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Immobilization of spent nuclear fuel in iron phosphate glass

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Abstract

Twenty-four iron phosphate compositions (15 wt% wasteloading) were evaluated to determine their suitability for vitrifying Al-clad, highly enriched uranium, spent nuclear fuel (SNF). In half the compositions melted, 80 wt% of the Al_2O_3 in the simulated SNF was removed prior to vitrification. All twenty-four compositions formed homogeneous glasses, many at temperatures as low as 1150°C. As little as 2.5 wt% Na_2O decreased melt viscosity and increased alumina solubility in those glasses of higher alumina contents (7.2 wt% Al_2O_3). None of the glasses contained undissolved uranium compounds as has been found in borosilicate glasses containing as little 4.4 wt% UO_2. The chemical durability (measured by the product consistency test (PCT)) of the iron phosphate wasteforms is as good as, and in many cases up to 15 times better than the approved reference material (ARM-1) borosilicate glass. © 1999 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, the US Department of Energy agreed to accept SNF elements containing US origin fuel from several foreign research reactors [1]. The fuel was accepted and returned to the Savannah River Site (SRS) in order to limit the commercial availability of highly enriched uranium that could potentially be used to produce nuclear weapons.

Although the current US policy is to store commercial SNF, there are several reasons why the SNF elements of SRS will not be placed in long-term storage. The primary reason is that the SNF contains highly enriched uranium (80%) which means there is a greater risk of criticality (nuclear explosion). Additionally, there is a concern about the durability of the Al-cladding of the SNF elements and its corrosion resistance in comparison to the zircalloy cladding more commonly used in commercial nuclear fuel elements.

For these reasons, vitrification of the A1-clad, highly enriched SNF elements is being considered. Current plans call for the SNF elements to be dissolved in a nitric acid solution, the solution fed to a furnace along with glass forming components, and the mixture melted to form a chemically durable glass. The vitrification process would be similar to that now being used to immobilize high level wastes at the defense waste processing facility [2].

Currently, scoping studies are in progress to identify potential glass compositions for vitrifying the SNF. Criteria that must be met by these glasses include good chemical homogeneity, ease of melting (low melt temperature and melt viscosity) and high chemical durability. Once candidate glass compositions are identified, more extensive evaluations will be undertaken to select a final glass composition for vitrifying the SNF elements. At this time, two glass families, borosilicates and iron phosphates, are considered candidates for use [3].

The objective of the current study was to determine the suitability of iron phosphate wasteforms for the vitrification of SNF in terms of their chemical homogeneity, melting temperature and melt viscosity, and chemical durability. A constant waste loading of 15 wt% simulated SNF, selected on the basis of desired production rates and critically risk, was used in the current study [3]. A statistical design matrix was used to formulate two groups of twelve compositions, one containing the SNF in its as-received condition, and one where 80% of the Al_2O_3 from the SNF was removed prior to vitrification. X-ray diffraction (XRD) and

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scanning electron microscopy (SEM) were used to determine the chemical homogeneity of the quenched melts. Finally, the chemical durability of selected wasteforms was determined using the PCT [4].

2. Selection of SNF surrogate composition

The primary components of the Al-clad, highly enriched SNF elements are metallic aluminium and uranium oxide. A small quantity of daughter products (<10% total weight) which are produced during use is also present. For the present study, the waste composition was simplified by ignoring minor components (most were <1 wt%) and normalizing to 100%. Table 1 gives the simplified SNF waste composition converted to oxide form.

Because of the high fissile (U-235) content, the SNF must be diluted to lower enrichments prior to virtrification to avoid criticality risks. The surrogate waste used for the current study contained additional depleted uranium oxide (UO_2) to reduce the enrichment to 8%.

In addition, scoping calculations were performed [3] to determine the glass production rate achievable for various enrichments and waste loadings. This was done to ensure the glass could be produced at a realistic production rate of $\sim 10^6$ pounds per year. In the current study, a wasteloading of 15 wt% (at 8% enrichment) was used. This enrichment is low enough to avoid criticality risks and the waste loading is high enough to give reasonable production rates. The general composition of the wasteform, designated PB100, is given in Table 2. A constant waste loading of 15 wt% is used throughout the current study, but the composition of the iron phosphate base glass was varied.

Table 1
Simplified SNF composition in oxide form

	Mol%	Wt%
Rb_2O	0.03	0.06
SrO	0.17	0.16
Y_2O_3	0.04	0.09
ZrO_2	0.58	0.66
MoO_3	0.46	0.60
RuO_2	0.21	0.26
RhO_2	0.05	0.06
PdO	0.04	0.04
CS_2O	0.12	0.32
BaO	0.14	0.19
La_2O_3	0.06	0.18
Ce_2O_3	0.12	0.36
Pr_2O_3	0.05	0.16
Nd_2O_3	0.18	0.56
Pm_2O_3	0.01	0.02
Sm_2O_3	0.03	0.09
Eu_2O_3	0.00	0.01
UO_2	3.66	8.90
NpO_2	0.02	0.05
PuO_2	0.02	0.05
Al_2O_3	93.99	87.18
Total	100.00	100.00

With additional processing prior to vitrification, up to 80% of the Al_2O_3 in the SNF could be removed. This waste composition would have a much higher U/Al ratio. Because it is often difficult to form a glass containing large amounts of Al_2O_3, this additional processing step may be beneficial. To determine if removing 80% of the Al_2O_3 from the SNF waste before vitrification would be beneficial in terms of glass formation, melt temperature and melt viscosity and chemical durability, twelve compositions were melted with 80% of the Al_2O_3 removed from the SNF. The general composition of this series is also listed in Table 2 and is designated PB20.

