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DISCLAIMER

STABILIZATION OF CONTAMINATED SOIL AND WASTEWATER WITH CHEMICALLY BONDED PHOSPHATE CERAMICS*

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ABSTRACT

At Argonne National Laboratory, we have developed chemically Bonded phosphate ceramic (CBPC) technology to stabilize the U.S. Department of Energy's problem mixed waste streams, for which no other stabilization technology is suitable. In this technology, solid waste is mixed with MgO and reacted with aqueous solutions of phosphoric acid or acid phosphates at room temperature to form a slurry that sets in ≈2 h into a hard and dense ceramic waste form. Initial studies involved stabilizing the surrogate waste streams and then testing the waste forms for leaching of contaminants. After achieving satisfactory performance of the waste forms, we next incorporated actual waste streams at bench scale and produced waste forms that were then tested with the Toxicity Characteristic Leaching Procedure (TCLP). This presentation deals with stabilization of soil contaminated with Cd, Cr, Pb, Ag, Ba, and Hg, and of low-level radioactive wastewater. To enhance the contaminant levels in the soil, we further spiked the soil with additional amounts of Cd, Cr, Pb, and Hg. Both the soil and the wastewater were incorporated in the same waste form by stabilizing them with the CBPC process. The waste forms had a total waste loading of ≈77 wt.% and were dense with an open porosity of 2.7 vol.% and a density of 2.17 g/cm^3. Compression strength was 4910 psi. The TCLP results showed excellent immobilization of all the RCRA metals, and radioactive contaminant levels were below the detection limit of 0.2 pCi/mL. Long-term leaching studies using the ANS 16.1 procedure showed that the retention of contaminants is excellent and comparable to or better than most of other stabilization processes. These results demonstrate that the CBPC process is a very superior process for treatment of low level mixed wastes; we therefore conclude that the CBPC process is well suited to the treatment of low-level mixed waste streams with high waste loading.

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INTRODUCTION

The chemically bonded phosphate ceramic (CBPC) process was developed at Argonne in response to a need at U.S. Department of Energy sites to treat "problem" low-level mixed wastes by non-thermal processes [1]. These waste streams are secondary waste streams that are either off-gases from the thermal treatment of waste streams or residues left after thermal destruction of organic streams. Such waste streams cannot be treated by any thermal process again and hence need a process that stabilizes their contaminants at room temperature.

In our earlier work, the CBPC process was shown to treat such waste streams very effectively [1-3]. Surrogate waste streams of ash containing hazardous contaminants and cerium as a surrogate of U and Pu, were shown to form hard and dense waste forms with excellent performance in short- and long-term leaching tests.

The process consists of reacting a mixture of MgO powder and the solid waste with a solution of H_3PO_4 or an acid phosphate. The aqueous slurry, formed by mixing these components for 30 min, is a homogeneous paste that hardens into a ceramic with mild exothermic reaction in approximately 2 h. The resulting ceramic waste form has a density of ≈ 1.8 g/cm^3 and an open porosity of 2-5 vol. Compression strengths of such ash ceramics are 2 to 3 times that of portland cement. The Toxicity Characteristic Leaching Procedure (TCLP) [4] tests have shown that the leaching levels are 1-2 orders of magnitude lower than the U.S. EPA Land Disposal Restrictions (LDRs) limits. Accelerated leaching tests such as the American Nuclear Society's ANS 16.1 [5] showed that retention of contaminants is far superior to that of other similar methods such as cement stabilization.

Encouraged by this superior performance of the CBPC waste forms, we tested the process on actual waste streams at bench scale. In this attempt, we demonstrated that one could stabilize a solid and a liquid waste stream simultaneously. The solid waste stream was contaminated hazardous soil and the liquid waste was U contaminated wastewater both from Argonne-E site. These two were stabilized in a ceramic waste form of ≈ 100 g. Its properties and leaching performance were tested to demonstrate that the CBPC process is an excellent approach for treating actual wastes; details are given below.

FABRICATION OF WASTE FORM

Contaminated soil, MgO, the phosphate powders, and a measured amount of waste water were mixed together in a plastic container. With a spatula, the mixture was stirred for 30 min. We also added a small amount of an alkali sulfide powder for efficient stabilization of Hg. Initially, the slurry cooled by few degrees when phosphate powder crystals dissolved in the water, but after 30 min, was back to room temperature and formed a paste with the consistency of engine oil. The amounts of each component used in this mixture are given in Table 1.

Table 1. Composition of the slurry

Component	Composition (wt.%)
MgO	5.4
alkali sulfide	0.24
soluble phosphate	18
Soil	55
Waste water	21
Total waste loading	76

The slurry was allowed to set for ≈ 2 h during which it warmed up steadily. The maximum temperature recorded was ≈ 65°C. At 55°C, however, it set into a hard mass. After several hours, it cooled as the heat dissipated.

