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LOW-TEMPERATURE SETTING PHOSPHATE CERAMICS FOR STABILIZATION OF DOE PROBLEM LOW LEVEL MIXED-WASTE:

I. MATERIAL AND WASTE FORM DEVELOPMENT*

Dileep Singh, Arun Wagh, Lerry Knox

Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439

and

John Mayberry

Science Applications International Corporation, Idaho Falls, ID 83402

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ABSTRACT

Chemically bonded phosphate ceramics are proposed as candidates for solidification and stabilization of some of the "problem" DOE low-level mixed wastes at low-temperatures. Development of these materials is crucial for stabilization of waste streams which have volatile species and any use of high-temperature technology leads to generation of off-gas secondary waste streams. Several phosphates of Mg, Al, and Zr have been investigated as candidate materials. Monoliths of these phosphates were synthesized using chemical routes at room or slightly elevated temperatures. Detailed physical and chemical characterizations have been conducted on some of these phosphates to establish their durability. Magnesium ammonium phosphate has shown to possess excellent mechnical and as well chemical properties. These phosphates were also used to stabilize a surrogate ash waste with a loading ranging from 25-35 wt.%. Characterization of the final waste forms show that waste immobilization is due to both chemical stabilization and physical encapsulation of the surrogate waste which is desirable for waste immobilization.

INTRODUCTION

Chemically bonded ceramics (CBCs) are dense and hard materials which can be processed at low temperatures (1, 2). It has been shown that CBCs, such as phosphates, have excellent durability in aqueous environments. Phosphates have high solid solution capacity to incorporate heavy metals, actinide, 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 media for stabilizing these contaminants. In addition, the durable natural analogue monazite and apatite minerals(5) suggests that phosphates may be good hosts to radionuclides. Present work is being conducted to utilize the attractive properties of phosphates in solidification and stabilization of mixed wastes, especially with volatile contaminants, because fabrication can be achieved at room or slightly elevated temperatures to minimize off-gas processing concerns.

The goal of this work is to develop chemically bonded ceramics (CBCs) for low-temperature treament and stabilization of Department of Energy (DOE) "problem" low-level mixed waste streams as identified by the Mixed Waste Treatment Project (MWTP) [6]. This paper is the first of the two part effort on the development of several low-temperature chemically bonded phosphate ceramics for stabilization of low level mixed wastes. Specifically, this paper deals with the fabrication routes and processing procedures that were used in developing Mg, Al, and Zr based phosphate ceramics. Setting characteritics of each of these phosphate ceramics was established. Also, waste forms incorporating surrogate ash wastes in the phosphate ceramics were fabricated to test the viability of these ceramics for waste stabilization . Physical and microstructural characterizations of the monolithic matrix materials and final waste forms were conducted and are presented in this paper to gain insight into the stabilization mechanisms in the phosphate ceramics and the durability of the final waste forms.

TARGET PHOSPHATE SYSTEMS

In a classic study, Kingery [7] investigated room-temperature setting behavior of phosphates formed by reaction of a number of oxides with phosphoric acid. He showed that phosphates of Mg, Cd, Pb, Al, La, Th, and Zr set and form cements in a short time. Following this lead, five different phosphate ceramics were investigated in this study. Targeted phosphates were: magnesium phosphate, magnesium ammonium phosphate, magnesium sodium phosphate, aluminum phosphate, and zirconium phosphate. Some of these ceramics such as magnesium phosphate, magnesium ammonium phosphate, and aluminum phosphate have been studied in the past and have been found to be insoluble in water. They also possess attractive physical properties as desired in a waste form material. However, very limited work on magnesium sodium phosphate and zirconium phosphate ceramics is available in the literature.

FABRICATION OF CHEMICALLY BONDED PHOSPHATE CERAMICS MONOLITHS

Phosphate bonded ceramics can be classified as acid-base type cements [8]. Typically, phosphates are produced by reacting a metal oxide or hydroxide with phosphoric acid or an acid salt and allowing the mixture or the slurry to set in a mold. The fabrication steps involved are quite similar for the various phosphates studied except for the aluminum phosphate cements. The processing details of the five different ceramics investigated are discussed below and the summary is given in Table I.