3. Composition determination

A statistical design matrix was used to select the base glass compositions in the current study. The design matrix uses predetermined high and low values to produce a set of statistically variable compositions. The values used for Fe_2O_3 and P_2O_5 in the current study, see Table 3, are based on other studies [5–9] of iron phosphate glasses.

A previous study [10] showed that adding 7 wt% CaF_2 to sludge-containing iron phosphate wasteforms increased the glass formation tendency and decreased the melt viscosity without affecting the overall good chemical durability of the wasteform. Consequently, additions of CaF_2 were included in the statistical design matrix (see the 7.5 value in Table 3). In addition, Na_2O was included to determine if the melt temperature and viscosity were decreased without decreasing the chemical durability of the waste form.

For the current study, the sum of the variables in Table 3 were normalized to 85%, the remaining 15 wt% being the SNF. The trial numbers in Table 3 were randomized and the glasses melted in this random order. Two groups of twelve compositions were melted, one for SNF with none of the Al_2O_3 removed (PB100 compositions) and one where 80% of the Al_2O_3 in the SNF was removed (PB20 compositions), see Table 4.

4. Experimental procedure

4.1. Glass formation

Fifty gram batches of the PB100 and PB20 compositions listed in Table 4, were prepared using reagent

Table 2
Weight percent composition of the two groups of iron phosphate wasteforms

Pb 100 compositions (No Al_2O_3 removed from SNF)		Pb 20 compositions (80% Al_2O_3 removed from SNF)	
Component	wt%	Component	wt%
Iron phosphate glass	85.0	Iron phosphate glass	85.0
SNF waste		SNF waste	
Al_2O_3	7.2	Al_2O_3	2.4
UO_2 [a]	7.5	UO_2 [a]	12.1
Premix [b]	0.3	Premix [b]	0.5
Total	100.0	Total	100.0

[a] One half from SNF and one half from depleted UO_2 added for dilution.

[b] Weight percent composition of premix was: 1.57 Rb_2O, 8.36 Cs_2O, 4.18 SrO, 4.96 BaO, 2.35 Y_2O_3, 4.70 La_2O_3, 9.40 Ce_2O_3, 4.18 Pr_2O_3, 15.14 Nd_2O_3, 2.35 Sm_2O_3, 0.26 Eu_2O_3, 15.66 MoO_3, 17.23 ZrO_2, 6.79 RuO_2, 1.83 RhO_2, 1.04 PdO.

Table 3
Statistical design matrix showing the high and low values that were used for the four parameters

	PB100 compositions		PB20 compositions	
	High(+)	Low(−)	High(+)	Low(−)
Fe_2O_3	40.0	20.0	40.0	20.0
Fe_2O_3/P_2O_5	0.35	0.20	0.40	0.25
CaF_2	7.5	0.0	7.5	0.0
Na_2O	7.5	0.0	7.5	0.0
Trial	Fe_2O_3	Fe_2O_3/P_2O_5	CaF_2	Na_2O
1	+	+	−	+
2	+	−	+	+
3	−	+	+	+
4	+	+	+	−
5	+	+	−	−
6	+	−	−	−
7	−	−	−	+
8	−	−	+	−
9	−	+	−	+
10	+	−	+	+
11	−	+	+	−
12	−	−	−	−

grade materials [1] and depleted uranium oxide. [2] All components except the P_2O_5 were weighed and mixed thoroughly in a glass container. Once thoroughly mixed, and just prior to melting, the P_2O_5 was mixed with the batch because of its extremely hygroscopic nature.

The batch was then placed into a high purity Al_2O_3 crucible [3] which was placed inside an electric furnace at room temperature. The furnace was heated to 1250°C in 1–2 h and was held at this temperature for 2 h. The melt was stirred twice with a high purity alumina rod [3] to aid in chemical homogenization. After 2 h, the melt was cast onto a steel plate and cooled to room temperature. The viscosity of each melt was noted as it was stirred and poured at 1250°C. All of the quenched melts were opaque and black in color.

To determine if these wasteforms could be prepared at lower temperatures, five of the PB20 compositions and six of the PB100 compositions were selected on the basis of their homogeneity and range of composition, and melted at 1150°C (Table 5).

4.2. Homogeneity

The homogeneity of the melts was determined using XRD and SEM. The crystalline compounds identified by XRD are given in Tables 4 and 5.

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[1] Fisher Scientific Corp., Fair Lawn, NJ, USA.

[2] Savannah River Laboratory, Aiken, SC, USA.

[3] Vesuvius McDanel, Beaver Falls, PA, USA.

