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**IRON PHOSPHATE GLASSES: AN ALTERNATIVE FOR VITRIFYING CERTAIN
NUCLEAR WASTES**

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EXECUTIVE SUMMARY

During the past year, iron phosphate glasses containing the following three types of nuclear waste, as recommended by the Tank Focus Area (TFA) group, have been investigated.

- (1) a high sodium/sulfate Hanford Low-Activity Waste (LAW)
- (2) a High Chrome Waste (HCW) at Hanford, and
- (3) a Sodium Bearing Waste (SBW) at Idaho National Engineering and Environmental Laboratory (INEEL)

Over three hundred trial melts, ranging in size from 50 g to more than 10 kg, have been evaluated. The experimental work consisted of

- (1) evaluating the melting behavior and characteristics,
- (2) measurement of the viscosity and electrical conductivity of promising melts over their melting range,
- (3) determining the chemical durability by the PCT and VHT methods of both glassy and partially crystallized iron phosphate wasteforms,
- (4) determining the solubility limit for chrome oxide in selected iron phosphate melts,
- (5) examining the feasibility of melting iron phosphate glasses by Cold Crucible Induction melting (CCIM), Hot Crucible Induction Melting (HCIM), and Microwave Melting,
- (6) and measuring the corrosion of Inconel 690 and 693, potential electrode materials, in an iron phosphate melt.

In the past year, the results of the above experimental work have been described in eight technical papers and reports that have been submitted for publication.

As an alternative glass for waste vitrification, the maximum waste loading of the three wastes listed above in iron phosphate glasses was found to be 75 wt% for the high chrome HLW at Hanford, 40 wt% for the sodium bearing waste (SBW) at INEEL, and 35 wt% for the high sodium, high sulfate, LAW at Hanford. Iron phosphate glasses as well as deliberately partially crystallized samples met the current DOE requirements for chemical durability.

1. INTRODUCTION

The United States of America has accumulated a large amount of nuclear wastes that is now stored temporarily at different Department of Energy (DOE) sites across the country. These wastes are spent fuel from nuclear reactors; liquid and solid wastes from spent fuel reprocessing for plutonium extraction; transuranic wastes which include clothing, tools, and other materials contaminated with plutonium, neptunium, and etc.; hazardous radioactive wastes from hospitals, research institutes, and remnants of decommissioned power plants; and uranium mill tailings. These wastes must be managed properly to avoid contaminating the environment and to minimize risks to the health of humans and other living species. The liquid wastes are of most concern because of their high mobility and radioactivity.

The overall idea behind the clean-up process for the mobile liquid waste is to immobilize the waste in a stable host matrix. Vitrification of liquid nuclear waste in a suitable glass is considered the most effective process for waste disposal, and DOE currently approves only borosilicate (BS) type glasses for such use. However, many liquid wastes, presently awaiting disposal, have complex and diverse chemical compositions, and often contain components such as phosphates, sulfates, chrome oxide, and heavy metals that are poorly soluble in BS glasses [1,2]. Such problematic wastes can be pre-processed and/or diluted to compensate for the incompatibility with the BS glass matrix, but this can be an expensive solution and involves risk to the operators. It is more desirable to avoid pre-treating or diluting the waste since these alternatives will greatly increase the wasteform volume and the overall time and cost for vitrification. Direct vitrification using an alternative glass that can incorporate the problematic components in the waste should minimize the wasteform volume and overall cost.

Our previous studies [3-24] have shown that iron phosphate glasses have the potential for vitrifying many nuclear wastes that are either completely unsuitable or poorly suitable in BS glasses in terms of reducing the wasteform volume and disposal cost. The present research is a continuation of our previous work and is focused on three specific wastes that are considered high priority by the Tank Focus Area (TFA) Report of Hanford [1]. The main objectives are to investigate the feasibility of vitrifying these wastes in iron phosphate glasses, with an aim to produce a wasteform having a higher waste loading combined with acceptable chemical durability, and to acquire

scientific and engineering knowledge that is needed to utilize iron phosphate glasses for vitrifying selected nuclear wastes on a production scale. The feasibility for melting iron phosphate glasses by the Cold Crucible Induction Melter (CCIM), Hot Crucible Induction Melter (HCIM), and Microwave Oven techniques has also been explored.

2. RESEARCH PROGRESS

At the recommendation of TFA, the following three types of nuclear wastes are being investigated.

- (1) a high sodium/sulfate Hanford Low-Activity Waste (LAW)
- (2) a High Chrome Waste (HCW) at Hanford, and
- (3) a Sodium Bearing Waste (SBW) at Idaho National Engineering and Environmental Laboratory (INEEL)

These wastes were chosen primarily because of their high sodium, high sulfate, and high chrome content, all of which can seriously reduce the maximum waste loading in BS glasses [1,2]. The iron phosphate glasses were expected to have a higher solubility limit for those components based on our previous studies [3-24] and, therefore, potentially higher waste loadings than can be achieved in BS glasses.

For the twelve months covered by this annual report, more than 300 iron phosphate glass wasteforms containing varying amounts of simulated LAW, HCW, and SBW were prepared and investigated. The results for all three wastes are very promising.

