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Stabilization and Solidification of Metal-Laden Wastes by Compaction and Magnesium Phosphate-Based Binder

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ABSTRACT

Bench-scale and full-scale investigations of waste stabilization and volume reduction were conducted using spiked soil and ash wastes containing heavy metals such as Cd, Cr, Pb, Ni, and Hg. The waste streams were stabilized and solidified using chemically bonded phosphate ceramic (CBPC) binder, and then compacted by either uniaxial or harmonic press for volume reduction. The physical properties of the final waste forms were determined by measuring volume reduction, density, porosity, and compressive strength. The leachability of heavy metals in the final waste forms was determined by a toxicity characteristic leaching procedure (TCLP) test and a 90-day immersion test (ANS 16.1). The structural composition and nature of waste forms were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

CBPC binder and compaction can achieve 80-wt % waste loading and 39–47% reduction in waste volume. Compressive strength of final waste forms ranged from 1500 to 2000 psi. TCLP testing of waste forms showed that all heavy metals except Hg passed the TCLP limits using the phosphate-based binder. When Na_2S was added to the binder, the waste forms also passed TCLP limits for Hg. Long-term leachability resistance of the final waste forms was achieved for all metals in both soil and ash wastes, and the leachability index was ~14. XRD patterns of waste forms indicated vermiculite in the ash waste was chemically incorporated into the CBPC matrix. SEM showed that waste forms are layered when compacted by uniaxial press and are homogeneous when compacted by harmonic press.

IMPLICATIONS

Hundreds of millions of dollars are spent by businesses and the government for the treatment and disposal of hazardous waste. This project researched a stabilization and solidification method involving CBPCs. This method reduces heavy metal mobility in soil and ash wastes by producing relatively inert waste forms with good structural properties. In addition, it reduces the final volume of the waste, leading to reduction in transportation and landfill disposal costs.

INTRODUCTION

The U.S. Department of Energy (DOE) has generated large volumes of low-level radioactive, hazardous, and mixed wastes as a result of its energy- and defense-related research over the last 60 years.[1] Having acknowledged this problem, the DOE has funded several projects in its research laboratories in an effort to find an easy, cost-effective, and safe means of disposing this waste. Much of the DOE waste streams containing heavy metals and radionuclides require solidification/stabilization (S/S) before final disposal to reduce the mobility of contaminants into the environment. The most common practice at DOE and commercial facilities is to solidify waste using Portland cement.

Although cement stabilization processes are inexpensive, readily available, and easy to process, there are limitations. In most commercial cement stabilization processes, contaminant metals are precipitated as insoluble hydroxides, which have minimum solubility between the pH range of 8 and 11 of cement.[2] Most surface and groundwaters tend to have a pH between 5.5 and 8, and when the cement-stabilized metal waste forms come in contact with these waters, there is a potential for metals leaching from waste forms. Furthermore, cement hardens by means of a chemical hydration reaction that is susceptible to interference by the waste. For example, many inorganic salts and heavy metals present in waste streams are known to inhibit cement hydration, leading to a reduced amount of waste that can be incorporated and/or result in poor quality waste forms.[2] Thus, low-cost cement S/S is offset by poor waste loading efficiency and potentially poor structural performance of waste forms in disposal.

Brookhaven National Laboratory has developed two thermoplastic processes for treating hazardous and mixed waste.[3] The modified sulfur cement waste forms in these two processes can encapsulate up to 43-wt % incinerator fly ash, while the maximum quantity of this waste in hydraulic cement is 16 wt %. Although the comparison is impressive, 57-wt % binder is required for waste S/S using sulfur cement thermoplastic methods. This will not reduce the final volume of waste, as any increase in weight has an associated volume increase.

The chemically bonded phosphate ceramic (CBPC) technology, developed at Argonne National Laboratory (ANL), has been very successful in the S/S of hazardous and low-level mixed wastes that are part of the mixed waste stream inventory at several DOE sites.[4] This technology is based on synthetically produced, newberyite-rich magnesium phosphate ceramic and is intended for stabilization of the DOE's low-level mixed waste streams.[5] Since newberyite[6] has high strength and low solubility (10^{-6}), the magnesium phosphate matrix can be a very stable ceramic in an aqueous environment, hence making it a good candidate for stabilizing waste streams. CBPC is formed by an exothermic acid-base reaction between a supersaturated solution of calcined magnesium oxide (MgO) at a pH of 10.4 and a solution of phosphoric acid (H_3PO_4) at a pH of 0. Free-energy calculations show an estimate of heat evolution.

$$H_3PO_4 + MgO + 2H_2O \rightarrow MgHPO_4{\cdot}3H_2O \qquad (1)$$
$$\Delta G = -97.94 \text{ kJ/mol}$$

In order to form newberyite, it is necessary to react a stoichiometric proportion of 40.3 g MgO with 98 g H_3PO_4 and 36 g of water.

