

IMMOBILIZATION OF As, Cd, Cr AND Pb-CONTAINING SOILS BY USING CEMENT OR POZZOLANIC FIXING AGENTS*

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Summary

The present work reports leaching data for a soil contaminated with four inorganic model wastes, Cd(II) and Pb(II) nitrates, sodium arsenite, and sodium chromate, at concentrations in the range of 10,000 to 12,200 ppm. Various combinations of Type I portland cement (OPC), Type F fly-ash, blast furnace slag, lime, and silica fume have been used to treat the contaminated soils, which are then leached using a slightly modified EP Tox¹ leaching procedure. In no case does fly ash improve performance when mixed with other binding agents. Slag offers superior performance compared to fly ash in any combination tested and has some potential for general utility in practice. In particular, several mixtures including slag are effective in immobilizing lead, which sometimes given problems in solidification with cement. Type I portland is a very versatile and dependable reagent compared to the other agents used. In the cases of As and Cr, the performance of portland alone is superior to that of any other reagent or combination, when comparisons were made at the same dosage level. Cement alone was not among the fixing agents tested for Cd and Pb, but several combinations with cement were included. In every case, inclusion of OPC results in leachate concentrations as low as or lower than the corresponding mixture without OPC.

Introduction

Solidification/stabilization often uses cement and cement-like materials (and water if necessary) in the treatment of soils which are contaminated with hazardous wastes, particularly when the wastes are largely inorganic. Indeed, the U.S. EPA's SITE program has already included two demonstration projects using cement or pozzolanic materials for which applications analysis reports have appeared [1], and further demonstrations are underway. In cases of some heavy metal-containing wastes, the technology appears both cost-effective and safe, since the metals are converted into (or retained as) highly insoluble salts

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¹EP Tox is short for toxicity characteristic extraction procedure.

which do not leach into groundwater at appreciable rates. Nevertheless, with a technology which is so cheap and easy to apply, there is a great tendency to use it in cases in which its reliability could be questioned — particularly with the mixed wastes characteristic of contaminated soils. There are in fact many reports in the cement literature of adverse effects (usually upon strength development) due to the presence of a variety of admixtures [2], and such deleterious effects on the cement matrix may affect waste immobilization. There are also reports that two common inorganic pollutants, arsenic and chromium, are not effectively immobilized by cementitious systems [3–5]. Arsenic, whether in the form of arsenite or arsenate, and chromium in the form of chromate, have completely different chemical behavior from that of the metal 2^+ or 3^+ ions. The latter form quite insoluble hydroxides or carbonates or mixed salts when treated with the very basic solidifying agents.

The As(III), As(V), or Cr(VI) species are not converted into less soluble forms just by contact with a basic aqueous system. They may be immobilized by some other mechanisms, such as mixed salt formation or simple encapsulation resulting from unconnected porosity, or they may not be immobilized at all.

The present work reports leaching data for a soil contaminated with four different inorganic model wastes, Cd(II) and Pb(II) nitrates, sodium arsenite, and sodium chromate, at concentrations in the range of 10,000 to 12,000 ppm, based on Cd, Pb, As, and Cr, respectively. Various combinations of Type I portland cement, Type F fly-ash, blast furnace slag, lime, and silica fume have been used to treat the contaminated soils, which are then leached using a slightly modified EP Tox leaching procedure. Cement, fly-ash, and lime are quite common solidifying agents. Blast furnace slag is another common, cheap pozzolanic material which has been widely investigated as a component of cements for construction purposes [6]. The slag is lower in aluminate content than ordinary portland cement (OPC) and thus produces a solidified concrete that is more sulfate resistant than OPC. In that sense it is similar to fly-ash, although it is much more consistent in composition than fly ash and higher in silicate content. The activated slag cement is denser than OPC, being high in calcium silicate hydrate (C-S-H) and low in calcium hydroxide.