2.1. Hanford Low-Activity Waste (LAW)

The DOE's Hanford Site in Washington State produced more than 55 million gallons of radioactive waste, which is stored in 177 underground storage tanks [25]. The waste will be retrieved from these tanks and separated into Low-Activity Waste (LAW) and High-Level Waste (HLW) fractions which will be separately vitrified in the Hanford Tank Waste Treatment Plant (WTP). The Hanford LAW composition is high in sodium and sulfate (Table 1). The maximum loading of this waste in the borosilicate (BS) waste glass is largely determined by the allowable fraction of sulfate in the waste. If the sulfate loading did not limit the loading of LAW in glass then the amount of glass produced at Hanford could be reduced by as much as 50% [26].

Table 1. Summary of Hanford LAW composition (wt% non-volatile oxides and halogens) and the simplified composition used in present study.

Oxide (wt%)	Min	Ave	Max	Simplified*
Al ₂ O ₃	0.68	13.19	35.62	4.4
Cl	0.00	0.89	2.61	0.6
Cr ₂ O ₃	0.00	0.33	1.64	0.4
F	0.00	0.94	5.38	1.6
K ₂ O	0.00	1.02	16.06	0.0
MoO ₃	0.00	0.01	5.06	0.0
Na ₂ O	32.24	75.25	97.93	75.3
P ₂ O ₅	0.29	4.08	48.72	7.7
SiO ₂	0.01	0.86	7.42	0.5
SO ₃	0.02	3.19	14.11	9.5
Other	0.01	0.23	1.61	0.0
Total		99.99		100.0

* LAW wastes with SO₃ concentrations above 7 wt% were averaged & simplified and used in iron phosphate glasses.

2.1.1. Glass Preparation. The appropriate amounts of the raw materials (Table 2) were mixed in a sealed plastic container for sufficient time to produce a homogeneous mixture. The IP27LAW, IP30LAW, IP32LAW, and IP35LAW glasses contained 27, 30, 32, and 35 wt% of the simplified Hanford LAW (given in the right-hand column of Table 1) and 73, 70, 68, and 65 wt% Glass Forming Additives (GFA), respectively. Table 2 lists the glass forming additives and possible raw materials required to produce these iron phosphate glasses. The most convenient method of combining the majority of the GFA constituents with the Hanford LAW is to melt a glass frit. The GFA constituents, marked with an “asterisk” in Table 2, have been successfully melted as a glass frit. The amount of P₂O₅ used in the GFA included an additional 5 wt% of the required amount in order to compensate for potential volatilization losses of P₂O₅ during melting of the frit (which will reduce P₂O₅ loss during LAW vitrification). This glass frit combined with the appropriate silica and alumina constitute the GFA.

Table 2. Composition of the iron phosphate glass (IP27LAW) containing 27 wt% LAW and the raw materials used.

Oxide (wt%)	Hanford LAW	27 wt% LAW	73wt% GFA	Raw material for GFA	IP27LAW Glass
Al ₂ O ₃	4.4	1.2	15.0	Al ₂ O ₃ , Al(OH) ₃ , kaolinite: Al ₂ SiO ₅ (OH) ₄	16.2
Cl	0.6	0.2	0.0		0.2
Cr ₂ O ₃	0.4	0.1	3.3*	Cr ₂ O ₃ , chromite: (Mg,Fe)O-(Cr,Al) ₂ O ₃	3.4
F	1.6	0.4	0.7*	CaF ₂	1.1
Na ₂ O	75.3	20.3	0.0		20.3
P ₂ O ₅	7.7	2.1	27.1*	P ₂ O ₅ , H ₃ PO ₄ , NH ₄ H ₂ PO ₄	29.2
SiO ₂	0.5	0.1	12.3	SiO ₂ , kaolinite: Al ₂ SiO ₅ (OH) ₄	12.4
SO ₃	9.5	2.6	0.0		2.6
Bi ₂ O ₃			2.7*	Bi ₂ O ₃	2.7
Fe ₂ O ₃			7.2*	Fe ₂ O ₃ , iron ore, iron phosphate waste**	7.2
La ₂ O ₃			1.2*	La ₂ O ₃	1.2
ZrO ₂			2.7*	ZrO ₂ , ZrSiO ₄	2.7
CaO			1.0*	CaF ₂	1.0
Total	100.0	27.0	73.2		100.2

* denotes GFA constituents that can be melted as a glass frit.

** Phosphate chemical conversion coating processes are used by the metal products fabrication industry to condition metal surfaces for subsequent processes such as painting. This processing generates iron phosphate waste in the form of a sludge that can be used in iron phosphate glasses.

All these iron phosphate glasses (IP27LAW, IP30LAW, IP32LAW, and IP35LAW) were melted in an electric furnace in air at 1000-1250°C for 2-3 hours in a dense high silica (DFC 83% silica 17% alumina) crucible. Each melt was stirred 3 to 4 times with a fused silica rod to insure chemical homogeneity. After melting, the glass was cast into bars that were annealed at 430-520°C for 5 hours and cooled to room temperature overnight in the annealing furnace. The annealing temperature was determined from differential thermal analysis (DTA) measurements.

