

CHEMICALLY BONDED PHOSPHATE CERAMICS FOR RADIOACTIVE AND MIXED-WASTE SOLIDIFICATION AND STABILIZATION

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ABSTRACT

Results of an initial investigation of low-temperature-setting, chemically bonded magnesium ammonium phosphate (MAP) ceramics as waste form materials for solidification and stabilization of radioactive and mixed waste are reported. The MAP was synthesized from calcined MgO and ammonium phosphate solution precursors. X-ray diffraction (XRD) studies showed that the material consists of unreacted MgO, which acts as a filler, and phosphate ceramic MAP which acts as a binding phase. Dense specimens with a compressive strength of ≈ 42 MPa (6000 psi) were prepared. Batch leach tests, in high purity water, carbonate solution, and Mg-brine at 24°C and 90°C showed that, although ammonia was initially released; the rate of release decreased with time until the leachable inventory was depleted. The leachate pH increased rapidly to a steady-state value of ≈ 10 , even in refreshed tests after leaching of ammonia had subsided. Phosphate concentrations were low in the leachate, demonstrating the chemical stability of the binding phase. Leaching of MgO was also low, but in carbonate leachate increased with time. This trace-level leaching of free MgO may be eliminated by a vacuum impregnation technique. The radiation stability was tested up to an absorbed dose of 200 Mrad. The results indicate that MAP is stable for such high dose in a variety of environments.

The suitability of MAP ceramics for solidifying and encapsulating waste materials was tested by encapsulating zeolites at loadings up to ≈ 50 wt%. The resulting composites exhibited very good compressive-strength characteristics. Microstructure studies showed that zeolite grains remain unreacted in the matrix. Potential uses for solidifying and stabilizing wastes are discussed.

INTRODUCTION

Chemically bonded ceramics (CBCs) can be processed at low temperatures (1, 2). They are attractive for applications, such as solidification and stabilization of radioactive waste, because fabrication can be achieved at room or slightly elevated temperatures to minimize off-gas processing concerns. Phosphates have high solid solution capacity to incorporate heavy metals, actinide, and rare-earth contaminants (3). Also the very low solubilities of heavy metals, actinide, and rare-earth phosphates (4) indicate that phosphate-bonded ceramics should be effective media for stabilizing these contaminants. The durable natural analogue monazite and apatite minerals (5) suggests that phosphates may be good hosts to radionuclides.

This paper reports the results of an initial investigation of a chemically bonded magnesium ammonium phosphate (MAP) ceramic, the chemistry of which is fairly well understood (6-8). It sets into a very hard cement (9). Concretes of this cement have been developed and their chemical composition (10) and mechanical properties (11), have been studied for structural applications. Connaway-Wagner et al. (12) who have compared the properties of magnesia-orthophosphate and tripolyphosphate cements. Tripolyphosphate cements exhibit a very high compressive strength of 90 MPa at a porosity of 16%. The orthophosphate cements with a compressive strength of 23 MPa at a porosity of 26%. These favorable properties of phosphates motivated the present systematic

study of phosphate CBCs for applications in radioactive waste management in our laboratory.

FABRICATION OF MAP CERAMICS

The details of the materials used for the syntheses of MAP are given in Table I. The MAP monoliths were synthesized by mixing calcined MgO with a concentrated solution of ammonium phosphate $[(\text{NH}_4)_2\text{HPO}_4]$ 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, where the column of the paste could be compressed by a plunger during the setting process. The mixture hardened in 15 m with an exothermic reaction to form cylindrical monoliths. The specimens were kept in the syringes for one week, then removed from the syringes, and cured in desiccators for another week. The diameter of the samples was ≈ 0.6 cm; average length was 1.64 cms. Typically the porosity was $\approx 30\%$, as measured by using fluid displacement method. Initial scanning electron microscopy (SEM) observations of fractured surfaces of the resultant material (Fig. 1) showed that the surfaces of the grains of MgO had reacted with the $(\text{NH}_4)_2\text{HPO}_4$ solution to yield an MAP ceramic. 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 MAP, the $(\text{NH}_4)_2\text{HPO}_4$ solution did not completely permeate through the pores. To react the residual MgO in the pores with the $(\text{NH}_4)_2\text{HPO}_4$ solution, the cylindrical samples were soaked overnight in that solution. Subsequently, the samples were

