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Low Temperature Setting Iron Phosphate Ceramics as a Stabilization and Solidification Agent for Incinerator Ash Contaminated with Transuranic and RCRA Metals

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LOW TEMPERATURE SETTING IRON PHOSPHATE CERAMICS AS A STABILIZATION AND SOLIDIFICATION AGENT FOR INCINERATOR ASH CONTAMINATED WITH TRANSURANIC AND RCRA METALS.

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ABSTRACT

Incineration of combustible Mixed Transuranic Waste yields an ash residue that contains oxides of Resource Conservation and Recovery Act (RCRA) and transuranic metals. In order to dispose of this ash safely, it has to be solidified and stabilized to satisfy appropriate requirements for repository disposal.
This paper describes a new method for solidification of incinerator ash, using room temperature setting iron phosphate ceramics, and includes fabrication procedures for these waste forms as well as results of the MCC-1 static leach test, XRD analysis, scanning electron microscopy studies and density measurements of the solidified waste form produced.

INTRODUCTION

The goal of this work is investigation and development of a new method for solidification of incinerator ash, containing oxides of RCRA and transuranic metals using low temperature setting iron phosphate ceramics. More specifically, this work seeks to elucidate the means in which the reaction rate of the setting process can be controlled, easily and economically, while still yielding a waste form with acceptable characteristics and performance. Iron phosphate ceramics represent a large group of acid-base cements, and their properties, as well as, some practical applications are well described in the literature (1-5). Iron phosphate ceramics are themselves a sub-

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group of the a larger body of ceramics that include other types, such as magnesia based ceramics, that have been investigated for immobilzation of transuranic wastes (6).

Solidification of the ash waste using this process results not only in micro- and macro- encapsulation of contaminants, but also in chemical binding of TRU and RCRA metals in the form of phosphates. Phosphates are known as host minerals for some actinides and heavy metals (7,8). This process has several distinct advantages over other methods: 1) it is very simple mechanically requiring minimal equipment, 2) the process does not produce secondary waste streams such as free standing liquids or off-gases, 3) the process proceeds at room temperature which eliminates the need for off-gas treatment and 4) the treatment is cost-effective from a processing standpoint.

EXPERIMENTAL

Waste stream

Solidification experiments were conducted using simulated incinerator ash. It was prepared and supplied by Dr. Wagh of Argonne National Laboratory East, Energy Technology Division, Ceramic Section. Composition of the waste stream is given in Table 1.

Table 1. Composition of Simulated Ash Waste.

Components	Concentration (g/kg)
Class F fly ash	387.96
Coal bottom ash	320.07
Vermiculite	193.98
Activated carbon	48.49
Cr_2O_3	14.18
NiO	6.16
PbO	5.22
CdO	5.54
CsCl	6.15
Ce_2O_3	5.70
$HgCl_2$	6.56

As is indicated in Table 1, oxides and chlorides of various metals were added to the ash to simulate actual waste ash. Cr_2O_3, PbO, $HgCl_2$ and CdO represented compounds of RCRA metals. Ce_2O_3 was used to simulate plutonium oxide. Natural CsCl was used to simulate fission product cesium.

Solidification Experiments

Solidification experiments were conducted in 50 ml plastic beakers according to the flow sheet shown on Figure 1.