The most important fixation mechanism for metals in S/S systems is chemical precipitation as low-solubility species. During formation of chemically bonded phosphate ceramics, the contaminants are first converted into their low solubility phosphates and then physically encapsulated in the magnesium phosphate matrix, yielding excellent waste forms for hazardous and radioactive waste.[5] Removal of lead from wastewater has been most efficient when it is precipitated as phosphate.[7] Solubility of metal sulfides and phosphates are much lower than hydroxides.[8] In fact, phosphates prove to be the least soluble of the heavy metal species. An exception to this is Hg, where HgS has a higher pK_{sp} value (52) compared with mercury phosphate ($pK_{sp} = 45$). Typically, phosphates have the ability to form insoluble complexes of hazardous metals over a relatively wide pH range.[9] The solubility of mercury phosphate is low in the groundwater pH range, but not sufficiently low to meet the stringent universal treatment standard (UTS) limit of 0.025 mg/L. The leaching level of Hg can be further reduced by converting it into HgS, which has an extremely low solubility product.[10]

There has been no specific attempt in the past at volume reduction of waste using CBPC binders. So far, little research has been done in finding a viable technology that would ultimately decrease the final waste volume even after the addition of binders. Researchers at Lawrence Livermore National Laboratory conducted a comparative cost analysis study in which low-level mixed waste was compacted using various industrial compactors.[11] Although their study provided some insight into available compaction systems, it did not include the stabilization aspect of waste disposal.

The objective of this research was to develop a high waste loading compaction technique for stabilizing the most common waste streams such as ash and soil using a CBPC binder, without compromising effective contaminant stabilization and high compression strength of waste forms. Maximizing binder loading and reducing the final volume of waste translates to shorter treatment time, an increase in available landfill space, and ultimately big savings in transportation and disposal costs.

EXPERIMENTAL METHODS

In order to develop a viable S/S technology, bench-scale samples were fabricated to determine a standard binder composition and optimum waste loading for compacting ash and soil waste. Brick-size samples were prepared using both a uniaxial press at ANL and a harmonic press at Denver University. Bricks produced using both presses were subjected to various tests in order to determine if compaction method dictates the production of a good waste form. Tests were conducted to evaluate their physical properties, compression strength, leach resistance (by toxicity characteristic leaching procedure [TCLP]), and long-term leaching resistance (using American Nuclear Society's ANS 16.1 test). The metals in the leachate were determined by atomic adsorption spectroscopy (AAS). Specific methods and materials are described in the following sections.

Surrogate Waste Preparation

The surrogate waste was prepared in the laboratory based on steps similar to those involved in the formation of actual waste. The DOE surrogate ash waste composition given in Table 1 closely represents one of the DOE ash waste streams.[1] It consists of fly ash, coal bottom ash, vermiculite, and activated carbon as its major constituents and salts of certain metals as hazardous contaminants.

Table 1. Components of surrogate ash waste.

Bulk Components	wt % of Bulk	Spiked Contaminants	wt % of Bulk
Class F fly ash	37	$Cr(NO_3)_3$•$9H_2O$	2.6
Coal bottom ash	30	$Cd(NO_3)_2$•$4H_2O$	1.4
Vermiculite	20	$Pb(NO_3)_2$	0.8
Activated carbon	5	$Ni(NO_3)_2$•$6H_2O$	2.5
		$HgCl_2$	0.7

Activated carbon is used to adsorb the contaminants in liquid waste streams, while the vermiculite absorbs the liquid. This explains the presence of these substances in the actual bulk waste. In order to simulate these effects in the surrogate waste, activated carbon was first loaded with the contaminants and was later mixed with the bulk waste containing Class F fly ash, coal bottom ash, and vermiculite. The surrogate ash waste was then mixed thoroughly for 24 hr on a vibratory shaker.

Soil was sampled from an old rifle firing range at ANL. The original soil was contaminated with elemental Pb at different levels, but over the course of time, it is likely that some of it was converted to oxide or other forms due to corrosion. This soil consisted of 76.07-wt % fraction below 0.15-mm particle size and the rest in the range >0.15 mm. XRD indicated that a third of the soil consisted of SiO_2 (Figure 1). Since SiO_2 is not reactive in an acidic environment,[12] it was unlikely that the major components of the soil would react with the CBPC binder. Acid digestion analysis and AAS indicated that significant levels of Ba, Cr, Cu, Pb, Ni, and Zn were present in the soil (Table 2). TCLP analysis of the soil showed that the untreated soil fails for Pb, and its level in the extract was 1791 mg/L. To test the CBPC-compaction process in a worst-case scenario, the soil was further spiked with nitrates of Cd, Cr, Pb, and $HgCl_2$ in a manner such that the added level of each metal in the soil was 5000 ppm (Table 3). The soil was then mixed with the contaminants and put on a vibratory shaker for 24 hr.

