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Abstract Radioactive fluoride wastes are generated during the operation of molten salt reactors (MSRs) and reprocessing of their spent fuel. Immobilization of these wastes in borosilicate glass is not feasible because of the very low solubility of fluorides in this host. Alternative candidates are thus an active topic of research including phosphatebased glasses, crystalline ceramics, and hybrid glass-ceramic systems. In this study, mixed fluorides were employed as simulated MSRs waste and incorporated into sodium aluminophosphate glass to obtain phosphate-based waste form. These waste forms were characterized by X-ray diffraction, Raman spectroscopy, and scanning electron microscopy. Leaching tests were performed in deionized water using the product consistency test A method. This study demonstrates that up to 20 mol% of simulated radioactive waste can be introduced into the NaAlP glass matrix, and the chemical durability is much better than that of borosilicate. The addition of Fe₂O₃ in the NaAlP glass matrix results in increases of the chemical durability at the expense of fluoride loading (to 6.4 mol%). Phosphate glass vitrification of radioactive waste containing fluorides is a potential method to treat and dispose of MSR wastes.

Keywords Molten salt reactor · Fluoride-containing radioactive wastes · Phosphate-based glasses

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1 Introduction

The molten salt reactor (MSR) is the only liquid-fuel reactor of the six generation IV candidate reactors for advanced nuclear energy. It utilizes liquid molten salts simultaneously as fuel and coolant [1-3]. The MSR fuel is dissolved in molten fluoride salts such as lithium fluoride and sodium fluoride. Many research efforts, including pyrochemical methods, have been devoted to the reprocessing of used fuel salts. These technologies generate wastes containing fission products and transuranic elements—likely in the form of fluorides [4, 5]. Waste storage in metal containers is only a short-term solution because of their eventual corrosion and subsequent radioactivity release. Some fluorides from these MSR wastes are soluble in water, and exposure must therefore be eliminated. Consequently, a new technology is needed for temporary storage and final disposal of wastes containing radioactive fluorides.

The immobilization of radioactive wastes in glass and ceramic hosts has been under investigation for many years [6, 7]. Currently, borosilicate glass is generally accepted as the first-generation waste form [7]. However, direct immobilization of these fluoride-containing wastes in borosilicate glass is not feasible because of their very low solubility values in this host: <5 wt% for actinides [8] and <1.0 wt% for fluorides [5]. This results in the formation of crystals during vitrification and a resulting reduction in the product quality. Moreover, some wastes containing significant amounts of heavy metal oxides (e.g., UO₂, La₂O₃) exhibit lower chemical solubility in most borosilicate glasses. Lower solubility reduces the waste loading. Consequently, the radioactive waste volume increases in an undesirable way. Thus, there is a strong incentive to



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reconsider previous candidate materials for immobilizing fluorides such as developing more advantageous processes or identifying new ones.

Phosphate glasses are particularly attractive because of their relatively high solubilities (Table 1) [9], low glass transition temperatures (T_g), low melting temperature, and high thermal expansion coefficient [10, 11]. Moreover, using phosphate glass for the vitrification of these fluoride-containing wastes can eliminate the need to reprocess them into oxides.

Halogens are generally viewed as troublesome components for glass processing because of their high volatility, which produces hazardous fumes and particulates. Mesko et al. [12] demonstrated that a part of the Cl and F was volatilized during melting, but very little of the surrogate waste materials (Cs and Sr) or the glass-forming materials (Fe and P) were volatilized from the batch during melting. One of the advantages of phosphate glass over borosilicate glass for fluoride immobilization is its lower melting temperature-this is essential in reducing the likelihood of volatiles such as F and ¹³⁷Cs. For example, NaF melts at 996 °C. Assuming that the glass is melted throughout and becomes connected at a temperature of approximately 900 °C, then all of the F is likely to be incorporated into the glass. Also, additional efforts can reduce the F volatility if necessary such as adding CaF_2 [13], decreasing the melt surface-to-volume ratio and reducing the melting temperature and time [14].

