

ANL/ET/CP--81294
CONG-940416--4

PHOSPHATE BONDED CERAMICS AS CANDIDATE FINAL-WASTE-FORM
MATERIALS*

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April 1994

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Paper submitted for the Proceedings of 96th Annual Meeting of the American Ceramic Society, Indianapolis, IN, April 24-28, 1994.

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

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ABSTRACT

Room-temperature setting phosphate-bonded ceramics were studied as candidate materials for stabilization of DOE low-level problem mixed wastes which cannot be treated by other established stabilization techniques. Phosphates of Mg, Mg-Na, Al and Zr were studied to stabilize ash surrogate waste containing RCRA metals as nitrates and RCRA organics. We show that for a typical loading of 35 wt.% of the ash waste, the phosphate ceramics pass the TCLP test. The waste forms have high compression strength exceeding ASTM recommendations for final waste forms. Detailed X-ray diffraction studies and differential thermal analyses of the waste forms show evidence of chemical reaction of the waste with phosphoric acid and the host matrix. The SEM studies show evidence of physical bonding. The excellent performance in the leaching tests is attributed to a chemical solidification and physical as well as chemical bonding of ash wastes in these phosphate ceramics.

INTRODUCTION

In the 95th meeting of the American Ceramic Society, we proposed chemically bonded phosphate ceramics for stabilizing low-level wastes [1].

This concept was generalized to develop phosphate systems for low-temperature treatment and stabilization of DOE "problem" low-level mixed waste streams as identified by the Mixed-Waste Integrated Program. These problem mixed wastes contain either volatiles or pyrophorics and hence cannot be treated by the well established vitrification technology.

We identified several phosphate systems which may be used for stabilization of mixed wastes containing RCRA metals and organics. The systems selected were phosphates of Mg, Mg-Na, Al and Zr. Here we present detailed progress made on these phosphates. For initial studies surrogate formulation of DOE ash waste, as provided by Mixed Waste Treatment Project (MWTP), was used. X-ray diffraction studies and differential thermal analyses were used to develop an insight into the chemical solidification and stabilization. Assessment criteria used in the study were compression strength, porosity, and Toxic Chemicals Leaching procedure (TCLP). Scanning electron microscopy was used for deeper insight into the physical encapsulation.

FABRICATION OF THE MATRIX MATERIAL AND THE WASTE FORMS

For fabrication of the phosphate ceramics, an acid-base reaction route was followed. The starter powder was a hydroxide of the appropriate metal. It was reacted with phosphoric acid solution in the case of Mg, Al and Zr phosphates and soluble dibasic Na phosphate solution for the Mg-Na phosphate system. Dilution level of the acids depended on the water of hydration needed for reactions, which was determined by trial and error at this stage. In the case of Mg phosphates, which set rapidly, it was necessary to retard the reaction by adding 15 wt.% of boric acid to the starter powder.

This was not needed in the case of Mg-Na polyphosphates as the setting reaction was slow. Al phosphate powder was precipitated from the reaction solution of $\text{Al}(\text{OH})_3$ and concentrated phosphoric acid at $^{\circ}60 \text{ }^{\circ}\text{C}$. Zr phosphate was formed by reaction of $\text{Zr}(\text{OH})_4$ and 90 wt.% concentrated phosphoric acid. The acid-base reactions in all the cases gave a thick paste, which could be packed in syringes and shaped into hard monolithic cylinders of radius 0.5 cm. The paste sets in a week, but hardens fully in 3 weeks.

We used 25-35 wt.% of the ash waste in the various phosphate ceramics described above. The surrogate waste was formulated as described in Ref. [2]. It was well powdered before mixing with the oxide powders. The waste was mixed with the powders and then the mixture was reacted with the solutions. Final ceramic waste forms were formed by the method as described above. The samples for compression strength measurements were prepared by pressing the reacted paste at $^{\circ}10,000$ psi to reduce the residual porosity in the final waste form.

CHEMICAL CHARACTERIZATION STUDIES ON THE WASTE FORMS

The surrogate waste used in these experiments was a mixture of fly ash (Class F), coal cinder ash and vermiculite as the major components, and activated carbon as a minor component. The fly ash content was 40 wt.%, coal cinder ash 33 wt.%, and vermiculite was 20 wt.%. Thus these three formed 93 wt.% of the total surrogate composition. Trace contaminants used were RCRA metal nitrates and RCRA organics. The concentrations of the metal nitrates were such that the metal concentration in the surrogate

waste was 0.5 wt.% of each the metal. Each of the organics was also 0.5 wt.% of the final waste form.

