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Immobilization of Simulated High Level Nuclear Wastes with Magnesium Phosphate Glasses

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The leaching behavior of magnesium phosphate glasses containing 45 and 55 mol% MgO loaded with simulated high level nuclear wastes (HLW) to water was examined. The leach rates of gross and each constituent element were determined from the total weight loss of the specimen and the leachate analyses by inductively coupled argon plasma spectroscopy (ICP). The gross leach rate of the glass waste form containing 55 mol% MgO and 45 mass% simulated HLW is of the order of 10^{-6} g/cm^2·day at 90°C, which is small enough as compared with the corresponding release from a currently used borosilicate glass waste form. It was found that the magnesium phosphate glass works well as a matrix to solidify HLW.

Key words: High level nuclear wastes, Immobilization, Magnesium phosphate glass, Leach rates, Thermal properties, Microstructure

1. INTRODUCTION

The disposal of radioactive waste generated by the nuclear fuel cycle is among the most pressing and potentially costly environmental problems. The high level nuclear wastes (HLW) are immobilized in a stable solid state and completely isolated from the biosphere.

Nuclear waste glasses are typically borosilicate glasses, and these glass compositions can experience phase separation at elevated concentrations of P_2O_5. The maximum P_2O_5 concentrations must be limited to between 1 and 3 mass%. For some waste streams, this can require considerable dilution and a substantial increase in the volume of the waste glass produced. Hence, there has been a continuing interest in developing phosphate glasses as waste forms. Further, typical borosilicate glasses are limited to no more than 5 mass% actinides (2 mass% for Plutonium). In contrast iron phosphate glass with up to 15 mass% P_2O_5 can accommodate up to 40 mass% of simulated HLW [1, 2].

Phosphate glasses have some advantages over borosilicate glasses, such as a lower melting temperature and higher solubility for problematic elements, such as sulfur, and were investigated as early as the 1960s. Later work on sodium-aluminum phosphate glass [3] and iron-aluminum phosphate glass [4] showed that some of these glasses had comparable or better chemical durability than the borosilicate glasses. Present efforts are focused on the development of lead-iron phosphate glasses [1, 5-10]. The main disadvantage of phosphate glass is that the melts are highly corrosive. Still, a number of the engineering problems were overcome and in the 1980s at Mayak in the Urals, considerable amounts of waste, approximately 1000 m^3, were immobilized in a phosphate glass [11]. Vitrification of wastes with Na-Al phosphate glass matrix continues today at the Mayak Production Association in Chelyabinsk where 300 million Curies of activity of HLW have been immobilized in glass. There have been studies to investigate the immobilization of Cs [12], CsCl and SrF_2 [13], mixed-waste sludge [14] and spent nuclear fuel [2] in iron phosphate glass compositions.

Magnesium phosphate glasses are classified as 'anomalous phosphate glasses', which exhibit anomalies in the relationship between physical properties, such as density and refractive index, and MgO/P_2O_5 (M/P) molar ratio around the metaphosphate composition (M/P=1). The structures of M-P glasses were studied [15]. Most of the phosphate glasses formed high polyphosphate consisting of chains of phosphate ions, while the structures of M-P glasses are of two types, one includes four membered rings of PO_4 tetrahedra at M/P<1 (type T) and the other contains dimmers of PO_4 tetrahedra at M/P>1 (type P).

In this study, M-P glasses are chosen as the base glass. Mixed metal oxide, which acts as the simulated nuclear waste (radioactive isotopes were not employed) [16], was incorporated into the base glass to study its effects on the properties of the glasses. The present article reports on the leach rates to water, some of thermal properties and microstructure.

2. EXPERIMENTAL

2. 1 Sample preparation

The M-P glass frit that is used to produce glass waste form can be prepared by combining appropriate amounts of magnesium oxide and phosphoric acid and by heating at 1250°C for 1h. The powder mixtures of the glasses containing 0, 25 and 45 mass% of simulated HLW were melted at 1250°C for 2h. The melt waste glass was poured into a stainless plate. The composition of the simulated HLW is shown in Table I.