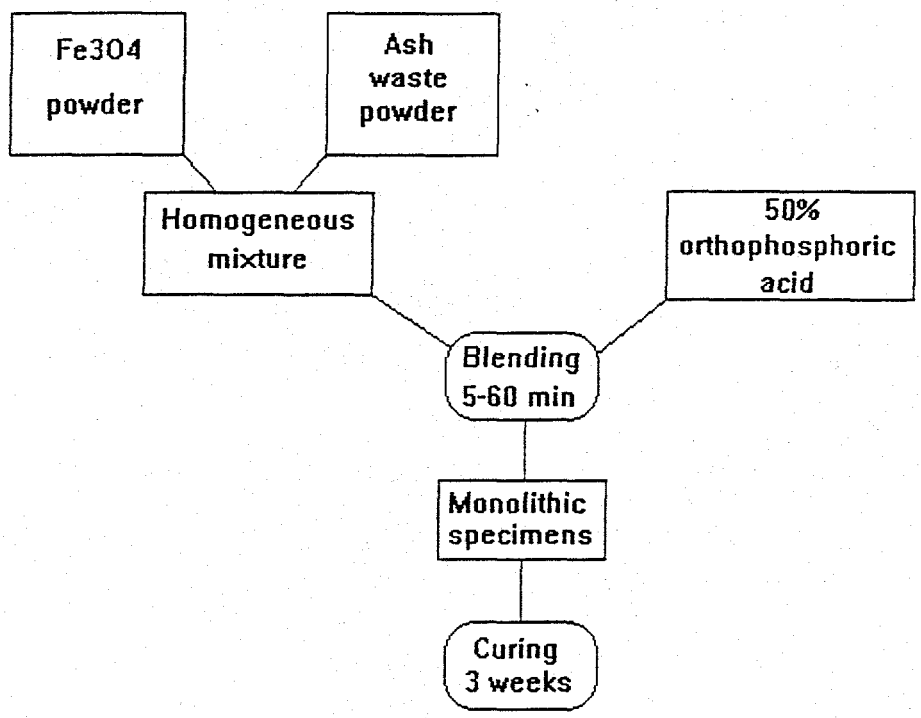

Figure 1. Flow chart for the process of ash waste solidification

The ratios of the constituents and the acid concentration were determined by an iterative method based on the composition diagram shown in Fig. 2. The key parameter used to narrow the area of interest in Fig. 2. was a visible inspection of the structural integrity of the waste form produced. A large number of cracks or a "crumbly" waste form was regarded as a non-attractive composition. The shaded area on the composition diagram (Fig. 2) corresponds to the waste form compositions for which solidification occurs. Investigations presented in this paper were focused on the compositions with a waste loading of 30 and 40%. The waste loadings sited in this paper are calculated so that the weight percent given, i.e., 30 or 40 wt%, is the fraction of the total mass, including waste, binder and phosphoric acid. multiplied by 100%.

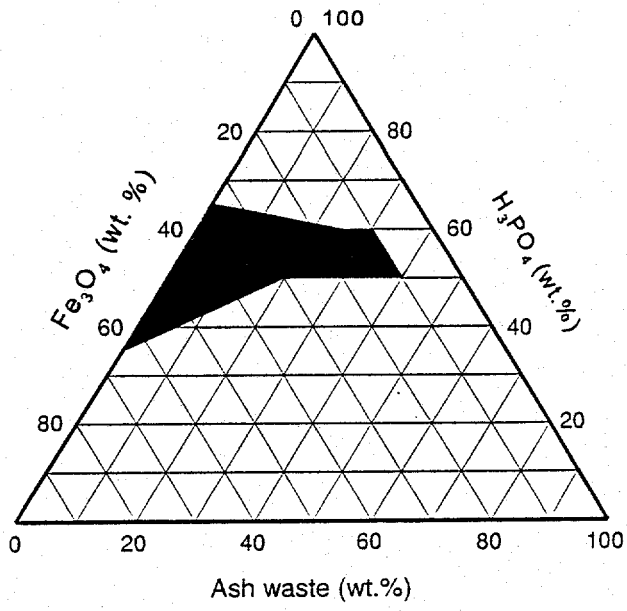

Figure 2. Composition Diagram for the Solidification Process.

Leach Tests

The leaching properties of the fabricated waste forms were investigated by conducting the MCC-1 static leach test (ASTM C1220-92). The procedure described in the MCC-1 method was modified in regard to the sample preparation steps. The monolith utilized was obtained via core drilling and the surface finish was 600 grit. The (surface area/volume) ratio was 10 m^{-1}. The leach tests were run for 7 days at 90 °C.

The normalized release rate (NRR) was evaluated using the equation:

$$NRR(i) = C_i V / f_i A d \qquad (1)$$

where C_i is the concentration of the element i in the leachate in g/ml, V is the volume of leachate in ml, f_i is the fraction of the element i in the solid initially, A is the macroscopic area of the solid in m^2, and d is the duration of the test in days. The surface area was calculated from the linear dimensions of the cylindrical samples. The monolithic specimens, obtained as a result of solidification, were cured for 21 days at room temperature, before they were submitted for the leach test.

Instruments Used for Analysis

1. Density measurements

Density of the samples was measured using Ultrapycnometer-1000 (UPY-2, Quantachrome Inc, Boyton Beach, FL).

2. Microscopy studies and EDS analysis

An ISI SS440 scanning electron microscope supplied by Topcon Technologies (Paramus, New Jersey) with a Kevex 7070 EDS system (Kevex Fisons Instruments, San Carlos, CA) was used for microscopy studies and EDS analysis.

3. Analysis of leachates

Leachates were analyzed using an ICP system that included a plasma unit consisting of a 40 MHZ, 1600 W generator and a torch box (ICP 16L, RFPP, New Jersey, USA). The torch box was fitted with a demountable Fassel type torch. A 1.5 path length monochromator, fitted with a 2400 lines per mm holographic grating (THR 1500, ISA Inc. Metuchen, NJ, USA) was used to detect analyte emissions from ICP. The monochromator stepper motor was controlled via a Spectrolink control unit, (ISA Inc., Metuchen, NJ, USA).

