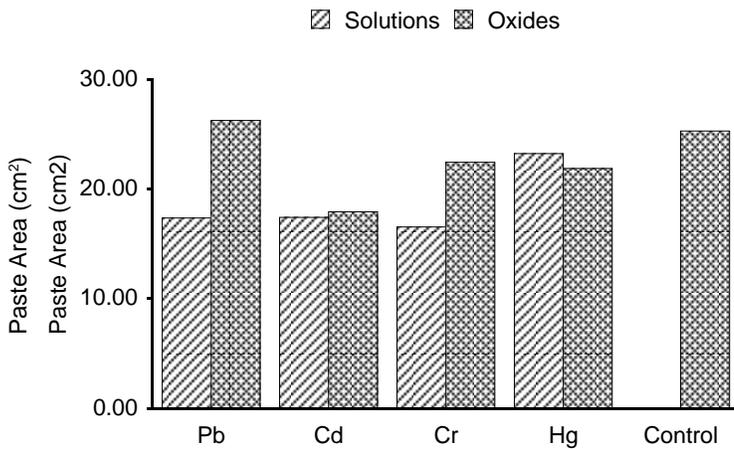


Figure 1-2. Minislump areas for Type I cements and metal solutions and high oxide contents.

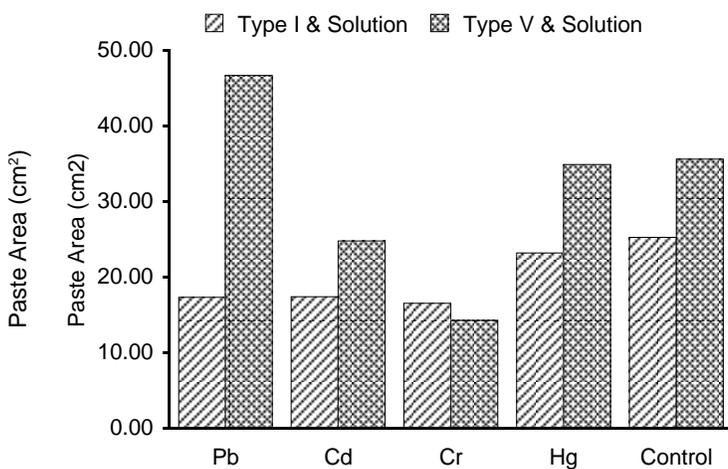


Figure 1-3. Minislump areas for Type I and Type V cements and metal solutions.

peak corresponds to the alite hydration reactions, which have calcium silicate hydrate gel (C-S-H) and calcium hydroxide (Ca(OH)₂) as the principal products. Initial peaks in the calorimeter output plots for Type V pastes are all lower than peaks for corresponding Type I cement pastes.

The highest initial peak values are for the two pastes made with chromium chloride, which also had the highest paste temperatures. Initial peak values for the paste with lead nitrate is also elevated relative to the control, indicating that a substantial hydration is occurring. This paste is also very slow to set. This effect is not surprising; the main C₃S hydration peak was delayed, and it is known that final set is dependent on significant progress in alite hydration. Judging from the strength of the initial heat peak, on the other hand, the lead nitrate apparently did not retard the initial aluminate reactions. Most induction times follow the same trend as the initial setting times.

Initial setting time tests. Initial set times for the Phase 1 and Phase 2 pastes (Figure 1-4) indicate chromium chloride is a set accelerator while cadmium oxide and both lead compounds are strong set retarders for Type I cement pastes. Lead and cadmium oxide at higher addition levels (Figure 1-5) have an even greater retarding effect. At both high and low addition levels, chromium (III) and mercuric oxides have little effect on the setting time. Judged on the basis of the admittedly fewer tests performed, similar behavior appears to be occurring with Type V cement pastes. Comparison of the soluble salts with Type I and Type V cement pastes indicates comparable setting times for mercury and chromium and greater retardation for cadmium and lead solutions in Type V cement pastes (Figure 1-6). It needs to be stressed that retardation implies only a delay in setting and strength-development behavior. Ultimately all the cements set and ultimate strengths were comparable to those of the control.

Chromium chloride vs chromium nitrate. To answer the question of whether

it is the chloride in CrCl_3 that causes set acceleration in the paste or the chromium, an equivalent molar amount of soluble $\text{Cr}(\text{NO}_3)_3$ was used to prepare Type I cement paste under identical experimental conditions. The same tests were repeated for this new system on the fresh as well as hardened pastes. The following results (Table 1-5) were obtained; data on CrCl_3 are given for comparison.

The similar behavior of both the fresh and hardened pastes containing chromium chloride or nitrate, i.e. high paste temperature, short initial setting time, and small mini-slump areas of the fresh paste and similar compressive strengths of the hardened paste, suggests that it is indeed chromium which is responsible for most of the set acceleration and the resulting high early strength.

Hardened Cement Pastes

Compressive strength tests. Compressive strengths at early ages reflect the apparent substantial interference with hydration reactions that gave rise to the large changes in fresh paste properties - especially to extreme changes in the initial setting times. Most notably for Type I cement pastes, 3-day strengths compared to the control were greater for chromium and cadmium, and less for lead and mercury when metals were added as solutions (Figure 1-7). Strength development of pastes with all four metals, although retarded in some cases at early ages and at 28 days, continued

under moist cure conditions. Relative to the control paste, the experimental pastes achieved equal or greater strengths at 90 days. For Type V cement, 3- and 28-day strengths for pastes containing Cr were higher than the control, but the 90-day strengths were lower (Figure 1-8). Except for Pb, the 90-day strengths of pastes with the remaining three metals were somewhat lower than the control. With cement paste in the absence of metals, this is usually attributed to the continued hydration of the cement, primarily to make C-S-H and a stronger matrix. It is believed that the mechanism for hydration of the

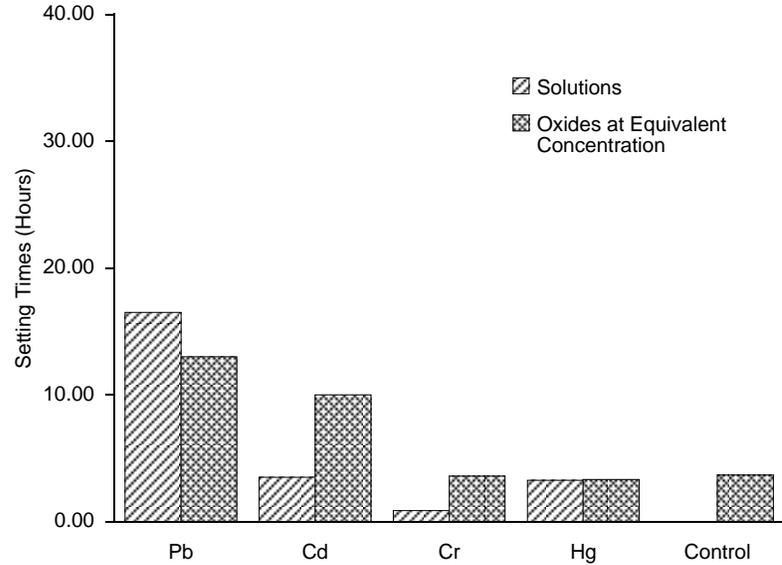


Figure 1-4. Initial setting time for Type I cements at low metal solutions and oxide levels.

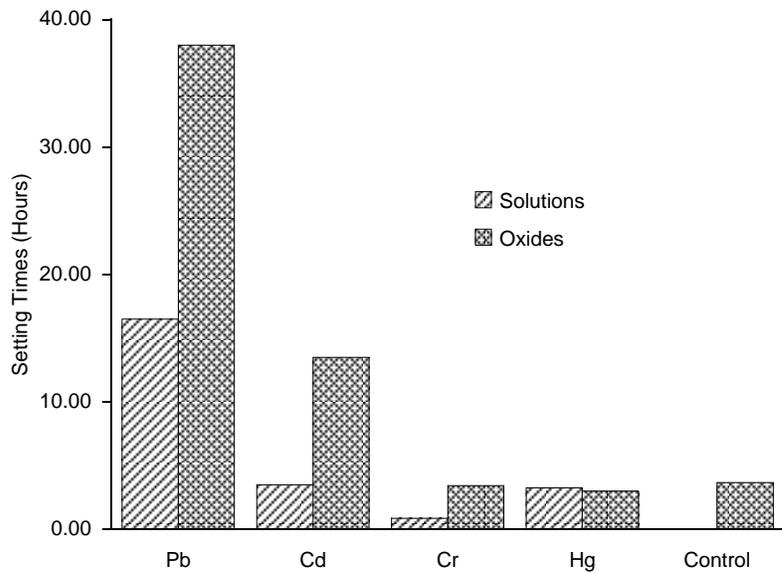


Figure 1-5. Initial setting time for Type I cements at high metal solutions and oxide levels.

metal paste combinations in this study is in most respects similar to that of the control paste.

In general, the addition of metal oxides produces pastes with 90-day strengths somewhat less than those of the respective control for both Type I and V cement pastes; the only exception is the Type V-PbO cement paste combination. Compressive strength development for Type I pastes with metal oxides at metal concentrations equal to those in pastes with solution addition are shown in Figure 1-9. Three-day strengths for pastes with each of the four metal oxides were less than the control at the

Table 1-5. Comparison of Type I Cement Pastes Performance Containing Equivalent Concentrations of Cr(NO₃)₃ and CrCl₃

| Chromium compounds | Fresh pastes | | | Hardened pastes | | |
|-----------------------------------|-----------------------|----------------|-------------------------------|---------------------|---------------------|----------------------|
| | Initial set (hrs:min) | Paste temp. °C | Slump area (cm ²) | 3-day strength, psi | 7-day strength, psi | 28-day strength, psi |
| Cr(NO ₃) ₃ | 1:09 | 38.0 | 12.13 | 10680 | 12770 | 15150 |
| CrCl ₃ | 0:52 | 36.8 | 16.56 | 11750 | 12750 | 16510 |

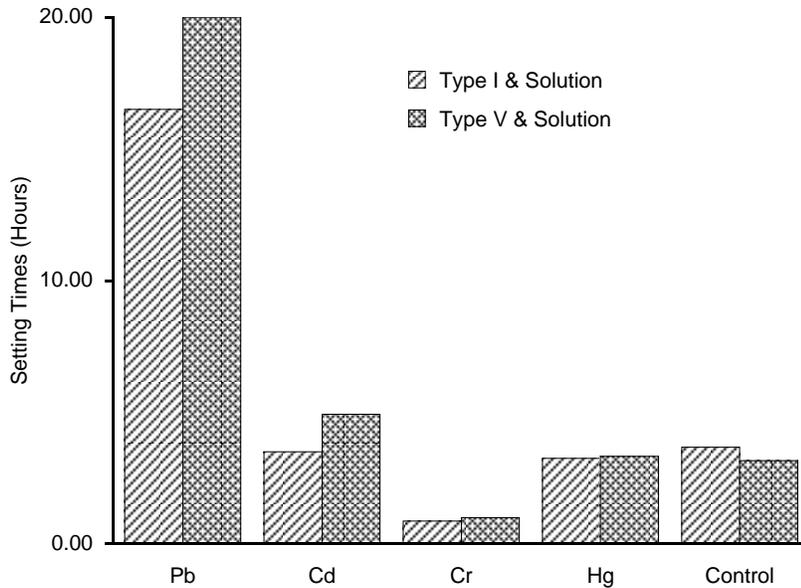


Figure 1-6. Initial setting time for Type I and Type V cements and metal solutions.

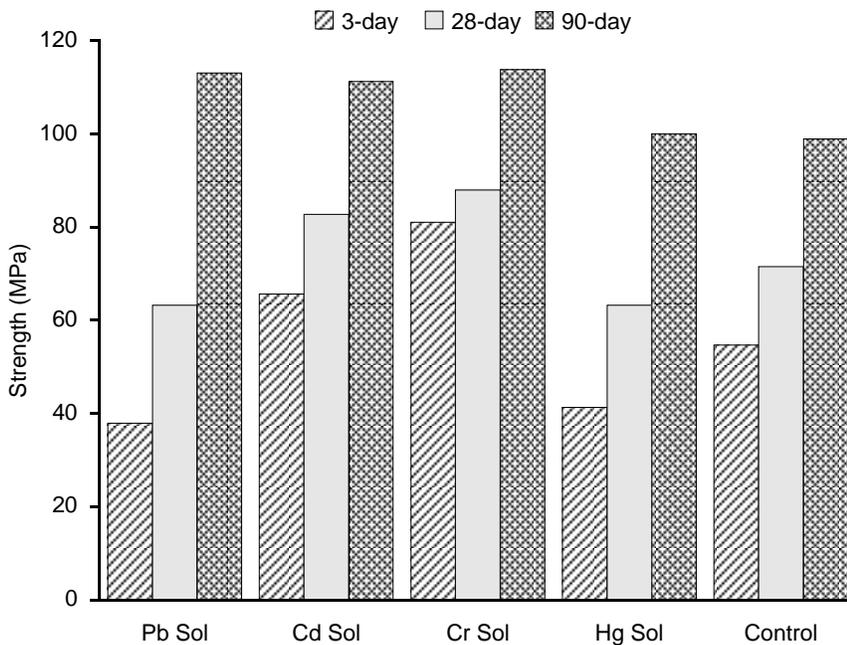


Figure 1-7. Compressive strength development for Type I cements with metals additions as solutions in the mix water.

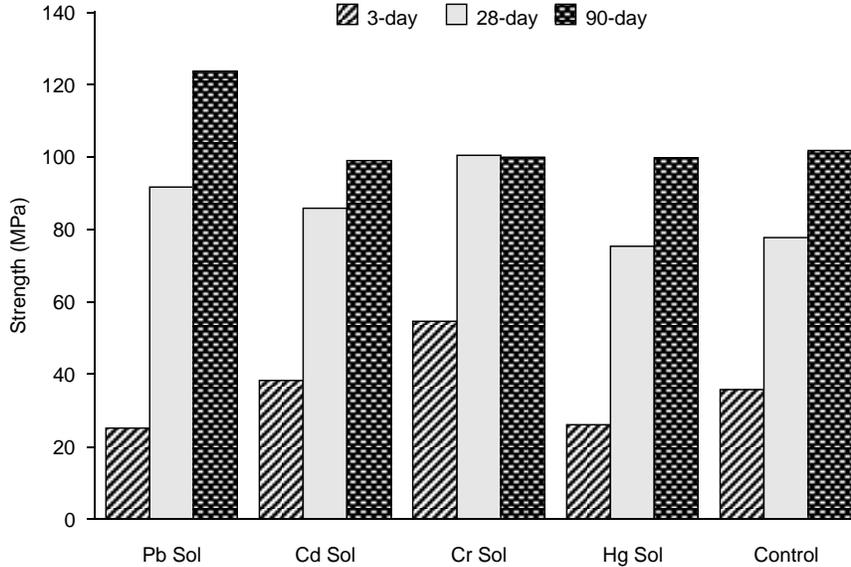


Figure 1-8. Compressive strength development for Type V cements with metal additions as solutions in the mix water.

same age. At 28 days, however, all modified pastes had strengths that exceeded the control. Strength development is more rapid between 3 and 28 days for metal oxide-containing pastes versus metal solution pastes, but the strength gains decrease, resulting in 90-day strengths (Figure 1-10) which are less than those of the control and the metal solution pastes. The same observations apply for Type V cement pastes (Figure 1-11) except that the 3-day strength for Pb-containing paste was not recorded because the paste was still plastic at the time.

TCLP leaching tests. With the exception of the high lead levels, leachability of the metals was uniformly

quite low, and for cadmium, chromium and mercury there was little difference, if metals levels were equal, between leaching from pastes made with solutions and those made with the metal oxides (Table 1-6). Cadmium and chromium leaching from Type I paste appear to give similar concentrations in the leachate at both levels of metal oxide in the study. Mercury and lead leaching, especially the latter, increases at higher levels of these oxides in Type I paste. This appears to be particularly true for very high levels (38,000 ppm Pb), and for the oxide as opposed to the solution. The specific surface area of the oxide is likely to be much lower than that achieved from the salts conversion to hydroxide, or

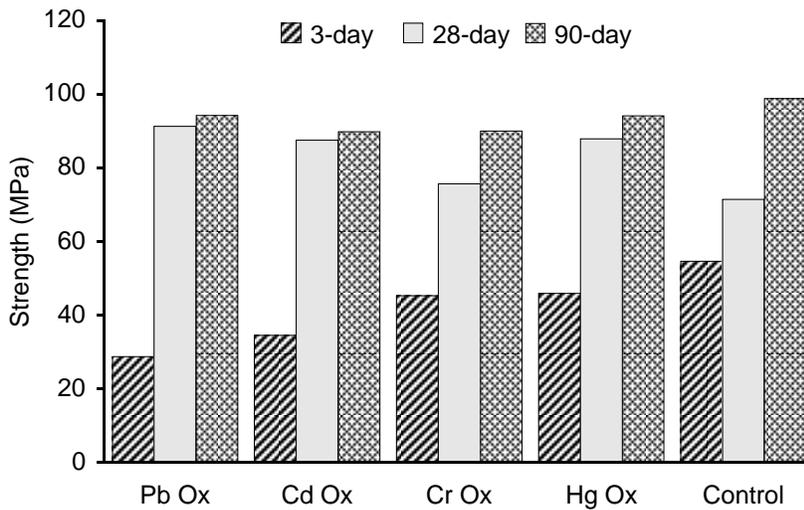


Figure 1-9. Compressive strength development for Type I cements with metals additions to cements as oxides.

for the hydroxide sludge itself, as will be seen in the next section on hydroxide sludges. Although there were some failures of TCLP (exceeding of the 5 mg/L extraction limit) with the oxide addition, it is not considered representative of the form typical of that found in most wastes. The column leaching tests were extremely stringent, and probably therefore not quantitatively accurate in prediction of actual field results either with respect to concentration of lead or to the exposure to acid. As will be shown, cadmium solubility appears to be principally a matter of the solution pH.

Table 1-6. Total vs Leached Metals (mg/L) from TCLP and Column Leaching (after 24 Hours) of 28-day-old Type I and V Cement Pastes Made with Metal Solutions and Oxides (Data on Controls Given for Comparison)

| Metals | Metal solutions | | | Metal oxides | | Control | |
|---------------|------------------------|-------------|-----------|--------------|-----------|-------------|-----------|
| | Total (mg/kg) in solid | TCLP (mg/L) | CL (mg/L) | TCLP (mg/L) | CL (mg/L) | TCLP (mg/L) | CL (mg/L) |
| Type I Cement | | | | | | | |
| Pb | 7 300 | 0.76 | 5.28 | 1.21 | - | <0.0058 | 0.113 |
| Pb | 38 000 | - | - | 8.27 | 37.80 | - | - |
| Cd | 5 800 | <0.0003 | 0.016 | 0.0007 | - | <0.0002 | <0.0005 |
| Cd | 12 600 | - | - | <0.0007 | 0.03 | - | - |
| Cr | 5 800 | 0.024 | 0.02 | 0.043 | - | 0.0136 | 0.0100 |
| Cr | 14 900 | - | - | 0.011 | 0.006 | - | - |
| Hg | 140 | 0.33 | 0.20 | 0.384 | - | <0.0007 | 0.0600 |
| Hg | 330 | - | - | 1.71 | 3.08 | - | - |
| Type V Cement | | | | | | | |
| Pb | 7 300 | 0.22 | 4.32 | - | - | 0.013 | 0.053 |
| Pb | 38 000 | - | - | 3.24 | 37.26 | - | - |
| Cd | 5 800 | 0.003 | 0.09 | - | - | <0.0002 | 0.00558 |
| Cd | 12 600 | - | - | 0.007 | 0.006 | - | - |
| Cr | 5 800 | 0.03 | 0.03 | - | - | 0.025 | 0.00864 |
| Cr | 14 900 | - | - | 0.009 | 0.006 | - | - |
| Hg | 140 | 0.40 | 0.84 | - | - | 0.00058 | 0.00524 |
| Hg | 330 | - | - | 2.02 | 4.05 | - | - |

All these solids are very cement-rich and probably more alkaline than many solidified waste matrices. The high alkalinity probably contributes to the high lead leaching levels.

For Type V cement the leaching is very similar to that for Type I. Other data from this project reported elsewhere [Bhatty and West, 1993] also indicate that at 90 days TCLP leachate concentrations are similar for cadmium and chromium while lead concentrations are slightly lower and those for mercury slightly higher. Comparable lead contents in cement samples consistently give slightly lower TCLP leachate values for Type V than for Type I cement at both 28 and 90 days. Subsequent tests on sequential batch leaching confirm these results.

Metals Interactions with Type I Cement

Mercury, both as the chloride and oxide, had very little effect on the properties of cement paste. This lack of influence may be due to the low concentration. The concentration was chosen as representative of a high level mercury waste and therefore such wastes should not affect the solidification process significantly. Mercury did decrease fresh paste flow

and resulted in somewhat lower early strengths but did not materially affect initial setting time.

Cadmium, as the chloride, changed cement paste properties less than did cadmium oxide. Both compounds decreased paste flow, but only the cadmium oxide significantly delayed initial set and lowered the 3-day strength. Lead oxide and nitrate substantially changed almost all cement paste properties causing slow strength development and severely retarding initial set and decreasing flowability as measured by the mini-slump pat area.

Chromium chloride and nitrate were very effective set accelerators; they raised the paste temperature and also caused rapid strength development. Chromium (III) oxide, on the other hand, hardly changed the cement paste setting time or strength but did decrease paste flow, as did all metal additions both as oxides and as soluble salts. For all these metals, whether they positively or negatively affected the fresh paste properties, the metal containing pastes had compressive strengths after 90 days quite close to the control strength. Pastes made with soluble salts were slightly stronger and those made with oxides slightly weaker than the control.

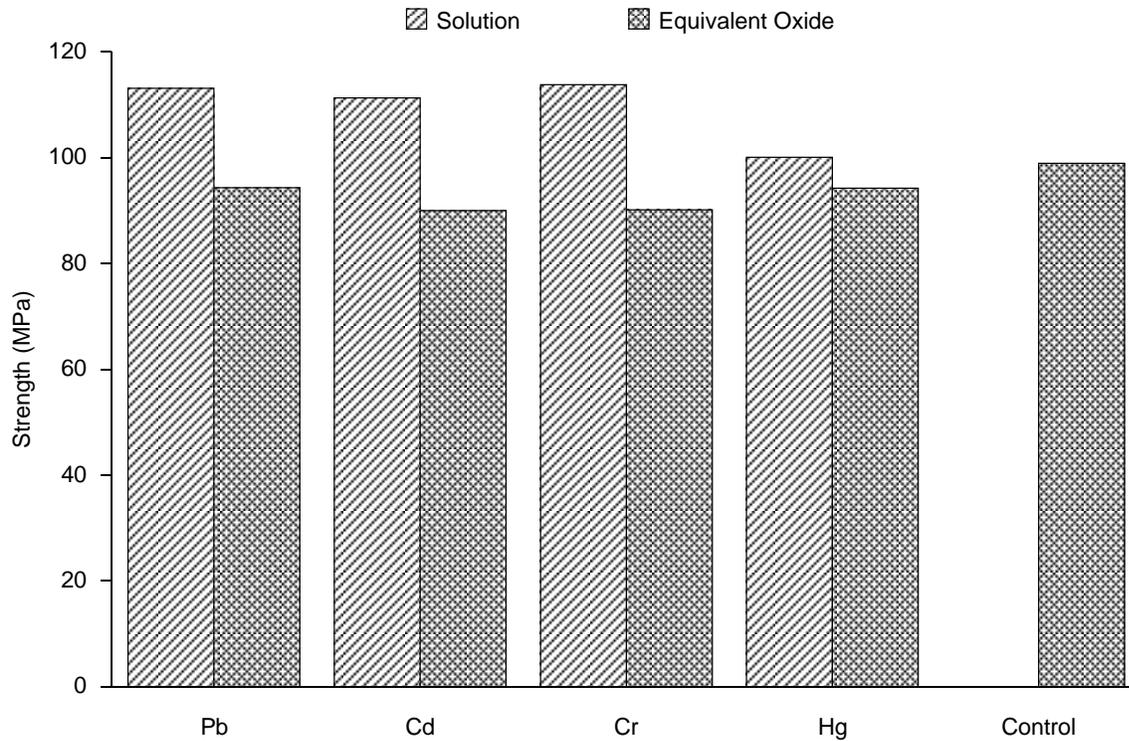


Figure 1-10. 90-day compressive strengths for Type I cement.

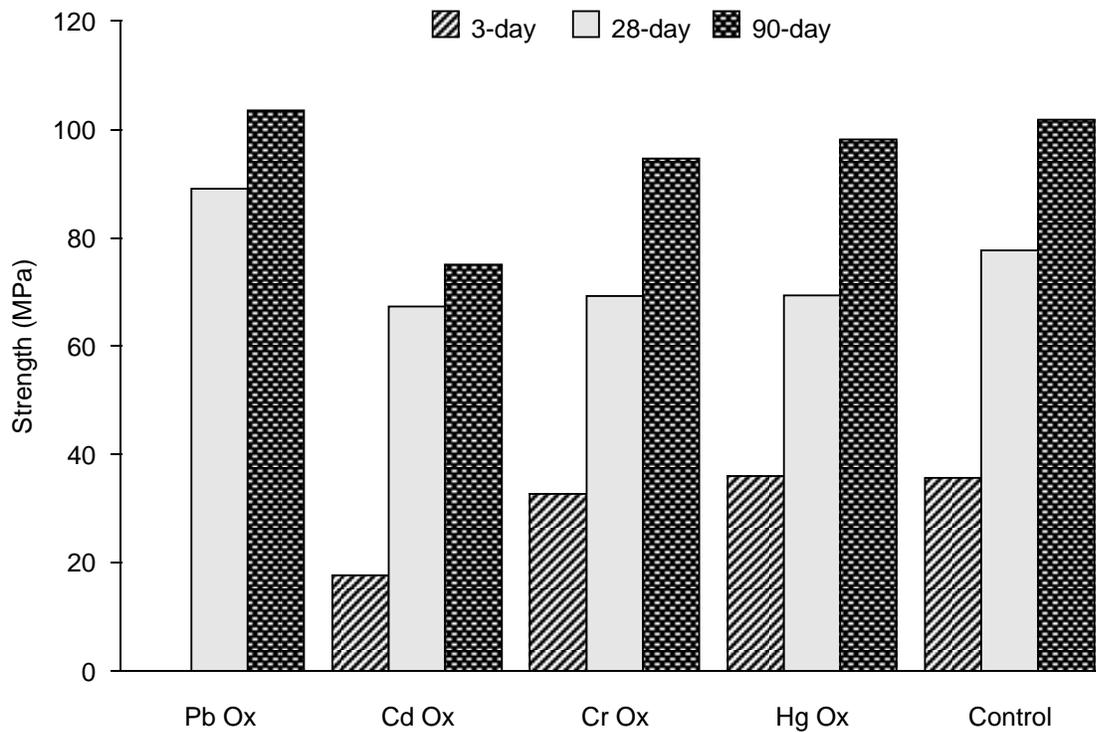


Figure 1-11. Compressive strength development for Type V cements with metal additions to cements as oxides.

Discussion and Interpretation of Results

Flowability was decreased in nearly all the cases studied with metal addition in either form. Both the soluble metal salts and the metal oxides in the highly alkaline environment of cement paste will react with water and, except for mercury, form metal hydroxides. The water consumed to make the hydroxides is unavailable for paste hydration, and additional water of solvation may also be tied up with the hydroxides. This effect will decrease paste flow and slump area. This is part of the reason why metal pastes have lower mini-slump areas than the control, but other mechanisms that interfere with paste hydration probably also contribute to decreasing paste flow. Analysis of the first conduction calorimetry peak, paste temperature changes, and other measures of initial paste hydration (roughly the first 15 minutes) may also be appropriate to increase the understanding of these early reactions. In order to elucidate the mechanism and improve the realism in interpretation of stabilization in cement pastes, investigations on paste systems with metal addition as fresh hydroxide are given in the succeeding chapters of this report.

Substantial retarding of initial paste setting time and delayed compressive strength development, such as occurs with lead nitrate and oxide, and cadmium oxide, involves changes in the middle and later cement-paste hydration reactions. Zhao et al. [1992] has suggested for cement systems containing lead that lead hydroxide coats unhydrated cement and causes retardation, and may limit water diffusion to the unreacted particles. A mechanism such as this would explain the observed changes in setting time and early strength development, but not the development of nearly full strength at 90 days. A two-part mechanism is necessary which might involve formation of an inhibiting coating to explain the middle reactions, but also provides a breakdown of the coating and the resumption of hydration reactions at later ages. As one possibility, if the lead hydroxide, an amphoteric material, were to dissolve in the increasingly high pH pore fluid, it would permit exposure of the unhydrated cement grains to ingress by water. This mechanism would be similar to that observed with retarding admixtures in general, and especially with fluoride, whose ultimate dissolution often permits a more controlled formation of hydration products, which is postulated to

result in better hydrate microstructure, and has been observed to lead to higher late-age (>28 days) compressive strengths.

Acceleration of early hydration in pastes containing soluble chromium is probably occurring and explains why flowability is decreased, initial set is accelerated, and strength gain is more rapid than for neat cement pastes. It is likely that acceleration occurs because of an interference with the soluble sulfate concentrations in the fresh paste. For neat pastes, soluble sulfate immediately reacts with the calcium aluminates slowing down what would otherwise be very fast reactions. It is believed that chromium in solution but not chromium oxide reacts with or adsorbs sulfate, making it less available for the reaction with calcium aluminate to form ettringite. Accelerated hydration in this mechanism is due to rapid hydration of the aluminate phase, which in neat pastes would be slowed down by sulfate, primarily derived from gypsum and plaster.

A portland cement binder was used in another study of agents that interfere with solidification/stabilization, but always in the presence of a mixed metal hydroxide synthetic sludge containing cadmium, chromium, nickel, and mercury. Compressive strength results were reported by Cullinane, Bricka, and Francingues [1987], and the heavy metal interfering agents used were copper, lead, and zinc nitrate. Leaching results [Jones, Bricka, and Cullinane, 1992] from the same study concentrate on the leaching changes of the metals in the sludge, not of the interfering agents. At the lowest lead addition level, a very slight decrease in 28-day strength was observed in the presence of the mixed sludge. In the present study, lead nitrate caused a significant decrease of 28-day strength, compared to neat paste.

CONCLUSIONS

In general, cement pastes appear highly suitable matrices for stabilizing trace metals, and therefore can be considered in the S/S systems for stabilizing metal wastes. While some significant retardation or acceleration may occur at early ages, sufficient hydration does occur at later ages (of 28 or 90 days) to form strong pastes. Metals as oxides and soluble salts generally decrease flow of cement pastes and may therefore lead to lower workabilities of plastic-state S/S matrices.

CHAPTER 2

Leachability of Single Metals from Cement Pastes Using Sequential Batch Acetic Acid Leaching

During the early stages of this project, PCA solicited reviews of the proposed work plan from researchers in government and industry familiar with solidification/stabilization. These were received after experiments making cement pastes with metal oxides and soluble salts of metals had already been carried out; these reviews indicated that metal hydroxide sludges freshly precipitated using hydrated lime were more realistic prototypes of actual solid metal-bearing wastes. Furthermore, project goals were modified to obtain additional information on the stabilization mechanism of metals with portland cement. In response, initial experiments investigating paste properties parallel to those run with solutions and oxides were done using freshly precipitated metal hydroxide sludges. Subsequently, to obtain information on durability, leaching properties, and on stabilization mechanisms, a sequential leaching regimen was adopted.

TCLP testing and the column leaching experiments, reported in Chapter 1, had not resulted in much information beyond the initial leaching characteristics. Good mechanistic information had been obtained in a study of metal stabilization by portland cement [Bishop, 1988] utilizing a sequential batch leaching test with acetic acid as the leachant. The sequential batch leaching regimen adapted for this work was modeled after the 1988 work and was modified to some degree so the first step was closer to a simulation of the TCLP test. The test adapted for this work is scaled down and similar, but not identical, to the TCLP test.

Cadmium, chromium and lead, as lime-precipitated metal hydroxide sludges, were incorporated individually into Type I portland cement pastes, and a lead hydroxide sludge was also mixed into a hydrating Type V portland cement. There were therefore a total of four samples. Data from earlier work in this project had indicated that lead may be better stabilized within a Type V portland cement matrix (see Table 1-6). The samples were moist-cured over 90 days before leaching. Over the course of the steps of this test, a

total of a ten percent excess of acetic acid is available to neutralize all the calcium in the solid samples; predictably this destroys almost all of the cement paste structure, leaving a silica-rich residue. The leachate pH initially is quite high, around 13.5, and decreases through the eleven leaching steps, performed sequentially on the same solid material, until the pH is less than 4.8. Remarkably the chromium and lead remain stabilized in the solid, with less than 3% of each metal going into solution after nine leaching steps. Cadmium remains stabilized until the pH falls below 8, but it rapidly goes into solution at lower pHs; about 70% (cumulative) dissolves by the end of the last batch leaching step.

The resistance of these portland cement-stabilized materials to acid attack implies they have a high degree of durability against increased leachability from factors such as acid rain and carbonation—the attack of an acidic gas, carbon dioxide. In ordinary practice S/S wastes are placed and covered daily in special landfills. For such a scenario, exposure to gaseous carbon dioxide is expected to be very low, and any changes to the portland cement stabilized wastes caused would be anticipated to be extremely small. Carbon dioxide dissolved in water has a greater access, but even here a monolithic matrix should be designed to limit groundwater ingress. It is not envisioned that a solidified/stabilized waste would ever be exposed to enough acid to destroy the matrix, but this destructive test regimen can provide valuable mechanistic information.

EXPERIMENTAL WORK

Preparation of Paste Specimens

Metal hydroxide sludges were prepared using anhydrous reagent grade lead nitrate ($\text{Pb}(\text{NO}_3)_2$), chromium (III) chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$), and cadmium chloride

($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$). The salts were dissolved in about one liter deionized water purified as described below, and $\text{Ca}(\text{OH})_2$ powder was added until the pH reached 11.0 and remained at that value for at least 30 minutes. The precipitates were vacuum-filtered using a Büchner funnel. A small sample was removed and oven-dried at 110°C to determine the moisture content. The remaining moist sludge was retained in a sealed container over water until the next day. The sludge was then used in a cement paste mix within the next 36 hours. Paste mixes combining hydroxide sludge of a single metal with cement and water were made using the following protocol.

Pastes were mixed in a standard Hobart “mortar” mixer (Model N-50) with total paste usually weighing 2320 grams. Single metal pastes were mixed at a water-cement ratio of 0.4. The amount of added mix water was reduced by the amount of water in the sludge; the water was placed in the bottom of the bowl, and then the fresh sludge was added. The two were mixed well to ensure that the metal hydroxide sludge was well dispersed. Cement was added, while the mixer was set on a speed of 1 (low speed), using a vibratory feeder set to deliver all the cement within one minute. The paste was then mixed for two minutes and the mixer stopped. The mixing blade and bowl were scraped down during this time period. After a rest period of three minutes, the mixer was restarted on a speed setting of 2 (medium speed) and mixing was continued for an additional two minutes. (This mixing procedure is the same one used by Kantro [1980]. He mentions that the rest period avoids the effects of false set on the cement paste flow measurement.) The bowl was then lowered and the blades and side of the bowl were scraped down again. The fresh paste was then used to perform a mini-slump cone test for flowability and to fill both 25.4-mm (1-inch) cube molds as well as several 100-mL plastic beakers. One of the beakers was set aside to perform a modified Vicat initial time-of-set measurement.

The pastes were molded into 25.4-mm (1-inch) paste cubes as follows:

Stainless steel 25.4-mm (1-inch) cube molds, which had been lightly coated with form oil, were placed on a small vibrating table. Paste was placed into the vibrating molds and each cube cavity filled to about 90% of its volume. A flat laboratory spatula was then used with an “up-and-down” motion, first on the sides and then in the corners of the mold, and finally working across the mold— first in one direction and then across the mold perpendicular to the first pass. This procedure was employed to remove any air bubbles that may have been trapped in the paste. The molds were then overfilled with paste (about 10% excess) and the

spatula again used sparingly with the same motion to obtain a bubble-free paste. The molds were placed in a standard moist curing cabinet and the paste allowed to cure for three days at 23°C and 100% relative humidity. On the third day the cubes were removed from the molds after using a wide and stiff spatula to remove excess hardened paste and to leave a smooth top surface, level with the top of the molds. The cubes for future strength tests were returned to the moist cabinet to continue curing. Three cubes were broken using a special jig for the one-inch cubes which mounts on the same pedestal used for 50-mm (2-inch) mortar cubes.

The following four pastes were prepared in this task:

- Type I portland cement with added lead at 0.7% concentration by mass of lead in the total mix designated as IPbH.
- Type V portland cement with added lead at 0.7% concentration by mass of lead in the total mix designated as VPbH.
- Type I portland cement with added cadmium at 0.5% concentration by mass of cadmium in the total mix designated as ICdH.
- Type I portland cement with added chromium at 0.3% concentration by mass of chromium in the total mix designated as ICrH.

The following Table 2-1 indicates the important weights of material used and the amount of metal in the fresh paste. The sum of the weights of cement, total water, and metal is less than the total weight; the difference is attributable to the added hydrated lime. The sum of the weights of sludge used, cement, and total water exceeds the total weight by the amount of water in the sludge.

Preparation of Deionized Water

Tap water was deionized to $>1 \text{ M}\Omega\text{-cm}$ in dual-bed service deionizers and polished to $18.3 \text{ M}\Omega\text{-cm}$ resistivity (Barnstead PCS, organic/colloid removal, dual ultrapure cartridges) then finally passed through a $0.2 \mu\text{m}$ final filter. The water was sufficiently pure to meet ASTM Type I water specifications.

Preparation of “Pseudo-TCLP” Leaching Solution

114 mL of ACS reagent grade glacial acetic acid (18 M) was added to deionized water, and the volume made up to 20 liters. The pH of this solution, nominally 0.1 N, was 2.88.

Table 2-1. Mix Designs of the Pastes with Lime Metal Hydroxide Sludges

| Mix designation | IPbH | VPbH | ICdH | ICrH |
|---|--------|--------|--------|---------|
| Weight of sludge used in mix including retained water (g) | 25.309 | 25.550 | 69.225 | 157.550 |
| Grams of metal in the sludge | 16.045 | 15.468 | 11.023 | 57.60 |
| Weight of cement (g) | 1640.0 | 1640.0 | 1640.0 | 1640.0 |
| Total weight of water in mix (g) | 660.0 | 660.0 | 660.0 | 660.0 |
| Total weight of the mix (g) | 2319.2 | 2319.2 | 2317.2 | 2326.1 |
| Heavy metal content in total mix (mg/kg) | 6920 | 6670 | 4760 | 2480 |

RESULTS

Physical Testing

Immediately after the paste mixing had been completed, the paste temperature was measured then a mini-slump cone test was performed. A sample of paste was set aside for the modified Vicat time-of-set test, and measurements were taken until the pastes set. These results are shown in Table 2-2.