Bench-Scale Fabrication

Bench-scale samples were prepared with the spiked soil waste on the uniaxial press. The soil was mixed with H_3PO_4 (85 wt % concentrated) for 15 min and with calcined MgO for another 15 min. The resulting mixture was transferred into a 0.8-in.-diameter cylindrical mold. Using a bench-top uniaxial press, the mixture was compacted at 2000 psi and held at that pressure for 10 min. When taken out of the mold, the samples (size 0.8-in. diameter and 2-in. length) held their structural integrity, but as yet had no load-bearing capacity. In previous studies,[5] it was determined that CBPC samples required a minimum of 21 days of curing time, during which period they developed strength. Three sets of samples were made using 10-, 15-, and 20-wt % binder and were stored in a humid environment. Binder denotes a mixture of H_3PO_4, MgO, and H_2O, determined stoichiometrically from eq 1.

Full-Scale Fabrication

Figure 2 shows the full-scale compaction process diagram. The ash/soil wastes were mixed with the stoichiometric amount of deionized water for 30 min. Often, the contaminants and the bulk waste do not form a homogeneous surrogate waste mixture. Mixing thoroughly with water helps disperse the contaminants evenly in the waste stream. The stoichiometric amount of H_3PO_4 (85-wt % concentration) was then added and mixed for 30 min. MgO was added to this mixture gradually and mixed for 15 min. Stoichiometric amounts of binder, comprising H_2O, H_3PO_4, and MgO,

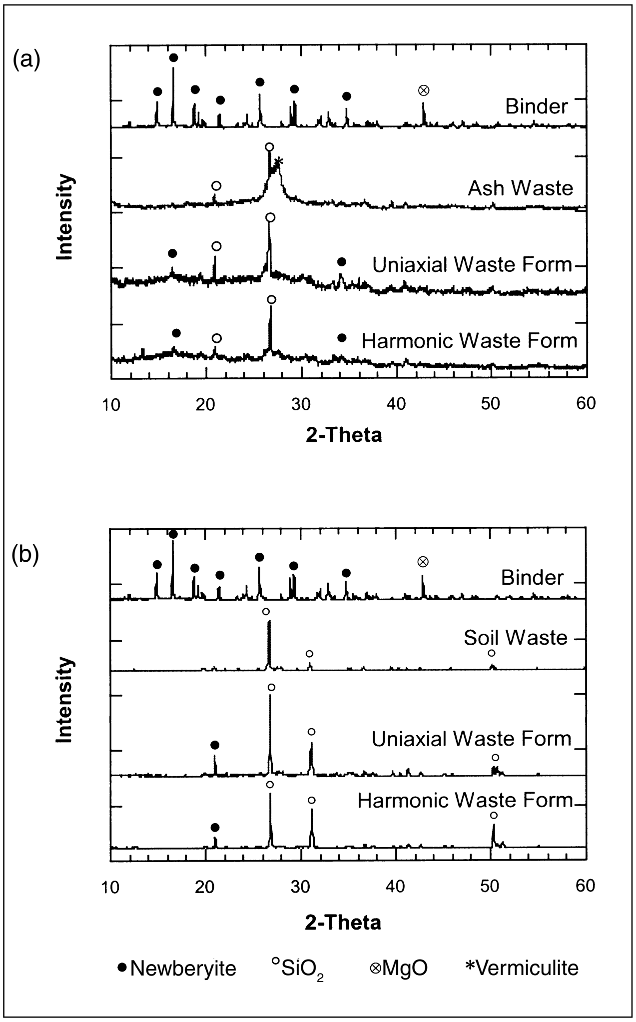


Figure 1. XRD images of (a) surrogate ash waste forms and (b) contaminated soil waste forms.

Table 2. Hazardous metals content in the unspiked and spiked soil.

Element	In Unspiked Soil of Size (ppm): 0.15–2mm	<0.15 mm	>2 mm	In Spiked Soil (ppm)
Ba	26.6	44.4	40.3	40.3
Cd	<1	<1	<1	5000
Cr	12.3	21.3	19.2	5019.2
Hg	0	0	0	5000
Cu	34.6	65.6	58.2	58.2
Pb	4750	825	1760	6760
Ni	17.8	24.1	22.6	22.6
Zn	85.4	14.6	73.8	73.8

Table 3. Composition of contaminated soil.

