86665-A

ANL/ET/PP--86665A

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CHEMICALLY BONDED MAGNESIUM PHOSPHATE CERAMIC*

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AUG 04 1997
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Revised November 1995

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MASTER

Submitted to Journal of Materials Research.

*Work supported by the U.S. Department of Energy, Office of Technology Development, as a part of the Mixed Waste Integrated Program, under Contract W-31-109-Eng-38.

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ABSTRACT

A novel newberyite-rich magnesium-phosphate ceramic, intended for the stabilization of the U.S. Department of Energy's low-level mixed-waste streams, has been developed by an acid-base reaction between magnesium oxide and a phosphoric acid solution. The reaction slurry, formed at room temperature, sets rapidly and forms a lightweight hard ceramic with low open porosity and a high compression strength of $\approx 6,200$ psi. It is a composite of stable mineral phases of newberyite, lünebergite, and residual Mg oxide. Using this matrix, we developed superior waste forms for a surrogate ash waste stream. The final waste form is a low-permeability structural-quality ceramic, in which hazardous contaminants are chemically fixed and physically encapsulated. The compression strength of the waste form is an order of magnitude higher than the land disposal requirement, even at high waste loading. The high compression strength is attributed to stronger bonds in the waste form that result from participation of ash waste in the setting reactions. Long-term leaching studies show that the waste form is stable in an aqueous environment. The chemically bonded phosphate ceramic approach in this study may be a simple, inexpensive, and efficient method for fabricating high-performance waste forms either for stabilizing waste streams or for developing value-added construction materials from high-volume benign waste streams.

I INTRODUCTION

Chemically bonded phosphate ceramics^{1,2} are a class of materials formed at low temperatures; hence, they are distinct from sintered ceramics. Formed by acid-base reactions between an inorganic oxide or hydroxide and phosphoric acid or a soluble acid phosphate,³ they are hard and dense and their fabrication is simple and comparatively less expensive than that of conventional ceramics. These advantages may well be exploited in several fields, including waste management and construction.

Kingery⁴ reported exploratory studies on the setting characteristics of phosphates produced by reactions between phosphoric acid and several inorganic oxides. He demonstrated that a wide variety of phosphate ceramics may be formed by using inorganic oxides. However, very few attempts have since been made to develop them further. Magnesium ammonium phosphate is the only ceramic material that has been extensively developed⁵⁻⁸ and is finding application in quick-setting concrete for road repair. However, ammonia is evolved continuously during and after formation of this material, and it is unsuitable as a matrix for waste stabilization applications because ammonia is likely to corrode the waste containers.

Some studies show that Al phosphate may be formed in desired berlinite-rich phases at temperatures between 120 and 200°C.⁹ Sliva and Scheetz¹⁰ used these phases to stabilize waste from the Idaho Chemicals Processing Plant. Their work demonstrates the potential of these materials to stabilize hazardous wastes without resorting to treatment at very high

temperatures. Similarly, phosphate waste forms have been made with bone char for plutonium-rich wastes.¹¹ Monazites and apatites, which are phosphate minerals, are known to be host minerals of uranium and thorium.¹² This demonstrates that radioactive as well as hazardous wastes (and hence mixed wastes) may be stabilized in phosphates.

The above-mentioned studies indicate great potential for the development of a class of chemically bonded phosphate ceramics for waste management applications. The phosphates are formed by acid-base reactions in which waste contaminants can be chemically converted to insoluble phosphate species. Subsequently, the paste formed by these reactions sets into a hard ceramic in which contaminants can be physically encapsulated in a phosphate matrix. This allows us to develop a superior waste form that can exploit the benefits of both chemical fixation and physical encapsulation.

We investigated several possible systems, including Mg phosphate, Mg-Na phosphate, Al phosphate, and Zr phosphate, all synthesized at low temperatures. We found that Mg phosphate is one of the simplest systems. Unlike Mg ammonium phosphate, no gas is evolved during synthesis of this material; it is formed by a simple acid-base reaction between calcined Mg oxide (MgO) and dilute phosphoric acid. In previous attempts,¹³ such a reaction formed a water-soluble phase of $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and hence this system generated little interest in practical applications. For this reason, Finch and Sharp¹³ developed an insoluble newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$)-rich phase by reacting MgO with soluble Al orthophosphate. We reexamined the Mg phosphate system and with some process modifications, developed an

insoluble newberyite-rich Mg-phosphate ceramic. Details of the development of this material and its properties are presented here.