Compressive strengths were obtained on the 25.4-mm (1-inch) cubes after curing at 23°C and 100% relative humidity for 3, 28, and 90 days; the results for these pastes with water/cement ratio = 0.40 are shown below in Table 2-3.

DISCUSSION

Physical Properties

Initial set was unaffected by cadmium, accelerated by chromium, and strongly retarded by lead; this behavior is generally similar to that observed in the tests involving introduction of the metals as solutions and oxides. Acceleration by chromium hydroxide was less pronounced than when the metal was added as a solution. Cadmium hydroxide affected initial set in a similar manner to cadmium chloride. Retardation was somewhat greater using lead hydroxide than for lead nitrate or lead oxide.

Slump areas were comparable or slightly greater when metal hydroxides were used as compared to solutions or oxides. In almost all cases slump area was significantly reduced compared to the control. Paste temperature effects were generally similar whether using oxides, solutions or hydroxides. The only significant difference was a much lower temperature with chromium hydroxide since use of chromium chloride solution resulted in a paste temperature near 38°C. Comparison of this paste data

Table 2-2. Initial Setting Times, Temperatures, and Slump Areas for the Type I and Type V Cement Pastes Containing Heavy Metals Added as Lime Sludges

| Metals (mg/kg) in dried & solidified paste | Added as hydroxide sludges | | |
|--|----------------------------|---------------|-------------------------------|
| | Initial set (hrs:min) | Paste temp °C | Slump area (cm ²) |
| Type I Cement | | | |
| IPbH (7,800 mg Pb/kg) | 23:30 | 27.5 | 15.35 |
| ICdH (5,300 mg Cd/kg) | 3:30 | 27.5 | 19.52 |
| ICrH (2,700 mg Cr/kg) | 2:25 | 27.4 | 16.02 |
| Control | 3:40 | --- | 35.63 |
| Type V Cement | | | |
| VPbH (7,500 mg Pb/kg) | 32:00 | 22.9 | 29.87 |
| Control | 3:10 | 24.5 | 35.63 |

to similar data with multiple metal addition obtained in later phases of this project appears in Appendix E.

Compressive strengths were all comparable between oxide, solution, and hydroxide series at 28 and 90 days.

Preparation of hardened pastes for leaching and the leaching regimen. To prepare the cubes for leaching after curing for 95 to 109 days, they were crushed and dried in an oven at 105°C then ground in a ring-and-puck mill. The ground material was sieved to pass a 74- μ m (No. 200 mesh) sieve; material not passing the sieve was ground in a mortar and pestle until fine enough to pass. The four samples were subjected to leaching using the following leaching regimen:

Table 2-3. Compressive Strengths of Pastes Made with Metal Hydroxides

| Metals Paste (mg/kg in solid) | Compressive strengths, MPa (PSI) | | |
|-------------------------------------|-------------------------------------|------------------|-------------------|
| | 3 days | 28 days | 90 days |
| Type I Cement | | | |
| IPbH (7,800 mg Pb/kg) | 31.95 (4630) | 82.97 (12030) | 93.88 (13620) |
| ICdH (5,300 mg Cd/kg) | 51.83 (7520) | 84.58 (12270) | 95.61 (13870) |
| ICrH (2,700 mg Cr/kg) | 62.70 (9090) | 93.77 (13600) | 79.06 (11470) |
| Control | 54.68 (7930) | 71.50 (10370) | 99.15 (14380) |
| Type V Cement | | | |
| VPbH (7,500 mg Pb/kg) | 15.17 (2200) | 68.72 (9970) | 92.18 (13370) |
| Control | 35.72 (5180) | 77.70 (11270) | 101.84 (14770) |

Sequential leaching of
 28.144 grams of IPbH paste,
 28.260 grams of VPbH paste,
 28.360 grams of ICdH paste, and
 28.368 grams of ICrH paste,

with 500 mL aliquots of pH 2.88 acetic acid for each of the first 3 days, then 450 mL aliquots for each of the last 8 days.

The weights were calculated so that each sample contained the same amount (about 9.0 g) of calcium to keep total alkalinity constant. Due to the drying process, the mg/kg of each metal for the dry samples was higher than that calculated for metals loading in the fresh paste. A complete description of the leaching regimen can be found in Appendix B. There were some modifications to that regimen at the beginning of this series of sequential leaching tests. The 500-mL bottles were first placed on a shaker table and it was left on overnight. The shaker broke down but the bottles were filtered and stored. The shaker was used again for leaching on the second through the fourth steps, but again it failed. For the fifth step until the end of the test, the rotating wheel described in Appendix B was used. After three leaching steps the amount of acetic acid leachant was reduced to 450 mL from 500 mL to avoid spillage of the filtrant during filtration and refilling of the leach bottles. Aliquots of the same 0.1 M acetic acid were used for all extractions.

In subsequent phases of this project, for sequential batch leaching of other paste materials, the concentration of the acetic acid was decreased after seven days leaching, the volume of leachant remained constant at 0.45 L, and the rotating wheel was used for all leaching steps.

Results of leaching tests. Leaching was evaluated in two different ways, first using the U.S. EPA TCLP test and second using the sequential batch leaching procedure on pastes at least 90 days old. The results for the TCLP tests and for the first sequential batch leaching step are shown in Table 2-4.

The sequential batch leaching test was designed to obtain information about the mechanism of metal stabilization in portland cement pastes and was modeled after the test reported by Bishop [1988]. In designing the test, an attempt was made to stay close to the specifications of the U.S. EPA TCLP test procedure. Size reduction to pass a No. 200 sieve was done to ensure the entire sample was exposed to the leachant from the beginning of the test. Although there were some differences, in other respects every effort was made to follow the TCLP protocol: the bottle of sample and leachant was rotated for 18±2 hours in a temperature controlled room; the specified glass fiber filter paper, properly acid washed, was used for the filtration; and metals analysis was performed in accordance with EPA SW-846 atomic absorption spectrometry methods. The differences between the TCLP and the sequential batch leaching test are shown in Table 2-5.

It is evident from Table 2-4 that the first step of the sequential batch leaching (SBL) test shows higher metals solubilities than does the TCLP test. It will be noted that the TCLP test utilizes a slightly larger ratio of leachant to solid sample than does the SBL test. Due to the greater amount of acid available in the TCLP test, the equilibrium pH was lower than in the 1st step of sequential batch leaching. A small change to lower pH tends to result in lower concentrations for lead and chromium. This is the pH range in which the amphoteric nature of these metals may cause them to be more soluble at higher pH. Cadmium differences are small, and within the error of test reproducibility. TCLP samples also are not dried before leaching, and this also may result in lower leach concentrations.

The figures in this chapter summarize the analytical results for leaching from pastes containing single metal hydroxides carried out using the sequential batch leaching test with nominal 0.1 M acetic acid.

In the sequential batch leaching test, the combined equilibrated solids and liquid are filtered to obtain the leachate after each leaching “day.” The pH and con-

Table 2-4. TCLP Results for Metals in Paste

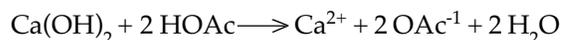
| Type of Paste | ICdH (mg Cd /L) | ICrH (mg Cr /L) | IPbH (mg Pb /L) | VPbH (mg Pb /L) |
|--------------------------|-----------------|-----------------|-----------------|-----------------|
| 28 days | 0.0004 | 0.06 | 0.73 | 0.24 |
| 90 days | 0.04 | 0.13 | 0.6 | <0.4 |
| ~100 days | | | | |
| 1st Seq Batch leach step | 0.12 | 0.22 | 2.4 | 1.9 |

Table 2-5. Comparison of TCLP and Sequential Batch Leaching Procedures

| | U.S. EPA TCLP | Sequential Batch Leaching |
|--|---------------------------------|---------------------------------------|
| Particle size | Through 9.5 mm (3/8") sieve | Through 74 µm (No. 200 mesh) sieve |
| Leachant | Acetic acid (pH=2.88) | Acetic acid (0.1 M) |
| Liquid volume | 2000 mL | 450 mL |
| Leaching container | about 2100 mL | 500 mL |
| Sample weight | 100 g | about 28 g |
| Ratio of milliliters leachant: Grams of sample | 20 | about 16 |
| Tumbling | Special rotary 30 rpm extractor | Larger diameter 23 rpm rotating wheel |

centration of elements (in mg/L) is determined for each daily (or incremental) leachate. In several of the following figures, selected elemental concentrations are plotted versus leach day number or pH (e.g., Figures 2-2 and 2-3). The volume and elemental concentration in the leachate are used to calculate the incremental amount of each element leached daily. The cumulative amount of an element leached is calculated from the sum of the amounts leached each day and, using the analysis of the initial solid paste, the cumulative percent of an element leached can be determined. Figures 2-1 and 2-4 are examples of cumulative percents of elements leached plotted versus leach day number and pH, respectively.

To understand this data, it is important to realize the changes that the leached paste undergoes through the steps of leaching. Sequential batch leaching of the ICdH paste will be discussed, but the general behavior of the pH, calcium, silicon, aluminum, and iron is similar in all the sequential batch leaching reported for this project. The high alkalinity of the paste easily neutralizes the acetic acid in the first step and the pH remains high, but considerable calcium goes into solution as can be seen in Figure 2-1. Until the pH falls below 11, calcium hydroxide is being leached from the hydrated paste, as shown in the following equation:



Below pH 11, the acetic acid is beginning to dissolve the calcium from the calcium silicate hydrate (C-S-H). [C-S-H is the principal hydration product of the cement clinker minerals alite (C₃S) and belite (C₂S).] In this series, calcium hydroxide is exhausted after the fourth cycle, when over 40% of the calcium has been leached and the pH is about 11. (The point in the leaching cycle at which Ca(OH)₂ is exhausted will depend on the C₃S content of the cement.) Between pH 11 and 6, calcium continues to go into solution, and leaching of silica slowly rises. From the first through the ninth cycle, the pH decreases from 13 to 6, and the solubility of iron and alumina is negligible. Only below pH 6 are significant amounts of aluminum and iron dissolved from the paste, after essentially all the calcium has been leached from the C-S-H in the paste. Cadmium has very low solubility above pH 9, but below that value, the solubility rapidly increases.

For ICdH after the 9th leaching day, the pH is 7.11 and 88% of the calcium has been leached. At this point, three percent of the silicon, 0.5% of the aluminum, 0.24% of the iron, and 5.6% of the cadmium has also been leached. After 11 cycles the pH is 4.18, and 93% of the calcium has been leached.

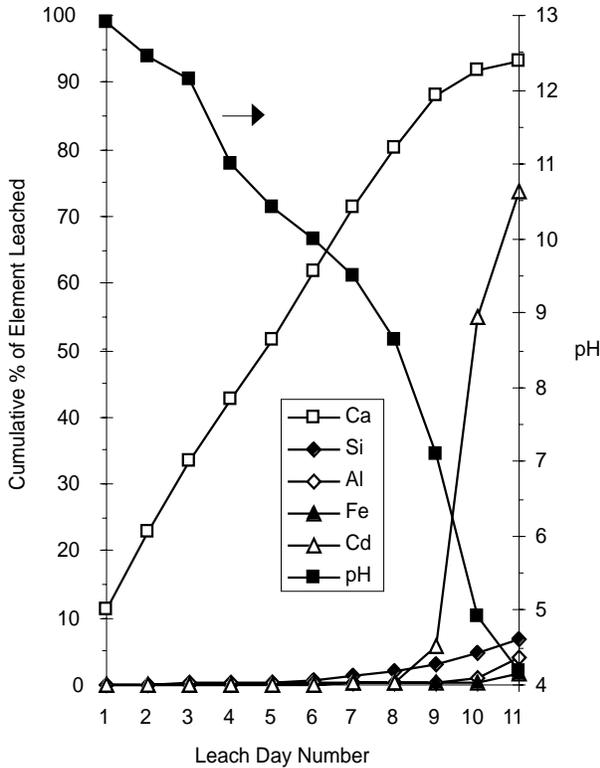


Figure 2-1. Leaching of cadmium with sequential acetic acid leaches.

Seven percent of the silicon, 4% of the aluminum, 2% of the iron, and 74% of the cadmium has also been leached. This is typical of the data for all four leached pastes with the exception of the other heavy metals. Lead and chromium do not leach nearly as much as cadmium.

Comparison of cadmium, chromium, and lead leaching. A comparison of leaching of the individual metals, obtained by combining information from the four separate leaching series, is presented in Figure 2-2. Lead leaches to a small degree in the first two days of leaching, but then has very low solubility until after the 9th leaching day, when its solubility again increases. Cadmium leaching was discussed above. Chromium has fairly low solubility at the beginning of the sequential leaching, but “bumps up” around the 5th and 6th leach days, then decreases until the pH is below 6.

Since solubility of the metals varies so strongly with pH, it is useful to plot this same data versus pH, as has been done in Figure 2-3. This graph more clearly shows the higher solubility of lead at high pH and the increased solubility of chromium around pH 10. Solubility of cadmium is so low that concentrations are near the detection limit, and the data are

therefore somewhat erratic. Cadmium concentrations are well below its toxicity characteristic limit of 1 mg/kg until the pH is below 8. Likewise lead and chromium remain significantly below their toxicity characteristic limit of 5 mg/kg until the pH is below about 6.5. It is important to recognize that at these pHs, the calcium is substantially depleted. Calcium leaching concentrations are very high, with behavior similar for all four paste materials; therefore for clarity of presentation, calcium concentrations are not shown.

The cumulative depletion of the four metals is shown in Figure 2-4, confirming the trends discussed above. Extremely little cadmium leaches above pH 8, but below this value its solubility increases dramatically. Chromium is steadily leached at low levels above pH 10; it is well stabilized between pH 6 and 10 and is increasingly leached below pH 6. Lead is well stabilized between pH 12 and 6 but is more soluble at the extreme pHs.

Metal and matrix interactions. One of the principal goals of this work was to obtain information to elucidate the mechanism of heavy metal stabilization with portland cement. Evidence from the leaching experiments indicates stabilization is not

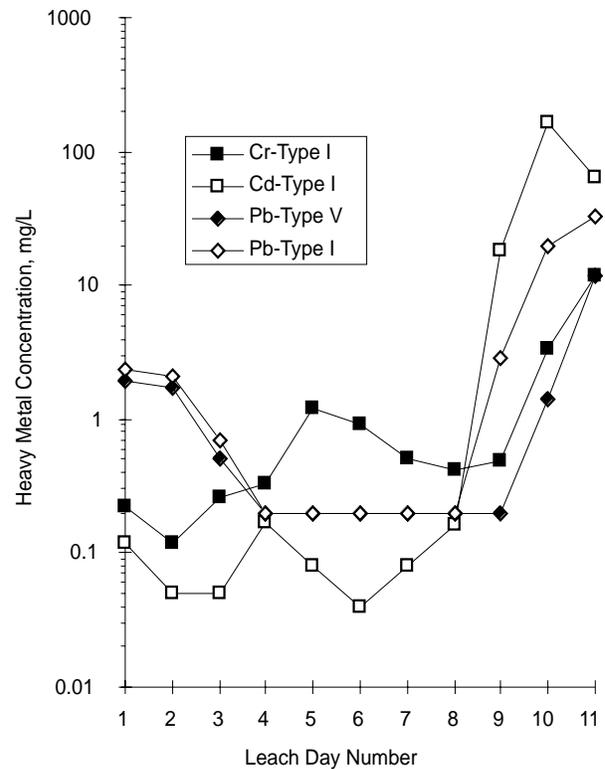


Figure 2-2. Leaching of individual metals vs leach day number.

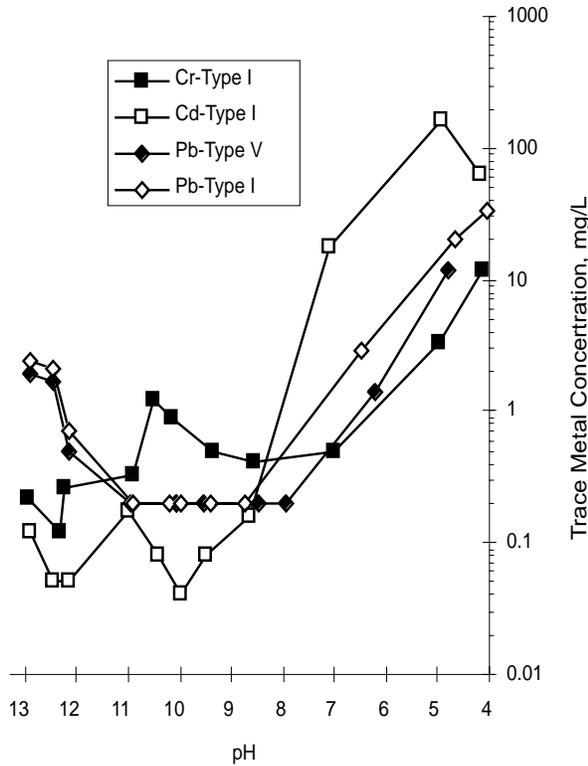


Figure 2-3. Leaching concentration of individual metals vs pH.

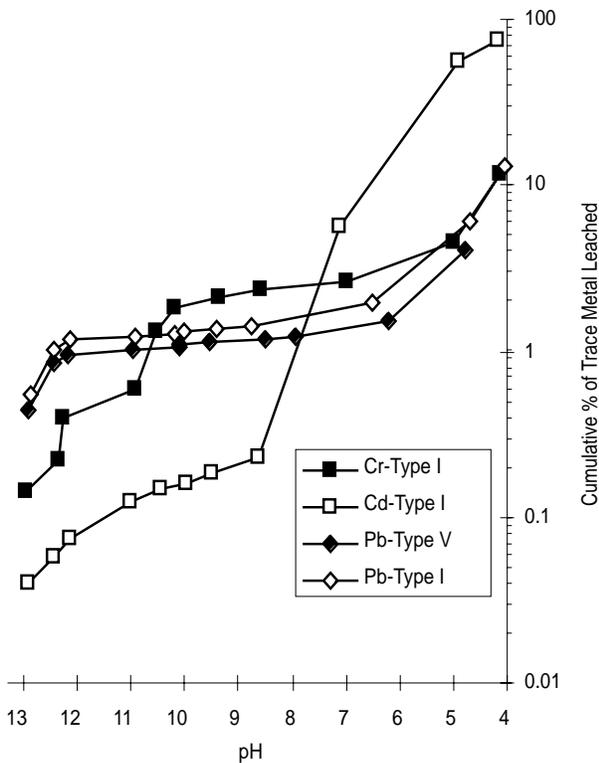


Figure 2-4. Cumulative leaching of individual metals vs pH.

simply a function of pH. Here the connection between leaching of the metals and the leaching of components of the cement indicate the complexity of the stabilization mechanism, but provides mechanistic data relative to the association of the hazardous constituents and cement components. Incremental leach quantities for lead, silicon, and aluminum are shown in Figures 2-5 and 2-6. The first data are from the Type I cement paste and the second from the Type V cement paste. A possible connection between lead and aluminum but not with silicon is suggested as a possibility. Similar data, with concentrations of chromium, silicon, and iron for leaching of mix ICrH, are shown in Figure 2-7. Above pH 10 chromium and silicon appear to increase in concert, however, below pH 9 concentrations of chromium and iron tend to move together.

All the matrix ions except calcium are shown in Figure 2-8, with the data derived from leaching of ICdH. No trend can be discerned, and it is suspected cadmium leaching is solely pH-dependent.

Cumulative leaching from the same leaching series shown incrementally in Figures 2-5 through 2-8 is presented in Figures 2-9 through 2-12. Lead leaching appears to be independent from silicon leaching behavior, but does appear to be correlated with alumina solubility. Concentration data from the chromium paste mix ICrH were confusing, but the cumulative data in Figure 2-11 suggest chromium and silicon may be bound together and dissolve together. Chromium solubility appears to be independent of iron solubility, but may be somewhat associated with aluminum solubility. In all the sequential batch leaching tests of pastes, aluminum and iron are solubilized at approximately the same pH. An example of this phenomenon can be seen in Figures 2-8 and 2-12.

Comparison of lead in Type I and V cement matrices. Lead appears to be better stabilized by a small but measurable amount with Type V cement compared to Type I cement as is shown in Figure 2-13. The difference is clearly not attributable to pH, and so must be related to the influence of differences in the cement hydration products.

TCLP and sequential batch leaching. The TCLP leaching results show full compliance with the TCLP limits, despite the relatively high levels of metals incorporated in the pastes. Cadmium leachability never exceeds 4% of the regulatory limit, chromium leachability remains below 3% of its limit, and lead solubility, in a Type I matrix, is less than 15% of the allowable limit. In a Type V matrix, the corresponding figure for lead is less than 8% of the limit. The initial high-pH leachability of lead is not surprising

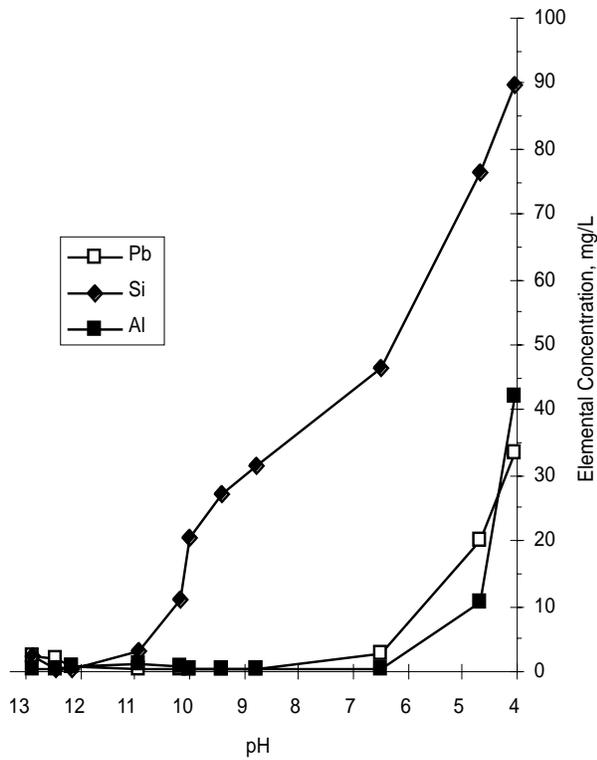


Figure 2-5. Pb/Al relationship in Type I cement mix IPbH.

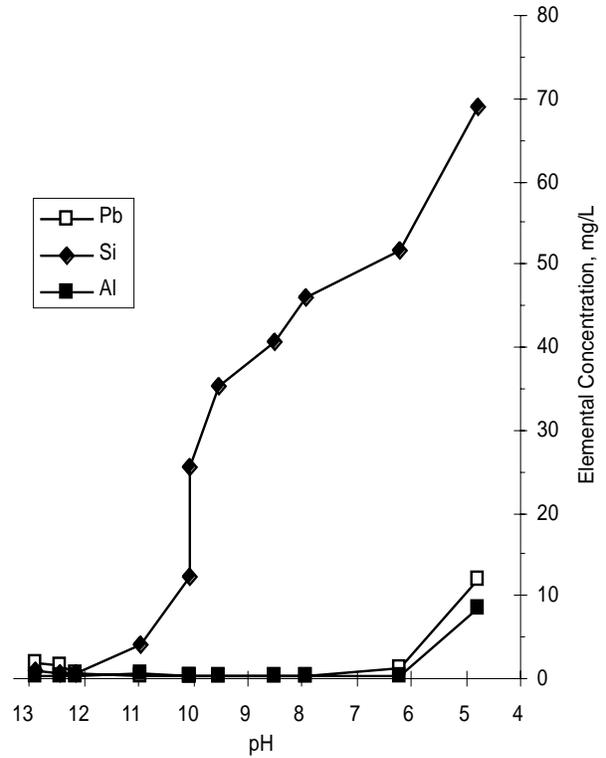


Figure 2-6. Pb/Al relationship in Type V cement mix VPbH.

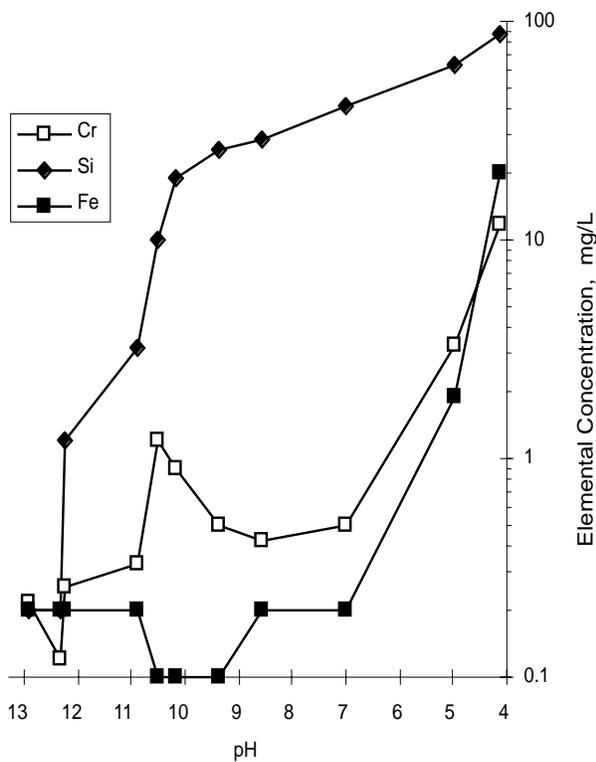


Figure 2-7. Cr/Fe/Si relationship in Type I cement mix ICrH.

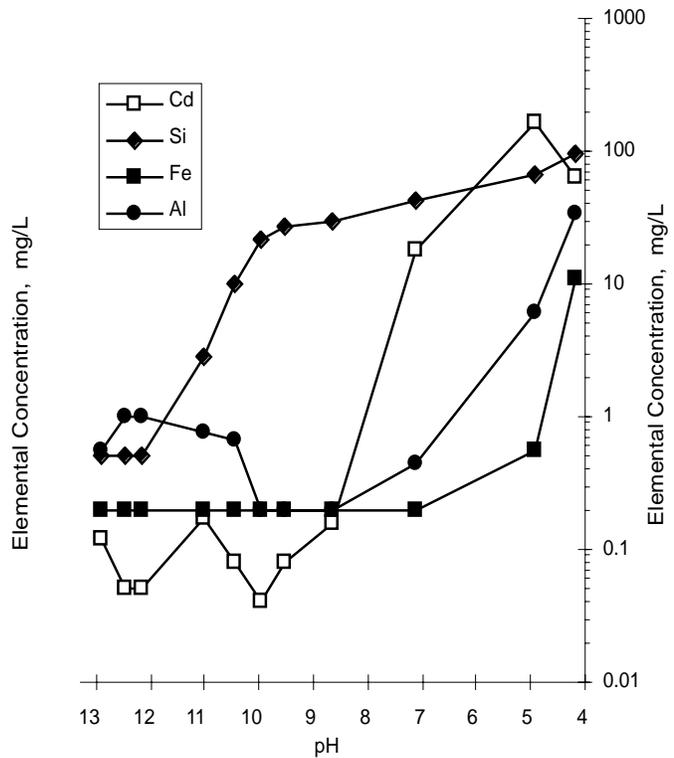


Figure 2-8. Metals concentration vs pH in Type I cement mix ICDH.

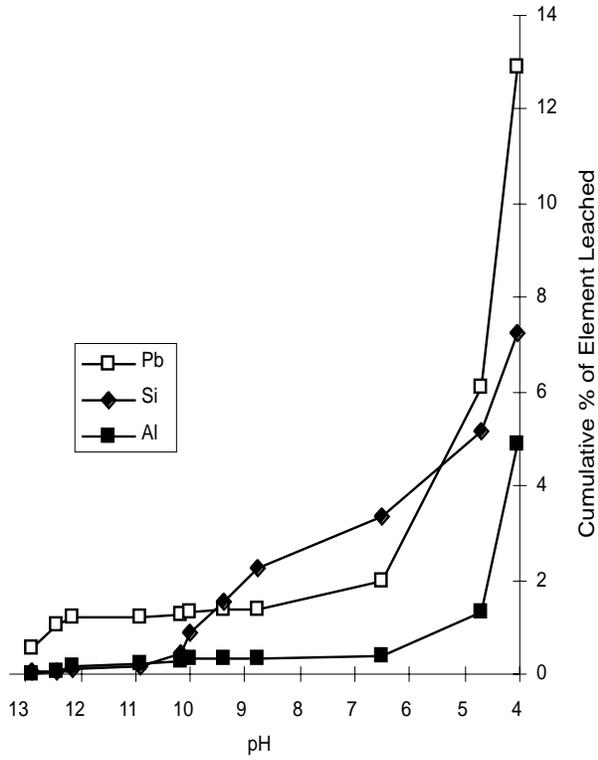


Figure 2-9. Pb/AI/Si leaching IPbH (Type I cement) vs pH.

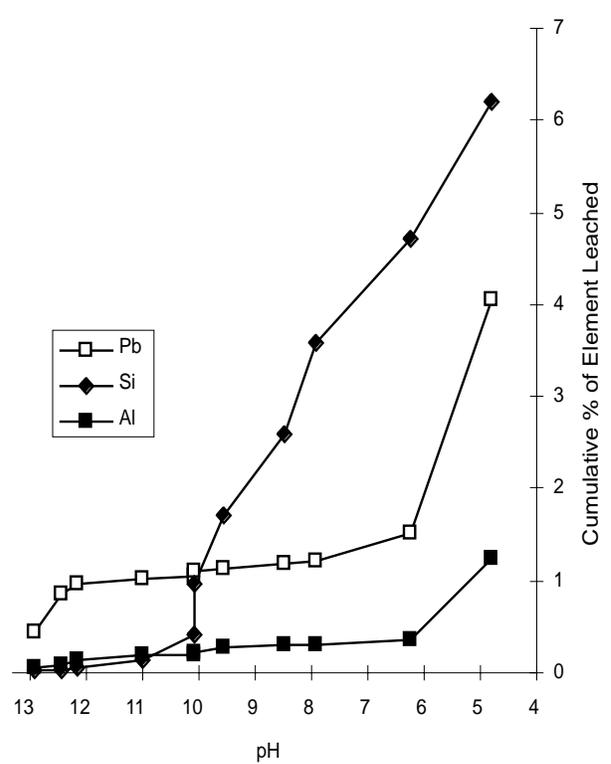


Figure 2-10. Pb/AI/Si leaching VPbH (Type V cement) vs pH.

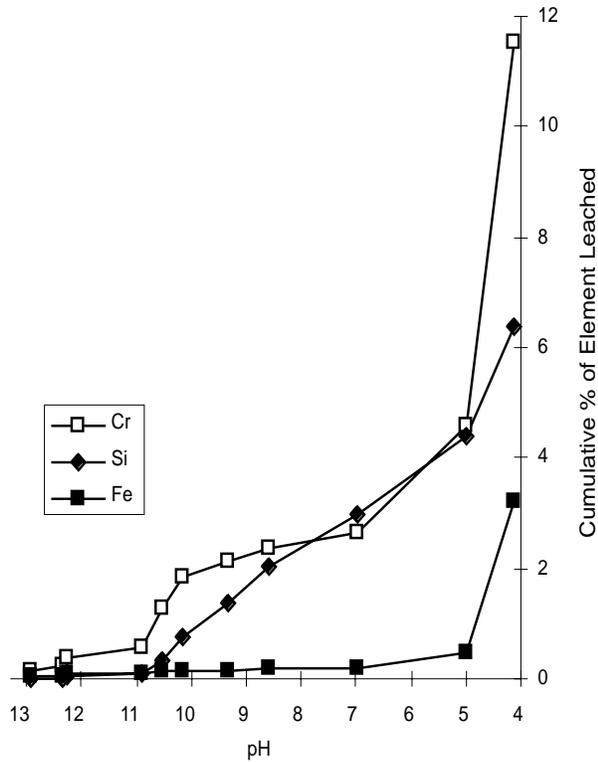


Figure 2-11. Cr/Fe/Si leaching ICrH (Type I cement) vs pH.

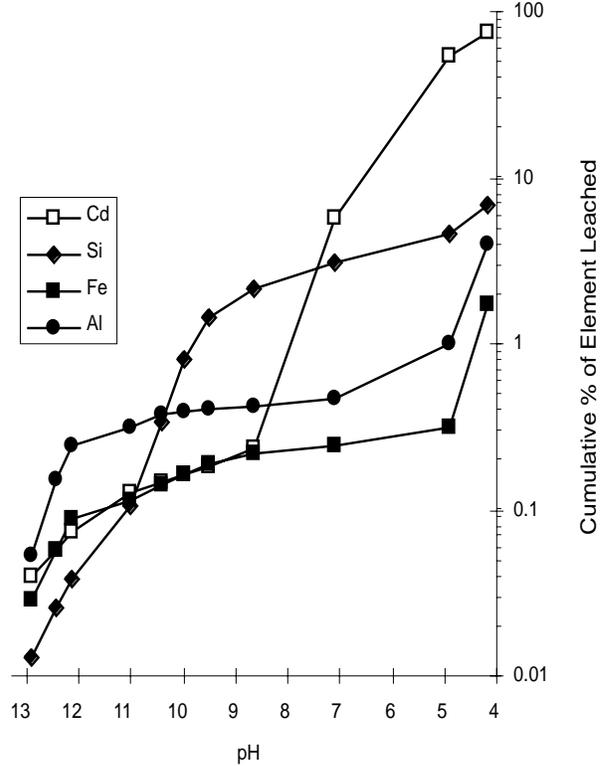


Figure 2-12. Cumulative % metals leached vs pH in Type I cement mix ICdH.

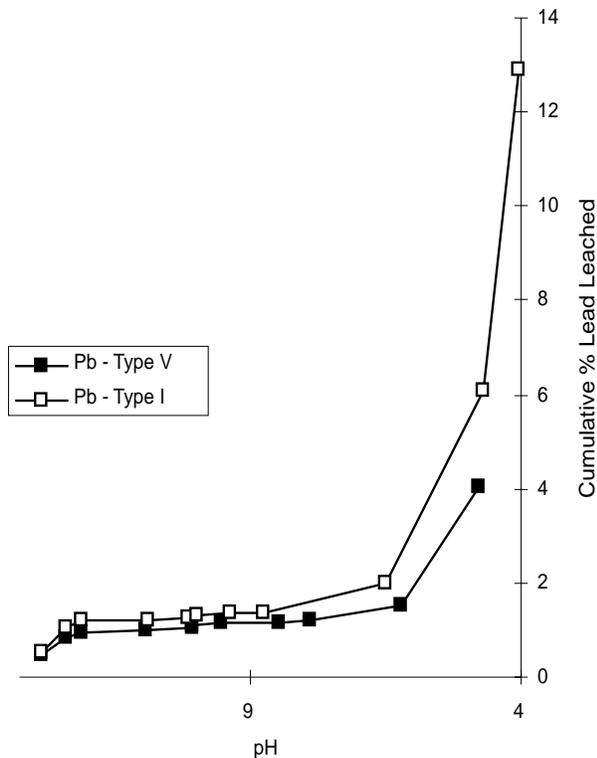


Figure 2-13. Cumulative % lead leached vs pH, Types I and V cement.

considering the amphoteric nature of lead oxide and hydroxide; any lead hydroxide or hydrous oxide not well stabilized in or adsorbed on calcium silicate hydrate or sulfoaluminate/sulfoferrite phases will be subject to enhanced solubility at high pH. This finding was the initial impetus for the study, to be discussed later, involving the use of silica fume to reduce the pH of the system during early sequential leaches. The fact that Type V cement outperformed Type I cement in lead stabilization suggests that low C_3A cements may be preferable in treating this particular metal. The scope of this project did not permit a determination of the leachabilities of chromium and cadmium from Type V S/S systems; this would be an interesting supplemental investigation.

Chromium, and in particular cadmium, were very well stabilized as judged by this standard. As we shall see, the sequential batch leaching results of multiple metal pastes confirm this conclusion.

In the sequential batch leaching experiments, as noted above, cadmium remains very well stabilized until the pH drops below about 8; thereafter it rapidly becomes easily leachable. The pH does not drop below a value of 8 until the hydrated cement matrix

is almost completely destroyed. Furthermore, as will be apparent in the subsequent work, additions of matrix modifiers such as silica fume, additional gypsum, or carbonate were unable to improve on the results obtained with portland cement alone. These findings represent the first solid indication, later to be repeatedly confirmed, that cadmium stabilization is primarily a matter of maintaining an adequately high pH.

Chromium shows low, but finite, leachability throughout the pH range, with concentrations between 0.1 and 1.2 mg/L (less than 25% of the allowable), until the pH drops below about 6. As earlier noted, this low of a pH is consistent only with virtually complete destruction of the hydrated cement matrix. The test results to be presented in subsequent chapters will bear out this conclusion. The SBL data show a probable correlation between chromium and silicon solubility, which would suggest (1) a possible substitution of chromium, probably as $Cr(OH)_4^-$ ion, for $[Si(OH)_4]$ units in the C-S-H system, or (2) possible chemisorption of hydrous chromium (III) oxide on the C-S-H phase. We will later also discuss the possibility that a small amount of trivalent chromium may be oxidized to hexavalent chromium by the oxygen of the air. An interesting supplemental experiment could involve the addition of ferrous sulfate or granulated blast furnace slag (GBFS) at low levels to prevent this air oxidation; this experiment would permit resolution of this question.

As in the TCLP testing, the lead leachability shows a higher-than-desirable peak at high pH, which declines to non-detect or nearly non-detect values from pH 10 down to pH 6, and then increases to unacceptably high values below about pH 6.5. The low pH leachability may be slightly ameliorated by low pH insolubility of lead sulfate, but in other respects is not easily resolved. The high pH solubility is believed to be associated with the availability of hydroxide ion at high pH. Removal of hydroxide ion, a natural result of the process during the sequential batch leaching, reduces the lead leachability. To reduce its leachability at the early stages, it will be necessary to "tie up" the hydroxide ion; this can be readily accomplished with an active pozzolan such as silica fume, slag, or a good reactive fly ash. Later in the report the beneficial action of silica fume is discussed. Its level was not optimized, nor was fly ash investigated. These studies would be logical extensions of the present work.