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TABLE I
Materials Used in the Fabrication of MAP Ceramics

Powder	Supplier	Characteristics
MgO (calcined)	Mallinkrodt	particle size $\approx 7-8 \mu\text{m}$ after recalcination
$(\text{NH}_4)_2\text{HPO}_4$ zeolite	Mallinkrodt Union Carbide	crystals particle size $7-8 \mu\text{m}$

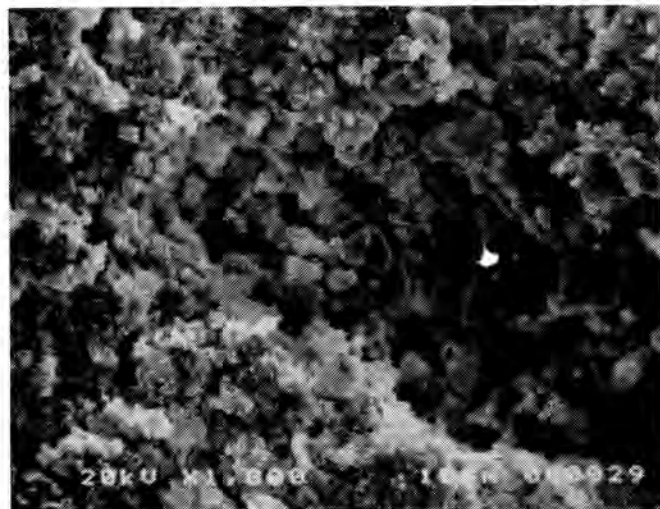


Fig. 1. Scanning electron photomicrograph of fractured surface of porous MAP ceramic.

cured for another week. Reaction of additional MgO with the $(\text{NH}_4)_2\text{HPO}_4$ 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 MAP near the sample surface. The inner core of the samples retained a porosity of $\sim 11\%$.

This procedure for the fabrication of dense samples may also be used to incorporate solid wastes in the MAP matrix. The procedure is to pulverize the solid waste to the grain size of the MgO powder ($\sim 8 \mu\text{m}$), mix the powder with the starter MgO powder before reacting the mixture with the $(\text{NH}_4)_2\text{HPO}_4$ solution. We investigated this procedure with feldspathoidic zeolites, which have been demonstrated to capture chloride salt wastes (13). Various proportions of zeolites were added to MgO powder and mixed a solution of $(\text{NH}_4)_2\text{HPO}_4$ as described above. It was possible to incorporate upto 50 wt% zeolites in the starter powder and obtain competent monoliths.

CHEMICAL AND PHYSICAL CHARACTERIZATION OF MAP CERAMICS

The product phases were characterized by X-ray diffraction analysis (XRD) (Fig. 2). The peaks are identical to those reported by Connaway-Wagner et al. for magnesium orthophosphate cement (11) and are very similar to those reported by Sugama and Kukacka (5). Identification of the major peaks shows that this is a polyphosphate ceramic that includes both struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and magnesium phosphate hy-

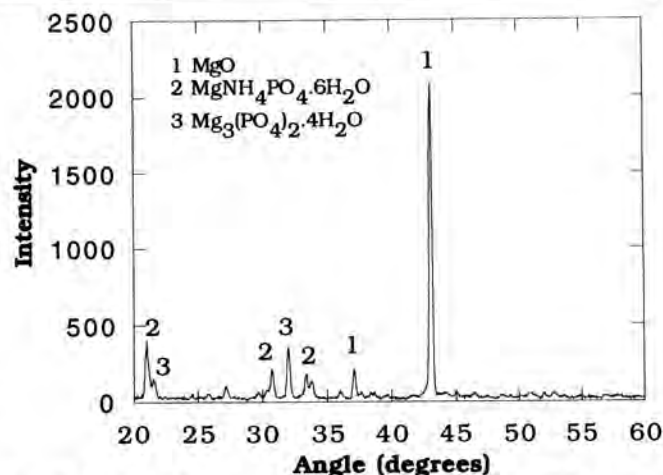


Fig. 2. X-ray diffraction pattern of As-fabricated MAP ceramic.