4. X-ray diffraction analysis were performed in order to identify the crystalline phase that is present in the ceramics. A Scintag X1 Powder X-ray Diffractometer (Scintag, Inc., CA) with a Theta-Theta type goniometer, Cu K-alpha x-ray tube with normal focus, and top loading powder sample holder was used for this purpose.

RESULTS AND DISCUSSION

The methodology pursued for this study revolved around first investigating the appropriate binder compositions to provide the desired setting kinetics, not too slow or too fast. Once the approximate composition was determined the waste loading was optimized and the final fine tuning of the components was attempted. The waste forms produced were characterized by means of SEM, XRD, density and setting times. The durability of the waste forms produced was assessed by the MCC-1 test.

A) Estimation of Reaction Rates and Setting Times

The quick setting behavior of the Fe_3O_4-H_3PO_4 system is caused by the rapid formation of normal and acidic iron phosphates (2). Since this reaction is exothermic, its rate can be monitored via the temperature rise of the slurry. As can be seen in Fig. 3, the reaction rate is controllable at several waste loadings of interest by the simple addition of a single agent. The reaction retardant is dissolved in phosphoric acid before the acid is reacted with the powder mixture of ash waste and magnetite. Varying concentration of the retardant in the acid from 0.025 g/ml to 0.1 g/ml, we

were able to fabricate waste ceramic waste forms with the setting time from 5 minutes to 2 hours. The degree of flexibility that this affords the process in the field can not be over-stated.

B) Density

Results of density measurements are summarized in Table 2. The true density of the fast setting compositions is less than that of the slow setting. A difference between the true and bulk density is explained by the presence of air voids, trapped in the matrix. Bulk density was determined using the macroscopic volume and mass. The higher the density, the lower the porosity and this should be reflected in better normalized release rates from the MCC-1 test. A method of removing this variable from the leach test would be to apply the product consistency test (PCT), ASTM 1285-94, which utilizes a crushed sample and not a monolithic one. Providing the compressive strength measurments are acceptable the PCT test may be the method of choice in the immediate future for our research needs.

Table 2. Densities and Setting Times of Selected Waste Form Compositions

Parameters		Fast setting compositions		Compositions with extended setting time							
Waste loading, %		30	40	30				40			
Amount of retardant added, g/ml H_3PO_4		0	0	0.025	0.05	0.075	0.1	0.025	0.05	0.075	0.1
Setting time, min		5	5	8	30	60	90	8	30	60	90
Density, g/cm^3	true	2.68	2.50	2.62	2.78	2.80	2.90	2.63	2.77	2.83	2.67
	bulk	1.46	1.57	1.37	1.58	1.67	1.63	1.79	1.57	1.67	1.68

C) Static Leach Results

The results of a 7 day MCC-1 results are presented in Table 3. These are normalized release rates for the cations of interest including Fe. Concentrations of Ce, Cs and RCRA metals in the leachate solutions were below detection levels. Relatively high weight losses of the samples are explained by leaching of unreacted phosphoric acid from the samples.

Table 3. Leach results

Parameters		Fast setting compositions		Compositions with extended setting time				
Waste loading, %		30	40	30		40		
Amount of retardant added, g/ml H_3PO_4		0.00	0.00	0.075	0.1	0.05	0.075	0.1
Weight loss, wt %		5.95	7.10	2.02	1.95	2.32	2.13	1.48
pH of the leacate solutions		3.47	3.32	3.36	3.33	3.51	3.55	3.37
Normalized release rate, $g/m^2/day$	Cr	<0.049	<0.037	<0.049	<0.051	<0.036	<0.037	<0.036
	Pb	<0.294	<0.220	<0.294	<0.305	<0.217	<0.219	<0.219
	Ce	<0.049	<0.037	<0.049	<0.051	<0.036	<0.037	<0.036
	Fe	0.042	0.038	0.018	0.039	<0.016	0.036	0.039

D) Scanning Electron Microscopy Analysis

Scanning electron microscopy combined with EDS analysis was used to characterize different phases present in monolithic waste forms. The samples were found to consist of a bulk matrix phase with smaller phases present in suspension. The bulk phase consisted of Al, Si, P and Fe (our EDS is incapable of detecting oxygen). The bulk phase appears as a dense amorphous material; its amorphoric character was confirmed by XRD analysis. The suspended particles present in the matrix were of non-uniform compositions consistent with the encapsulated nature of the waste form. It was found that major constituents of the ceramic matrix are Al, Si, P and Fe. SEM images of selected monolithic waste forms are presented in Fig. 4. Fig. 4a) and 4b) correspond to the fast setting compositions with the waste loading of 30 and 40% respectively. Fig. 4c) and 4d) correspond to the slow setting compositions with the same waste loading. It was observed that slow setting compositions have fewer pores and cracks compared to fast setting, which suggests that slow setting is more favorable for the solidification process.

