

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. Polyphosphate MAP was synthesized using calcined MgO and ammonium phosphate solution as precursors. XRD studies show that the material consists of large amount of unreacted MgO, which acts as a filler, and that the phosphate cement which acts as a binding phase. Resoaking porous MAP, we have made denser specimens with a compressive strength of ~ 42MPa (6000 psi). Batch leach tests, using experimental procedures MCC-1 in high purity water, carbonate solution and Mg-brine at 24 °C and 90 °C show that, although ammonia evolved initially, the rate of release decreases with time until leachable inventory is depleted. The leachate pH increases rapidly to a steady state value of ~10 even in refreshed tests after leaching of ammonia has subsided. Phosphate concentrations were low in the leachate demonstrating

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the chemical stability of the binding phase. Leaching of MgO was also low, however, it was found to increase with time. It is argued that this trace level leaching of free MgO may be eliminated by a vacuum impregnation technique, which can mask the free MgO grains by more stable MAP. The radiation stability was tested with a radiation dose of 200 Mrad with a rate of 0.3 Mrad/h, and it was shown that ionizing radiation is not detrimental in establishing the suitability of MAP for radioactive waste applications.

The suitability of MAP 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 show that zeolite grains remain unreacted in the matrix. Potential uses for solidifying and stabilizing wastes are discussed.

Introduction

Chemically bonded ceramics (CBCs) are materials, which can be processed at low-temperature (1, 2). Some of the CBCs, such as phosphates of Mg, Al and Zr are refractory. They are ideal for applications, such as containment of radioactive waste, where fabrication can be achieved at room temperature or at warm temperature, but service conditions require stability of the material at elevated temperatures. Phosphates have high solid solution capacity to incorporate heavy metal, actinide and rare earth contaminants (3). Also their very low solubilities of heavy metal, actinide and rare earth phosphates (4) indicates that phosphate bonded ceramics should be effective media for stabilizing these contaminants. A natural analogue of monazites and apatites (5) suggests that phosphates may be natural hosts to radioactive species and rare earths. Earlier results of leach testing for grouted phosphate wastes at Argonne, support this view. These favorable properties of phosphates motivated the present systematic study of this material for applications in radioactive waste management in our laboratory.

This paper reports the results of an initial investigation of a chemically bonded Magnesium ammonium phosphate (MAP) ceramic. Its chemistry is fairly well understood (6 -8). It sets into very hard cement (9). Concretes of this cement have been developed and their chemical composition (10) and mechanical properties (11) have been well studied for structural applications. Connaway-Wagner et al. (12) have compared the properties of magnesia-orthophosphate and tripolyphosphate cements, and they show that tripolyphosphates have very high compressive strength of 90 MPa with a porosity of 16% as compared to the orthophosphate with a compressive

strength of 23 MPa at a porosity of 26%. Based on these earlier investigations, an application oriented study was done to investigate MAP as a waste form material and the results of this study are reported here.

Fabrication of MAP Ceramics

The details of the materials used for the syntheses of MAP are given in Table I. It was synthesized by contacting calcined MgO with concentrated solution of $(\text{NH}_4)_2\text{HPO}_4$ in distilled water in the weight ratio of 17 :10. This ratio was determined by the workable consistency of the paste, so that it could be quickly transferred to syringes, where the column of the paste was compressed by a plunger to form cylindrical specimens. The mixture hardened in few minutes with an exothermic reaction and the paste set into hard cylinders in ~ 15 minutes. The specimens were kept in the syringes for one week, then removed from the syringes, and cured in desiccators for another week. The samples had a diameter of ~0.6cm and an average length of 1.64 cms. Typically the porosity was ~ 30% measured by using fluid displacement method. Initial SEM investigations of fractured surface of the material formed (Figure 1) showed that the surfaces of the grains of MgO had reacted with the ammonium phosphate solution to yield MAP cement. The inner parts of MgO grains might have remained unreacted however. In addition, the inner regions of the pores contained unreacted MgO. Thus during the formation of MAP, $(\text{NH}_4)_2\text{HPO}_4$ solution did not permeate through the pores. To react the residual MgO in the pores with the

TABLE I : Materials used in the fabrication of specimens

Powder	Supplier	Characteristics
MgO (calcined)	Mallinkrodt	Particle size ~ 7 - 8 μm after recalcination
Ammonium phosphate (dibasic)	Mallinkrodt	crystals
zeolite	Union carbide	particle size 7 - 8 μm

(NH_4)₂HPO₄ solution, the cylindrical samples were soaked overnight in that solution. Subsequently, they were cured for another week. The reaction of additional MgO with the ammonium phosphate solution resulted in the reduction of the open porosity to ~11%. An attempt to reduce the porosity further with vacuum impregnation of the solution only resulted in an impermeable barrier on the surface of the samples, which gave an apparent porosity of ~4%. This was due to the rapid reduction of the surface porosity due to the formation of MAP. The inner core of the samples still retained a porosity of ~11%.