Magnesium Phosphate

Magnesium phosphate was prepared by reacting acid washed MgO powder with a mixture of phosphoric acid and deionized water. The starting MgO powder (Mallinkrodt, Inc.) was of a particle size ≈8 μm. In general, MgO powder forms a layer of carbonate on the particle surface which inhibits any chemical reaction. To overcome this, MgO powder was first washed by a solution of 0.28 M nitric acid to strip off the surface carbonate layer. Subsequently, the powder was washed in deionized water, to remove any traces of nitric acid, and dried. This acid washing procedure resulted in a major phase of $Mg(OH)_2$ with a particle size of ≈5 μm.

The acid washed powder was mixed with 10 wt.% boric acid and added to a solution of phosphoric acid and water mixed in equal amounts by weight. The purpose of adding boric acid was to retard the rate of reaction between $Mg(OH)_2$ powder and the acid solution. The powder was continuously added to the acid solution and the mixture was rigorously mixed to a desired consistency and quickly transferred to a syringe where the column of the paste could be compressed by a plunger during the setting process. The mixture hardened in 15 minutes with an exothermic reaction to form cylindrical monoliths. The specimens were kept in the syringes for eight days, then removed from the syringes. The diameter of the final samples was ≈0.6 cm; average length was 1.5 cms.

Magnesium Sodium Phosphate

Magnesium sodium phosphate was prepared by reacting acid washed MgO powder [$Mg(OH)_2$] with saturated sodium phosphate solution. Subsequent fabrication steps involved were same as described for magnesium phosphate ceramics.

Magnesium Ammonium Phosphate

The MAP monoliths were synthesized by mixing acid washed MgO powder [$Mg(OH)_2$] with a concentrated solution of ammonium phosphate [$(NH_4)_2HPO_4$] in distilled water in the weight ratio of 17:10. This ratio was determined by the workable consistency of the paste required to allow quick transfer to syringes and compression using the plunger. Specimens were removed from the molds after eight days of curing.

Aluminum Phosphate

Aluminum phosphate powder was prepared by first reacting aluminum oxide powder (Johnson Mathey, Ward Hill, MA) with phosphoric acid. This reacted mixture was added to boiling water and cured for ≈4 h at 100°C. Subsequently, excess water was decanted and the resulting powder was collected, air dried, and crushed to ≈7 μm particle size. This powder was pressed in a cylindrical steel die at a pressure of 35 ksi. The resulting monolith was hard and dense and was allowed to cure for several days.

Zirconium Phosphate

The starting powder for zirconium phosphate fabrication was zirconium hydroxide (Atomergic Chemetals Corp., Farmingdale, NY) with a particle size of 20 μm. This powder was reacted with a concentrated phosphoric acid. The fabrication steps were again similar to magnesium phosphate, however the setting time was much longer on the order of 21 days.

TABLE I Summary of Fabrication Details of Various Chemically Bonded Ceramics

Phosphate System	**Starting Powder**	**Acid Solution**	**Setting Time**
Magnesium Phosphate	$Mg(OH)_2$ + boric acid	Phosphoric acid + water (50 wt.%)	8 days
Magnesium Ammonium Phosphate	$Mg(OH)_2$	Saturated ammonium phosphate	8 days
Magnesium Sodium Phosphate	$Mg(OH)_2$	Saturated sodium phosphate	8 days
Aluminum Phosphate	$Al(OH)_3$	Phosphoric acid (≈60°C)	Reacted powder pressed at 35 ksi
Zirconium Phosphate	$Zr(OH)_4$	Phosphoric acid	21 days