Table 4
Batch composition (wt%) and XRD results for PB100 and PB20 compositions melted at 1250°C

ID#	Base glass components				Simulated SNF			XRD
	Fe_2O_3	P_2O_5	CaF_2	Na_2O	UO_2	Al_2O_3	Premix	
100-1	21.0	60.0	3.9	0.0	7.5	7.2	0.3	$AlPO_4$
100-2	14.2	70.8	0.0	0.0	7.5	7.2	0.3	$AlPO_4$
100-3	22.0	63.0	0.0	0.0	7.5	7.2	0.3	$AlPO_4$
100-4	21.0	60.0	0.0	3.9	7.5	7.2	0.3	glass
100-5	20.1	57.4	3.8	3.8	7.5	7.2	0.3	glass
100-6	13.3	66.7	2.5	2.5	7.5	7.2	0.3	glass
100-7	13.3	66.7	5.0	0.0	7.5	7.2	0.3	$AlPO_4$
100-8	13.3	66.7	0.0	5.0	7.5	7.2	0.3	glass
100-9	20.1	57.4	7.5	0.0	7.5	7.2	0.3	$AlPO_4$
100-10	14.2	70.8	0.0	0.0	7.5	7.2	0.3	$AlPO_4$
100-11	20.1	57.4	0.0	7.5	7.5	7.2	0.3	glass
100-12	12.6	63.0	4.7	4.7	7.5	7.2	0.3	glass
20-1	23.0	57.6	4.3	0.0	12.1	2.4	0.5	glass
20.2	17.0	68.0	0.0	0.0	12.1	2.4	0.5	glass
20-3	24.3	60.7	0.0	0.0	12.1	2.4	0.5	glass
20-4	23.0	57.6	0.0	4.3	12.1	2.4	0.5	glass
20-5	21.9	54.8	4.1	4.1	12.1	2.4	0.5	glass
20-6	15.8	63.3	3.0	3.0	12.1	2.4	0.5	glass
20-7	15.8	63.3	5.9	0.0	12.1	2.4	0.5	glass
20-8	15.8	63.3	0.0	5.9	12.1	2.4	0.5	glass
20-9	21.9	54.8	8.2	0.0	12.1	2.4	0.5	glass
20-10	17.0	68.0	0.0	0.0	12.1	2.4	0.5	glass
20-11	21.9	54.8	0.0	8.2	12.1	2.4	0.5	glass
20-12	14.8	59.1	5.5	5.5	12.1	2.4	0.5	glass

Table 5
PB20 and PB100 compositions (wt%) melted at 1150°C and XRD results

ID#	Base glass components				Simulated SNF			XRD
	Fe_2O_3	P_2O_5	CaF_2	Na_2O	UO_2	Al_2O_3	Premix	
20-3	24.3	60.7	0.0	0.0	12.1	2.4	0.5	glass
20-6	15.8	63.3	3.0	3.0	12.1	2.4	0.5	glass
20-9	21.9	54.8	8.2	0.0	12.1	2.4	0.5	glass
20-11	21.9	54.8	0.0	8.2	12.1	2.4	0.5	glass
20-12	14.8	59.1	5.5	5.5	12.1	2.4	0.5	glass
100-4	21.0	60.0	0.0	3.9	7.5	7.2	0.3	$Al_2O_3/AlPO_4$
100-5	20.1	57.4	3.8	3.8	7.5	7.2	0.3	$AlPO_4$
100-6	13.3	66.7	2.5	2.5	7.5	7.2	0.3	glass
100-8	13.3	66.7	0.0	5.0	7.5	7.2	0.3	glass
100-11	20.1	57.4	0.0	7.5	7.5	7.2	0.3	$AlPO_4$
100-12	12.6	63.0	4.7	4.7	7.5	7.2	0.3	$Al_2O_3/AlPO_4$

4.3. Chemical durability

The chemical durability of the eleven compositions (Table 5) melted at 1150°C was determined by the PCT following the procedures described in ASTM C 1285-94. Approximately 1.5 g glass powder (from −100 to +200 mesh) was immersed in 15 ml of distilled water in a stainless steel vessel and held at 90°C for seven days. After completion of the PCT, the leachate was filtered and the concentration of ions in the leachate solution was measured. Inductively coupled plasma-emission spectroscopy (ICP-ES) was used to determine the concentration of ions released into the leachate solution, except for uranium. Uranium cannot be accurately detected by ICP-ES so the amount of uranium released from the iron phosphate wasteforms was not determined in the present work. The chemical durability of the iron phosphate wasteforms were compared to a reference borosilicate glass (ARM-1) [11].

5. Results

5.1. Glass formation

At 1250°C, the six PB100 compositions containing Na_2O, see Table 4, had a lower viscosity (~5 P) than the six PB100 compositions containing no Na_2O. All the quenched melts appeared glassy after casting, but upon closer inspection, the soda-free compositions were found to contain small (<1 mm) white particles in the glassy matrix. XRD analysis showed that these six soda-free compositions contained a small amount (5%) of crystalline $AlPO_4$ (JCPDS card #11-500) in a glassy matrix (Table 4). SEM and XRD showed that the six compositions containing 2.5–7.5 wt% Na_2O were chemically homogeneous and completely glassy.

