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CHEMICALLY BONDED PHOSPHATE CERAMICS FOR LOW-LEVEL MIXED WASTE STABILIZATION*

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Abstract

Novel chemically bonded phosphate ceramics (CBPCs) are being developed and fabricated for low-temperature stabilization and solidification of mixed waste streams which are not amenable to conventional high-temperature stabilization processes due to presence of volatiles such as heavy metal chloride and fluorides and/or pyrophorics in the wastes. Phosphates of Mg, Mg-Na and Zr are being developed as candidate matrix materials . In this paper, we present the fabrication procedures of phosphate waste forms using surrogates compositions of three typical mixed wastes streams - ash, cement sludges, and salts. The performance of the final waste forms such as compression strength, leachability of the contaminants, durability in aqueous environment were conducted. In addition, parameteric studies have been conducted to establish the optimal waste loading in a particular binder system. Based on the results, we present potential applications in the treatment of various mixed waste streams.

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Introduction

Currently, there is approximately 250,000 m^3 of the mixed low-level wastes (MLLW) within the U.S. Department of Energy (DOE) complex [1]. Major components of these waste streams are comprise of 39% aqueous liquids, 17% inorganic sludges and particulates, 25% heterogeneous debris, 3% soils and 5% organic liquids. It is expected that the current volume will increase to 1,200,000 m^3 in the next five years. Due to the diverse nature of the physical and chemical compositions of the waste streams it is accepted that there is no single solidification and stabilization technology that can successfully treat and dispose of all the low-level mixed wastes.

The low-level mixed wastes contain both hazardous chemical and low-level radioactive species. Stabilization of such wastes requires that contaminants of both kinds be immobilized effectively. Often the contaminants are volatile compounds and hence cannot be treated effectively by high-temperature processes [2]. These volatiles are usually in the form of chlorides or fluorides of heavy metals and actinides. Fluorine and chlorine is introduced in the wastes from plastics such as PTFE and polyvinyl chloride. In a conventional vitrification or plasma hearth stabilization processes, such contaminants may be captured as secondary waste streams as scrubber residues or as off-gas particulates that need further low-temperature treatment for stabilization. It may not be viable to continuously recycle these secondary waste streams in the feed stream of the high-temperature process because of the build-up of contaminant levels. These secondary waste streams, thus, will require low-temperature treatment to meet the Land Disposal Restrictions (LDRs). Also, some of these waste streams may contain pyrophorics that will ignite spontaneously during thermal treatment causing hot spots which may require expensive control systems and demanding structural integrity on equipment [3]. Therefore, there is a critical need for a low-temperature treatment and stabilization technology to effectively stabilize these secondary wastes generated by high-temperature treatment processes as well as those wastes which are not amenable to thermal treatment. To this end, a low-temperature treatment and stabilization technology based on chemically bonded phosphate ceramics is being developed and demonstrated.

Fabrication of Chemically Bonded Ceramics

Three different phosphate systems were investigated in this study are namely: Mg, Mg-Na, and Zr phosphates. The choice of using these systems was based on ease of fabrication, low-cost of the process, and attractive properties such as high strength [4], durability in aqueous environments [5], and heavy metal retention characteristics [6]. For fabrication of phosphate ceramics, an acid-base reaction route was followed. The starter powder was an oxide or hydroxide of the appropriate metal which was reacted with a phosphoric acid solution or an acid-phosphate solution. For the Mg phosphates, which sets rapidly, it was necessary to retard the reaction by mixing additives to the starter calcined MgO powder. This was not needed in the case of Mg-Na or Zr phosphates because the setting reaction was slow. For the Mg-Na phosphate system, crystals of soluble dibasic Na phosphate were mixed with calcined MgO to which water was added to initiate the reaction. Zr phosphate was formed by reaction of $Zr(OH)_4$ and 90 wt.% concentrated phosphoric acid. The acid-base reactions in all cases produced a thick paste or slurry that could be packed in a die or poured in a mold. Time required for complete hardening ranged from one week for magnesium phosphate to three weeks for zirconium phosphate.