PHYSICAL & CHEMICAL CHARACTERIZATIONS OF MONOLITHIC PHOSPHATE CERAMICS

Porosity measurements made on the various monolithic phosphates using fluid displacement method gave a typical value of ≈30%. However, for pressed aluminum phosphate, the porosity was < 3%. Initial scanning electron microscopy (SEM) observations of fractured surfaces of the magnesium ammonium phosphate material (Fig. 1) showed that the surfaces of the grains of MgO had reacted with the $(NH_4)_2HPO_4$ solution to yield magnesium ammounium phosphate. However, the inner parts of the MgO grains remained unreacted. In addition, the inner regions of the pores contained unreacted MgO. Thus, during the formation of magnesium ammonium phosphate, the $(NH_4)_2HPO_4$ solution did not completely permeate through the pores. To react the residual MgO in the pores with the $(NH_4)_2HPO_4$ solution, the cylindrical samples were soaked overnight in that solution. Subsequently, the samples were cured for another week. Reaction of additional MgO with the $(NH_4)_2HPO_4$ solution resulted in a reduction of the open porosity to $\approx 11\%$. An attempt to reduce the porosity further by vacuum impregnation of the solution only resulted in an impermeable barrier on the sample surface, which exhibited an apparent porosity of $\approx 4\%$. This was attributed to the rapid reduction of surface porosity due to formation of magnesium ammonium phosphate near the sample surface. The inner core of the samples retained a porosity of $\sim 11\%$. Figure 2 shows the microstructure of a MAP specimen with 11% porosity. When compared with the microstructure from Fig. 1, one can see that the porosity is considerably less in Figure 2. In addition, the magnesium ammonium phosphate cement phase in Fig. 2 is much greater than that in Fig. 1 and the MgO grains are less visible. This indicates that the reaction of MgO grains with $(NH_4)_2HPO_4$ solution has resulted in densification during soaking. Similar procedures are being applied in the other phosphate systems to reduce the porosity levels.

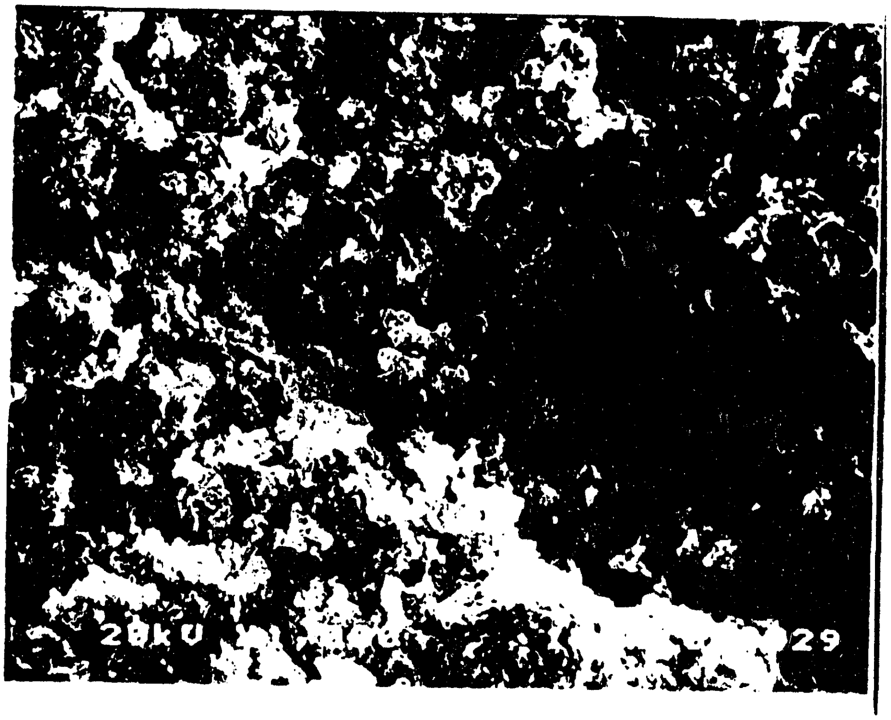

Figure 1. Scanning Electron Photomicrograph of Fractured Surface of Porous Magnesium Ammonium Phosphate Ceramic