Phosphate glasses usually suffer from poor chemical durability, rapid devitrification, and high corrosiveness in the molten stage. However, the addition of some oxides (e.g., Al_2O_3 , Fe_2O_3 , or PbO) can resolve or mitigate these issues. Recently, phosphate has been found to immobilize special categories of radioactive waste. Iron phosphate (IP) glasses have been proposed for the immobilization of CsCl and SrF₂ extracted from high-level radioactive waste (HLW) tank sludge [12]. Aluminofluorophosphate glasses have been recommended for immobilizing the melt containing alkali metal chlorides used as diluents in the reprocessing of spent fuel [15]. Of the compositions under

Table 1 Solubility of elements in phosphate glass (wt%)

Element	Solubility	Element	Solubility
Zr, Mo	≥0.7	Te	≥0.1
Fe	0.5	La	1.1 - 1.4
Ru, Rh	$(2-6) \times 10^{-3}$	Se	1.2-1.6
Cr, Ni	5×10^{-2} -0.2	Nd	2-2.4
Ag	≥0.26	Sm	2.8-3.2
Ра	$(3-6) \times 10^{-2}$		

study, sodium aluminophosphate (NaAlP) glasses are the most intensively studied for their suitability as hosts. Phosphate-based glasses without network modifiers usually consist of PO₄ groups in the ring structures with many nonbridging oxygen atoms. This leads to poor chemical resistance. The addition of network modifiers (e.g., Na₂O) and network intermediates (e.g., Al₂O₃) results in structural strengthening of the glass network and hence an increase in chemical resistance. The expected presence of a larger proportion of AlPO₄ groups in NaAlP glasses explains the structural stability (and durability) of this glass versus binary alkali phosphate glasses [16]. The NaAlP glass has been selected as the glass matrix for HLW in the former Soviet Union and was recently studied by the Atomic Weapons Establishment (AWE) for treating chlorine-containing radioactive wastes generated during the pyrochemical reprocessing of Pu metal [8, 17].

This study investigated the feasibility of employing NaAlP glasses as an immobilization host for simulated MSR wastes. The properties of the waste forms were characterized by several technologies including X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM). Leaching tests were performed in deionized water with the product consistency test A (PCT-A) method. This test simulates extreme conditions of underground repositories (moist air and high temperature).

2 Experimental

2.1 Sample preparation

The designated non-radioactive simulated waste contains cesium, strontium, zirconium, cerium, and samarium fluorides (Table 2). In this paper, MF_n represents the mixed fluorides in the simulated waste.

Samples of NaAlP(-Fe) glass (compositions listed in Table 3) were prepared by melting a mixture of ammonium dihydrogen phosphate (NH₄H₂PO₄), sodium hydroxide (NaOH), aluminum oxide (Al₂O₃), iron oxide (Fe₂O₃), and the raw material of the simulated wastes (Table 2). Wellmixed powders for each batch were first preheated to 300 °C (with a heating rate of 10 °C/min) in alumina crucibles and maintained at this temperature for 3 h to

Table 2 Composition of the non-radioactive simulated waste

Fluoride	CsF	SrF_2	ZrF_4	CeF ₄	SmF ₃
Mol%	8.4	8.3	29.7	15.8	37.8

 Table 3 Compositions of sodium aluminum phosphate-based glasses (mol%)

Samples	Na ₂ O	Al ₂ O ₃	P_2O_5	Fe ₂ O ₃	MF _n
NaAlP1	38.7	18.9	38.7	/	3.8
NaAlP2	37.4	18.2	37.4	/	7.4
NaAlP3	35.3	17.2	35.3	/	13.8
NaAlP4	33.6	16.4	33.6	/	19.6
NaAlP5	31.5	15.4	31.5	/	27.5
NaAlP-Fe1	34.1	11.0	40.3	10.3	4.4
NaAlP-Fe2	32.8	15.6	38.8	6.8	6.4
NaAlP-Fe3	32.8	10.6	38.8	10.0	8.5
NaAlP-Fe4	30.9	14.7	36.5	6.4	13.1
Fe–P	/	/	55.9	37.2	7.4

evaporate ammonia and water. The batches were then melted in air at 950-1200 °C (according to their components) for 30 min. The fused glass masses were poured into a preheated steel mold, held at 450-475 °C for 1 h to relieve internal stresses, and then cooled to room temperature.

The experiments aimed to establish the maximum amount of fluoride that could be incorporated into these glasses. The melting schedules were adjusted according to the viscosity of the melt and the observed volatility. The Fe_2O_3 was added to improve the thermal stability and resistance to crystallization of NaAlP glass. For comparison, IP glasses containing mixed fluorides (the simulated waste) were also prepared.

2.2 Characterization of samples

The XRD was used to identify the crystalline phases present in the glass samples (D8 Advance, Bruker, Germany). Raman spectra on glass powder were recorded using a 532-nm laser and a spectrometer coupled with an optical microscope (HR800, Renishaw, England). The surfaces of the glass powder were investigated by SEM (LEO 1530VP).