Based on the data provided by the suppliers of these components, the amorphous silica content in the surrogate waste was found to be *20-33 wt.%. Thus a high percentage of the surrogate waste contained amorphous silica. As is well known in cement chemistry, this amorphous silica is responsible for formation of cementitious bonds with pozzalanic reactions. Thus, due to its reactivity, it is expected that this component will participate in setting reactions to develop hard ceramic final waste forms. Therefore phosphate formations and reaction of amorphous silica will govern the kinetics during setting of the final waste forms.

X-ray diffraction studies

Fig. I is an X-ray diffraction output of the surrogate waste, and the reaction product of the waste and phosphoric acid. The results on the waste show a mixture of highly crystalline and amorphous phases. The crystalline phases are listed in Table I. The large hump at low angles (10° to 20°) is due to the amorphous silica content. Silica is present in the surrogate waste as an amorphous component and as crystalline alumino-silicates.

When the waste reacts with phosphoric acid, the amorphous hump vanishes, indicating that the amorphous material has reacted with the phosphoric acid. The reaction product may be pressed into fairly hard ceramic, but in the absence of an appropriate phosphate binder, it is not stable in an aqueous medium. Therefore, phosphates are needed as binders. Thus the stabilization in the final waste form is both physical due to phosphate binder-matrix, and chemical due to this reaction.

TABLE I. Notations of minerals and their host materials

Mineral	Symbol	Formula	Host matrix
Mullite	@	$3\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$,	Ash waste
Boehmite	\$	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	„
Gibbsite	◆	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	„
Tridymite	&	SiO_2	„
Mg-hydrophosphate	*	$\text{MgPO}_4(\text{OH})$	
Newberyite	Σ	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Mg phosphate
Anhydrous Mg phosphate	®	$\text{MgPO}_4(\text{OH})$	„
Brucite	+	$\text{Mg}(\text{OH})_2$	Mg and Mg-Na phosphate
Mg-Na phosphate	○	$\text{Na}_{14}\text{Mg}_9(\text{P}_2\text{O}_7)_8$	Mg-Na phosphate
Cristobalite, Tridymite	X	AlPO_4	Al phosphate
Berlinite	Δ	AlPO_4	„
Zr phosphate	#	$\text{Zr}_3(\text{PO}_4)_4$	Zr phosphate

Figure 2 contains the X-ray diffraction patterns of the host materials and the corresponding waste forms after a loading of 25-35 wt.% of the surrogate waste. Several observations may be made from these X-ray diffraction patterns.

The matrix materials contain highly crystalline structures. The crystalline phases identified from these outputs are listed in Table 1. As one may see from Fig. 2, magnesium phosphate contains newberyite as the major reacted phase along with anhydrous Mg phosphate and a hydrophosphate ($\text{MgPO}_4 \cdot \text{OH}$). Considerable $\text{Mg}(\text{OH})_2$ remains unreacted in the matrix.

The situation is similar in Mg-Na phosphate. The main phase is $\text{Mg}(\text{OH})_2$, while Mg-Na-phosphate is formed due to reaction of $\text{Mg}(\text{OH})_2$ and sodium phosphate solution. It is likely that the reaction products are formed due to surface reaction of the $\text{Mg}(\text{OH})_2$ grains with phosphoric acid or phosphate solutions. Long time curing of the samples may increase the content of the reaction products and reduce the residual $\text{Mg}(\text{OH})_2$ content.

Figure 2 shows strong peaks of Zr phosphate, and no peaks of $\text{Zr}(\text{OH})_2$ are visible. It is also interesting to note that, though the setting reactions in these phosphates are hydration reactions, no hydrated phases are found in the X-ray diffraction outputs. This may be because the hydration products are non-crystalline. The samples in all the cases were found to be hard and stable. Even a small cementitious phase can bind the particles together like a small amount of portland cement binding gravel to form cement concrete.