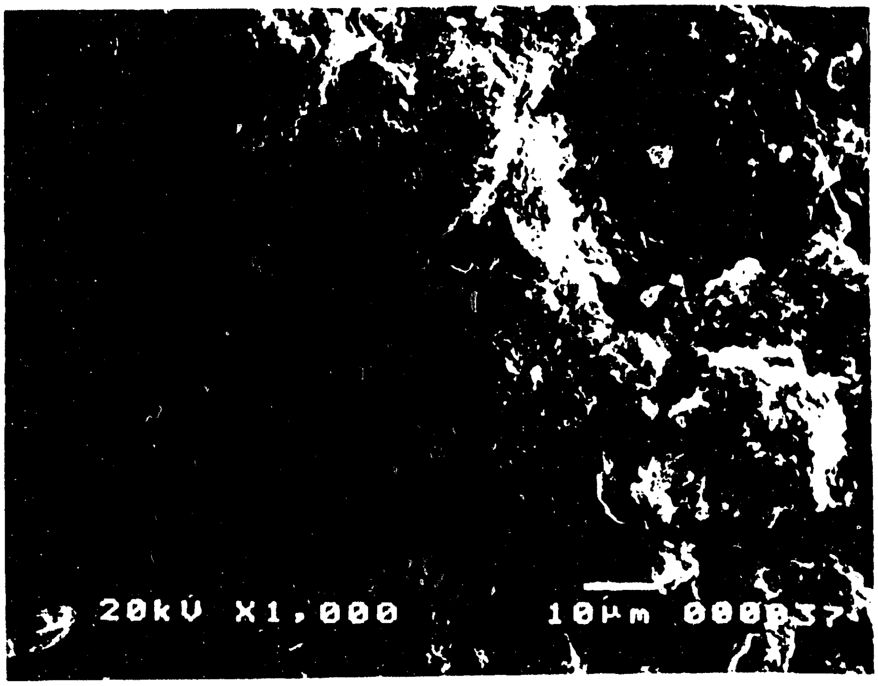

Figure 2. Scanning Electron Photomicrograph of Fractured Surface of Magnesium Ammonium Phosphate Ceramic After Densification by Resoaking

The product phases in the phosphate ceramics were characterized by X-ray diffraction analysis (XRD). Figure 3 shows the XRD peaks obtained for magnesium ammonium phosphate ceramics. The peaks are identical to those reported by Connaway-Wagner et al. for magnesium orthophosphate cement [9] and are very similar to those reported by Sugama and Kukacka [10]. Identification of the major peaks shows that this is a polyphosphate ceramic that includes both struvite ($MgNH_4PO_4.6H_2O$) and magnesium phosphate hydrate ($Mg_3(PO_4)_2.4H_2O$) phases. The strong MgO peaks suggest that considerable unreacted MgO remains in the material. Sugama and Kukacka [10] have shown that, except for the release of free water, magnesium ammonium phosphate phases are stable upto 930 °C.

Similar phase analyses on the other phosphates were conducted and their results are discussed in the Part II of this paper. However, at this point it is sufficient to mention that in other systems strong peaks of corresponding phosphate phases were evident. Also, the particular cementitious binding phases in each of the phosphate systems is discussed in detail in the companion paper.

The physical properties of magnesium ammonium phosphate ceramics are listed in Table 2. The negligible water-intrusion value also shows that vacuum impregnation may be a way to make the magnesium ammonium phosphate monolith impermeable to water intrusion. The mechanical properties of the