The principal types of silica fume consist largely of SiO_2 , but contain other oxides in varying amounts depending upon the silicon alloy being produced [7]. Silica fume is itself pozzolanic, and when it is blended with cements, one of the main effects is the combination of the extra silica with lime, resulting in a cement paste which has a higher proportion of C-S-H and a lower proportion of calcium hydroxide. One of the main applications is in the formation of high-strength concrete made with silica fume, portland cement, and superplasticizers. The high strength is accompanied by low permeabilities. The ultrafine silica fume particles pack densely in the cement pore spaces (in part because the particles are spherical) and also undergo pozzolanic reactions. Another

added benefit of such materials is increased frost resistance. Fly ash, slag, and silica fume all have silica microspheres which can potentially act in the manner just described, but the purity of the silica increases greatly in the order listed.

Methods and materials

The soil used for the work was a Mississippi loess with a 2 percent organic content. The soil was freshly contaminated with an aqueous solution of the appropriate inorganic salt prior to solidification. After curing for periods of 48 h, 7 days, or 28 days, the materials were tested with a pocket penetrometer to determine whether a compressive strength of at least 50 psi (3.5 bar) had been obtained. If so, the materials were crushed and leached as described below.

Solidification procedure

Each solidified sample was prepared from fresh soil which was contaminated with one of the four inorganic salts immediately before the solidifying agents were added. The soils were weighed into a 120 mL plastic cup and mixed, using a stainless-steel stirring rod, with aqueous solutions of NaAsO_2 , $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Na}_2\text{CrO}_4 \cdot \text{H}_2\text{O}$ or $\text{Pb}(\text{NO}_3)_2$, respectively, in order to produce a mixture that was in the range of 10,000 to 12,000 ppm of the contaminant, i.e., As, Cd, Cr, or Pb, measured as weight of contaminant per weight of dry soil + inorganic salt. The following mixtures were used: (a) 45.7 g of soil with 5 mL of an aqueous solution containing 0.115 g As per mL giving a concentration of 12,200 ppm As; (b) 48.6 g of soil with 5 mL of a solution of 0.100 g of Cd per mL giving a concentration of 10,000 ppm Cd; (c) 38.7 g of soil with 5 mL of a solution of 0.100 g of Cr per mL giving a concentration of 12,200 ppm Cr, and (d) 45.0 g of soil with 5 mL of a solution of 0.100 g of Pb per mL giving a concentration of 10,900 ppm Pb.

The compounds to be mixed with the soil were weighed into a separate plastic cup, to which 15 mL of water was added. The amounts of solidifying agents added are indicated in the tables which appear in the discussion section of this paper. After stirring to form a slurry, the slurry was added to the contaminated soil, stirred thoroughly, then sealed with an airtight lid and stored in the dark at room temperature ($23 \pm 2^\circ\text{C}$).

Several experiments were carried out in order to determine whether the initial distribution of water between soil and solidifying agents made an appreciable difference in the leaching results. The following variations were tried: 5 mL of water to the soil and 15 mL to the solidifying agents; 10 mL to the soil and 10 mL to the agents; and 15 mL to the soil and 5 mL to the agents. These experiments were run with slag and lime as the binding agents, with four different weight ratios of slag to soil and two ratios of lime to slag. There was no significant difference in the concentrations of any of the contaminants in the leachates, and hence this variable was not investigated further.

At time intervals of 48 h, 7 days, and 28 days, the plastic cups were opened, and a pocket penetrometer with a maximum reading of 62.5 psi (4.3 bar) was inserted into the matrix. If the compressive strength reading exceeded 50 psi, the sample was subjected to leaching as described below. If not, the sample was resealed and returned to the storage drawer.

Leaching procedure

A modification of the U.S. EPA Toxicity Test [8] was employed. The solidified matrix described above was removed from the plastic cup and placed into a mortar, where a piece of approximately 15 g weight was cleaved from the large sample. The latter was replaced in the cup, which was sealed and returned to the storage drawer. The smaller piece was crushed with a pestle, so that it could pass through a 9.5 mm sieve. Of the crushed material 10 g were then placed in a 250-mL plastic bottle, to which 160 mL of deionized water and 40 mL of 0.5 M acetic acid were added. The bottle was then placed in an agitator for 24 h. Thus, the procedure differs from the EP Tox in using a tenth of the amount of sample and correspondingly less leaching solution. Furthermore, all 40 mL of the acetic acid solution was added at the beginning and not simply when the pH rose above 5.2. The pH of all solutions was measured at the conclusion of the agitation, and all samples had a pH above 5.2, verifying that an excess of acetic acid solution was not added.