As the first application of this material, we examined stabilization of U.S. Department of Energy (DOE) low-level mixed waste. The DOE Mixed Waste Treatment Project (MWTP) has identified a need for alternative waste forms for problem mixed waste¹⁴ that contains volatiles and pyrophorics, for which conventional thermal treatment is not suitable and room-temperature stabilization seems to be the best approach. DOE has formulated several surrogate waste streams¹⁵ that contain hazardous materials as defined by the Resource Conservation and Recovery Act (RCRA), including metals, organics, and radioactive contaminants. Contaminated ash, one of these waste streams, is produced as a secondary waste during thermal destruction of bulk waste by incineration, vitrification, molten metal, or plasma hearth treatments. In these processes, bulk waste is treated at high temperatures, typically at 900-1500°C. At these temperatures, hazardous components with lower boiling points, such as salts of Pb, As, Hg, Cd, Cr, and Ni, volatilize and are captured along with other emissions in a baghouse or electrostatic precipitator. Stabilization of these secondary waste streams comprising these contaminated emissions and radioactive components requires an alternative low-temperature treatment. The chemically bonded phosphate ceramic approach may fulfill this need. Using the DOE surrogate ash waste stream, we developed an Mg-phosphate-based waste form. Detailed development of this waste form, its properties and its regulatory-performance characteristics are presented here.

II. FABRICATION OF CHEMICALLY BONDED Mg PHOSPHATE CERAMIC

Magnesium oxide powder reacts too quickly with phosphoric acid (H_3PO_4) and the reaction product is formed as a precipitate. To retard this reaction, it is necessary to precalcine MgO so that practical ceramics can be formed. Eubank¹⁶ has shown that calcination to 1300°C reduces the reactivity of MgO by increasing the particle size and reducing the porosity of the particles. For this reason, commercial, precalcined, chemical-grade MgO powder with a particle size of $\approx 8 \mu\text{m}$ (supplied by Mallinckrodt) was used in this study. This powder was further calcined at 1300°C for 1 h and repowdered back to approximately its original size. The H_3PO_4 used in this study was an 85 wt.% concentrated commercial-grade acid solution. It was diluted to net 50 wt.% concentration, which not only retarded the reaction, but also provided part of the water needed to form hydrated phosphate phases.

The reaction between calcined MgO and H_3PO_4 solution is exothermic and the paste formed by this reaction sets into ceramic form within minutes. To make consistently good samples, it was necessary to further retard the reaction. Literature on the formation of Mg ammonium phosphates cites addition of several retardants, including boric acid and borates,^{6,8} for this purpose. Sarkar¹⁷ studied the kinetics of retardation of such a system with boric acid; he reports that boric acid aids in the development of a polymeric coating on the MgO grains and thus retards the setting rate. Our preliminary experiments showed that addition of 15 wt.% powdered boric acid to the MgO powder adjusted the setting time for fabrication of cylindrical samples 1 cm in diam and few centimeters in

length to ≈ 15 min. Smaller additions of boric acid did not give a comfortable working time, whereas a larger amount crystallized excess boric acid on the surface of the sample. Unlike the earlier studies, retardation of the reaction with boric acid also formed a ceramic that was dominated by the newberyite phase and was not soluble in water. For this reason, all of the samples were made with 15 wt.% boric acid in the starter MgO powder.

To form newberyite, it is necessary to react a stoichiometric proportion of 40.3 g MgO with 98 g H_3PO_4 , and 36 g of water. To retain the 50 wt.% concentration of the acid, however, the amount of water had to be increased to 98 g. In practice, such a composition results in a dilute gel that does not set into a solid form. To form a structural ceramic, the MgO content may be increased so that the surface of the MgO particles will react with the H_3PO_4 solution and the unreacted core of the particles will provide nucleation sites for the newberyite crystals to grow. Preliminary experiments showed that 4 g of a mixture of MgO and boric acid, when reacted with 6 g of 50 wt.% H_3PO_4 solution formed a slurry with exothermic reaction and that set into dense ceramics in ≈ 15 min; hence, this composition was used in making the test samples.