2.3 Chemical durability test

The product of any competent radioactive waste treatment process should be highly resistant to corrosion by water (leaching) and not readily dispersible (i.e., monolithic, not "dusty"). Experiments were performed to evaluate the leaching resistance of phosphate glasses and were conducted according to the product consistency test A (PCT-A) [18], which has become the DOE's de facto standard leaching test. The glass samples were crushed manually in an agate mortar and sieved to 75–150 μ m. Powders were washed following the PCT operating procedure, 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 completion of each testing period, the normalized elemental mass loss was determined by chemical analysis of the leachate using ICP-AES (Na, Al, P, Fe) and ICP-MS (Cs, Sr, Zr, Ce, Sm). The data were corrected by subtracting the normalized values for accompanying blank solutions. A fluorine-ion electrode was used to analyze the F-ion concentration. A typical density of 3.0 g/cm³ was assumed for glasses, and the surface area was then calculated to be 1.79 m²/g. The leaching data were converted to leachability units (g/m²) using the formula:

$$L = C_i V / f_i A \tag{1}$$

where, C_i is the concentration of species *i* in the leachate in g/mL, *V* is the volume of the leachate in mL, f_i is the initial fraction of species *i* in the solid, and *A* is the surface area of the solid in m².

After the PCT test, the powder from the leaching container was washed again with pure water, transferred to a clean watch glass, and dried at 90 °C. At this temperature, the adsorbed moisture is removed but not the water of hydration. The surface of the glass powder was investigated after drying.

3 Results and discussion

3.1 X-ray diffraction

Figure 1a presents the XRD patterns of the xMF_{n-} (100-x) NaAlP glass system with x = 4, 7, 12, 20, and 28 mol%. No crystalline phases were detected by XRD for compositions containing up to 14 mol% of MF_n in the glasses. For samples with MF_n ratios ≥ 20 mol%, the crystalline phase was clearly detected as indicated by sharp peaks. The major crystalline phase is identified as monazite (Sm, Ce, Zr)PO₄. The results indicate that devitrification increases with increasing fluoride content. This feature is related to the atomic percentage of the modifier cation Mⁿ⁺ (Sm, Ce, Zr) [19]. Previous studies have shown that the aluminum atom appears in four-, five-, and sixfold coordination environments [16]. While the (Sm, Ce, Zr) atom coordination number is six or higher [20, 21], a strong polymerization effect may result.

Figure 1b presents XRD patterns of the xMF_n -(100-x) (Fe-NaAlP) glass systems with x = 4.4, 6.4, and 8.5 mol%. The XRD patterns of the Fe₂O₃-modified NaAlP glasses show that the structure of this glass is more susceptible to fluoride addition: For samples with MF_n ratios



Fig. 1 XRD patterns: **a** NaAlP glasses $(xMF_n-(100-x)NaAlP)$ and **b** NaAlP-Fe glasses $(xMF_n-(100-x)NaAlP-Fe)$

 \geq 8.5 mol%, numerous additional crystalline phases including FePO₄, AlPO₄, and Na₃PO₄ are observed.

3.2 Raman spectroscopy

The short-range order (SRO) of phosphate glasses is best described by considering the dependence of the fractions of different tetrahedral phosphate species Q^n on composition (the superscript "*n*" represents the number of bridging oxygens on a PO₄ tetrahedron). Raman spectra of the fluoride-containing glass samples NaAlP(1–5) and NaAlP-Fe(1, 3) are shown in Fig. 2.

Versus the spectra of the crystalline materials, the vibrational modes in amorphous materials can be expected to become broader because of the thermally excited distribution of local geometries and vibrational coupling. The peaks in the spectra can be assigned to their vibrational mode according to known frequencies from iron [22], sodium [23], sodium aluminum [16], and calcium [24] phosphate glasses (Table 4).



Fig. 2 Raman spectra of NaAlP and NaAlP-Fe glasses containing MFn

The most intense peak in each spectrum is near 1050 cm^{-1} and can be assigned to the symmetric stretch of a non-bridging oxygen on a Q^1 -tetrahedron in the $(PO_3)_{sym}$ mode. The higher-frequency shoulders evident in each spectrum could result from asymmetric PO₃ modes associated with Q^1 -tetrahedra, but could also be from symmetric PO₂-stretching modes associated with Q^2 -tetrahedra. Likewise, the lower-frequency shoulders could be assigned to other PO₃ modes associated with Q^1 -tetrahedra or to PO₄ modes associated with Q^0 -tetrahedra units in the glasses.