This procedure of fabrication of dense samples may also be used to incorporate solid wastes and second phase materials for the containment in the MAP matrix. The procedure is to powder the solid waste to the grain size of the MgO powder used (~8 μm) and to mix with the starter powder of MgO prior to the reaction of the powder and ammonium phosphate. We investigated this procedure with feldspathoidic zeolites, which have been demonstrated to be acceptable media to capture chloride salt wastes [13]. Various proportions of zeolites were added to MgO powder and the mixed powder was contacted with ammonium phosphate solution using the method described above. Even upto

60wt% of the zeolites in the starter powder could be incorporated and the samples set well.

Chemical and Physical Characterization of MAP Ceramics

To identify the reacted paste, X - ray diffraction analysis of the samples was done. The XRD output is shown in Figure 2. The peaks are identical to those reported by Connaway-Wagner et al., for magnesium orthophosphate cement [11] and are also very similar to those reported by Sugama and Kukacka [5]. Detailed identification of the major peaks shows that this is a polyphosphate cement, which includes both struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) and magnesium phosphate hydrate ($\text{Mg}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$). The strong peaks of MgO suggest that considerable unreacted MgO remains in the material. Sugama and Kukacka [5] have shown that, except for the release of free water, this material is stable at high temperatures. With this temperature stability and the high density, MAP may form a suitable containment matrix for contaminants.

Figure 3 shows the microstructure of a MAP specimen with 11% porosity. When compared with the microstructure from Figure 1, one may see that porosity is considerably less in Figure 3. In addition, content of MAP cement in this Figure is much more than that in Figure 1 and MgO grains are less visible now. This implies that the reaction of grains of MgO from the pores with ammonium phosphate has resulted in the densification during the soaking.

The physical properties of MAP ceramics are listed in Table 2. The submicron pore sizes may make this material leach-resistant. In addition, the

negligible water intrusion value also shows that vacuum impregnation may be a way to make the monolith impermeable to water intrusion.

The mechanical properties of the material were measured using an Instron machine on samples with ~11% porosity. The flexural strength was measured by three point bend test on rectangular bars cut out from the

TABLE II : Properties of magnesium ammonium phosphate cement

Property	Data
density (g/cc)	2.76 for resoaked samples
connected porosity (P)	32% in as formed MAP and ~ 11 after soaking in ammonium phosphate solution.
water intrusion after vacuum impregnation (cc/g)	0.019 + 0.005
pore size distribution	bimodal around 0.018 μm and 0.5 μm
compression strength (MPa)	23 \pm 3.8 before resoaking, 41.92 \pm 3.8 after resoaking
flexural strength (MPa)	21.7 \pm 3.6
compressive strength (MPa) when zeolite is added.	~28 MPa for 50 wt% zeolite in MgO

cylinders using a diamond saw. The observed compressive strength is high as compared to the one measured by Connaway-Wagner et al. [11], because of the

higher density of these samples. This value is considerably higher than that of Portland cement. The flexural strength is also comparable to most of the room temperature setting materials such as Portland cement and polymers such as resins.

The compressive strength of samples with 20 wt% zeolite in the starter powder seems to dramatically increase. This may be due to toughening resulting from the particle reinforcement of the matrix. When 50 wt% zeolite is added, the strength decreases, but is still comparable to Portland cement. This implies that MAP may be a suitable material for containment of zeolites and may form a final waste form with an acceptable strength.

Chemical Durability

The chemical durability of the MAP was examined by exposing the samples of an average porosity ~ 11% to a variety of aqueous environments. In order to span a broad range of possible ground water environments (14), leaching tests were conducted in high purity water (HPW), a 0.01M carbonate solution, and a high magnesium brine and at room temperature and 90 °C. These tests were conducted using the MCC - 1P leaching procedure (15). In the case of HPW, the leaching behavior was also confirmed by ANS 16.1 procedure (16), but is not reported here. In the case of MCC - 1P tests, the leachate was recharged to an initial 50ml level at the end of each test method. The samples were rinsed and cleaned in an ultrasonic bath prior to testing. They were then dried and weighed. Small dry weight gains were observed, which were probably due to solids residues from drying, and are consistent with corresponding observations of porosity decreases following the tests. 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.

