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**EFFECT OF AQUEOUS ENVIRONMENT ON LONG-TERM DURABILITY OF
PHOSPHATE-BONDED CERAMIC WASTE FORMS***

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EFFECT OF AQUEOUS ENVIRONMENT ON LONG-TERM DURABILITY OF PHOSPHATE-BONDED CERAMIC WASTE FORMS*

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ABSTRACT

Over the last few years, Argonne National Laboratory has been developing room-temperature-setting chemically-bonded phosphate ceramics for solidifying and stabilizing low-level mixed wastes. This technology is crucial for stabilizing waste streams that contain volatile species and off-gas secondary waste streams generated by high-temperature treatment of such wastes. Magnesium phosphate ceramic has been developed to treat mixed wastes such as ash, salts, and cement sludges. Waste forms of surrogate waste streams were fabricated by acid-base reactions between the mixtures of magnesium oxide powders and the wastes, and phosphoric acid or acid phosphate solutions. Dense and hard ceramic waste forms are produced in this process. The principal advantage of this technology is that the contaminants are immobilized by both chemical stabilization and subsequent microencapsulation of the reaction products. This paper reports the results of durability studies conducted on waste forms made with ash waste streams spiked with hazardous and radioactive surrogates. Standard leaching tests such as ANS 16.1 and TCLP were conducted on the final waste forms. Fates of the contaminants in the final waste forms were established by electron microscopy. In addition, stability of the waste forms in aqueous environments was evaluated with long-term water-immersion tests.

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INTRODUCTION

Chemically bonded phosphate ceramics are dense and hard materials that can be processed at low temperatures [1,2]. Phosphates exhibit high solid-solution capacity for incorporating heavy metals, actinides, and rare-earth contaminants [3]. Also, the very low solubilities of phosphates of heavy metals, actinides, and rare earths [4] indicate that phosphate-bonded ceramics should be effective in stabilizing these contaminants. In addition, the durable natural analogs monazite and apatite minerals [5] suggest that phosphates are good hosts to radionuclides. The present developmental program on phosphate waste forms is being conducted to utilize their attractive properties in solidifying and stabilizing of mixed wastes, especially those that contain volatile contaminants, because fabrication can be achieved at room temperature or slightly elevated temperatures to minimize off-gassing.

The goal of this work is to incorporate surrogate ash wastes in magnesium phosphate ceramics and perform long-term durability tests of the resulting waste forms in aqueous media with various pH values and modeled after actual disposal scenarios. In addition, physical and microstructural characteristics of the final waste forms are determined in order to gain insight into the stabilization mechanisms in the phosphate ceramics and the durability of the final waste forms. The results of this study show that phosphate ceramics are a viable stabilization/solidification technology for treating low-level mixed wastes.

FABRICATION OF MAGNESIUM PHOSPHATE CERAMIC WASTE FORMS

Phosphate-bonded ceramics can be classified as acid-base cements because they are fabricated by chemical reactions between an oxide powder and an acid solution. Magnesium phosphate ceramic was prepared by reacting calcined magnesium oxide powder with a mixture of phosphoric acid and deionized water. Particle size of the starting magnesium oxide powder (Mallinckrodt, Inc.) was $\approx 8 \mu\text{m}$. Boric acid (15 wt.%) was added to the magnesium oxide powder to control the rate of reaction. In addition, certain other additives were incorporated in the premix. The powder was continuously added to the acid solution, and the mixture was vigorously mixed to a desired consistency and then transferred to a mold and allowed to set. The mix hardened in ≈ 2 h to form hard and dense monoliths. After complete curing for >7 days, the monoliths are removed from the molds for physical and chemical evaluation.

To demonstrate solidification and stabilization of the magnesium phosphate binder, an ash waste stream was selected. Principal components of the ash waste were: fly ash, coal ash, vermiculite, and activated carbon; details

on composition is given in the DOE/MWIP-16 report [6]. Various contaminants were used to spike the ash wastes. In the first case, cerium oxide and cesium chloride were added to simulate radioactive contaminants such as uranium and cesium. In second case, RCRA heavy metals such as lead, cadmium, chromium, and nickel in their soluble nitrate forms were incorporated. The third ash waste was spiked with mercury in its chloride form. Contaminant levels, however, were identical in all three waste streams. The proportion of each contaminant was such that individual metal content in the waste was 0.5 wt.%.

