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STABILIZATION AND DISPOSAL OF ARGONNE-WEST LOW-LEVEL MIXED WASTES IN CERAMICRETE™ WASTE FORMS*

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DISCLAIMER

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Abstract

The technology of room-temperature-setting phosphate ceramics or Ceramicrete™ technology, developed at Argonne National Laboratory (ANL)-East, is being used to treat and dispose of low-level mixed wastes through the Department of Energy complex. During the past year, Ceramicrete™ technology was implemented for field application at ANL-West. Two debris wastes were treated and stabilized: (a) Hg-contaminated low-level radioactive crushed light bulbs and (b) low-level radioactive Pb-lined gloves (part of the MWIR # AW-W002 waste stream). In addition to hazardous metals, these wastes are contaminated with low-level fission products. Initially, bench-scale waste forms with simulated and actual waste streams were fabricated by acid-base reactions between mixtures of magnesium oxide powders and an acid phosphate solution, and the wastes. Size reduction of Pb-lined plastic glove waste was accomplished by cryofractionation. The Ceramicrete™ process produces dense, hard ceramic waste forms. Toxicity Characteristic Leaching Procedure (TCLP) results showed excellent stabilization of both Hg and Pb in the waste forms. The principal advantage of this technology is that immobilization of contaminants is the result of both chemical stabilization and

subsequent microencapsulation of the reaction products. Based on bench-scale studies, Ceramicrete™ technology has been implemented in the fabrication of 5-gal waste forms at ANL-West. Approximately 35 kg of real waste has been treated. The TCLP is being conducted on the samples from the 5-gal waste forms. It is expected that because the waste forms pass the limits set by the EPA's Universal Treatment Standard, they will be sent to a radioactive-waste disposal facility.

Introduction

The technology of chemically bonded phosphate ceramics (CBPC), i.e., Ceramicrete™ technology, has been developed at Argonne National Laboratory (ANL) over the last several years[1-2] and is based on the fabrication of dense, strong, and insoluble ceramics at room temperature by using acid-base reactions.[3-5] Among the reaction/immobilization systems that have been developed are those that use magnesium phosphate and magnesium potassium phosphate (MKP). In addition, Ceramicrete™ technology has been scaled up to fabricate 55-gal waste forms from soil wastes. Currently, the technology is being used to stabilize various low-level mixed wastes throughout the Department of Energy complex and in the commercial sector.

The rationale for using phosphate materials for hazardous and radioactive waste stabilization is that the resultant phosphates of the contaminants are extremely insoluble compounds. In addition, natural phosphate minerals such as monazite ([Ce, La, Y, Th]PO_4) are hosts to radioactive elements and are insoluble in groundwater.[6] Thus, by treating hazardous and radioactive wastes with phosphate-bonding technology, e.g., Ceramicrete™ technology, one can form insoluble phosphate compounds of the contaminants and thereby chemically fix them. In addition, the contaminants are encapsulated in a durable phosphate matrix that serves as a superior containment system. Because this treatment takes place at low temperatures, it presents no contaminant volatilization problems such as those faced in high-temperature stabilization technologies. Several solid and aqueous wastes, including ash, soils, and sludges, have been stabilized by Ceramicrete™ technology.

The goal of this effort was to apply Ceramicrete™ technology to treat and stabilize two low-level-debris mixed-waste streams at ANL-West (ANL-W). The intent was to demonstrate the technology in the solidification/stabilization (S/S) (a) 18 gal (32 kg) of Hg-contaminated low-level radioactive crushed light bulbs and (b) 1 gal (3 kg) of low-level radioactive Pb-lined gloves (part of the MWIR #AW-W002 waste stream). Both waste streams are contaminated with low-level fission products. Major tasks included (a) demonstrating S/S of the waste streams, the result being durable, bench-scale final waste forms; (b) implementing phosphate-bonded immobilization technology on low-level mixed waste at the 5-gal size; and (c) disposing of the fabricated final waste forms.

Waste Stream Composition

Hg-contaminated crushed light bulbs

The glass waste used in our experiments consisted of crushed fluorescent light bulbs from the Fuel Conditioning Facility (FCF) at ANL-W. Visual inspection revealed that the particle size of 90 vol.% of this waste is <60 mm; thus, this waste cannot be classified as a debris waste according to the Environmental Protection Agency's (EPA's) 40 CFR 268.45. Typical size of the crushed glass ranged from 2-3 cm long by 1-2 cm wide down to fine particulates.

