Preliminary Study on the Vitrification of Molten Salt Reactor Radwastes Containing Fluorides by Phosphate Glass

Yan-bo Qiao, Ya-ping Sun, Xue-yang Liu, Zheng-hua Qian, Shuai Wang and Hong-jun Ma

Abstract The fluoride-containing waste from molten salt reactor should be embedded in a stable, chemically resistant matrix for final disposal, and the matrix should be easily stored or disposed. However, the solubility of halides in borosilicate-based glasses is so low that the traditional glasses are inappropriate for the immobilization of radioactive waste containing fluorides because of the poor load capacity. In this paper, the vitrification of MSR fluoride-containing waste by phosphate glass was performed. The research investigated the source item of MSR fluoride-containing waste, and simulated nonradioactive waste was prepared. Sodium aluminophosphate and iron phosphate glasses were chosen as host matrixes in our preliminary experiment. The material structure and properties of the wasteforms were analyzed by XRD, Raman, and SEM. Chemical durability was carried out by the product consistency test method. The results showed that the metal fluorides could be well solidified in the phosphate-based glasses. The wasteforms exhibited good performance with high-effective waste loading, lower cost, and fine stability. Our work is of great significance for the scientific management and safety disposal of radwastes from molten salt reactor and contributes to the long-term sustainable development of molten salt reactor.

Keywords Vitrification · Radioactive waste treatment · Molten salt reactor · Fluorides

1 Introduction

Molten salt reactors (MSRs) use the liquid molten salt as the fuel solvent and coolant. Different form light water reactors (LWRs), molten salt reactor does not have fuel pellets; instead, its nuclear fuel is dissolved in molten fluoride salts such as lithium fluorides or sodium fluorides [1–4]. The fuel and molten salt reprocessing

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Y. Qiao (✉) · Y. Sun · X. Liu · Z. Qian · S. Wang · H. Ma
Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, China
e-mail: qiaoyanbo@sinap.ac.cn

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could reduce the volume of the high-level wastes; however, significant quantities of radwastes containing fluorides are still left. These wastes will bring particular problems because of their high-level radioactivity and complex chemical properties. Storage of the waste in metal containers is only a short-term solution because of the eventual corrosion of metal containers and resulting release of radioactive. Some fluorides in MSR waste are soluble in water and require no exposure to water. This made it necessary to embed the fluoride-containing radioactive wastes in a stable, chemically resistant matrix for final disposal, and the matrix should be more easily stored or disposed.

Glass solidification is the most widely used technology for the treatment of high-level liquid waste. Borosilicate glass is the generally accepted wasteform for the oxide radwastes from the LWRs [5]. However, the immobilization of the fluoride-containing wastes in borosilicate glass directly is not feasible due to the very low solubility of fluorides [6, 7]. The low solubility usually results in phase distribution during the vitrification and lowers the quality of the wasteform. Some wastes containing significant amounts of heavy metal oxides (e.g., UO_2, La_2O_3) also have lower solubilities in borosilicate glasses. This decrease in the waste loading will make the volume of the wasteform undesirably large. Based on these considerations, alternative type of wasteform should be developed; in particular, a feasible approach is to seek other glass matrix.

Phosphate-based glasses possess apparent advantages of lower melt temperatures and lower viscosity relative to borosilicate glasses, so they were originally investigated as potential hosts for spent nuclear fuel waste, but these early glasses had poor durability and the melts were generally highly corrosive. However, some researches based on the adjusting of the glass composition (e.g., addition of Al_2O_3 and Fe_2O_3) have improve the durability of the phosphate glasses and the refractory corrosion [8]. Iron phosphate glasses have been proposed for immobilizing CsCl and SrF_2 extracted from HLW tank sludges because of their high radioactivity and short half-lives [9]. Aluminofluorophosphate glass matrix was recommended for immobilizing spent melt containing alkali-metal chlorides which as the diluents in reprocessing of spent fuel for fast reactors by the pyroelectrochemical method [10]. Certain calcium aluminosilicate glasses have been suggested for treating chloride-containing incinerator wastes [11]. Sodium aluminophosphate glass was chosen as the glass matrix for HLW in the former Soviet Union [12]. Even the recent studies proposed that glass compositions based on iron phosphate could be as an alternative host for the vitrification of HLW which contains relatively high concentrations of actinide elements, because the actinides solubilities in these glasses being higher than that of silicate-based glasses [13].