To avoid overheating during the mixing process, the mixture of powders was stirred into the H_3PO_4 solution slowly. The paste formed by the reaction was thick but flowing; it was poured into cylindrical syringes 1 cm in diameter. The slurry set in a few minutes, but hardened well after one day. The excess water partially evaporated or remained as unreacted free water separated from the consolidated sample. When taken out of the syringes after one day, the ceramic samples were hard monoliths. All of the

samples were cured for three weeks to ensure full strength. They were cut into $\approx$ 2-cm lengths and were used for further study.

III. WASTE FORM DEVELOPMENT

The DOE ash waste stream¹⁵ contains materials generated by incineration of radioactive and nonradioactive waste streams. Its surrogate composition, presented in Table 1, is designed to closely represent this waste at various DOE facilities. The surrogate ash waste stream, mixed in the laboratory according to a prescribed procedure in Ref. 15 as MWTP # 3111, consists of fly ash, bottom ash, and activated C as major components and RCRA metals as contaminants. The levels of the inorganic contaminants in the waste streams were adjusted so that the metal concentration was 0.5 wt.% of the total waste. In addition, the procedure also recommends addition of dichlorobenzene and naphthalene to demonstrate that the setting reactions are not affected by typical organic contaminants that exist in such DOE waste streams. Cesium chloride (0.3 wt.%) was also added, as a surrogate for radioactive Cs.

The elemental compositions of the fly ash and the bottom ash used in this formulation were estimated by ICP analysis. The major elements found (in wt.%) were Al, 11.5 and 12.9 wt.%; Si, 21.8 and 22.3 wt.%; Fe, 4.16 and 9.36 wt.%; and C, 8.8 and 1.3 in the bottom ash and fly ash respectively. When these compositions are compared with the elemental composition of a typical DOE waste stream, such as transuranic (RFP TRU) incinerator ash¹⁵ from Rocky Flats with a wt.% composition of C, 25 wt.%; Al, 2 wt.%; Si, 21 wt.%; and Fe, 0.1 wt.%, one realizes that the fly ash and bottom ash are

mainly deficient in C, which is high in the actual waste stream. Activated carbon is used to adsorb contaminants from liquid waste streams and is then disposed of in the actual waste. In addition, the actual waste also contains ≈ 20 wt.% vermiculite which is used to absorb liquids. For these reasons, these two components are added in the surrogate waste formulation.

The detailed composition of the simulated ash waste is given in Table 1. When the surrogate waste is simulated, activated C is first loaded with the contaminants and then mixed with the bulk waste that contains ash and vermiculite. It is difficult to stabilize such a high-C waste stream with high loadings in conventional portland cement.¹⁸ This is one reason why we decided to explore the potential for phosphate ceramics to stabilize this waste stream.

The waste stream mixture was ground to nearly the same size as the starter MgO powder, and this ground mixture served as the surrogate ash waste stream during the entire investigation. It was mixed with the starter powder in concentrations ranging from 35 to 70 wt.%. In all of the cases, the best samples were obtained when the powder and solutions were used in equal proportions. The sample fabrication procedure for forming the ceramic was the same as that given above for the Mg phosphate ceramic. The slurry set exactly the same way as the matrix material and formed hard monolithic cylinders. They were cured for three weeks before they were used in various investigations.

IV. PHASE COMPOSITION AND PHYSICAL PROPERTIES OF CERAMIC MATRIX

To identify crystalline phases in the Mg phosphate ceramic and its ash waste form, X-ray diffraction studies were performed. Figure 1 shows the X-ray diffraction pattern of the Mg phosphate ceramic. Newberyite and residual MgO were the main phases. In addition, a boron compound, lünebergite ($\text{Mg}_3\text{B}_2(\text{PO}_4)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$),¹⁶ was also present as a result of the use of boric acid in the process. Both newberyite and lünebergite are natural minerals. Newberyite has been extensively studied by Sutor,¹⁹ and Boistelle and Abbona.²⁰ On the other hand, literature on lünebergite is scarce and the only serious investigation conducted on this mineral was by Senagupta et al.²¹ Because both newberyite and lünebergite are natural stable minerals, the Mg phosphate matrix is likely to be very stable and hence a good candidate for treating different waste streams and developing durable waste forms. Newberyite is the only durable phase among the Mg phosphate hydrate systems that have been identified.²² This is the reason, we believe, earlier attempts to develop a durable chemically bonded Mg phosphate ceramic, in which newberyite was not a constituent phase, were not successful.¹³