Leaching aliquot samples obtained at each of the sampling periods were analyzed to determine the pH, magnesium, ammonium and phosphate concentrations. The results are shown in Figure 4. After an initial transient release, the ammonium release decreases 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 the corresponding tests at room temperature. This is reflected in the more rapid depletion of the available inventory at the higher temperature.

The behavior of the magnesium and phosphate ion concentrations are better 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 should reflect the dissolution of the aggregate material. The Mg concentration has been low in HPW and in brine, but shows increase with time in CO₃ environment. This increase, however, is not accompanied by phosphate, which means that the leaching of Mg is due to release of MgO rather than MAP. It is likely that this release may be retarded

by vacuum impregnating the monolithic samples with the phosphate solution. As mentioned earlier, such a procedure plugs the surface pores, reduces the intrusion of the leachate and should reduce leaching of free MgO.

Effects of Gamma Radiation

The stability of MAP with respect to gamma irradiation was investigated by irradiating the samples for 34 days in a gamma radiation field of 0.2 Mrad/hr 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, are possible. The matrix of the tests is shown in Table III. These tests were designed to investigate the effects of irradiation when the MAP samples were immersed in water and humid air environments and homogeneously irradiated with the environment. The second test was designed to determine if irradiation of the MAP would lead to significant outgassing. After each test the gas phase was analyzed for condensible and non condensible gases (H₂, O₂, N₂, CO, CO₂, N₂O, NO_x, and NH₄⁺).

TABLE III. : Details of the samples and environments for gamma irradiation test.

Test number	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

The results show, as expected, that the effect of gamma radiation on the MAP is small for the set of conditions examined. There was no visible change, and little change in density of 0.8% was associated with the irradiation. The compressive strength tested for sample irradiated in vacuum was 23.1 MPa, which is consistent with the strength observed for porous samples (as given in Table II) and indicates that the samples did not deteriorate. There was no evidence of significant change in the morphology observed by SEM or mineralogy investigated by XRD (Fig. 5) due to gamma radiation. The gas phase results and the results from the irradiated leachant indicated 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 due to reaction of the dissolved oxygen 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 indicated that the combined effects of irradiation of the sample and the environment were not significantly different from that of the environment alone.

Conclusions

The investigations reported here on magnesium ammonium phosphate as a containment material reveal that this material is a physically, chemically and mineralogically stable material, with its properties superior to other room temperature setting cements. The material can be synthesized at room temperature and can also be densified by impregnation of ammonium phosphate solution. The fact that zeolites can be encapsulated in this material without a significant strength loss implies that wastes, such as the chlorides from the Integral Fast Reactor, can be encapsulated in this material. In addition, this material may be very suitable for containment of low level and mixed wastes, and may have applications as a grout in waste management. This work is only an initial study in that direction, and detailed studies are necessary for each of these applications.