Studies with differential thermal analyses

X-ray diffraction studies (DTA) can only detect crystalline phases. Differential thermal analyses can shed light on non-crystalline phases also. For this reason, DTA studies were done on the matrix materials and on the corresponding waste forms to identify noncrystalline phases. In addition, we have also provided the results on the DTA of the surrogate waste. The results are shown in Fig. 3.

In the DTA output of the surrogate waste, except for the detection of free water release below 100 °C, no strong endotherm is observed, implying no transformation of major phases occurred. The nitrates in the waste will decompose at high temperatures, but this will not be seen in the DTA due to small amount of these salts in the waste.

The endotherm at ≈ 180 °C in the Mg phosphate as well as in its waste form is due to the occurrence of insoluble newberyite [2,3]. The endotherm at 425 °C in the matrix is due to decomposition of Mg(OH)_2 to form free MgO. This endotherm is not seen in the waste form. This implies that Mg(OH)_2 reacts better in the waste form than in the base material. This was noticeable in the X-ray diffraction output also. Thus both X-ray diffraction studies and DTA confirm a better chemical reaction in the waste form than in the base material.

The Mg-Na-phosphate matrix material has only one endotherm, i.e., that of Mg(OH)_2 . It appears that the only phosphate phase $\text{Na}_{14}\text{Mg}_9(\text{P}_2\text{O}_7)_8$, which is an anhydrous phase detected by X-ray diffraction, is a stable phase and is unaffected by the heating. The endotherm for Mg(OH)_2 both in the matrix material as well as in the waste form (slightly shifted, possibly due to the effect of the environment) indicates that there exists considerable amount of unreacted Mg(OH)_2 in both the matrix and in the waste form.

Finally, in the curve for ZrPO_4 or in the waste form no endotherm or exotherm are present indicating no new unstable phases are formed in the waste form.

III. PERFORMANCE ASSESSMENT TEST RESULTS

Tests were done on the waste forms containing RCRA metal wastes as nitrates. Table 2 provides details of the waste forms tested and the results of the study. We have also given the results of the leaching tests done on the waste itself and the allowable regulatory limits on the leachability. The results show that all the three phosphate systems show good promise in

retaining RCRA metals. Further studies are in progress on samples cured for longer durations.

Compression strength measurements were done on the specimens using an Instron machine in a uniaxial mode. The open porosity was measured by water displacement method. Table 3 contains the average compression strength measured on three samples and the porosity.

The data shows that all three phosphate systems have good strength. The ASTM requirements for the waste forms is 500 psi, and the phosphate waste forms have a strength an order of magnitude higher than this value. The strength of Zr phosphate waste form has been the best and its porosity has been the lowest. Comparatively lower strength of Mg and Mg-Na phosphates may be due to higher porosity.

Table 2. Results of TCLP studies on phosphate waste forms

Matrix	Waste form composition	Concentration in leachate (mg/litre)			
		Cd	Cr	Ni	Pb
Surrogate waste		196	40.4	186	99.7
Mg phosphate	RCRA metal nitrates, Total waste 35 wt. %	1.64	.05	9.63	<0.1
Mg-Na phosphate	Same	0.03	0.05	0.05	<0.1
Al phosphate	Same	0.04	0.91	1.9	<0.1
Zr phosphate	Same	0.07	0.16	11.0	<0.1
Zr phosphate	RCRA metal nitrates, Total waste 20 wt. %	0.02	0.06	0.45	<0.1
Regulatory level		1	5	1*	5

* Since Ni is not a RCRA metal, no regulatory level was available, instead, we used the stringest drinking water level for comparison.

Table III: Compression strength and porosity of the phosphate waste forms

Waste form, loading (wt.%)	Compression strength (psi)	Porosity (Vol.%)
Mg phosphate, 35	2923	26
Mg-Na phosphate, 35	2561	40
Zr phosphate, 20	7572	^a 16
Zr phosphate, 35	4675	^a 16

IV. SCANNING ELECTRON MICROSCOPIC OBSERVATIONS

During the period of this report, preliminary studies on microstructure of the phosphate ceramic waste forms were done. Figure 4 consists of typical microstructures of Mg-Na, and Zr.

The overall microstructure of these waste forms appears to be derived from the ash. Spherical silica from the ashes are well distributed. One may also notice platelets which are likely to be vermiculite. These components of the waste are surrounded by the continuous amorphous phosphate cement phases, which indicates good physical encapsulation. This encapsulation is crucial for the bonding of the waste with the matrix material.