Surrogate Waste Stream Compositions

To demonstrate solidification and stabilization of the phosphate binders three waste streams were selected: (a) ash waste, (b) contaminated cement sludge, and (c) salts. Compositions of the surrogate waste streams used in our investigations are given in Table 1. Each of the waste streams differs in the bulk composition. The bulk compositions form nearly 91 wt% of the total waste streams. The contaminant levels, however, are the same in all the three waste streams. They contain heavy metals added as soluble nitrates. The proportion of each of the nitrate was such that the individual metal content in the waste was 0.5 wt.%. To spike these metals, the total nitrate content of the contaminants added was approximately 7wt.%, which was a significant proportion of the total waste. The organics were added to see their effect on the stabilization process. We also simulated radioactive cesium isotope by adding cesium chloride. Details of the mixing sequence can be found in Ref. [7].

Fabrication of Waste Forms

Figure 1 shows the flow-sheet for fabricating final waste forms using phosphate ceramics based on acid-base reactions [8]. Both solid and liquid wastes can be treated by this process. Solids such as contaminated ashes and cements may be crushed and mixed with the starter powder and then reacted with the liquid. On the other hand, if the waste is a liquid, one may mix it with the liquid component and then react the solution with the base powder. Thus, treating

TABLE 1: Composition of the Surrogate Waste Streams

Ash waste		Salt waste		Cement sludge	
Components	Wt.%	Component	Wt.%		
		Bulk ingredients			
Activated carbon	4.7	Activated carbon	5	Activated carbon	10
Fly ash	37.5	$Na_2(CO)_3$	58	Fly ash	10
Coal ash	30.9	Cation exchange resin	5	Water	10
Vermiculite	18.7			Concrete	50
		Water	10	Plaster of Paris	10
		NaCl	5	Haematite (Fe_2O_3)	3
		$NaNO_3$	10	Alumina	3
		$Na_2(PO_3)$	5	Perlite	1.5
		$Na_2(SO_4)$	5		
RCRA metal salts (for all three wastes)					
$Cr(NO_3).6H_2O$				2.6	
$Ni(NO_3)_2.6H_2O$				2.3	
$PbNO_3)$				0.75	
$Cd(NO_3)_2.4H_2O$				1.3	
RCRA organics (for all three wastes)					
Naphthalene ($C_{10}H_8$)				0.47	
Dichlorobenzene ($C_6H_4Cl_2$)				0.47	
Radionuclide surrogate(for all three wastes)					
CsCl				0.3	

both solid as well as liquid wastes with acid-base reactions to form phosphate ceramics widens applicability of this technology. In addition, since this process is based on the reaction between an acid and a base it can occur over a wide range of pH.

All the three waste streams were used in powder form. They were ground to an approximate particle size of 8-10 microns. In the case of ash and cement wastes, they were mixed with the starter oxide or hydroxide powders at desired weight percentages in a vibratory shaker mixer. Salt waste, however, was reacted with phosphoric acid first to get rid of CO_2 that was formed during the reaction, and then was mixed with the powder. In all three cases, the resulting powders were added at a slow rate to the respective acid solution and thoroughly mixed using a mixer. Since the chemical reactions are exothermic, the mixture was cooled using water around the container. The slurry was then poured in a mold and was allowed to set. In the case of zirconium phosphate, the slurry was allowed to thicken first and then was pressed into uniform shapes in a mold at low pressures. After complete setting all of them formed into hard ceramics.

It was interesting to note that organics such as dichlorobenzene and naphthalene did not interfere with the stabilization process. This indicates that the organic traces may not affect stabilization of actual waste streams in the chemically bonded phosphate systems, which further confirms suitability of phosphate ceramics for mixed waste treatment.