Continuous melting experiments were also conducted for selected glasses (Figure 1). The batch was continuously charged to a crucible from the top using a mechanical feeder and the glass melt was drained to a cast mold through a hole at the bottom of the crucible.

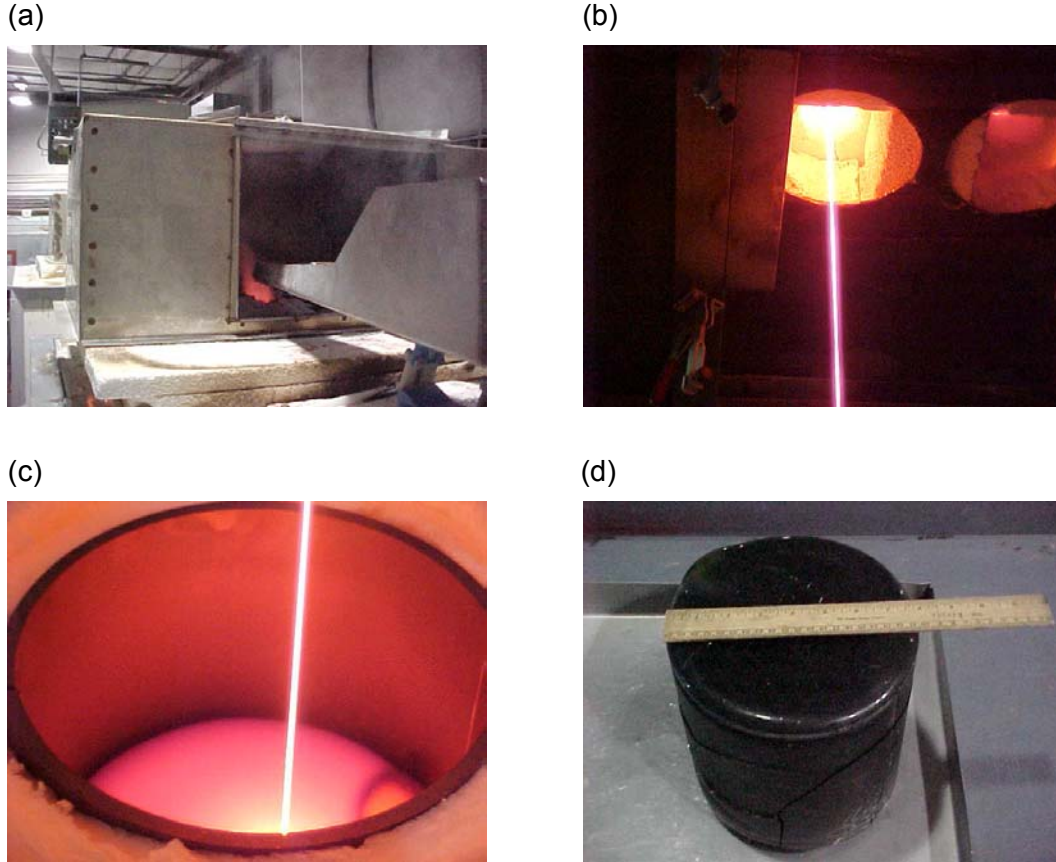


Figure 1. Continuous melting of iron phosphate wasteform (IP27LAW) at 1200°C. (a) continuous charging of dry batch into crucible; (b) bottom view of furnace where iron phosphate glass is being drained into cast iron mold; (c) close up of iron phosphate glass accumulating in the mold; (d) as cast iron phosphate glass wasteform (~8" x ~10").

A sample of the IP27LAW melt was cooled according to the simulated immobilized LAW canister centerline cooling (CCC) profile [27]. For the IP32LAW and IP35LAW, samples were slowly cooled ($\sim 2^{\circ}\text{C}/\text{min}$), designated as SC, in the furnace instead of performing the fully programmed CCC treatment. The controlled cooling experiment was not performed for the IP30LAW melt.

2.1.2. Glass Formation. The chemical composition of each glass was calculated from the batch composition and was also measured by inductively coupled plasma-emission spectroscopy (ICP-ES) as well as by the Leco method for sulfur analysis (Table 3). The batch and measured compositions were in reasonable agreement.

Table 3. Batch and analyzed (ICP-ES) compositions (wt%) of iron phosphate glasses containing 27, 30, 32, and 35 wt% LAW (IP27LAW, IP30LAW, IP32LAW, and IP35LAW, respectively).