Some interesting microstructure is also noticeable in Zr phosphate waste form. A network structure is formed on the grains. Such a network exhibits the inorganic polymer structure of these phosphates. Currently efforts are in progress to characterize such microstructure using energy dispersion X-ray analyses and back scattering method.

VI. CONCLUSIONS

Several conclusions may be drawn from this study on chemical stabilization of ash waste using phosphate systems.

1. Phosphates and phosphate based ash waste forms set at room temperature into hard ceramics. The setting rates are controllable. The raw materials and processing methods are low-cost and hence phosphates may form a good alternative for stabilization of low-level mixed waste.
2. Phosphates of Mg, Mg-Na, Al and Zr provide insoluble, fairly dense and mechanically strong matrix to stabilize waste.
3. The ash waste chemically reacts with acid solutions during fabrication of the waste form, resulting in chemical solidification by forming insoluble phosphates.
4. Leaching tests on samples cured for one week show a good stabilization of heavy metals in these phosphate systems.

It is also necessary to reduce the porosity of these waste forms, optimize their composition and microstructure, and achieve optimum loadings. Current efforts are directed along these lines

REFERENCES

1. Wagh Arun S., Dileep Singh, Waseem Subhan, and Nikhilesh Chawla, Proc. 95th Annual Meeting of the Amer. Ceram. Soc., Cincinnati, OH, April 18-22, 1993.
2. Bostick W. D., D. P. Hoffman, J. M. Chiang, W. h. Hermes, L. V. Gibson, Jr., A. Richmond and J. Mayberry, Surrogate formulations for thermal treatment of low-level mixed waste: Part II: Selected mixed waste treatment project waste streams, DOE/MWIP-16.
3. Wilson A. D., and H. W. Nicholson, Acid-base cements, Cambridge Univ. Press (1993) p. 222.