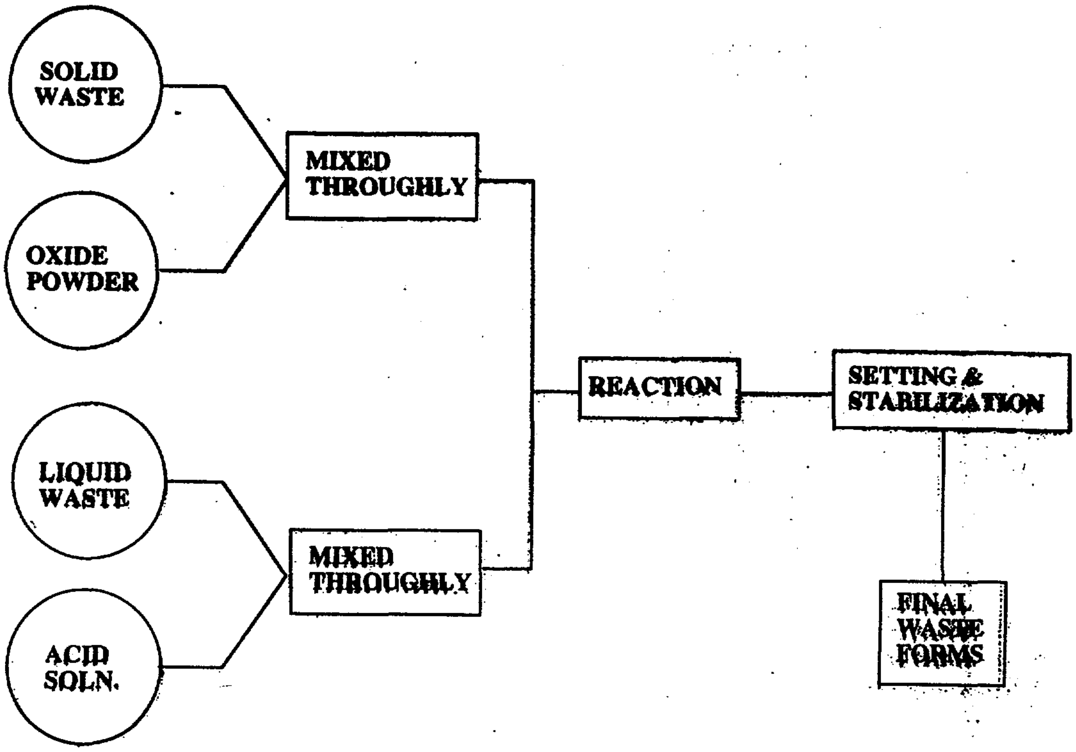

Figure 1. Schematic representation of the fabrication steps for phosphate based final waste forms.

Physical and Mechanical Properties of Waste Forms

The density and porosity of the final waste forms were dependent on the phosphate system and waste loadings. Density values ranged from 1.3 g/cm^3 for Mg-Na phosphate to 1.7 g/cm^3 for Mg-phosphate with 50 wt.% ash waste loadings. The corresponding porosities were 37% and 10%, respectively. For Zr-phosphate with ash waste of 20 wt.% had a density of 1.98 g/cm^3 and porosity of 16%.

Compression strengths on fully cured waste form samples were measured using an Instron machine. Figs. 2 & 3 show the measured strength of Mg and Mg-Na phosphate based waste forms as a function of the waste type and loading. For Mg-phosphate systems the compression strengths showed very interesting results. For ash wastes, the strengths were over 6000 psi at waste loadings as high as 70wt.%. These strength values are higher than that of other room-temperature-setting materials such as portland cement. Whereas, for salt and cement sludge wastes, as expected, the strength decreased with increasing waste loadings. In any case these strengths are significantly higher than the regulatory requirements. Preliminary Nuclear Magnetic Resonance (NMR) studies suggest that the ash waste helps stabilization process in the Mg phosphate system and hence Mg phosphate system is the most suitable for stabilization of ash waste stream.

For Mg-Na phosphate with ash waste loadings the strengths ranged from 1500 psi at a waste loading of 50 wt.% to 1200 psi at 70 wt.%. These strengths were relatively lower than Mg-phosphate due to the higher porority levels in these materials. For Zr-phosphate with 20 wt.% ash waste the strengths were over 7000 psi.