drate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) phases. The strong MgO peaks suggest that considerable unreacted MgO remains in the material. Sugama and Kukacka (5) have shown that, except for the release of free water, MAP phases are stable upto 930°C .

Figure 3 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 Fig. 3. In addition, the MAP cement in Fig. 3 is much greater than that in Fig. 1 and the MgO grains are less visible. This indicates that the reaction of MgO grains with $(\text{NH}_4)_2\text{HPO}_4$ solution has resulted in densification during soaking.

The physical properties of MAP ceramics are listed in Table II. The negligible water-intrusion value also shows that vacuum impregnation may be a way to make the MAP monolith impermeable to water intrusion. The mechanical properties of the material were measured with an Instron machine on samples with $\approx 11\%$ 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. (11), because of the higher density

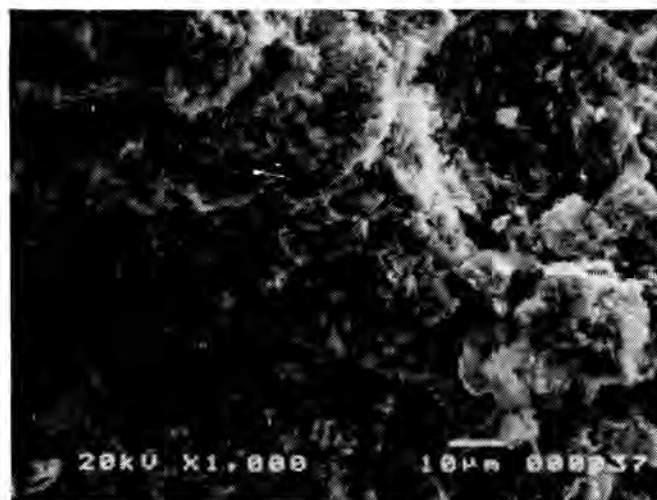


Fig. 3. Scanning electron photomicrograph of fractured surface of MAP ceramic after densification of resoaking.

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 (MPa)	
as formed	23 ± 3.8
resoaked	41.92 ± 3.8
flexural strength (MPa)	21.7 ± 3.6
compression strength (MPa) when 50 wt% zeolite is added.	~28 MPa

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. The strength of MAP-zeolites was also good. When 50 wt% zeolite was added, the strength was still comparable to Portland cement.

CHEMICAL DURABILITY

The chemical durability of the MAP 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 (14), 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 (15). For the MCC-1P tests, the leachate was recharged to an initial 50-ml level at the end of each test period. The samples were rinsed and cleaned in an ultrasonic bath prior to testing. They were then dried and weighed. Observed small dry weight gains were probably due to solids residues from drying. They are consistent with corresponding observations of porosity decreases following the tests.

Leaching aliquot samples obtained at each of the sampling periods were analyzed to determine the pH, and the concentration of magnesium, ammonium, and phosphate. The results are shown in Fig. 4. After an initial transient release, the NH₃ release decreased to a very low rate. This behavior is consistent with the expected leaching of the ammonium hydroxide that is formed in the MAP binding reactions. The initial transient release of ammonia in the leaching tests is consistent with release of the limited inventory of this very soluble phase; it does not, however, reflect the alteration or dissolution of the MAP binding phases. In general, the MAP samples appeared to release ammonium more rapidly at 90°C than in corresponding tests at room temperature. This is reflected in the more rapid depletion of the available inventory at the higher temperature. The pH of the solution increased in the

HPW and carbonate leachant tests until it reached a steady state value approaching 11. The steady state value for the brine tests was about 2-3 pH units lower.