After agitation, the samples were vacuum filtered through a 0.45 μm glass fiber filter. The filtrate was then analyzed by AAS-ICP using a Jarrell-Ash AtomComp direct-reading inductively coupled argon plasma spectrometer. It should be noted that the spectrometer response is linear with concentrations up to 100 mg/L for Cd, Cr, and Pb, and up to 75 mg/L for As. Higher concentrations, which are encountered in this work, should be corrected for the non-linear response (this has not been done). The instrument was standardized each day before any samples were run and checked after each 5 to 7 samples. Three standards were used: a blank sample containing deionized water; a solution containing 10 ppm each of Cd, Cr, and Pb; and a solution containing 10 ppm of As. The latter solutions were prepared by dilution of 1,000 ppm laboratory standard solutions. A drift in the results of more than 2 percent for any of the metals in the standard solutions was used as an introduction of the need for recalibration of the instrument.

Results

Slag/lime combinations have been investigated recently for use in construction applications because of their rapid setting characteristics and their production of a dense, durable matrix [6]. In preliminary work related to that reported here, we have investigated appropriate ratios of lime to slag to water in order to produce a rapidly setting matrix. We have carried out scanning

electron microscopic investigations of the solids produced and have noted little porosity. Part of the motivation for the current work was the assumption that a dense matrix with little porosity would be favourable from a mechanical point of view in solidification/stabilization.

The current work is related to the general problem of immobilization of inorganic species in soils contaminated with hazardous wastes at relatively high concentrations. The species chosen include heavy metal ions (Cd^{2+} and Pb^{2+}), as well as two troublesome complex ions (AsO_2^- and CrO_4^{2-}). The immobilizing agents being used are common ones, including Type I portland cement and Type F fly-ash, as well as slag, lime, and silica fume.

Cd-contaminated soils

Our previous work [9] and that of others [3,4] has indicated that Cd(II) is in general effectively immobilized by cement and pozzolanic fixing agents. Our view of the interactions of Cd(II) with setting cement [9] suggests that very insoluble $\text{Cd}(\text{OH})_2$ is precipitated very early in the process of cement hydration and that it serves as nuclei for crystallization of calcium silicate hydrate gel (C-S-H). The leaching results from the soil samples investigated in the present work are shown in Table 1. Cement alone and cement/fly-ash mixtures were not investigated, since we and others have found them to be effective. The regulatory limit under the EP Toxicity Waste Characterization is 1.0 mg/L of

TABLE 1

Cadmium contaminated soil (10,000 ppm), binding agents and leachability

Weight of additive per 100 g of soil					Leachate EP, ppm
Cement	Fly ash	Slag	Lime	Silica	
0.0	0.0	0.0	0.0	0.0	338
0.0	0.0	10	0.3	0.0	— ^a
0.0	0.0	21	0.6	0.0	82
0.0	0.0	21	1.2	0.0	93.5
0.0	0.0	41	1.2	0.0	0.08
5	0.0	5	0.0	0.0	195
10	0.0	10	0.0	0.0	0.48
21	0.0	21	0.0	0.0	0.02
0.0	5	5	0.3	0.0	200
0.0	10	10	0.6	0.0	137
0.0	10	10	1.2	0.0	134
0.0	21	21	1.2	0.0	43.9
0.0	0.0	10	0.3	0.5	144
0.0	0.0	20	0.6	1	13
0.0	0.0	20	1.2	1	16.8
0.0	0.0	39	1.2	2	0.05

^aSample did not set to at least 50 psi compressive strength.

