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ABSTRACT

Across the DOE complex, large quantities of contaminated debris and irradiated lead bricks require disposal. The preferred method for disposing of these wastes is macroencapsulation under U.S. Environmental Protection Agency Alternative Treatment Standards. Chemically bonded phosphate ceramics serve as a novel binder, developed at Argonne National Laboratory, for stabilizing and solidifying various low-level mixed wastes. Extremely strong, dense, and impervious to water intrusion, this material was developed with support from the U.S. Department of Energy's Office of Science and Technology (DOE OST). In this investigation, CBPCs have been used to demonstrate macroencapsulation of various contaminated debris wastes, including cryofractured debris, lead bricks, and lead-lined plastic gloves. This paper describes the processing steps for fabricating the waste forms and the results of various characterizations performed on the waste forms. The conclusion is that simple and low-cost CBPCs are excellent material systems for macroencapsulationg debris wastes.

INTRODUCTION

Phosphate-bonded ceramics have been developed at Argonne National Laboratory over the last several years. This technology is based on fabrication of dense, strong, and insoluble ceramics at low temperatures by using acid-base reactions. Among the phosphate systems that have been developed are magnesium phosphate and magnesium potassium phosphate. Currently, these systems are being used to stabilize a variety of low-level mixed wastes.

The rationale for using phosphate materials for hazardous and radioactive wastes is that the resulting 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.[1] Thus, by treating hazardous and radioactive wastes with phosphate-bonding technology, we 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 process occurs at low temperatures, it presents no contaminant volatilization problems such as those faced in high-temperature stabilization technologies. Using this process, we have stabilized several solid and aqueous wastes, including ash, soils, and sludges[2].

Recently, the U.S. Environmental Protection Agency has defined in 40 CFR 268.45 that debris wastes with dimensions greater than or equal to 60 mm can be immobilized by Alternative Treatment Standards such as macroencapsulation. The macroencapsulation (MACRO) process is defined as applying surface-coating materials such as polymeric organics or a jacket of inert inorganic materials to substantially reduce surface exposure to potential leaching media. There are no federal regulatory requirements for structural integrity or leaching tests for macroencapsulated low-level wastes, as there are for microencapsulation. However, design acceptance criteria for waste forms at disposal facilities, such as Envirocare of Utah, require a uniform monolithic encapsulant layer of at least 2 in. completely around the waste. This conservative criterion ensures that soluble contaminants will not leach out in appreciable quantities in the event of water permeation into the waste form.

Because phosphate ceramics are insoluble dense inorganic materials, they are the logical choice for providing an impermeable barrier in a macroencapsulation system. Phosphate ceramics are prepared in an easily pourable aqueous slurry form that makes possible the intimate encapsulation of the waste. Since the phosphate process can handle significant water, it does not require pretreatment operations on waste, such as drying. Phosphate ceramics have excellent self-adhesion properties, which is highly desirable for macroencapsulation. Moreover, these ceramics are fabricated under ambient conditions, thus requiring minimum energy costs. The purpose of this investigation was to establish the feasibility of tphosphate ceramics as a viable macroencapsulant material system. Several waste streams, including cryofractured debris, lead bricks, and lead-lined plastic gloves are being investigated for macroencapsulation. This paper presents the results to date on our ongoing effort in the area of macroencapsulating low-level radioactive and mixed wastes with phosphate ceramics.

EXPERIMENTAL PROCEDURE

Fabrication of Waste Forms

Three waste streams have been used to demonstrate macroencapsulation using phosphate ceramics: cryofractured debris, lead bricks, and lead-lined plastic gloves. Fabrication procedures related to each of the waste streams are discussed below.

Cryofractured Debris

Uncontaminated cryofractured waste debris from the FY-92 Office of Technology Development project at the Idaho National Engineering Laboratory (INEL) was shipped to Argonne-East. This debris contained metals, wood, bricks, rocks, and plastics of various shapes and sizes. Some of the debris items were shredded so they would fit easily in the 2 gallon drum in which the waste form was to be produced. Typically, all pieces of debris were less than one-third the diameter of the drum. The waste debris was bonded by mixing the waste with the phosphate ceramic slurry that had been prepared by stirring premixed powders of calcined magnesium oxide and fly ash with an acid phosphate (magnesium potassium phosphate) solution in a 5-gallon Hobart mixer. The ratio of these ingredients was 1:4.4:5.8, respectively. After the slurry was mixed to the desired consistency, it was transferred to the drum containing the cryofractured debris. As the slurry was poured into the drum, the waste was stirred continuously to produce a homogeneous mixture, which was then allowed to set in the drum. Following this procedure, two waste forms were produced with volumes of 1.4 and 3 gallons. Final loading of the waste by weight was 35% in both waste forms, and density of the waste form was 1.81 g/cm^3. There was a volume reduction of about 4% as the debris waste was incorporated into the phosphate ceramic. Total loading of debris by volume was ≈29% in the final waste form.

Because the phosphate-bonding technology is based on acid-base reactions, it generates heat. Therefore, it is important to monitor heat generation (temperature) in the large waste forms samples fabricated with cryofractured debris waste. Temperature variations were recorded by a thermocouple inserted in the 3 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 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 there will be no heat generation problems during large-scale production of the waste forms. It is expected that similar temperature profiles would be observed irrespective of the waste type being macroencapsulated.