CHAPTER 3

Leachability of Multiple Metals from Paste Matrices Using Acetic Acid, Deionized Water, and “Synthetic Acid Rain” Leachants

INTRODUCTION

Based on the results obtained with single metal hydroxide sludges, the system of three metal hydroxides in the cement paste system was investigated. Because the TCLP leaching regimen is extremely rigorous, simulating extreme conditions in a municipal waste landfill with a high concentration of organic acid present, a sequential leaching regimen using acetic acid (the initial step closely simulating the TCLP testing method) was supplemented with two additional leaching schemes. In one such scheme, deionized water was used, while in the second such scheme, the leachant was a “synthetic acid rain” which was a mixture of nitric and sulfuric acids in water (60% H_2SO_4 /40% HNO_3), added to deionized water in a quantity such that the final pH was 3.0. This acid rain is prepared as described in Paragraph 5.2 of U.S. EPA Method 1320 “Multiple Extraction Procedure,” from the SW-846 Methods, and dated September 1986.

The preponderance of the leaching tests was carried out with wastes stabilized with Type I portland cement. Members of the sponsoring committee, however, felt that in addition it would be helpful to investigate masonry cement. Their reasons for this additional study included:

- The acid neutralization capability of the limestone comprising about 50% by weight of the masonry cement,
- The lower pH anticipated for masonry cement in the early leaching cycles, and the expected reduction in early chromium and lead leaching that might thereby ensue.

Chronologically, these studies were carried out before those involving contaminated soils or oily wastes. It was anticipated that the mechanistic information derived from these results would be helpful in optimizing efficiency by minimizing duplicative testing with the soil experiments.

In summary, the multiple metals testing provided a number of significant findings. The cement system proved to be a better stabilizing medium for two of these three metals (lead and chromium) than would be anticipated from pH considerations alone. Even for cadmium, the stabilization was better than pH considerations would predict. As will be apparent from the results, both the calcium silicate hydrate matrix and the ettringite/ C_4AF hydrate system were seemingly effective in immobilizing these metals even after the vast majority of the calcium in the system had been dissolved.

EXPERIMENTAL WORK

Preparation of Deionized Water

Tap water was deionized to $>1 \text{ M}\Omega\text{-cm}$ in dual-bed service deionizers and “polished” to $18.3 \text{ M}\Omega\text{-cm}$ resistivity (Barnstead PCS, organic/colloid removal, dual ultrapure cartridges) then finally passed through a $0.2 \mu\text{m}$ final filter. The water was sufficiently pure to meet ASTM Type I water specifications.

Preparation of Synthetic Acid Rain

6 mL of concentrated ACS reagent grade sulfuric acid (18 M) and 4 mL of concentrated ACS reagent grade nitric acid (12 M) were added to deionized water and volume made up to 1 liter. 100 mL of this solution was further diluted to 20 liters with deionized water to make up the acid rain. The pH of this solution was 3.0. The fluid used for extraction is that outlined in U.S. EPA’s Method 1320 (“Multiple Extraction Procedure”) from the SW-846 analytical methods. In the method, the Multiple Extraction Procedure is described as “designed to simulate the

leaching that a waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill.”

Preparation of Acetic Acid Leaching Solution

114 mL of ACS reagent grade glacial acetic acid (18 M) was added to deionized water, and the volume made up to 20 liters. The pH of this solution, nominally 0.1 N, was 2.88.

Preparation of Paste Specimens

Multiple metal hydroxide sludges were prepared using anhydrous reagent grade lead nitrate ($\text{Pb}(\text{NO}_3)_2$), chromium (III) chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$), and cadmium chloride 2.5-hydrate ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$). The salts were dissolved in about one liter deionized water purified as described above, and reagent grade $\text{Ca}(\text{OH})_2$ powder was added until the pH reached 10.0 and remained at that value for at least 30 minutes. The precipitates were vacuum-filtered using a Büchner funnel. A small sample was removed and oven-dried at 110°C to determine the moisture content. The remaining moist sludge was retained in a sealed container over water until the next day. The sludge was then used in a cement paste mix within the next 36 hours. Cement pastes were prepared with a water/cement ratio of 0.6 (the higher water/cement ratio was required for adequate fluidity, to ensure that the materials were well-homogenized). Mixes were made using the following protocol:

Pastes were mixed in a standard Hobart “mortar” mixer (ASTM C 305-94, nominal capacity 4.73L) with total paste usually weighing 1800 grams. Multiple metal pastes were mixed at a water-cement ratio of 0.6. The mix water was placed in the bottom of the bowl and then the fresh sludge was added. The two were mixed well so the metal hydroxide sludge was well-dispersed. Cement was added, while the mixer was set on a speed of 1 (low speed), using a vibratory feeder set to deliver all the cement within one minute. The paste was then mixed for two minutes and the mixer stopped. The mixing blade and bowl were scraped down during this time period. After a rest period of three minutes, the mixer was restarted on a speed setting of 2 (medium speed), and mixing was continued for an additional two minutes. The bowl was then lowered and the blades and side of the bowl were scraped down again. The fresh paste was then used to perform a mini-slump cone test for flowability and was used to fill both 25.4-mm (1-inch) cube molds as well as several 100

mL plastic beakers. One of the beakers was set aside to perform a modified Vicat initial time-of-set determination.

The following series of pastes were prepared in this task:

- Series 1 - Type I portland cement, with added lead, chromium, and cadmium (each at 1% [10,000 ppm] concentration in the total paste by mass on a metal basis) designated as IMM2.30K
- Series 2 - Type I portland cement, with added lead, chromium, and cadmium (each at 1000 ppm concentration in the total paste by mass on a metal basis) designated as IMM3.3K
- Series 3 - Type N masonry cement, with added lead, chromium, and cadmium (each at 1% [10,000 ppm] concentration by mass in the total paste on a metal basis) designated as NMM2.30K

Initial paste consistency (mini-slump method), paste temperature, and time-of-set measurements were carried out on the pastes, with results as shown in Appendix E, which compares these results (designated as “Multiple Metals”) with those obtained on the single metal pastes, and on those pastes made with matrix modifiers (to be discussed later in this report). The pastes representing the present work were then molded into 25.4-mm (1-inch) paste cubes. Cubes were molded as follows:

Stainless steel 25.4-mm (1-inch) cube molds which had been lightly coated with form oil were placed on a small vibrating table. Paste was vibrated into the molds and each cube cavity filled to about 90% of its volume. A flat laboratory spatula was then used with an “up-and-down” motion, first on the sides and then in the corners of the mold, and finally working across the mold—first in one direction and then across the mold perpendicular to the first pass. This procedure was employed to remove any air bubbles that may have been trapped in the paste. The molds were then overfilled with paste (to compensate for shrinkage) and the spatula again used sparingly with the same motion to obtain a bubble-free paste. The molds were placed in a standard moist curing cabinet at 23°C and 100% relative humidity, and the paste allowed to cure for three days. On the third day the cubes were removed from the molds after using a wide and stiff spatula to remove excess hardened paste and leave a smooth top surface which was level with the top of the molds. The cubes for future strength tests were returned to the moist cabinet to continue curing. Three cubes were broken using a special jig for the 25.4-mm (1-inch) cubes, mounted on the same pedestal used for 50-mm (2-inch) mortar cubes.

Table 3-1. Compressive Strength Measurements

| Cement type | Metals addition level | Compressive strength, MPa (psi) | | | |
|-------------|-----------------------|---------------------------------|-------------|-------------|-------------|
| | | 3 days | 7 days | 28 days | 90 days |
| I | 1000 ppm | 24.7 (3580) | 35.2 (5100) | 55.5 (8050) | 61.0 (8850) |
| I | 1% | 31.6 (4580) | 36.9 (5350) | 52.6 (7630) | 56.1 (8180) |
| N | 1% | 7.9 (1140) | 13.4 (1950) | 21.1 (3060) | 29.1 (4220) |

Compressive strength measurements were made at 3, 7, 28, and 90 days, with results as shown in Table 3-1 (water/cement ratio = 0.60).

To prepare the cubes for leaching after curing for 90 days, they were crushed to pass a 74- μm (No. 200 mesh) sieve and dried with acetone. They were subjected to leaching using one of three leaching regimens:

Regimen A: Sequential leaching of 28.01 grams of IMM2.30K paste, 26.39 grams of IMM1.3K paste, and 29.76 grams of NMM2.30K paste, with 450 mL of pH 2.88 acetic acid.

Regimen B: Sequential leaching of the above pastes, with 450 mL of deionized water purified as described above.

Regimen C: Sequential leaching of the above pastes with 450 mL of synthetic acid rain, prepared as described above.

Series 1 and series 2 pastes (Type I portland cement) were subjected to all three leaching regimens; series 3 pastes (Type N masonry cement) were subjected to the acetic acid ("Regimen A") leaching solution only.

RESULTS

The figures below summarize the analytical results for leaching carried out for the multiple metals study. In this chapter, the daily (or incremental) results have been expressed as the amount of metal leached (in mg) in many of the figures. Previously in Chapter 2, the incremental results were expressed as elemental concentration (mg/L). Here the amount leached was calculated from the elemental concentration and the daily volume of leachate, which was a constant 0.45 L in all leaching tests.

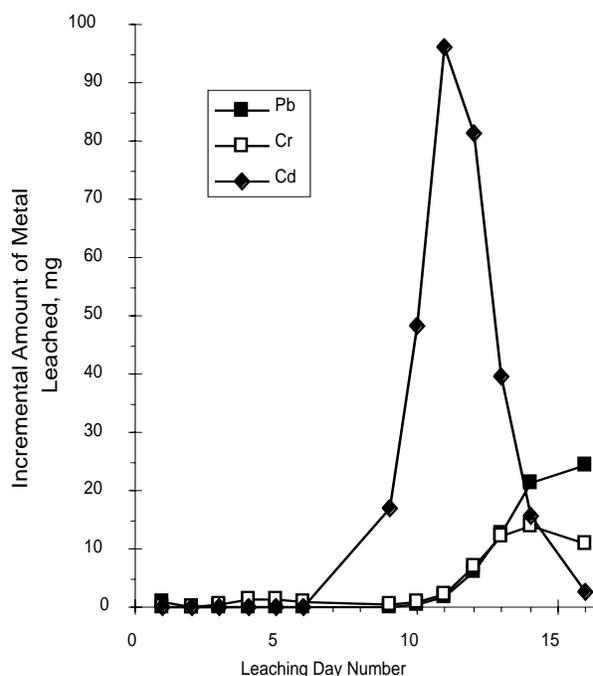


Figure 3-1. Metal concentration vs leach day number.

Series 1

Figure 3-1 shows the incremental amount of metal leached in each sequential batch leach, for the Type I cement system containing 1% of each heavy metal. Cadmium is extremely well stabilized for the first six leaches; then its leachability increases greatly. Lead is leached to some degree in the very early leach cycles, then is very stable until about the tenth leach. Chromium has only a small solubility from the fourth to the ninth day, then begins to be more susceptible in later steps, where the pH has dropped considerably. Figure 3-2 plots the same solubility data against pH. Cadmium does not begin to leach

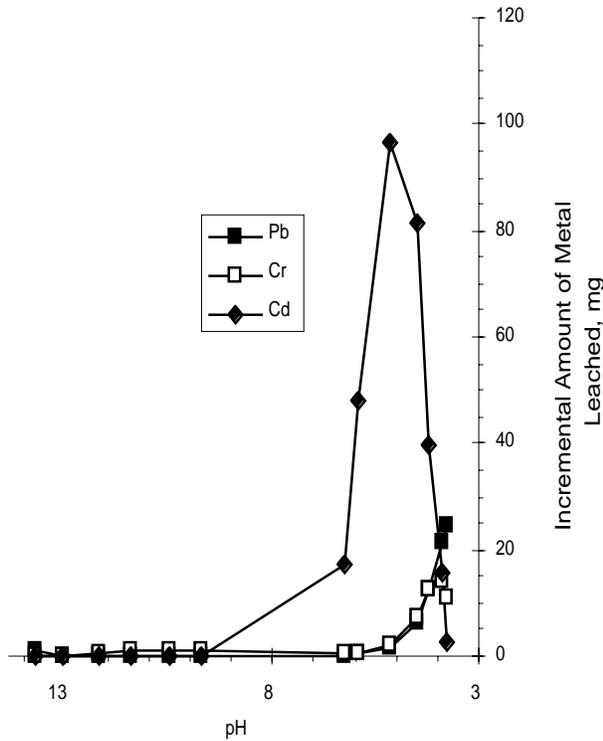


Figure 3-2. 1% metals/acetic acid-mg leach vs pH.

until the pH is below about 9.5, but increases rapidly thereafter. Lead has an initial “bump” of solubility above pH 13, then is well stabilized to below pH 6. Chromium has a low but always finite solubility from high pH down to pH 6; it is increasingly leached below this pH value.

Figure 3-3 shows the cumulative percent leached of the three metals and confirms that lead is leached at very high pH and again below pH 7. Cadmium shows almost no solubility above pH 9.5, but very high solubility below this value. Chromium leaches to some extent from pH 13 down to pH 9, and again below pH 6. In between, chromium is very well stabilized.

The incremental leach quantities of lead and aluminum from a 1% metals paste are depicted in Figure 3-4. The very close correspondence strongly suggests that there are synergies in the leaching of these two elements as there are between chromium and silicon, as seen in Figure 3-5. Cadmium, by contrast, shows a leach vs. pH curve (Figure 3-6) that does not appear to correlate with that of any of the amphoteric oxides of cement (silica, alumina, or ferric oxide). Its solubility seems related almost exclusively to pH. The corresponding cumulative data

for Pb/Al, Cr/Si, and Si/Al/Fe/Cd are given in Figures 3-7 through 3-9. These data are considered even more persuasive than the incremental data.

Series 2

Starting with Figure 3-10, the subject is the leaching from paste mix with 0.1% (1000 ppm) of each heavy metal. Although there are quantitative differences between the results, qualitatively the trends are identical. An overview of incremental heavy metals leached versus leach day and pH, respectively, is shown in Figures 3-10 and 3-11. The cumulative percent heavy metals leached appears in Figure 3-12. Again, the lead and aluminum appear to be related in their leaching characteristics (Figures 3-13 and 3-16), as do the silicon and chromium (Figures 3-14 and 3-17). Furthermore, the cadmium solubility seems again to be nearly exclusively dictated by the pH (Figures 3-15 and 3-18).

Series 3

Starting with Figure 3-19, the subject is leachability from a masonry cement paste matrix. Since masonry cement is a mixture of ground limestone, clinker and gypsum, there is a buffering capacity in the system, which keeps the pH from dropping so low so soon. In this matrix as in the straight Type I matrix, there is a correlation between the leaching behavior of lead and aluminum, and between the behavior of chromium and silicon, as can be seen in Figures 3-20 and 3-22, and in Figures 3-21 and 3-23, respectively. (The erratic appearance of the lines around pH 5 are occasioned by the similarly erratic pH values in this range.) The dependence of cadmium leachability on pH can be seen in Figure 3-24 along with cumulative percents leached of three elements from the cement matrix.

Leaching data from series 2 (0.1% metal pastes) is used to demonstrate that there appears to be no correlation between cadmium and silicon leaching behavior, and between lead and silicon, as shown in Figures 3-26 and 3-28. Figure 3-27, however, which shows the chromium and aluminum leaching results together, can be interpreted to indicate that there is some mutual synergy. This is not surprising, as will be discussed later.

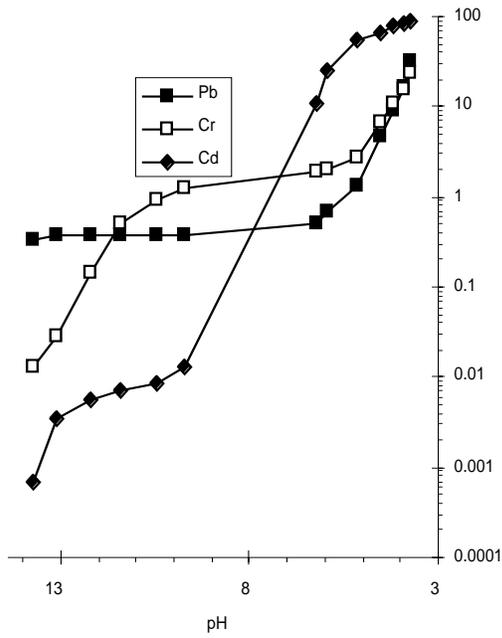


Figure 3-3. Summary of metals leach - 10,000 ppm.

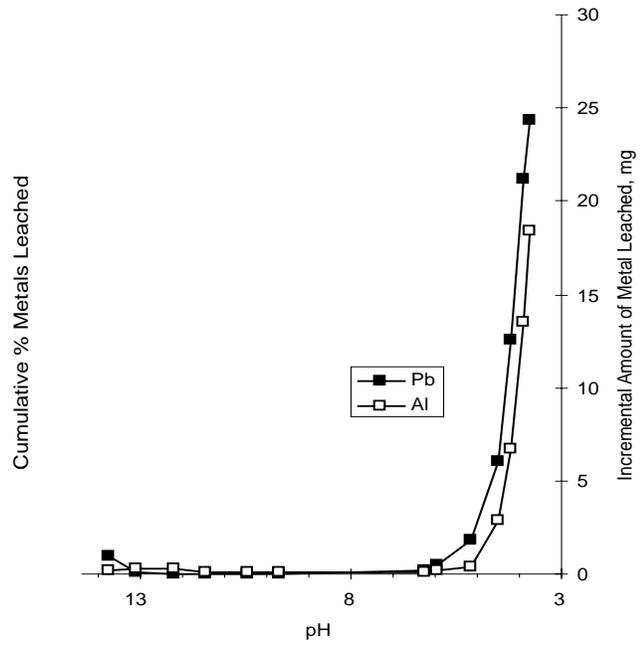


Figure 3-4. 1% metals, acetic acid-Pb/Al relationship.

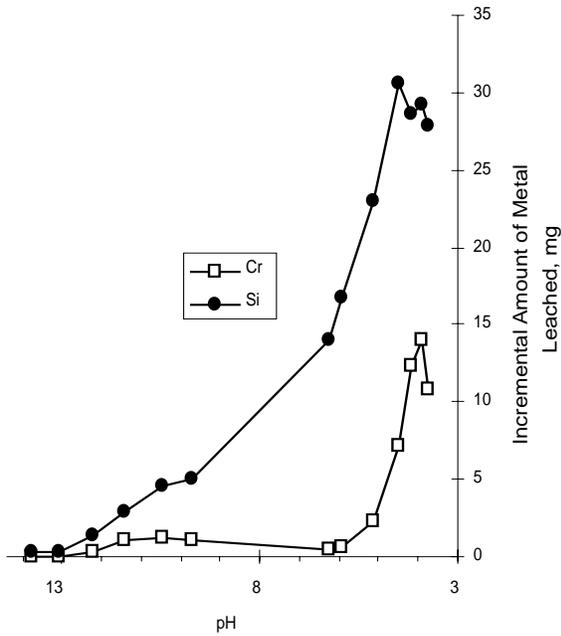


Figure 3-5. 1% metals, acetic acid- Cr/Si relationship.

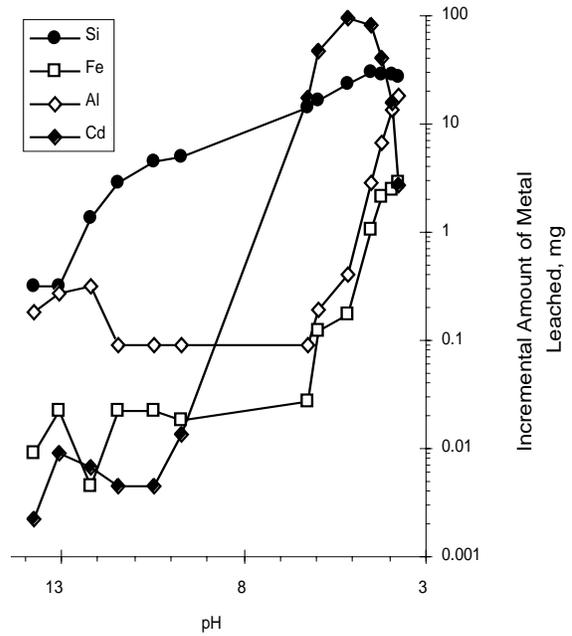


Figure 3-6. Concentrations of metal vs pH, 1% metals.

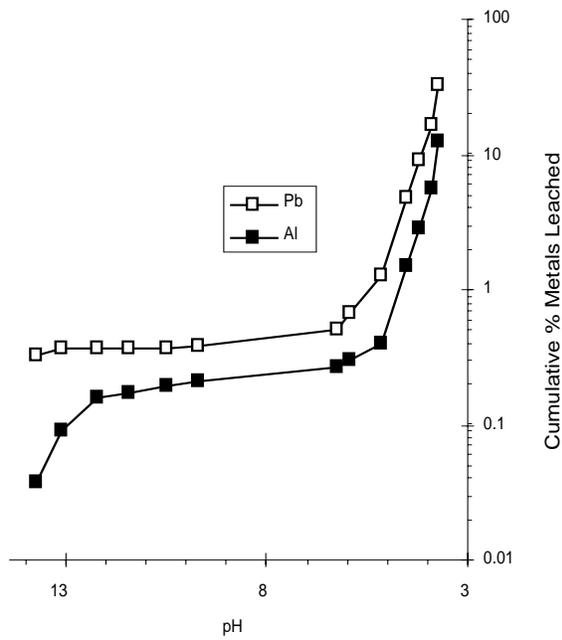


Figure 3-7. Al/Pb leaching, 1% lead, Type I cement.

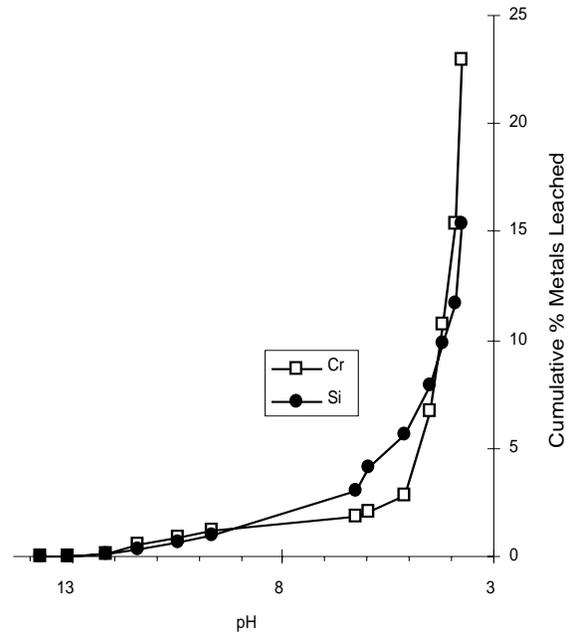


Figure 3-8. Si/Cr leaching, 1% chromium, Type I cement.

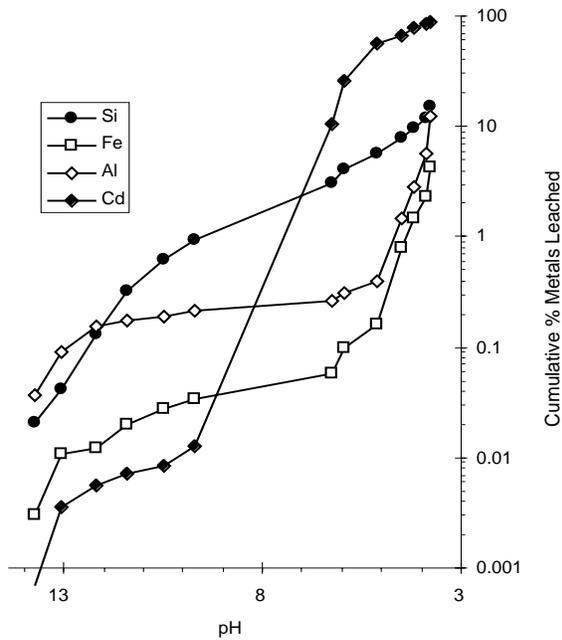


Figure 3-9. Si/Al/Fe/Cd leaching, 1% cadmium, Type I cement.

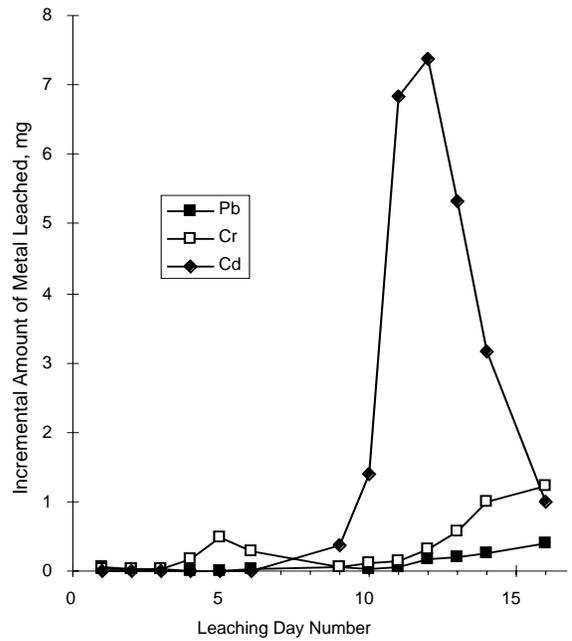


Figure 3-10. Metal concentrations vs leach day number 1000 ppm metals.

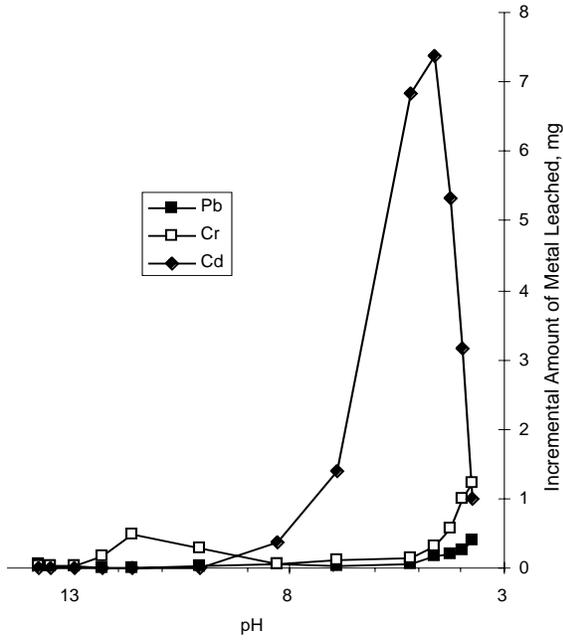


Figure 3-11. 1000 ppm metals/acetic acid-mg leach vs pH.

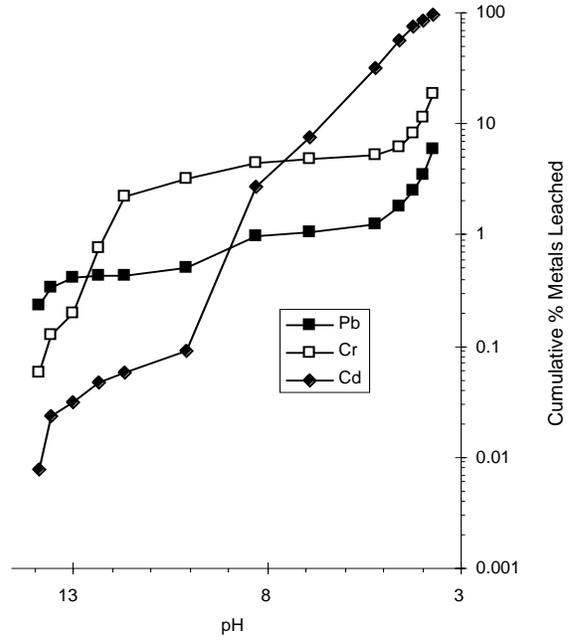


Figure 3-12. Summary of metals leached 1000 ppm.

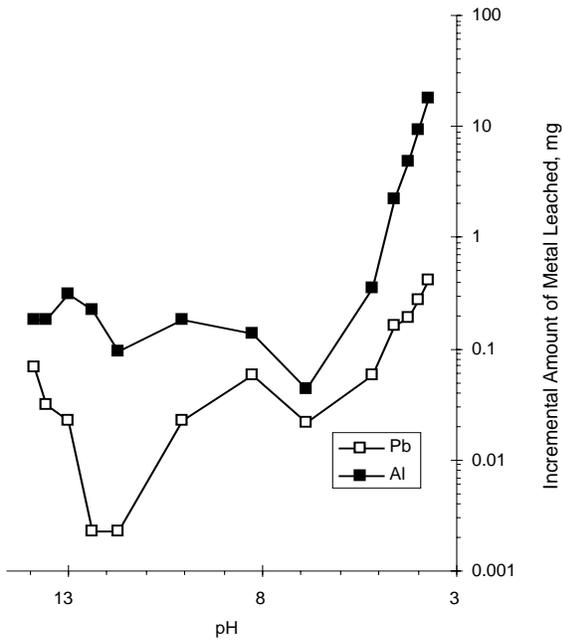


Figure 3-13. 0.1% metals, acetic acid-Pb/Al relationship.

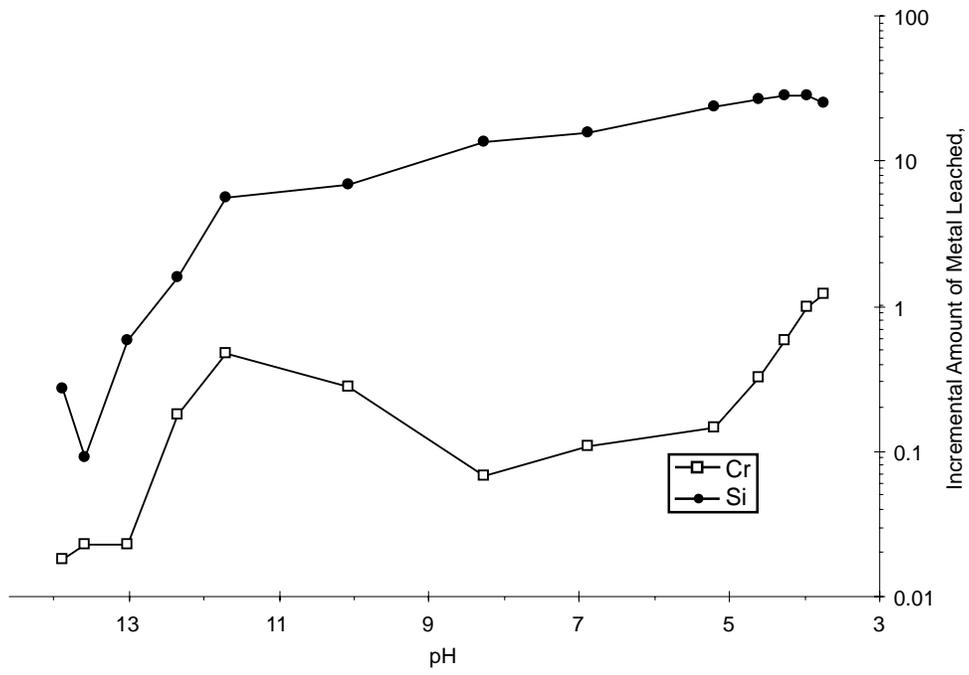


Figure 3-14. 0.1% metals, acetic acid-Cr/Si relationship.

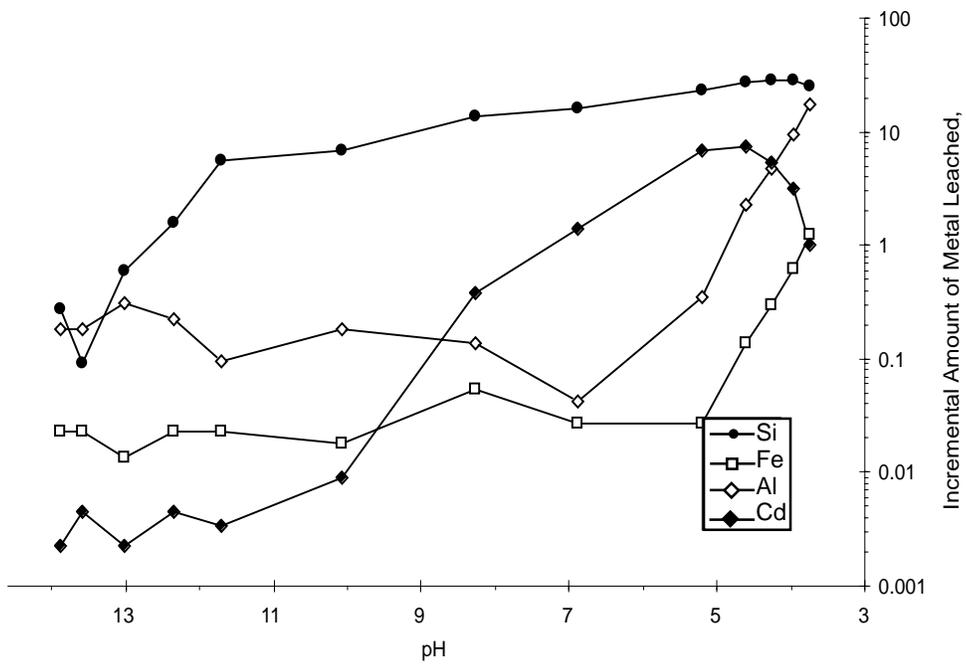


Figure 3-15. Concentrations of metals vs pH, 0.1% metals.

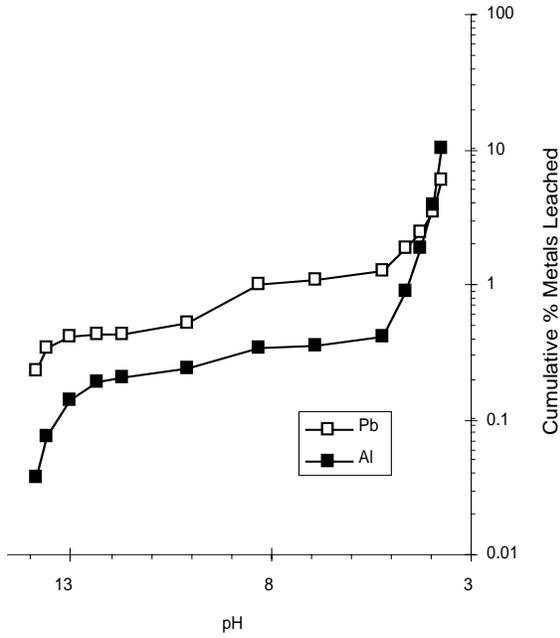


Figure 3-16. Al/Pb leaching, 0.1% lead, Type I cement.

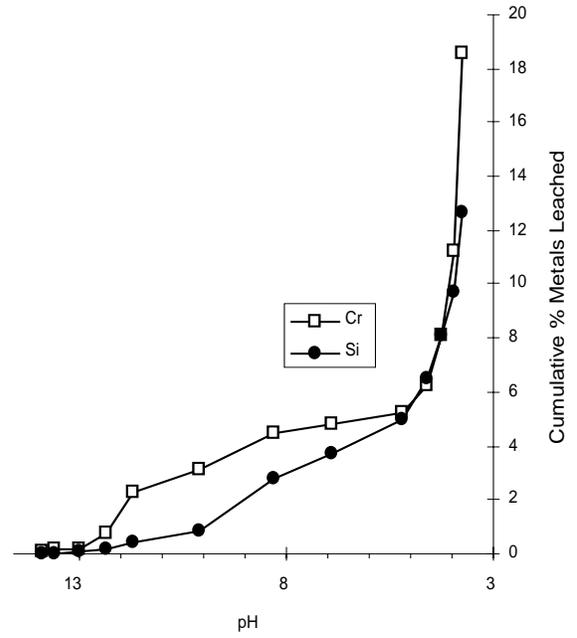


Figure 3-17. Si/Cr leaching, 0.1% chromium, Type I cement.

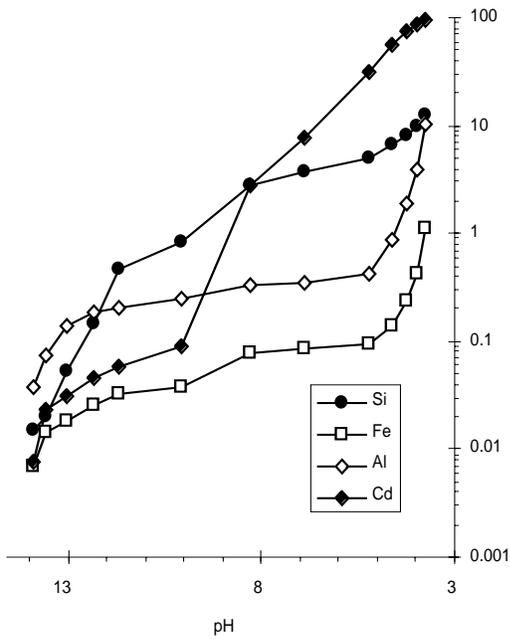


Figure 3-18. Si/Al/Fe/Cd leaching, 0.1% cadmium, Type I cement.

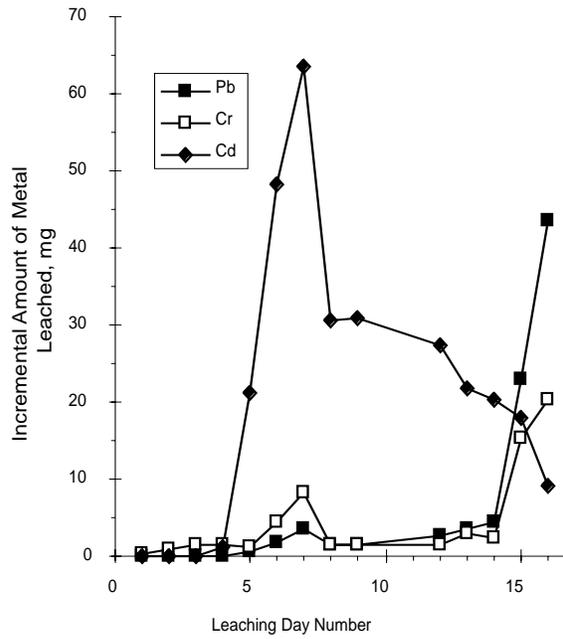


Figure 3-19. Metal concentration vs leach day number Type N masonry cement.

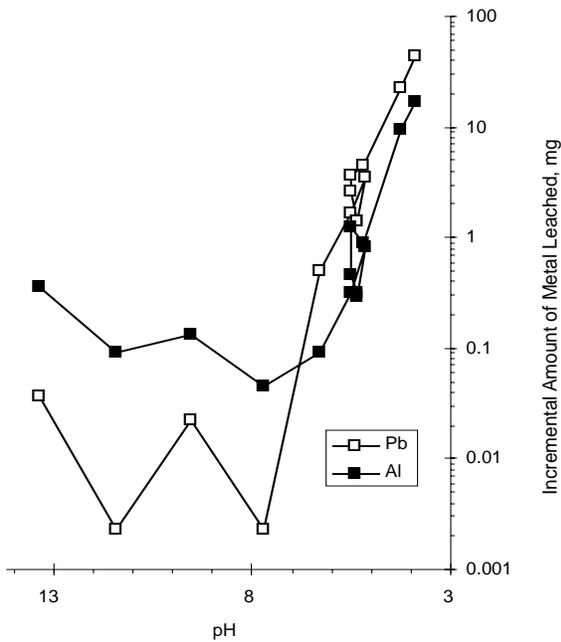


Figure 3-20. 1% metals, HOAc, Type N, Pb/Al Synergy.