On the other hand, all 12 PB20 melts were very fluid at 1250°C having a viscosity of only a few poise. After casting, all of the quenched melts appeared glassy and chemically homogeneous. This was confirmed by XRD and SEM of the quenched melt.

The six PB100 compositions that were free of crystalline material after melting at 1250°C, see Table 4, were also melted at 1150°C to determine if this lower temperature was suitable. The PB100 melts (Table 5) had a viscosity estimated at 20 P at 1150°C. Each quenched melt appeared glassy after casting, but upon closer inspection, four contained small (<1 mm) white particles in a glassy matrix. XRD analysis showed that these white particles were crystalline Al_2O_3 (JCPDS card #19-173) and, or $AlPO_4$ (JCPDS card N0. 10-173) (Table 5). The PB100-6 and 8 compositions were completely glassy when melted at 1150°C and air quenched.

Since all of the PB20 compositions in Table 4 formed chemically homogeneous glasses when melted at 1250°C, the five compositions in Table 5, considered to be representative of the range of compositions, were also melted at 1150°C to determine if this lower temperature was suitable. The PB20 melts at 1150°C had a slightly higher viscosity (estimated at ~20 P) than those melts at 1250°C, but they could still be stirred and poured easily. All five of the quenched melts appeared to be glassy and XRD and SEM analysis confirmed that no crystalline material was present (Table 5).

In summary, the PB100 (high Al_2O_3 content) compositions in Table 5 formed a homogeneous glass when melted at 1250°C only when 2.5–7.5 wt% Na_2O was present in the batch. Soda-free compositions contained ~5% crystalline $AlPO_4$ in the glassy matrix. When the soda-containing compositions were melted at 1150°C, Table 5, only two were completely glassy and the other four contained ~5% crystalline $AlPO_4$ or Al_2O_3. All of the PB20 compositions in Tables 4 and 5 formed a homogeneous glass when melted at 1250°C and 1150°C, respectively.

5.2. Chemical durability

Fig. 1 shows the concentration of P, Na, and Ca ions found in the PCT leachate from the PB20 and PB100 wasteforms melted at 1150°C. Phosphorus was the most abundant ion in solution, but the absolute quantity was small, only 4–123 ppm. Small amounts, usually <20 ppm Ca and Na were also in the leachate from the wasteforms containing CaF_2 and Na_2O. Fe_2O_3 and Al_2O_3 were present in large concentrations in all the wasteforms (up to 24.3 and 7.2 wt%, respectively) but barely detectable amounts ($\leqslant 3$ ppm) of Fe or Al were present in the leachate.

Fig. 2 shows the total ion release from the iron phosphate wasteforms containing SNF compared to the ARM-1 reference borosilicate glass. The iron phosphate wasteforms had a total ion release that ranged from 10 to 180 ppm compared to the ARM-1 reference glass (150 ppm). The total ion release from the iron phosphate wasteforms was dependent on the Fe_2O_3 content. Wasteforms with a higher Fe_2O_3 content (20–25 wt%) had a better durability than those with a lower Fe_2O_3 content (12–16 wt%). For the wasteforms of higher Fe_2O_3 content, the total ion release into distilled water was ~10

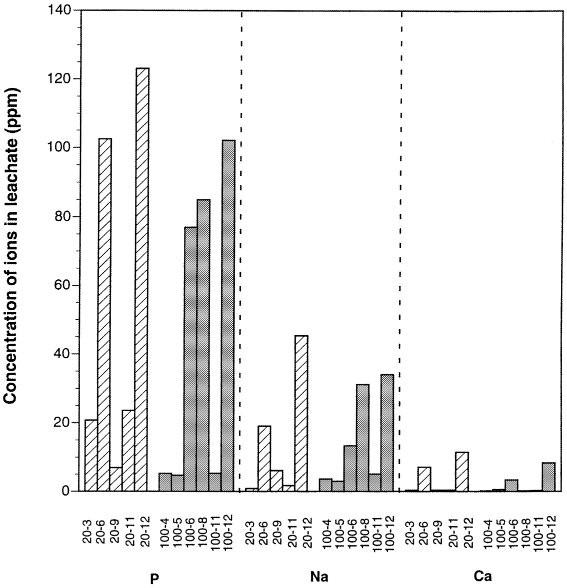

Fig. 1. Concentration of P, Na, and Ca ions in the leachate solution after PCT testing of the PB20 (hashed bars) and PB100 (solid bars) iron phosphate wasteforms containing 15 wt% simulated SNF and melted at 1150°C. PCT conducted in distilled water at 90°C for seven days.