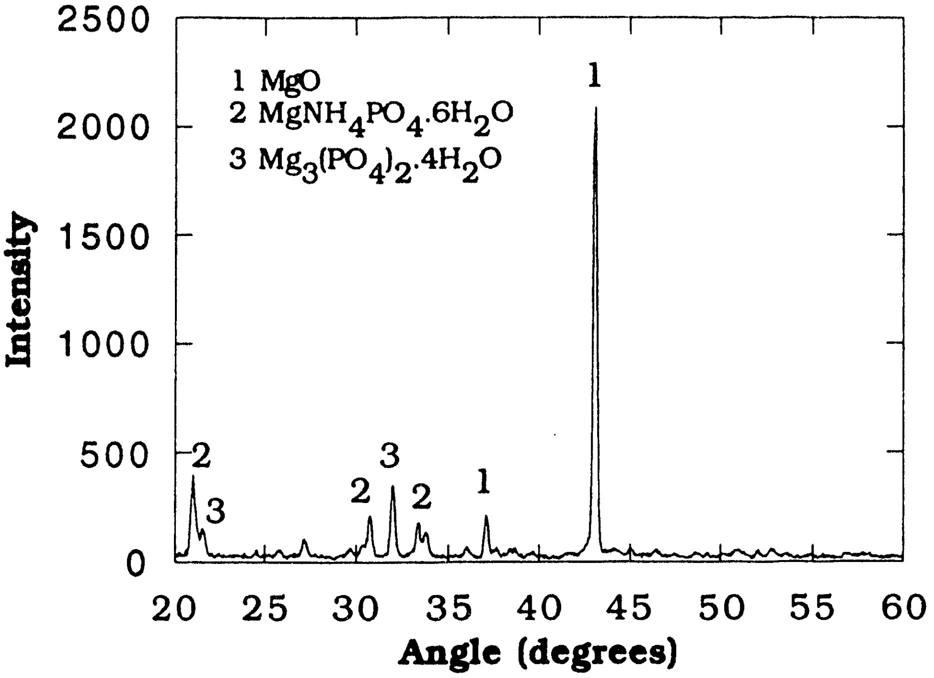

Figure 3. X–Ray Diffraction Pattern of As–Fabricated Magnesium Ammonium Phosphate Ceramic

material were measured with an Instron machine on samples with ≈11% porosity. The flexural strength was measured by the three-point bend test on rectangular bars cut from the cylinders with a diamond saw. The observed compressive strength was high compared with that measured by Connaway-Wagner et al. [9], because of the higher density of these samples. The measured compression strength was approximately twice that of Portland cement concrete, which is ≈3,000 psi. The flexural strength was also comparable to that of most room temperature-setting materials e.g.,Portland cement and polymers. Currently, investigations are underway for characterization of mechanical properties of other phosphate systems.

The chemical durability of the magnesium ammonium phosphate ceramic was examined by exposing samples of an average porosity of ≈11% to various aqueous environments. To span a broad range of possible ground water environments (11), leaching tests were conducted in high purity water (HPW), in a 0.01M carbonate solution, and in a high magnesium brine at room temperature and at 90 °C. For these tests, we followed the MCC-1P leaching procedure (12). The results of this work has been reported earlier [13]. The behavior of the magnesium and phosphate ion concentrations are good indicators of the degradation and dissolution of the MAP binding phases. The phosphate concentrations in the HPW showed a decreasing trend with time and after fifty days, were below the detection limits. As pointed out earlier, MgO is a major aggregate component of the magnesium ammonium phosphate samples. Hence the leaching behavior of the magnesium may reflect the

TABLE II Properties of the Magnesium Ammonium Phosphate Ceramic

Property	Data
density of resoaked samples (g/cc)	2.76
connected porosity	
as formed	≈32%
resoaked	≈11 %
water intrusion after vacuum impregnation (cc/g)	0.019 + 0.005
pore size	bimodal around 0.018 μm and 0.5 μm
compression strength (psi)	
as formed	3338 ± 551
resoaked	6100 ± 551
flexural strength (psi)	3193 ± 522

dissolution of the aggregate material. The Mg concentration is low in HPW, but shows an increase with time in the carbonate environment. This increase, however, is not accompanied by phosphate, which suggests that this dissolution of Mg is due to dissolution of MgO rather than magnesium ammonium phosphate. It is likely that this release may be retarded by vacuum impregnating the monolithic samples with phosphate solution, which will reduce the free MgO available for leaching.

PROCESSING ROUTES, FABRICATION, AND CHARACTERIZATION OF CHEMICALLY BONDED PHOSPHATE CERAMICS WASTE FORMS

Figure 4 shows the various processing routes that can be undertaken for fabrication of final waste forms using phosphate based chemically bonded ceramics. The specific processing route that is used will be dependent on the whether the waste is in solid or liquid form. For a solid waste, first metal oxide/hydroxide powder is mixed with the waste powder and then reacted with the acid solution. Following, the mixture is allowed to set for appropriate amount of time. This leads to setting and stabilization of the waste form. It is important to ensure that waste powder has approximately the same particle size or less than the starting powders. This may require a pulverization step for solid wastes. In the event of a liquid waste, it is reacted with the acid solution and then mixed with the oxide powder and allowed to set and stabilize.