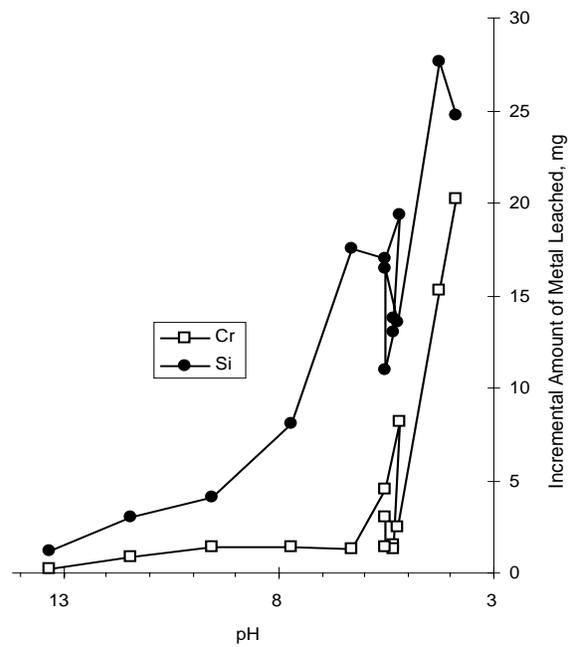


Figure 3-21. 1% metals, HOAc, Type N, Cr/Si synergy.

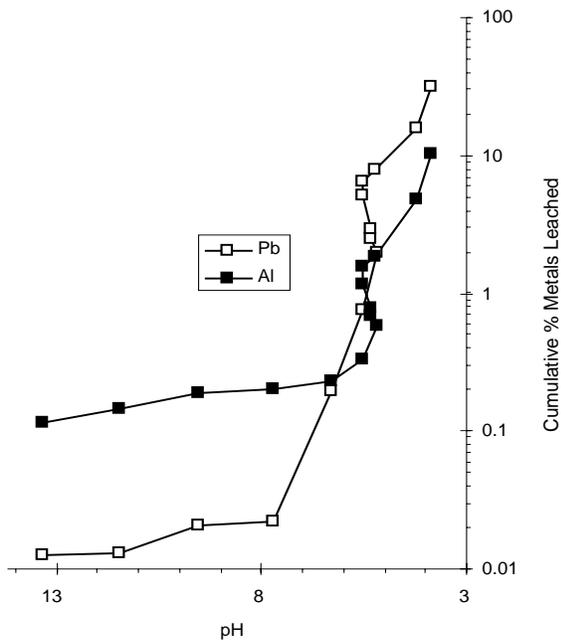


Figure 3-22. Al/Pb leaching, 1% lead, masonry cement.

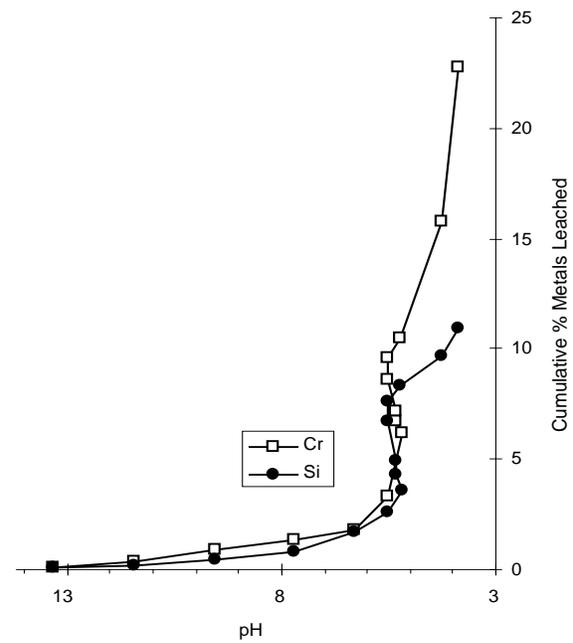


Figure 3-23. Si/Cr leaching, 1% chromium, masonry cement.

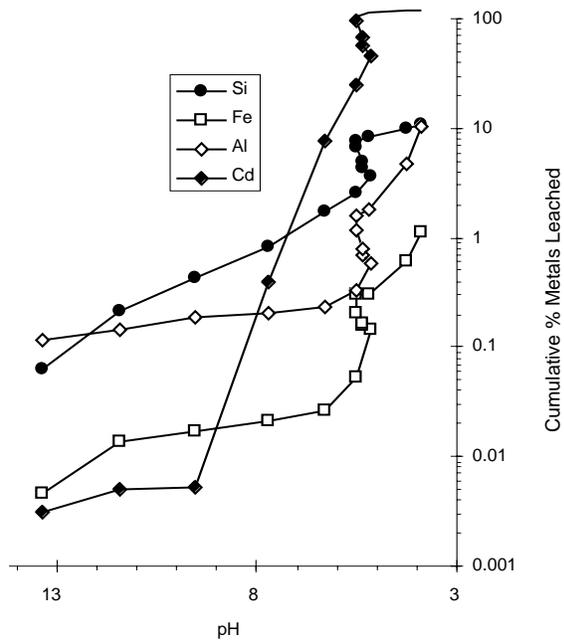


Figure 3-24. Si/Al/Fe/Cd leaching, 1% cadmium, masonry cement.

DISCUSSION (ACETIC ACID LEACHES—“PSEUDO-TCLP”)

It is of interest for the following discussion to review the solubility of the metal hydroxides of interest, as a function of the pH of the system. Figure 3-25 details this information, derived from a presentation by Conner, Cotton and Lear [1992].

Lead

Results of this investigation justify the suitability of Type I portland cement as a solidification/stabilization reagent for wastes containing cadmium, chromium and lead impurities. Portland cement is amazingly efficient at insolubilizing these three metals. The results provide strong evidence that the mechanism involves more than simple pH control, at least insofar as lead and chromium are concerned. At pH values greater than about 11.5, lead shows some leachability, probably as a result of the amphoteric nature of the hydroxide. The lead tied up in either aluminate or silicate phases may be converted to plumbite ion:

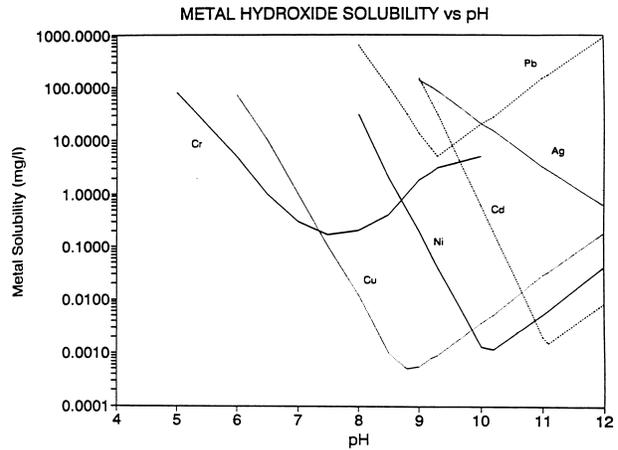
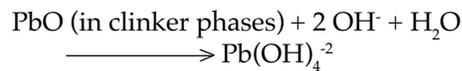
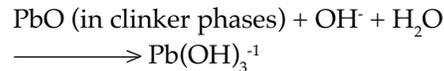


Figure 3-25. Metal hydroxide solubility vs pH.



or



However, at pH values from 11.5 down to about 7, the solubility of lead is virtually nil. Thereafter, of course, as the solution becomes acidic, lead solubility again rises. However, at a pH of 5, only 1% of the total stabilized lead was leached, and for 10% of the lead to be leached, the pH had to be below about 3.6. At this pH level, lead hydroxide (Pb(OH)_2) is very soluble. The solubility of Pb(OH)_2 at room temperature is 0.0155 g/100 cc. This translates to a K_{sp} of 1.064×10^{-9} . At a pH of 3.6, the hydroxide ion concentration is 3.98×10^{-11} M. Therefore, lead hydroxide should be completely soluble at this pH; with respect to other anions present, lead acetate is highly soluble, and although lead sulfate is quite insoluble ($K_{sp} = 1.96 \times 10^{-8}$ at 25°C), the sulfate ion is largely tied up in an even more insoluble ettringite phase. However, only about 10% of the lead has dissolved to this point. The picture is further clarified by looking at the pH at which 1% of the lead has dissolved. At pH 9, the hydroxide ion concentration is 10^{-5} M. Therefore, even at this pH, some lead hydroxide should dissolve, but 99% of it does not. Therefore, lead must be stabilized in a form other than the simple hydroxide (or hydrous oxide, which has a similar solubility).

It is revealing in this regard to compare the leaching behavior of lead with that of the aluminum from the cement. As noted earlier, Figure 3-7 shows the

leaching behavior of both metals as a function of pH for the 1% metals case. It appears as though a significant fraction of the lead may be associated with the alumina in either ettringite or ferrite, since it only begins dissolving when the alumina becomes solubilized. This association probably does not involve simple substitution since the ionic radius of lead is so large [Cotton and Wilkinson, 1962].

Chromium

With respect to chromium, the picture is rather similar. As previously indicated, in these experiments the Cr was all introduced in the trivalent state, because of the known high solubility of most hexavalent chromium salts. At very high pH values, there is limited solubility of chromium (III). Chromium (III) hydroxide probably does not exist as such, but the hydrous oxide ($\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) has some appreciable solubility in both acid and base. Therefore, at the very high pH values at the beginning of each leaching cycle, chromium solubility would be expected to be appreciable. In fact, it is very low, and becomes even lower at the intermediate pH values of 6-10. At low pH, the solubility is higher, but not nearly as high as would be anticipated assuming that the chromium exists in cement pastes as hydroxo- or sulfato- complex anions. Figure 3-27 shows the parallelism of the patterns of chromium (at the 0.1% level) and aluminum leaching, although the chromium line lies above the alumina line in terms of "% leached." Figure 3-8 shows the correspondence between chromium leaching pattern and silica for the 1% metals case. The correspondence is striking, and suggests that at least some of the chromium may be stabilized in or adsorbed on the CSH system. The ionic radii of $\text{Cr}(\text{OH})_4^{-1}$ and $\text{Si}(\text{OH})_4$ are fairly closely comparable.

Cadmium

The situation with cadmium is clearly different. Cadmium is the least soluble of the three metals at high pH, but becomes soluble at pH values somewhere around 9, regardless of the cement used. It becomes soluble at a point where there is still a significant amount of calcium silicate hydrate left. An example of its behavior in acetic acid leaching regimen is shown in Figure 3-26 for silica and 0.1% cadmium stabilized by Type I cement. The curves for silicon and cadmium cross at about pH 8; in other words, silica is more amphoteric than cadmium hydroxide, but below pH 8, cadmium hydroxide dissolves. The

situation with aluminum (Figure 3-9) leads to similar conclusions; once the pH drops, the cadmium dissolves, irrespective of aluminum behavior.

These results reveal that the cadmium is either not stabilized in the matrix of hydrated clinker minerals, or is very weakly so, and depends upon a high level of alkaline calcium compounds for stabilization. According to the *Handbook of Chemistry and Physics* (Chemical Rubber Company, 1988-9), $\text{Cd}(\text{OH})_2$ has a solubility of 2.6×10^{-3} grams/liter at 25°C. This equates to a solubility product of 5.6×10^{-15} . At a pH of 8, the hydroxide ion concentration is 10^{-6}M , which would yield a cadmium ion concentration of 0.0056 M, ignoring activity coefficients. At a pH of 7, however, the concentration of cadmium ion could increase to 0.56 M. This in general terms is what seems to be occurring with cadmium in the systems investigated here.

In summary then, the data provide good evidence that the cement matrix insolubilizes and immobilizes certain metals [lead and chromium (III)] far more effectively than could be projected from pH effects alone. It appears likely that this stabilization occurs by one or both of the following mechanisms:

- substitution of the metals in the lattice of either the calcium silicate hydrates or the calcium sulfoaluminate hydrates. (This appears to apply even to C-S-H that is depleted in calcium.)
- physical or chemical adsorption or encapsulation of the metal ions on the surface of the above hydrated cement phases.

In the case of cadmium, by contrast, it appears that pH is the dominant mechanism by which cement immobilizes the metal.

COMPARISON OF PORTLAND CEMENT AND MASONRY CEMENT MATRICES

A comparison of the leaching of the target metals, as a function of pH, from a masonry cement matrix and from a Type I portland cement matrix is shown in Figure 3-29. The most striking difference is with respect to lead. In the early leaching steps, and indeed down to a pH of about 6.0, the masonry cement is a superior stabilization reagent. In more acidic solution, the portland cement outperforms the masonry. At high pH, with the exception of the first leaching cycle, the leachability of cadmium from a Type I matrix is also slightly higher, while in acid, once more, the portland cement is more effective. For chromium, with the exception of the pH range from about 6 to about 11, the portland cement performs better.

Even in this intermediate pH range, the advantage of the masonry cement is slight; the difference is probably of the order of analytical uncertainty.

RESULTS AND DISCUSSION (DEIONIZED WATER AND SYNTHETIC ACID RAIN)

The deionized water and the synthetic acid rain are much less aggressive leaching solutions than the acetic acid solution. This is not surprising when the actual number of moles of acid (hydrogen ion) available for leaching is calculated for the three systems. The acetic acid solution was 0.10 M, with a pH of 2.88, which represents 0.046 moles of acid per 450 mL leaching aliquot. The synthetic acid rain (pH of 3.0) contained 0.00024 M nitric acid and 0.00054 M sulfuric acid (0.00108 N), for a total normality of 0.00132 N. 450 mL of this solution therefore contained 0.000594 moles of acid. This is only about 1.3% as much acid as supplied by the acetic acid aliquot, and so would require about 77 leach cycles to furnish an amount of acid equivalent to that furnished by one acetic acid leach cycle. Therefore, with deionized water or synthetic acid rain as leachants, the pH never dropped below 13.0. As a result, the degree of leaching experienced was much lower than that observed with the acetic acid leaching solutions; on the other hand, the initial high-pH leachability of lead and chromium was observed to continue for several cycles. The total amount leached, however, is very low for all metals, even after 16 sequential leaches. The synthetic acid rain leached a small amount more chromium and cadmium, while the distilled water leached a very small amount more lead than the synthetic acid rain, presumably because the pH of the latter solution was a little lower due to the nitric and sulfuric acid content. The summary of the cumulative distilled water leaching observed for cadmium, chromium, and lead is shown in Figure 3-30, and for the synthetic acid rain, in Figure 3-32. The corresponding data showing incremental quantities of each metal leached for synthetic acid rain are given in Figure 3-31.

COMPARISON OF RESULTS OF LEACHING IN SINGLE METAL AND MULTIPLE METAL SYSTEMS—SYNERGETIC CONSIDERATIONS

It is interesting to note that there appears to be a small degree of suppression of leachability of all metals apparently related to the presence of the other trace metals in the stabilized paste system. In Fig-

ure 3-33, we see the comparison of cumulative leachability of lead, for the single metal batch leaching sample (SBL) and the multiple metals leaching system. Lead is less soluble at any given pH in the multiple metals (MM) leaching system. For chromium, between pH values of 11 and 4, the picture is similar as seen in Figure 3-34, although at the very high pH levels there seems little to choose between the results. For cadmium, above pH 5.5, the solubility for the multiple metals system is again somewhat lower. Elucidation of the reasons for these effects would require some detailed scanning electron microscopy and/or x-ray diffraction studies to pinpoint the phases in which the metals reside, and the form which they have taken when present together.

COMPARISON OF THE SOLUBILITY OF THE TRACE METALS WITH THEIR THEORETICAL SOLUBILITY

As a means of documenting the effectiveness of portland cement stabilization of cadmium, lead, and chromium, plots have been constructed comparing the solubility of metals as a function of pH for the various leaching steps, together with the calculated data on the solubility of the corresponding hydroxide or hydrous oxide obtained from the data of Conner, Cotton and Lear [1992]. Figure 3-36 shows the comparative data on cadmium solubility, for the metal hydroxide, and for the portland cement S/S matrix. In the range of pH from about 11-12, the cadmium proves to be more soluble in the cement matrix than the hydroxide, but above and below this pH range, the solubility is far lower for the cement-stabilized cadmium. In fact, around pH 9-10, it is more than one order of magnitude less soluble than would be predicted by the theoretical solubility of $\text{Cd}(\text{OH})_2$.

The picture is even more dramatic for lead. Figure 3-37 shows the comparison of the theoretical solubility of lead as a function of pH, and that actually observed. The ratio of solubilities is often as high as 1000—that is, the lead is nearly three orders of magnitude less soluble than would be predicted by the solubility of $\text{Pb}(\text{OH})_2$. For lead in particular, the evidence for effects other than those of pH is obvious.

The case of chromium is slightly more complex. As can be seen in Figure 3-38, the cement-stabilized chromium is far less soluble than the theoretical for hydrated Cr_2O_3 above pH 9 and below pH 7. There are no data for the intermediate pH range. This probably has little practical significance in actual field applications, because a pH less than 9.0 would not be reached in most cases. The reason for the discrepancy may lie in the possible oxidation of some

of the Cr^{+3} to Cr^{+6} during the process of repeated handling of these pastes. The separations of solid and liquid were carried out in air, the pH was high enough for improved stability of hexavalent Cr, and some oxidation was perhaps inevitable. As noted earlier, hexavalent chromium is much more soluble than trivalent chromium in alkaline media. Since these plots are on a logarithmic scale, a small amount of hexavalent chromium would remain soluble in this pH range and skew the data. It would be interesting to see whether a small addition of ferrous sulfate or other reducing agent could inhibit this oxidation of chromium and lower the leachabilities for this element.

Another possible explanation is the fact that the none of the pH values actually obtained in the experiments fell between 7 and 9; had there been an actual measurement in this range, it may have reflected a lower chromium solubility.

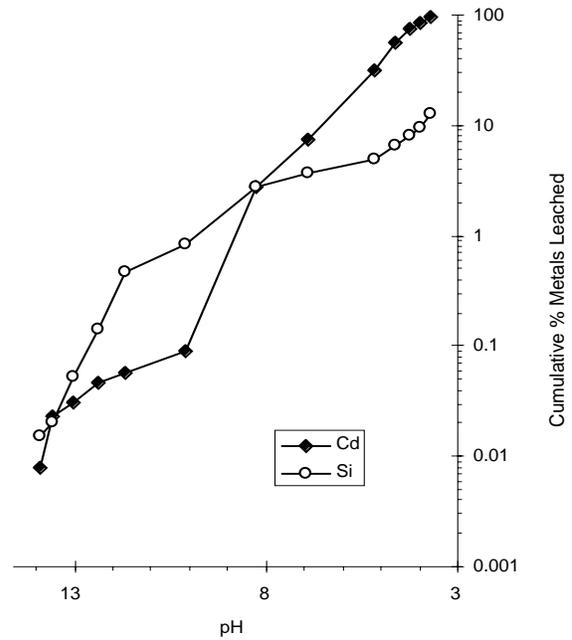


Figure 3-26. Cadmium/silica leaching vs pH-0.1% metals.

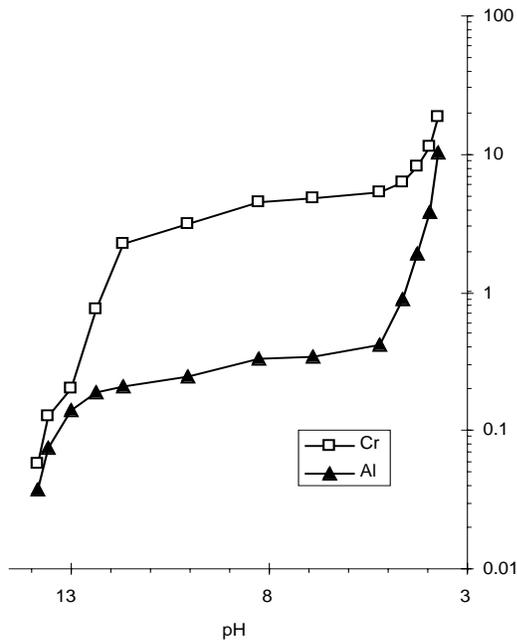


Figure 3-27. Al/Cr leaching vs pH-0.1% metals.

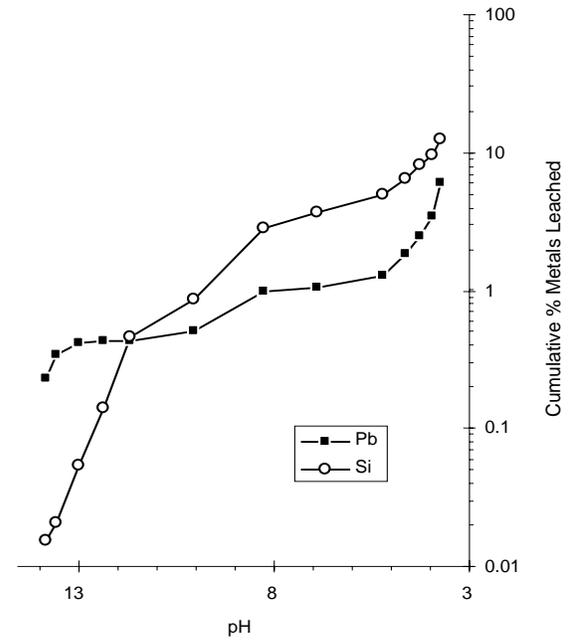


Figure 3-28. Silica/lead leaching vs pH-0.1% metals.

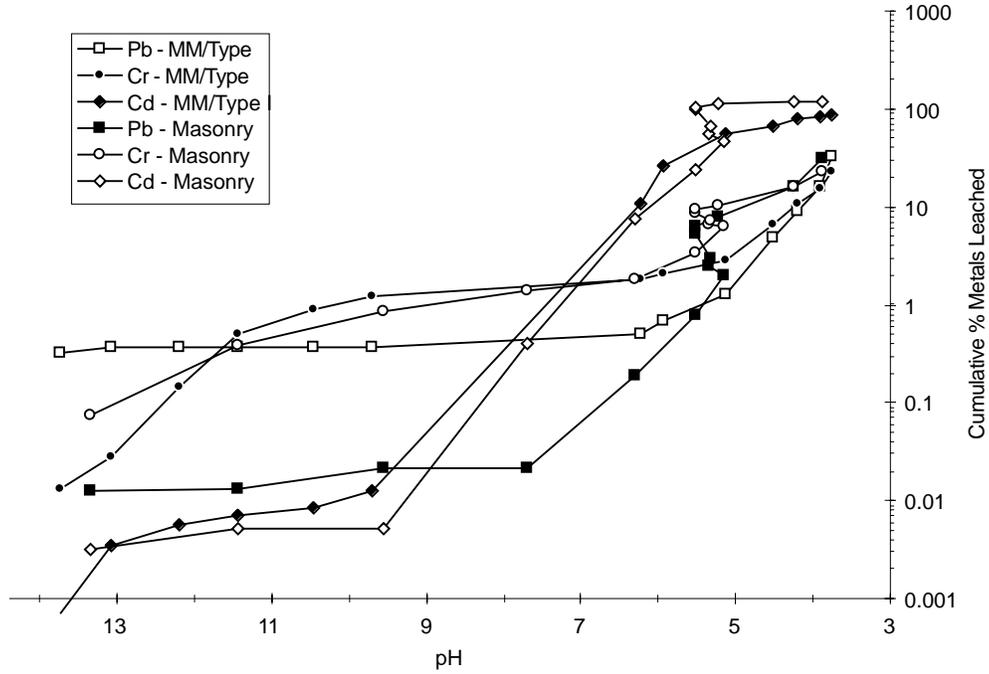


Figure 3-29. Comparison of Type I vs masonry for stabilization.

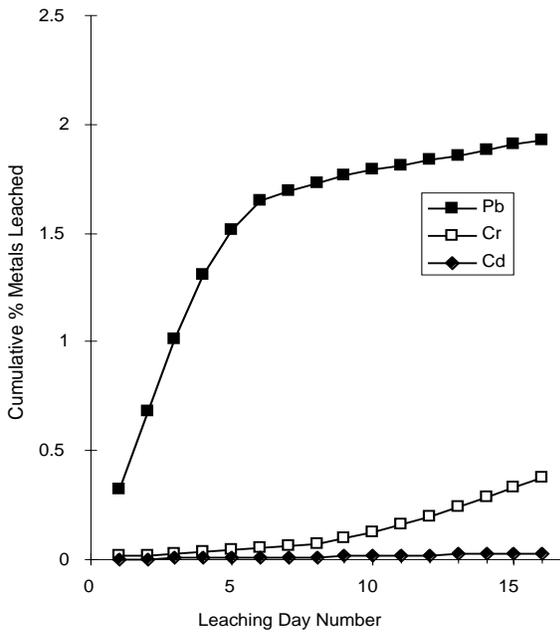


Figure 3-30. Cumulative % leached-1% metals-DI water.

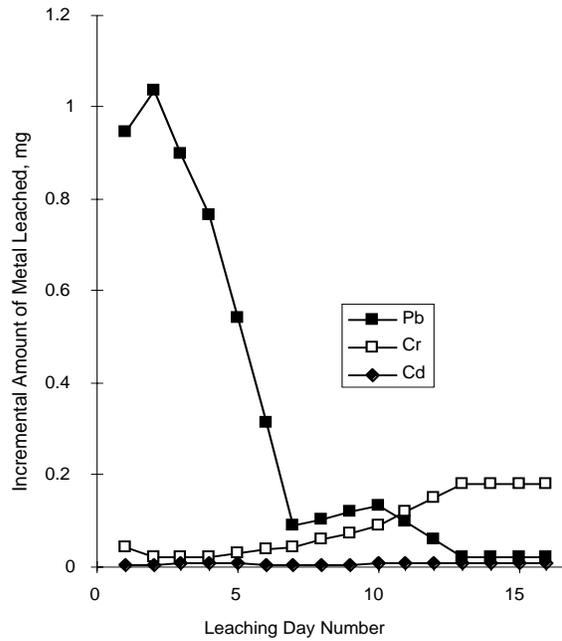


Figure 3-31. Incremental leach of metals-synthetic acid rain leach.

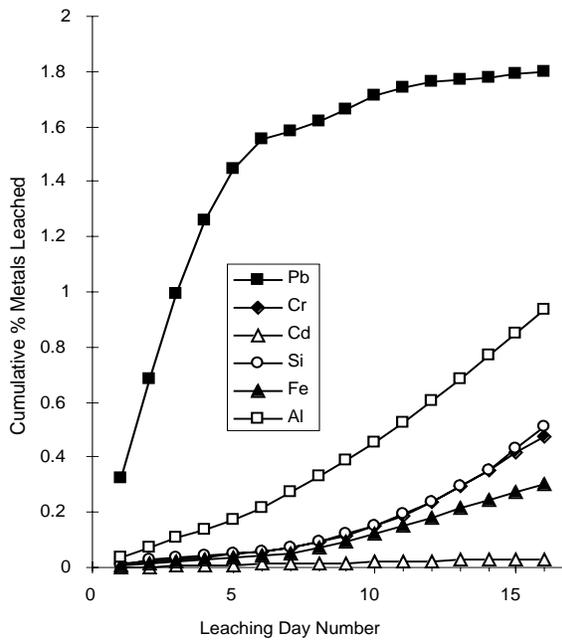


Figure 3-32. Synthetic acid rain, 1% metals, cumulative leach vs cycle.

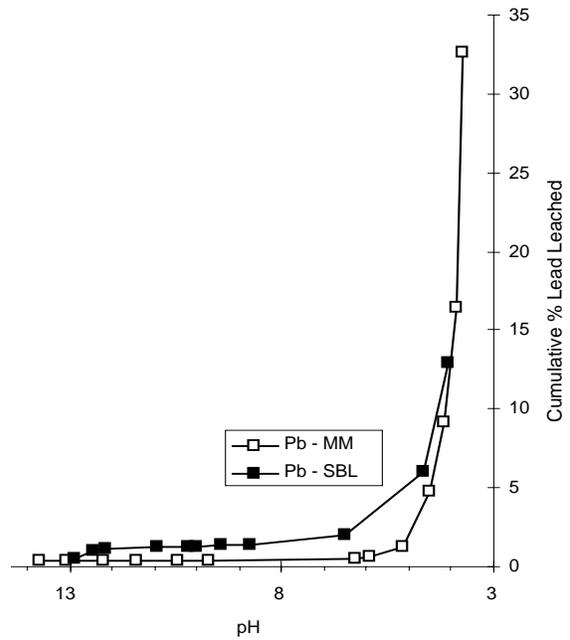


Figure 3-33. Comparison of Pb leach-SBL vs MM.

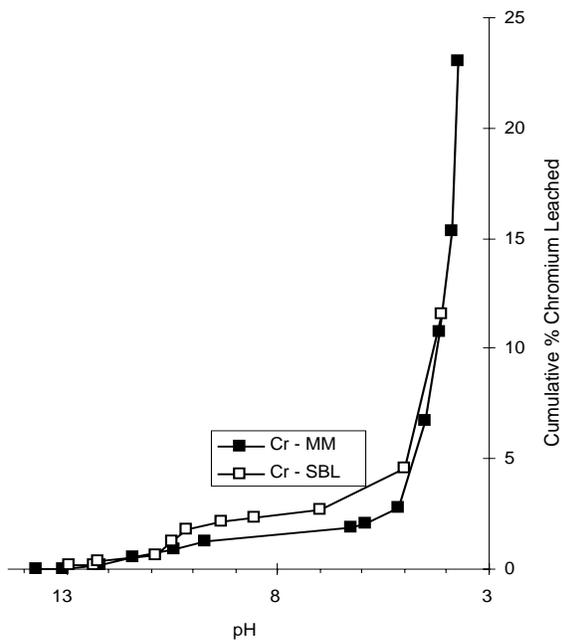


Figure 3-34. Comparison of Cr leach-SBL vs MM.

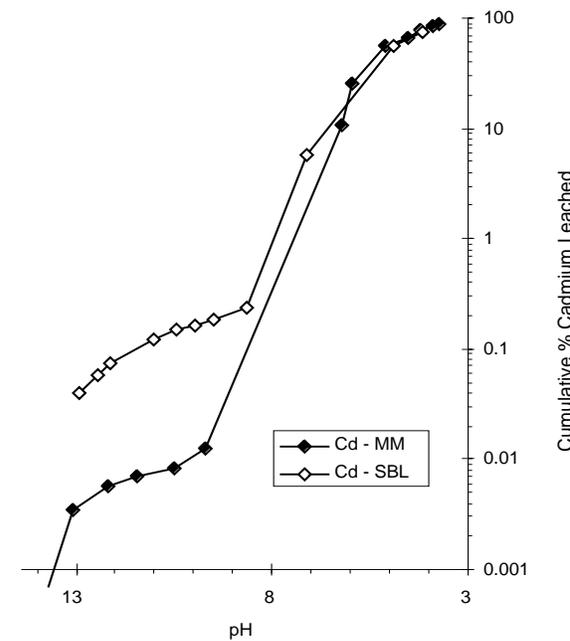


Figure 3-35. Comparison of Cd leach-SBL vs MM.

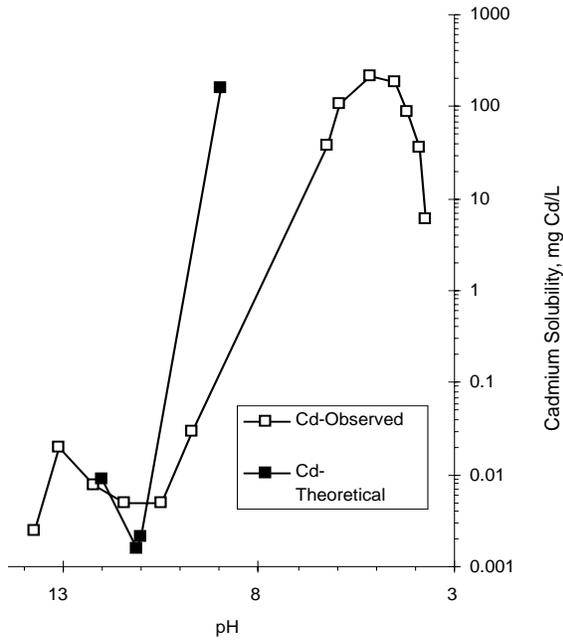


Figure 3-36. Solubility of cadmium hydroxide theoretical vs observed (S/S matrix).

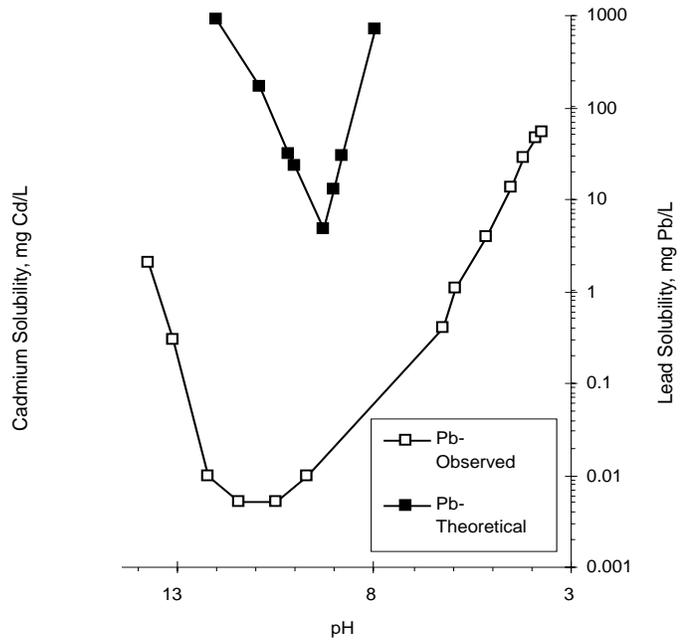


Figure 3-37. Solubility of lead hydroxide theoretical vs observed (S/S matrix).

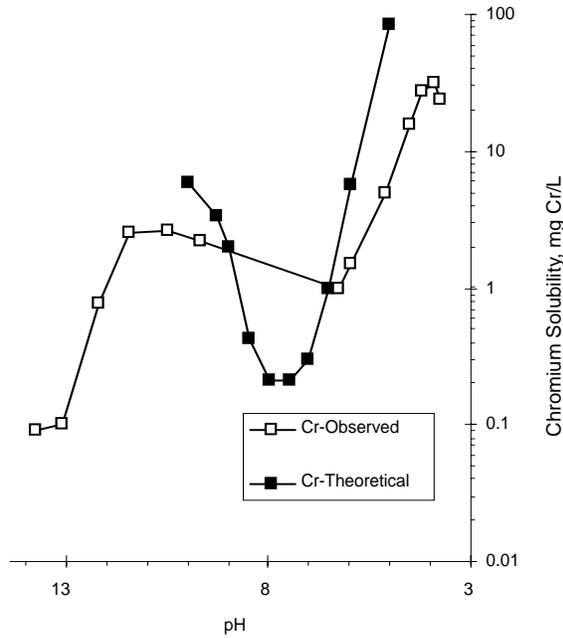


Figure 3-38. Solubility of chromium hydrous oxide theoretical vs observed (S/S matrix).

CHAPTER 4

Leachability of Multiple Metals from Contaminated Soils and Oily Waste

This discussion will concentrate on the behavior of cadmium, chromium, and lead in soil-cement matrices, with and without the contamination of oil. This task was the logical extension of the work done with multiple metals in cement paste, but with the inclusion of soil matrices. The soils used were put together according to the procedure outlined by the U.S. EPA (1988). The following materials were required (Table 4-1).

The materials were air dried by spreading out on a large clean area. The lumps of the dried topsoil

contained an hydroxide sludge of cadmium, chromium, and lead. The TSC2 and TSC3 series were identical, except with respect to the relative humidity at which the samples were cured. The TSC2 samples were cured at 100% R.H., while the TSC3 samples were cured at 80% R.H. This soil also was used for mix TSC4, which contained, in addition to the sludge, 8% oil. This oil was a commercially available SAE 10 W oil (without additives). The oil was aged prior to incorporation into the soil matrix by oven heating, in ambient laboratory air, to 100°C for

Table 4-1. Materials Proportions Required in the Soil-Mix

| Soil ingredients | Proportion (wt. %) | Sources for the first soil |
|------------------|--------------------|---|
| Gravel (No. 9) | 5.7 | Material Service Corporation, Elgin, IL |
| Sand | 31.5 | Material Service Corporation, Elgin, IL |
| Silt | 28.3 | Material Service Corporation, Elgin, IL |
| Bentonite | 5.4 | Mississippi |
| Kaolinite | 9.4 | Kraft clay |
| Topsoil | 19.7 | Local garden store |

were crushed in a jaw crusher and later ground to pass No. 16 mesh.

For the first soil, the materials were proportioned as given above to prepare four soil batches of about 11 kg (25 pounds) each. The materials were loaded into a pre-dried rotary drum mixer and mixed for several minutes. The mixer was intermittently stopped for examination to ensure complete mixing. After mixing, the soil was stored in five-gallon buckets lined with plastic liners. This first soil was of calcareous type, in which the gravels and sand contained substantial dolomite. This soil was used in the metal stabilization studies for contaminated soil-cement mixes TSC2 and TSC3, which

72 hours. The TSC4 samples were cured at 100% relative humidity.

A second soil was prepared specifically for use in the subsequent arsenic testing program, and for preparation of TSC5, which contained oil and an hydroxide sludge containing cadmium, chromium, and lead. A siliceous soil-mix was made using the same recipe for particle size distribution, but using the siliceous gravels and sand from Eau Claire, Wisconsin. It was felt that the siliceous soil matrix would represent a more severe challenge than the dolomitic matrix, since it had no inherent acid-neutralization capacity of its own. The silt required in the mix was prepared by grinding the Eau Claire sand to appro-

appropriate fineness. A type of topsoil similar to that used in the dolomitic soil mix was used, after drying, crushing, and grinding to pass a 1.19-mm sieve (No. 16 mesh). The mixing was done in a drum-mixer in two batches of 11.34 kg (25 pounds) each, to prepare 22.7 kg (50 pounds) of siliceous soil.

Rapid X-ray fluorescence analysis was carried out on the prepared base soils, both for the dolomitic soil and for the siliceous material used for the arsenic studies. The results are shown in Table 4-2.