In this study, we have investigated the feasibility of employing sodium aluminophosphate as immobilization hosts for simulated MSR radwastes containing both actinide and fluorides. The structure and properties of the wasteforms were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy. Leaching tests were performed in deionized water using the product consistency test A (PCT-A method), which simulate extreme conditions of underground repositories (moist air and high temperature). Our results indicated that sodium aluminophosphate glass exhibited high solubility and desirable chemical stability.

2 Experimental

2.1 Waste Stream Compositions

The commonly simulated non-radioactive waste was employed to represent a number of specific radioactive wastes generated during the reprocessing of used TMSR fuel. The designated non-radioactive-simulated fluoride-containing wastes consist of Cs, Sr, Zr, Ce, and Sm, with the compositions shown in Table 1. Sm was used as a surrogate for tetravalent radionuclides; Cs for Ru, Cs; ^{88}Sr for ^{90}Sr, Ba; Ce and Zr for itself actinide elements (U, Pu, Th); and Sm for surrogated trivalent actinide elements (Am, Cm). MF_n was used to represent the various fluorides as shown in Table 1.

2.2 Sample Preparation

The glasses with compositions listed in Table 2 were prepared from mixtures of reagent grade constituents. Well-mixed powders were first preheated to 300 °C (heating rate is 10 °C/min) in alumina crucibles and kept for 3 h to evaporate ammonia and water in the batches. Then, the batches were melted in air at 1000–1250 °C for 30 min. The fused glass mass was poured into a preheated steel mold, held at 450 °C for 1 h to relieve internal stresses, and then cooled to room temperature. The experiments aimed at establishing the maximum amount of fluorides that could be incorporated into the glasses. Melting schedules were adjusted according to the viscosity of the melt and the observed volatility.

2.3 Characterization

X-ray diffraction (XRD) was employed to performed identification the limits of glass formation and crystalline phases present in the glass samples (D8 advance, Bruker, Geman) using a Ultima IV diffractometer with CuKα radiation. Raman spectra on glass powders are recorded by using a laser of wavelength 532 nm

Table 1 Compositions of the MSR-simulated waste

Fluoride	CsF	SrF_2	ZrF_4	CeF_4	SmF_3
mol%	8.4	8.3	29.7	15.8	37.8

Table 2 Compositions of sodium aluminum and iron phosphate glasses (mol%)

Sample	Na_2O	Al_2O_3	P_2O_5	Fe_2O_3	Simulated wastes (mol%)
NAP1	40.2	19.6	40.2	0	3.8
NAP2	40.2	19.6	40.2	0	19.6
NAP3	40.2	19.6	40.2	0	27.5
NAFP1	35.6	11.5	42.1	10.8	4.4
NAFP2	34.9	16.6	41.3	7.2	6.4
NAFP3	35.6	11.5	42.1	10.8	8.5

radiation and a Renishaw in Via spectrometer coupled with an optical microscope (HR800, Renishaw, England). Chemical durability measurements have been conducted according to Product Consistency Test A (PCT-A) [14]. The glass samples were crushed manually in an agate mortar and sieved to 75–150 µm. Powders were washed abiding by PCT operating procedure, then mixed with distilled water at a ratio of 10 ml/g, and held at 90 °C for 7 days in a stainless steel vessel. Upon the completion of each test period, the normalized elemental mass was determined by chemical analysis of the leachate using the ICP-AES (Na, Al, P, Fe) and ICP-MS (Cs, Sr, Zr, Ce, Sm) methods.