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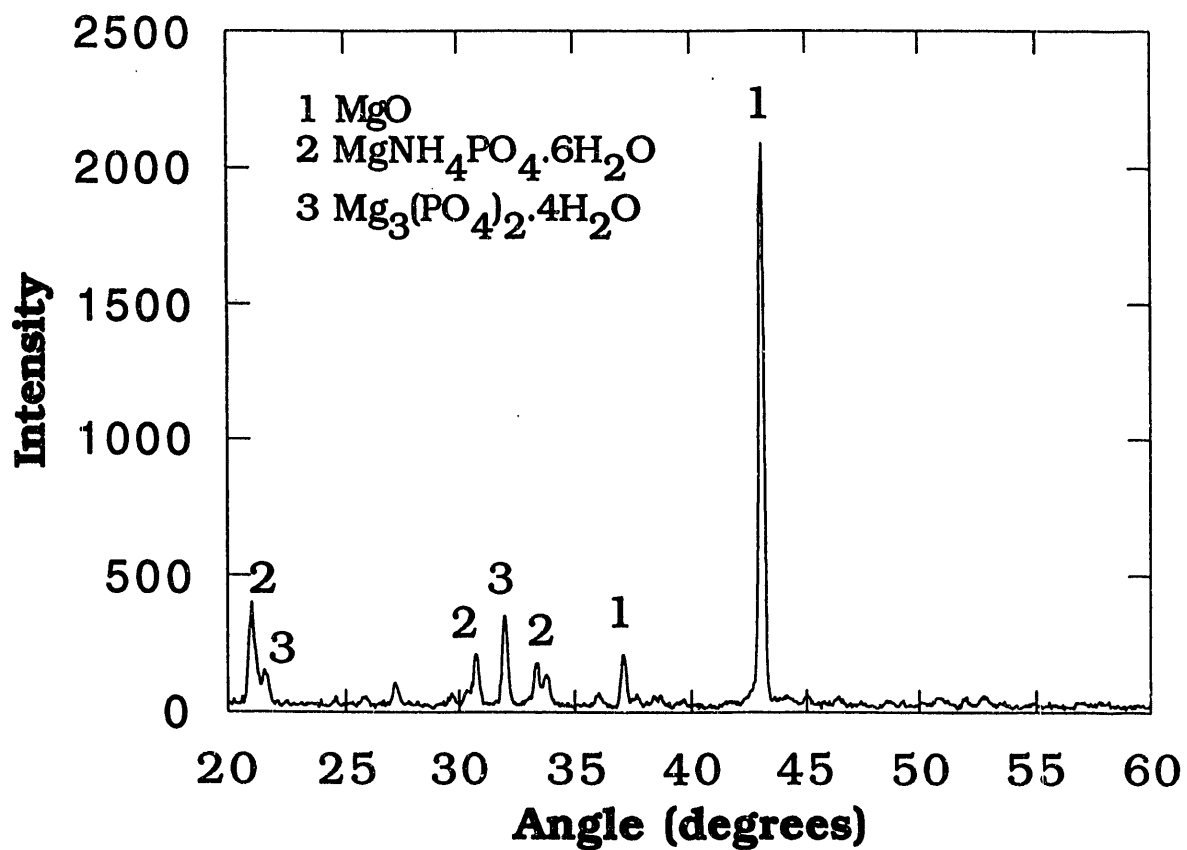


Figure 1. X-Ray Diffraction Pattern for As-Fabricated Magnesium Ammonium Phosphate (MAP) Specimen

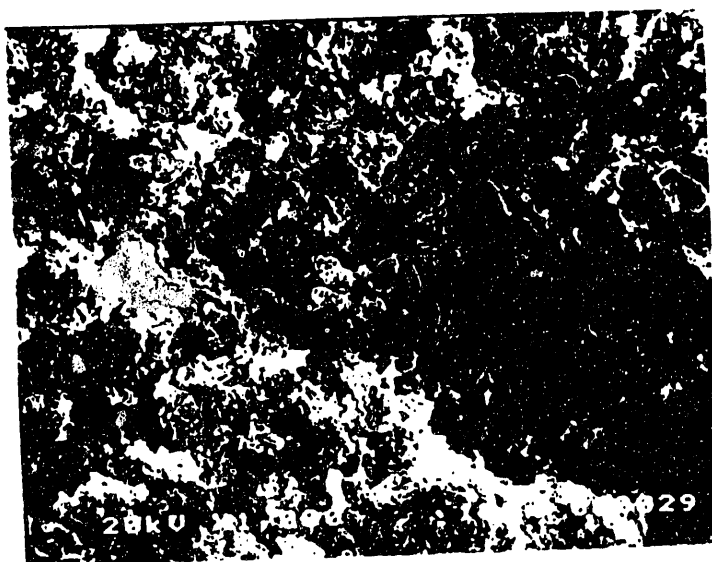


Figure 2. Scanning Electron Micrograph of Fractured Surface of Porous Magnesium Ammonium Phosphate (MAP) Specimen