The bands between 700 and 800 cm⁻¹ are related to the symmetric P–O–P-stretching modes associated with linkages to Q^1 -tetrahedra. Indeed, the Raman spectra reveal the existence of Q^1 and Q^0 units in the glasses with a trace of Q^2 . With increasing fluoride content, the Q^n units shift slightly in relative amplitude and frequency. It is interesting that the PO₄ symmetric stretch (Q^0) mode exhibits a greater relative intensity in the NaAlP5 glass than in the other glasses. Distinct Raman line structure appears in the NaAlP5, in which crystallization is observed by XRD.

In contrast to other phosphate glasses (e.g., Refs. [16, 22, 23]), the Raman spectra in Fig. 2 show that the NAIP(-Fe) glasses containing fluorides have no long-chain phosphate structures, which is similar to the results observed in CaO-P₂0₅ by Kasuga [24]. In Refs. [25, 26], it is argued that a fluorine atom can replace an oxygen atom in a Q^n unit to slightly reduce network connectivity in the glass. This may be indirect evidence of fluorine's ability to break the phosphate network into smaller parts that are less constrained by neighboring units.

3.3 Chemical durability

The leaching rates (g/m^2) were calculated based on the normalized elemental mass loss (Table 5). The leaching

Vibrational mode glass type	Band position						
	Fe ₂ O ₃ -P ₂ O ₅	$xNa_2O-(1-x)P_2O_5$	$40Na_2O-10Al_2O_3-xTiO_2-(50-x)P_2O_5$	CaO-P ₂ 0 ₅			
P–O–P symmetric stretch (Q^2)	680–720	690	693,737	/			
P–O–P symmetric stretch (Q^1)	720–780	810,910	/	748			
PO_4 symmetric stretch (Q^0)	990-1010	927–950	/	950–960			
PO ₃ symmetric stretch (Q^1)	1030-1100	1037–1064	1010–1050	1044			
PO ₃ asymmetric stretch (Q^1)	~ 1200	1170	1100	1104			
PO ₂ symmetric stretch (Q^2)	1050-1220	1105–1121, 1190–1195	1147–1160	/			
PO ₂ asymmetric stretch (Q^2)	1250-1310	1207-1228, 1269-1287	1174–1277	/			
$(P = O)_{sym}$ stretch (Q^3)	/	1280–1390	1	/			

Table 4 Summary of Raman frequency ranges for iron, sodium, sodium aluminum, and calcium phosphate glasses (cm⁻¹)

data for the samples indicate that all release values are $\leq 0.2 \text{ g/m}^2$ in the test period—this meets the requirements of EJ 1186–2005 (<1 g/(m²d)) [27]. The release rates of Sr²⁺, Ce^{3+/4+}, Zr⁴⁺, and Sm³⁺ are an order of magnitude lower than Na⁺, P⁵⁺, Fe³⁺, Al³⁺, F⁻, and Cs⁺. In addition, the quantity released did not change substantially when the waste form crystallized (NaAlP5).

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The good chemical durability of NaAlP glasses is primarily due to the presence of strong and hydration-resistant Al–O–P bonds [12], which replace unstable P–O–P bonds. The latter become depolymerized upon hydration through the formation of terminal –OH groups [8, 17]. This result is consistent with the Raman spectra results, which indicate that the NaAlP glasses contain few Q^2 units, but Q^3 units are not evident. It is known that the addition of Fe₂O₃ can also improve durability. This oxide acts as both an intermediate and a glass-modifying oxide and can be present in the glass network in both Fe²⁺ and Fe³⁺ states to replace P–O–P bonds with the more durable P–O–Fe²⁺ or P–O– Fe³⁺ bonds [28, 29]. This is consistent with the leaching results of the NaAlP-Fe samples. However, the addition of Fe₂O₃ to NaAlP glasses decreases the fluoride loading markedly. It might therefore be prudent to limit the addition of Fe_2O_3 in NaAlP glasses.

In practice, the performance of any candidate HLW form on the PCT test relative to the DOE's benchmark has come to define whether or not it is "satisfactory." Data from FZ-1 [6], ARM-1 [30, 31], and CVS-IS [6] leaching tests conducted under similar conditions were also converted to leachability units for comparison. As shown in Table 6, the release rates of sodium, phosphorus, aluminum, strontium, and iron are quite low—typically less than the quantity released from ARM-1 and CVS-IS borosilicate glasses. The dissolution rate of these phosphate glasses in distilled water is lower than that of these borosilicate glasses and is as low as that of the IP glass FZ-1 in distilled water.