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ID: WASTE+PHOSPHERIC ACID

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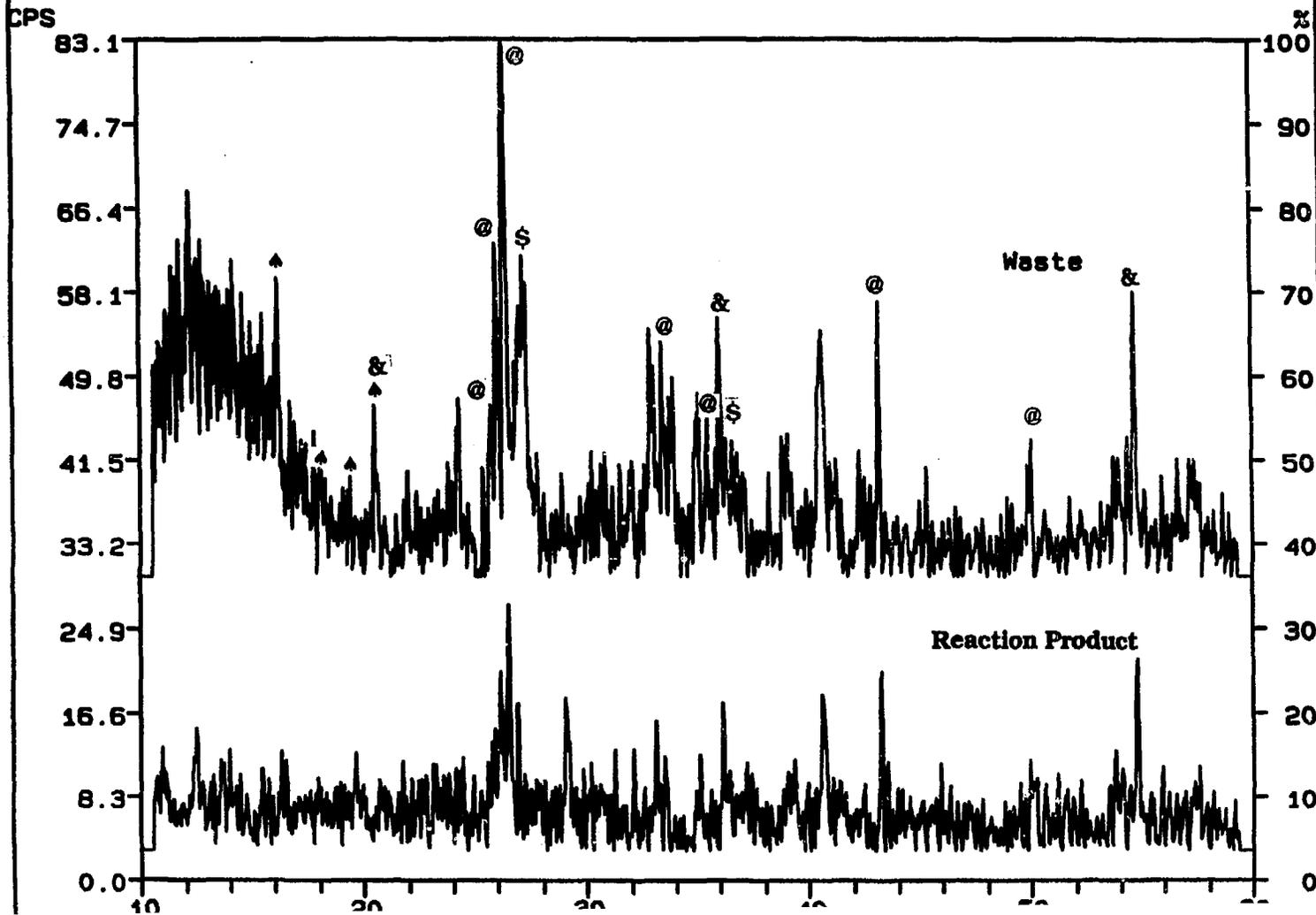
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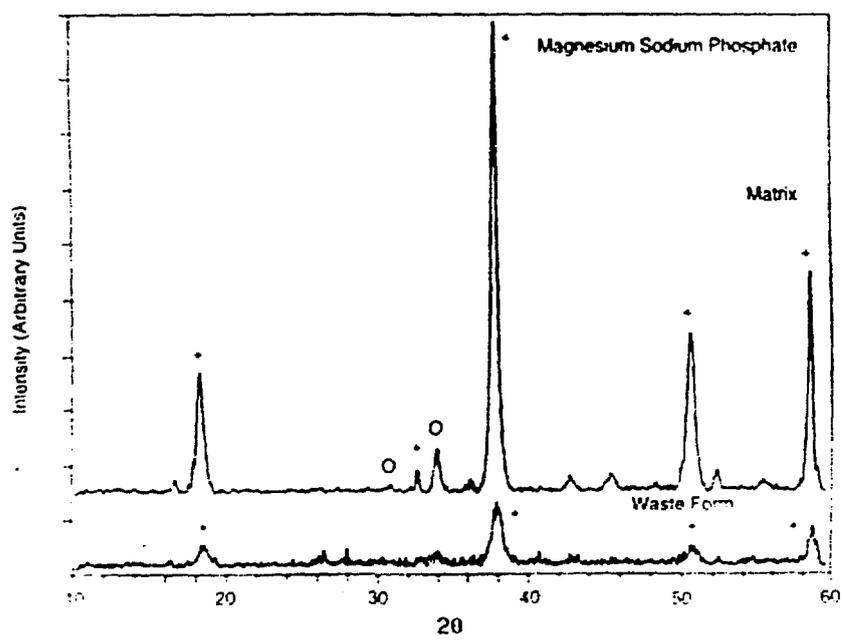
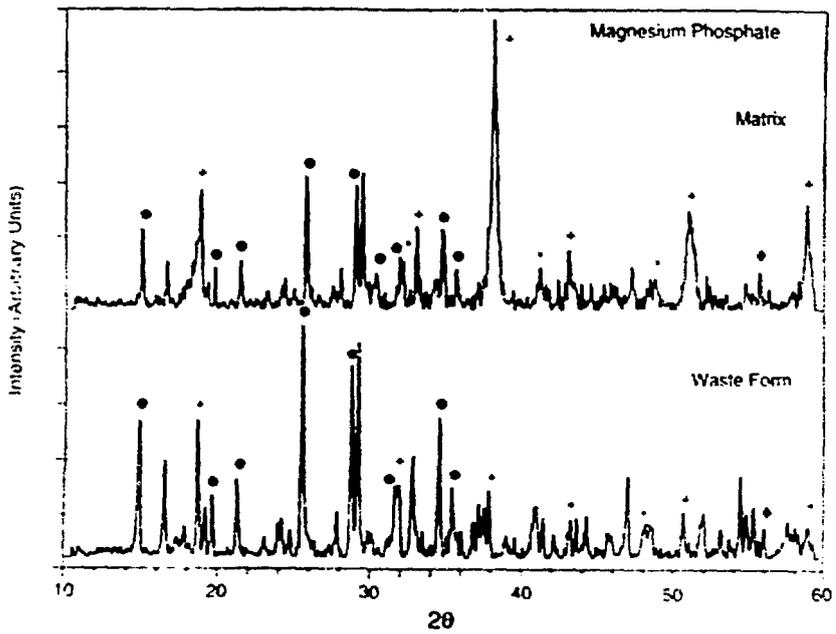