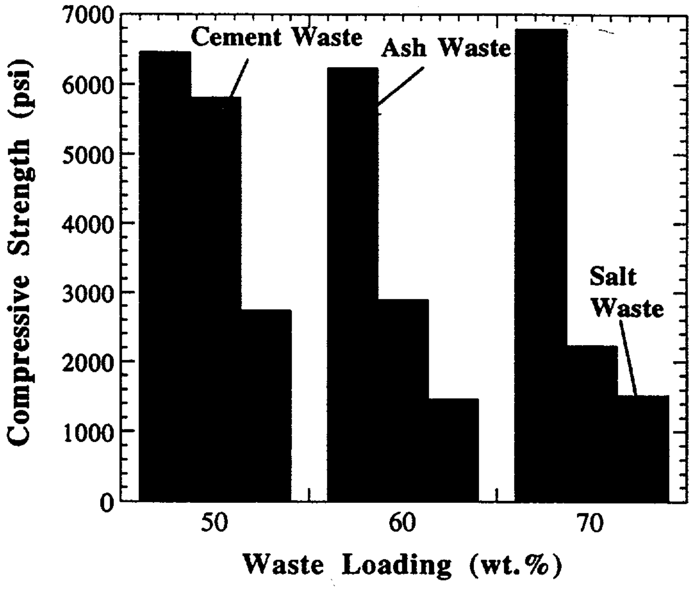

Figure 2. Variation of Compression Strength of Mg-phospahte Waste Forms as a Function of Waste Stream and Waste Loadings

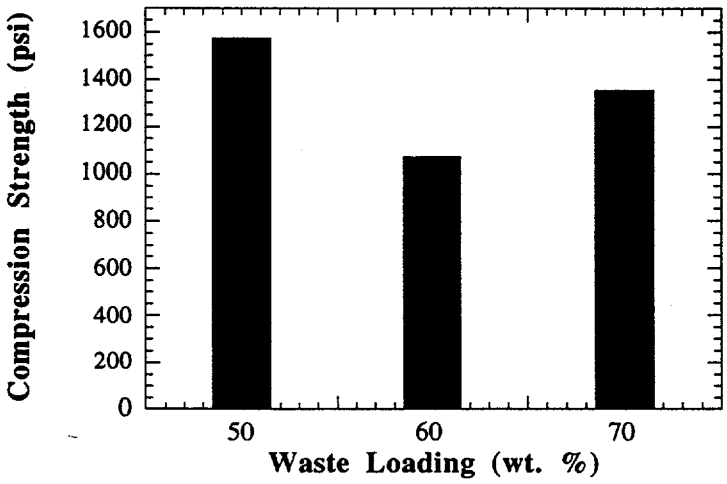

Figure 3. Variation of Compression Strength of Mg-Na phosphate Ash Waste Forms as a Function of Waste Loadings

Microstructural and Phase Characterizations of Waste Forms

Scanning electron microscopy (SEM) was conducted on Mg-phosphate ash waste form to identify and establish the various phases and the fate of the contaminants in the waste form. Microscopy and phase analysis were conducted on other phosphate systems as well, however, results of magnesium phosphate waste forms are only presented here. Figure 4 is a typical micrograph showing the fracture surface of the waste form. The waste form appears to be quite dense which attests the high compressive strength and low porosity measurements on these waste forms. It is believed that there are both crystalline as well as noncrystalline binding phases. Further, both crystalline as well as noncrystalline phases contain both Mg phosphates as well as silicates arising from the ash waste, possibly forming complex phospho-silicate structures. This is has been confirmed using Nuclear Magnetic Resosnace techniques in collaboration of University of Illinois at Urbana-Champaign. Energy Dispersive X-ray (EDX) analysis was performed to identify the crystalline phases in the waste form and is shown in Figure 4. The major phase in magnesium phosphate system is newberyite ($MgHPO_4.3H_2O$), which is an insoluble phase. Analysis of noncrystalline phases is much more complex and requires combination of techniques and is currently the focus of our work.

Mapping of the area shown in Figure 4 was done to determine the fate of the heavy metal contaminants and the results are shown in Figure 5. It is clear that the various contaminants are well distributed and physically microencapsulated by the phosphate matrix. It is belived that this phenomenon along with chemical stabilization leads to excellent performance of the phosphate systems in preventing the leaching out of the contaminants during leaching tests as discussed below.