The composition revealed by the X-ray diffraction studies was further confirmed by differential thermal analysis (DTA). The results are shown in Fig. 2. The endotherm near $\approx 100^\circ\text{C}$ is due to evaporation of the free water from the sample. The endotherm at $\approx 180^\circ\text{C}$ is due to newberyite.²³ These findings suggest that newberyite is the major phase formed during the acid-base reaction. In addition to this, an endotherm is also noticeable at $\approx 220^\circ\text{C}$.

From the earlier studies by Senagupta et al.,²¹ this endotherm appears to be due to lünebergite. The endotherms at ≈ 180 and 220°C confirm the results obtained by X-ray diffraction.

Using this information and stoichiometric calculations, we estimated the overall composition of the Mg phosphate ceramic. We assumed that all the boric acid and H_3PO_4 reacted to form newberyite and lünebergite phases and left excess MgO in the material. The excess water escaped partially during mixing; the rest remained on the surface and sides of the set sample. This information allows us to estimate the overall stoichiometric compositions. The results are given in Table 2.

As we see from the estimates, newberyite is the major phase in the material. In addition, because lünebergite exhibits a high molecular weight, it forms the second largest phase in the material even though only a small percentage of boric acid was added during fabrication. Of the 36 wt.% MgO added during fabrication, 14.75 wt.% reacted to form newberyite and lünebergite, and 21.25 wt.% remained unreacted. Of the 31.25 wt.% water that was added to the material, only 11 wt.% reacted; the rest escaped as free water.

The samples appeared dense and the surface of the samples was smooth. However, fractured surfaces of both newberyite and lünebergite showed evidence of closed porosity. To investigate the physical structure of these materials, density and open porosities were measured. The density, measured by determining the mass and geometrical volume, was 1.706 g.cm^{-3} , which is lower than the densities of the major components, i.e.,

newberyite, lünebergite, and unreacted MgO. Based on the theoretical densities of these three components (2.12, 2.05, and 3.58 g.cm⁻³, respectively), and using the composition given in Table 2, we determined that the theoretical density of the matrix ceramic to be 2.42 g.cm⁻³. This finding implies that total porosity must be 29.5%. Open porosity, estimated by the water immersion method, was 8%, which suggests that closed porosity is 21.5%; this high closed porosity must have arisen because of air trapped during mixing of the slurry and the rapid setting of the ceramic.

The compression strength of the matrix material was measured on an Instron machine in a uniaxial mode. The strength of the material was 3079 psi, which is in the same order of magnitude as that of portland cement. We believe that the strength of the matrix can be higher if the closed porosity is reduced.

The microstructure of the matrix material was investigated by scanning electron microscopy (SEM). Figure 3 is an SEM photomicrograph of a fractured surface of Mg phosphate ceramic. The granular structure connected by a glassy phase is clearly visible in the left half of the image; the granular structure contains grains of residual MgO, the presence of which was confirmed by energy-dispersive X-ray (EDX) analysis. In the lower right corner, oblong platelets of crystalline newberyite can be seen; they are distributed throughout the specimen and grow in voids. The granular and glassy structures seem to depend on the ratio of MgO to H₃PO₄ solution; higher ratios seem to provide more granular structure, whereas excess solution gave glassy structures. Excess glassy phase tended to

produce microcracks on the surface of the samples, and hence excess MgO was necessary to form good samples.

V. WASTE FORM COMPOSITION AND PHYSICAL PROPERTIES

Figure 4 shows the X-ray diffraction output of the untreated ash waste and the ash waste form ceramic. The output for untreated ash exhibits, in addition to a broad peak of vermiculite between 28° and 29° , definite crystalline phases of quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The overall pattern also shows a broad low-angle hump that suggests occurrence of an amorphous phase typical of ashes. Some of the crystalline peaks are retained in the waste form, others do not show up in the overall pattern because of dilution effect. The peak of vermiculite in the waste form is absent probably due to a coating of the phosphate layer of this material, which will make it inaccessible to X-rays. In addition, when the output of the waste form in Fig. 4 is compared with that of the matrix material in Fig. 1, we realize that all of the major crystalline phases of the matrix also exist in the waste form. Thus, the waste form contains crystalline phases of both the matrix and the waste. The DTA studies (Fig. 5) also confirmed the existence of newberyite in the waste form. All of these phases are stable and durable in the waste form and contaminants are hosted in them.