3 Results

3.1 X-Ray Diffraction (XRD)

Figure 1a shows the XRD patterns of the sodium aluminum phosphate glasses with different waste loadings. No crystalline phases were detected by XRD when the simulated waste content is low. For those samples with simulated wastes ratio more than 19.6 mol%, the crystalline phase was detected and the major crystalline phase is monazite (Sm, Ce, Zr)PO_4(46-1392). Figure 1b shows the XRD patterns of the iron phosphate glasses with different waste loadings. For those samples with high waste loading, peak regime revealed the presence of a number of additional crystalline phases, including monazite $FePO_4$ (29-0715), $AlPO_4$ (31-0029,11-0500), and Na_3PO_4 (33-1272).

3.2 Raman

Raman spectra of fluoride-containing glasses of NAP and NAFP are shown in Fig. 2. The peaks in the spectra from the glasses occur at similar frequencies as those from the phosphates glasses of iron, calcium, sodium, and sodium aluminum phosphate, and similar assignments can be made for the peaks in the spectra from

Fig. 1 XRD patterns of sodium aluminum and iron phosphate glasses

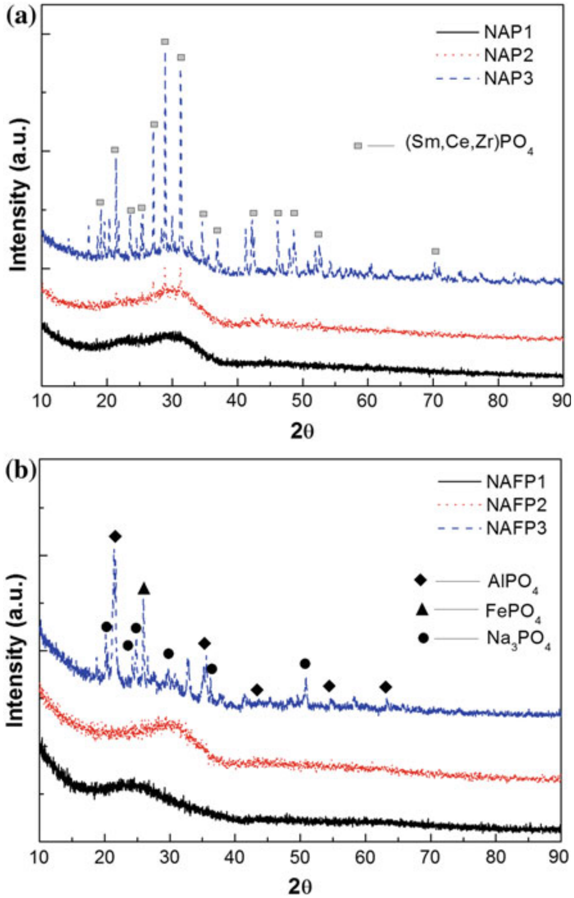
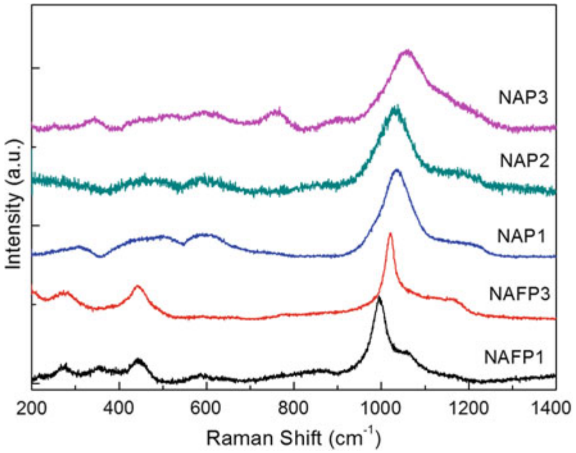