Leaching Properties of Waste Forms

Leaching studies on the waste forms were conducted by using the standard Toxicity Characteristics Leaching Procedure of EPA [9] and the results are shown in Table 2. We also performed leaching studies on untreated surrogate wastes to compare the leaching data of the stabilized materials with the untreated waste. Regulatory limits on the leaching levels for the contaminant metals as prescribed by EPA are shown in Table 2.

EDX Output On
Mg Phosphate Waste Form
With Ash Waste

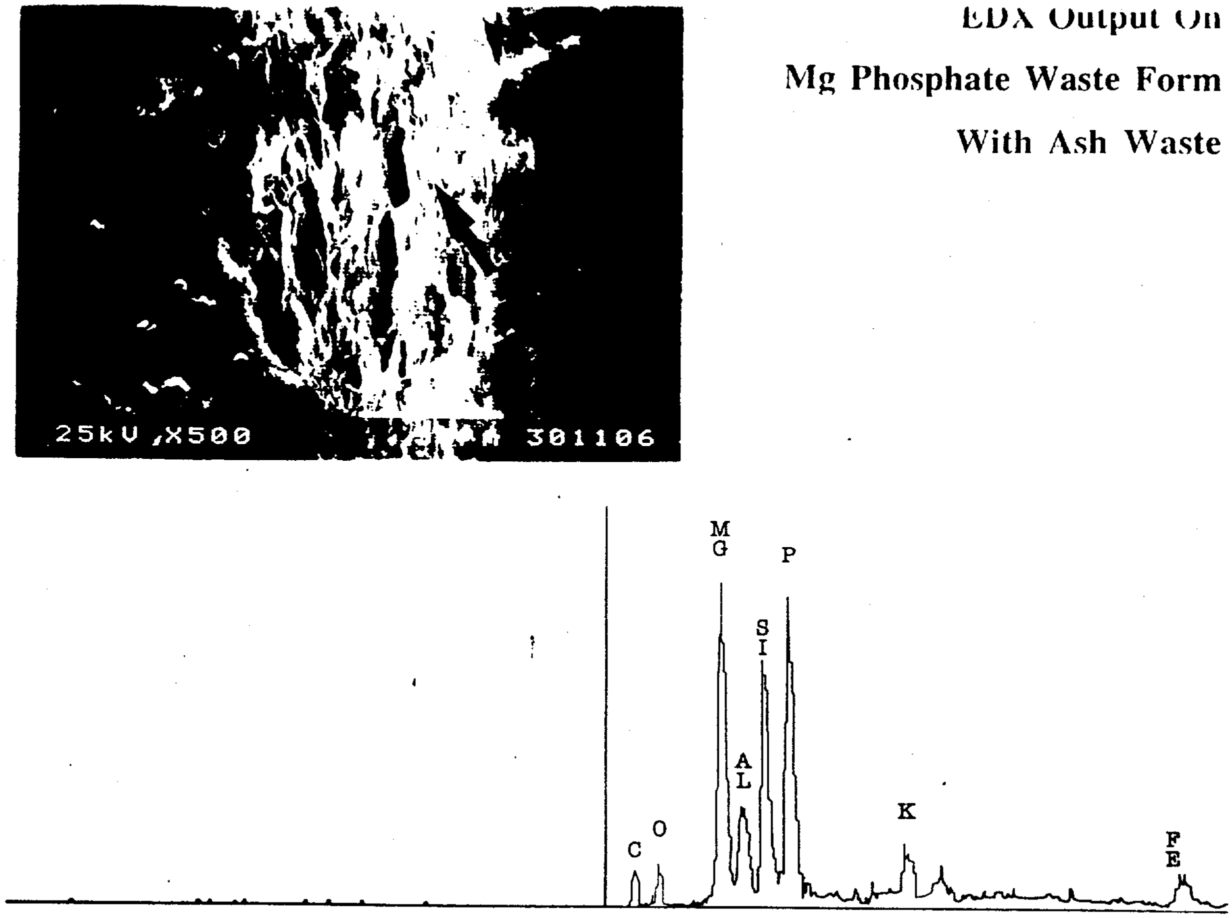

Figure 4. Typical Fracture Surface and Associated Energy Dispersive X-ray Pattern of Magnesium Phosphate Ash Waste Form