Based on the phases identified by the above studies, stoichiometric calculations were made to estimate the composition of the waste form. As an approximation, we ignored any reactions of the waste components with the matrix materials. This allowed us to calculate the phases quantitatively in a manner similar to that done in developing Table 2. The results of these

calculations, for a waste loading of 70 wt.% in the starter powder, are newberyite, 44.8%; lünebergite, 10.7%; MgO, 2.73%; and ash waste, 41.7%.

These results show that newberyite is the major phase, followed by the ash waste. When compared with the matrix material, the residual content of MgO is significantly reduced. It forms only a minor component of the entire waste form and this is indicated by the reduced peak in the X-ray diffraction pattern in Fig. 4. The residual MgO in the matrix and the ash waste particles in the waste form play an important role in providing particle reinforcement to the respective materials. By optimizing the waste-to-MgO powder ratio, it may be possible to react all of the MgO and leave the nucleation sites solely to ash waste particles.

Such a threshold, that determines the maximum waste loading for our process, was found to be 74.5 wt.% of ash loading in the original powder, and translates into ≈ 44.4 wt.% waste loading in the final waste form. Our preliminary studies showed, however, that higher than this calculated optimum waste loading was possible (we made waste forms with 80 wt.% ash in the original powder) because the ash waste appears to also participate in the reaction and alters the matrix. In our stoichiometric calculations, we ignored these interactions for the sake of simplicity. Thus, our estimations were only approximate. The occurrence of interaction between the ash waste and the matrix material was observed in a limited study using nuclear magnetic resonance (NMR) undertaken at the University of Illinois by W. Klemperer and J. F. Young,²⁴ who investigated structural changes that occurred in the Mg phosphate system because of incorporation of the ash waste. Figure 6 shows outputs of the (a) Mg phosphate system without ash

waste and then, (b) the waste form with 50 wt.% the ash waste in the starter powder. The additional dominant peak in the waste form near the maximum suggests that a distinct matrix modification has occurred in the waste form in the presence of the ash waste in the system. This modification indicates that ash waste itself participates in the stabilization reaction. It is likely that an interaction occurs between the amorphous phases of the waste stream and the matrix material during the formation and setting of the reaction slurry. This aspect needs detailed study and will be pursued in the future.

As was done in the case of the matrix material, theoretical density of the waste form and total porosity were calculated on the basis of the stoichiometric composition estimated above. The theoretical density was 2.248 g.cm^{-3} , and measured density was 1.756 g.cm^{-3} . Based on these numbers, total porosity was 21.89 vol.%. The measured open porosity in this material was 8 vol.%, which implies that the closed porosity is ≈ 14 vol.%.

The compression strength of the waste forms for various waste loadings is given in Fig. 7. As stated previously, the strength of the matrix was nearly the same as that of portland cement. However, once it was loaded with ash waste, the compression strength increased by more than two-fold. In spite of the moderately high closed porosity in these samples, compression strength in all cases was high, i.e., in the range of 6223-6487 psi; it was not affected by the extent of waste loading and was nearly the same at all waste loadings. The very high strength of the waste forms when compared with the matrix material must be due to the strengthening of bonds between the

particles in the waste forms as a result of the alteration of the matrix detected by NMR studies. The nature of this strength enhancement is important in optimizing the properties of the waste form as a structural material and must be studied further. As a waste form, however, Land Disposal Restrictions require a minimum strength of 500 psi, and the strength of the ash waste form is one order of magnitude higher than this value.

An important factor that affects the choice of a particular stabilization process in waste management is the final volume of the waste form. To ensure economic disposal of the stabilized waste form, waste loading, which may be defined as the ratio of the volume of the waste form to the free volume of the waste, must be minimized. We calculated this ratio by stabilizing a predetermined loosely compacted volume of free ash in the final waste form at a stoichiometric composition estimated before, and determined the waste loading to be 0.91. This result shows that there has been, in fact, a small volume reduction of 9%.