Components	wt %
Lead-contaminated soil	93.9
$Cd(NO_3)_2{\cdot}4H_2O$	1.4
$Cr(NO_3)_2{\cdot}9H_2O$	3.9
$Pb(NO_3)_2$	0.2
$HgCl_2$	0.6

were calculated from eq 1. The temperature of the mixture increased slightly due to the reaction between MgO and H_3PO_4. The mixture was then transferred to the mold for compaction. In the case of uniaxial compaction, the plunger was lowered very slowly to release any trapped air within the ash/soil and the mold. It took 3–4 min to attain the full pressure of 1000 psi. This pressure was maintained for a total of 10 min and was then released. In the case of the harmonic compactor,[13] the whole process of compacting the ash/soil takes only 5 sec. In both cases, samples (size 8 × 3.5 × 3 in.) were removed from the molds and were allowed to cure for 21 days before they were subjected to various performance tests.

Procedural Modifications

TCLP results of samples made according to the procedure described above indicated that some of the contaminant metals in the wastes failed to stabilize effectively. Also, Hg could not be sufficiently stabilized by conversion into phosphates. The addition of a small amount of sulfide stabilizes Hg as HgS (cinnabar).[10] Therefore, procedural modifications were made in making brick waste forms. Twice the stoichiometric amount of sulfur needed for stabilizing Hg was added as Na_2S in the binder powder. Since any unreacted Na_2S would immediately react with the concentrated H_3PO_4, producing foul-smelling H_2S, the concentration of the acid was reduced to 50 wt %. Due to the reaction of H_3PO_4 with the major constituents of fly ash, it was possible that the phosphate required for contaminant stabilization would be reduced.[14] Hence, the binder loading was increased to 20% from the 15% previously used. The waste form fabrication procedure remained the same with the exception of mixing the waste with the stoichiometric amount of H_3PO_4 (50 % wt.) for 60 min, then adding MgO to this mixture and further mixing for 15–30 min.

Waste Form Testing and Characterization

Physical properties, such as the bulk density of the ceramic waste form, its open porosity, and its compression strength, provide sufficient quantitative information on its physical integrity. Land disposal regulations (LDR) require a minimum compression strength of 500 psi for waste forms.[2] Compression strength is defined as the maximum compressive stress at failure. It was determined for small-scale cylindrical samples by ASTM C109/C109M method using a universal testing system (model 4505, Instron Corp.). In the case of full-scale samples, each brick was cut into 2- × 2- × 2-in. size cubes using a diamond-coated disc ceramic cutter. Compression strength was measured by ASTM C39 method, prescribed for bricks.

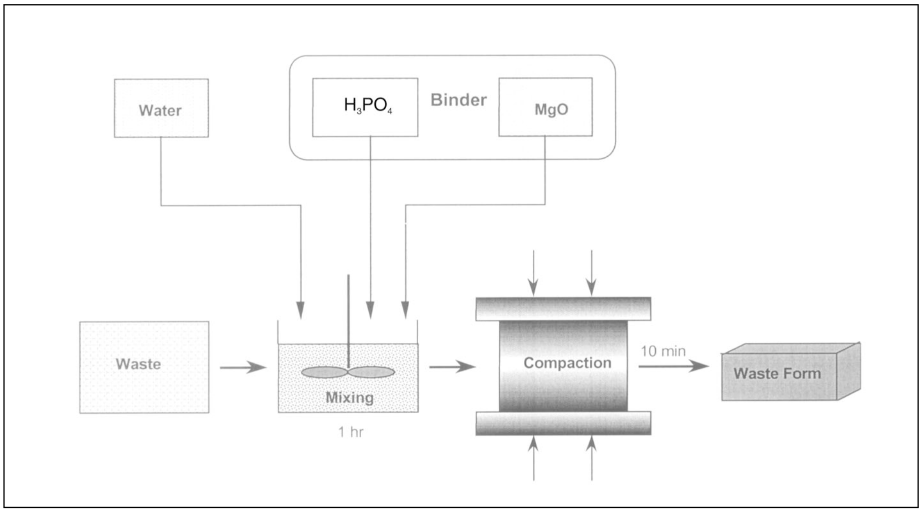


Figure 2. Process diagram for S/S of wastes using CBPC binder and compaction.

The XRD technique was used to identify crystalline phases of the waste forms. Phases of the specimens were analyzed by XRD with a Scintag XDS 2000 using CuK^a radiation. The 2ϕ range of 10–60° was scanned in steps of 0.03° at 2 sec per step. The physical structure of the matrix at grain level was investigated by SEM. Fractured surfaces of the samples were sputter-coated with a thin film of gold-palladium and the microstructural characteristics of phosphate ceramic waste forms were studied using SEM, JEOL JSM 5400. Homogeneous physical structure at grain level indicates good microencapsulation of contaminants, isolating them from the groundwater. On the other hand, a microstructure exhibiting microcracks may indicate structural failure due to crack growth. Similarly, voids and agglomeration of single phases indicate poor quality of waste form matrix.