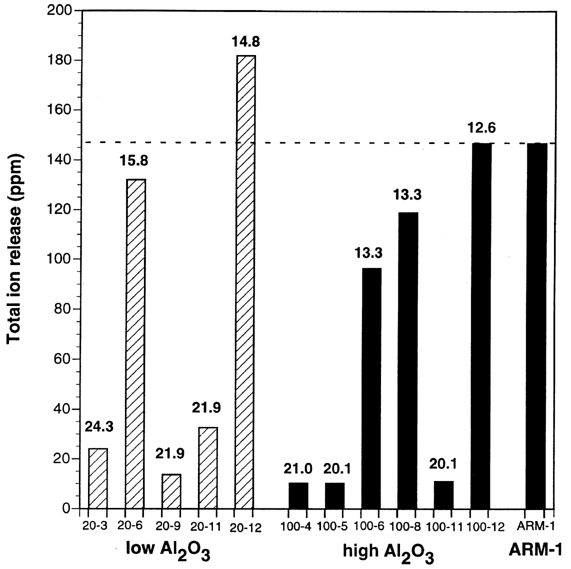

Fig. 2. Total ion concentration in the leachate (distilled water) after PCT of iron phosphate wasteforms made with 15 wt% simulated SNF melted at 1150°C. Fe_2O_3 content of each wasteform is given above each bar. Striped bars represent wasteforms made with SNF with 80% Al_2O_3 removed and solid bars represent wasteforms made with SNF with none of the Al_2O_3 removed. PCT conducted in distilled water at 90°C for seven days. The ARM-1 borosilicate reference glass is shown for comparison.

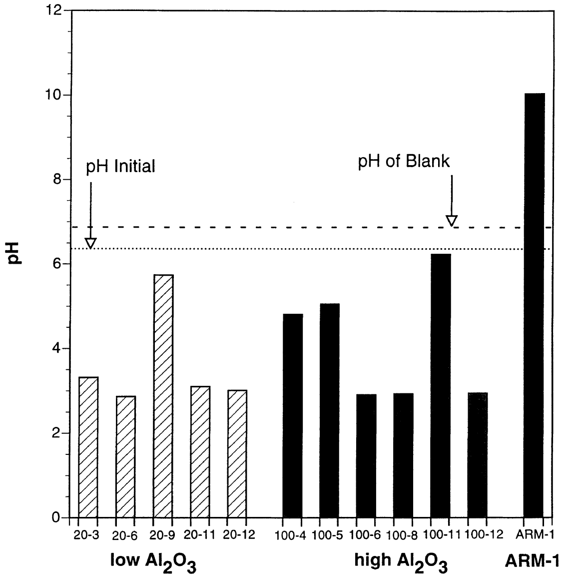

Fig. 3. pH of leachate solution after PCT of iron phosphate wasteforms containing 15 wt% simulated SNF and melted at 1150°C. Striped bars represent wasteforms made with SNF with 80% Al_2O_3 removed and solid bars represent wasteforms made with SNF with none of the Al_2O_3 removed. PCT conducted in distilled water at 90°C for seven days. The ARM-1 borosilicate reference glass is shown for comparison. The initial and final pH's of a blank is also given for reference.

ppm which is 15 times lower than the total ion release from the ARM-1 reference borosilicate glass (150 ppm). Only one iron phosphate wasteform, PB20-12, released more ions than the ARM-1 borosilicate glass. Clearly, a higher alumina content improved the chemical durability of the wasteforms of lower, 12–15 wt% Fe_2O_3 content.

At the conclusion of the PCT test, the pH of the leachate solution was measured and compared to the pH of a blank (a vessel containing only distilled water). Fig. 3 shows that the pH of the leachate from the iron phosphate wasteforms is neutral to acidic ($pH = 3–6$) while the leachate from the ARM-1 reference glass has a much higher final pH ($\sim$10). This is due to the 'buffering action' that results from the simultaneous release of P along with Na and Ca during the dissolution of the iron phosphate wasteforms. Since iron phosphate glasses have their highest chemical durabilities in neutral to slightly acidic solutions [8], this 'buffering action' contributes highly to their low dissolution rate.

6. Discussion

6.1. Glass formation

The most extensive use of phosphate glasses for vitrifying nuclear wastes has been in the former Soviet Union [12], where several thousand tons of nuclear waste has been vitrified using a sodium aluminophosphate glass. Lead phosphate glasses, some containing iron oxide, have also been investigated [13] for vitrifying nuclear waste, but have not been used in actual practice. The iron phosphate glasses investigated in the present work have properties that are significantly different from the traditional phosphate glasses such as the sodium aluminophosphate glass used in the former Soviet Union.

For example, the chemical durability of a phosphate glass is dramatically increased by adding iron. In fact, the dissolution rate of a sodium phosphate glass can be decreased nearly five orders of magnitude [6] when it contains 20 wt% Fe_2O_3. Many studies [5,6,8–10] have focused on determining why iron phosphate glasses have such an excellent chemical durability, comparable to the chemical durability of borosilicate glasses such as the CVS-IS, developed at Hanford, the R7T7, developed in France, and the DWPF-EA, used at Savannah River.

Mössbauer spectroscopy [5,6,14] on glasses near the ferric pyrophosphate ($2Fe_2O_3{\cdot}3P_2O_5$) composition show that approximately 20% of the Fe^{3+} which is present in the batch as Fe_2O_3 is reduced to Fe^{2+} during melting in air. The glass, therefore, is more accurately described as a ferric/ferrous pyrophosphate glass. The structure of such a glass is believed to be close to that of the ferric/

ferrous pyrophosphate crystal [15] (Fe_2^{3+} Fe^{2+} $(P_2O_7)_2$), whose structure contains 33.3% Fe^{2+} in an unusual trigonal prism coordination as shown in Fig. 4. The unusually large quadrupole splitting in the Mössbauer spectrum of these glasses [16] is a result to the unusual coordination of Fe^{2+} in the glass. Typically Fe^{2+} present in a phosphate glass occupies octahedral coordination and acts as a network modifier [6]. For good chemical durability and glass formation, iron in the 3+ valence state is typically preferred.