Chemical analysis of this waste indicated a Hg concentration of ≈2.5 ppm. In addition, emissions from isotopes of ^{60}Co (1.1 x 10^{-5} μCi/g), ^{137}Cs (4 x 10^{-4} μCi/g), and ^{154}Eu (4 x 10^{-6} μCi/g) were detected.

Radioactively contaminated lead-lined gloves

This waste was essentially Pb-lined gloves that had been used in various hot-cell operations. Radioactive contamination in the gloves was from ^{137}Cs (5 x 10^{-7} μCi/g). To stabilize this waste, the gloves were first cryofractured by using liquid nitrogen and a high-speed blender. Typical debris size generated by this operation ranged from powder to pieces as large as a few millimeters; thus, this material also is not classified as debris waste according to 40 CFR 268.45; hence, stabilization of the waste is required. Chemical analysis indicated that ≈11.3 wt.% Pb was present in the waste.

Waste Form Fabrication

Ceramicrete™ or magnesium potassium phosphate (MKP) was used to stabilize the two ANL-W debris waste streams. The Ceramicrete™ binding phase is obtained by reacting calcined magnesium oxide powder with a solution of dibasic potassium phosphate. The reaction that occurs can be represented by

$$MgO + KH_2PO_4 + 5H_20 \text{ -----> } MgKPO_4.6H_2O \text{ (MKP).}$$

The resultant MKP phase is extremely stable, with a solubility product of 2.4×10^{-11} under ambient conditions.[7] In addition, fly ash up to 50 wt.% is added to the binder mix to enhance the structural integrity of the set product.

Fabrication of bench-scale waste form samples was similar for the two types of waste streams. Bench-scale studies were conducted on simulated and real wastes. In each case, the requisite amount of waste was first placed in a plastic container. Subsequently, binder powder and water were added and the mixture was stirred with a spatula to form a homogeneous slurry. Typical waste loading ranged from 35 to 40 wt.% . For the glass wastes, small amounts of potassium sulfide were added to the binder mixture to stabilize Hg by converting it into its least-soluble cinnabar (Hg_2S) form. After mixing for ≈30-35 min, the resultant slurry was poured into plastic molds for setting and curing. The waste form samples were removed from the molds after 14 days of curing.

The fabrication procedure for 5-gal waste form samples was similar to that used for the bench-scale sample. However, a modified Hobart mixer was used to mix the waste, Ceramicrete™ binder powder, and water in a 5-gal container. Figure 1 shows the setup used in the fabrication of the 5-gal waste forms. After mixing the ingredients, the slurry was allowed to set in the bucket itself. Figure 2 shows the slurry that was formed with actual waste during the Ceramicrete™ process. Using this setup, we first fabricated waste forms and subsequently with actual wastes. In each case, before setting occurred, a small slurry sample was removed and allowed to set in a plastic container. After complete curing, this sample was sent for testing by the Toxicity Characteristic Leaching Procedure (TCLP).[8] For the actual wastes, three waste form monoliths were fabricated. The first two contained ≈13 kg of glass waste only, whereas the third monolith contained 6 kg of glass waste and 3 kg of crushed Pb-lined gloves.

Because Ceramicrete™ technology is based on acid-base reactions, it generates heat. Therefore, it is important to monitor heat generation (temperature) in the large waste form samples fabricated with debris waste. Temperature variations were recorded by a thermocouple inserted in the 5-gal waste form. The tip of the thermocouple was approximately at the center of the specimen. The temperature rapidly increased with time, reaching a peak value of 72°C at ≈50 min after the waste mixture was poured into the mold. Thereafter, the temperature dropped, although at a much slower rate. Because the maximum temperature during the entire setting process remained well below the boiling point of water, we believe that heat generation will not be a problem during large-scale production of the waste forms.

Results on Bench-Scale Waste Forms

Bench-scale (150-g) waste form samples with both surrogate and actual wastes were subjected to various tests to determine porosity, density, and compression strength; they were also subjected to the TCLP.[8] Results are reported in Tables 1 and 2. Physical properties of the two waste forms are more than adequate from the disposal standpoint. However, the compression strength of the cryofractured gloves is lower than glass waste forms because the waste form behaves inelastically and the reported strength is based on the load at which the waste form began to deform. In any case, compression strengths are significantly higher than the NRC's recommendation of 500 psi.