The final waste forms were fabricated by mixing the respective ash wastes with the starter magnesium oxide powder at desired weight percentages in a vibratory shaker. Subsequently, the resulting powders were added at a slow rate to the phosphoric acid solution and thoroughly mixed. The slurry was then poured into a mold and allowed to set. After complete setting, all of the specimens formed hard ceramics that were used for further evaluations.

RESULTS AND DISCUSSION

Physical properties

The densities of the monolithic magnesium phosphate and the final fabricated waste forms with 35 wt.% ash waste loading were 1.8 g/cm^3 and 1.7 g/cm^3 , respectively. The corresponding porosities were 6% and 12%, respectively. Such low porosity values are highly desirable to minimize water intrusion in the final waste form.

Phase analysis

Figure 1 shows an X-ray diffraction (XRD) pattern of the magnesium phosphate ceramic. The major phase in the magnesium phosphate system is newberryite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), a highly insoluble phase. In addition, there is some unreacted magnesium oxide. Using XRD on the final waste forms, we determined that both crystalline and noncrystalline phases of magnesium phosphate are present as the binding phases. Further, these two phases contain both Mg phosphates and silicates arising from the ash waste, possibly forming complex phospho-silicate structures. This has been confirmed by nuclear magnetic resonance (NMR) performed in collaboration with investigators at the University of Illinois at Urbana-Champaign [7]. Analysis of noncrystalline phases, which is much more complex and requires a combination of techniques, is currently the focus of our work.

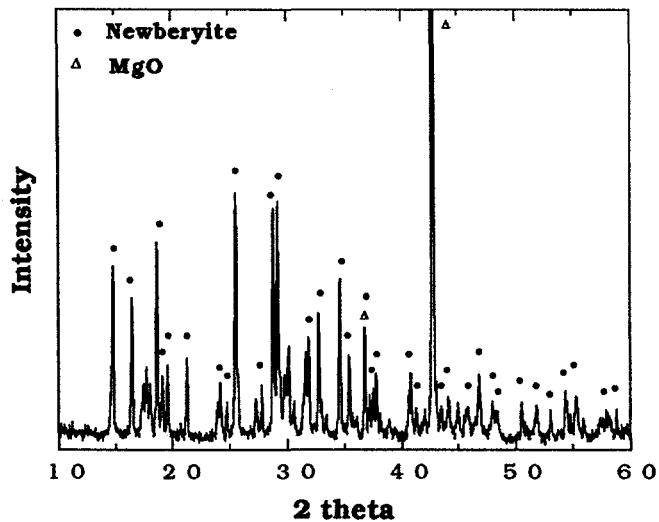


Fig. 1. XRD Pattern of Monolithic Magnesium Phosphate Ceramic.

Microstrucrural analysis

Figure 2 is a photomicrograph of the fracture surface of magnesium phosphate ceramic. As seen in this figure, the fabricated ceramic is extremely dense. Needlelike crystals of the newberryite phase are evident. Scanning electron microscopy (SEM) was also used to map the distribution of the metal contaminants in the magnesium phosphate final waste form (Fig. 3). The various contaminants are well distributed and physically microencapsulated by the phosphate matrix, and we believe that this phenomenon, along with chemical stabilization, leads to excellent performance of the phosphate systems in preventing leaching of the contaminants during the tests discussed below.

Compression Strength

Compression strength of fully cured waste form samples was measured with an Instron machine on samples of 0.5 in. diameter and 1-2 in. length. For monolithic magnesium phosphate specimens, the average compression strength was \approx 4000 psi. This value is higher than those of other room-temperature-setting materials such as portland cement. For the final waste



Fig. 2. SEM Photomicrograph of Fracture Surface of Magnesium Phosphate-35 wt.% Ash Final Waste Form.