Lead Bricks

To macroencapsulate the lead brick, we used a phosphate ceramic composition of 60 wt.% ash, 25 wt.% binder (MgO and KH_2PO_4 powders mixed in 1:1 molar ratio), and 15 wt.% water. These ingredients were combined by a table-top mixer at a low speed for 30 min to form a uniform slurry, which was then poured into the container to form the lower, 2-in-thick base level. The slurry began to set, and after ≈1 h, had sufficient strength to bear the weight of a lead brick. At that time, a small amount of newly mixed slurry was poured to form a thin layer on the already set phosphate ceramic, and the brick was placed on it at the center of the container. The thin layer was used to avoid air gaps between the set slurry and the brick surface in contact. Additional new slurry was then poured all around the brick and above the brick so that the brick was evenly covered by at least 2-in. on all sides, including the top of the brick. This was allowed to set for one week and then the entire sample was cut horizontally and vertically to expose the cross sections.

Lead-lined Plastic Gloves

Low-level radioactive lead contaminated debris, including lead-lined gloves (which are a portion of the MWIR # AW-W002 waste stream), is located at ANL-W at a total inventory of 5 gallons (≈100 lb). Apart from the presence of heavy metals, these wastes contain low-level (5×10^{-7} μCi/g) contamination by fission and/or activation products such as ^{137}Cs.

Fabrication of the waste forms involved first packing contaminated gloves in a metal cage and suspending it in a 5 gallon container. The cage was centered so there was more than 2 in. clearance on the sides and bottom of the container. Subsequently, the phosphate slurry was prepared according to the procedure described above and poured out in the 5 gallon container. Care was taken to ensure that the cage did not shift during pouring. After the slurry had set, the wire from which the cage was suspended was cut. At that point, another batch of slurry was prepared and poured over the top so that it covered the top surface by 2 in., thus ensuring no pathways for water intrusion. After complete setting of the waste form, it was cut and examined.

CHARACTERIZATION AND RESULTS

Phase Analysis

X-ray diffraction (XRD) was conducted on the fabricated final waste forms to analyze the various crystalline phases. The XRD pattern for the waste form showed major peaks of magnesium potassium phosphate ($MgKPO_4.6H_2O$) and unreacted magnesium oxide. Magnesium potassium phosphate provides excellent durability to the waste form samples. Other peaks were due to the fly ash.

Physical Properties of Matrix Material

The physical properties evaluated for the phosphate-bonded ash waste forms were density, porosity, and compression strength. These evaluations were conducted on waste form samples measuring 0.5 in. in diameter and 1.0 in. long. Density was measured by using the mass and volume of the specimen. Open porosity was determined by the water intrusion method, in which the samples were weighed, then immersed in hot water (≈70°C) and held there for 2 h so that entrapped air in the pores is expelled and replaced by water. After they were removed from the water and dried, the specimens were weighed again. The weight difference provides the weight of water that intruded into the pores, from which the volume of the pores can then be determined. Compression strength was measured on cylindrical samples on an Instron machine in a uniaxial mode.

Density of the matrix material was 1.8 g/cm^3, which indicates that the phosphate-bonded ash waste samples are lightweight and dense. Open porosity was <4%. Due to this extremely low open porosity, these waste forms have minimal water intrusion, a highly desirable characteristic for macroencapsulation. Compression strengths were 5000-7000 psi. Although for macroencapsulation there are no regulatory limits for structural integrity, these values easily exceed the Land Disposal Restrictions (LDRs). The high strengths imply that a 5 gallon macroencapsulated waste form will bear loads as high as 50,000 lb.

Microstructural and Interface Analysis

Each of the waste form samples was cut horizontally and vertically to expose the cross sections, and the interior was examined for trapped air pockets or bubbles. Cross sections of each waste form showed that the matrix was very homogeneous, dense, and free of air pockets. The interface between the waste and the matrix was free of air gaps. During cutting of the sample, rough handling and vibration from the cutting tools did not damage the interfaces, which suggests that the bonds were very rigid.

Bonding between phosphate ceramic matrix and waste, specifically lead, was characterized quantitatively by preparing modulus-of-rupture bar specimens made of two pieces of lead joined by phosphate ceramic. These bars were broken in a bending mode, and measured strength was 1132 ± 203 psi. In addition, we observed that failure occurred in the phosphate ceramic phase rather than at the lead/phosphate matrix interface. This implies a superior bond due to excellent chemical adhesion between the lead surface and phosphate ceramic.

Scanning electron microscopy was used on the cut surfaces of the waste forms to evaluate their microstructures at the phosphate ceramic and waste interface. In the case of the lead bricks, we found that at microstructural level there is complete wetting of the lead brick and continuous adhesion; there were no gaps or air pockets at the interface. Also, similar binding was observed at the phosphate/phosphate interface, as created in the macroencapsulated Pb-lined gloves due to multiple pouring of the phosphate slurry on the surface. This ensures that there are no pathways available for water intrusion within the macroencapsulated waste forms.

SUMMARY

- A room-temperature chemically bonded phosphate ceramic process has been successfully demonstrated to macroencapsulate various wastes, including cryofractured debris, lead bricks, and Pb-lined plastic gloves.
- Phosphate-bonded macroencapsulated waste forms were scaled upt o volumes as large as 3-4 gallons. The fabricated waste forms were dense, strong, and impermeable to water.

- The phosphate-bonded matrix shows superior physical and mechanical properties. Compression strengths of the waste forms were significantly higher than those specified in the Land Disposal Requirements.
- Microstructural evaluation shows excellent bonding between the phosphate matrix and waste. No trapped-air pockets were observed in the phosphate matrix or at the matrix/waste interfaces.
- This simple technology can be used to encapsulate large objects such as irradiated bricks, tools, machine parts, and any other heterogeneous debris that require safe disposal.

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