TCLP testing shows that both Hg and Pb are well immobilized in the waste forms. Hg levels in the leachate are well below the EPA's Universal Treatment Standard (UTS) of 25 ppb, whereas the Pb level was below 0.1 ppm, as compared with the UTS limit of 0.37 ppm. Thus, leaching tests indicate that the waste forms pass the regulatory limits and are thus out of RCRA classification and can be sent to a radioactive disposal facility.

Scanning electron microscopy was conducted on the fractured surfaces of MKP waste forms that contained glass and cryofractured gloves. Figures 3 and 4 show glass chips and cryofractured plastic gloves completely encapsulated within the MKP matrix, which is highly desirable.

Results from 5-gal Waste Forms

Large-scale (5-gal) applications of Ceramicrete™ technology was examined at ANL-E by using simulated waste and at ANL-W by using actual waste. Figure 5 shows a cut section of a 5-gal waste form that contained 40 wt.% simulated glass waste. The interior of the waste form is homogeneous and exhibits no trapped porosity. It is expected that the interior of 5-gal. waste forms with actual waste will also be homogeneous because the physical characteristics of the simulated and actual wastes were similar and the processing steps are identical.

In addition, to ensure waste form performance, the TCLP was conducted on a 5-gal waste form with 40 wt.% simulated glass waste. Total concentration of Hg in the waste form was 80 ppm and in the leachate 0.41 ppb; thus, confirming Hg stabilization in the large-scale waste form. Similar stabilization