The SEM images of glass particles of samples $NaAlP_2$ and NaAlP-Fe1 are shown in Fig. 3. The NaAlP glass has high surface area (Fig. 3a, b), and the treated NaAlP glass particles are covered with a thin layer of a honeycomb structure consisting of nm-sized spherules and pores (Fig. 3b). In contrast, the NaAlP-Fe glass tested for 7 days at 90 °C (Fig. 3d) did not show obvious signs of corrosion

Table 5 Normalized elemental mass release from sodium aluminophosphate waste forms after 7-day PCT (g/m²)

Samples	F	Na	Al	Р	Fe	Cs	Zr	Sr	Ce	Sm
NaAlP1	0.055	0.026	0.175	0.187	1	0.204	4.31×10^{-3}	7.94×10^{-4}	8.30×10^{-3}	/
NaAlP2	0.044	0.082	0.083	0.094	/	0.122	8.95×10^{-4}	3.14×10^{-5}	1.01×10^{-3}	/
NaAlP3	0.031	0.052	0.048	0.060	/	0.073	3.25×10^{-4}	3.77×10^{-4}	4.74×10^{-3}	8.61×10^{-6}
NaAlP4	0.048	0.022	0.111	0.172	/	0.036	7.73×10^{-3}	4.68×10^{-4}	4.92×10^{-3}	/
NaAlP5	0.028	0.082	0.133	0.178	/	0.037	1.39×10^{-3}	1.53×10^{-4}	4.87×10^{-4}	/
NaAlP-Fe1	0.005	0.009	0.000	0.010	4.50×10^{-5}	0.013	/	5.18×10^{-4}	/	/
NaAlP-Fe3	0.004	0.022	0.002	0.027	6.76×10^{-5}	0.088	1.58×10^{-5}	1.38×10^{-2}	1.65×10^{-4}	4.77×10^{-5}
NaAlP-Fe4	0.025	0.066	0.084	0.131	/	0.078	7.58×10^{-4}	3.52×10^{-4}	3.67×10^{-4}	2.28×10^{-4}
40 %Fe-P	0.007	/	/	0.010	2.46×10^{-5}	0.022	3.26×10^{-6}	1.96×10^{-4}	/	/

Normalized mass release	NaAlP1	NaAlP-Fe1	FZ-1 ^a	ARM-1 ^b	CVS-IS ^c
Al	0.175	0.000	0.795	0.09	/
Na	0.026	0.009	0.723	0.27	1.1-1.5
Р	0.187	0.010	0.246	/	/
F	0.055	0.005	/	/	/
Fe	/	0.000	<10	0.17	/
Cs	0.204	0.013	/	/	0.06-0.13

Table 6 Performance of sample NaAlP(-Fe) and glass standards versus the durability of known standards and other glasses (g/m²)

^a FZ-1 is an iron phosphate glass waste form made at UMR ($18Na_2O \cdot 26Fe_2O_3 \cdot 46P_2O_5 \cdot 10$ other, 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 53.3 SiO₂, 10.5 B₂O₃, 11.3 Na₂O₃, 3.7 Li₂O₃, 2.4 Al₂O₃, 7.0 Fe₂O₃, 3.9 ZrO₂, and 1.3 Nd₂O₃ and 6.6 others, wt%



Fig. 3 SEM micrographs of surface: a pristine NaALP₂, b NaALP₂ after a 7-day PCT test, c pristine NaALP-Fe1, and d NaALP-Fe1 after a 7-day PCT test

(Fig. 3c). The absence of sharp scratches in Fig. 3c and the absence of a detectable corrosion layer on the surface in Fig. 3d provide clear evidence of the excellent chemical durability of these waste forms as detailed in Table 5.

4 Conclusion

We studied the immobilization of fluoride-containing wastes in phosphate-based glasses. Non-radioactive simulated wastes were added and reacted in air at 950–1200 °C. Waste forms based on NaAIP glass were created by adding mixed fluorides at high loading. The tendency to crystallize increases with concentrations of the simulated waste and with monazite phases (Sm, Ce, Zr)PO₄ observed for

 $x = 20 \text{ mol}\% \text{ MF}_n$ in the NaAlP glass. The addition of the Fe₂O₃ constituent (~10 mol%) to the glass decreases the MF_n loading at which crystallization is observed to 8.5 mol%, but improves the chemical durability. The phosphate chain length is shortened, and the asymmetric bridging oxygen content increases upon increasing the incorporated simulated waste. The PCT analysis for leaching indicates that the dissolution rate for the NaAlP(-Fe) glasses is less than for the borosilicate ARM-1 and CVS-IS glasses used as benchmarks. It is equal to or even less than that for the IP glass FZ-1. This study demonstrates that the MSR wastes containing fluorides can be satisfactorily incorporated into sodium aluminophosphate glasses. The waste forms exhibit good performance with high effective waste loading, low cost, and good stability. It is

expected that this study will contribute to the waste management needs of MSR energy systems.

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