Preparation of Soil-Cement Matrices

The preparation of the soil-cement test specimens, both with and without oil addition, are outlined in detail in Appendix C. These were molded in 50-mm (2-inch) mortar cube molds. Emulsifiers were used to ensure the best homogenization of oil and water. Once the specimens had been cured for the requisite amount of time, strength tests were carried out at 7, 28, and 90 days of curing. The results are given in Table 4-3.

Appendix B describes the methods used for the preparation of leach samples and leaching regimen used to produce the results discussed below. Particular attention should be paid to the incorporation of oil and methods of drying used in test series TSC 4D, TSC 4O, and TSC 5.

RESULTS AND DISCUSSION

With the previous results obtained on cement pastes with multiple metals, it was perhaps predictable that the patterns of stabilization behavior noted for cadmium, chromium, and lead in those systems might be mirrored, to some extent, by behavior in stabilized soil matrices. In all cases, the leachant was acetic acid, with concentration adjusted to maintain the same ratio of acetic acid-to-cement used in the paste studies. Details on acetic acid concentrations used can also be found in Appendix B. Five separate test series were carried out in this segment of the work as shown in Table 4-4.

Table 4-2. Analysis of Base Soils Used for Soil-Cement/Metal System

| Oxides | Base soil for TSC2, TSC3, & TSC4 | Base soil for ASC series & TSC5 |
|--------------------------------|----------------------------------|---------------------------------|
| SiO ₂ | 37.14 | 75.27 |
| Al ₂ O ₃ | 8.02 | 10.02 |
| Fe ₂ O ₃ | 2.27 | 3.15 |
| CaO | 14.47 | 1.67 |
| MgO | 9.63 | 0.88 |
| SO ₃ | 0.14 | 0.05 |
| Na ₂ O | 0.41 | 0.75 |
| K ₂ O | 0.78 | 1.33 |
| TiO ₂ | 0.45 | 0.58 |
| P ₂ O ₅ | 0.07 | 0.09 |
| Mn ₂ O ₃ | 0.05 | 0.05 |
| SrO | 0.03 | 0.03 |
| LOI | 26.62 | 7.24 |
| Total | 100.08 | 101.11 |

Table 4-3. Compressive Strength of Soil-Cement Cubes

| Sample | Remarks | Compressive strength, MPa (psi) | | |
|--------|-----------------|---------------------------------|------------|------------|
| | | 7 days | 28 days | 90 days |
| TSC1 | Not Leached | 1.10 (160) | 1.45 (210) | 2.28 (330) |
| TSC2 | Standard Cure | 1.24 (180) | 1.59 (230) | 2.55 (370) |
| TSC3 | 80% R.H. Cure | 1.72 (250) | 2.34 (340) | 4.76 (690) |
| TSC4 | With Oil | 1.17 (170) | 1.72 (250) | 3.17 (460) |
| TSC5 | W/Oil-Sil. Soil | 1.24 (180) | 1.79 (260) | 2.34 (340) |

Table 4-4. Soil-Cement Test Series

| Designation | Soil matrix | Oil added? | Relative humidity curing conditions | Drying before leach |
|-------------|-------------|------------|-------------------------------------|---------------------|
| TSC2 | Dolomitic | No | 100% | Acetone |
| TSC3 | Dolomitic | No | 80% | Acetone |
| TSC4O | Dolomitic | Yes | 100% | Air |
| TSC4D | Dolomitic | Yes | 100% | Acetone |
| TSC5 | Siliceous | Yes | 100% | Air |

100% Relative Humidity Cure, Dolomitic Contaminated Soil without Oil (TSC2)

In the case of cadmium, there was essentially no leaching until the pH was below about 8.5, at which point it became suddenly highly leachable. Lead and chromium were initially slightly leachable at the very high pH values, but below pH 10.0, lead became essentially unleachable, and the incremental leachability of chromium declined until it was minimum at about pH 7. On the low pH side, below about pH 5.5, the incremental lead leachability increased sharply, while the incremental chromium leachability stayed low. Incremental chromium leachability never declined to levels as low as observed for the

other two metals at their minimum solubility. These results are summarized in Figure 4-1.

The cumulative percent of each metal leached as a function of pH is shown for this contaminated soil in Figure 4-2. Cadmium leachability is negligible above pH 9, and chromium leachability for this soil is only weakly dependent on pH. Lead is more leachable below pH 6 or above pH 11 than between these two pH values. It seems clear that the alkalinity of the soil itself provides protection against chromium leaching.

80% Relative Humidity Cure, Dolomitic Contaminated Soil Without Oil (TSC3)

The comparable data for incremental and cumulative leachability of the three metals in question, for a system which has been cured at 80% relative humidity, are given in Figures 4-3 and 4-4 respectively. The results are roughly the same as for the 100% relative humidity cure. However, there are differences, as can be seen by consulting Figures 4-5 and 4-6, for a comparison of incremental and cumulative leaching, respectively, for the two different relative humidities. In Figure 4-5 it is apparent that the higher relative humidity cure is marginally beneficial for stabilization of chromium, as the curve for 100% R.H. (TSC2) lies below that for the 80% R.H. cure (TSC3). The opposite seems to be the case for lead above pH 10; curing at 80% R.H. reduces leachability relative to that for 100% R.H. curing. The difference for cadmium seems to be very small. When viewed on the basis of cumulative leachabilities, displayed in Figure 4-6, these trends can perhaps be seen more clearly. The differences may or may not be statistically significant.

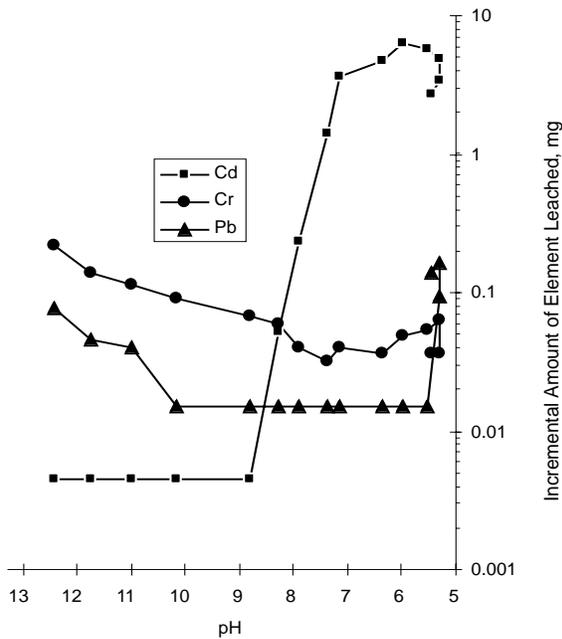


Figure 4-1. Increment leach of metals, TSC2 soil-cement.

Oily Wastes, Dolomitic Contaminated Soil (TSC4O and TSC4D)

This study was a combination of two series of leachability runs, one with cured oily soil-cement (8% by

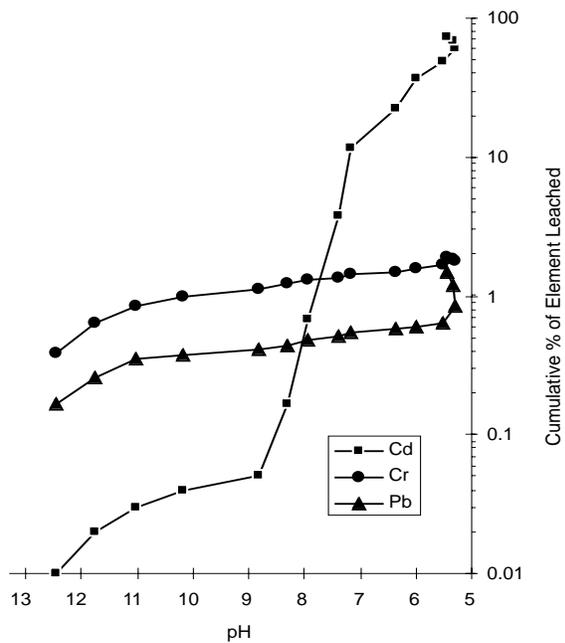


Figure 4-2. Cumulative leach of metals, TSC2 soil cement.

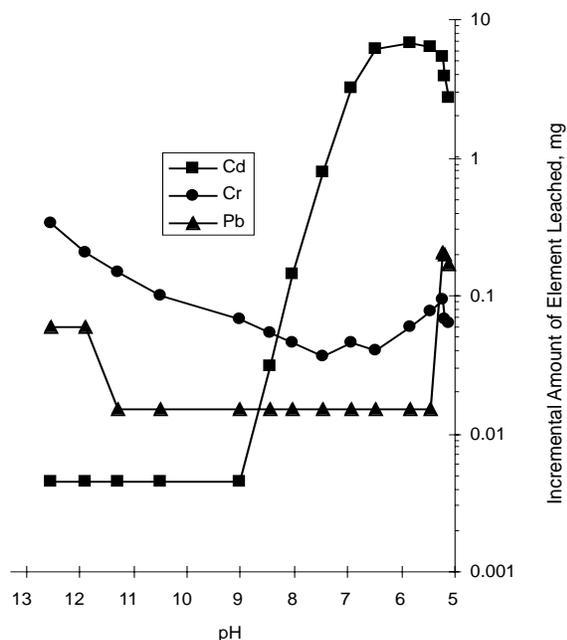


Figure 4-3. Incremental leach of metals, TSC3 soil-cement.

mass each aged oil and portland cement stabilizer) dried with acetone prior to commencing the leaching steps (referred to as sequence TSC4D), and another, identical in other respects, which was subjected only to air drying (designated as sequence TSC4O). The reason that two series were performed was to ensure that any leaching aberrations possibly caused by the removal of oil by the acetone could be determined, and yet that direct comparisons with the other soil-cement studies, where acetone drying had been used, could also be made.

For the acetone-dried samples (TSC4D), Figure 4-7 shows the incremental leach of cadmium, chromium, and lead vs. pH; the general patterns are very similar to those obtained for the contaminated soils without oil. The cumulative behavior as a function of pH, displayed in Figure 4-8, is likewise similar to its contaminated soil counterpart. The behavior of the oily samples dried in air (TSC4O) is likewise shown in Figures 4-9 and 4-10. The comparison of the cumulative percent leached for samples dried with acetone and dried in air is shown in Figure 4-11; here it emerges that the samples dried with acetone prior to leaching had a uniformly lower leachability than those dried in air for all three heavy metals, especially at high pH. For cadmium, at pH values below about pH 7, the air-dried sample was generally less leachable.

Another comparison of interest for waste stabilization feasibility determinations is the effect of the oil on stabilization of inorganic sources of the metals. Figure 4-12 shows the relative values of cumulative % leached against pH for the air dried oily waste samples (TSC4O) and the 100% relative humidity-cured contaminated soil without oil (TSC2). This comparison is for the dolomitic soil. For lead, the oily waste in fact stabilized the metal more effectively than did the soil without oil. The chromium results are almost indistinguishable, although at very high pH (>11.5) and at low pH (<8), the oil-free material had better performance. In the case of the cadmium, it was less leachable in the oil-free material at high pH (<10), and less leachable in the oil-contaminated material at pH values less than about 8.

Comparison of Oily Waste, Oil-free Soil-Cement, and Paste vs. pH

In an effort to discover the effect of the dolomitic aggregate on the effectiveness of stabilization, other than the pH buffering that was expected, a plot of pH vs cumulative leachability of the three metals was constructed, shown as Figure 4-13. Data for acetic acid leaching for multiple metals paste (MM

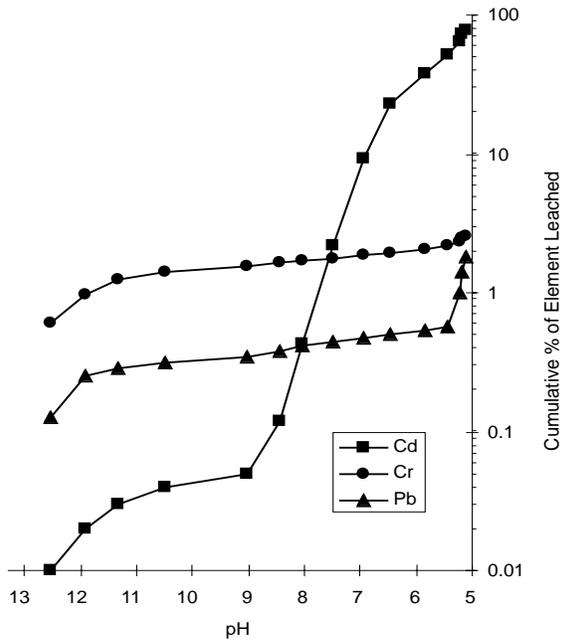


Figure 4-4. Cumulative leach of metals, TSC3 soil cement.

paste), previously discussed in Chapter 3, is shown for comparison.

With respect to cadmium, the cement paste kept leaching to a minimum below about pH 8. Between pH values of about 8 and about 6, all three systems appear approximately equivalent, while from pH 6 down, the paste again is the most efficient system. For example, for 10% of the total cadmium to be leached, the paste system had attained a pH of 6, the oily waste a pH of about 6.6, and the oil-free contaminated soil-cement a pH of about 7.0. For chromium, the cement paste was again most effective at high pH, in this case at pH values greater than about 10.0. Below this pH, chromium appears to be better stabilized in soils than in pastes. This may have something to do with the siliceous clay minerals in the soil, which may adsorb chromium effectively in a zeolitic or lattice substitution for aluminum. By contrast, the leachability for lead is again higher in the neat paste matrix than it is in the dolomitic soil matrix. The oil-contaminated system (perhaps counterintuitively) did the best job of stabilizing lead of these three systems.

Studies of a Soil-Cement System Incorporating Siliceous Soil

The previously mentioned studies evaluating a dolomitic soil matrix were in a sense a “best case” scenario, since the dolomite component of the soil

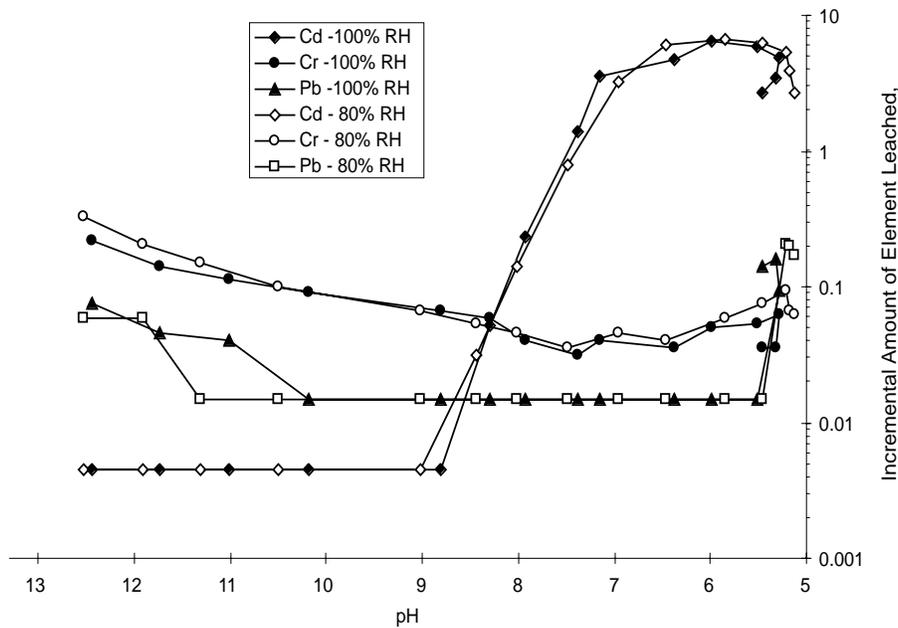


Figure 4-5. Comparison of incremental leach, as function of relative humidity.

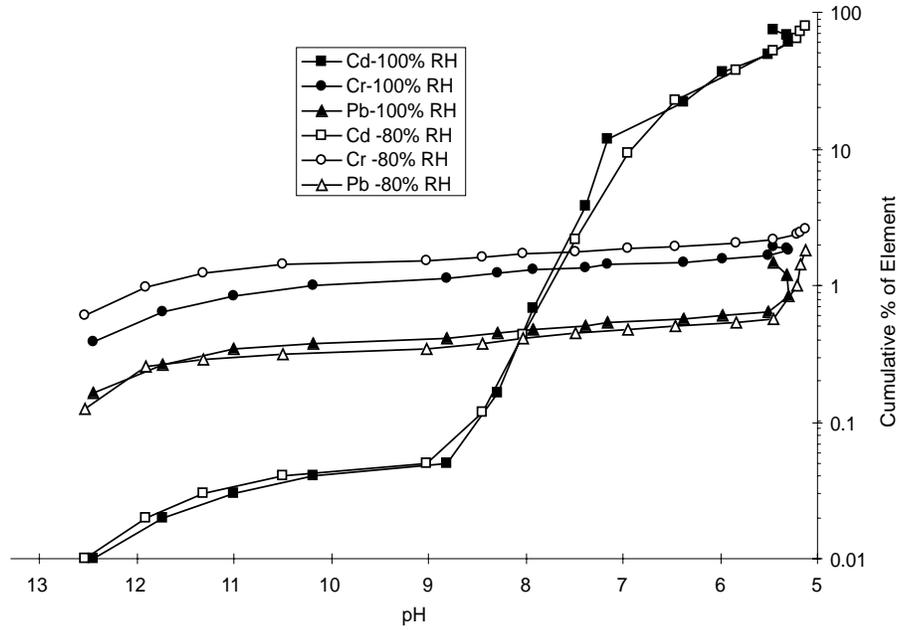


Figure 4-6. Cumulative leach, soil-cements, vs relative humidity.

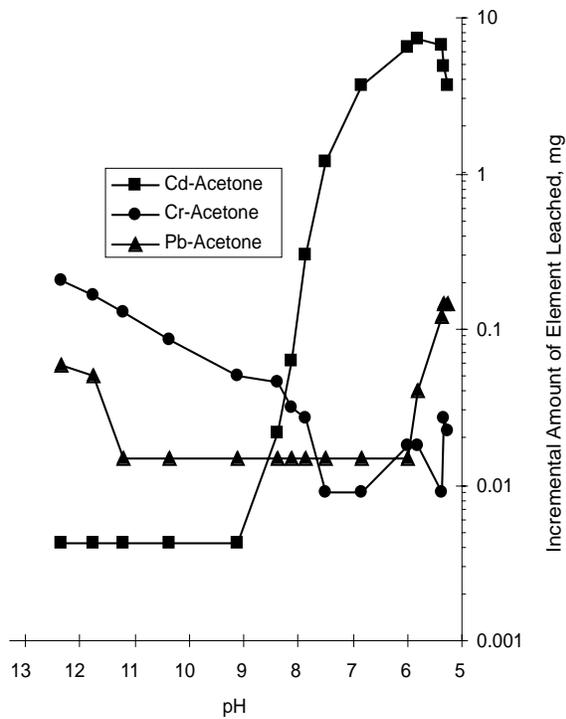


Figure 4-7. Incremental leach of metals, TSC4D soil cement.

could itself neutralize some of the acetic acid and thereby increase the buffering capacity of the system. To provide a “worst case” scenario, the dolomitic sand and pea gravel components were replaced with siliceous substitutes. This new soil system was also contaminated with 8% aged oil (by mass), and when stabilized with 8% portland cement and contaminated with metals at a level comparable to those previously employed, was designated as system TSC5. The incremental amount of each of the three metals leached from this system as a function of pH is given in Figure 4-14. While the cadmium results do not appear to differ significantly from those obtained with a dolomitic soil, the chromium and lead are more leachable, particularly at the lower pH values. For a given amount of acetic acid used, of course, the siliceous soil system attained a much lower pH than its dolomitic equivalent, because of the neutralizing capacity of the dolomite.* The corresponding cumulative results are given in Figure 4-15.

* The dolomite, although alkaline, obviously dissolved quite slowly at a pH of around 5.0. There was a significant amount of unreacted calcium left in the sample at the end of thirteen leach cycles, in spite of the acidic pH. This calcium was principally in the form of unreacted dolomite.

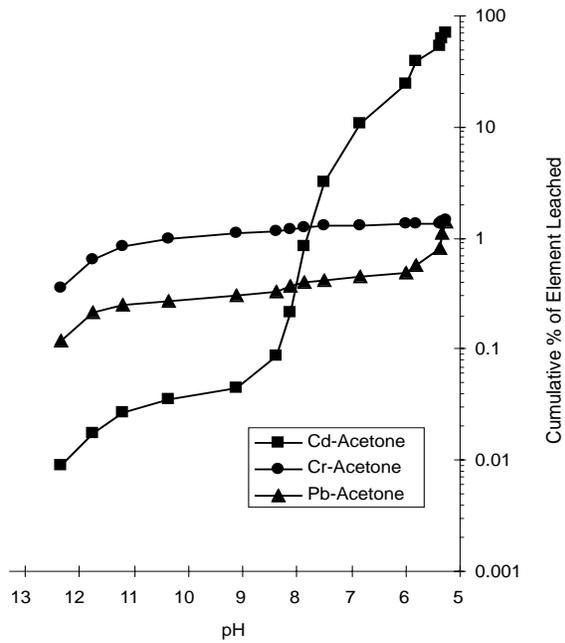


Figure 4-8. Cumulative leach of metals, TSC4D cement.

One key comparison, of course, involves the leachability of the metals in the contaminated soil system (TSC2), the oily waste with dolomitic soil (TSC4O), and the oily waste with siliceous soil (TSC5). This comparison, shown in Figure 4-16, reveals a number of interesting contrasts:

- for stabilizing chromium, the calcareous soil appears to be more effective in all pH ranges;
- for cadmium, the calcareous soil outperforms the siliceous soil at pH values above 8.0, but lags at lower pH values;
- for lead, the siliceous soil is better at very high pH values above 11, but is less efficient than its dolomitic counterpart below this pH.

Because it has already been demonstrated that cadmium control is principally a matter of pH, these findings seem to clearly demonstrate that dolomite has a beneficial effect on the stabilization of heavy metals, where the system may be subjected to significant acid attack. Dolomite would appear to be a low-cost additive to cement S/S systems for acidic wastes, because it has the capability to “stretch” the effectiveness of the portland cement used.

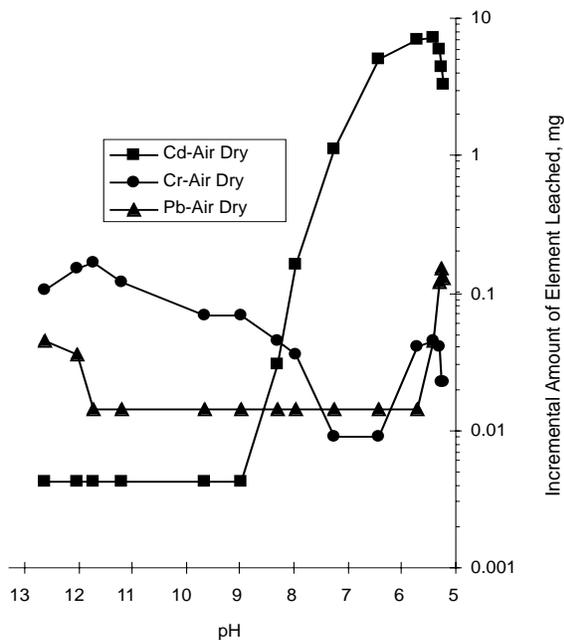


Figure 4-9. Incremental leach of metals, TSC4O soil-cement.

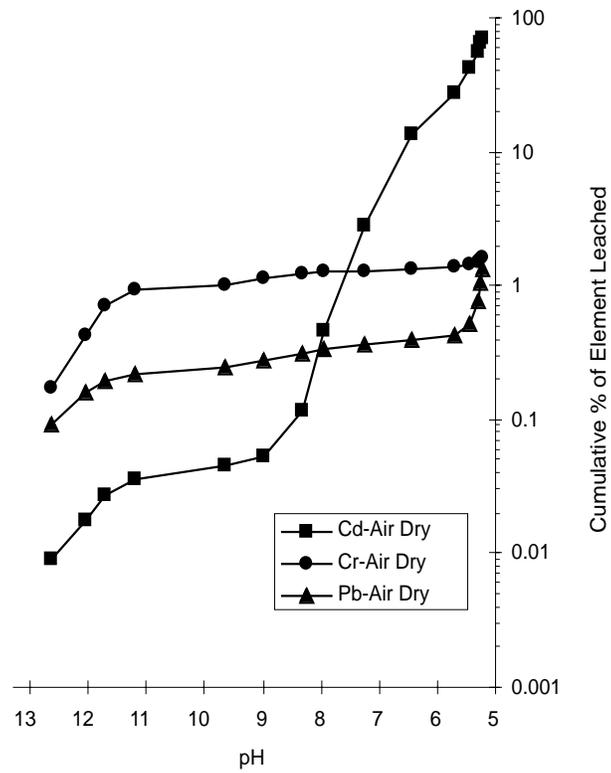


Figure 4-10. Cumulative leach of metals, TSC40 soil-cement.

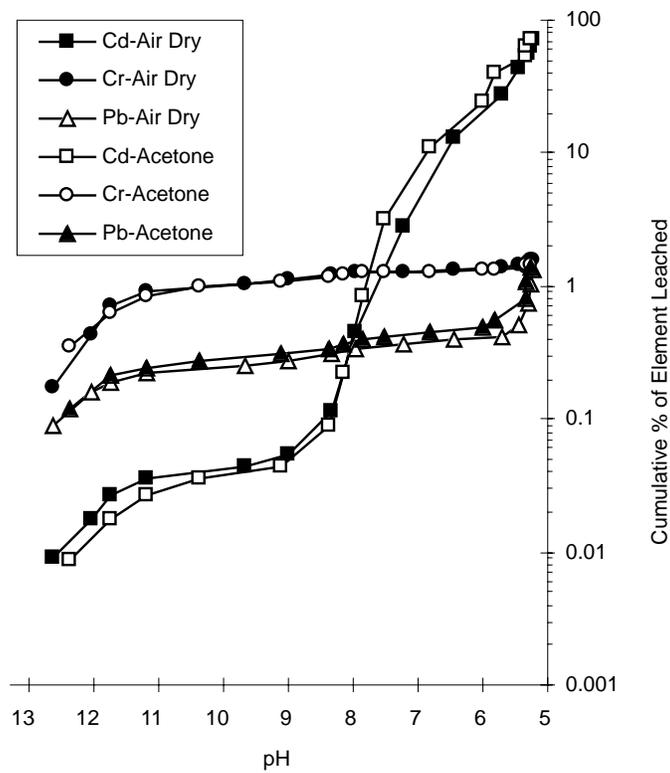


Figure 4-11. Comparison of metals leached vs cube drying method-oily waste.

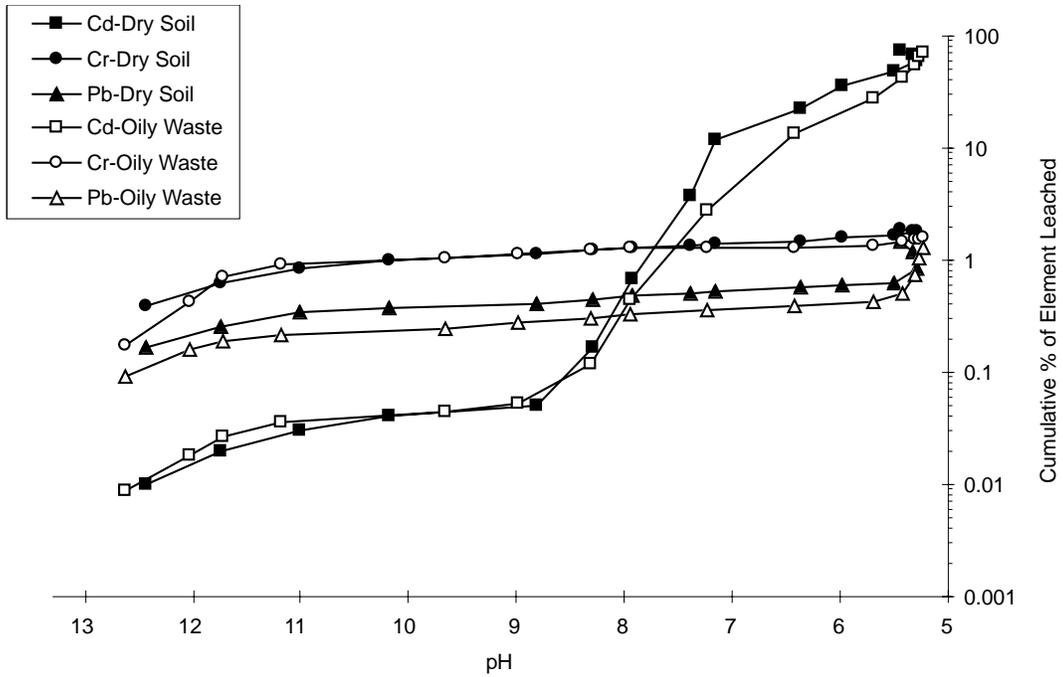


Figure 4-12. Comparison of cumulative leach vs pH, oily waste vs non-oily waste.

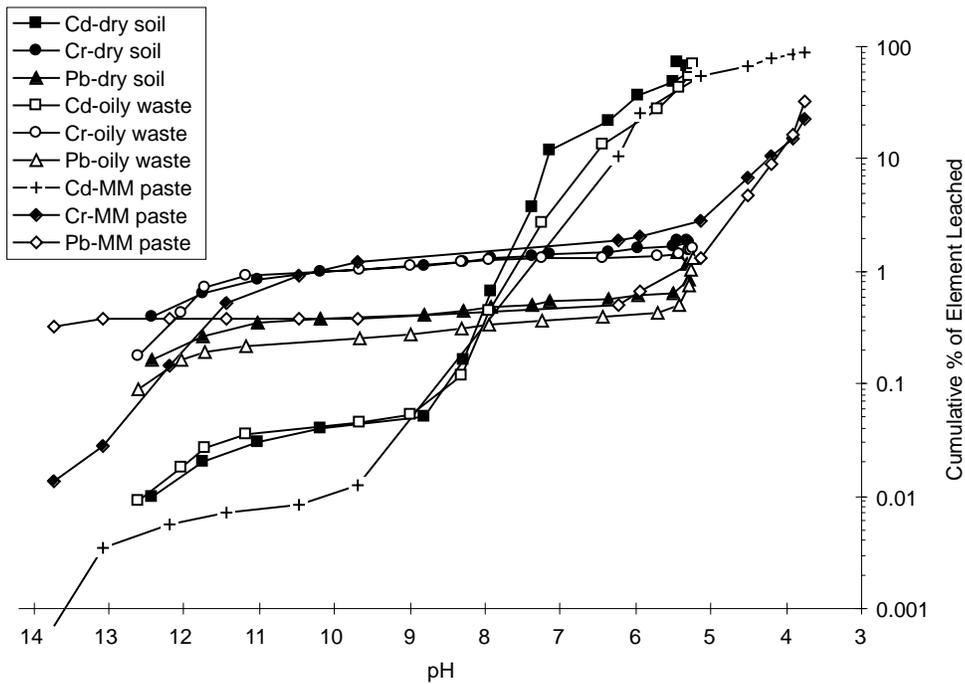


Figure 4-13. pH dependence of cumulative leach paste, soil, oily waste.

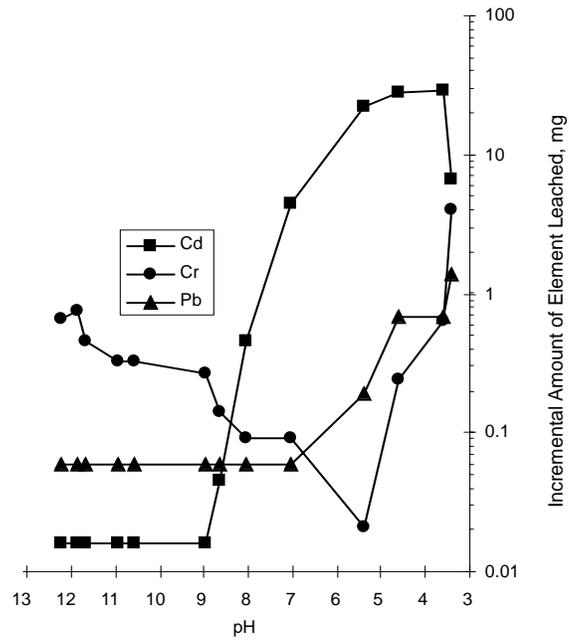


Figure 4-14. Incremental leach of metals, TSC5 soil-cement (siliceous).

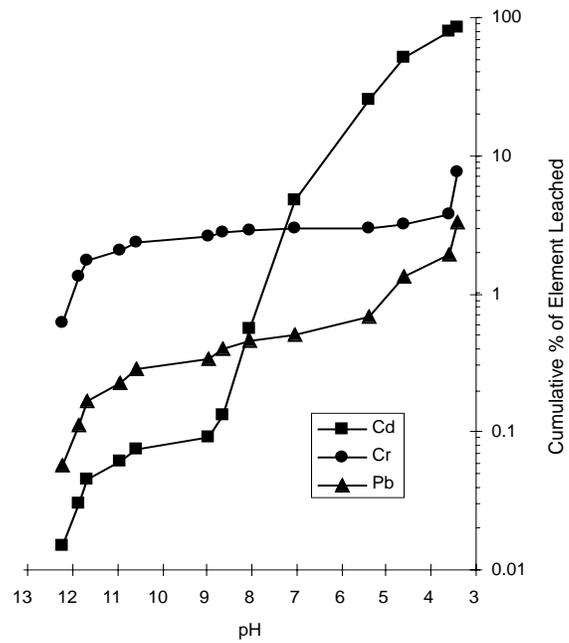


Figure 4-15. Cumulative leach of metals, siliceous soil-cement.

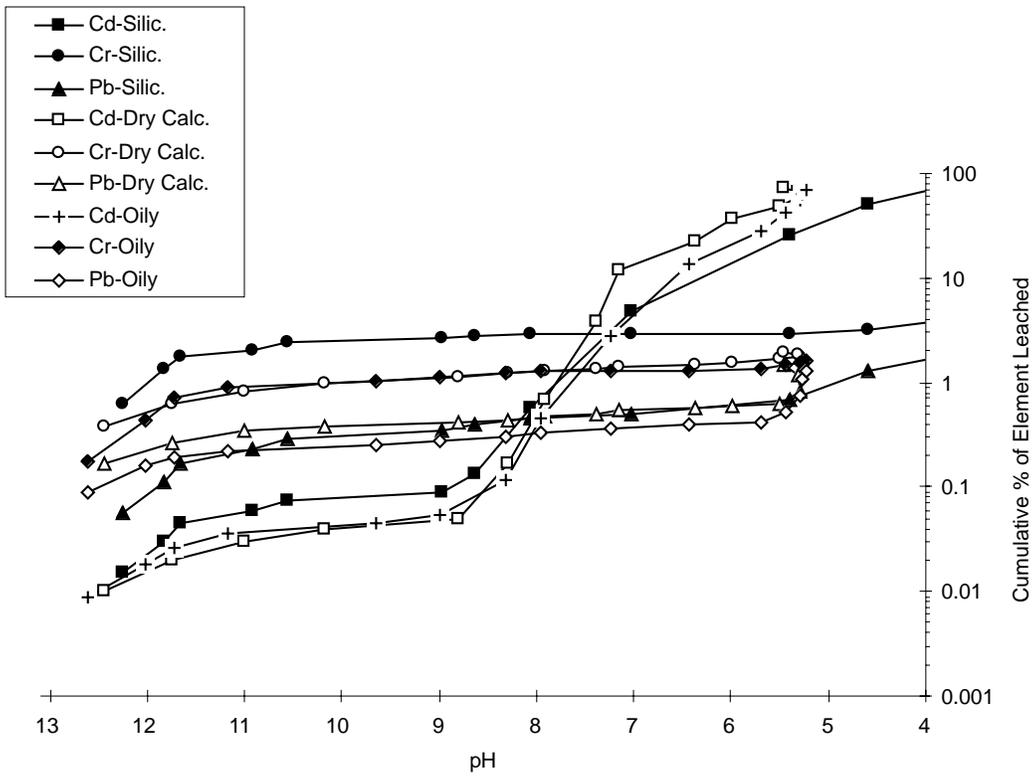


Figure 4-16. Comparison - cumulative % leach for oily waste calcareous soil, and siliceous soil.

CHAPTER 5

Use of Matrix Modifiers to Improve Metals Stabilization to Acetic Acid Leaching

As noted above in the discussions of the single metals and multiple metals leaching experiments, there had been a tendency for small, but potentially significant, levels of lead and chromium to leach out in the early batch leaching steps, when the pH was high. In addition, the results suggested that these two metals did not begin to leach appreciably until the aluminum also began to appear in the leachate in a significant concentration. These results led to the inference that the metals, perhaps particularly chromium by virtue of its ionic size, might have been stabilized in the ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) crystal lattice. It is well known that ettringite is far less soluble than calcium monosulfoaluminate hydrate ($C_3A \cdot CaSO_4 \cdot 12H_2O$).

These results, in turn, suggested that the initial early solubility of lead and chromium might be suppressed if a system could be devised that would:

- Avoid the high pH conditions that appeared to increase lead solubility, and
- Increase the amount of tricalcium aluminate that was converted to ettringite, rather than to monosulfate, hence providing more ettringite for potential ionic substitution.

Clearly, the addition of supplemental gypsum to the paste mixes would have the potential to increase the amount of ettringite formed, relative to monosulfate. Furthermore, the addition of the very reactive silica fume should tie up calcium hydroxide as generated more effectively than, for example, fly ash, since it is much finer and is ordinarily also higher in pozzolanic reactivity.

It was recognized that there could be an optimum amount of gypsum for this application. Even if more ettringite were obtained from a very high gypsum dosage rate, it would detract from the overall alkalinity of the system by dilution, and might thus be less effective for stabilization of cadmium. In addition, too high a gypsum content could actually retard ettringite formation by building a

boundary layer of ettringite between the anhydrous C_3A and the gypsum. For these reasons, two supplemental gypsum levels were selected, representing (1) 2/3 of the amount of gypsum required to convert all C_3A to ettringite, and (2) the full complement of gypsum required to convert all C_3A to ettringite. There was no effort to optimize the amount of silica fume added to the mix; the amount chosen was that quantity stoichiometrically equivalent to all the calcium hydroxide that would be generated by hydration of the calcium silicate phases in the cement. (Probably, the optimum is less than this amount, but it was not within the scope of this project to determine such optimum.)