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 MAP samples. Hence the leaching behavior of the magnesium may reflect the 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 MAP. 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.

EFFECTS OF GAMMA RADIATION

The stability of the MAP ceramic with respect to gamma irradiation was investigated by exposing the samples to a gamma radiation field of 0.2 Mrad/hr for 34 days to achieve a total dose of 163 Mrad. The tests were conducted at 28°C. Since gamma radiation has a low rate of linear energy transfer (LET), little direct degradation due to atomic displacement is expected. However, radiolytic effects, such as radiolytically induced outgassing and interactions with the environment, were possible. The matrix of tests conducted is shown in Table III. These tests were designed to investigate the effects of irradiation when the MAP ceramics were immersed in water and humid air environments and irradiated homogeneously with the environment. A second test was designed to

TABLE III
Details of the Samples and Environments for
Gamma Irradiation Test

Test No.	Sample Wt. (g)	Porosity (%)	Environment
1	1.7243	28	HPW, 740 torr, 10ml
2	4.2688	21	vacuum
3	1.6255	26	740 torr, moist air

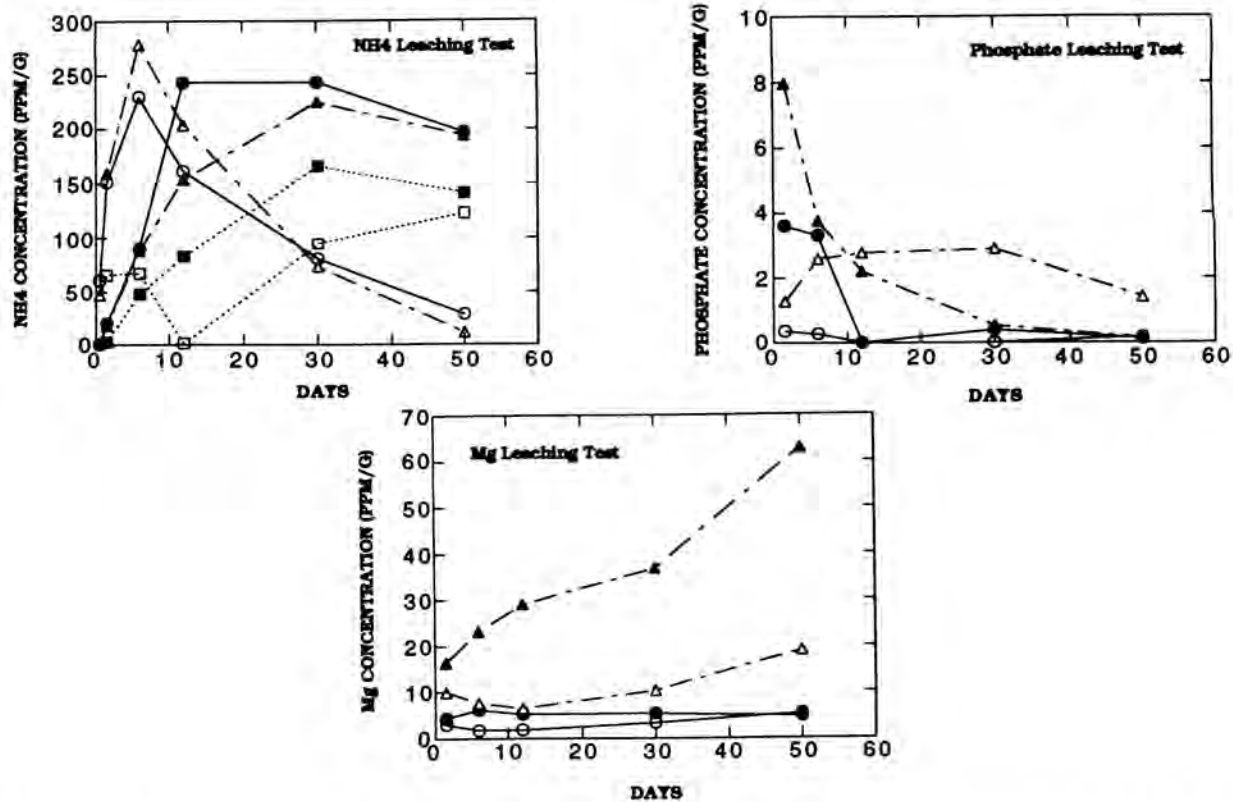


Fig. 4. Leaching characteristics of MAP: The leaching environment is given by 1) —○— HPW, 90 °C, 2) —●— HPW, 24 °C, 3) —△— 0.01 M CO_3^{2-} , 90 °C, 4) —▲— 0.01 M CO_3^{2-} , 24 °C, 5) —□— brine, 90 °C, 6) —■— brine, 24 °C.

determine if irradiation of the MAP ceramic would lead to significant outgassing. After each test, the gas phase was analyzed for condensable and non-condensable gases (H_2 , O_2 , N_2 , CO , CO_2 , N_2O , and NH_4^+).