Contaminant Leaching Tests

The leaching performance of waste forms was determined by the U.S. Environmental Protection Agency (EPA)-prescribed TCLP test to evaluate the toxicity of hazardous wastes and stabilized waste forms.[15] UTSs are the regulatory leaching levels for the TCLP test, provided by EPA 40 CFR, Part 268, in September 1994, for treated wastes. The ANS 16.1 test is a 90-day immersion test prescribed by the American Nuclear Society to demonstrate the long-term retention of contaminants in waste forms. Samples were prepared from the brick waste forms and the ANS 16.1 test was performed as prescribed.[16] The leachant metals data obtained were then used to calculate the diffusion constant of the contaminants through the matrix. The negative natural logarithm of the normalized diffusion constant, called leaching index, was used as the measure of the retention of the contaminants in the matrix. A value greater than 6 is usually acceptable. The larger the number, the better the retention of metals in solidification media.

RESULTS AND DISCUSSION

Bench-Scale Waste Forms

Table 4 shows that the density and porosity of the spiked soil waste forms remain constant at ~2 g/cm^3 and ~10%, respectively, for 10-, 15-, and 20-wt % binder loading. Compression strength of the 15-wt % binder samples is about twice that of the 10-wt % binder samples. It further increases to ~2332 psi with the increase of binder loading to 20 wt % (Table 4). Although samples made with 10-wt % binder loading meet the LDR requirement of 500 psi, higher strength is desired for safe handling and transportation. Samples made with 15- and 20-wt % binder loading more than meet the LDR requirement, as the compression strength is greater than 3–4.5 times the minimum needed for disposal.

The TCLP results given show that in all cases, samples passed both the TCLP and UTS limits (Table 5). From these results, it can be inferred that 10-wt % binder loading is the threshold minimum amount required to stabilize the contaminants. At least at bench scale, there is only a marginal improvement in the TCLP performance between samples made with 15- and 20-wt % binder loading. It was thus concluded that 15-wt % binder loading may be adequate for effective contaminant stabilization along with good compression strengths. With this as the basis, a full-scale study was conducted using 15-wt % binder loading.

Table 4. Physical properties of small-scale soil samples.

Binder Loading (wt %)	Density (g/cm^3)	Open Porosity (%)	Compression Strength (psi)
10	2.04	10.5	759.0
15	2.04	9.5	1568.5
20	2.10	9.55	2332.5

Table 5. TCLP results of small-scale soil samples.

Binder Loading	TCLP Results (mg/L)		
(wt %)	Cd	Cr	Pb
10	0.07	0.28	<0.1
15	0.05	0.18	<0.1
20	0.03	0.13	<0.1
TCLP limits	0.69	2.77	0.69
UTS limits	0.19	0.86	0.37

Large-Scale Waste Forms

Table 6 presents the physical properties of large-scale bricks prepared using soil waste and ash waste with 15-wt % binder loading. Volume reduction data indicate that compaction reduces waste volume considerably. The compaction pressure can be varied in the uniaxial compaction technique. Depending on this pressure, the extent of volume reduction will vary. A pressure of 1000 psi was applied, resulting in volume reduction of 39% for ash and 46% for soil. Comparatively, the volume reduction for harmonic compaction was slightly more. In any case, an average of 44% volume reduction can be achieved by either method.

Compression strengths of the samples are significantly higher than the land disposal requirements of 500 psi (Table 6). In both cases of compaction, the measured strengths were ~1550 psi for ash and ~2000 psi for soil. This is the level of compression strength seen in most construction components, such as building blocks and bricks. While most of the bricks used in the construction industry are sintered, it is important to note that the same strength was achieved here using a room-temperature binder and a compactor.

Table 6. Physical properties of large-scale bricks with 15-wt % binder.