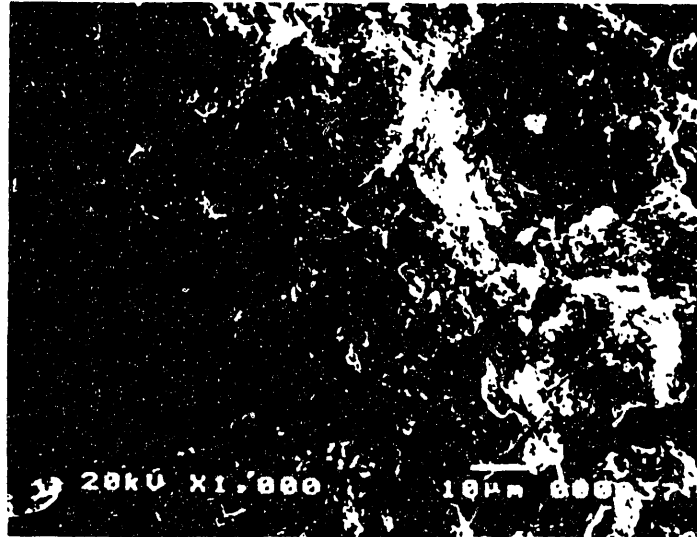
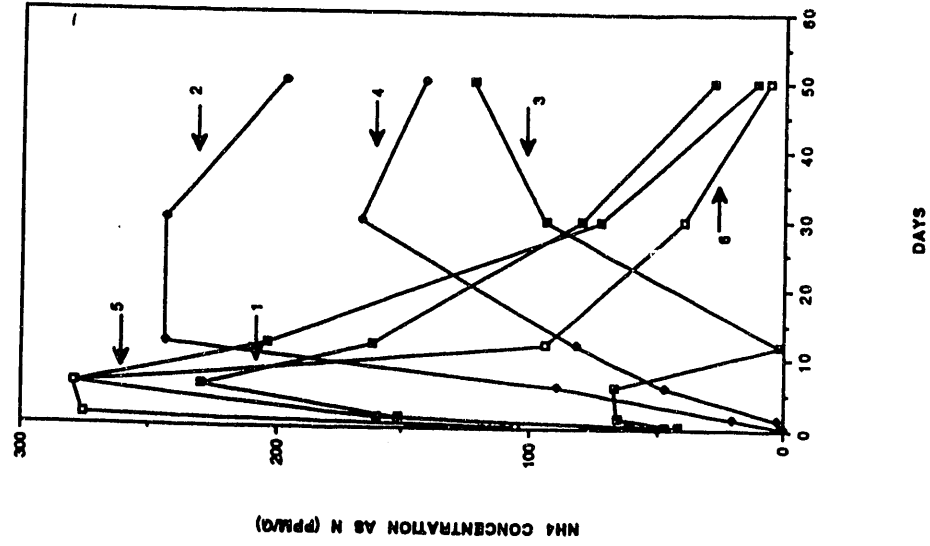
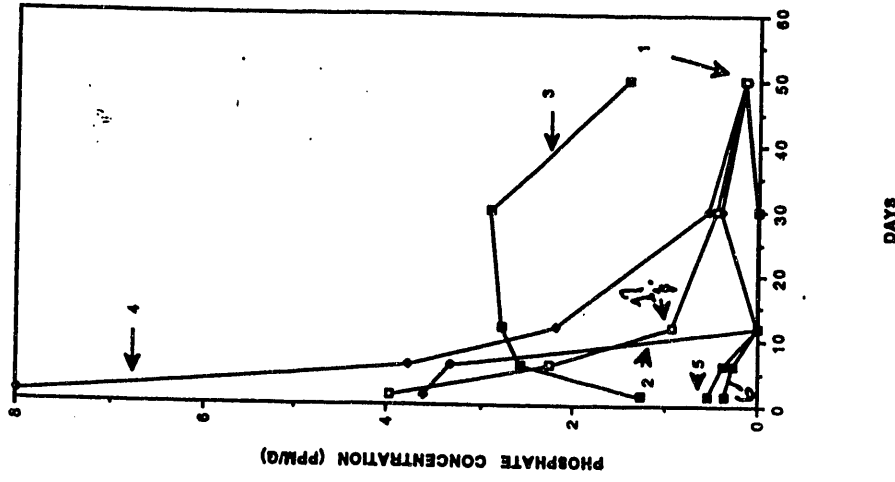


Figure 3. Scanning Electron Micrograph of Fractured Surface of Magnesium Ammonium Phosphate (MAP) Specimen After Densification by Re-soaking

Data from "NH₄ data normalized"