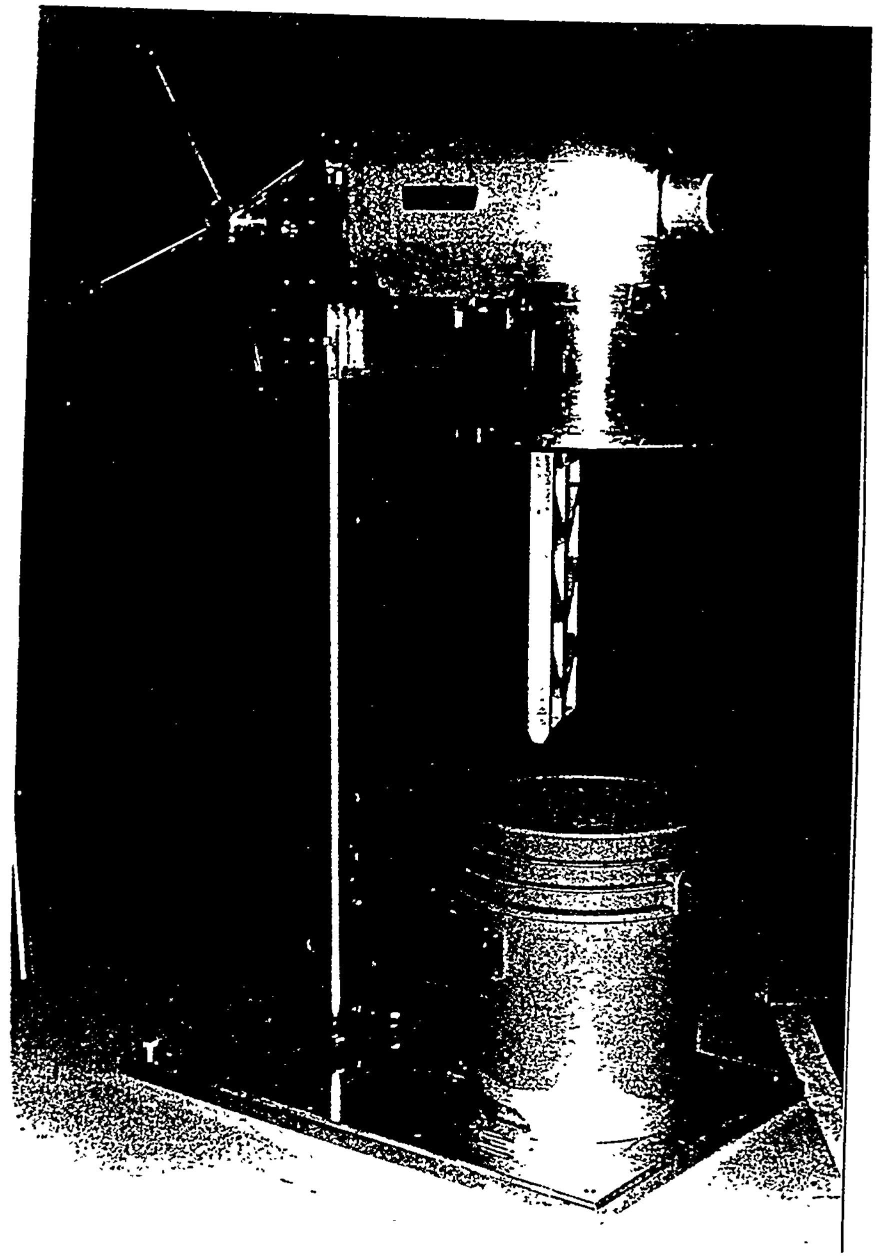

Fig. 1. Photograph of the mixer modified at ANL-E
for fabrication of 5-gal waste forms.

Fig. 2. Ceramicrete™ slurry and glass waste after mixing in 5-gal container.

Table 1. Physical properties of MKP final waste forms

Waste Form Description	Waste Loading (wt.%)	Density (g/cm^3)	Open Porosity (vol.%)	Compression Strength (psi)
MKP + simulated glass waste	40	2.0	4.2	5200 ± 654
MKP + simulated Pb-lined gloves	35	1.3	3.6	1200 ± 183

Table 2. TCLP Results on MKP Waste Forms

Waste Form Description	Contaminant Concentration in Waste Form	TCLP on Waste	TCLP on Waste Form
MKP + 40 wt.% real waste	Hg: 1000 ppb	24.4 ppb	0.05 ppb
MKP + 40 wt.% simulated waste	Hg: 80,000 ppb	202 ppb	<0.04 ppb
MKP + 35 wt.% cryofractured Pb-lined gloves	Pb: 4 wt.%	328 ppm	<0.1 ppm

Fig. 3. Photomicrograph of MKP-40 wt.% glass waste form.

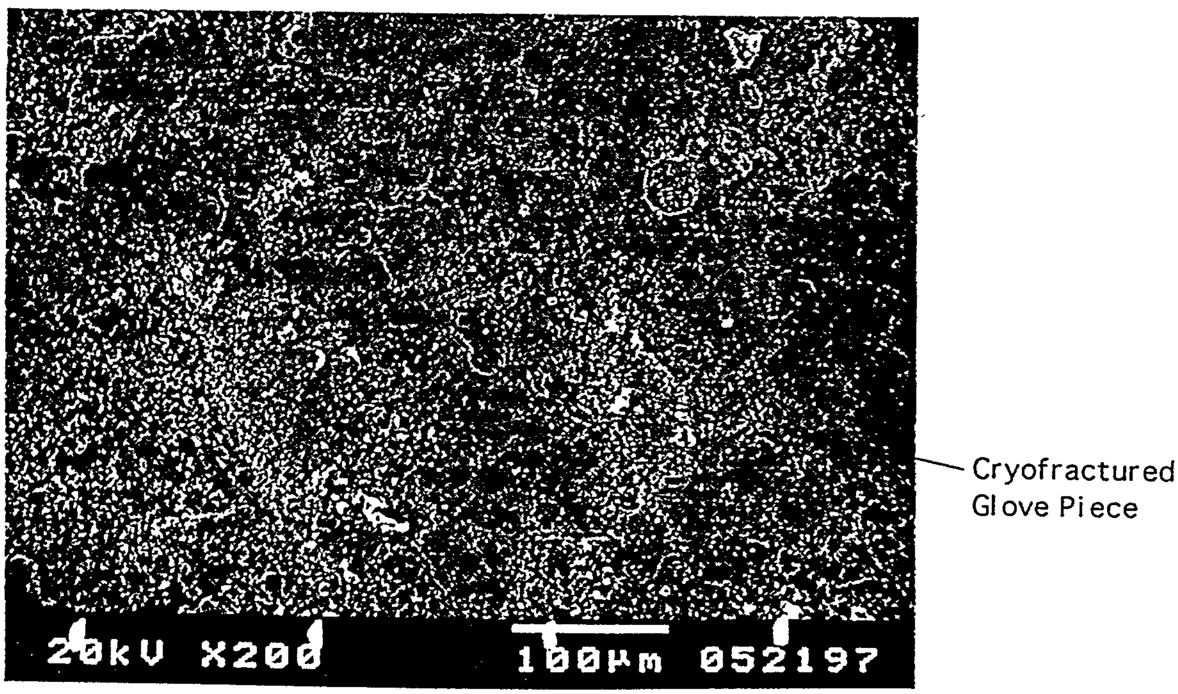

Fig. 4. Photomicrograph of MKP-35 wt.% cryofractured plastic glove waste form.