Fig. 2 Raman spectra of sodium aluminum and iron phosphate glasses



the glasses [16–19]. The most intense peak in each spectrum, at frequencies from ~1060 to ~1100 cm^{-1}, can be assigned to the symmetric stretch of a non-bridging oxygen on a Q^1-tetrahedron, the (PO_3)sym mode. The higher frequency shoulders evident in each spectrum could be due to asymmetric PO_3 modes associated with the Q^1-tetrahedra, but also could be due to symmetric PO_2-stretching modes associated with Q^2-tetrahedra. Likewise, the shoulders near ~1000 cm^{-1} could be assigned to other PO_3 modes associated with the Q^1-tetrahedra, or to PO_4 modes associated with the Q^0-tetrahedra units in the glasses. The bands of NAFPs between 700 and 800 cm^{-1} are related to the symmetric P–O–P-stretching modes associated with linkages to Q^1-tetrahedra. Raman modes observed at 200–600 cm^{-1} are typical of rocking motion of PO_4 tetrahedra and/or the motion of cationic polyhedra. With increasing waste loading, the (PO_1)sym band increases in relative amplitude without significant frequency shift, whereas the high-frequency (P = O)sym band decreases in relative intensity and decreases in frequency.

3.3 Chemical Durability

On the completion of each test period, the normalized elemental mass was determined by chemical analysis of the leachate using the method by ICP-AES or ICP-MS. Data were corrected by subtracting the normalized analysis for accompanying blank solutions. Fluorine ion electrode was used to analyze F ion concentration, and the pH values of the leachate were also measured during the tests. The lower the ion concentration in the leachate, the better chemical stability will be. PH of leachate can also characterize the chemical stability of the sample, variate as small as possible (PH for all the sample initial leachate is 7).

Table 3 Chemical stability performance of NAP and NAFP compared with the other glasses (g/m^2)

Normalized mass release	NAP1	NAFP1	FZ-1[a]	ARM-1[b]	CVS-IS
r_{Al}	0.175	0.000	0.795	0.09	
r_{Na}	0.026	0.009	0.723	0.27	1.1–1.5
r_P	0.187	0.010	0.246		
r_F	0.055	0.005			
r_{Fe}		0.000	<10		
r_{Cs}	0.204	0.013			0.06–0.13
PH_i/PH_f	8.4/7	8.92/7	5.4/9.4	10.47/–	5.9/~10.3

[a] FZ-1 is an iron phosphate glass waste form made at UMR (18Na2O·26Fe2O3·46P2O5·10other, wt%) and tested (PCT) at PNNL

[b] ARM-1 is a standard reference borosilicate glass used at Savannah River Laboratory

[c] CVS-IS is a standard glass made by Pacific Northwest National Labs (PNNL) and has a nominal composition of 53.3SiO2, 10.5B2O3, 11.3Na2O, 3.7Li2O, 2.4Al2O3, 7.0Fe2O3, 3.9ZrO2, 1.3Nd2O3, and 6.6 others, wt%

The leaching rate (g/m^2) was calculated on the basis of the normalized elemental mass loss. The leaching of samples demonstrates that the normalized all ions release ≤ 0.2 g/L within the 2 g/m^2 Hanford specification [15]. The releases of Sr^{2+}, $Ce^{3+/4+}$, Zr^{4+}, and Sm^{3+} are lower than Na^+, P^{5+}, Fe^{3+}, Al^{3+}, F^-, and Cs^+, which indicates that the former are likely bonded differently or in different phases. The deionized water pH used in the PCT test is from 8 to 9.5 for the NAP and from 4.5 to 9 for the NAFP wasteforms. PH increase is potentially detrimental to the glass durability since the corrosion of glass is more readily. Furthermore, it is noted that the quantity releasing from the wasteforms did not change clearly if the wasteform is crystallized.

The chemical stability performance of the NAP and NAFP glass is shown in Table 3. The data from FZ-1, ARM-1, and CVS-IS are used to compare with the results in this study. Sodium, phosphorus, aluminum, strontium, and iron released are quite low, typically less than released from the two borosilicate glasses as