Oxide (wt%)	IP27LAW		IP30LAW		IP30LAW-A**		IP30LAW-C**		IP32LAW		IP35LAW	
	Batch	ICP-ES	Batch	ICP-ES	Batch	ICP-ES	Batch	ICP-ES	Batch	ICP-ES	Batch	ICP-ES
Al ₂ O ₃	16.2	18.5	1.3	3.4	11.3	13.6	1.3	3.0	15.4	14.3	14.9	16.4
Cl	0.2	NM	0.2	NM	0.2	NM	0.2	NM	0.2	NM	0.2	NM
Cr ₂ O ₃	3.4	3.0	0.1	0.1	0.1	0.1	3.1	2.8	3.2	2.3	3.0	2.5
F	1.1	NM	0.5	NM	0.5	NM	0.5	NM	1.1	NM	1.1	NM
Na ₂ O	20.3	19.2	22.6	23.1	22.6	22.4	22.6	22.5	24.1	24.5	26.4	25.1
P ₂ O ₅	29.2	27.8	52.2	53.9	52.2	52.6	52.2	54.0	27.7	26.1	26.8	26.2
SiO ₂	12.4	15.4	0.2	0.1	0.2	0.1	0.2	0.1	11.7	14.6	11.2	15.7
SO ₃	2.6	1.1*	2.9	1.3*	2.9	1.5*	2.9	1.5*	3.0	2.1*	3.3	2.4*
Bi ₂ O ₃	2.7	NM	NP	NM	NP	NM	NP	NM	2.5	NM	2.4	NM
Fe ₂ O ₃	7.2	7.1	20.0	17.2	10.0	9.4	17.0	15.3	6.7	6.9	6.4	6.7
La ₂ O ₃	1.2	NM	NP	NM	NP	NM	NP	NM	1.1	NM	1.1	NM
ZrO ₂	2.7	NM	NP	NM	NP	NM	NP	NM	2.5	NM	2.4	NM
CaO	1.0	1.3	NP	NM	NP	NM	NP	NM	1.0	1.6	1.0	1.2
Total	100.2	93.4	100.0	99.1	100.0	99.7	100.0	99.2	100.2	92.4	100.2	96.2

* Analyzed by Leco (All of the Leco and ICP-ES analyses in the present study were conducted by Acme Analytical Laboratories Ltd. in Vancouver, Canada.).

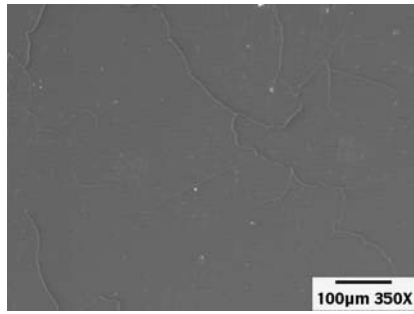
NM = not measured.

NP = not present.

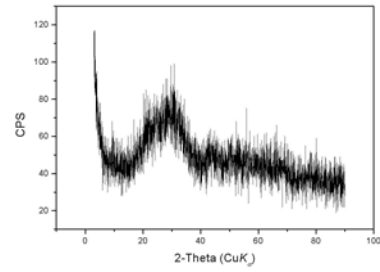
** IP30LAW-A and IP30LAW-C glasses are wastefoms slightly modified from the IP30LAW composition. An additional 10 wt% Al₂O₃ or 3 wt% Cr₂O₃ was added to the IP30LAW glasses, respectively, by replacing the same amount of Fe₂O₃.

No evidence of any type of segregation was found either from the visual appearance of the crucible or scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis or powder X-ray diffraction (XRD) of the quenched melt (Figure 2). There was no observable sulfate “gall” layer on the surface of the molten iron phosphate glass, as has been reported [28] for borosilicate melts that contained > 1 wt% SO₃. Leco analysis indicated that 42 to 73% of the SO₃ originally present in the waste was retained in the glasses (Table 3). The sulfate retention (ranging from 1.1 to 2.4 wt% SO₃) in iron phosphate glasses was found to depend upon the glass composition and melting conditions such as atmosphere and temperature. The quenched samples of IP27LAW, IP32LAW, IP35LAW had trace amounts (< 1%) of crystalline (Cr,Fe)₂O₃ (solid solution of Cr₂O₃ and Fe₂O₃) and the CCC treated IP27LAW sample contained crystalline sodium iron phosphates (NaFeP₂O₇ and Na₃Fe₂(PO₄)₃) as well as crystalline (Cr,Fe)₂O₃. No crystalline phase was found in the quenched samples of IP30LAW, IP30LAW-A, and IP30LAW-C.

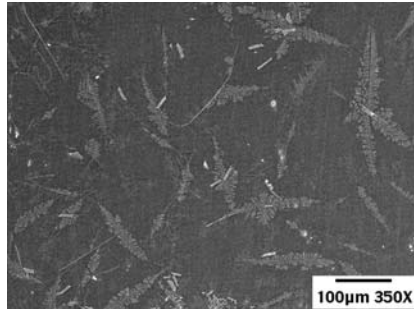
(a) IP27LAW (glass)



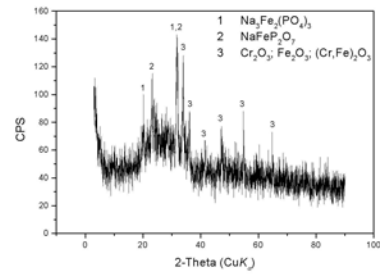
(a') IP27LAW (glass)