2. 2 Leach test

The leach test for the glass waste forms was conducted in distilled water. About 1 g of each sample crushed to 10~20 mesh was dipped into 50 ml of water

Table I Composition of simulated nuclear wastes.

Waste element	Raw material	mass%
Na	$NaNO_3$	64.8
Sr	SrO	2.9
La	La_2O_3	16.1
Mo	MoO_3	7.5
Mn	MnO_2	1.2
Fe	Fe_2O_3	6.6
Te	TeO_2	0.9

in a teflon beaker within an oven kept at 90°C for 20 days. The total surface area of the grains was estimated by the following:

$$S=W\cdot S_0/\rho \qquad (1)$$

where W and ρ are the mass in g and the density in g/cm^3 of sample, and S_0 the specific surface of crushed specimen, respectively.

The leach rates of gross and each constituent were determined from the total weight loss of the specimen and the leachate analyses by inductively coupled argon plasma spectroscopy (ICP).

2. 3 Density, XRD, DTA and SEM

The density of the waste forms was measured at room temperature using the Archimedes method with kerosene as the immersion fluid. Powder X-ray diffraction (XRD) analysis of the as-quenched melt was used to verify the amorphous state of the samples. The differential thermal analyses (DTA) were performed in flowing nitrogen at a heating rate of 10°C/min. The microstructure of the waste forms was investigated with the scanning electron microscope (SEM)

3. RESULTS AND DISCUSSION

3. 1 Vitrification of wastes with M-P glass matrix

The composition and density of the M-P glass waste forms prepared in this study were listed in Table II, where the structure of 45M55P0W (M/P<1) glass is referred to as the type T, and that of 55M45P0W (M/P>1) glass is referred to as the type P. The density increases with increase in simulated HLW content. The appearance of the base glass is colorless and transparent. The colors of the glasses, which contain mixed metal oxides, are dark brown and turn darker with increasing the mixed oxides content.

To understand the effect of temperature on the crystallization of M-P glass wastes, the samples were annealed isothermally at 500°C for 2h. The glass states were confirmed by the absence of XRD peaks. The results of XRD measurement are shown in Table III. The glass forming tendency decreased with the increasing M/P ratio, and the tendency of the compositions with high simulated HLW contents decreased and these samples partially crystallized during cooling, except the sample 55M45P45W. It was found that the 55M45P45W was thermally stable form. The borosilicate glasses are limited to no more than 5 mass% actinides. In contrast M-P glass with up to 55 mass% P_2O_5 can accommodate up to 45 mass% of simulated HLW.

3. 2 Leach rates of samples in water

The gross leach rates and the leach rates of each constituent element of the sample in water at 90°C were determined from the total weight loss of the specimen and chemical analysis of leachate solution. The results are summarized in Tables IV and V. The chemical durability of the glasses was greatly improved as the addition of simulated HLW. Table IV shows that 55M45P45W has the gross leach rate of the order of 10^{-6} $g/cm^2\cdot day$, which is fairly low as compared with that of the borosilicate waste glass. Of the elements in most phosphate glasses, Na shows higher leach rate than others, probably because of rather higher solubility of its polyphosphate consisting of chains of phosphate ions. No effect of Na in the M-P glass waste form on its leachability was found. These results can be attributed to the glass structure.

3. 3 Thermal properties of glass waste form

It is important to obtain information about the thermal stability of the glass waste form, since the crystallization of glass waste can mostly increase the undesirable aqueous corrosion rate of the form, probably due to the

Table II Composition and density of glass waste forms prepared in this study.

Composition (mol%)	**$MgO:P_2O_5=45:55$**			**$MgO:P_2O_5=55:45$**		
Simulated waste content (mass%)	0	25	45	0	25	45
Waste forms	45M55P0W	45M55P25W	45M55P45W	55M45P0W	55M45P25W	55M45P45W
Density (g/cm^3)	2.44	2.66	2.65	2.45	2.66	2.88

Table III The results of XRD measurement of glass waste forms.

Waste forms	**45M55P0W**	**45M55P25W**	**45M55P45W**	**55M45P0W**	**55M45P25W**	**55M45P45W**
before heat-treatment	V	V	C	V	C	V
after heat-treatment	V	V	C	V	C	C

V; vitreous C; crystalline

Table IV Surface area and leach rate of glass waste forms.