In this study, three different waste streams are being targeted using chemically bonded phosphate ceramics. These waste streams include ash, cement and sludges, and salts. To date, only ash waste stream has been stabilized using the phosphate ceramics. Surrogate ash wastes were prepared following the recipe provided in the DOE/MWIP-16 [6]. Major components of this waste stream are fly ash (Class F), vermiculite, bottom ash, and activated carbon. In addition, to study the leaching characteristics of the final waste forms, several

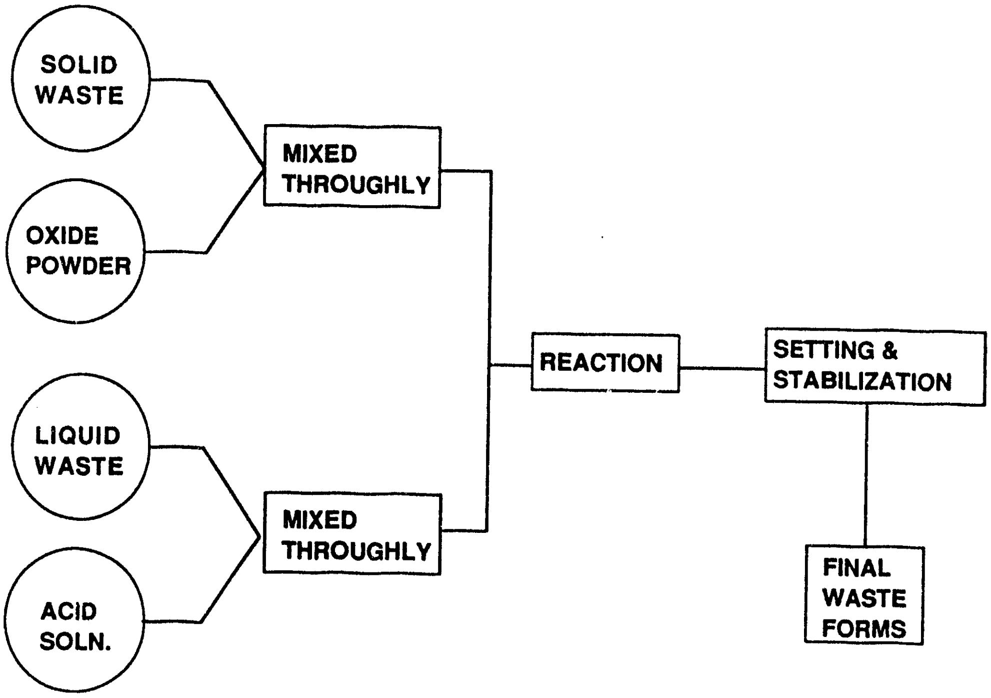

Figure 4. Schematic of the Fabrication Steps for Phosphate Based Final Waste Forms.

RCRA metals (Cr, Ni, Pb, Cd), organics (napthalene, dichlorobenzene), and radionuclide surrogate (CsCl), were added to the waste in trace amounts.

The fabrication of the waste forms required crushing of the ash waste and mixing it with the starting powder of the particular phosphate sytem and subsequently reacting the mix with the appropriate acid solution. Again, after reaching a workable consistency of the reacted mix, the slurry/paste was transferred to a syringe and compressed for few minutes. Thereafter, it was allowed to cure for several days prior to removing the set waste form from the syringe mold. In the case of aluminum phosphate a slightly different procedure was followed. Here the waste powder was mixed with the aluminum phosphate powder and the mix was pressed in a cylindrical steel die (0.5 in. dia.) at a pressure of 35 ksi. The pressed specimens were allowed to cure for over two weeks. Figure 5 compares the aluminum phosphate monolith and 35 wt.% waste loaded specimens. It is clear that waste additions do not deteriorate densification of the matrix material.

Scanning electron microscopy was conducted on a fractured specimen of aluminum phosphate loaded with 35 wt.% ash wastes and is shown in Figure 6. It is clear from the micrograph that the waste form is extremely dense. Aluminum phosphate grains are clearly visible along with the waste particles. It seems that in this phosphate systems stabilization is occuring from both chemical reaction/stabilization as well physical encapsulation. From extensive X-ray analysis it has been shown that the waste does chemically react with the