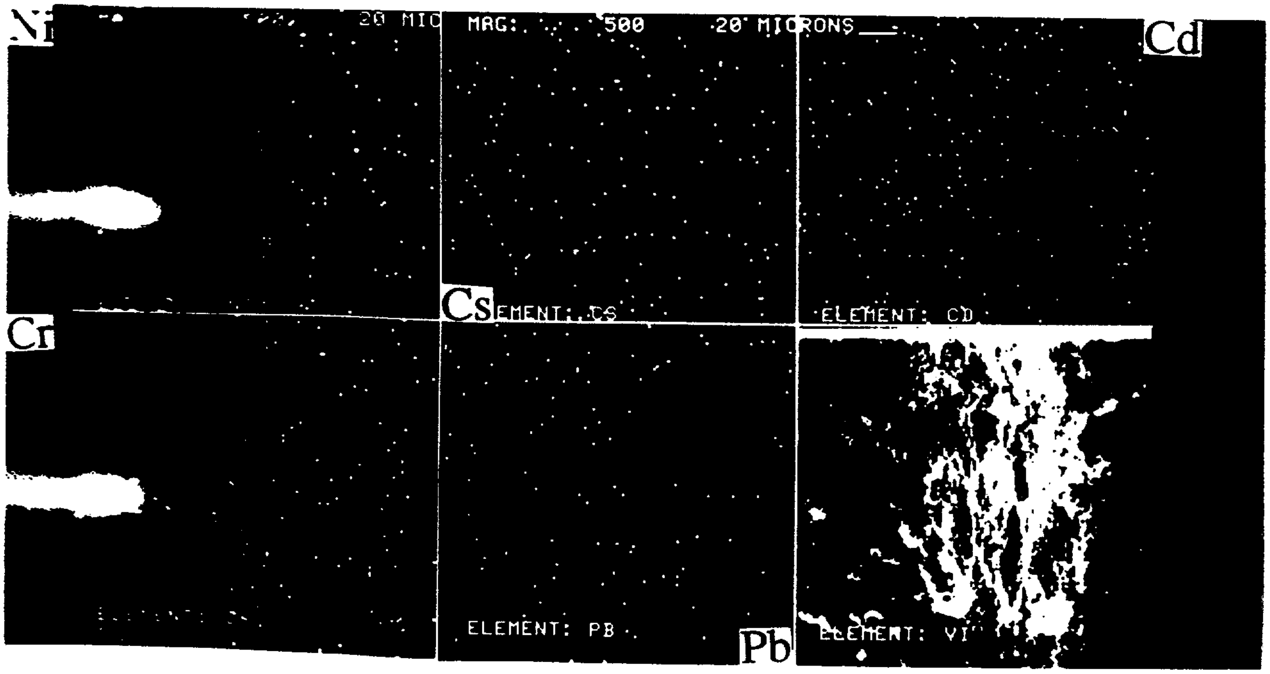

Figure 5. Distribution of Various Contaminants in Magnesium Phosphate Ash Waste Form.

The results show that all the phosphate systems are very effective in stabilizing heavy metal contaminants. A comparison between the leaching levels for the untreated waste and the stabilized samples shows that the leaching levels in the stabilized waste are by an order of magnitude lower than those for the untreated waste. Further they are much below the regulatory limits even at a high loading of 70 wt.% of the waste. The reason for this superior immobilization is the chemical stabilization of the contaminants in the matrix due to reaction between contaminant metal salts and the acid solution followed by the physical encapsulation within the dense phosphate matrix. It is believed that the nitrates of heavy metals are converted to insoluble phosphates by chemical reactions and hence they do not leach out into the leachate during TCLP. Also, physical encapsulation immobilizes the contaminants in the matrix, thus forming an excellent final waste form.