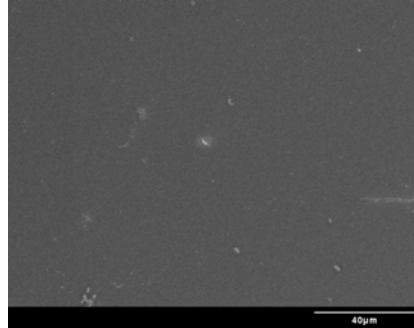
(b) IP27LAW (CCC treated)



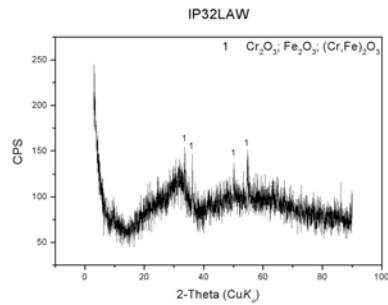
(b') IP27LAW (CCC treated)



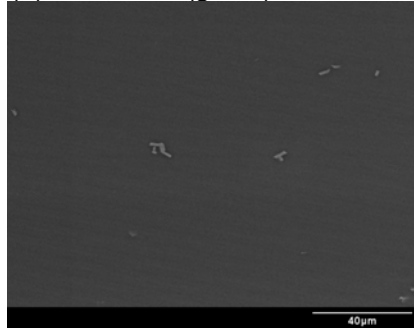
(c) IP32LAW (glass)



(c') IP32LAW (glass)



(d) IP35LAW (glass)



(d') IP35LAW (glass)

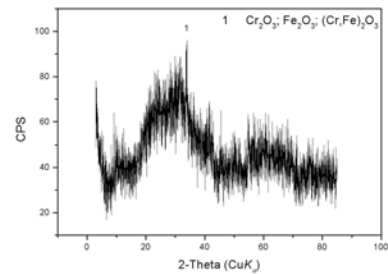


Figure 2. SEM micrographs and XRD patterns of iron phosphate glasses containing 27, 32, and 35 wt% LAW (IP27LAW, IP32LAW, and IP35LAW, respectively).

2.1.3. Physical Properties. The density of each sample was measured at room temperature by the Archimedes' method using deionized water as the suspending medium. The density was 2.74 to 2.88 g/cm³ for the glass samples and less than 2% higher for the CCC treated or slowly cooled samples (Table 4). The thermal expansion coefficient (TEC) was determined by dilatometry. The liquidus temperature (T_L) was measured per ASTM C 829-81 [29] procedures in a temperature gradient furnace using a platinum tray in which glass particles were fused to form a thin (~3 mm) layer of melt. The TEC and T_L for the iron phosphate glasses are summarized in Table 4.

Table 4. Density, thermal expansion coefficient (TEC), and liquidus temperature (T_L) of iron phosphate wasteforms.

Wasteform	Density (g/cm ³)		TEC from 35 to 300°C (x 10 ⁻⁷ /°C)	T_L (°C)
	Glass	CCC/SC*		
IP27LAW	2.76±0.01	2.82±0.01	138±3	762±5
IP30LAW	2.88±0.01	NA	168±3	NM
IP30LAW-A	2.77±0.01	NA	165±3	NM
IP30LAW-C	2.87±0.01	NA	163±3	NM
IP32LAW	2.77±0.01	2.82±0.01	NM	NM
IP35LAW	2.74±0.01	2.77±0.01	NM	736±5

* CCC treated for IP27LAW and Slowly Cooled (~2°C/min) for IP32LAW and IP35LAW samples (No controlled cooling experiment was performed for IP30LAW samples.). NM = not measured.

2.1.4. Chemical Durability. The chemical durability of the iron phosphate glasses was determined by the product consistency test (PCT) following the procedures in ASTM C 1285-97 [30]. After completion of the PCT, the concentration of ions in the leachate was measured by ICP-ES.

The normalized elemental mass release, r_i , was calculated from the concentration of each element in the leachate and from the mass fraction of element in the glass. The mass release of Na, Si, P, Al, Cr, Fe, and Ca from the iron phosphate wasteforms is summarized in Table 5. The current PCT specification for Hanford LAW borosilicate glass is that the r_i of Na, Si, and B should be less than 2 g/m² from a 7-day test at 90°C [31] (Table 5). Given that the iron phosphate glasses in this study do not contain boron, no boron value can be given. The r_i 's for i = sodium and silicon for the annealed and CCC/SC treated samples of IP27LAW and IP32LAW, and for i = sodium for the annealed samples of IP30LAW, IP30LAW-A, and IP30LAW-C are well below the

current DOE specification for LAW and the Environmental Assessment (EA) glass values. The chemical durability of IP35LAW is not quite as good as that of IP27LAW, IP30LAW(-A,C), and IP32LAW, but is still comparable to that of the EA glass [32]. The mass release of the IP27LAW-CCC and IP32LAW-SC samples suggests that any crystallization that occurred during CCC treatment or slowly cooling at $\sim 2^{\circ}\text{C}/\text{min}$ did not significantly change the chemical durability of these iron phosphate glasses. In fact, the r_{Na} and r_{P} values for the IP32LAW-SC sample are smaller than those for the normally annealed sample. The amount of crystals present in the SC and CCC iron phosphate samples has not been determined.