EXPERIMENTAL WORK

The following series of cement pastes were prepared in this task:

- Series 1 - Type I portland cement, with added gypsum, calculated to convert 2/3 of the available tricalcium aluminate to ettringite (95.3% cement, 3.01% gypsum, 1.69% hemihydrate- $CaSO_4 \cdot 0.5H_2O$). This series was referred to as the "Low Gypsum, Three Metal", or LGTM, system. No provision to convert the aluminoferrite phase to ettringite was made.
- Series 2 - Type I portland cement, with added gypsum, calculated to convert all of the available tricalcium aluminate to ettringite. This series was referred to as the "High Gypsum, Three Metal", or HGTM, system.
- Series 3 - Type I portland cement, with silica fume added in sufficient quantity (14.4% by weight of cementitious materials, or 16.8% by weight of cement) to react with all the calcium hydroxide calculated to be generated in the hydration of the tricalcium silicate and dicalcium silicate. This series was referred to as the "Silica Fume, Three Metal", or SFTM, system.

The pastes were prepared and molded into 25.4-mm (1-inch cubes) as described for the multiple metals leaching experiments (designated "Preparation of Paste Specimens"). In the case of the silica fume study, it was necessary to add a high-range water reducer or "superplasticizer" to overcome the high water demand of the system. Twenty (20) grams of superplasticizer were used with an 1800-gram batch (about 1.1% by weight).

The fresh pastes were examined for paste consistency (mini-slump), paste temperature, and initial time-of-set, for comparison with the pastes from the single metal and multiple metals studies. These results are given in Appendix E. Compressive strength measurements were made at 3, 7, and 28 days, with results as shown in Table 5-1 below.

Not surprisingly, the over-optimum gypsum content causes a strength loss relative to the control, while the silica fume-modified cement shows excellent strengths at all ages of measurement. To prepare the cubes for leaching after curing for 90 days, they were crushed to pass a 74- μ m (No. 200 mesh) sieve and dried with acetone. They were subjected to leaching using the dilute acetic acid leaching regimen described in Appendix B.

Table 5-1. Compressive Strength Measurements

| LGTM, HGTM, and SFTM compressive strengths, MPa (psi) | | | |
|---|-------------|-------------|-------------|
| | 3-day | 7-day | 28-day |
| LGTM | — | 22.8 (3300) | 43.9 (6370) |
| HGTM | — | 17.4 (2530) | 23.4 (3400) |
| SFTM | 33.8 (4900) | 46.9 (6800) | 68.7 (9970) |

RESULTS AND DISCUSSION

Incremental Leaching, LGTM System

The elemental concentrations of the three trace metals are plotted against the pH in Figure 5-1. The lead has a small leachability at the very high pH values greater than about 11.5, but then remains unleachable down almost to pH 4. Below this pH, the leachability of lead increases sharply. Cadmium also has an initial slightly higher leachability at very high pH, but then remains essentially completely stabilized until the pH is less than about 8, at which point the solubility becomes rapidly higher. Chromium has a low, but measurable, leachability below about pH 11.5, with small peaks at pH 11 and pH 7.

However, it does not increase above about 0.3 mg/L until the pH decreases below about 4.

Incremental Leaching, HGTM System

The elemental concentrations of the metals in the HGTM system are plotted against pH in Figure 5-2. Lead has no initial high pH leachability, but starts to become soluble as the pH decreases at about pH 6, which is a higher threshold than found in the LGTM system. For cadmium, the solubility seems to increase already at pH 10, indicating that this stabilization system is less effective than the LGTM system for stabilizing this metal. Chromium has a peak in leachability at pH 11. In other respects, it seems to be less soluble than in the LGTM system at medium high pH, and more soluble at lower pH (<6) and very high pH (>11). Neither of the enhanced-gypsum systems seem to be advantageous for chromium stabilization relative to the cement alone. This will be discussed later in greater detail.

Incremental Leaching, SFTM System

The elemental concentrations from each sequential leach for the SFTM system are shown in Figure 5-3. Lead begins to be soluble already at a pH of about 6.5, though the slope of the curve is more gentle than for the other systems. Cadmium already begins to become soluble at a pH around 9.5, which is disadvantageous relative to the lower pH threshold for the LGTM system. Chromium exhibits the same peak in leachability at pH 11, but in other respects appears to be far better stabilized than in the other two matrix modified systems.

Incremental Leach, Lead Comparison

Figure 5-4 summarizes the comparison of the effectiveness of the three systems in stabilizing lead. The initial high pH bump for the LGTM system is not duplicated in the other two systems; but thereafter, down to a pH of almost 4, there is no additional leachability. Leachability in the other two systems begins in the pH range of 6.5-7.0. Hence, if the system could be maintained at high pH, perhaps the silica fume modification might be the most effective of the three under study.

Incremental Leach, Chromium Comparison

Figure 5-5 summarizes the situation with chromium. Here, it is clear that the silica fume-modified system

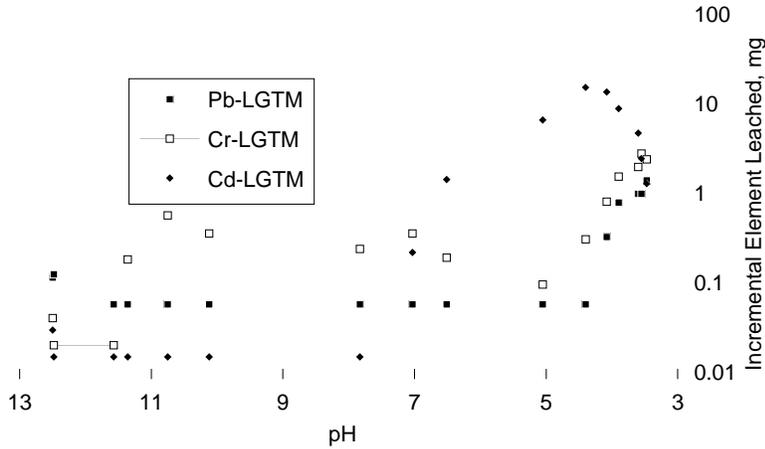


Figure 5-1. Trace metal incremental leach vs pH-LGTM.

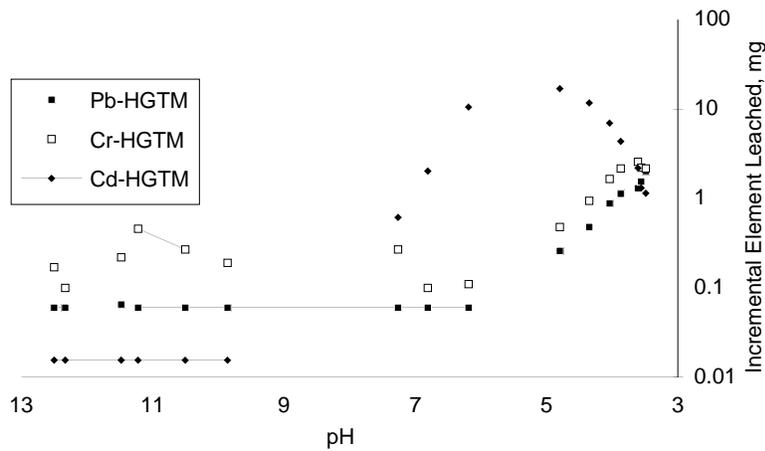


Figure 5-2. Trace metal incremental leach vs pH-HGTM.

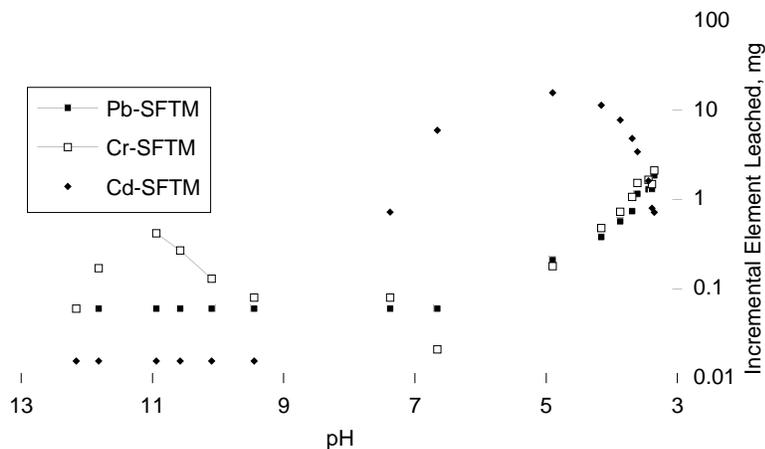


Figure 5-3. Trace metal incremental leach vs pH-SFTM.

is the most successful throughout a wide pH range. At the very high pH levels, the LGTM system appears to result in the lowest leachability.

Incremental Leach, Cadmium Comparison

As can be seen in Figure 5-6, with the exception of the very high pH range above 12.5, the LGTM system is by far the most effective stabilizer of the three evaluated. Leachability begins at a much lower pH than for the other two systems, and remains significantly lower at all pH values above pH 5. There is little difference between the other two systems.

Cumulative Leaching Data

Of course, all the above results are for the incremental leach per cycle. The data for cumulative leaching may be more meaningful. In this comparison, we will also include the data from the multiple metals study without matrix modifier (“neat paste,” referred to on the graphs as “Pb,” to distinguish from “Pb-SF,” for example).

The leachability of the metals lead and cadmium can be conveniently discussed in three pH ranges:

1. From pH 14 down to about pH 11
2. From about pH 11 to about pH 5
3. Below pH 5

LEAD

In the case of lead, there are some definite leachability reductions at high pH associated with using either silica fume or excess gypsum. Figure 5-7 shows the relative cumulative leachabilities, as a function of the pH of the system, for lead in the Type I cement matrix, the low gypsum and high gypsum matrices, and the Type I cement/silica fume matrix. For high pH values, the matrix containing silica

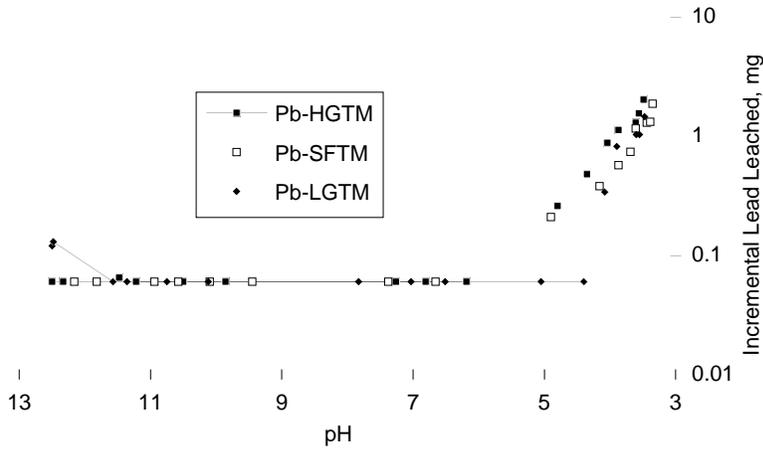


Figure 5-4. Incremental lead leach, matrix modified system.

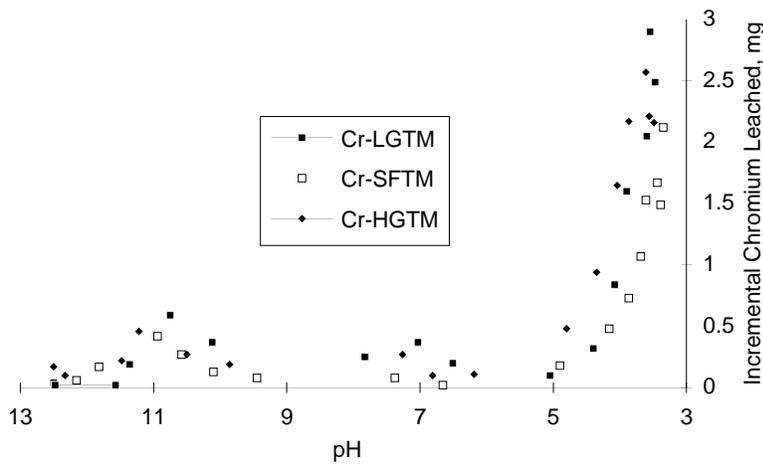


Figure 5-5. Incremental chromium leach, matrix modified systems.

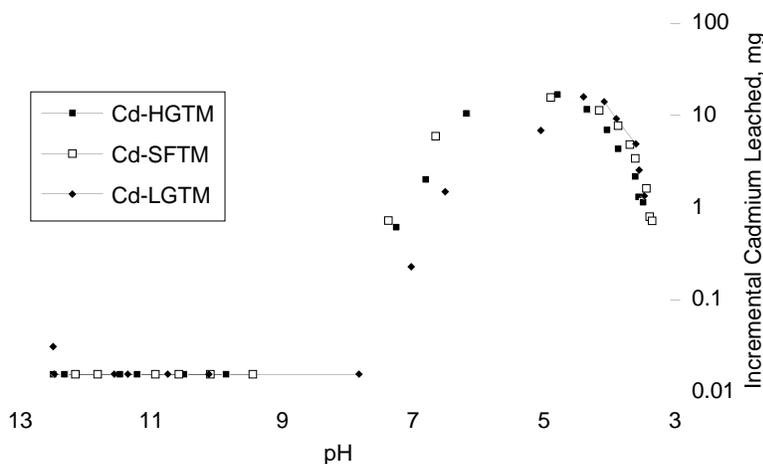


Figure 5-6. Incremental cadmium leach, matrix modified systems.

fume gives the best results, then the high gypsum system. In the broad intermediate pH range, from about 10 to about 5, the neat cement matrix outperforms any of the modified systems; however at low pH < 5, the neat cement shows considerably higher leachabilities than any of the modified systems. The silica fume-modified system performs the best at low pH, as might be expected. Chemisorption or physical adsorption of lead on the calcium depleted C-S-H phase appears to be indicated; since the silica fume matrix has the highest concentration of this phase, the results would be anticipated. The lower leachabilities of the gypsum-modified cements relative to the unmodified material at low pH may be due to stabilization in, or adsorption on, aluminate phases, or it may simply be due to the reduced solubility of lead sulfate in excess sulfate ion. Depending, therefore, on the pH to be anticipated in the stabilized waste, if lead is the principal metal to be stabilized, it may be appropriate to use silica fume modification, or perhaps some gypsum augmentation, or both.

As discovered in the multiple metals studies, lead leaching seems to be significantly associated with alumina leaching, as can be seen in Figure 5-10. In addition to the other mechanisms suggested, this may be the case because lead and alumina are both substituted in the C-S-H phase, and the solubilization of both occurs roughly at the same pH value. Scanning electron microscopy/energy dispersive x-ray analysis would be very helpful in distinguishing among these various explanations.

CHROMIUM

Chromium's behavior is somewhat more complex than that of either cadmium or lead. Figure 5-8 shows the relative cumulative leachabilities, as a function of the pH of the system, for chromium in the Type I cement matrix, the low gypsum and high gypsum ma-

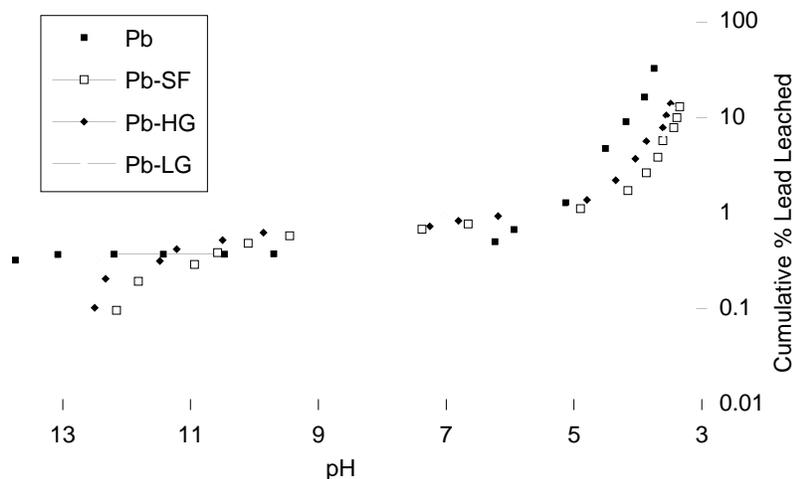


Figure 5-7. Leachability of lead vs pH.

trices, and the silica fume-modified matrix. At very high pH there appears to be a tendency for the lower-sulfate augmented gypsum sample to outperform the other systems. This would be consistent with chromium substitution in the additional ettringite that has been generated. The highest sulfate level material, however, does not perform as well as the control to the extent that differences are statistically significant. Between about pH 11 and about pH 5.5, the control outperforms all the modified materials, with the silica fume-modified sample performing better than either gypsum-modified sample. This would appear to suggest that some of the chromium may be tied up with the C-S-H phase—this is not surprising in light of the findings in the multiple metals leaching study, and as found by Bishop [1988]. Below about pH 5.5, the silica fume-modified system clearly outperforms all other systems, and the gypsum-modified systems marginally outperform the control below pH 5. This latter effect may mirror the lower solubility of ettringite vis-a-vis monosulfate; the former supports the effectiveness of C-S-H as a stabilizing medium. Again, as observed in the multiple metals leaching and as shown in Figure 5-11, the chromium and silica leaching appears to follow a similar path. The correlation with the aluminum leaching (Figure 5-12), while still quite close, does not appear to be as plainly visible as that with silica.

One factor potentially complicating the interpretation of the chromium results is the possibility that chromium could be undergoing some oxidation to the hexavalent state. Chromium was added to the system as Cr^{3+} , since it was known that hexavalent chromium was far more difficult to stabilize. The longer the material remains at high pH, the more risk there is that some of the trivalent chromium may be

oxidized to hexavalent chromium. The oxidation potential for the transformation of trivalent Cr to hexavalent Cr is favorable at high pH, and highly unfavorable in acid. The lower the pH, therefore, the less likelihood there is that the rather easily stabilized Cr^{3+} is being converted to the relatively soluble Cr^{6+} .

CADMIUM

In the case of cadmium, the picture is again quite simple, as it has been for all the previous systems studied. The effective stabilization of cadmium again appears to be principally a case of pH. The cement without any additives has the highest pH for the longest time and therefore is the best stabilization medium. Figure 5-9 shows the relative leachabilities of cadmium, as a function of the pH of the system, for cadmium in the Type I cement matrix, the low gypsum and high gypsum matrices, and the silica fume matrix. At high pH (above 8.0) the silica fume matrix is marginally better than the two mixes with enhanced gypsum, but not nearly as effective as the neat cement paste matrix. Below pH 7, the four mixes are all poor, and almost indistinguishable. At very low pH values below about 5.0, the stabilization with silica fume may be marginally better than the other matrices.

With respect to synergies between the leaching of cadmium and that of any other of the major elements, none were discovered, as had been the case with the multiple metals pastes, and as can be seen in Figures 5-13, 5-14, and 5-15. As a consequence, it seems even more clear that cadmium is not appreciably substituted in the lattice of any of the cement hydration minerals, irrespective of their relative quantities, and that the effectiveness of cadmium stabilization is based principally on the maintenance of a high pH.

In summary then, the data provide good evidence that, while the cement matrix by itself insolubilizes and immobilizes certain metals very effectively, it appears likely that especially under certain pH conditions, the addition of a pozzolan (viz. silica fume) may enhance stabilization of lead and chromium. Under very high and low pH conditions, the augmentation of sulfate content in the cement may also result in improved immobilization. However, with respect to cadmium, pure cement appears to be the most effective of the S/S reagents tested.

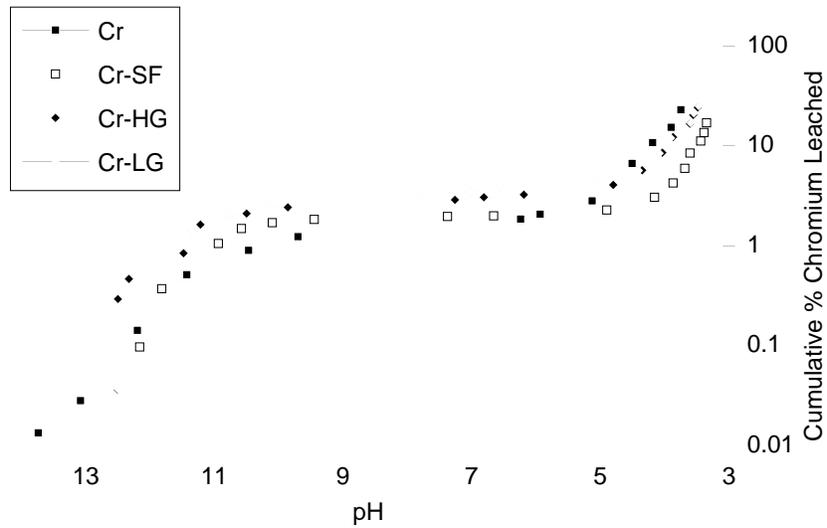


Figure 5-8. Leachability of chromium vs pH.

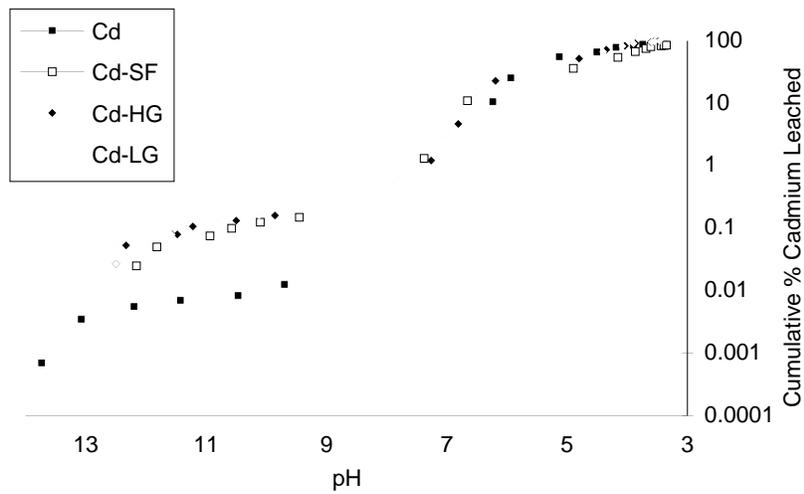


Figure 5-9. Leachability of cadmium vs pH.

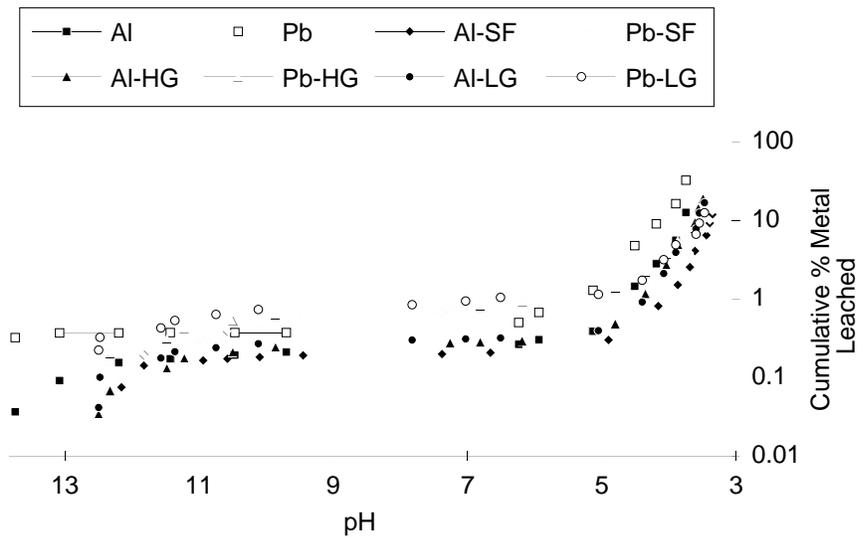


Figure 5-10. Leachability of lead and alumina with HOAc.

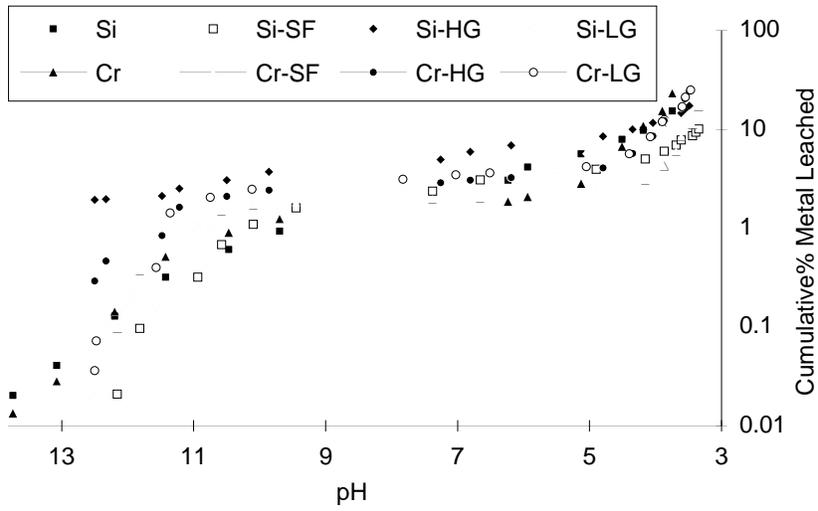


Figure 5-11. Silicon and chromium vs pH-LG,HG,SF,R.

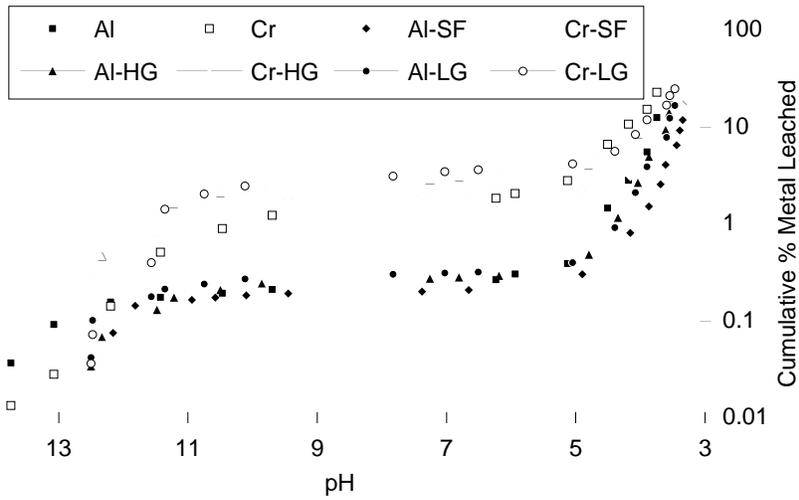


Figure 5-12. Aluminum and chromium vs pH-LG,HG,SF,R.

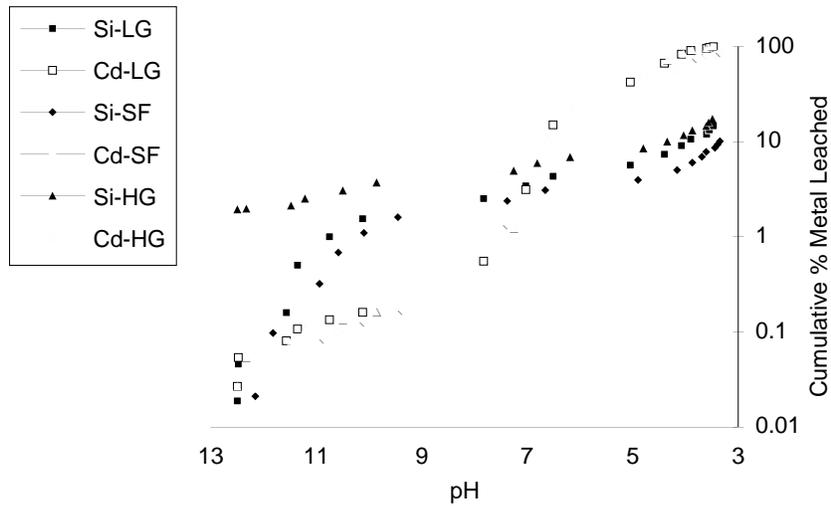


Figure 5-13. Silicon and cadmium vs pH-LG,HG,SF.

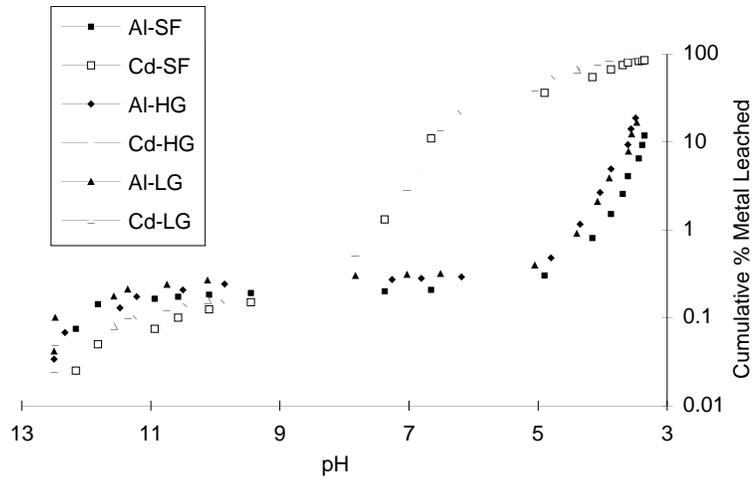


Figure 5-14. Aluminum and cadmium vs pH-LG,HG,SF.

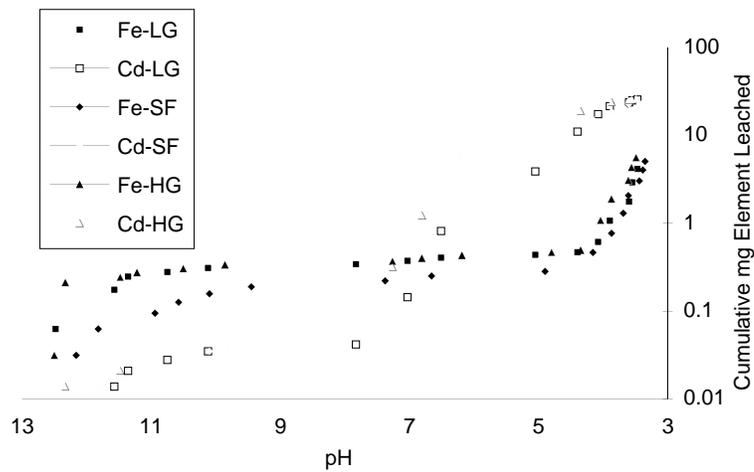


Figure 5-15. Cadmium and iron vs pH-LG,HG,SF.

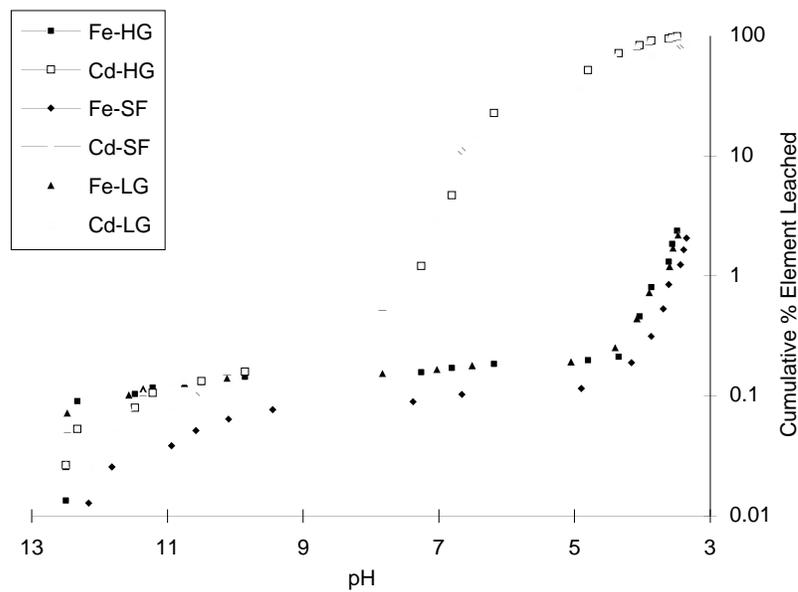


Figure 5-16. Cadmium and iron vs pH-LG,HG,SF.

CHAPTER 6

The Special Problems of Arsenic Stabilization

Arsenic is a metalloid and exhibits some amphoteric behavior; that is, it would tend to be more soluble at both low and high pH, than at intermediate pH, in an unstabilized system.

Arsenic has been claimed to be toxic to the human liver, kidneys, and peripheral nerves. It is also reportedly implicated in skin, digestive, glandular, blood and respiratory problems. Limited data indicate that it may cause spontaneous abortion, and it is a suspect, and even probable, human carcinogen. At very low pH and reducing conditions a highly toxic gas (arsine, AsH_3) forms. Toxicity to animals and plants has also been demonstrated. Thus it is prudent that leachate levels be kept to a reasonable minimum.

Further complicating the problem is that the disposal techniques ideally should result in products stable "for all time." Most likely, maintaining the very low TCLP leach concentration of 5 mg/kg will be the most serious restriction, since government limits very likely will be even stricter in the future. Also sludges and semi-solids tend to be highly variable in composition. Perhaps contaminant concentrations varying by a factor of five to one are likely in the same waste. Thus, disposal schemes must be *extremely robust* to handle the vagaries of extended time, regulations, and changes in the storage environment.

Most empirical disposal schemes have been found to work for only a limited scope of materials. This is especially true for arsenic wastes, because of the complexity of arsenic chemistry. Arsenic exists in several oxidation states (-3,+3, and +5), although the latter two are the most common. In water, arsenic is not present as a simple metal ion, but rather as the arsenite (+3 oxidation state) or arsenate (+5 oxidation state). Furthermore, unlike lead, cadmium, and chromium, arsenic does not form insoluble hydroxides or hydrous oxides. Data by Robins [1988] shows the complex ions present at various pH values as a function of oxidation potential (Figure 6-1).

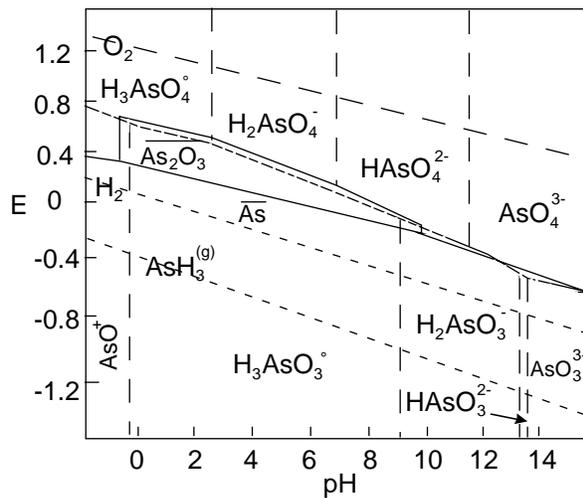


Figure 6-1. Complexions at various pH values. Robins 1988.

Since initial pH in a hydrated cement matrix ($E_h = +0.1$) is 12 to 12.5 and a plentiful supply of Ca^{2+} ion is available from the calcium silicate hydration, calcium arsenate [$\text{Ca}_3(\text{AsO}_4)_2$] is the predominant arsenic compound present. It is interesting to note that calcium arsenate is much less soluble than calcium arsenite, as shown in Figure 6-2 by Stefanakis and Kontopoulus [1988]. This confirmed earlier work by Robins [1983]. Peroxide oxidation can be used to convert the arsenite to the arsenate. Less costly oxidation with air or oxygen may be possible at higher temperatures with adequate exposure of new surface area (vigorous stirring). Conner [1990] indicated that organoarsenic compounds may require oxidative decomposition before solidification/stabilization treatment can be successfully employed.

Calcium arsenate was in fact the form used in the past to stabilize arsenic. Based on studies by Twidwell et al. [1994], Lear and Conner [1992], and Nishimura et al. [1988], calcium arsenate is now considered unstable with respect to carbonation, the

end-product being calcium carbonate in high pH systems. This may be more of a problem in aerated lagoons than in a cement matrix. Even after many years, carbonation does not extend far into normal low permeability cement matrices. If the disposal site is sealed with an impermeable layer of, for example, clay, carbonation may not be a problem, except perhaps in the very long term. The literature indicates that the arsenate does not substitute in the calcium silicate hydrate gel; rather, it is encapsulated or adsorbed. In another proposed stabilization mechanism, arsenic as the oxyanion may substitute for sulfate in ettringite [Hassett et al., 1989]. This substitution is similar to what happens with boron and selenium, two other semi-metallic elements which also exhibit amphoteric tendencies. Such a substitution may be hard to accomplish in a high sulfate environment where the excess sulfate is competing with the oxyanion to substitute in the ettringite. Ettringite is very insoluble at high pH, but is also subject to carbonation. For the long term, additional protection of the arsenic is prudent. Such protection might be accomplished by a reactive silica (fly ash or silica fume) which would react with excess lime to form calcium silicate hydrate, which does not carbonate as easily as hydrated lime. Tashiro et al. [1977] indicated that arsenates do not seem to be powerful retarders for cement hydration, although Sheikh et al. [1988] showed that a very high level (7.5% addition) reduced the strength by about 45%.

RATIONALE FOR EXPERIMENTAL MATRIX SELECTION

Most successful arsenic stabilization schemes do not rely on S/S with cement alone. Many of the successful methods additionally use either iron (+2) or iron (+3) sulfates as additions. Although the pure compounds are quite expensive, ferrous sulfate is available as a waste (K001). (This is a RCRA listed hazardous waste, and land ban leachability limits may apply.)

Robins [1988] reports, significantly, that Fe^{2+} does not reduce As^{5+} . D004/D005 wastes were treated by Taylor and Fuessle [1994] with cement and fly ash using a pre-oxidation step. They concluded that Fe^{3+} was not as effective a precipitant as Fe^{2+} over wide ranges of mix designs and over the long term. The rationale for this difference was that encapsulation of the ferric hydroxy-arsenic complex, a larger molecule, was harder to achieve than it was with the smaller ferrous arsenic compound. Their recommended Fe^{2+} -to-arsenic mole ratio was at least 6. The failure of Fe^{3+} was attributed to the fresh cement

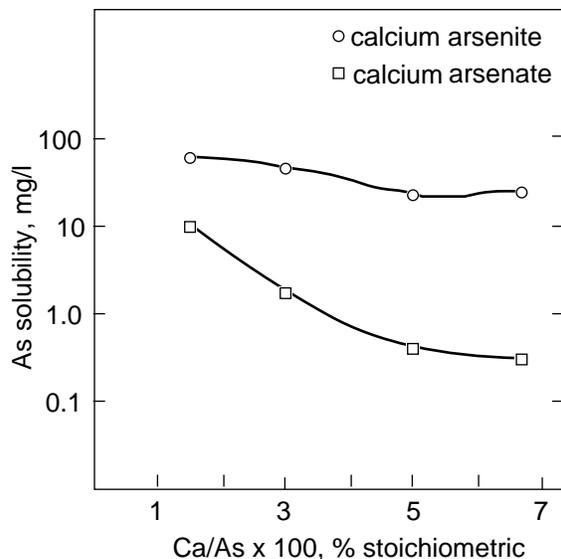


Figure 6-2. Stefanakis and Kontopoulus 1988.

paste absorbing the ferric ion. An inspection of their data indicates that the best overall short term (2-day) and also long term (540-day) stabilization was achieved with a 0.40 binder-to-waste ratio. The arsenic leaching showed a continuous drop with age indicating excellent long term potential. On the other hand, a 0.15 binder-to-waste ratio, although acceptable at 2 and 60 days, showed definite instability after 60 days of cure. This study at Bradley University [Taylor and Fuessle, 1994] indicated that the *results of leachings after short term cures may be entirely inadequate* to indicate long term ultimate stability.