Cd. A 1:1 ratio of cement/slag produced a waste form that leached about 0.5 ppm of Cd when the weight ratio of soil to fixing agent blend was 1:0.2. At higher ratios of soil to fixing agent blend (1:0.42) performance was even better for both 1:1 cement/slag, and for slag/lime mixtures. Slag/lime at lower dosages was significantly less effective, as was slag/fly ash at all dosages tested. Silica fume as an additive improved the performance of slag/lime mixtures, both with respect to increasing the rate of attainment of a 50 psi compressive strength (as shown from pocket penetrometer readings at 48 h and 7 days) and reducing the concentration of Cd in the leachate. While mixtures containing slag showed satisfactory performance in some of the cases tested, there is no compelling evidence that slag alone or in combination with other agents has special attributes that make it more effective.

Pb-contaminated soils

In our previous work with Type I portland, lead salts produced deleterious effects on immobilization performance in several respects [9]. Lead salts have a major rate-retarding effect on cement hydration reactions, and also produce a mature cement matrix that has a different composition in terms of silicate species than that of cement alone. These differences are accompanied by a leachability that is 100-times or more greater than that of cadmium salts. Our view of the process of cement hydration in the presence of lead salts, which is supported by the results of others [10,11], accounts for the greater mobility of lead in the following terms. Lead is precipitated under basic conditions in the form of a number of mixed salts and principally on the surfaces of the solids present. These salts dissolve and reprecipitate throughout the course of the cement hydration process, leading to a mature cement paste that has a high surface concentration of lead species. Thus, the solidified lead salts are much more accessible to leaching solutions than are the cadmium salts.

The results for Pb-contaminated soils are shown in Table 2. The EP Toxicity regulatory limit for Pb is 5.0 mg/L. In contrast to cement alone, which was investigated without soils present, mixtures containing slag were effective at immobilizing Pb in the soil samples. The 1:1 cement:slag mixtures were notably effective at dosages of greater than 20 percent by weight compared to the weight of soil being treated. Fly ash/slag mixtures were notably less effective than cement/slag or slag/lime at comparable dosages. As with Cd results, silica fume enhanced the performance of slag/lime mixtures, both with respect to achievement of acceptable compressive strength and reducing leachability. At an approximately 23 wt.% dosage rate, slag/lime is marginally acceptable in terms of leachability, but it is notably more effective in the presence of a small amount of silica fume.

The rate-retarding effect associated with lead salts is not apparent in Table 3, because most of the samples attained a 50 psi compressive strength after 28 days. However, many of the 48 h and 7 day tests with the pocket penetrometer

TABLE 2

Lead-contaminated soil (10,900 ppm), binding agents and leachability

Weight of additive per 100 g of soil					Leachate EP, ppm
Cement	Fly- ash	Slag	Lime	Silica	
0.0	0.0	0.0	0.0	0.0	379
0.0	0.0	11	0.3	0.0	— ^a
0.0	0.0	22	0.7	0.0	7.02
0.0	0.0	22	1.3	0.0	3.69
0.0	0.0	44	1.3	0.0	0.55
5.5	0.0	5.5	0.0	0.0	105
11	0.0	11	0.0	0.0	0.28
22	0.0	22	0.0	0.0	0.18
0.0	5.5	5.5	0.3	0.0	— ^a
0.0	11	11	0.7	0.0	75.2
0.0	11	11	1.3	0.0	76.7
0.0	22	22	1.3	0.0	2.56
0.0	0.0	11	0.3	0.6	88.9
0.0	0.0	21	0.7	1.1	1.85
0.0	0.0	21	1.3	1.1	0.55
0.0	0.0	42	1.3	2.2	0.18

^aSample did not set to at least 50 psi compressive strength.

TABLE 3

Arsenic-contaminated soil (12,200 ppm), binding agents and leachability

Weight of additive per 100 g of soil					Leachate EP, ppm
Cement	Fly- ash	Slag	Lime	Silica	
0.0	0.0	0.0	0.0	0.0	420
44	0.0	0.0	0.0	0.0	4.56
22	22	0.0	1.3	0.0	111
0.0	36	0.0	7.7	0.0	201
0.0	0.0	11	0.3	0.0	322
0.0	0.0	22	0.7	0.0	241
0.0	0.0	22	1.3	0.0	241
0.0	0.0	44	1.3	0.0	134
0.0	0.0	77	2.2	0.0	91.7
0.0	0.0	109	3.3	0.0	74.9
5.5	0.0	5.5	0.0	0.0	292
11	0.0	11	0.0	0.0	162
22	0.0	22	0.0	0.0	57.7
0.0	11	11	0.7	0.0	291
0.0	11	11	1.3	0.0	297
0.0	22	22	1.3	0.0	215
0.0	0.0	10	0.33	0.55	320
0.0	0.0	21	0.7	1.1	207
0.0	0.0	21	1.3	1.1	215
0.0	0.0	42	1.3	2.2	126