Table 5. Normalized elemental mass release (g/m^2) from iron phosphate wasteforms containing up to 35 wt% Hanford LAW after PCT in deionized water at 90°C for 7 days.

Wasteform	r_{Na}	r_{Si}	r_{P}	r_{Al}	r_{Cr}	r_{Fe}	r_{Ca}
IP27LAW	0.51	0.19	0.24	0.21	< 0.01	0.03	< 0.01
IP27LAW-CCC*	0.48	0.22	0.21	0.23	< 0.01	0.02	< 0.01
IP30LAW	0.91	NA	0.52	0.38	NA	0.37	NA
IP30LAW-A	0.62	NA	0.28	0.19	NA	0.03	NA
IP30LAW-C	0.67	NA	0.28	0.17	0.08	0.06	NA
IP32LAW	1.81	0.16	1.43	0.61	0.09	0.03	< 0.01
IP32LAW-SC**	1.02	0.21	0.83	0.53	0.09	0.02	< 0.01
IP35LAW	4.85	0.08	3.37	1.06	0.85	0.15	0.01
IP35LAW-SC**	5.70	0.11	4.09	1.39	0.83	0.80	0.03
DOE limit for LAW***	2	2	NA	NA	NA	NA	NA
EA glass***	6.67	1.96	NA	NA	NA	NA	NA

* CCC treated sample.

** Slowly Cooled sample.

*** DOE limit for Hanford LAW borosilicate glass [31] and Environmental Assessment (EA) glass value [32] after PCT (90°C for 7 days).

The chemical durability of the iron phosphate glasses was also evaluated by the vapor hydration test (VHT). A complete description of the VHT can be found in reference [33], whose procedures were used in the present work. Optical micrographs of a cross section of the VHT samples after 7-day tests at 200°C are shown in Figure 3. The VHT corrosion rate (mass of specimen dissolved per unit surface area) was calculated from the initial specimen thickness and the thickness of the glass remaining at the end of the test [33]. The VHT corrosion rates (estimated by assuming a constant rate from time = 0) for the annealed and for the CCC treated or slowly cooled iron phosphate wasteforms except IP30LAW are considerably smaller than the current DOE limit of $50 \text{ g}/\text{m}^2/\text{day}$ [31]

(Table 6), indicating that these iron phosphate wastefoms have an outstanding chemical resistance to the humid conditions existing at 200°C for 7 days.

The chemical durability of the IP30LAW wastefom satisfied the DOE requirement for PCT but did not meet the VHT requirement. However, the wastefoms IP30LAW-A and IP30LAW-C satisfied the current DOE requirements for both PCT and VHT. The better chemical durability of the IP30LAW-A and IP30LAW-C glasses compared to that of the IP30LAW glass suggests that the presence of Al_2O_3 or Cr_2O_3 in the IP30LAW-A and IP30LAW-C glasses, respectively, significantly improved their chemical durability.