The photomicrograph in Fig. 8 shows the fractured surface of the ash waste form. Figure 8(a) shows spherical structures that are silica spheres (cenospheres) from the ash waste. These spheres are covered and well joined to the matrix by a glassy phase, which is actually responsible for the physical encapsulation of the waste particles. Microcracking was much reduced in the ash waste form, possibly because the ash particles provide the necessary particle reinforcement to the sample. As one may see in Fig. 8(b), profuse growth of newberyite crystals similar to those found in the Mg phosphate ceramic in Fig. 3 is found in the void regions on the fractured

surfaces of the waste forms. The waste form was rich in these crystalline growths, even though total phosphate content was not high in the final waste form.

These studies reveal that the structure of the Mg phosphate waste form with ash waste is very complex and contains both crystalline and noncrystalline phases. Among the crystalline phases, newberyite and lünebergite are natural mineral phases and hence are insoluble in a groundwater environment. In addition, residual MgO remains as a component in the waste form and in the matrix material.

VI. LEACHING AND IMMERSION STUDIES

Regulatory performance of the final waste forms was demonstrated by leaching and immersion studies.

A. Toxicity Characteristic Leaching Procedure

Toxicity Characteristic Leaching Procedure (TCLP) studies are recommended by the U.S. Environmental Protection Agency (EPA)²⁵ as a regulatory requirement for the final waste form. This procedure was used in this project to assess the performance of the final waste forms in acidic aqueous environments.

The untreated waste and the waste forms were subjected to TCLP tests. In addition, to demonstrate the role of H_3PO_4 in the chemical stabilization of heavy metals, we also performed TCLP studies on ash waste that was reacted

directly with H_3PO_4 solution; results are given in Table 3, which also includes regulatory limits on leaching levels for the contaminant metals.

The first row of the table shows that considerable leaching occurs from the unstabilized surrogate ash waste stream under TCLP conditions. However, when the ash waste is reacted with H_3PO_4 solution (second row), the leaching levels are reduced. This reduction is due to the reaction between the contaminant metal salts and the acid solution, which converts the heavy metal nitrates into insoluble phosphates. As a result, they do not leach into the acidic leachate water used in the TCLP. The numbers show that this chemical stabilization has been very effective.

The leaching levels shown in the remaining three rows of the table are further reduced by two orders of magnitude. This superior immobilization of the contaminants is due to the subsequent physical encapsulation of the contaminants within the dense phosphate matrix. The encapsulation may be due to incorporation of the contaminants in the crystalline structures of the various phosphate phases of the matrix or to formation of an impermeable phosphate glassy cover on these contaminants. The SEM photomicrograph in Fig. 8 reveals some evidence of this latter mechanism, where ash particles are coated with a continuous phase.

A limited study was also done to investigate the ability of the Mg phosphate ash waste form to retain Cs. The leaching level of Cs from the stabilized waste form with 70 wt.% ash waste in the starter powder was 11 ppm. When one considers that there is no viable technology to stabilize

Cs, this result is encouraging. Efforts are currently underway to develop phosphate-bonded ceramics that are especially suited to stabilize Cs.

The glassy phase very likely also coats the contaminant particles of heavy metals, helping to eliminate direct contact with the ground water. This may be why Ni, although not chemically well stabilized, was not leached out in the TCLP studies after the waste was incorporated in the phosphate ceramics.

B. Immersion Studies on Final Waste Form

To study the durability of the final waste forms in an aqueous environment, immersion studies were initiated. Samples were immersed in distilled water that was changed periodically to compensate for any evaporation loss. The samples were periodically removed, dried, and weighed to detect any weight loss. The procedure followed was similar to ANS method 16.1.²⁶ In addition, we also monitored the pH of the solution. After 90 days, specimens were tested for compression strength. Weight change and pH readings are presented in Figs. 9 and 10, respectively, and the compression strength after the immersion study is shown in Fig. 11. Figure 9 shows the change in weight of an Mg phosphate specimen with 70 wt.% ash waste loading in the starter powder. Weight change percentage was computed with respect to the weight of the waste form at the beginning of the immersion study.