Assuming the glass is similar to the crystal, the glass would contain individual P_2O_7 (pyrophosphate groups) bonded together by Fe–O groups. The excellent chemical durability of the ferric/ferrous pyrophosphate glass is attributed to the large number of Fe–O–P bonds which are more hydration resistant than P–O–P bonds [17]. In the structure in Fig. 4, only one out of the 14 oxygens participate in the P–O–P bonds.

One of the primary components present in the iron phosphate glasses in the current study is UO_2. In glass, uranium is typically present in the 4+, 5+ and 6+ valence states, and less commonly as U^{3+} in halide melts [18]. The chemistry of uranium in silicate and borosilicate glasses has been studied since these glasses are candidates for nuclear waste disposal glasses [19,20]. As phosphate glasses have become of more interest for nuclear waste disposal, studies of uranium in phosphate glasses have been undertaken also.

In phosphate glass, as with the silicate glasses, uranium may be present as 4+, 5+ or 6+ ions. [18]. The coordination number of the U^{4+} ion in most phosphate glasses is eight. Typically, only about 10 wt% UO_2 is soluble in phosphate glasses before UO_2 precipitates from the glass. U^{5+} in phosphate glass occurs as a $(UO_2)^+$ 6-coordinated species. Finally, U^{6+} most likely exists as the $(UO_2)^{2+}$ uranyl ion within the glass. U^{6+} may form complexes between the uranyl ion and phosphate (PO_4) groups, much like that proposed for the Fe^{3+} ions in iron phosphate glasses [18].

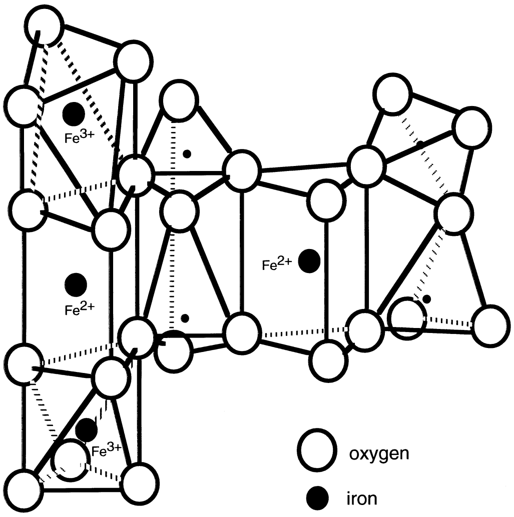

Fig. 4. Structure of crystalline ferric/ferrous pyrophosphate β-$Fe_3(P_2O_7)_2$ from Ref. [15].

A study [18] of sodium aluminophosphate glasses containing up to 15 wt% U_3O_8 showed that the uranium valence depends strongly on the melting atmosphere. In reducing conditions, U^{4+} was primarily present which lead to the precipitation of UO_2 from the melt. Under oxidizing conditions, U^{5+} and U^{6+} were present which are both very soluble in the phosphate glass. Since the PB20 wasteform contained up to 12 wt% UO_2 (Table 4) without precipitating UO_2 from the glass, it is likely that at least a portion of the uranium is present as U^{5+} or U^{6+} in the iron phosphate glasses.

It should be noted that since uranium is present in an iron phosphate glass in the current study, the redox chemistry between the U^{4+}–U^{5+}–U^{6+} and the Fe^{2+}–Fe^{3+} systems is a concern. When iron phosphate glasses are melted in air, about 20–30% of the iron is present as Fe^{2+} and the balance is present as Fe^{3+}. Recent work [14] has shown that when uranium is present in iron phosphate glasses it acts as an oxidizing agent, thereby reducing the Fe^{2+} content from 20% or 30% to about 10%. The lower Fe^{2+} content is considered beneficial from both a property and glass stability view point. For maximum chemical durability, there is a slight preference for Fe^{3+} as opposed to Fe^{2+} in the iron phosphate glasses [6].

Also, a high concentration of Fe^{2+} has been found [14,21] to increase the crystallization tendency and when the Fe^{2+} concentration exceeds about 60% nearly all the iron phosphate melts crystallize during cooling. This behavior suggests that the Fe^{2+} ions, which are in octahedral coordination, act as structural modifiers in iron phosphate glass.

In the current study, Fe^{2+}/Fe^{3+} concentrations were not determined, but the exceptionally good chemical durability of the iron phosphate wasteforms indicates that the iron is predominately present as Fe^{3+}.

A recent study [3] focusing on the immobilization of SNF in a borosilicate glass (SRS Frit 165) reported that uranium compounds crystallized from a melt containing only 4.4 wt% UO_2. This is in strong contrast to the iron phosphate glasses in the current study which were able to accommodate up to 12 wt% UO_2. In fact, even larger amounts of UO_2 (22 wt%) have been vitrified in an iron phosphate glass [16]. In terms of uranium solubility alone, wasteloadings much higher than the 15 wt% SNF used in the current study could be achievable with the iron phosphate glasses.