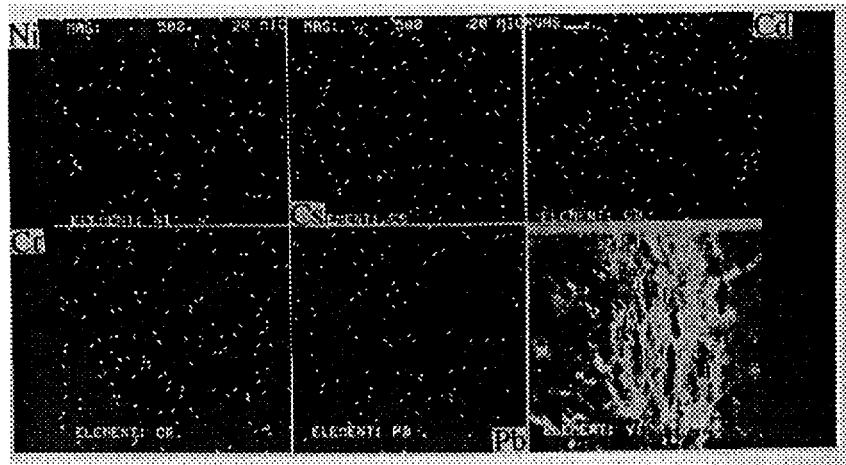


Fig. 3. Distribution of Various Contaminants in Magnesium Phosphate-35 wt.% Ash Final Waste Form.

forms with 35 wt.% ash waste, compression strengths were 3190 ± 440 psi., and these high values are believed to be due to chemical interaction between the ash waste and magnesium phosphate. NMR studies showed peak splitting in the presence of ash wastes as compared to a single peak obtained for monolithic magnesium phosphate; suggesting a chemical interaction [7].

Toxicity Characteristic Leaching Procedure

Leaching studies on the fabricated waste forms were conducted according to the standard Toxicity Characteristic Leaching Procedure (TCLP) and the American Nuclear Society's ANS 16.1 test [8,9]. Results from the TCLP are shown in Table 1, which indicates excellent stabilization of the heavy metals and cerium in the phosphate matrix system. The reason for this superior immobilization is chemical stabilization of the contaminants in the matrix due to reaction between the contaminant metal salts and the acid solution, followed by physical encapsulation within the dense phosphate matrix. We believe that the nitrates of heavy metals are converted to insoluble phosphates by chemical reactions and hence do not leach out into the leachate.

Also, physical encapsulation immobilizes the contaminants in the matrix, thus forming an excellent final waste form. It is not clear yet why the stabilization of cesium is not as good as that observed for other contaminants.

ANS 16.1 Test

The American Nuclear Society's ANS 16.1 Standard Test was followed to evaluate the diffusion constants and the leachability indexes for the various contaminants. Results are presented in Table 2. As expected, diffusivity of the contaminants is extremely low. The determined leachability indexes range from 15 for Cs to as high as 24 for Ce, significantly higher than Nuclear Regulatory Commission's passing criterion of 6. Higher leachability index indicates better retention of the contaminant in the final waste form. These results are further evidence of the superior containment characteristics of the magnesium-phosphate-bonded final waste forms.

Table 1. TCLP results on magnesium phosphate waste forms

Sample specification	Contamination levels (ppm)						
	Cd	Cr	Ni	Pb	Hg	Ce	Cs
Magnesium phosphate with 30 wt.% ash waste	0.04	0.03	2.5	<0.1	0.014	<0.02	35.5
Regulatory limits	0.19	0.86	5	0.37	0.2	---	---

Table 2. Diffusion constants and leachability indexes for various contaminants in magnesium-phosphate-ash final waste forms

Contaminant	Diffusion constant (cm ² /s)	Leachability Index
Ce	1 x 10 ⁻²³	24
Cs	5 x 10 ⁻¹⁴	15
Pb	7 x 10 ⁻²⁰	20
Ni	3 x 10 ⁻²¹	21
Cd	1 x 10 ⁻²¹	22
Cr	1 x 10 ⁻²¹	22
Hg	2 x 10 ⁻¹⁸	18

Long-Term Water Immersion Study

To study the long-term durability of the final waste forms in an aqueous environment, water immersion studies were initiated. As per the ANS 16.1 standard, samples were immersed in deionized water (pH≈5.5) and 0.003 M acetic acid solution (pH≈4). Samples were removed at regular intervals, dried, and weighed to observe any weight change. In addition, we also monitored the pH of the aqueous solutions in which the samples were immersed. Results for magnesium-phosphate ash waste forms exposed to solutions with two different pH values are shown in Figures 4 and 5. After 84 days, only a small increase was seen in the weight of the specimens immersed in both the deionized and acidic solutions. For specimens immersed in deionized water, weight increased by ≈0.5%, while for specimens immersed in the acid solution, weight loss was ≈1%. The larger weight increase in the acid-solution specimens is probably due to further reaction between the residual magnesium oxide and the acid.