E) XRD Results

XRD analysis was performed to identify the crystalline phases present in the solidified product. Crystalline phases include those identified in the surrogate waste starting material (i.e. silicate or aluminum-silicate phases, carbon, mullite), unreacted magnetite (Fe_3O_4) and possibly an iron phosphate phase ($Fe_3H(PO_6)\ 6H_2O$). It appears the fast setting composition has a greater amorphus content than the slow setting material.

CONCLUSIONS

The preliminary study presented in this paper using surrogate fly ash has demonstrated the potential of the iron phosphate ceramic system for application to actual TRU containing waste. Furthermore, the results show promise and the need for further work in this area using both surrogates and actual TRU containing fly ash. The following points deserve emphasis as the significant findings of this work:

1) High, 40 wt%, waste loadings of surrogate fly ash containing Cs, Ce and RCRA metals have been successfully immobilized using an iron phosphate ceramic waste form.

2) The ceramic waste form shows preliminary normalized release rates for the RCRA metals that are promising.

3) The setting time of the waste form compositions is easily controlled in a wide range using a retardant.

4) The method outlined in this work is quick, effective, economical and displays a significant waste loading.

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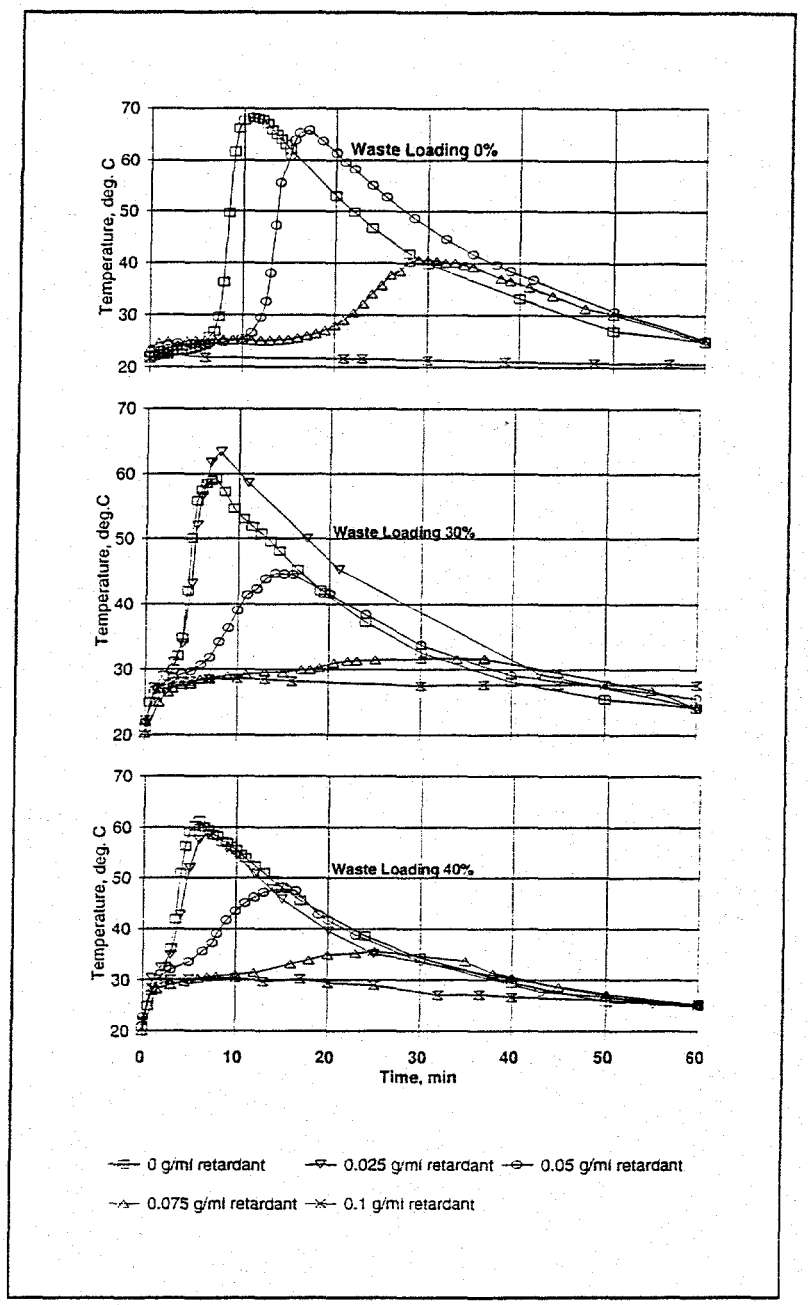

Figure 3. Temperature rise during setting of iron phosphate ceramics
Amount of the retardant added is in grams per milliliter of phosphoric acid.