In a previous study [22] of waste-containing lead iron phosphate glasses, Al_2O_3 present in the waste caused the formation of $AlPO_4$ crystals. In the current study, all of the PB20 wasteforms (containing 2.4 wt% Al_2O_3) were chemically homogeneous, as were the PB100 wasteforms (containing 7.2 wt% Al_2O_3) which contained between 2.5 and 7.5 wt% Na_2O. All of the soda-free PB100 wasteforms contained $AlPO_4$ crystals. It appears that adding a small amount of Na_2O prevents the crystallization of $AlPO_4$ from the PB100 compositions.

Although up to 80% of the Al_2O_3 in SNF could be removed with additional processing, there are obvious advantages to vitrifying the SNF waste directly. The present study shows that SNF can be directly vitrified to an iron phosphate glass without removing any of the Al_2O_3 as long as a small amount (as little as 2.5 wt%) of Na_2O is present in the batch.

Soda not only improved the glass formation tendency for the high alumina (PB100) waste compositions, but it also lowered the melt viscosity even in small (2.5 wt%) concentrations. Most of the soda-containing PB100 melts had a viscosity of a few Poise at 1250°C and a viscosity estimated at $\sim$20 P at 1150°C. At the same time, a few weight percent soda did not appear to lower the chemical durability of the wasteforms, see Fig. 2. For these reasons, it is considered beneficial to add a small amount of soda to the batch when vitrifying SNF.

Calcium fluoride was also added to the wasteforms for the purpose of determining if the glass formation, melt viscosity, or chemical durability would be affected. The present results indicate that adding calcium fluoride to the iron phosphate wasteforms had no noticeable effect.

6.2. Chemical durability

The excellent chemical durability of the iron phosphate glasses has been attributed primarily to the presence of Fe–O–P bonds which are more hydration resistant than P–O–P bonds [17]. Since the number of Fe–O–P bonds depends upon the iron content of the glass, it is expected that the chemical durability would be higher for wasteforms with a higher Fe_2O_3 content.

As expected, the wasteforms in Fig. 2 of higher iron content ($Fe_2O_3 = 20$–25 wt%) typically released a much lower quantity (15–20%) of ions than the wasteforms with a lower iron content ($Fe_2O_3 = 12$–16 wt%).

In addition to the Fe–O–P bonds, Al–O–P bonds should also be present [23] when an iron phosphate glass contains alumina. Like the Fe–O–P bonds, Al–O–P bonds are also more hydration resistant than P–O–P bonds [23]. The dissolution rate is plotted versus the total number of Fe–O–P and Al–O–P bonds per mole in Fig. 5 and decreases as the number of Fe–O–P and Al–O–P bonds increase. The total number of Fe–O–P and Al–O–P bonds was calculated from the batch composition (Table 4) assuming all of the iron present in the glass forms Fe–O–P bonds and no Fe–O–Fe bonds are formed.

The results from the current study are consistent with data from studies on other iron phosphate glasses [5,24], where the dissolution rate is also found to decrease with increasing number of Fe–O–P and Al–O–P bonds, see Fig. 5. The data points plotted in Fig. 5 tend to fit two lines rather than one. The points on the upper line are for phosphate glasses which contain either iron or alumina, whereas the points for the lower line are for glasses that contain both iron and alumina. This may indicate the benefit of an increased chemical durability when a phosphate glass contains both iron and alumina.

Another factor contributing to the good durability of the iron phosphate wasteforms is the self-buffering action which occurs when a phosphate glass dissolves in distilled water. At the conclusion of the PCT, the leachate solutions in which the phosphate glasses were tested were neutral to slightly acidic (pH 3–6) while the pH of the leachate from the ARM-1 borosilicate glass had increased from 7 to 10 (Fig. 3). The buffering effect of phosphate glasses occurs because any phosphate groups dissolving from the iron phosphate glass tend to lower the pH which counteracts the increase in pH caused by the release of the alkali and alkaline earth cations when they ion exchange with H_3O^+ ions. This buffering action helps to maintain a neutral to acidic leachate pH which helps to minimize the dissolution rate

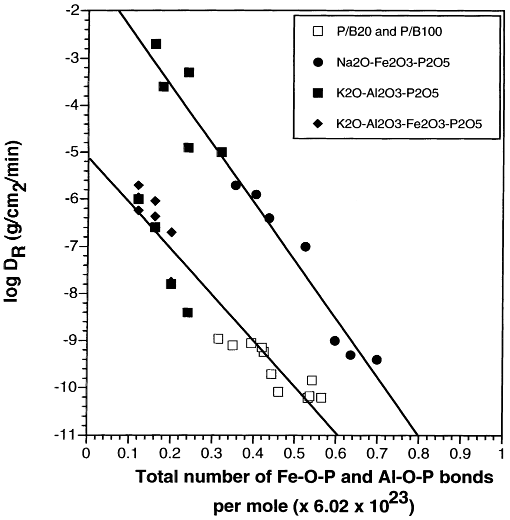

Fig. 5. Log dissolution rate (D_R) of iron phosphate glasses containing 15 wt% SNF measured in distilled water at 90°C (open symbol) plotted vs. total number of Fe–O–P and Al–O–P groups calculated from the batch. Sodium iron phosphate (●) glasses from Ref. [6], potassium aluminium phosphate (■) glasses from Ref. [24] and potassium iron aluminium phosphate (◆) glasses from Ref. [24] plotted for comparison. Top curve for glasses that contain either Fe_2O_3 or Al_2O_3 singularly. Bottom curve is for glasses which contain both Fe_2O_3 and Al_2O_3.

because iron phosphate glasses have their lowest dissolution rate in neutral solutions [8].