Variation in pH of the solutions in which waste forms were exposed is shown in Figure 6. The initial large increase in pH suggests a loss of excess magnesium oxide from the waste form surface; this oxide is an artifact of the waste form fabrication process. Thereafter, there is no further release of unreacted magnesium oxide, leading to stabilization of pH in the leachate solution. The final pH of both deionized water and acid solution is on the basic side (≈8-9).

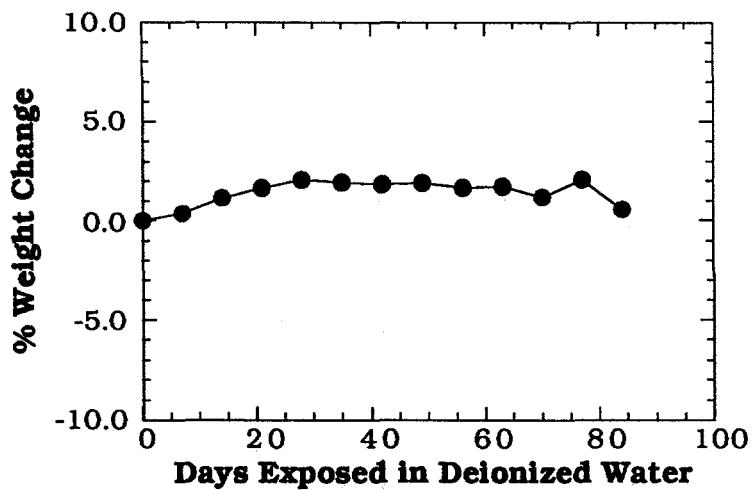


Fig. 4. Variation in Weight of Magnesium-Phosphate/35 wt.% Ash Final Waste Forms Exposed to Deionized Water.

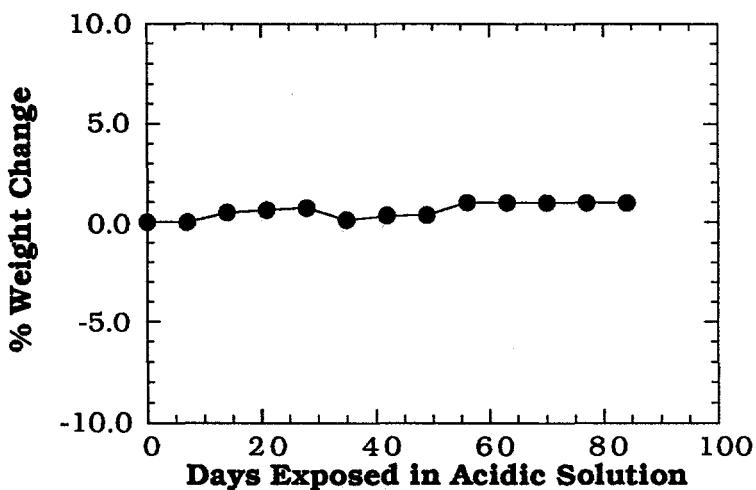


Fig. 5. Variation in Weight of Magnesium-Phosphate/35 wt.% Ash Final Waste Forms Exposed to Acidic Solution.