Waste forms	45M55P0W	45M55P25W	45M55P45W	55M45P0W	55M45P25W	55M45P45W
Surface area (cm^2)	37.82	32.66	33.26	38.94	34.09	31.96
Leach rate (g/cm^2·day)	1.37×10^{-3}	1.48×10^{-4}	3.37×10^{-5}	1.27×10^{-3}	9.80×10^{-5}	5.79×10^{-6}

Table V Leach rate of each constituent element of glass waste forms.

Waste forms	45M55P25W	45M55P45W	55M45P25W	55M45P45W
Mg	1.64×10^{-5}	2.51×10^{-7}	7.17×10^{-6}	4.79×10^{-7}
P	5.28×10^{-5}	1.20×10^{-6}	3.70×10^{-5}	1.08×10^{-6}
Na	8.98×10^{-6}	5.29×10^{-6}	1.23×10^{-5}	7.35×10^{-7}
Sr	4.20×10^{-8}	3.00×10^{-9}	4.20×10^{-8}	1.00×10^{-9}
La	2.00×10^{-9}	3.00×10^{-9}	2.00×10^{-9}	n.d.
Mo	3.00×10^{-6}	1.23×10^{-5}	4.00×10^{-6}	1.80×10^{-7}
Mn	5.00×10^{-8}	2.00×10^{-9}	1.50×10^{-8}	2.00×10^{-9}
Fe	1.60×10^{-8}	2.00×10^{-8}	1.00×10^{-8}	1.60×10^{-8}
Te	2.00×10^{-9}	n.d.	4.00×10^{-9}	1.00×10^{-9}

Leach rate ; g/cm^2·day

formation of somewhat more soluble crystals or the increase in surface area.

Fig. 1 shows the DTA curves of the samples. The starting temperature of the crystallization peaks (Tx) and glass transition temperature (Tg) determined from the DTA curves and the stability of the waste forms (Tx-Tg) are listed in Table VI. It indicates that both Tx and Tg decrease with increasing simulated HLW content. The 55M45P45W waste form was thermally stable.

3. 4 Microstructure

Fig. 2 shows SEM photographs for samples with simulated waste content of 25 and 45 mass%. In the 45M55P45W and 55M45P25W forms, crystalline grains were observed. The 45M55P25W and 55M45P45W forms were vitreous state, and phase separation was observed in the former composition. The above-mentioned fact corresponds to the result of XRD measurement well.

Table VI The results of DTA measurement of glass waste forms.

Waste forms	45M55P0W	45M55P25W	45M55P45W	55M45P0W	55M45P25W	55M45P45W
Tg (℃)	504	496	484	558	516	485
Tx (℃)	608	580	546	686	573	565
Tx-Tg	104	84	62	128	57	80