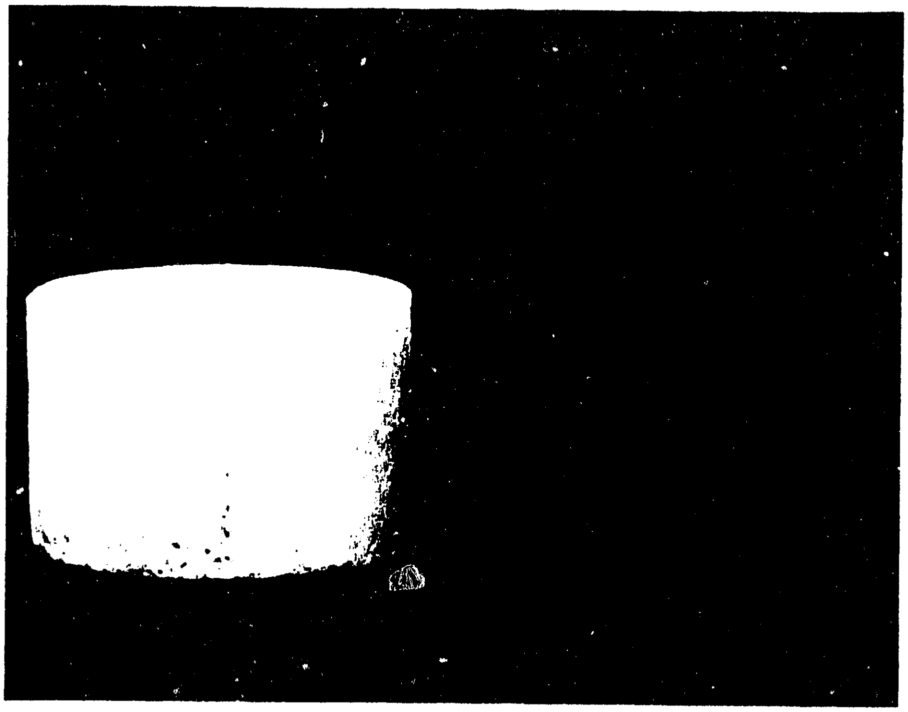

Figure 5. Photograph of Typical Aluminum Phosphate Ceramics Without (Light) and With (Dark) Ash Waste Additions.

acid solution and forms silicates. It is believed that the chemical reaction forms stable silico-phosphate bonds which makes the stabilization process much more efficient. The details of this are discussed in the campanion paper. In addition to chemical stabilzation, due to the high density of the matrix material waste particles are completely surrounded and physically trapped in the matrix. Due to the operation of the two waste stabilization mechanisms the final waste form produced will have superior physical and chemical characteristics. Similar stabilization mechansims are expected to operate in other phosphate systems.

CONCLUSIONS

This paper reports the processing procedures required for the devlopment of phosphate bonded ceramics for waste stabilization at low-temperatures. The investigations reported here are on magnesium phosphate, magnesium ammonium phosphate, magnesium sodium phosphate, aluminum phosphate, and zirconium phosphate as a candidate waste form materials. Initial physical and chemical characterizations of magnesium ammoinium phosphate material has shown it to be physically, chemically, and mineralogically stable material, with its properties that are superior to those of other room temperature-setting cements. In addition, an ash surrogate waste stream has been incorporated and stabilized in the abovementioned phosphates with a loadings of 25-35 wt.%. Characterization of the aluminum phosphate waste form shows that waste immobilization is due to both chemical stabilization and physical encapsulation of the waste. Similar mechansims are expected to operate in other phosphate systems.