Properties	Surrogate Ash Waste		Contaminated Soil	
	Uniaxial	Harmonic	Uniaxial	Harmonic
Volume reduction (%)	39	45	46	47
Compression strength (psi)	1590	1525	2042	2076
Density (g/cm^3)	1.73	1.63	1.98	2.04
Open porosity (vol %)	14.7	15.2	13.6	11.0

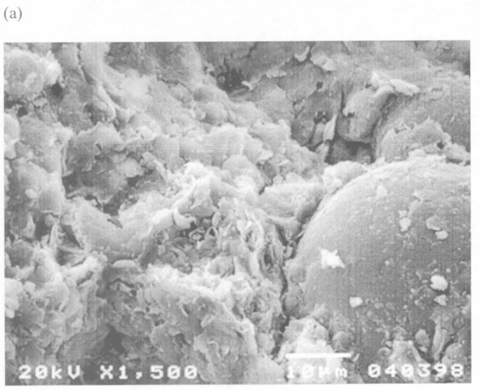
The density of the ash bricks was ~1.65 g/cm^3 and the soil bricks ~2.0 g/cm^3 (Table 6). This indicates that the CBPC binders, when used with the compaction technique, can produce lightweight products. Considerable reduction in the open porosity in the samples is due to compaction. However, the porosity was still high, ~15 vol % for ash and ~12 vol % for soil bricks. For superior products, this porosity needs to be reduced, otherwise freeze-thaw properties of the products will be poor in colder climates.

XRD Patterns

XRD patterns in Figures 1a and 1b indicate the predominant constituents of the binder, waste (ash and soil), and the final waste forms for both uniaxial and harmonic compaction. The purpose of this test is to study the changes waste goes through during the S/S process and to check whether the binder is well incorporated into the final waste form. The ash waste has significant amounts of SiO_2 and vermiculite (Figure 1a). As can be seen from Table 1, this is to be expected, since the waste has 20-wt % vermiculite, and both Class F fly ash and coal bottom ash are made up of high levels of SiO_2. Waste forms show total breakdown of vermiculite, but the SiO_2 is still present as a result of its high solubility. It is also clear from Figure 1b that the soil waste has a considerable amount of SiO_2. Not much evidence of the binder can be found in either ash or soil waste forms. This was expected, since only 15-wt % binder loading was used; it is highly unlikely to find high intensity peaks of newberyite in the final waste form.

Microstructural Evaluation

Figures 3 and 4 show the SEM micrographs of the fractured surface of the waste forms. In the case of ash waste forms, both the compression processes produce waste forms with similar microstructures (Figure 3). The spherical particles of the fly ash seem to be well encapsulated in the binder matrix. The micrographs do not indicate the presence of voids and agglomeration of single phases, implying good quality of the waste form matrix.



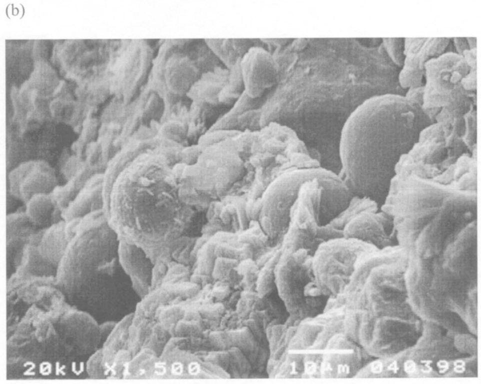


Figure 3. SEM micrographs of surrogate ash waste forms using (a) uniaxial compaction and (b) harmonic compaction.

Uniaxially compacted soil bricks appear to have a layered structure, while those harmonically compacted seem to be more homogeneous and dense (Figure 4). This difference must be due to the vibration of the waste-binder mixture during compaction in the harmonic press.[13] The vibrations appear to be ineffective on ash waste. This could be explained by the presence of vermiculite (often used as packing material) in ash waste. Vermiculite has good shock-absorbing properties and also inhibits volume reduction. The dense matrix of the harmonically pressed soil waste forms indicates that harmonic compaction provides a more uniform structure and is better suited for forming superior waste forms (Figure 4b).

Leaching Performance

At a binder loading of 15 wt %, the soil waste forms made by uniaxial compaction failed for Cd, but the harmonically pressed bricks passed the TCLP limits (Table 7). Ni in ash waste fails for both presses. The waste forms pass the TCLP test very effectively for both Cr and Pb. In fact, for both of these contaminants, the leaching levels are consistently below the detection limits of AAS and, hence, pass not only the TCLP but also the UTS limits.

Tables 7 and 8 show that Hg leaching levels at 15-wt % binder loading for both uniaxial and harmonic waste forms fail the regulatory limits. The large difference in Hg