PO 4 LEACHING TEST



MG LEACHING TEST

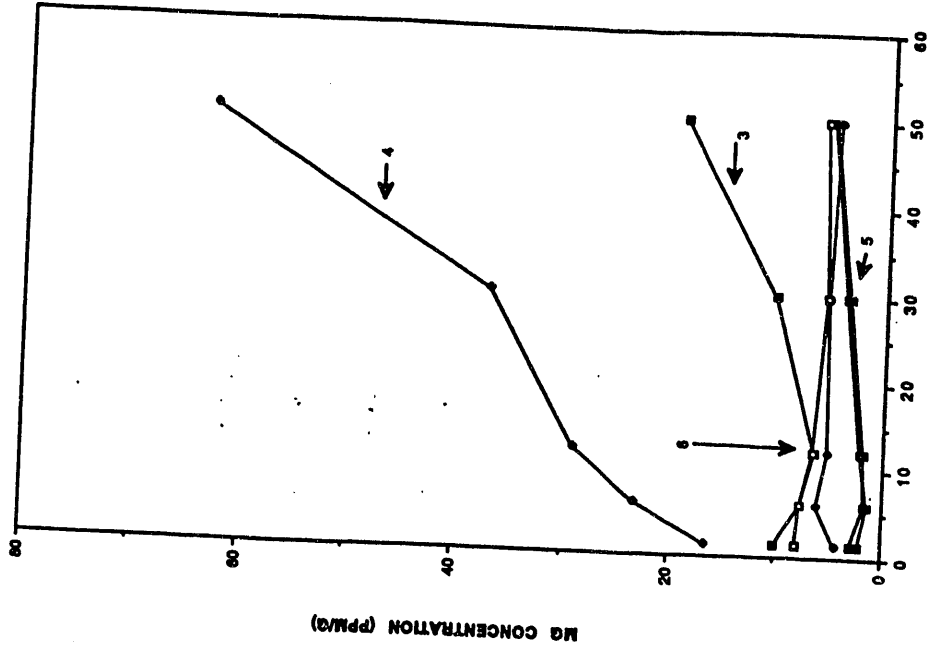


Figure 4. Leaching Characteristics of MAP. The Leaching Environment is given by 1) HPW, 90 °C, 2) HPW, 24 °C, 3) 0.01 M CO₃²⁻, 90 °C, 4) 0.01 M CO₃²⁻, 24 °C, 5) brine, 90 °C, 6) brine, 24 °C

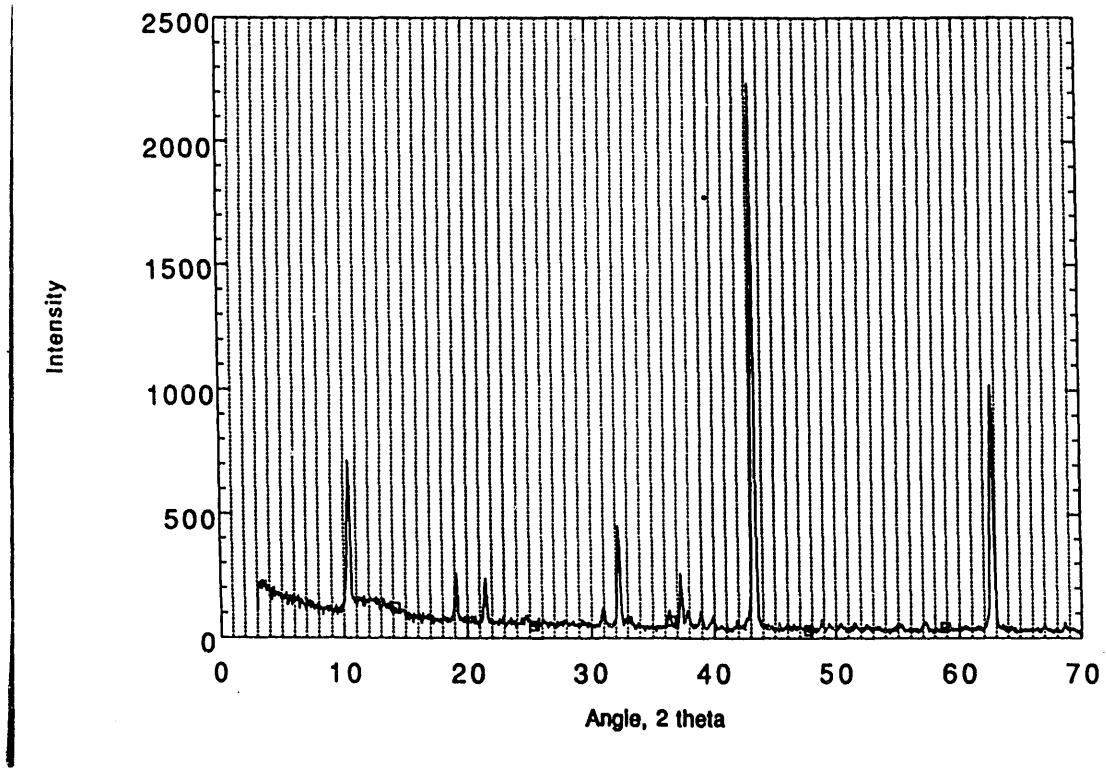


Figure 5. X-Ray Diffraction Pattern for Irradiated MAP Specimen

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