Table 4 : TCLP Results on Phosphate Waste Forms

Sample specification	Contamination levels (ppm)			
	Cd	Cr	Ni	Pb
Ash waste unstabilized	40.4	196	186	99.7
MgP with 50% ash waste	0.09	<0.05	0.21	<0.2
MgP with 60% ash waste	0.12	<0.05	1.27	<0.2
MgP with 70% ash waste	0.06	<0.05	3.71	<0.2
MNP with 50% ash waste	0.03	0.12	0.04	<0.2
MNP with 60% ash waste	0.06	0.11	0.05	<0.2
MNP with 70% ash waste	0.13	0.12	0.08	<0.2
MgP with 50% cement waste	0.03	<0.05	0.13	<0.2
MgP with 60% cement waste	0.04	<0.05	0.26	<0.2
MgP with 70% cement waste	0.06	<0.05	0.74	<0.2
Zr phosphate with 20 wt.% ash waste	<0.02	0.04	0.55	<0.1
Regulatory limits	1	5		5

Water Immersion Studies

To study the durability of the final waste forms in an aqueous environment, immersion studies were initiated. Samples were immersed in distilled water and periodically the water was charged to compensate for evaporation loss. Samples were taken out at regular intervals, dried and weighed to observe any weight loss. The procedure followed was similar to that outlined in ANS 16.1 [10]. In addition, we also monitored the pH of the water solution with time. At the end of 90 days specimens were tested for compression strength. Preliminary results on magnesium phosphate/ash waste forms for weight change, pH, and compression strength at the end of 90 day period are shown in Figures 6-8, respectively. Figure 6 shows the change in weight of a Mg-phosphate specimen with 70 wt.% ash waste loading. The percentage change in weight is computed with respect to the weight of the waste form at the begining of the immersion study. The results indicate some weight loss in the early stages of the measurements. Thereafter, the weight of the waste form is more or less constant. The initial weight loss is believed to be due the free phosphoric acid in the waste form which is released in the water. This is confirmed with pH measurements for the same waste form as shown in Figure 7. There is a striking similarity between the results shown in Figures 6 and 7. The initial large drop in pH suggests that there is loss of excess phosphoric acid from the waste form. Once this excess acid is released, the pH and the waste form weight is stabilized.

Figure 8 shows the variation in the compression strength of the magnesium phosphate waste forms as a function of the waste loadings. Also, for comparison purposes, the strength of the Mg-phosphate waste forms which were not exposed to water are presented. It is clear that there is no significant degradation in the strength of the magnesium-phosphate waste form with loadings of 50 and 60 wt.% ash wastes. However, for 70 wt.% loading there is a more noticeable drop in strength to a value of ≈4000 psi from an initial value of ≈7000 psi for unexposed waste forms. In any case, the resultant strength of the waste forms are exceptionally good and satisfy the regulatory requirements after 90 day exposure to aqueous environment with waste loadings of as high as 70 wt.%. The results given here on weight change and compression strength clearly indicate that chemically bonded phosphates have the potential to form durable waste forms.

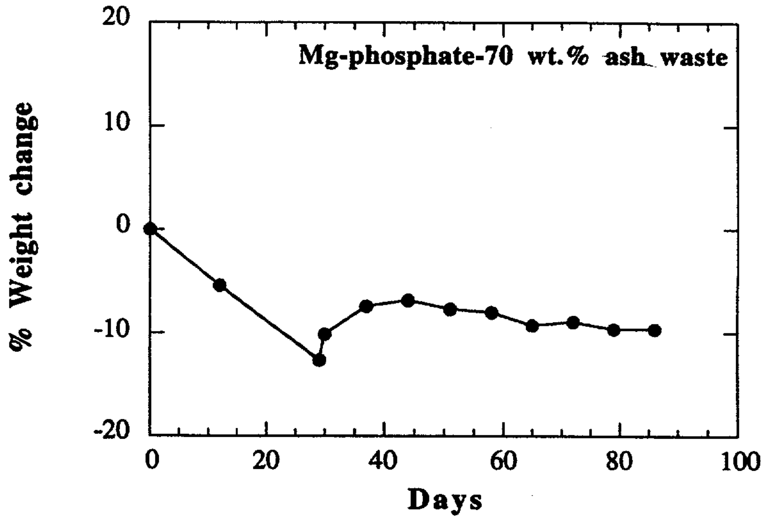

Figure 6. Weight Change of the Mg-phosphate-70 wt.% Ash Waste Loaded Waste Form During Water Immersion Studies.