did indicate low compressive strengths at these earlier times. The effect was more pronounced in the slag/lime and slag/fly-ash/lime mixtures than in the slag/cement mixtures. Nevertheless, except for the dosages in the 10 percent range, all samples tested did reach a compressive strength of 50 psi within 28 days.

Arsenite-contaminated soils

As expected from previous work in the literature, performance with respect to leachability is much less satisfactory with arsenite-contaminated soils than with the heavy metal cation contaminants. The results are shown in Table 3. These results, and the ones to follow for chromate, contain direct comparisons of samples containing slag with those prepared from cement, cement/fly-ash, and fly ash/lime. The EP Tox regulatory limit for As is 5.0 mg/L, and the only sample in the current study showing reasonable performance is portland cement alone at a dosage of 1 part soil in 0.44 part cement. Cement/fly-ash and fly-ash/lime mixtures at comparable dosages showed poorer leachability results. All of the slag-containing samples show relatively poor performance,

TABLE 4

Chromium (VI)-contaminated soil (12,200 ppm), binding agents and leachability

Weight of additive per 100 g of soil					Leachate EP, ppm
Cement	Fly ash	Slag	Lime	Silica	
0.0	0.0	0.0	0.0	0.0	441
52	0.0	0.0	0.0	0.0	90.8
26	26	0.0	1.5	0.0	199
0.0	43	0.0	9.0	0.0	265
0.0	0.0	13	0.4	0.0	343
0.0	0.0	26	0.8	0.0	168
0.0	0.0	26	1.5	0.0	211
0.0	0.0	52	1.5	0.0	62.1
0.0	0.0	90	2.6	0.0	54.7
0.0	0.0	129	3.9	0.0	38.5
6.5	0.0	6.5	0.0	0.0	287
13	0.0	13	0.0	0.0	197
26	0.0	26	0.0	0.0	58.5
0.0	6.5	6.5	0.4	0.0	293
0.0	13	13	0.8	0.0	263
0.0	13	13	1.5	0.0	265
0.0	26	26	1.5	0.0	197
0.0	0.0	12	0.4	0.6	274
0.0	0.0	25	0.8	1.3	192
0.0	0.0	25	1.5	1.3	199
0.0	0.0	49	1.5	2.6	64

even at a dosage greater than 1:1 soil/slag. Fly-ash/slag/lime showed poorer immobilization than slag/lime, and in contrast to the earlier results for Cd and Pb, silica fume improved performance only marginally.

Chromate-contaminated soils

The results with chromate-contaminated soils parallel those with arsenite, and are shown in Table 4. As with the arsenite samples, all solidified samples that contain chromate showed reduced leachability compared to the contaminated soil alone, however, none of the leachate levels were reduced to near the regulatory limit of 5.0 mg/L. At a dosage of approximately 52 parts of binding agent to 100 parts of soil, all of the following binding agents give comparable reductions in leachability: cement, cement/slag, and slag/lime. Again, incorporation of fly ash results in deterioration in performance. Inclusion of silica fume with the slag/lime formulations does not yield appreciable improvement.

Discussion and conclusion

The data presented above reveal a number of trends and lead to some significant conclusions regarding solidification/stabilization practice. In the cases of the arsenite- and chromate-contaminated soils, seven different formulations of binding agents, at approximately the same dosage rate, can be compared among themselves and compared to soil without binder. Figures 1 and 2 present a graphical representation of relative efficiency of immobilization in these two cases, and several conclusions stand out. In no case does fly-ash improve performance when mixed with other binding agents. This is a surprising conclusion, since fly ash is sometimes claimed to offer significant benefits. Slag offers superior performance compared to fly ash in many combinations tested and has some potential for general utility in practice. In particular, several mixtures including slag are effective in immobilizing lead, which sometimes gives problems in solidification with cement.