Based on the literature study and taking into account the time and funding constraints, the following test matrix was selected:

The selected molar ratio of iron to arsenic was 6.0. The soil was siliceous and contained no intentionally added dolomite. ASC1 was selected to form the more sparingly soluble precipitate as found in the Bradley University study. The ethylenediamine tetraacetic acid (EDTA) in ASC2 was selected to chelate the lime in the ASC3 mix and to provide a lower lime environment to possibly encourage the formation of iron and/or arsenic-substituted ettringite; note that a lime-starved condition is the basis for rapid set ettringite cements [Ost et al., 1975]. ASC2 did not, however, contain added aluminum or iron compounds, which would have enabled the production of more ettringite than that possible with the portland cement alone. Thus this mix should be considered a preliminary one to indicate the effect (if any) of EDTA alone on arsenic stabilization. The ASC4 mix evaluated stabilization of arsenite, while

Table 6-1. Contents of Arsenic Test Mixes

| Mix No. | Soil | Cement | Arsenate | Arsenite | FeSO ₄ | Other |
|---------|------|--------|----------|----------|-------------------|-------------------------------|
| ASC1 | X | X | X | | X | EDTA |
| ASC2 | X | X | X | | | |
| ASC3 | X | X | X | | | |
| ASC4 | X | X | | X | X | H ₂ O ₂ |
| ASC5 | X | X | | X | X | |
| ACP | | X | X | | X | |

ASC5 employed hydrogen peroxide (H₂O₂), selected to oxidize the arsenite in the ASC4 mix. ACP was included as reference to omit the complications of the soil presence, and to provide an arsenic-containing paste sample as companion to the data base for the other metals studied.

EXPERIMENTAL WORK

The following specific mix designs and ratios were used:

The volume increase (final volume/waste volume) was estimated from the density of aged cubes or cube fragments (obtained by weighing in and out of water) and the dry soil bulk density (obtained in a graduated cylinder). The Type I cement was the same whose analysis is given in Chapter 1 of this report, dealing with the addition of metals as solu-

tions or oxides. The siliceous soil preparation and analysis is shown in Appendix D.

The arsenic compounds were Baker reagent-grade sodium arsenate, dibasic, 7-hydrate, granular (m.w. 312.01) and sodium meta-arsenite (m.w. 129.91). The arsenic concentration was chosen to be 2% of the cement level to explore how the stabilization procedures would work at a relatively high contaminant level such as might be encountered due to variations of the contaminant level in actual semi-solid wastes. It was assumed that methods effective on a relative basis at high levels would most likely also be effective at low levels. The FeSO₄ source was Fisher laboratory-grade ferrous sulfate, 7-hydrate (m.w. 278.02). The ethylenediamine tetraacetic acid (EDTA) was Baker A.C.S. reagent grade (m.w. 292.255). The EDTA addition rate (0.5% of the soil matrix) was equivalent to 3.3% on the basis of the

Table 6-2. Contents of Arsenic Test Mixes

| Mix Identifier | ASC1 | ASC2 | ASC3 | ASC4 | ASC5 | ACP |
|---|------|------|------|------|------|------|
| Cement | 600 | 600 | 600 | 600 | 600 | 721 |
| Soil | 2284 | 2806 | 2823 | 2291 | 2291 | 0 |
| Water | 798 | 524 | 527 | 821 | 821 | 697 |
| Na ₂ AsO ₄ ·7H ₂ O | 50 | 50 | 50 | 0 | 0 | 60 |
| NaAsO ₂ | 0 | 0 | 0 | 21 | 21 | 0 |
| FeSO ₄ ·7H ₂ O | 267 | 0 | 0 | 267 | 267 | 321 |
| EDTA | 0 | 20 | 0 | 0 | 0 | 0 |
| Total weight, grams | 4000 | 4000 | 4000 | 4000 | 4000 | 1800 |
| Hydrogen peroxide, in mix water | | | | | 6 | |
| Arsenic in waste, ppm | 5100 | 4200 | 4200 | 5200 | 5200 | 24% |
| Arsenic/cement, % | 2 | 2 | 2 | 2 | 2 | 2 |
| Cement/total weight | 0.15 | 0.51 | 0.15 | 0.15 | 0.15 | 0.40 |
| Fe/As molar ratio | 6.00 | 0.00 | 0.00 | 6.00 | 6.00 | 6.00 |
| Cement/(waste+FeSO ₄ ·7H ₂ O) | 0.23 | 0.21 | 0.21 | 0.23 | 0.23 | 1.89 |
| (Cement+FeSO ₄ ·7H ₂ O)/waste | 0.37 | 0.21 | 0.21 | 0.38 | 0.38 | 17.4 |
| Cement/waste | 0.26 | 0.21 | 0.21 | 0.26 | 0.26 | 12.0 |
| Water (w/ sulfate water)/cement | 1.63 | 0.98 | 0.99 | 1.63 | 1.63 | 1.20 |
| Water (w/o sulfate water)/cement | 1.43 | 0.98 | 0.99 | 1.43 | 1.43 | 1.00 |
| EDTA, % of total mix | 0.00 | 0.50 | 0.00 | 0.00 | 0.00 | 0.00 |
| Volume increase, % (waste to final) | 46.3 | 13.8 | 12.0 | 46.5 | 46.8 | N.A. |

Note: Waste=soil+arsenic compound

cement content. For mix ASC5, enough hydrogen peroxide was supplied (about 6 grams on a solid basis) as a 30 percent solution, as part of the mix water, to provide stoichiometry to convert 110% of the arsenite to arsenate.

The batch for the ACP mix was reduced in size because compressive strengths for the paste could be determined using one-inch cubes instead of the 50-mm (2-inch) cubes used for the other mixes. The mixing procedure for soil-cements and pastes was that shown in Appendix A. Whenever the ferrous sulfate was used, the water/cement ratio had to be increased by an additional 0.40 over the increase of 0.20 already provided by the water-of-hydration of the sulfate. This indicates the likelihood that a gypsum precipitation similar to false set occurred. The iron could probably react to form an iron hydroxide gel. Another reaction path—that of forming an iron substituted ettringite—is possible. Sample preparation and test regimens were as follows:

PREPARATION OF LEACH SAMPLES AND LEACHING REGIMEN

Samples containing arsenic were prepared by the procedure described in detail in Appendix A. Briefly, sample ACP (which had been subjected to hydration for 28 days) was ground and acetone-washed until fine enough to pass a 74- μm (No. 200 mesh) sieve; a sample weighing 32.01 g was leached. Each ASC series (soil-cement/arsenic) leaching sample was prepared from one of the 2-inch cubes tested for strength at 28 days. Each soil-cement cube of the ASC series was ground to separate aggregate from the remainder of the sample and then material passing a No. 20 sieve was ground and acetone-washed until that fraction passed a 74- μm (No. 200 mesh) sieve. This fine material was recombined with its associated aggregate; then a 32.01-g sample was weighed and used for the sequential batch leaching.

Leaching for all the ASC series samples was done with 0.03 M acetic acid. The ACP sample was leached with 0.1 M acetic acid for seven days and then the leachant was changed to 0.05 M acetic acid for the subsequent leaching, in order to avoid obscuring critical transitions by bypassing pH values of importance. A detailed description of the sequential leaching procedure appears in Appendix B. The leachate pH was measured each day and, when the pH of both the ACP and all the soil-cement/arsenic, ASC series, samples were less than 4.0, leaching was stopped. All samples were sequentially batch leached for 11 days.

RESULTS

Chemical Analytical Data

The chemical analysis was done by a graphite furnace method on acidified extracts. The mg/L detection limits were Ca:0.15, Si:0.6, Fe:0.12, Al:0.19 and As:0.05. Whenever an element was indicated by the chemical analysis to be below the detection limit, one half of that level was used to plot the curves, in order to use the same convention as used for the other metal studies. The following figures summarize the analytical results for leachings carried out for the arsenic study.

All mixes showed a relatively low starting arsenic concentration of 0.23 to 0.60 mg/L with the soluble arsenic in the EDTA mix being the lowest and that in the unoxidized arsenite mix being the highest.

All mixes had a maximum arsenic solubility at a pH of about 9.5. The two mixes without ferrous sulfate had excessive solubility at this point (29 and 52 mg/L). The solubility of As in the unoxidized arsenite mix slightly exceeded 5 mg/L. The oxidized arsenite and the arsenate soil mixes, both with ferrous sulfate, had a maximum solubility of about 3 mg/L. The cement paste mix released a maximum of only 1.4 mg/L. It should be noted that a definite decrease in the silicon solubility occurred at this pH of 9.5 for all mixes containing added iron compounds. The aluminum and iron solubility was below the detection level at this point for all mixes. There was also some indication that a relative increase in the calcium solubility may have occurred here, although hard to distinguish from the overall high calcium solubility.

At the end of eleven cycles of leaching, all the extracts were in the pH range between 3.3 and 3.6. The two mixes without ferrous sulfate and the unoxidized arsenite mix still were releasing approximately 1 mg/L of arsenic per cycle. The paste mix was releasing about 0.1 mg/L whereas the oxidized arsenite and the arsenate soil mixes both with ferrous sulfate were at or below the analytical detection level indicating a good level of stabilization.

The cumulative % of arsenic released during the 11 leaching cycles was exceptionally high (40 to 45%) for the two mixes without ferrous sulfate. It was 10% for the unoxidized arsenite mix, and 4% for the oxidized arsenite and arsenate soil mixes all with ferrous sulfate. The paste mix released only 0.7% of the available arsenic.

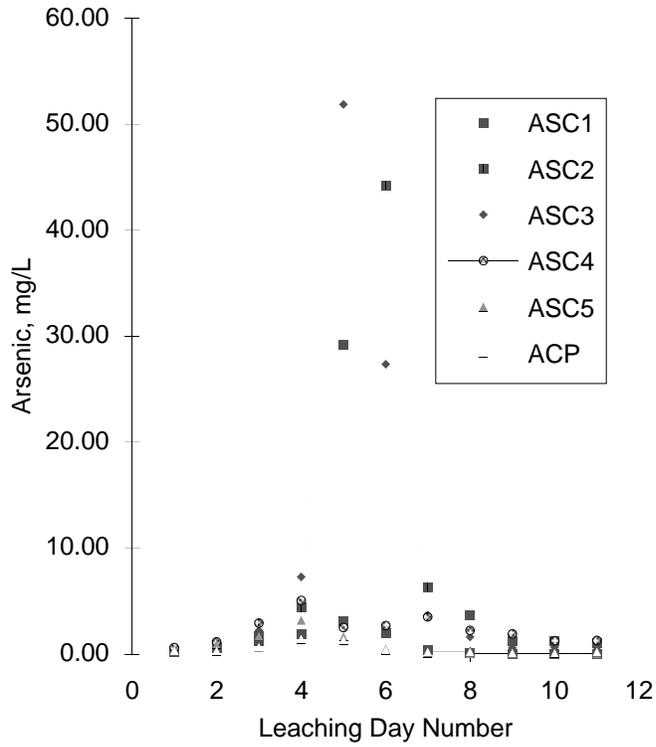


Figure 6-3. Arsenic concentration vs leaching day number.

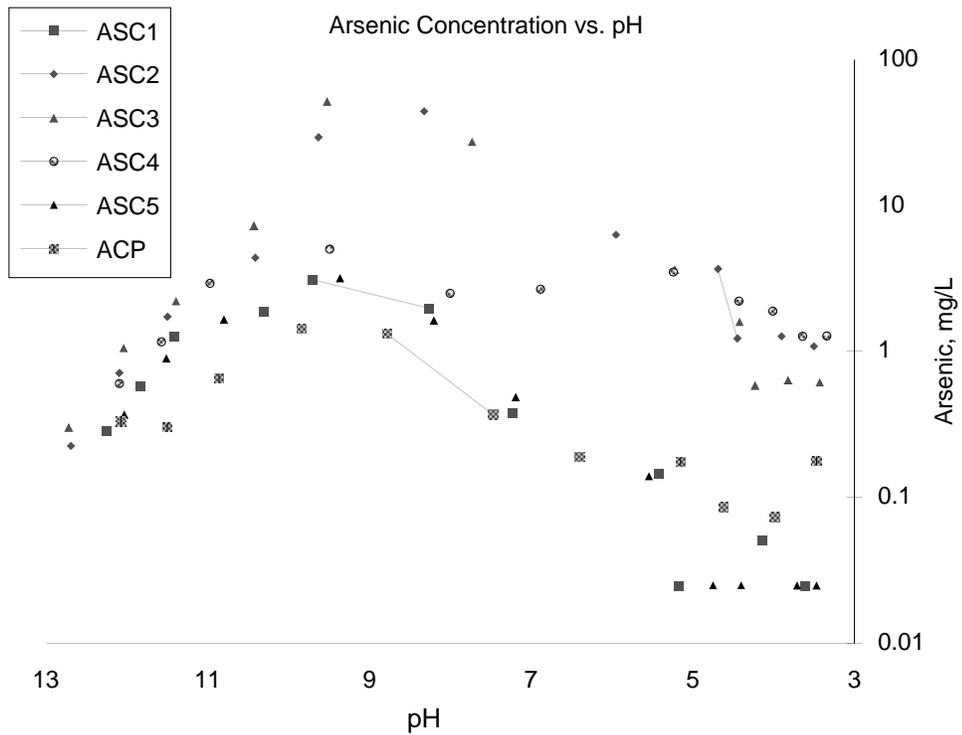


Figure 6-4. Arsenic concentration vs pH (all mixes).

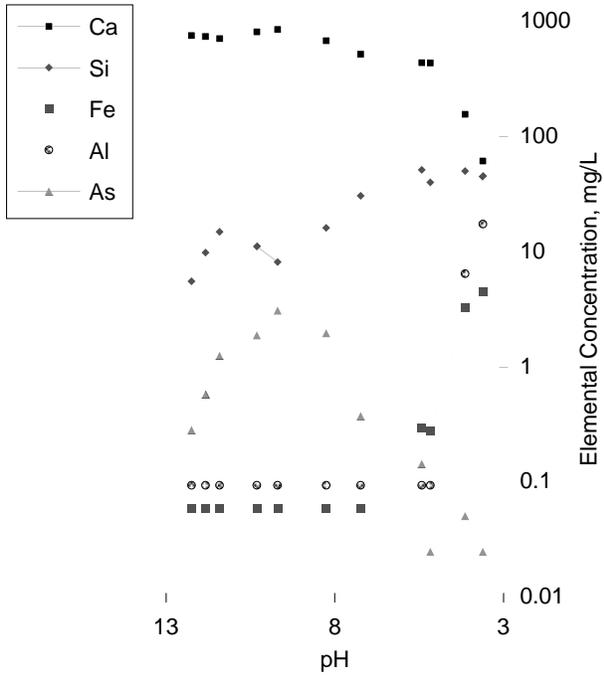


Figure 6-5. ASC1 Element concentrations vs pH.

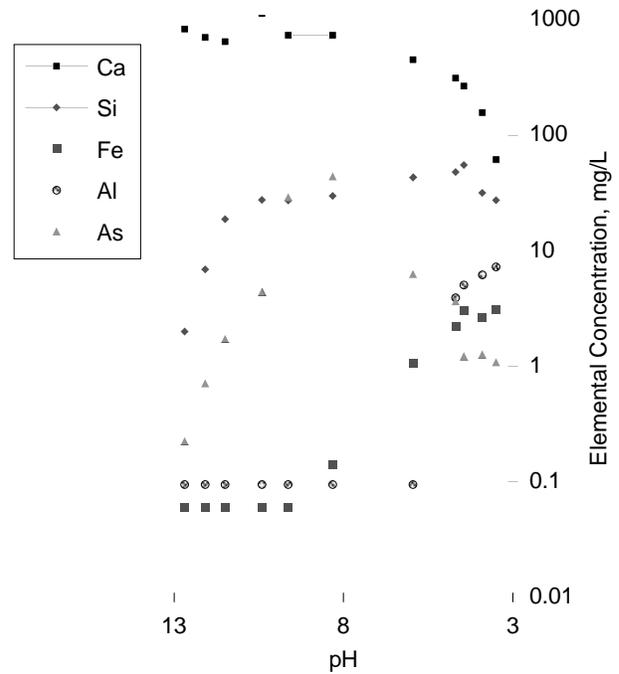


Figure 6-6. Soil, As(+5), EDTA, No FeSO_4 .

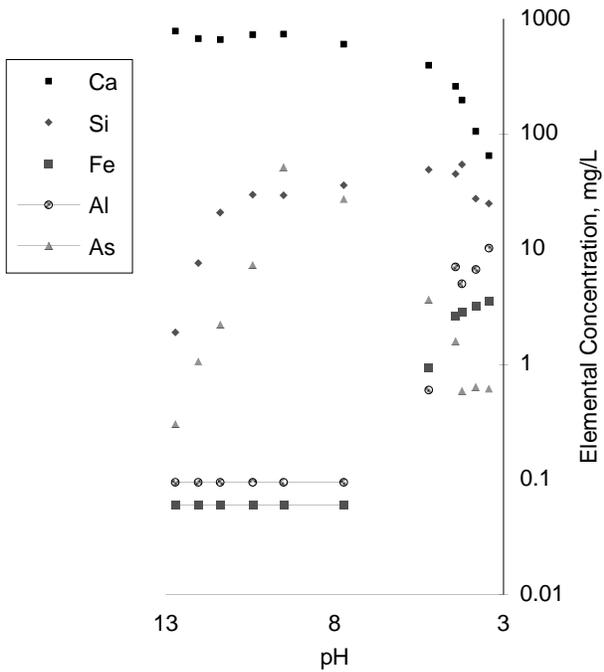


Figure 6-7. Soil, As(+5), No FeSO_4 .

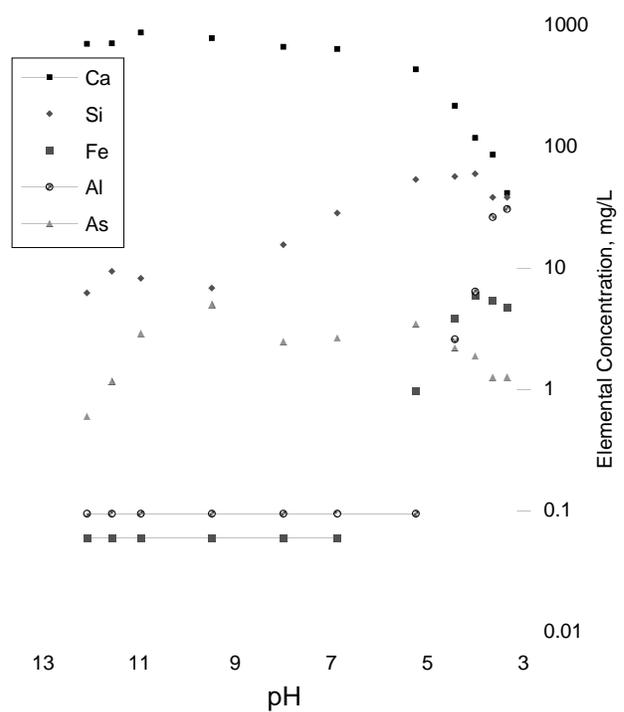


Figure 6-8. Soil, As(+3), FeSO_4 .

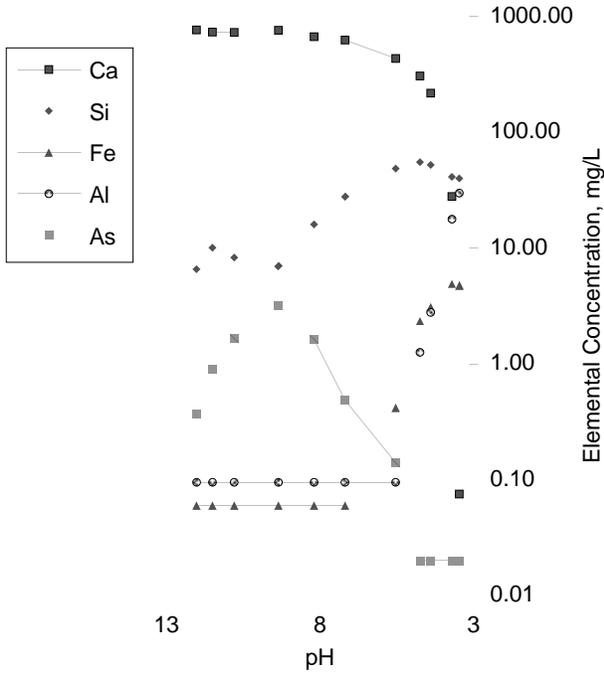


Figure 6-9. Soil, As(+3), H₂O₂, FeSO₄.

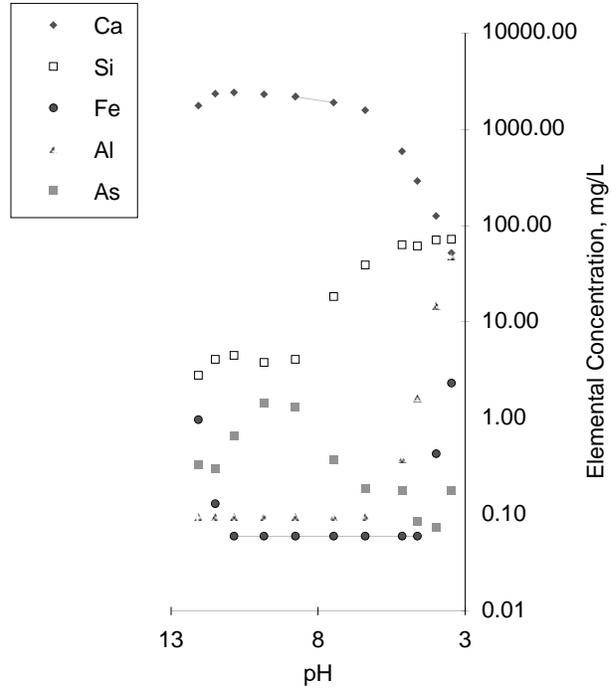


Figure 6-10. No Soil, As(+5), FeSO₄.

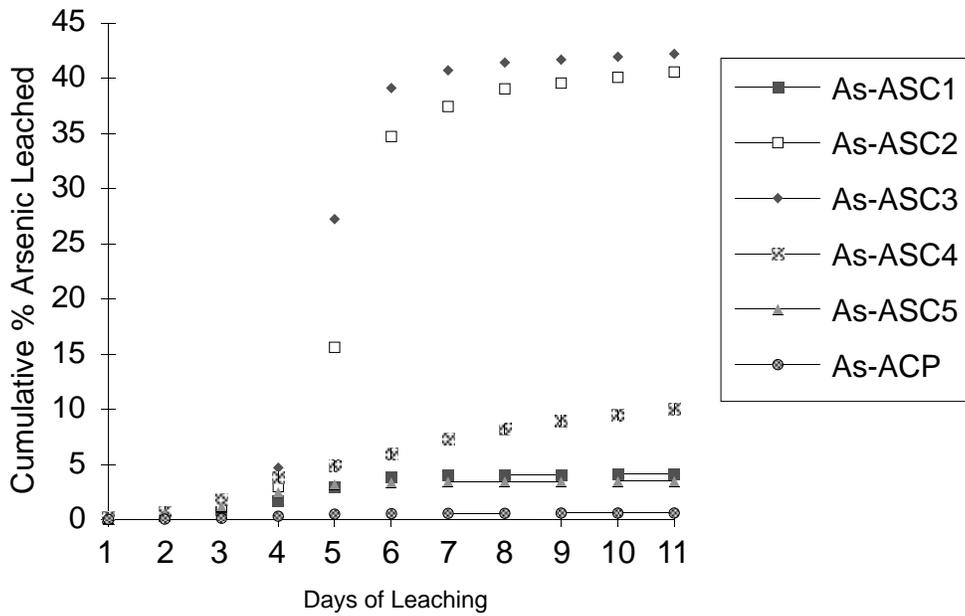


Figure 6-11. Summary of test results.

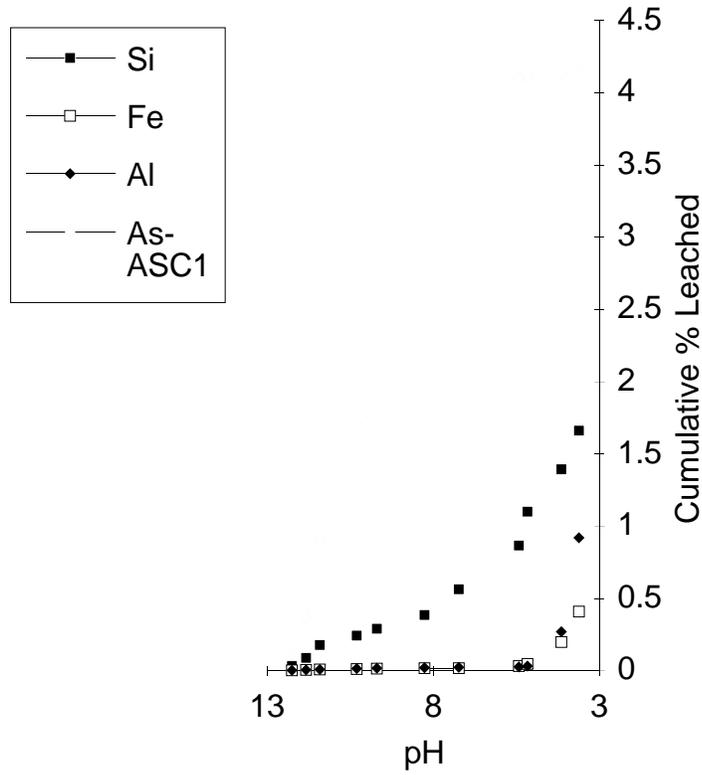


Figure 6-12. Soil, As(+5), FeSO₄.

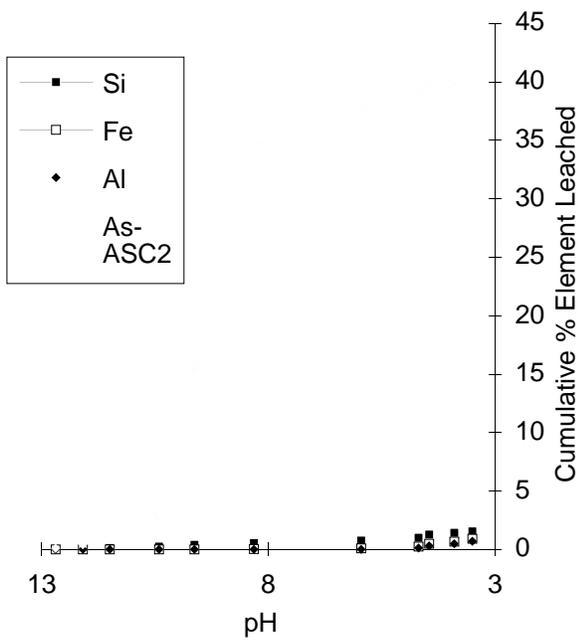


Figure 6-13. Soil, As(+5), EDTA, No FeSO₄

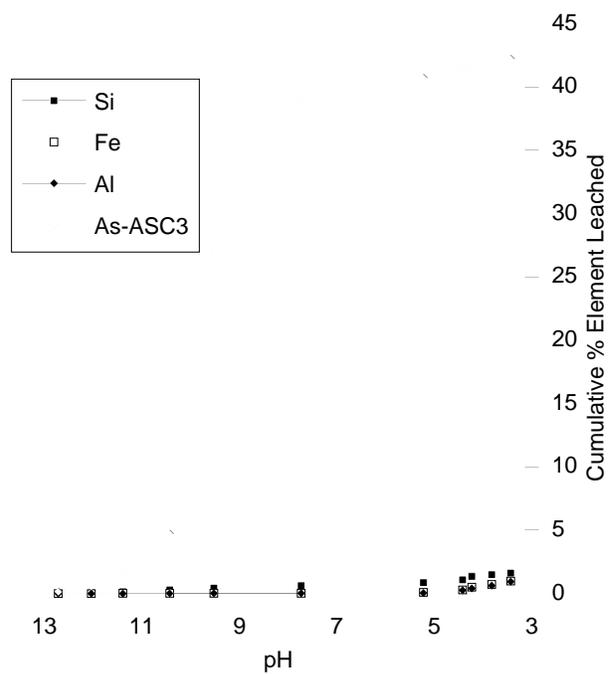


Figure 6-14. Soil, As(+5), No FeSO₄.

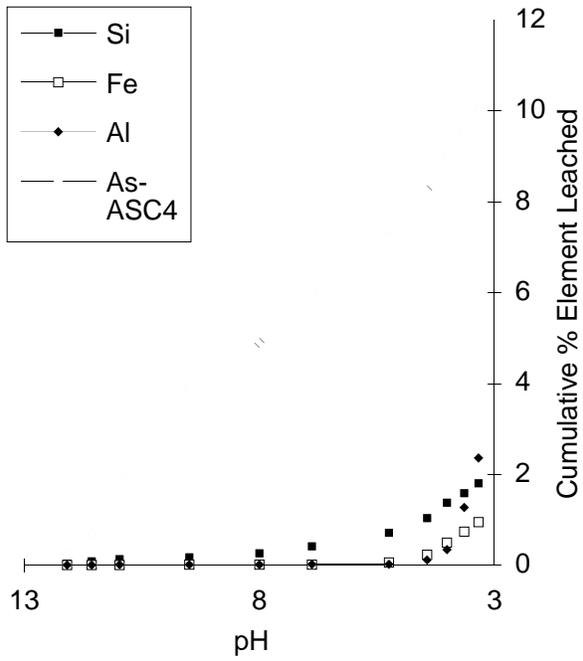


Figure 6-15. Soil, As(+3), FeSO₄.

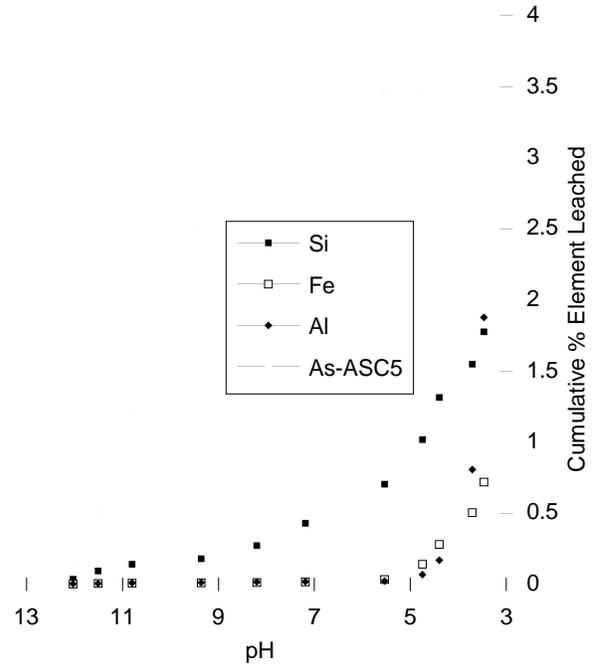


Figure 6-16. Soil, As(+3), H₂O₂, FeSO₄.

Compressive Strengths of Arsenic-Modified Systems

Two-inch cubes for the soil mix samples and 25.4-mm (1-inch) paste cubes for the paste mix were cast. Some problems in stripping the molds at one day were encountered with all mixes except ASC4. These difficulties are largely attributable to the very low compressive strength of these specimens after 1-3 days. Arsenate ion is shown to be a potent retarder for hydration. The following average compressive strengths in MPa (psi) were obtained:

Table 6-3. Compressive Strengths

| Mix | 4 Days | 7 Days | 28 Days |
|------|-----------|------------|------------|
| ASC1 | | 0.34 (70) | 3.10 (450) |
| ASC2 | | 1.31 (190) | 3.38 (490) |
| ASC3 | | 1.03 (150) | 1.72 (250) |
| ASC4 | | 0.69 (100) | 6.00 (870) |
| ASC5 | | 0.28 (40) | 3.10 (450) |
| ACP | 0.34 (50) | | 6.34 (920) |

DISCUSSION OF SOME POSSIBLE REASONS FOR THE ACETIC ACID LEACHING BEHAVIOR OF ARSENIC IN CEMENT MATRIX SYSTEMS

The cement paste system, whether in the presence or in the absence of soil, starts out at a very high pH of between 12.5 and 13.0. In this pH region, the As(V) species of highest stability is the arsenate ion (AsO_4^{3-}). The pH is too high for $HAsO_4^{2-}$ to be stable. The calcium ion concentration is limited by the solubility product for calcium hydroxide and for gypsum, but is still significant compared to the concentration of any other cations (except alkali metal cations). Therefore, calcium arsenate can precipitate. It is very insoluble at high pH, and therefore there was little leaching in the first two steps.

As the pH decreases to the range of about 6.5-11, and especially at the intermediate pH of about 9.5, arsenate ion becomes protonated to $HAsO_4^{2-}$. Calcium monohydrogen arsenate is much more soluble than is $Ca_3(AsO_4)_2$. Furthermore, the concentration of iron cations (Fe^{2+} or Fe^{3+}) is limited by the very low solubility of the respective hydroxides in this pH range. Therefore, the arsenic is more soluble in this pH range.

As the pH decreases below about 6, the $HAsO_4^{2-}$ ion becomes unstable relative to the dihydrogen arsenate ion. Also, and very importantly, the iron

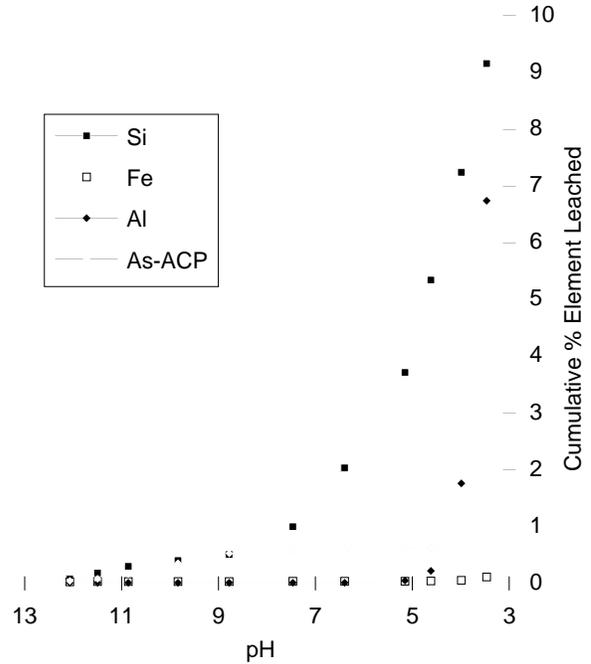


Figure 6-17. No soil, As(+5), $FeSO_4$.

compounds become much more soluble as the hydroxide ion concentration is dramatically reduced. As a result, iron arsenate compounds can form. These are very insoluble; their use as the basis for insolubilization of arsenic in waste stabilization has been well documented in the literature (for example, Twidwell [1994], Robins [1988], Taylor and Fuessle [1994]). The literature also mentions the use of aluminum sulfate as a precipitant for arsenic, indicating that aluminum-arsenate complexes are also relatively insoluble. Our test results confirm that when the concentration of aluminum and iron cations in the system increase, arsenic solubility is dramatically reduced. As a result, the stabilization of arsenic again improves at low pH values. The maximum solubility of arsenic therefore appears to occur at about pH 9.5, which is very close to the point of minimum solubility for lead and chromium. Careful balance would therefore be needed if all four metals (including cadmium) required simultaneous stabilization.

Overall there is little indication that the arsenic substituted for silica in the calcium silicate hydrate. In fact, whenever ferrous sulfate was used, the silica solubility showed a distinct drop at pH 9.5 where the arsenic had the maximum solubility. The supplemental calcium ion released by calcium arsenate dissolution probably temporarily suppressed the solubility of the C-S-H.

One X-ray diffraction pattern taken after 28 days of curing but before the leaching tests showed the presence of a significant amount of AFt phase, probably iron-substituted ettringite. The arsenate ion probably could not substitute into the ettringite crystal lattice to a significant degree because of competition from the high excess sulfate concentration. In systems in which no ferrous sulfate was added (the cement and cement/EDTA systems), the aluminum, iron, and sulfate concentrations are low enough that the arsenate ion may be able to compete for substitution in the AFt phase either for the sulfate, or for aluminate or ferrite. Such a stabilization may play a role in arsenic stabilization when massive amounts of sulfate are not present. As previously noted, this mechanism is probably not operational when ferrous sulfate is present. In this situation the thermodynamics would favor an iron-rich AFt phase, because of the higher concentrations of iron and sulfate.

Further evidence that arsenic is probably not stabilized to any significant degree in the AFt phase is provided by the low concentration of arsenic at low pHs in the sequential batch leaching experiments. Below pH 6 the stability of the AFt phases decreases and calcium, aluminum, iron, and sulfate would be solubilized. If arsenic were present in the AFt phase by substitution, then that arsenic would also be solubilized and its concentration would increase in the leachate. However, there is no indication of increased arsenic concentrations at low pHs. An alternate explanation of this observation is possible. The arsenic may be substituted in the AFt phase

but as soon as it dissolves at low pH, it immediately reacts with iron in solution to form an insoluble iron arsenate compound or complex.

RECOMMENDATIONS FOR TREATMENT OF ARSENIC WASTES

The study confirmed that the stabilization of arsenic is difficult but possible, but that special care has to be taken in the presence of other common toxic materials which usually show maximum stabilization at the pH (about 9.5) where the arsenic is most difficult to stabilize. On the other hand, the study indicated that adequate stabilization quite likely can be obtained by increasing the binder-to-waste ratio to a value higher than that used in the study (0.21-0.26). The present results, taken together with the results of Taylor and Fuessle [1994] suggest that a binder-to-waste ratio of about 0.4 may be suitable. The study also provides a means to calculate a first order estimation of the amount of oxidizer needed for a given ratio of arsenite-to-arsenate in the waste. In some cases, long term stabilization may require a simultaneous increase in both the binder-to-waste and iron-to-arsenic ratios. Further work may be needed into means to avoid the large increase in the water-to-cement ratio when ferrous sulfate is used. Perhaps a common retarder such as citric acid or a superplasticizer could be used, or a non-sulfate ferrous compound could be substituted; Taylor and Fuessle [1994] showed good results with ferrous acetate.