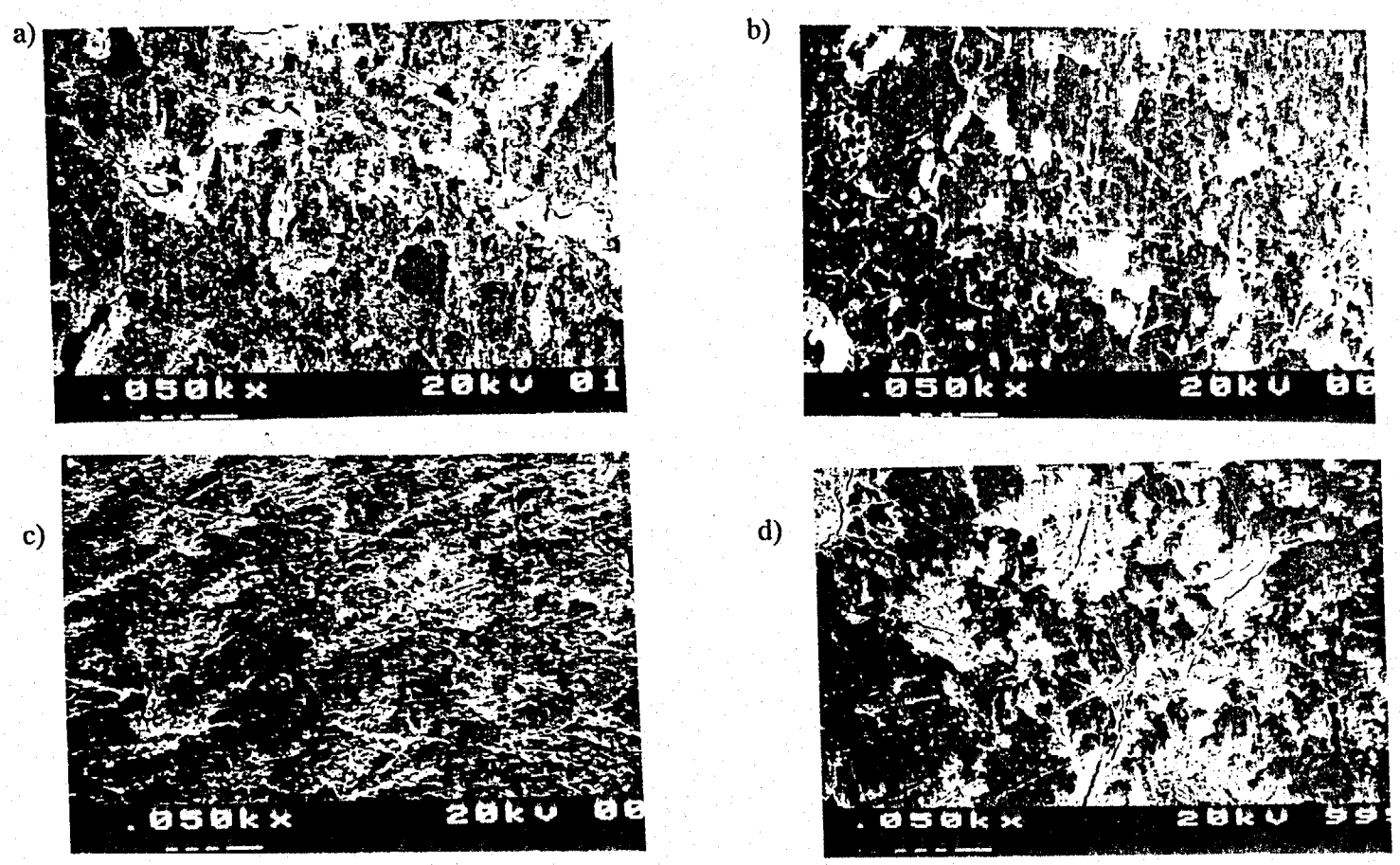

Fig. 4 SEM images of selected compositions
a) fast setting composition, waste loading 30%; b) fast setting composition, waste loading 40%; c) slow setting composition, waste loading 30%; d) slow setting composition, waste loading 40%