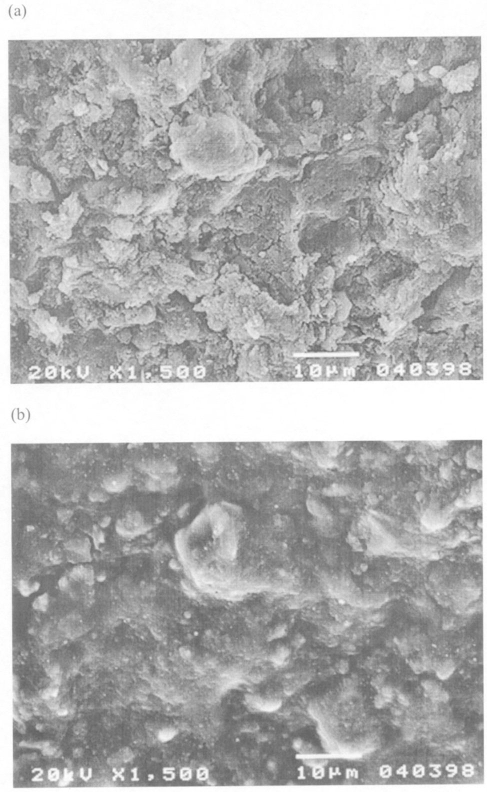


Figure 4. SEM micrographs of contaminated soil waste forms using (a) uniaxial compaction and (b) harmonic compaction.

leaching levels between uniaxial and harmonic processes only emphasizes the inconsistency in Hg treatment. Two factors can be attributed to the failure of Hg stabilization in the 15-wt % waste forms: lack of sufficient phosphates due to the minimal binder loading used, and the absence of a stabilizing agent to facilitate the conversion of Hg into its insoluble forms. To overcome the problem of Cd and Hg stabilization, a number of soil waste forms were prepared with various modifications made to the binder. Bricks were prepared with an increase in binder loading to 20 wt %. This helped to some extent in bringing down the leaching levels of Cd and Hg but was not effective enough.

Table 7. TCLP results of large-scale stabilized soil waste forms.

Compaction Method	TCLP Results (mg/L)			
	Cd	Cr	Pb	Hg
Uniaxial 15-wt % binder	1.01	<0.2	<0.2	0.608
Harmonic 15-wt % binder	0.42	<0.2	<0.2	23.8
Uniaxial 20-wt % binder	0.18	<0.2	<0.2	3.06
Uniaxial 20-wt % binder + K_2CO_3	0.29	<0.2	<0.2	2.70
Uniaxial 20-wt % binder + Na_2S	0.1	<0.2	<0.2	0.087
TCLP limits (mg/L)	0.69	2.77	0.69	0.2
UTS limits (mg/L)	0.19	0.86	0.37	0.025

Table 8. TCLP results of large-scale surrogate ash waste forms.

Compaction Method	TCLP Results (mg/L)				
	Cd	Cr	Ni	Pb	Hg
Uniaxial 15-wt % binder	1.46	<0.2	17.75	<0.2	23.87
Harmonic 15-wt % binder	1.4	<0.2	11.0	<0.2	3.18
Uniaxial 20-wt % binder + Na_2S	0.77	<0.2	10.68	<0.2	0.006
Uniaxial 20-wt % binder + K_2CO_3 + Na_2S	0.38	<0.2	0.72	<0.2	0.065
TCLP limits (mg/L)	0.69	2.77	3.98	0.69	0.2
UTS limits (mg/L)	0.19	0.86	5.0	0.37	0.025

It was then hypothesized that the highly acidic (~0 pH) environment created by the H_3PO_4 in the binder was detrimental to the contaminant stabilization process. In order to increase the pH of the solution, a phosphate solution was prepared and incorporated in the binder as a substitute for the 50-wt % concentration H_3PO_4 solution. The phosphate solution was prepared according to the following equation:

$$2H_3PO_4 + K_2CO_3 \rightarrow 2KH_2PO_4 + H_2O + CO_2 \qquad (2)$$

The pH of the resulting solution was ~1. Subsequent soil waste forms showed no improvement in the contaminant leaching results. But there was a significant improvement in the Cd and Ni leaching levels of the surrogate ash waste forms. This indicates that it might be necessary to modify the binder composition when treating ash wastes. This could be the result of concentrated H_3PO_4 (pH ~0) reacting with the components of fly ash, whose main constituents are oxides of Ca, Al, and Si.[12]

Due to this, a lesser amount of phosphates might be available for the conversion of the contaminants into their insoluble phosphate forms. Without the addition of a source of S, the waste forms fail the TCLP test for Hg, but pass with the addition of Na_2S.[10] Hence, for wastes containing Hg, it is recommended that a small amount of sulfide be incorporated during the stabilization process.

Ash and soil waste forms were not prepared using the harmonic compactor for 20-wt % binder loading and for samples with modifications made to the binder. Also, all physical characterization tests were conducted only for bricks prepared using 15-wt % binder loading. The contaminants pass the TCLP test for a binder loading of 20 wt % (Tables 7 and 8). In other words, the CBPC binder effectively stabilized the metal contaminants even though a very low binder loading was used.

