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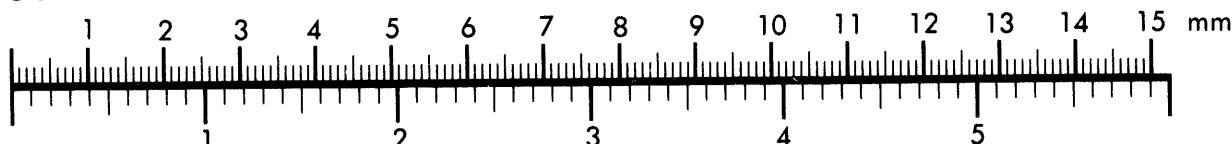
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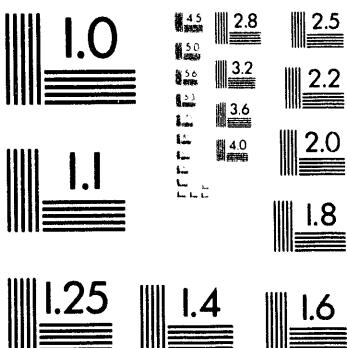
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STABILIZATION OF LOW-LEVEL MIXED WASTE IN
CHEMICALLY BONDED PHOSPHATE CERAMICS*

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STABILIZATION OF LOW-LEVEL MIXED WASTE IN CHEMICALLY BONDED PHOSPHATE CERAMICS

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I. INTRODUCTION

Mixed waste streams, which contain both chemical and radioactive wastes, are one of the important categories of DOE waste streams needing stabilization for final disposal.¹ Recent studies have shown that chemically bonded phosphate ceramics may have the potential for stabilizing these waste streams, particularly those containing volatiles and pyrophorics.² Such waste streams cannot be stabilized by conventional thermal treatment methods such as vitrification. Phosphate ceramics may be fabricated at room temperature into durable, hard, and dense materials. For this reason, room-temperature-setting phosphate ceramic waste forms are being developed to stabilize these "problem waste streams."

Of the several phosphate systems that can be employed, the phosphates of Mg and Zr are being explored in detail in our study. Phosphates of Mg, Mg-Na, Mg-NH₄, and Zr may be formed by acid-base reactions of the oxide or hydroxide of Mg and Zr with appropriate acid phosphate or phosphoric acid. These phosphates are being investigated for stabilization of several problem waste streams, including contaminated ashes, salts, and cement sludges. The contaminants are RCRA metal nitrates and organics, as well as radioactive nuclides. Based on our investigations of waste forms with different loadings of surrogates of these wastes in the various phosphate ceramics, we conclude that the

phosphate waste forms are highly suitable for treating low-level mixed wastes.

II. COMPOSITION OF SURROGATE WASTE STREAMS

Three surrogate wastes were formulated to simulate the DOE waste streams;³ Table I gives their composition.

The major constituents vary in each surrogate, but the contaminants are the same. Heavy metals were added as nitrates, and the content in the final composition was 0.5 wt.% for each metal. Each of the organics was also 0.5 wt.%, and CsCl content was 0.3 wt.%.

III. FABRICATION OF PHOSPHATE WASTE FORMS

The phosphate systems were used to stabilize the three surrogate waste streams discussed above. Fabrication procedures for the ash waste forms in different phosphate systems have been reported in Ref. 4. Depending on the major constituents in the three different waste streams, the setting reactions of the waste forms and hence the setting characteristics are expected to differ. Thus, some variations in fabrication were needed for each of the waste forms. For example, ash waste is a powder that may be mixed with the oxide or hydroxide powder and reacted with phosphoric acid or acid phosphate. The cement waste is a sludge that, when dry, can be mixed

Table I. Composition of surrogate waste streams

Components	Ash Waste	Salts	Cement
Major components	Activated carbon, fly ash, bottom ash, vermiculite	Activated carbon, cation exchange resin, Na_2CO_3 , NaCl , Na_2SO_4 , NaNO_3 , Na_3PO_4	Activated carbon, Set cement, plaster, perlite, hematite, alumina, activated carbon and cation exchange resin, water
RCRA metals	Cd, Cr, Ni, and Pb		
RCRA organics	Naphthalene and dichlorobenzene		
Radioactive surrogate	CsCl		

with and reacted with the acid components. In the case of salt wastes, however, sodium carbonate decomposes during synthesis of the phosphate waste form. This requires reacting the waste with the acid component, mixing with the powder, and then reacting the resulting mixture with additional acid or acid phosphate. In each of the three cases, the reaction results in a paste that can be poured or packed into molds. After setting, the paste is formed into hard ceramics. The samples set fully in three weeks, but in several cases the initial strength was obtained in one week. The samples for this study were cured for three weeks.

As an illustration of the various waste forms pursued in this study, we present detailed properties and performance of ash waste forms in this paper. A full account of the properties and performance of other waste forms will be presented in the future.