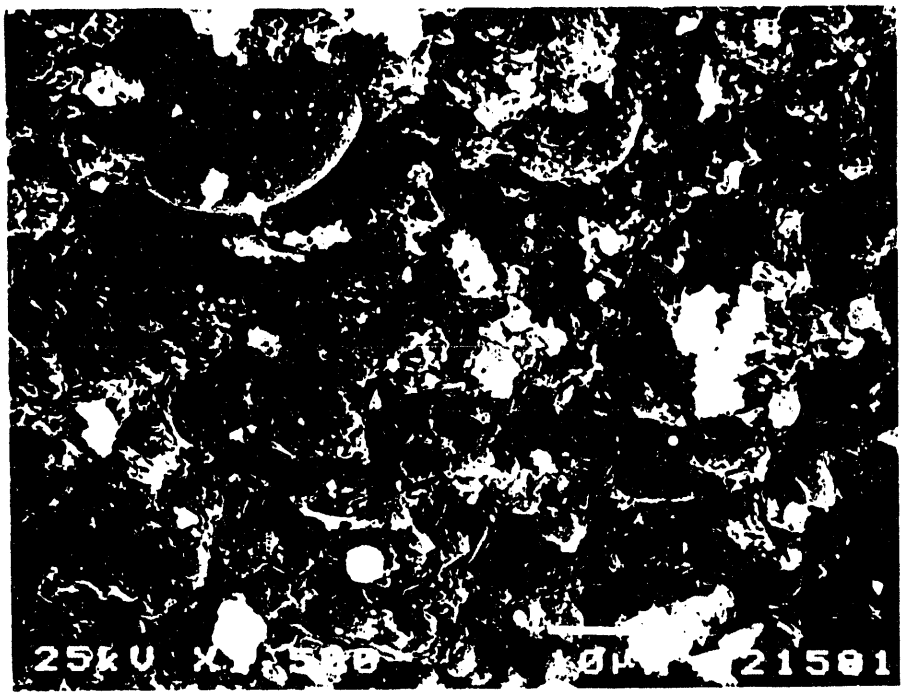

Figure 6. Scanning Electron Micrograph of Fractured Surface of Aluminum Phosphate with 35 wt.% Ash Waste Loading.

REFERENCES

1. D. M. ROY, "New Strong Cement Materials: Chemically Bonded Ceramics," Science **235** (1987) 651 - 658.
2. D.D. DOUBLE, "Chemically Bonded Ceramics: Taking the Heat Out of Making Ceramics," J. Mater. Educ., **12** (1990) 353 - 381.
3. A. E. REISENAUER and L. L. AMES, Removal and Recovery of Plutonium from 234-5 Building Sump Waste with Phosphate Rock, HW-70041 (1961).
4. IAEA Technical Report Series No. 326, "Conditioning of Alpha Bearing Wastes ", International Atomic Energy Agency, Vienna (1991).
5. G. J. McCARTHY, W. B. WHITE, D. K. SMITH, A. C. LASAGA, R. C. EWING, A. W. NICOL and R. ROY, "Mineral Models for Crystalline Hosts for Radionuclides in Radioactive Waste Disposal," Vol. 1, The Waste Package, ed. Rustum Roy, Pergamon Press 91982) 184 - 232.
6. W. D. BOSTICK et al., Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste: Part II: Slecetd Mixed Waste Treatment Project Waste Streams," DOE/MWIP-16, Spetember, 1993.
7. W. D. Kingery, "Fundamental Studies of Phosphate Bonding in Refractories: II. Cold-bonding Properties," J. Am. Ceram. Soc., **33** 242-247 (1950).
8. A. K. SARKAR, "Phosphate Cement-Based Fast-Setting Binders," Ceram. Bull. **69** (1990) 234 - 238.

9. M. C. CONNAWAY-WAGNER, W. G. KLEMPERER, and J. F.YOUNG, "A comparative study of magnesium orthophosphate and magnesium tripolyphosphate cements", Ceram. Trans. **16**, Am. Ceram. Soc. Westerville, OH (1991) 679-688.
10. T. SUGAMA and L. E. KUKACKA, "Magnesium Monophosphate Cements Derived from Diammonium Phosphate Solutions," Cem. Concr. Res., **13** (1983) 407 - 416.
11. D. M. STRACHAN, L. R. PEDERSON, AND R. O. LOKKEN, "Results from the Long-Term Interaction and Modeling of SRL-131 Glass with Aqueous Solutions", Mater. Res. Soc. Symp. Proc. **50** (1985) 195- 202.
12. Nuclear Waste Materials Handbook (Test Methods), Prepared by the Materials Characterization Center, DOE report DOE/TIC-11400 Pacific Northwest Laboratory, Richland, WA.
13. A. S. WAGH, J. C. CUNNANE, D. SINGH, D. T. REED, S. ARMSTRONG, W. SUBHAN, and N. CHAWLA, "Chemically Bonded Phosphate Ceramics for Radioactive and Mixed-Waste Solidification and Stabilization," in Waste Management 93, Vol. 2, eds R. G. Post and M. E. Wacks, WM Symposia Inc., Tucson, AZ.

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