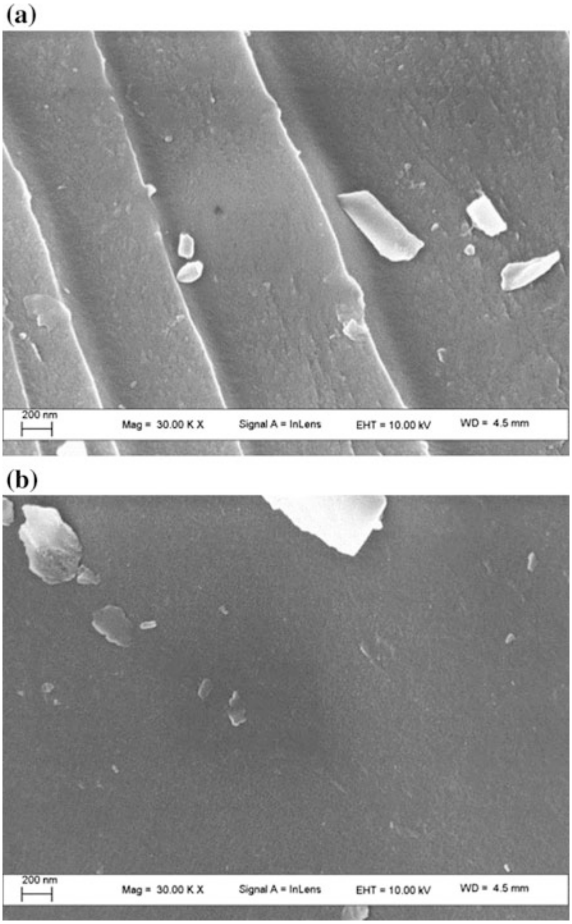


Fig. 3 SEM photographs of before PCTs of the **a** NAP1 and **b** NAFP1 glasses

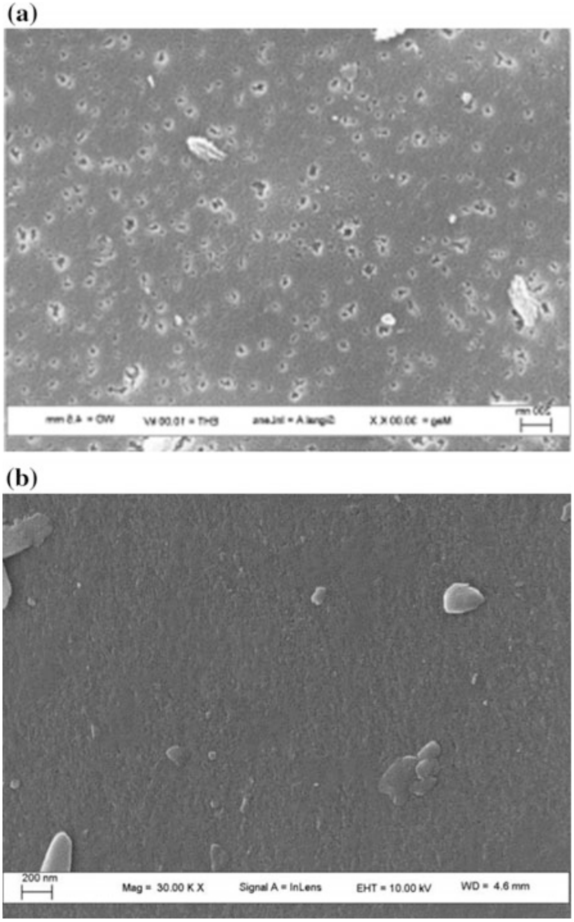


Fig. 4 SEM photographs of after 7 days PCTs of the **a** NAP1 and **b** NAFP1 glasses

shown in Table 3. The dissolution rate of these phosphate glasses was better than that of the borosilicate ARM-1, CVS-IS glasses, and as good as even better iron phosphate glass FZ-1 in distilled water.

The visually noticeable corrosion of the NAP and NAFP glasses particles was confirmed by their appearance after PCT testing. The SEM photographs of before PCT tests of the NAP and NAFP glasses are shown in Fig. 3a and b. The SEM photographs of after 7 days PCT tests of the NAP and NAFP glasses are shown in Fig. 4a and b. The SEM images of the glasses show sharp corners and edges as shown in Fig. 3. And the glasses after PCT tests are also absent of any detectable corrosion layer on the surface, which is a clear evidence of the excellent chemical durability of NAP and NAFP wasteforms which also can conclude from Table 3.