The results show, as expected, that the effect of gamma radiation on the MAP ceramic is small for the set of conditions examined. No visible change was observed, and a little change in density was associated with the irradiation. The compressive strength of a sample irradiated in vacuum was 23.1 MPa, which is consistent with the strength observed for porous samples (as shown in Table II) and indicates that the samples did not deteriorate. There was no evidence of significant change in morphology, observed by SEM, or mineralogy as shown by XRD (Fig. 5). The gas phase results and the results from the irradiated leachant indicate that the interactions with these environments were small. Hydrogen was the predominant gaseous radiolytic product observed in all the tests. As expected, oxygen depletion was significant in Test 1, because dissolved oxygen reacted with aqueous radiolytic species. The leachate results for Test 1 were very similar to those obtained for corresponding conditions in the absence of radiation, which indicates that the combined effects of irradiation and the environment were not significantly different from those of the environment alone.

CONCLUSIONS

The investigations reported here on magnesium ammonium phosphate (MAP) as a candidate waste form material indicate that this material is a physically, chemically, and mineralogically stable material, with its properties that are superior to those of other room temperature-setting cements.

The material can be synthesized at room temperature and can be densified by impregnation with $(\text{NH}_4)_2\text{HPO}_4$ solution. The fact that zeolites can be encapsulated in this material without significant strength loss implies that wastes, such as salt loaded zeolites may be encapsulated in this material. In addition, this material may be suitable for stabilization and solidification of low-level and mixed wastes, and may have applications as a grout in waste management. Detailed studies are necessary for each of these applications.

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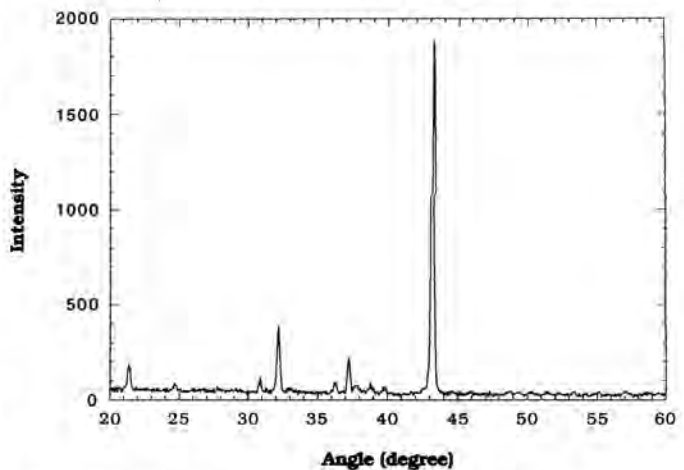


Fig. 5. X-ray diffraction pattern for irradiated MAP ceramic.

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