CHAPTER 7

Durability of Waste Forms, Especially with Respect to Carbonation

The original intention was to carry out tests evaluating the weathering characteristics of cement-based stabilization/solidification (S/S) wasteforms, concentrating on the potential effects of carbonation with atmospheric CO₂. This discussion is based on a quick literature survey designed to “hit the high points” of work that has been published to date on long term durability considerations with portland cement-stabilized systems.

The cement-based stabilization/solidification (S/S) process has been a common practice to immobilize trace heavy metals in metal-containing wastes. The immobilization of metals is largely attributed to the chemical interaction between the metals and the hydrating cement phases, although some physical containment (encapsulation) may also be occurring. According to Macphee and Glasser [1993], dispersion of waste in the matrix at micrometer, or perhaps nanometer scale, can affect the physical factors such as porosity, permeability, etc. of the stabilized matrix, thereby controlling the mobility of solubilized species.

Macphee and Glasser [1993], and Glasser [1992, 1994] have reviewed the science of metal immobilization and the application of a number of cement-based systems for toxic waste stabilization. Examples of the reactions between cement and metallic components such as Cr (III), Cr (VI), Ni, Mo, As, Zn, Cd, Pb, Ba, and U and the formation and stabilities of the reaction products are frequently cited. Metal-cement interactions, chemical considerations involved in effective stabilization, and waste conditioning are specifically reviewed in some details. Some of the issues, problems, and perspectives in the use of cement for treating and conditioning the toxic and hazardous wastes with respect to technical, economical, and disposal scenarios have also been discussed for predicting stability and long-term performance of the S/S wasteforms. Conner [1990]

also gives a comprehensive review of these economic considerations.

Since the stability of the hydrates of portland cement is pH controlled, the stability of the hydration products incorporating metals can be affected by any environmental change causing pH to fluctuate. Exposure to sulfates, carbonates, and environmental CO₂ is one of the factors that has been reported to cause adverse effects on the stabilized/solidified matrices, resulting in metal release. For instance, in the case of arsenic fixation in cement based S/S systems, Robbins [1988] has noted a risk of long term arsenic resolubilization by environmental carbonation. It was concluded that the atmospheric CO₂ rendered the simple metal arsenates unstable. Appreciable decrease was observed in the stability of magnesium, cadmium, lead, and copper arsenates. However, the effect on amorphous ferric arsenate was less noticeable.

In a very stringent experimental test, Bonen and Sarkar [1995] studied the effects of CO₂ exposure (in the form of carbonic acid) on the morphology and the leachability of a cement matrix. The cement matrix used was Type V cement at $w/c=0.5$, and contained oxides of nickel, cadmium, lead, and mercury. The report concluded that a considerable amount of calcium was leached out and deposited both at the bottom of the vessels as a finely divided powder and on the surfaces of the specimens. A significant amount of calcium carbonate was found deposited in the pores. After 180 days of subjection to a saturated aqueous CO₂ solution at a pH of 6.25 ± 0.25 , there were three distinct zones found: a surface layer showing considerable leaching, a CaCO₃-rich layer, and an unleached core. The C-S-H gel was decalcified, and there were pseudomorphs of incompletely hydrated grains composed of amorphous silica gel. A great deal of porosity had also developed.

Bonen and Sarkar believed that the metals had been incorporated into the aluminate phases, and that there was no substitution in the C-S-H gel. They found evidence that the grains of metal oxides (nickel and cadmium) may have coatings of hydroxide. The mercuric oxide was unaffected. They were not able to characterize the fate of the lead, but concluded that it was the best stabilized of the metals examined. The cadmium and nickel began to leach when the pH dropped below 9, consistent with results obtained in the present work. Incorporation of the heavy metals reduced the $\text{Ca}(\text{OH})_2$ buffering capacity of the cement paste and increased its susceptibility to carbonation.

McCarthy and Solem-Tishmack [1994] discussed the implications of secondary thaumasite ($\text{Ca}_6\text{Si}_2(\text{SO}_4)_2(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$) formation on the durability of sulfoaluminic cementitious materials, such as Class C fly ash that can furnish sources of calcium, alumina, and sulfate to form calcium sulfoaluminate hydrates and contribute some solidification and/or stabilization to a system.

Although the work does not specifically deal with cement-stabilized wastes, it mentions prominently the formation of ettringite in the materials studied, and its conversion to thaumasite by weathering or the formation of thaumasite from other precursors. Any waste stabilization method that relies upon ettringite to stabilize metals may be subject to weathering that converts some or all of this ettringite to thaumasite, which is a well-known cause, and/or symptom, of physical degradation.

It was also pointed out that thaumasite formation affects consolidation and permeability of the

sulfoaluminic materials, and that thaumasite was probably more stable geochemically than ettringite in lower pH ground waters. On the other hand, high-pH solubilizable silica provided by cementitious materials such as fly ash components in a S/S system may play a pivotal role in forming thaumasite.

On the premature conversion of ettringite to thaumasite, Lukas [1976] has reported that silica, especially from reactive silica sources like fly ash, may be able to form a material with the X-ray diffraction behavior of ettringite in the presence of excess calcium sulfate, even without a source of carbonate; the carbonate could come in later. This may have some important implications in S/S technology, or if the groundwater in the stabilized waste disposal region is sulfate-rich, it may be advisable not to use fly ash or silica fume in the cement system in order to avoid the premature formation of thaumasite.

Gouda et al. [1975] reported the effects of prolonged contact of sulfate-containing ground water on the deterioration of soil-cements. They also attributed the deterioration to the formation of expansive thaumasite or possibly to a solid solution between thaumasite and ettringite (thaumasite formation need not be expansive). High dolomite contents of soil can also possibly promote the formation of thaumasite. According to van Aardt and Visser [1975], the formation of thaumasite is most favorable at low temperatures ($\sim 5^\circ\text{C}$); however, recent studies [McCarthy and Solem-Tishmack, 1994] have shown that thaumasite can form in significant quantities even above 20°C .

CHAPTER 8

Interpretation of X-Ray Diffraction (XRD) Results

It was decided that it would be advantageous to establish, using x-ray diffraction techniques, what hydrated cement compounds were present in the samples whose leachability was being determined. This was considered of interest especially since the metals solubility was so much lower than would be predicted from hydroxide solubility data, and determination of simultaneity between disappearance of a hydrated cement phase and increase in leachability could be helpful in further defining the mechanism of stabilization.

Multi-metallic pastes were examined before and after the leaching experiments but also at intervals throughout the test. Parallel bottles of the pastes were prepared for leaching, placed on the mixing wheel overnight, and filtered; then the solid was again leached with fresh solution. This XRD leaching series varied from the standard leaching in the following respects: 1) approximately every other day about 1.5 g of the filtered solid was removed and put into a vial of acetone, and 2) the volume of fresh acetic acid leachant was reduced to maintain the pH as close as possible to that of the standard test leachate. After the sequential leaching was complete, the solid samples in acetone were filtered, washed with additional acetone, and dried. X-ray diffraction patterns were obtained and interpretation of those patterns are as follows:

The freshly ground 100-day old pastes (before any leaching) made from Type I paste and the mixed cadmium-chromium-lead hydroxide sludge contained $\text{Ca}(\text{OH})_2$ and ettringite as the principal crystalline components. Weak intensity peaks were observed for C-S-H, C_2S , and tetracalcium aluminoferrite. A broad and weak peak at 0.81 nm is attributed to a partially substituted calcium hemi-carboaluminate hydrate or monosulfoaluminate hydrate with acetate substitution for some of the hydroxide or sulfate (hereafter referred to as "substituted AFm phase"). This hypothesis is based on

other work done at CTL which indicated formate ion from formic acid substituted in this compound and resulted in a similar XRD pattern. Acetone-washing of the sample did not affect the $\text{Ca}(\text{OH})_2$, but did decrease the intensity of the peaks for C-S-H, ettringite, and substituted AFm phase.

During the leaching test, a sample was obtained on the 7th leaching day, and the associated filtrate had a pH of 10.02. No calcium hydroxide was detected, but a substantial amount of CaCO_3 was observed. Ettringite was still present, and other weak peaks were attributed to C_2S , C-S-H, and tetracalcium aluminoferrite. A very weak peak at 0.776 nm was believed to be the substituted AFm phase; further acetate substitution most likely caused the shift of peak position. Another sample had a pH of 7.95; the compound composition was predictably widely different. The sample was strongly carbonated, and calcite peaks predominated among the crystalline components. Small residual ferrite peaks and peaks of the substituted AFm phase remained; no evidence for C-S-H or ettringite could be found. The beginnings of amorphous humps centered around 0.33 nm, presumably attributable to silica gel, and alumina gel began to be discernible.

The next sample had an associated filtrate of 7.78 pH and, though still containing calcite, was less carbonated than the previous sample. Extensive carbonation of the previous sample is thought to be due to the air exposure after filtration more than to carbonation during the leaching cycle. In this sample, the weak peak at 0.78 nm attributed to the substituted AFm phase is still present along with very weak peaks for dicalcium silicate, tetracalcium aluminoferrite, and the broad peak for silica gel.

The solid sample separated from a filtrate of pH 5.99 showed only a slight amount of carbonation. No C_2S was observed and only a small amount of ferrite appeared on an increasingly large broad peak for silica gel. An XRD pattern obtained on the resi-

due at the end of the standard leaching series (after 16 cycles) was nearly featureless except for the very broad silica gel peak centered at 0.33 nm. From the leaching results, it is known that below pH 6 most of the silicon, iron, aluminum and about 5% of the calcium is still present. Apparently these metals are all present as amorphous oxides or hydroxides, possibly encapsulated in extensive amounts of silica gel with most of the lead and chromium that had been originally added to the paste. The amorphous gels of hydrous oxides of these elements appear to have good adsorptive capability for chromium and lead.

The ettringite appeared to decompose somewhere between pH 10 and pH 8; the substituted AFm phase remained even in the pH 7 range. Although it is very difficult to quantify the amount of C-S-H due to its poor XRD characteristics, there was no obvious shift in its XRD response as the pH dropped.

Perhaps at least in the early stages it is not undergoing any substantive change in lattice parameters as its calcium content decreases; this might help explain its effectiveness.

Unfortunately, no samples were available for pH values about 8.5-9.5, or for values around pH 11. Having the capability to examine such samples would help significantly in evaluating when the ettringite disappeared, when the C-S-H was first not detectable, etc. In addition, these samples should be examined by techniques of scanning electron microscopy/energy dispersive x-ray analysis to pinpoint the phases containing the highest concentrations of the metals. This study would permit the confirmation or refutation of many of the hypotheses for the mechanism of portland cement solidification/stabilization advanced in this report.

ACKNOWLEDGMENT

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APPENDIX A

Arsenic Soil-Cement and Arsenic Paste Mixes**SOIL-CEMENT MIXING PROCEDURE WITH ARSENATE AND ARSENITE SALTS**

All soil-cement preparations followed a mixing protocol similar to the protocol in ASTM D558 (Moisture-Density Relations of Soil-Cement Mixtures, section 5), but were modified to accommodate the mixing of more components. The ASTM procedure in section 5 specifies a soil sample which entirely passes a 4.76 mm (No. 4 mesh) sieve; for this work the small amount of aggregate in the sample too coarse to pass this size sieve was included in the sample.

Arsenic solutions were prepared in advance using warm deionized water. Mixes ASC1, ASC2, and ASC3 were made with solutions of 150 mL water and 49.97 g of dibasic sodium arsenate, 7-hydrate. Solutions were heated to about 40°C with stirring to aid dissolution of the salt. The arsenic solution for mix ASC4 was made by dissolving 20.81 g of sodium meta-arsenite in 170 mL of water, and this solution also was heated and stirred. The solution for mix ASC5 used the same amount of this salt dissolved in 200 mL warm deionized water, and the solution was allowed to cool to about 30°C. Twenty milliliters of a 30% aqueous solution of hydrogen peroxide was then added slowly to the solution with stirring continuing for 30 minutes.

The total amount of soil each mix required was placed in a large size Hobart mixer, and about one-half the added water was introduced while the mix was being stirred; mixing was continued an additional 2.5 minutes. For all mixes, the warm arsenic solution was added while mixing; the mixing continued throughout the addition and for an additional two minutes. The mixer was stopped, the bowl removed, and the material was turned over and scraped from the bowl to break up lumps and soil

caked on the walls. The bowl was again placed in the mixer and 600 g of Type I cement was added as the stirring continued.

For mix ASC3, the last 100 mL of mix water was added during this last-mentioned mixing step. For mix ASC2, the EDTA and the last 100 mL of mix water was added at the same point. For the other three mixes no additions were made during this mixing step.

All five soil-cements were mixed for 2.5-minutes after cement addition was completed. The mixer was again stopped, the bowl scraped down, and the material turned over as described above. These two steps, consisting of 2.5-minute mixing and scraping down the bowl, were repeated. This procedure is followed to obtain intimate mixing of the soil and cement.

From this point on the mixing procedure for the individual mixes varied somewhat for each mix. Descriptions below are grouped because of the similarities of procedure.

Mixes ASC2 and ASC3 were both covered with plastic for a five-minute rest period to allow more complete moisture absorption by the soil-cement. This was followed by a final 2.5-minute mixing period; then the bowl was scraped down and any caked material was broken up. The material was then tamped into 50-mm (2-inch) mortar cube molds as described below.

Ferrous sulfate solutions were prepared in advance for mixes ASC1, ASC4, and ASC5 using 250 mL of warm deionized water and 267.2 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Solutions were stirred and heated to about 40°C until the salt was completely dissolved. Solutions were somewhat cooler when added to the arsenic/soil-cement mixes.

Mixing was resumed with addition of the ferrous sulfate solution during mixing, and stirring was continued for an additional 2.5 minutes. The bowl was removed, sides scraped, lumps broken up, and

the mixer reassembled. The mixer was started with addition of the final amount of water and stirring continued for 2.5 more minutes. (This step was included because cement paste mixes with sodium arsenate and ferrous sulfate would stiffen noticeably and heat up. Retempering water was required to restore some flow to the mix.) The amount of water added in this step was 100 to 200 mL, depending on the water added at the beginning to dampen the soil. When mixing was stopped, the bowl was removed, scraped down, lumps broken up, and the material tamped into molds to make twelve 50-mm (2-inch) mortar cubes.

To make 50-mm (2-inch) cubes, the same procedure for filling and tamping the material as is described in ASTM C 109/C 109M-95 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, section 10.4) was followed. The molds were filled, then tamped in 3 layers and leveled with a trowel. Extra material was placed and tamped in a similar manner into a 300 mL plastic beaker. The molds were then placed in a standard moist curing room at 100% relative humidity and 23°C. Since the cubes were not expected to have much strength, the molds were not stripped until at least the third day.

Stripping the molds was quite difficult because the material adhered to the sides and many cubes split when the two sides of the mold were released. A non-standard procedure was implemented so that some strength data could be obtained. A spatula was used in between the cube and the wall of the mold to break the adhesion and then the cubes were crudely extruded. This usually resulted in cubes with very rough sides and broken corners but generally uncracked. Cubes that were not used immediately for strength tests were placed in open plastic bags and returned to the moist room. The poor quality of the cubes contributed substantially to the wide range of individual cube strengths obtained for each mix and generally lower strengths.

ARSENIC CEMENT PASTE MIXING PROCEDURE

A solution of 60.1 g of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ was prepared in advance using 300 mL of warm deionized water which was stirred until the salt was completely dissolved. Paste mixing was done in a stainless steel bowl with a small standard mortar mixer. The solution was put in the bowl and, while stirring at slow speed, the Type I cement was added with a vibratory feeder over a one minute period. At a mixer speed setting of 1 (slow speed) the paste was mixed for 3 minutes. Mixing was stopped, the sides of the bowl scraped down, and mixing resumed after 2 minutes. At a mixer speed of 2 (medium speed) the paste was mixed 3 minutes and the sides of the bowl were again scraped down.

A ferrous sulfate solution was prepared in advance with the iron salt and 300 mL of deionized water; the solution was heated and stirred until the salt dissolved. This solution was added while stirring the paste at a mixer setting of 1 and a mix time of five minutes. The mixer speed was increased to the #2 setting and mixing continued an additional 5 minutes. The bowl was scraped down and the final 97 mL of water was added slowly while the paste was being mixed at the higher speed over a 10 minute period; mixing continued an additional 5 minutes after the end of the water addition. The extensive mixing time was necessitated by the thick rheology of the mix and the ongoing precipitation of iron hydroxides. The bowl was scraped down and the paste was used for the following steps.

First a mini-slump cone was filled and leveled then lifted to form a paste pat. The area of the pat was later calculated as a measure of the flowability of the paste. Five 100 mL plastic beakers were filled while on a vibratory table. Molds to make fifteen 25.4-mm (1-inch) paste cubes were filled while they were on a vibrating table and a procedure followed to remove air bubbles from the cubes was followed. One plastic beaker was used to determine an initial setting time. The other plastic beakers and cube molds were placed in a standard moist cabinet for three days and then the cubes were removed from the molds. Cubes not tested for strength were returned to the moist cabinet.

APPENDIX B

Preparation of Leach Samples and Leaching Regimen

LEACH SAMPLE PREPARATION

The solidified/stabilized solids, both cement paste/contaminant metal samples and soil-cement/contaminant metal samples, were all cured for a minimum of 28 days and then portions of all samples were prepared for leaching in a similar manner. Generally, all samples were prepared by reducing the cement paste portions to a fine powder before leaching. In the U.S. EPA TCLP test (Toxicity Characteristic Leaching Procedure), solid samples are required only to be reduced to a particle size fine enough to pass a 9.5-mm (3/8-inch) standard sieve; no lower size limit is specified. Technically, the procedure adopted meets the TCLP criteria, however, it was felt the reduction to a very fine powder may provide a more leachable material and stringent test than material reduced to meet the minimum TCLP size criteria. (It was subsequently learned [Bishop, 1988] that in some cases, the coarser sample may be more susceptible to leaching because the cement dissolves more slowly, resulting in a temporarily lower solution pH.)

The sequential batch leaching procedure was used to obtain a stepwise chemical breakdown of the solidified material and determine whether certain chemical constituents of the cement paste were breaking down at the same time as the stabilized metals were being leached. Fine particle size material reduces complications from diffusion effects and differing rates of leaching. The leaching solution and the particles come to chemical equilibrium more rapidly and the resulting data can then presumably be interpreted in a more unambiguous manner. It is for these reasons that the cement paste portions of the samples were reduced to fine powders.

Cement paste/contaminant metal samples that contained cement but no soil were prepared from solidified paste that had been molded in 100 mL plastic beakers and cured in a standard moist cabinet

for a minimum of 28 days. The solids were broken up with a mortar and pestle until the whole sample passed a 0.84-mm (No. 20 mesh) sieve. This material was dried by washing it two times with acetone and recovering the solid by filtration. Oven drying was not used so as to avoid dehydration of cement paste phases such as ettringite. The size of this coarse material was then reduced by a combination of grinding with a ring-and-puck mill and grinding using a mortar and pestle until all the material passed a 74- μ m (No. 200 mesh) sieve. This material was again washed twice with acetone for further drying. After filtration and air drying, a sample portion was weighed directly into a 500-mL HDPE plastic leaching bottle.

Soil-cement/contaminant metal samples were prepared for leaching by taking one of the 50-mm (2-inch) cubes after at least 28 days curing and breaking it up in a mortar and pestle. When necessary, this material was passed through a 0.84-mm (No. 20 mesh) sieve and the coarser material returned to the mortar for more gentle grinding to break up the paste fraction without pulverizing the aggregate. The combined finer material and aggregate was split and about one-half was washed twice with acetone, then filtered and dried. No acetone washing was used for samples TSC40 and TSC5 in order to avoid removing the oil from the samples prior to leaching, but they were air-dried to remove free water. This dried material was sieved, and the material passing a 0.84-mm (No. 20 mesh) sieve was reduced to a point where it all passed a 74- μ m (No. 200 mesh) sieve in the same way that the cement pastes were size-reduced. This fine material and the dried aggregate not passing the 0.84-mm (No. 20 mesh) sieve were recombined and then washed twice with acetone, filtered and air-dried. Samples TSC40 and TSC5 again were not acetone washed in this step. The leaching sample was taken from this dried material and a weighed amount placed in each leaching bottle.

SEQUENTIAL BATCH LEACHING REGIMEN

Especially for the cement paste/contaminant metal samples, the first step of the leaching procedure was similar to the U.S. EPA TCLP method, and subsequent leaching steps were done in a similar manner. For the soil-cement/contaminant metal samples, more dilute acetic acid was used. This leaching procedure was modeled on the leaching procedure described by Bishop [1988]. The combination of sample weight and concentration of acetic acid was chosen so that the total number of moles of acetic acid (for approximately 12 to 15 steps) was about 2.5 to 3 times as great as the number of moles of calcium from cement and sludge in the sample. The solid leaching samples weighed between 24 and 32 grams and were leached using 450 mL of acetic acid or other leaching solution. These leaching experiments, therefore, started with a leachant to solid weight ratio of between 14 and 19; the TCLP procedure uses a ratio of 20. The leachant was 0.1 M acetic acid for all cement paste/contaminant metal samples for the first seven (7) steps of all the acetic acid leaching series. This is virtually identical to the TCLP extraction fluid # 2, specified as 5.7 mL of glacial acetic acid diluted to 1 liter with reagent water; the solution should have a pH of 2.88 ± 0.05 . The calculated pH from the ionization constant for 0.1 M acetic acid is 2.88.

From the eighth step until the end of the sequential batch leaching, the leachant was 0.05 M acetic acid for the cement paste/contaminant metal samples except for the cement pastes made with a single metal hydroxide. This reduction in acid concentration was an effort to decrease the amount leached at each step and to determine any correlation between leaching of either aluminum or iron and the leaching of the contaminant metals. It was anticipated that more detailed information could be obtained from the experiments by spreading out the leaching over more steps.

Soil-cement/contaminant metal samples contained less cement and, correspondingly, the acetic acid leachant used was more dilute. The freshly mixed TSC samples contained 8% cement and the ASC series contained 15%. For these samples the leachant remained the same throughout the sequential batch leaching series. The leachant solution was 0.012 M acetic acid for mixes TSC2, TSC3, TSC4D, and TSC4O; the leachant solution for TSC5 was 0.0125 M acetic acid. Leaching for the ASC series of samples was done with 0.03 M acetic acid.

To each plastic bottle containing a solid sample for leaching, 450 mL of the leaching solution was added. These leaching bottles were attached near the rim of a 0.6-m (2-foot) diameter wheel, which rotated about a horizontal axis. The wheel was rotated overnight for 16 to 20 hours. At the end of the leaching period, the bottles were removed and the material allowed to settle for roughly 30 to 120 minutes. The material in the leaching bottles was filtered through Büchner filter funnels, using glass fiber filters, and the leachate collected. Acid-washed glass fiber filters (0.7 μm pore size) meeting TCLP criteria were used. The solid on the filter paper and filter paper were returned to the original leaching bottle; this bottle was filled with another 450 mL of fresh leaching solution for the next day of leaching. The filter paper in the bottle was cleaned as much as possible leaving the solid material in the bottle, and the filter paper was removed and compressed to permit a maximum of leaching solution in the bottle.

The leachate pH was measured; a sample of the leachate was acidified and submitted for AAS (atomic absorption spectrometry) measurement for the concentration of calcium, silicon, aluminum, iron and any contaminant metals that had been added to the original solid.

The leaching bottle, with the solid being leached and the fresh leaching solution, was returned to the wheel and rotated overnight to begin the next day of sequential leaching.

APPENDIX C

Soil-Cement Mixes with Three-Metal Sludge

In designing the soil-cement mix preparations, a sequence was adopted to first provide a homogeneously contaminated soil. Soil and fresh sludge with some water were first thoroughly mixed. Oil was added next to this mixture for mixes TSC4 and TSC5 in order to coat both soil and metal components with oil. This was an attempt to provide a worst case scenario in which it would presumably be difficult to combine the cement paste matrix with the metal and soil components. It also provides a contaminated material analogous to the type found at some waste sites. In commercial practice, solidification/stabilization specialists would then add cementitious material to treat the waste. In a similar sequence for these laboratory experiments, cement, water, and other additives were added and thoroughly mixed with the previously homogenized contaminated soil; details of this preparation procedure are described immediately below.

All soil-cement preparations followed a mixing protocol similar to the protocol in ASTM D558 (Moisture-Density Relations of Soil-Cement Mixtures, section 5), but were modified to accommodate the mixing of more components. In Section 5 of ASTM D558, it specifies a soil sample which laterally passes a 4.76-mm (No. 4 mesh) sieve; for this work the small amount of aggregate in the sample too coarse to pass this size sieve was included in the sample. Preparation of the synthetic soil is described in Appendix D. The siliceous synthetic soil was used for Mix TSC5; the dolomitic synthetic soil was used for Mixes TSC2, TSC3, and TSC4.

All of the TSC series of soil-cement batches were prepared in 5 kg batches containing 8% (400 g) of Type I cement. The amount of water needed was estimated from one experimental series with only soil and cement to determine the moisture content required for maximum density (ASTM D558). All of the soil-cement mixes contained 7.0 g each of cadmium, chromium, and lead. This mixture of metals

was added as a freshly prepared wet sludge, made by addition of calcium hydroxide to a solution containing nitrate salts of all three metals, and the sludge was recovered by filtration. Preparation of the sludge was the same as the sludge preparation for the pastes containing multi-metallic hydroxides and is described in detail in the section on multiple metal pastes. For each metal this is about 10000 ppm added to a paste of 640 g with a w/c ratio of 0.6; the cement paste/metal sludge portion of the soil-cement mixes should be the same as for paste mix IMM.H.30K, described in the referenced section.

The procedure for preparing sample mixes TSC2 and TSC3, which contain no oil, is described first; description of sample preparation for TSC4 and TSC5, which both contain oil, is described second. Samples TSC2 and TSC3 were prepared in the same manner but were cured differently. Cured cubes of mix TSC4 were prepared for leaching in two different ways to make the leaching samples TSC4D and TSC4O.

SOIL-CEMENT MIXING PROCEDURE WITH NO OILS

The amount of soil required by each mix was placed in a large size Hobart mixer (Model # C-100), dry mixed for one-half minute, and, without stopping the mixer, the following additions were made. For both mix TSC2 and mix TSC3, the freshly prepared wet metal sludge and 80 mL water were added during mixing at slow speed; the mixing continued throughout the addition and for an additional four (4) minutes. The mixer was stopped, the bowl removed, and the material was turned over and scraped from the bowl to break up lumps and loosen soil caked on the walls. The bowl was again placed in the mixer and mixed an additional two (2) minutes. Cement and water were then added while mixing continued.

Four hundred (400) grams of Type I cement and the remaining water were added. The amount of added water, about 400 ml, varied a little due to varying water content of the fresh sludge; the total water content was the same in both mixes. Soil-cements were mixed for 2.5 minutes after cement and water addition was completed. The mixer was again stopped, the bowl scraped down, and the material turned over as described above. These two steps (the 2.5-minute mixing and scraping down of the bowl) were repeated, but mixing was done at medium speed. This procedure is followed to obtain intimate mixing of the contaminated soil and cement.

Soil-cement mixes were covered with plastic for a five-minute rest period to allow more complete moisture absorption by the soil-cement. Both mixes TSC2 and TSC3 were mixed for a final two (2) minutes after the plastic was removed. Standard 50-mm (2-inch) cube molds were then filled following the procedure described below, for mixes with and without oil.

SOIL-CEMENT MIXING PROCEDURE WITH OIL

All the soil each mix required was placed in a large size Hobart mixer (Model # C-100), dry mixed for one-half minute, and without stopping the mixer the following additions were made. For both mix TSC4 and mix TSC5, the freshly prepared wet metal sludge and 40 ml water were added during mixing at slow speed; the mixing continued throughout the addition and for an additional four (4) minutes. The mixer was stopped, the bowl removed, and the material was turned over and scraped from the bowl to break up lumps and loosen soil caked on the walls. The bowl was again placed in the mixer and mixed an additional two (2) minutes. Oil was then added while mixing continued for five (5) minutes after addition. This oil was aged SAE 10 W oil (without additives). The aging of the oil had been done in air in large rectangular pans with an oil depth of 15 mm to provide a large surface for evaporation and air oxidation. These pans of oil had been placed in an oven at 100°C for 72 hours for the simulated aging process. The bowl with the oil and metal-sludge-contaminated soil was then scraped down and the lumps broken up.

In previous experiments it had been determined that oil and water, saturated with calcium hydroxide, in the same proportions as mix TSC4 and TSC5, were well emulsified by a combination of two emulsifiers. The surfactants replaced 6.7% of the total

water and were used at 3 parts Triton X-45 and 1 part Triton X-100. Triton X series surfactants are made by Union Carbide Corporation and are non-ionic alkylaryl (specifically octylphenol) polyether alcohols. Nonionic surfactants have the advantage over anionic surfactants in that they do not form insoluble salts with calcium. Triton X-100 is miscible with water and insoluble in aliphatic hydrocarbons. Triton X-45 is borderline; it is described as dispersible in water and somewhat soluble in aliphatic hydrocarbons. For the 5-kilogram batches, 31 g of X-45 and 10 g of X-100 were added to the remaining water and the container was vigorously shaken.

The reassembled mixer was started and the cement, then the water and surfactant mixture, were added; mixing continued 2.5 minutes after the additions were complete. Four hundred (400) grams of Type I cement and the remaining water were added. The amount of added water, about 370 mL, varied a little due to varying water content of the fresh sludge; total water content was the same in both mixes. The mixer was again stopped, the bowl scraped down, and the material turned over as described above. These two steps (the 2.5-minute mixing and the scraping down of the bowl) were repeated, but mixing was done at medium speed. This procedure is followed to obtain intimate mixing of the contaminated soil and cement.

The oily soil-cement mixes were covered with plastic for a five-minute rest period to allow more complete moisture absorption by the soil-cement. Both mixes TSC4 and TSC5 were mixed for a final 2 minutes after the plastic was removed. After scraping down the bowl and breaking up any lumps, standard 50-mm (2-inch) cube molds were then charged with material, following the procedure described below, for mixes with and without oil.

To make 50-mm (2-inch) cubes, the same procedure for filling and tamping the material as is described in ASTM C 109/C 109M-1995 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, section 10.4) was followed. The molds were filled, then tamped in 3 layers and leveled with a trowel. Extra material was placed and tamped in a similar manner into a 300-mL plastic beaker. The molds were then placed in a standard 100% relative humidity and 23°C moist curing room. Since the cubes were not expected to have much strength, the molds were not stripped until at least the third day.

The preparation of the samples for leaching is described in Appendix B.

APPENDIX D

Preparation of Two Synthetic Soils for Metals Stabilization Project

Several years ago the U.S. EPA prepared a synthetic soil matrix intended to be representative of the typical uncontaminated soil at Superfund sites. Using this base soil, the EPA prepared four contaminated soil mixes with high and low levels of metal and organic contaminants. These sample soils were made available to parties interested in evaluating effectiveness of various waste treatment methods. In late 1994, the EPA no longer had any of the uncontaminated base soil, and the contaminated soils that were available were not considered suitable for this project. Specifically, the contaminant levels were considered too low, and it was decided that higher contaminant levels that were more challenging for solidification/stabilization by portland cement would be prepared using a similar base soil. The soils were prepared as per the EPA recipe for the Synthetic Soil Matrix [U.S. EPA (1988)]. The following materials were required:

and mixed for several minutes. The mixer was intermittently stopped for examination to ensure complete mixing. After mixing, the soil was stored in five-gallon buckets lined with plastic liners. The soil was of calcareous type in which the gravels and sand contained substantial dolomite. The first soil was used in the metal stabilization studies for contaminated soil-cement mixes TSC2 and TSC3, which contained an hydroxide sludge of cadmium, chromium, and lead. This soil also was used for mix TSC4 which contained, in addition to the sludge, 8% oil.

A second soil was prepared specifically for use in the subsequent arsenic testing program, and for preparation of TSC5, which contained oil and an hydroxide sludge containing cadmium, chromium, and lead. A siliceous soil-mix was made using the same recipe for particle size distribution, but using

Table D-1. Materials Proportions Required in the Soil-Mix

| Soil ingredients | Proportion (wt. %) | Sources for the First Soil |
|------------------|--------------------|--|
| Gravel (No. 9) | 5.7 | Material Services Corporation, Elgin, IL |
| Sand | 31.5 | Material Services Corporation, Elgin, IL |
| Silt | 28.3 | Material Services Corporation, Elgin, IL |
| Bentonite | 5.4 | Mississippi |
| Kaolinite | 9.4 | Kraft clay |
| Topsoil | 19.7 | Local garden store |

The materials were air dried by spreading out on a large clean area. The lumps of the dried topsoil were crushed in a jaw crusher and later ground to pass a 1.19-mm (No. 16 mesh) sieve.

For the first soil, the materials were proportioned as given above to prepare four soil batches of approximately 11.3 kg (25 pounds) each. The materials were loaded into a pre-dried rotary drum mixer

the siliceous gravels and sand from Eau Claire, Wisconsin. The silt required in the mix was prepared by grinding the Eau Claire sand. A similar type of topsoil was used after drying, crushing, and grinding to pass a 1.19-mm (No. 16 mesh) sieve. The mixing was done in a drum-mixer in two batches of approximately 11.3 kg (25 pounds) each, to prepare 22.7 kg (50 pounds) of synthetic soil.

No chemical analysis was available for the EPA mixed soils. However, the use of the radically different dolomitic and siliceous soils was expected to span the soil mineralogy ranges likely to be encountered in the field. Rapid XRF analysis was carried out on the prepared base soils, both for the dolomitic soil and for the siliceous material used for the arsenic studies. The results were as follows:

Table D-2. Analysis of Base Soils Used for Soil-Cement/Metal Systems

| Oxides | Base soil for TSC2, TSC3, & TSC-4 | Base soil for ASC series & TSC-5 |
|--------------------------------|-----------------------------------|----------------------------------|
| SiO ₂ | 37.14 | 75.27 |
| Al ₂ O ₃ | 8.02 | 10.02 |
| Fe ₂ O ₃ | 2.27 | 3.15 |
| CaO | 14.47 | 1.67 |
| MgO | 9.63 | 0.88 |
| SO ₃ | 0.14 | 0.05 |
| Na ₂ O | 0.41 | 0.75 |
| K ₂ O | 0.78 | 1.33 |
| TiO ₂ | 0.45 | 0.58 |
| P ₂ O ₅ | 0.07 | 0.09 |
| Mn ₂ O ₃ | 0.05 | 0.05 |
| SrO | 0.03 | 0.03 |
| LOI | 26.62 | 7.24 |
| Total | 100.08 | 101.11 |

Table D-3. Analysis of Soil-Cement/Metal Systems before Leaching

| Oxides | TSC-2 | TSC-3 | TSC-4 | TSC-5(soil only) |
|--------------------------------|-------|-------|--------|------------------|
| SiO ₂ | 35.54 | 37.42 | 36.23 | 75.27 |
| Al ₂ O ₃ | 6.81 | 7.00 | 7.08 | 10.02 |
| Fe ₂ O ₃ | 2.16 | 2.16 | 2.13 | 3.15 |
| CaO | 17.93 | 17.41 | 17.35 | 1.67 |
| MgO | 8.27 | 7.80 | 7.48 | 0.88 |
| SO ₃ | 0.29 | 0.29 | 0.034 | 0.05 |
| Na ₂ O | 0.37 | 0.39 | 0.37 | 0.75 |
| K ₂ O | 0.72 | 0.82 | 0.72 | 1.33 |
| TiO ₂ | 0.38 | 0.39 | 0.4 | 0.58 |
| P ₂ O ₅ | 0.06 | 0.06 | 0.06 | 0.09 |
| Mn ₂ O ₃ | 0.05 | 0.05 | 0.04 | 0.05 |
| SrO | 0.03 | 0.03 | 0.03 | 0.03 |
| LOI | 26.71 | 25.77 | 27.26 | 7.24 |
| Total | 99.32 | 99.59 | 99.184 | 101.11 |

Method of compounding soils derived from: U.S. EPA, *Synthetic Soil Matrix (SSM-SARM) User's Manual*, December, 1988

APPENDIX E

Table of Fresh Paste Temperatures, Mini-Slump Areas and Setting Times

| Mix Designation | Added as Hydroxide Sludge | | |
|---|---------------------------|-----------------------|-----------------------------|
| (mg/kg) in Solidified Paste | Initial Set (hrs:min) | Paste Temp °C Area | Slump (cm ²) |
| Single Metals-Type I Cement at w/c=0.4 | | | |
| IPbH (7 800 mg Pb/kg) | 23:30 | 27.5 | 15.35 |
| ICdH (5 300 mg Cd/kg) | 3:30 | 27.5 | 19.52 |
| ICrH (2 700 mg Cr/kg) | 2:25 | 27.4 | 16.02 |
| Control | 3:40 | ... | 35.63 |
| Single Metals-Type V Cement at w/c=0.4 | | | |
| VPbH (7 500 mg Pb/kg) | 32: | 22.9 | 29.87 |
| Control | 3:10 | 24.5 | 35.63 |
| Multiple metals at w/c=0.6 | | | |
| IMMH.3K | 8:50 | 24.7 | 77.25 |
| IMMH.30K | 7:15 | 26.9 | 10.38 |
| NMMH.30K | 13:00 | 23.1 | 11.00 |
| IMMH.3K (w/c=0.4) | 6:25 | 26.7 | 16.08 |
| Supplemental Gypsum and Silica Fume Mixes at w/c=0.6 | | | |
| LGTM | 9:04 | 25.1 | 77.86 |
| HGTM | 8:30 | 26.4 | 65.67 |
| SFTM | 7:35 | 26.1 | 11.72 |

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WARNING: Contact with wet (unhardened) concrete, mortar, cement, or cement mixtures can cause SKIN IRRITATION, SEVERE CHEMICAL BURNS (THIRD-DEGREE), or SERIOUS EYE DAMAGE. Frequent exposure may be associated with irritant and/or allergic contact dermatitis. Wear waterproof gloves, a long-sleeved shirt, full-length trousers, and proper eye protection when working with these materials. If you have to stand in wet concrete, use waterproof boots that are high enough to keep concrete from flowing into them. Wash wet concrete, mortar, cement, or cement mixtures from your skin immediately. Flush eyes with clean water immediately after contact. Indirect contact through clothing can be as serious as direct contact, so promptly rinse out wet concrete, mortar, cement, or cement mixtures from clothing. Seek immediate medical attention if you have persistent or severe discomfort.

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