4 Discussion

The low melting temperatures and poor chemical resistance of phosphate-based glasses are related to PO_4 groups in ring structures. For strengthening structural of the glass network and hence increasing chemical resistance, network modifiers (e.g., Na_2O) and network intermediates (e.g., Al_2O_3) were added. The ratio of Na_2O to P_2O_5 in the present samples is 1.00, and the Al_2O_3-to-P_2O_5 ratio is 0.49. Hudgens et al. [18] have reported that the structure of glasses around this composition consists predominantly of $AlPO_4$ groups together with some tetraphosphate and/or triphosphate groups. The expected presence of a larger proportion of $AlPO_4$ groups explains the structural stability (and durability) of this glass compared to binary alkali phosphate glasses. The generally good chemical durability is primarily due to the presence of strong, hydration-resistant Al–O–P bonds in these glasses [9]. This consistent with Raman spectra that the NAP glasses consist of the Q^1 and Q^0 units with a little/without the Q^2 units, and the latter own poor chemical durability of the waste glasses was attributed to dominance of easily hydrolysable P–O–P bonds, which upon hydration get depolymerized through formation of terminal −OH groups.

XRD shows that devitrification tendency increases with increasing fluorides content. This tendency can be explained by a broadly linear relation between the modifier cation field strength, Z/r^2 (Z, r represent ionic charge and ionic radius, respectively), and the atomic percentage of modifier cation [19]. In the study, ionic field strength is lowing with the M^{n+} (Sm^{3+}, Ce^{4+}, Zr^{4+}) addition. This is related to higher crystallization tendency of phosphate glasses with partial replacement of Al^{3+} by M^{n+} up to 20 mol%. The previous studies show that aluminum atoms appear in a environment of four-, five-, and sixfold coordinations [19], while the (Sm, Ce, Zr) atom coordination numbers are six or greater than six [20]. The higher crystallization tendency with the content of incorporation (Sm, Ce, Zr) may be related to the higher coordination number, which can lead to a strong polymerization effect easier.

Fe_2O_3 can act as both an intermediate and a glass-modifying oxide in phosphate glass, which presents in the glass network in both the Fe^{2+} and Fe^{3+} states and provides the greatest durability by replacing P–O–P bonds with more durable P–O–Fe^{2+} or P–O–Fe^{3+} bonds. But the addition of Fe_2O_3 to NAP glasses decreases waste loading markedly, and the crystallization tendency increasing with the addition of Fe_2O_3 may demonstrate that iron ions break the phosphate network into smaller parts and make them less constrained by the neighboring units [21]. Therefore, it might be prudent to limit the addition of Fe_2O_3 into the NAP glass.

5 Conclusions

The immobilization of fluoride-containing waste in glass has studied in the paper. Phosphate glasses were mixed with simulated wastes and reacted in air in the temperature range of 1000–1250 °C. Crystallization tendency increased with the simulated non-radioactive waste content, and monazite (Sm, Ce, Zr)PO_4 crystalline phases were found in the NAP glasses with high waste loading. The addition ($\sim$10 mol%) of Fe_2O_3 constituent decreases the waste loading, but improved the chemical durability significantly. The length of phosphate chain will be shortened, and the asymmetric BO increases with increasing incorporated simulated wastes. The PCT in distilled water conducted on these samples indicated the dissolution rate of phosphate glasses in this work was better than that of the borosilicate ARM-1, CVS-IS glasses, and as good as even better iron phosphate glass FZ-1.

The waste forms exhibit good performance with high-effective waste loading, low cost, and fine stability. Our work is of great significance for the scientific management and safety disposal of radwastes from molten salt reactor and contributes to the long-term sustainable development of molten salt reactor.

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Author Biography

Yanbo Qiao received his PhD degree from Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences in 2009. Then, he worked as a postdoctoral fellow in National Institute of Advanced Industrial Science and Technology (AIST), Japan. He joined Shanghai Institute of Applied Physics, Chinese Academy of Sciences in 2012. His current research interests are the management of radioactive wastes, molten salt reactor radwastes disposal and vitrification of high-level wastes.