Long-Term Leaching of Contaminants

The long-term leaching tests were conducted using the American Nuclear Society's ANS 16.1 test on waste forms produced with 15-wt % binder.[16] The testing was done for all the contaminants from samples produced using both the presses. The concentrations of metals in the leachates were below detection limits for Cr, Pb, Cd, and Ni in the case of both ash and soil wastes. For Hg, the concentrations were at a measurable level; the leaching index of Hg was calculated. Figure 5 gives the leaching profile as a function of time, and Table 9 provides the leachability index of Hg.

These results indicate that the long-term retention of Hg is independent of the compression method. Furthermore, these numbers are relatively very high when compared with a leaching index of 6 for Cs from cement waste forms.[17] This demonstrates that the retention of Hg in the CBPC waste form is 6 orders of magnitude higher than that in cement waste forms. The leachability index is the negative natural logarithm of the normalized diffusion constant.[16] If the leachability index of 6 for Cs were to be interpreted in simpler terms using this definition, it would take ~11 days for the metal to diffuse into 1 cm^2 of the waste form matrix. On the other hand, a leachability index of 14 for Hg theoretically translates to a time of ~3,170,980 years for Hg to diffuse into 1 cm^2 of the CBPC matrix. These results demonstrate that CBPCs are ideal for micro-encapsulation of metal contaminants in hazardous waste streams.

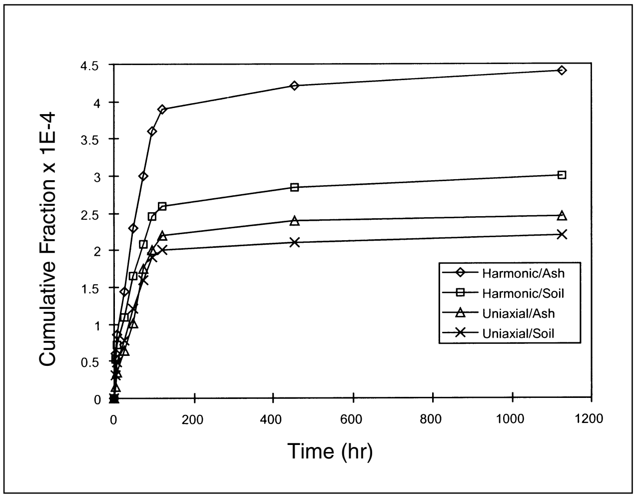


Figure 5. Cumulative fraction of Hg leached as a function of time.

Table 9. Leachability index of Hg.

Waste Stream/Compaction Method	Leachability Index
Soil waste/uniaxial	14.4
Soil waste/harmonic	14.3
Surrogate ash waste/uniaxial	14.4
Surrogate ash waste/harmonic	14.0

CONCLUSIONS

The objective of this research was to develop an S/S technology with high waste loading capability and reduction of final waste form volume. The two most important aspects of S/S, specifically, compression strength and contaminant leaching of final waste forms, have been investigated in this research. Based on the results from this research, the following conclusions can be made:

(1) Up to 80-wt % waste loading can be achieved by S/S with CBPC and compaction.

(2) Up to a 40% reduction in final waste volume can be achieved using either uniaxial or harmonic compaction methods.

(3) Comparing the results of mechanical testing and TCLP extraction, no significant difference can be observed between waste forms made by either uniaxial or harmonic compaction methods.

(4) Compression strengths between 1500 and 2000 psi were achieved, which are 3–4 times the LDR limits set by the EPA. Since soil waste forms had 25% more compression strength compared with ash-based waste forms, it is possible that CBPC binders could fail to solidify high carbon content incinerator ashes due to carbon being inert toward the binder.

(5) The advantage of harmonic compaction lies in its faster production of waste forms. Thus, much larger volumes of waste can be treated in each batch and at a higher throughput rate. Also, SEM micrographs suggest that the harmonic compaction produced denser waste forms.

(6) At larger scale, it was observed that 15-wt % binder loading was insufficient for effective stabilization of contaminants in waste streams. Optimum binder loading was found to be 20 wt % for larger scale waste forms.

(7) All metals in waste forms passed the TCLP limits, proving that the CBPC process is ideally suited for stabilizing a wide range of heavy metals.

(8) The long-term leaching test (ANS 16.1) showed that all the metals except Hg were below detection limits when immersed in water over a period of 3 months. Although the concentration of Hg

was at a measurable level, the calculated leaching index was very high, ~14. This indicates the effective long-term leach resistance of Hg in the CBPC matrix.

The compaction process using the CBPC binder may be a simple and cost-effective method to reduce the disposal volume of heavy metal-contaminated ash and soil waste streams. This technology could help set new standards in the S/S of hazardous wastes. Further studies could involve attempts at stabilizing and solidifying low-level radioactive waste streams using this process.

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