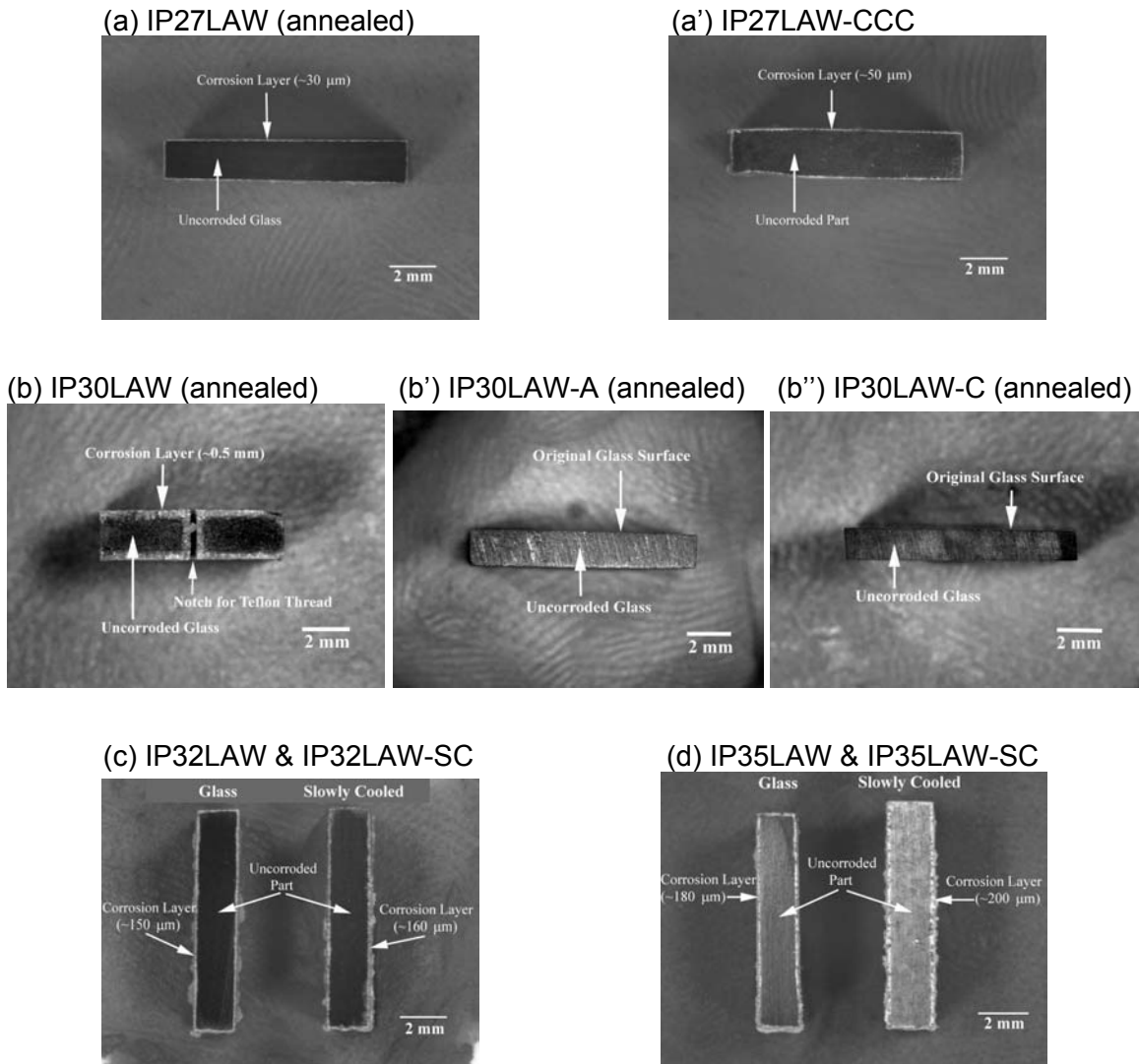


Figure 3. Optical micrographs of the cross section of iron phosphate wastefoms containing 27, 30, 32, and 35 wt% LAW after VHT at 200°C for 7 days.

Table 6. VHT corrosion rates (g/m²/day) for iron phosphate wasteforms containing up to 35 wt% LAW tested at 200°C for 7 days. DOE limit for corrosion rates as given in reference [31].

Test	VHT Corrosion Rate (g/m ² /day)									
	IP27LAW		IP30LAW	IP30LAW-A	IP30LAW-C	IP32LAW		IP35LAW		DOE Limit
	Annealed	CCC*	Annealed	Annealed	Annealed	Annealed	SC**	Annealed	SC**	
7-day	5.9	10.1	200.0	< ~1.0	< ~1.0	28.9	31.8	35.4	38.2	50 [31]

* CCC treated sample.

** Slowly Cooled sample.

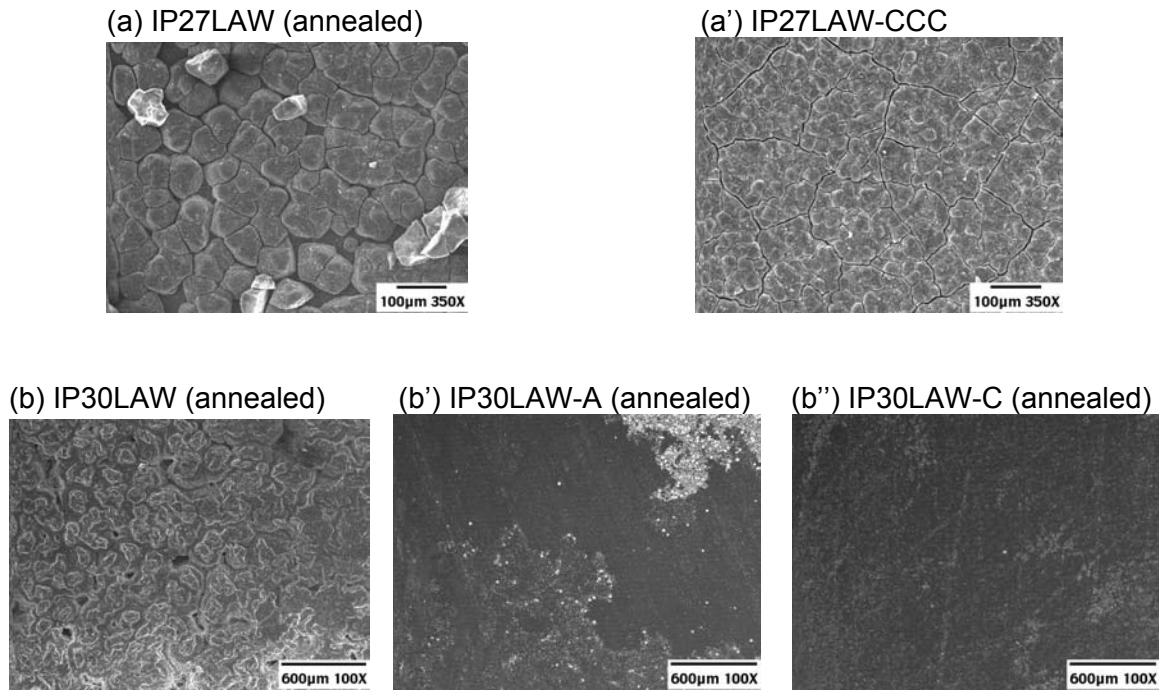


Figure 4. SEM micrographs of the external surface of IP27LAW and IP30LAW(-A,C) wasteforms after VHT at 200°C for 7 days.