Table 2: Stabilization of unspiked soil and water

	Concentration (mg/L)				
Contaminant	In as received soil	In water	In waste form	TCLP result on waste form (mg/L)	TCLP limit (ppm)
As	<100		<57	<0.5	5
Cd	44.3	0.63	25.25	<0.01	0.19
Mo		9.84	5.6	2.04	No Limit
Se	<100	243	138.5	<0.1	0.16
Ba	191	6.05	112.3	0.06	7.6
Cr	310		176.7	0.02	0.86
Pb	1457		830.5	<0.2	0.37
Ag	18.5		10.55	<0.03	0.3
Hg	2.27		1.29	0.00015	0.0025

We made two sets of samples. The first one was with the as-received waste streams. Because this soil had very low concentration of some of the hazardous metals, we spiked it with Cd, Cr, Hg, and Pb to test the process for higher levels of the contaminants, and made a second set of samples. The soil was spiked with soluble nitrates of Cd, Cr, and Pb, and chloride of Hg. The detailed concentrations of the 'as-received' soil and the waste water are given in columns 2 and 3 of Table 2, and those for the spiked soil are given in Table 3. All of the hazardous contaminants that were part of either the soil or the wastewater, exist in the waste form at significant levels. These levels are given in the column 4 of Tables 2 and 3.

Table 3: Data on stabilization of spiked soil and water

Contaminants	In soil (mg/L)	In water (mg/L)	In waste form (mg/L)	TCLP result on waste form (ppm)
Cd	1044.3	0.63	595.7	0.18
Cr	1310		746.7	0.03
Pb	2457		1400.5	<0.2
Hg	1002.27		571.29	0.0015

LEACHING PERFORMANCE TESTS

After curing the samples for 3 weeks they were subjected to Toxicity Characteristic Leaching (TCLP) Studies [4]. The results are given in columns 5 of Table 2 and 3, while the EPA limits are given in the 6th column of Table 2 for comparison.

A comparison of columns 5 and 6 show that the leaching levels are well below the EPA standards in both Tables. Even the results on spiked samples given in Table 3 show that stabilization has been very effective.

Table 4. Radioactive contaminants

	Concentrations			
Contaminants	In soil (mg/L)	In water (pCi/mL)	In waste form (pCi/mL)	TCLP result on waste form (pCi/mL)
Cs^{137}		83	47.31	<0.2
U^{238}		32	18.24	<0.2
U^{235}		0.6	0.34	
Am^{241}		0.7	0.40	<0.2

Table 4 contains the leaching results on the radioactive contaminants. The levels of Cs^{137}, U, and Am^{241} are significant in the water and hence in the waste form. However, no contaminants were detected in the leached water at the detection limit of 0.2 pCi/mL.

Table 5. Long-term leaching (ANS 16.1) results on waste form

Contaminant	Diffusion constant (cm^2/s)	Leaching index
Cr	$<4.12 \times 10^{-15}$	>14.66
Cr	$<2.62 \times 10^{-15}$	>14.85
Hg	2.52×10^{-17}	16.42
Pb	2.15×10^{-17}	16.57
U	1.88×10^{-15}	14.52

The American Nuclear Society's ANS 16.1 Standard Test [5] was followed to evaluate the diffusion constants for the various contaminants in the spiked soil and waste water form. Samples were immersed in leachants of deionized water; results are presented in Table 5. The determined leachability indexes range from 14.52 for U to as high as 16.57 for Pb, significantly better than the recommended criterion of 6 [6]. These results are further evidence of the superior containment characteristic of the CBPC final waste forms.

Some insight has been gained on the stabilization mechanisms since our earlier study. Chemical conversion of the contaminants such as Pb, Cd, and Cr into their insoluble phosphate forms followed by their microencapsulation in the dense ceramic matrix, leads to such superior stabilization in the phosphate matrix. Hg, on the other hand, is stabilized into its sulfide form. Investigation is underway on the other remaining metals to identify the exact stabilization mechanisms.

PHYSICAL PROPERTIES OF WASTE FORMS

Physical properties of the simulated soil waste forms were investigated. The results are given in Table 6. Density of the waste forms is approximately 20% lower than that of portland cement products. Open porosity is also extremely low, while compression strength is comparable to that of portland cement products. The low porosity clearly contributes to good encapsulation of the contaminants in the waste forms, while the lower density and good compression strength makes the waste form a lightweight but strong product for transportation and storage.

Table 6. Physical properties of simulated soil waste form

Soil loading (%)	Density g/cm^3	Porosity %	Compression strength, psi
50	2.06	2.7	4910
60	2.17	2.8	3007

CONCLUSIONS

This study on real waste has demonstrated that hazardous and radioactive contaminants can be efficiently stabilized in the CBPC matrix by this room-temperature process. In particular, the following findings are very attractive for use of this method in stabilizing aqueous and soil waste streams.

1. Contaminated soil and wastewater can be successfully stabilized in the same waste form, thereby increasing the total waste loading to 77 wt.%. To our knowledge, no other low-temperature process can achieve such a high waste loading.

2. Due to consolidation of the soil in the waste form, the waste form volume was nearly the same as that of the soil. Thus, the net volume decrease was equal to that of wastewater or ≈21 vol.%.

3. TCLP results showed that leaching levels of all hazardous contaminants are well below the most severe EPA testing standards. This ensures that the process is very rugged and is tolerant to variations in contaminant levels in the waste streams.

4. TCLP results on radioactive contaminants are below the most severe detection limits of the instrument. This ensures that no detectable leaching of the radioactive contaminants occurs.

Due to the low temperature nature of the process, its simplicity, and its volume reduction, we believe that use of this process will provide considerable cost savings in waste management operations.

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