IV. PROPERTIES OF ASH WASTE FORMS

All ash waste forms appeared to be dense and hard. For example, the Mg phosphate ceramic with ash waste was glassy in appearance. Its porosity, measured by water displacement, was 9%. Porosity of the Zr phosphate was 16%. These values are low compared to those of cement grouts, which have porosities of 20-30%. Compression strength of the Mg phosphate was 2923 psi (at 26% porosity), while that of the Zr phosphate was 7572 psi (at 16% porosity). These values are comparable to those of any other cement grout, which indicates that the phosphate-system waste forms will have adequate strengths.

Typical X-ray diffraction outputs for Mg and Zr phosphate waste forms are given in Fig. I. They indicate that all Mg phosphate waste forms contain residual oxides or hydroxides of Mg. In the Zr phosphate, however, ZrO_2 has completely reacted into Zr phosphate. The reaction products were complex phases characteristic of the waste compositions. It shows peaks of mullite, quartz, gibbsite, and boehmite, which are crystalline constituents of ashes. An MgO peak is also prominent, indicating that unreacted MgO remains in the matrix. Much of the material was noncrystalline, as can be seen from Scanning Electron Microscopy(SEM) photographs (Fig. II), and hence could not be detected by X-ray diffraction. Further investigations involving infrared(IR) and nuclear magnetic resonance(NMR) spectrometry are needed to identify these phases, and such studies are being pursued.

V. MICROSTRUCTURE OF WASTE FORMS

Figure II shows SEM photographs of phosphate waste forms of Mg and Zr. One may notice that the structures are dense and mostly noncrystalline. In both images, spherical structures are visible; these are silica structures arising from the ash components of the waste and are embedded into the matrix and bonded by the noncrystalline cementitious phase. One may also

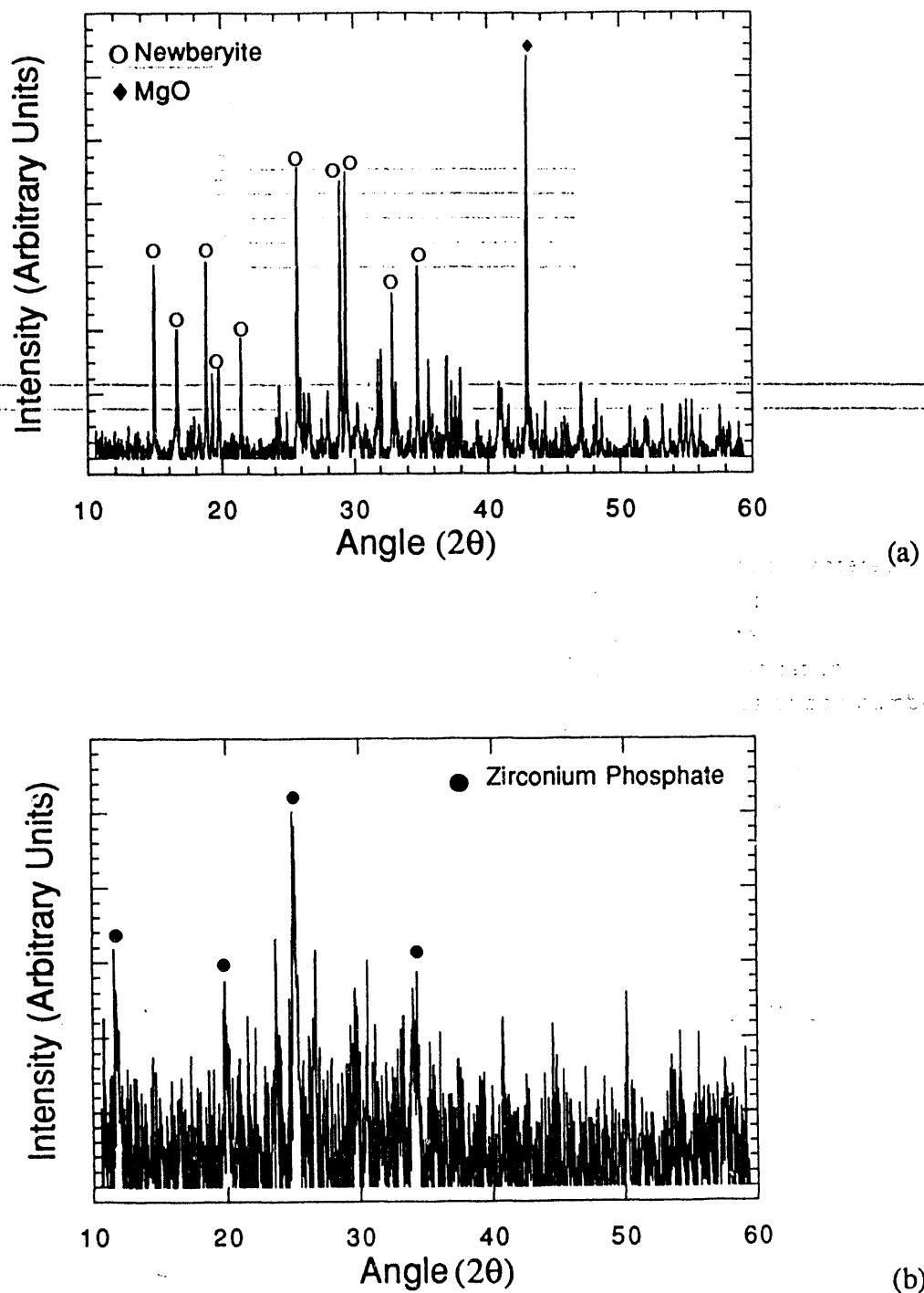


Fig. I. X-ray diffraction patterns for (a) magnesium phosphate waste form, (b) zirconium phosphate waste form.