Tg ; glass transition temperature Tx ; starting temperature of crystallization

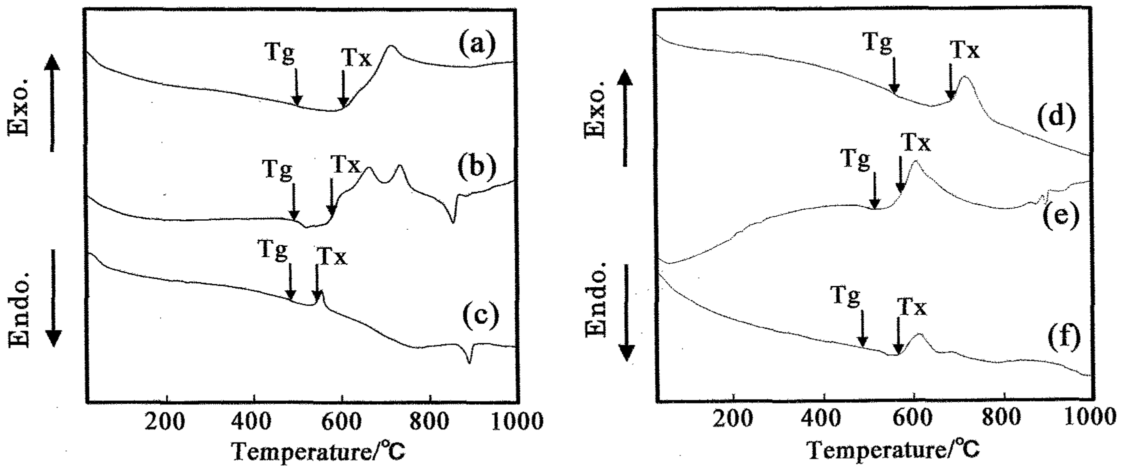

Fig. 1 DTA curves for samples with simulated waste content (0, 25 and 45 mass%).
(a) 45M55P0W, (b) 45M55P25W, (c) 45M55P45W, (d) 55M45P0W, (e) 55M45P25W, (f)55M45P45W

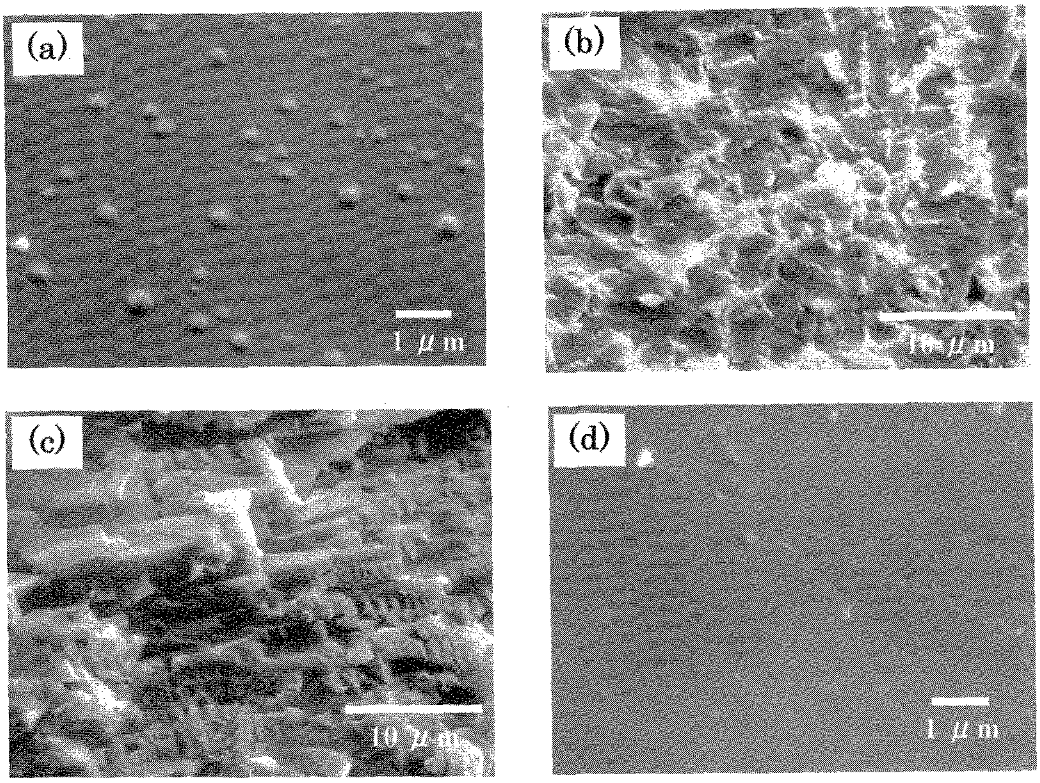

Fig. 2 SEM photographs for samples with simulated waste content of 25 and 45 mass%.
(a) 45M55P25W, (b) 45M55P45W, (c) 55M45P25W, (d) 55M45P45W

4. CONCLUSIONS

M-P glasses were proposed as the potential nuclear waste glasses. The leach rates and some thermal properties of M-P glasses loaded with simulated HLW were examined. It was found that the 55M45P45W glass waste form was thermally stable. The gross leach rate of the 55M45P45W form is of the order of 10^{-6} g/cm^2·day at 90°C, which is fairly low as compared with that of the borosilicate waste glass. Further works on effects of radiation on the leaching of the form are required.

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