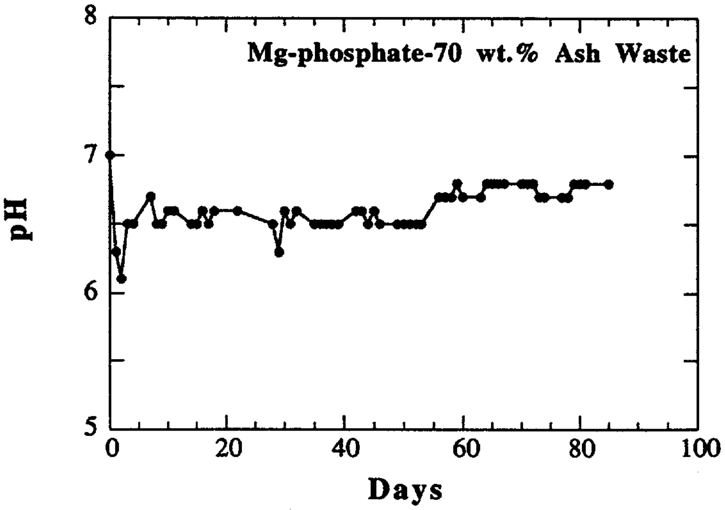

Figure 7. Variation of pH of the Water During the Water Immersion Studies of Mg-phosphate with 70 wt.% ash waste loading.

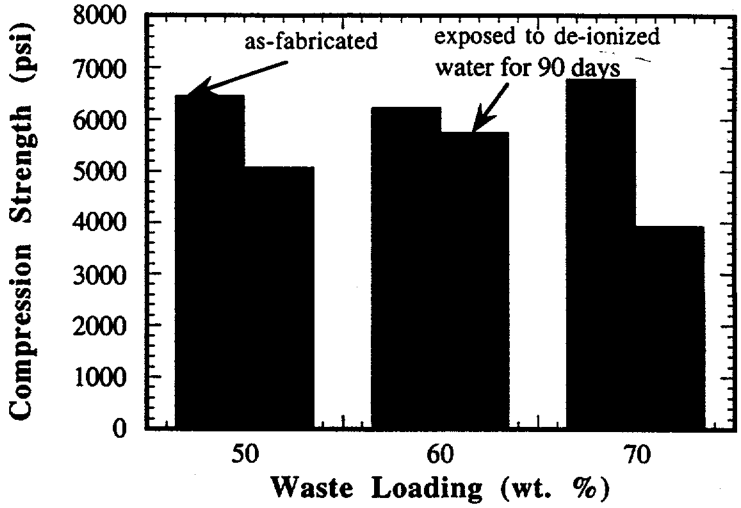

Figure 8. Variation in Compression Strength of Mg-phophate Waste Forms with Ash Wastes after Exposure in Water.

Summary

The overall efforts of these studies are to develop phosphate systems to immobilize problem mixed wastes. This first phase of investigation reveals the suitability of phosphate systems to stabilize contaminants by both chemical as well as physical means in a one step process. This should be a very effective and economical way to stabilize chemical waste. Since this process needs no thermal treatment, stabilization may be done on site economically without capital intensive equipment and high transportation costs. Preliminary calculations on volume reduction suggest that the ash waste may be consolidated by this process to 80 vol.% of its original volume. Such a volume reduction may reduce disposal costs.

We have highlighted results on contaminated ashes. We observe similar results on contaminated cement sludges and salts. The results on chemical stabilization may be very general, since in these acid-base systems, the acid phosphates seem to react with the contaminants irrespective of the bulk composition of the waste stream. This implies that chemically bonded phosphate ceramics may have wide applications in stabilization of different types of waste streams. Considering the fact that both solid, liquid as well as sludge waste streams may be incorporated in these systems, their applications may widen. Our investigations demonstrate only the potential of these materials. A wider scope of applicability may be revealed in the future with further research and development.

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