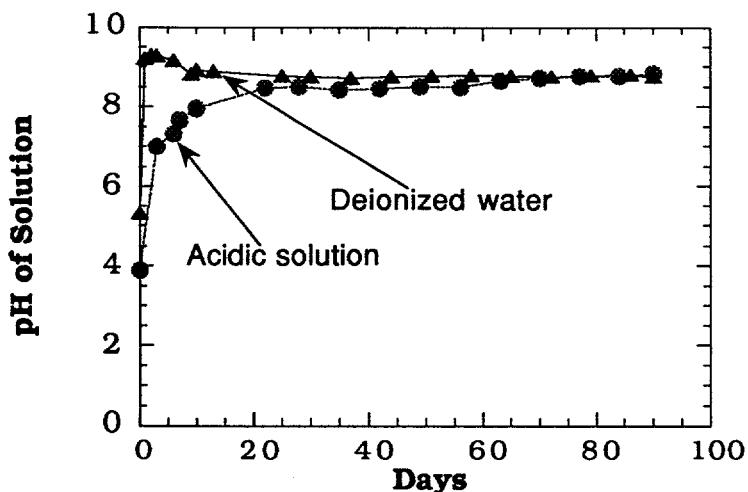


Fig. 6. Variation of pH of deionized water and acidic solutions in which magnesium phosphate-ash waste forms were immersed.

Compression strength before and after water immersion test

Figure 7 compares the average compression strength of the magnesium-phosphate waste forms before and after long-term (84-day) water immersion tests. Specimen strength after exposure to deionized water and acidic solutions were 3253 ± 950 and 3918 ± 980 psi, respectively. These values are higher than the average strength of the waste form before the long-term durability test (~ 3200 psi.). The higher values observed for specimens immersed in acidic solutions could be due to smaller fabrication-related inherent flaws in those specimens or to additional reaction of residual magnesium oxide. It is clear that no significant degradation occurs in the strength of the magnesium phosphate waste forms when exposed to aqueous solutions with various pH values. The resulting strength of the waste forms is exceptionally good and satisfies the regulatory requirements after a 90-day exposure to an aqueous environment. The results given here for weight change and compression strength clearly indicate that chemically bonded phosphates will be durable waste forms.

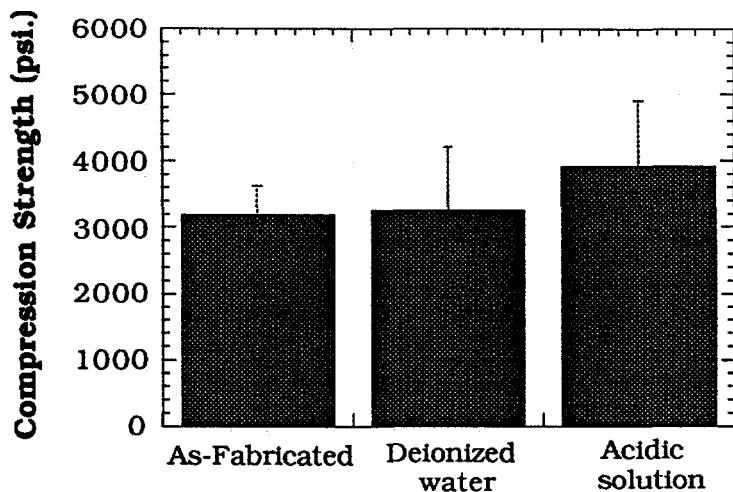


Fig. 7. Compression Strengths of Magnesium-Phosphate/35 wt.% Ash Waste Forms Exposed to Various Aqueous Solutions.

SUMMARY

This paper reports on the durability of magnesium-phosphate-bonded ceramics for waste stabilization at low temperatures. Physical and chemical characterization of magnesium phosphate materials has shown them to be physically, chemically, and mineralogically stable, with properties superior to those of other room-temperature-setting cements. In addition, an ash surrogate waste stream has been incorporated and stabilized in the magnesium phosphates at loadings of \approx 35 wt.%. Long-term durability studies using (ANS 16.1 standard test) showed excellent containment of the radioactive surrogates (Ce, Cs) and heavy metals (Pb, Cd, Cr, Hg, and Ni) in the phosphate matrix when exposed to deionized water and an acid solution with a pH of \approx 4. Excellent retention of contaminants in the magnesium phosphate matrix was further confirmed by the TCLP test. In addition, magnesium-phosphate-based final waste forms showed no significant weight changes after exposure to aqueous media for \approx 90 days, indicating the highly insoluble nature of the phosphate matrix.

ACKNOWLEDGMENTS

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