Finally, it should be emphasized that though the current work was intended as a scoping study of a wide range of iron phosphate compositions, all but one (PB20-12 in Fig. 2) of the iron phosphate wasteforms had a total ion release lower than the ARM-1 reference borosilicate glass. The overall good chemical durability of the iron phosphate wasteforms in the current study whose composition covers a fairly wide range suggests that the chemical durability of iron phosphate glasses is not overly dependent on composition.

6.3. Advantages of vitrifying SNF in iron phosphate glass

The primary reason iron phosphate glasses were studied for the vitrification of SNF is that they can accommodate 22 wt% UO_2 [16] and form a homogeneous glass. On the other hand, Frit 165 borosilicate glasses [3] contained crystalline uranium compounds when only 4.4 wt% UO_2 was present. In the current work, a constant wasteloading of only 15 wt% simulated SNF was used successfully, but the high solubility of uranium in iron phosphate glass suggests a much higher waste loading may be possible. The maximum SNF wasteloadings that can be vitrified in an iron phosphate glass remains to be determined.

An additional advantage to using iron phosphate glass to vitrify SNF is that lower melting temperatures could be used. Iron phosphate glasses have a viscosity 100–200 cP [10] at temperatures as low as 1150°C. Borosilicate glasses can be melted at 1150°C as well, but their higher viscosity (several hundred Poise) requires longer melting times and lower production rates, all other factors being equal. For this reason, borosilicate glasses are typically melted above 1150°C. Lower melting temperatures are preferred because of lower energy costs, lower potential for volatility, and longer refractory/furnace life.

Finally, many nuclear wastes, such as SNF, can be vitrified to iron phosphate wasteforms by only adding small amounts of Fe_2O_3, P_2O_5 and Na_2O to the nuclear waste. The glass forming components for iron phosphate compositions come from any convenient source such as Fe_2O_3, Fe_3O_4, H_3PO_4, Na_2CO_3, etc. In contrast, the borosilicate wasteforms require more and larger amounts of components (B_2O_3, Li_2O, CaO, Na_2O, SiO_2 and others) to form a glass. These glass forming components are typically added as a glass powder or frit. However, iron phosphate glass forming components can be added directly to the nuclear wastes rather than added as a glass frit. This eliminates the additional costly step of melting the frit separately, sizing the frit to the proper size particles, and transporting it to the site where it will be fused with the nuclear waste.

7. Conclusion

Iron phosphate glasses containing 15 wt% SNF (8% enrichment) were easily melted at 1150°C and were free of crystalline uranium compounds, which is in contrast to UO_2 containing borosilicate glasses studied previously. [7] It was not necessary to remove any of the Al_2O_3 from the SNF to form a homogeneous glass, although a small amount of Na_2O helped prevent devitrification in compositions containing 7.2 wt% Al_2O_3.

The current work was a scouting study so wasteforms of both high and low chemical durability were expected. However, all of the iron phosphate wasteforms had good chemical durability such that the total quantity of ions released in the PCT test was less than the ARM-1 reference borosilicate glass, with one exception, see Fig. 3. In fact, the total ion release from the majority of the iron phosphate glassy wasteforms (~10 ppm) was up to 15 times lower than the amount released from the ARM-1 borosilicate glass (150 ppm). Although the results from a single PCT cannot definitively predict the long term stability of a potential nuclear waste disposal glass, they do illustrate the generally good chemical durability of the iron phosphate wasteforms.

The chemical durability of the glassy iron phosphate wasteforms increased as the total number of Fe–O–P and Al–O–P bonds increased in the wasteform. This relationship was also followed when the dissolution rate of iron phosphate glasses from other studies were plotted against the number of Fe–O–P and Al–O–P bonds. The lower D_R of glasses containing both Fe_2O_3 and Al_2O_3 indicates that glasses made with a mixture of Fe and Al have a better chemical durability than glasses made with either Fe_2O_3 or Al_2O_3 alone.

Iron phosphate glasses have several advantages for immobilizing SNF due to their ease of processing. For example, the SNF would not require pre-processing to remove Al_2O_3 as long as ~2.5 wt% Na_2O was added to the batch. The only components that would need to be added to the waste to form a homogeneous glass would be convenient sources of iron, phosphorus and sodium (for example Fe_2O_3, Fe_3O_4, H_3PO_4, $NH_4H_2PO_4$ and Na_2CO_3). The glassy wasteforms would then be melted at 1150°C in 2 h.

In short, iron phosphate glasses, due to their high uranium solubility, high chemical durability, low melting temperature, and fluidity, make them ideal candidates for vitrifying aluminum-clad SNF.

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