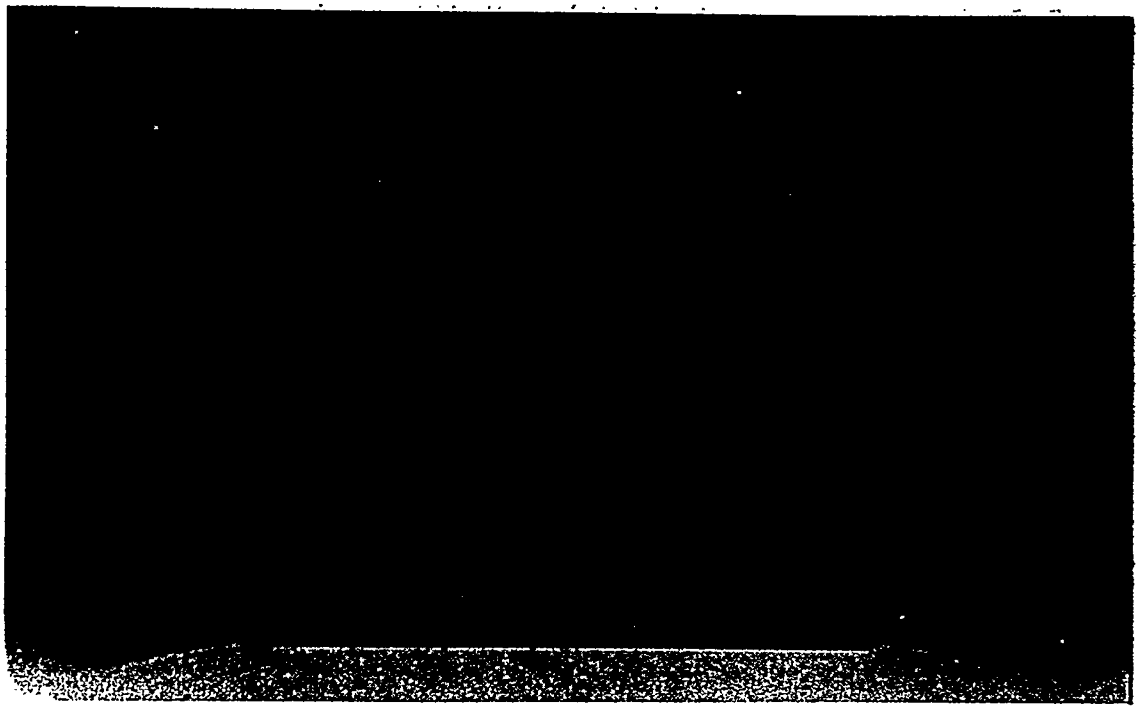

Fig. 5. Cut section of 5-gal MKP/40 wt.% glass debris waste form.

of Pb is expected because stabilization mechanism for both contaminants is chemical fixation in Ceramicrete™. The leaching results from the waste forms fabricated with actual waste have not been received at the time of this writing.

Summary

We have demonstrated the bench-scale application of Ceramicrete™ technology to the stabilization of Hg-contaminated light bulbs and cryofractured Pb-lined gloves.

The TCLP shows that the waste forms easily pass the EPA's UTSs for Hg and Pb. In addition, physical properties of the waste forms meet disposal requirements. Ceramicrete™ technology was scaled up to 5-gal waste forms to stabilize and dispose of 35 kg of low-level mixed debris wastes that consisted of crushed light bulbs and cryofractured Pb-lined gloves. Currently, the TCLP is being conducted on the fabricated final waste forms. Upon passing the regulatory levels for Hg and Pb, the final waste forms will no longer be under RCRA classificaiton and will be shipped for disposal to the Radioactive Waste Management Complex at the Idaho National Engineering and Environmental Laboratory.

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