Fig. 2

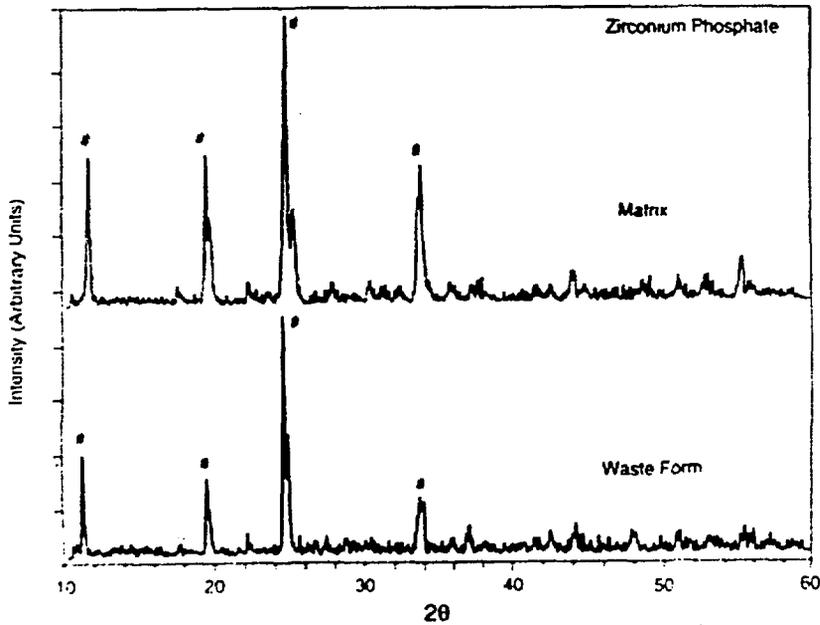
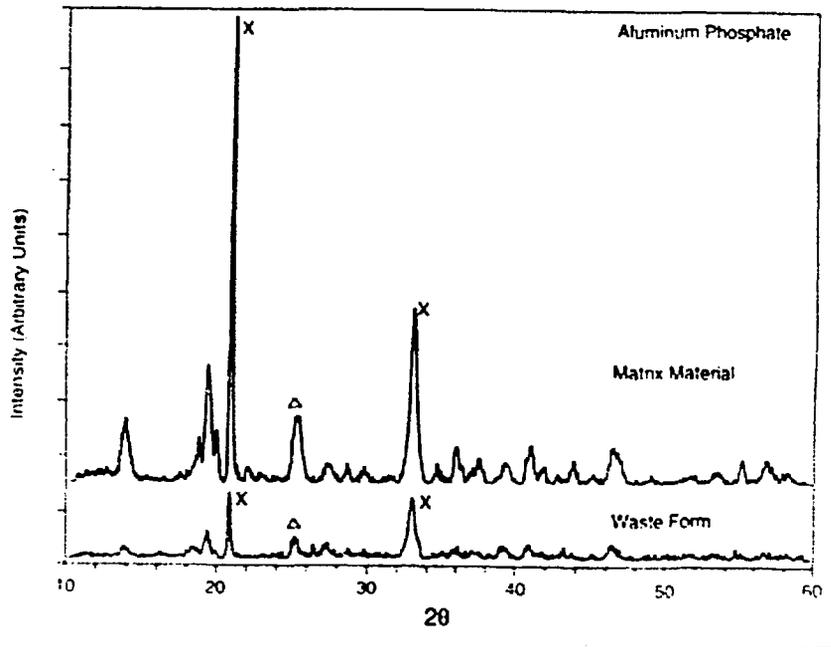