The results indicate some early weight loss; thereafter, the weight of the waste form was nearly constant. The initial large drop in weight is

accompanied by a similar drop in pH, which suggests a loss of excess H_3PO_4 from the waste form. Thereafter, unreacted MgO is released (although at a much slower rate), leading to a further decrease in weight and a recovery in pH. Once the excess acid and unreacted MgO are completely released, the pH and weight of the waste form remain constant. Currently, acid-base compositions are being improvised to eliminate this initial loss.

Figure 11 shows the variation in compression strength of the Mg phosphate waste forms as a function of the waste loading. For comparison, the strength of Mg phosphate waste forms not exposed to water are presented in the same figure. No significant degradation occurred in the strength of the Mg phosphate waste form at lower waste loadings. However, for the 70 wt.% loading in the starter powder, we observed a more noticeable drop in strength, to ≈ 4000 psi from an initial value of ≈ 7000 psi for unexposed waste forms. This implies that 70 wt.% waste loading is probably the upper limit for the durability of the waste form. Below this loading, the strength of the waste forms is exceptionally good and satisfies the regulatory requirements after a 90-day exposure to an aqueous environment. Thus, chemically bonded phosphates have the potential to form durable waste forms.

C. Contaminant Distribution in Waste Form

The waste form microstructures were further analyzed by EDX and X-ray mapping of the contaminants. A sample of Mg phosphate ceramic with ≈ 25 vol.% ash waste was polished and exposed to energy-dispersive X-rays. Figure 12 shows the surface of this sample along with the composition of

two distinct areas. One area, at the center of the photomicrograph, appears to be crystalline, while the surrounding area is featureless or glassy. The EDX studies show that both areas contain Si, Al, Mg, and P, implying they are made of alumino-silicates arising from the ash waste together with Mg phosphates. It is likely that some silico-phosphates also might have been formed; these thermally stable phases would not be detected in DTA studies. Thus EDX analysis shows a homogeneous distribution of the waste components in both the crystalline and glassy phases of the final waste form.

Figure 13 shows the distribution of the contaminant heavy metals within the same area of the photomicrograph shown in Fig. 12. The contaminant metals are evenly dispersed in the picture, and the heavy metals have not segregated into localized clusters. In addition, they exist in both crystalline and noncrystalline phases, which indicates that the contaminant distribution is not dependent on the morphology of the final waste form. Because of this even distribution, even though the samples were powdered and subjected to leaching in the TCLP test, they did not leach out.

VII. DISCUSSION

We have developed a room-temperature-setting chemically bonded Mg-phosphate ceramic that is most suitable for stabilization of ash waste streams. The approach is based on the principle that for superior performance of a waste form, the contaminants should be chemically fixed, and physically encapsulated in a stable and durable matrix. In our process, both are achieved in one step.

Chemical fixation is best achieved by converting the contaminants into insoluble phosphates. Divalent contaminant metals such as Pb^{2+} , Cd^{2+} , and Ni^{2+} will be converted into monohydrophosphates. This was confirmed with Pb^{2+} by reacting Pb nitrate with H_3PO_4 solution and using X-ray diffraction to identify the reaction product. The solubility product constant K_{sp}^{27} of this product is 1.4×10^{-10} , which is low, and hence an insoluble product is formed. Similarly, the trivalent contaminant metals (such as Cr^{3+}) form orthophosphates, where K_{sp} is even lower; K_{sp} for CrPO_4 is 2.4×10^{-23} . The low solubility of these reaction products is reflected in the TCLP results shown in Table 3. Comparison of the leaching data on the contaminated ash waste with data obtained from the waste reacted with H_3PO_4 solution indicates that these contaminants are chemically fixed by the phosphate conversion.

The physical stabilization is achieved by encapsulating the chemically fixed contaminants in the dense ceramic matrix of Mg phosphate; the SEM photomicrographs in Fig. 8 and the EDX output in Fig. 12 reveal this. In these figures, ash particles are encapsulated in a dense matrix of Mg phosphate. For durable physical encapsulation, it is necessary that this matrix be formed of durable minerals. Natural minerals are the best candidates for this. Newberyite and lünebergite are such mineral analogs of Mg and B phosphates. The X-ray diffraction data in Fig. 1 show evidence of these phosphates in the matrix and do not indicate formation of any other phases of Mg phosphate. The endotherm of only newberyite and lünebergite in the DTA results in Fig. 2 confirms that probably no other phases of Mg phosphate are formed in the material, and that even the noncrystalline phases are most likely newberyite and lünebergite.