Fig. II. SEM micrographs of (a) magnesium phosphate waste form, (b) zirconium phosphate waste form.

see platelets of vermiculite, which are also bonded into the matrix. These physical bonds provide a firm structure to the waste form.

Some energy-dispersive X-ray (EDX) studies were carried out on these micrographs. We found that the spherical structures were covered with phosphates of Mg and Zr, which indicated microencapsulation of the waste-component grains. Contaminants were distributed uniformly throughout the structures. Thus, the waste form microstructures indicate that excellent physical encapsulation of the waste components has occurred in the matrix.

VI. LEACHING STUDIES

To evaluate performance of the waste forms in a leaching environment, the toxicity characteristics leaching procedure (TCLP) was used. Details of this performance test are given in Ref. 5.

Table II summarizes the results of the TCLP testing on the final waste forms, and on the surrogate waste itself (first row of the table).

The data in Table II demonstrate the ability of the various phosphate ceramics to stabilize heavy metal wastes. Concentration of heavy metals in the leachates is several orders of magnitude lower than in the waste leachate itself. This suggests that the phosphate ceramics are very effective in stabilizing heavy metals. A comparison of these results with the regulatory limits (given in the last row of the table) suggests that most of the phosphates can stabilize Cr and Pb very effectively. Cd leaching is higher than the allowable level only in the Mg phosphate. This suggests that Cd may also be stabilized in other phosphate systems. Because nickel is not a RCRA metal, no regulatory limits are available for this metal. However, this metal is also well stabilized in the Mg-Na and Mg-NH₄ phosphates.

TABLE II. Results of TCLP testing

Sample	Waste loading (wt.%)	Concentration in leachate (ppm)
Surrogate waste		Cd=196, Cr=40.4, Ni=186, Pb=99.7
Mg-Phosphate	35	Cd=1.54, Cr=0.05, Ni=9.63, Pb=<0.1
Mg-Na- Phosphate	70	Cd=0.22, Cr=0.09, Ni=0.22, Pb=<0.1
Mg-NH ₄ - Phosphate	50	Cd=0.22, Cr=0.07, Ni=1.0, Pb=<0.1
Zr-Phosphate	35	Cd=0.07, Cr=0.16, Ni=11.0, Pb=<0.1
Regulatory limits		Cd=1.0, Cr=5.0, Pb=5.0

VII. DISCUSSION

We have limited our discussion in this paper to results from the ash waste forms. However, the behavior and characteristics of other waste forms are similar in all because of the chemical reactions between the acid phosphates and the heavy metal components which convert the metal components into insoluble compounds. These compounds are then encapsulated in the dense matrix of the phosphate ceramic. This

simultaneous chemical and physical stabilization of wastes in phosphates is a process superior to other low-temperature stabilization processes in cement grouts and polymers, in which stabilization occurs mainly because of physical encapsulation.

There are several other advantages to using phosphate bonded ceramics for waste stabilization. Because acid-base reaction is used to fabricate the phosphate ceramic waste forms, the reaction occurs over a wider range of pH in these phosphates. This means that the process is not very sensitive to the waste pH. Because the conventional cement grouts set in a high pH range only, the reaction is very sensitive to the pH of the paste and hence to that of the waste. A second advantage is that, as shown above, phosphates form denser ceramics. And the natural occurrence of monazites and apatites, which are host minerals of uranium, thorium, and rare earths, indicate that phosphates are stable hosts for long-term storage of radioactive isotopes. This is because heavy metals have good solid-solution solubility in phosphates.

Our studies demonstrate only the potential of phosphate systems for stabilizing mixed low-level wastes. To qualify the final waste forms, several other investigations are needed, including the accelerated leaching test (ALT) and immersion testing. To understand the chemistry of stabilization, detailed analyses of the final waste form are also necessary. These studies are now underway. Once the performance tests demonstrate the full potential of these final waste forms, stabilization of actual DOE waste streams will be undertaken. The studies reported here show promise in that direction.

ACKNOWLEDGMENTS

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The image consists of three separate, abstract black and white geometric shapes arranged vertically. The top shape is a central white rectangle with two solid black vertical bars, one on the left and one on the right, extending from the top edge to about two-thirds of the way down. The middle shape is a trapezoid with a thick black border. A diagonal line, also black, runs from the top-left corner to the bottom-right corner. The bottom shape is a large, thick black U-shaped cutout, centered on a white background.

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