The major conclusion of the current research must be that Type I portland (OPC) is a very versatile and dependable reagent compared to the other agents used. In the cases of As and Cr, the performance of portland alone is superior to that of any other reagent or combination, when comparisons are made for the same dosage level. Cement alone was not among the fixing agents tested for Cd and Pb, but several combinations with cement were included. In every case, inclusion of OPC results in leachate concentrations as low as or lower than the corresponding mixture without OPC. We cannot, of course, extrapolate these conclusions to all inorganic contaminants or to all soils, and certainly not to aqueous waste streams containing these contaminants. In particular, the performance of OPC alone with Pb-containing aqueous wastes has been shown to present problems with both rate of setting and leachability [9].

We are continuing our research to make a broad survey of potential fixing

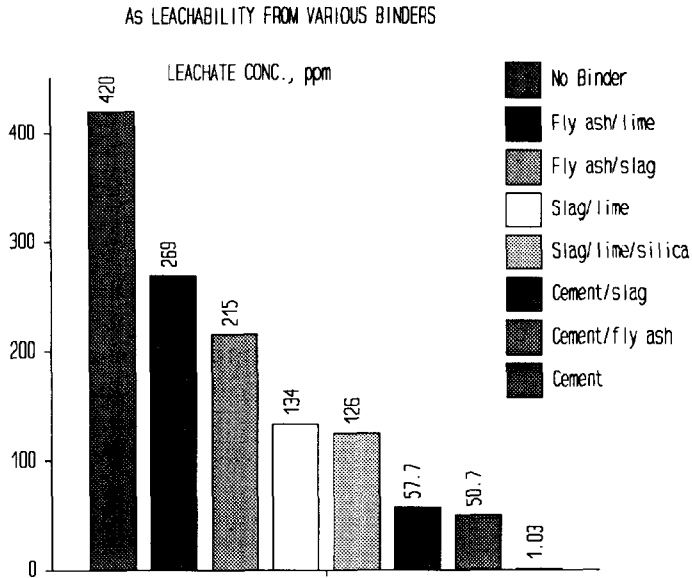


Fig. 1. Relative leaching rates from soils contaminated with sodium arsenite (12,200 ppm As), solidified and cured for 28 days.

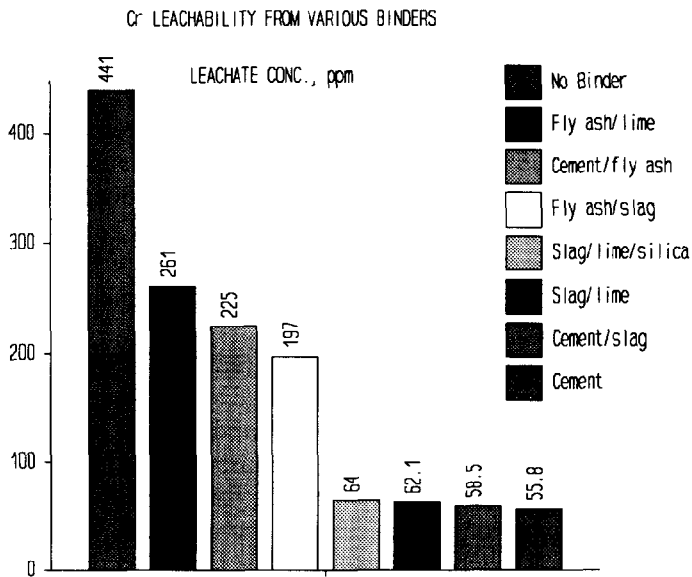


Fig. 2. Relative leaching rates from soils contaminated with sodium chromate (12,200 ppm Cr), solidified and cured for 28 days.

agents for inorganic wastes, including solutions and sludges, as well as contaminated soils. In subsequent papers we will report on other combinations as well as thorough microscopic and spectroscopic characterization of the samples that show promising performance.

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