The chemically bonded Mg phosphate ceramics with this newberyite-rich phase may be used to stabilize incinerator ash from utility industries, waste-to-energy incinerators, and fluidized-bed incineration of agricultural wastes. For these wastes, a low-cost stabilization method is needed and the methods reported here fill that need. Currently, the work is being extended to the stabilization of low-level radioactive waste, so that the method may be applicable to mixed waste streams. This study also reveals that ash waste participates in the setting reactions and contributes to the overall strength of the ceramics. Therefore, superior structural ceramics may be fabricated from ash waste. A detailed understanding of the exact nature of this strength enhancement in the ash waste form is needed. Such a study may lead to optimization of the strength characteristics and thus to superior structural ceramics.

ACKNOWLEDGMENTS

The authors thank Walter Klemperer and J. Francis Young of the University of Illinois at Urbana-Champaign for performing the NMR studies. Assistance in the leaching tests from J. C. Cunnane and D. Graczyk of Argonne National Laboratory is appreciated. This work is supported by the U.S. Department of Energy, Office of Technology Development, as a part of the Mixed Waste Integrated Program, under Contract W-31-109-Eng-38.

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Table 1. Composition of Ash Surrogate Waste

Bulk Components	wt. %	RCRA Metal Salts	wt. %
Activated carbon	5	$\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	2.6
Vermiculite	20	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.3
Class F fly ash	40	$\text{Pb}(\text{NO}_3)_2$	0.75
Coal bottom ash	33	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	1.3

RCRA Organics	wt. %	Radionuclide Surrogates	wt. %
Naphthalene (C_{10}H_8)	0.47	CsCl	0.3
Dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$)	0.47		

Table 2. Estimated Composition of the Mg Phosphate Ceramic

Component	wt. %
Newberyite	51.3
Lünebergite	26.5
Residual MgO	21.2
Bound Water	11

Table 3. Toxicity Characteristic Leaching Procedure Results from Fully Cured Samples

Sample Specification	Contamination Levels (ppm)			
	Cd	Cr	Ni	Pb
Ash waste unstabilized	40.4	196	186	99.7
Ash waste reacted with H_3PO_4 solution	1.5	0.12	57.5	<0.5
Stabilized waste form with 50% ash waste in starter powder	0.09	<0.05	0.21	<0.2
Stabilized waste form with 60% ash waste in starter powder	0.12	<0.05	1.27	<0.2
Stabilized waste form with 70% ash waste in starter powder	0.06	<0.05	3.71	<0.2
Regulatory limits	1	5	5	5

Fig. 1: X-ray diffraction output of Mg phosphate ceramic:

• newberyite, Δ MgO, $\circ$ lünebergite

Fig. 2. DTA curves of Mg phosphate ceramic

Fig. 3. SEM photomicrograph of fractured surface of the Mg phosphate ceramic.

Fig. 4. X-ray diffraction output of ash waste and its Mg phosphate ceramic waste form. # vermiculite, @ quartz, + mullite, • newberyite, Δ MgO, ° lünebergite

Fig. 5. DTA output of ash waste and newberyite waste form

Fig. 6. Nuclear magnetic resonance spectra of (a) Mg phosphate ceramic, and (b) its waste form with ash waste.

Fig. 7. Compression strength as a function of waste loading

Fig. 8. SEM photomicrographs of waste form: (a) fractured surface, (b) growth of newberyite in voids.

Fig. 9. Weight change in Mg phosphate waste form with 70 wt.% ash waste after 90-day immersion test

Fig. 10. Variation of pH of water during water immersion studies of Mg phosphate with 70 wt.% ash waste loading

Fig. 11. Variation in compression strength of Mg phosphate waste forms with ash wastes after exposure in water

Fig. 12. Photomicrograph from EDX analysis of two locations fractured surface.

Fig. 13. Contaminant distribution in waste form shown in Fig. 11.