Fig. 2 (contd)

Differential Thermal Analysis

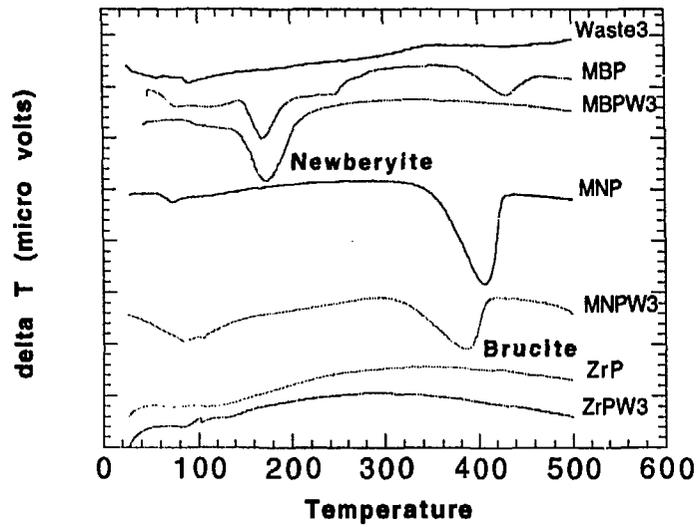
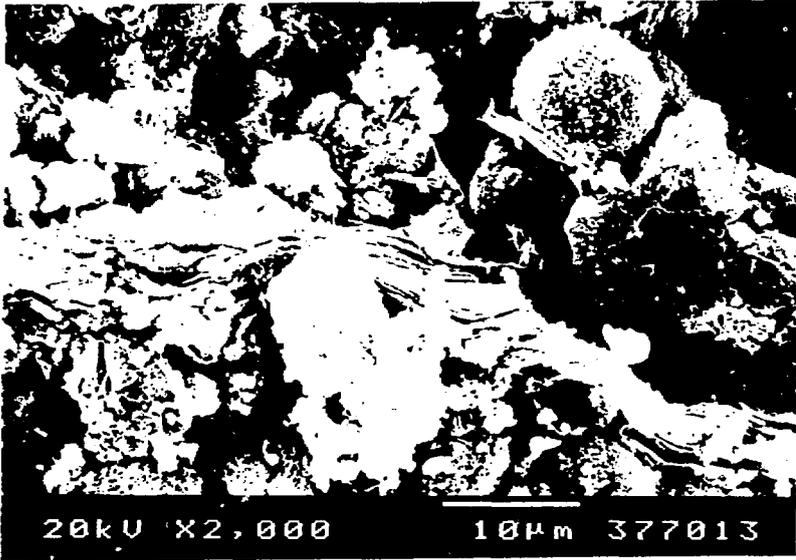
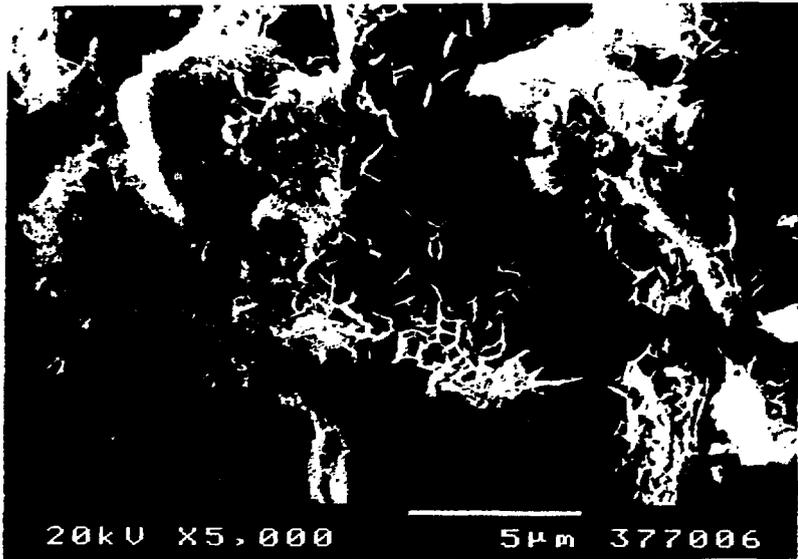


Fig. 3



(a)



(b)

Fig. 4