The corrosion layers (products) on the surface of the annealed and CCC treated IP27LAW samples after the VHT (200°C, 7 days) were identified by XRD to be mainly the zeolite, $\text{Na}_4(\text{Al}_4\text{Si}_{12}\text{O}_{32})(\text{H}_2\text{O})_{14}$ (Figure 4(a,a')). The corrosion products on the IP32LAW and IP35LAW wasteforms have not been identified by XRD, but are expected to be similar to that for the IP27LAW samples due to the similarities in composition and alteration extent. The corrosion products on the IP30LAW sample consisted mainly of three phases $\text{NaFe}_3\text{P}_2\text{O}_7(\text{OH})_3 \cdot \text{H}_2\text{O}$, $\text{Na}_3\text{Fe}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, and $\text{NaFeH}_2(\text{PO}_4)_2$ (Figure 4(b)). For the IP30LAW-A and IP30LAW-C samples, the polishing lines on the external surface

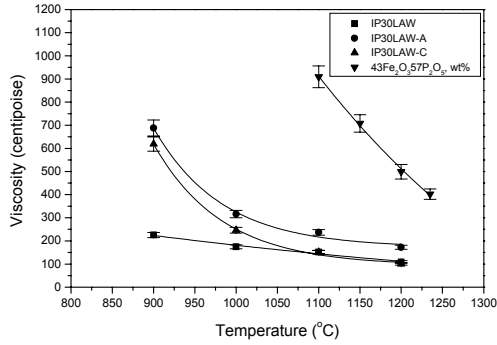
were still observable, and only small amounts of corrosion products, heterogeneously distributed on the surface, were visible (Figure 4(b',b'')). These small particles (corrosion products) could not be identified by XRD, but SEM-EDS analyses indicated that they were a sodium-iron-phosphate phase(s) for both glasses.

2.1.5. High Temperature Viscosity and AC Electrical Conductivity. The viscosity (η) for selected iron phosphate glass melts (IP30LAW, IP30LAW-A, and IP30LAW-C) was measured from 900 to 1200°C in 100°C increments and is shown in Figure 5(a) as a function of temperature. The viscosity for the compositionally simpler iron phosphate melt, 43Fe₂O₃·57P₂O₅, wt% (F43), is also included in Figure 5(a) for comparison. The lower viscosity at any temperature for the three melts containing LAW compared to that for F43 is consistent with their higher soda content. The IP30LAW-A and IP30LAW-C melts had a slightly higher viscosity than the IP30LAW melt, which may be due to the Al₂O₃ or Cr₂O₃ in the IP30LAW-A and IP30LAW-C melt, respectively.

The plot of log viscosity (η) versus 1/T in Figure 5(b) indicates that the viscosity obeyed the Arrhenius equation over the melting range. The activation energy (Q) for viscous flow, as calculated from the slope of the curves in Figure 5(b), was 35.3, 54.7, 74.1, and 108.3 kJ/mol for the IP30LAW, IP30LAW-A, IP30LAW-C, and baseline iron phosphate F43 melt, respectively. These values for the iron phosphate melts are considerably smaller than the reported [34] Q of 514.9 kJ/mol for SiO₂ (1600-2500°C) or 173.7 kJ/mol for P₂O₅ (545-655°C) melts.

The viscosity of the borosilicate melts at the Defense Waste Processing Facility (DWPF), Westinghouse Savannah River Co. [35] ranges from approximately 4,500 to 9,000 centipoise. The iron phosphate melts are, therefore, 10 to 50 times more fluid than the borosilicate melts now in use. At their melting temperature (1000-1050°C), the viscosity is approximately 200 to 400 centipoise so a melting time of only a few hours is typically adequate to achieve a chemically homogeneous melt free of all batch materials and gas bubbles.

(a)



(b)

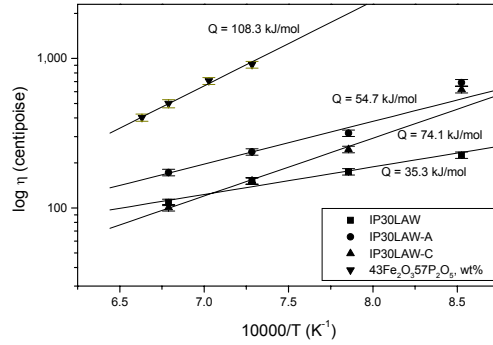


Figure 5. Viscosity (η) of melts IP30LAW, IP30LAW-A, and IP30LAW-C over their melting temperature range. Data for a 43Fe₂O₃·57P₂O₅ (wt%) glass is shown for comparison. (a) viscosity (centipoise) vs. temperature (°C); (b) viscosity (centipoise-log scale) vs. temperature (K⁻¹). Activation energy (Q) for viscous flow was determined from the slope log η vs. $1/T$.

The ac electrical conductivity (σ) of the three iron phosphate melts shown in Figure 6 was essentially the same at any temperature from 800 to 1200°C and followed an Arrhenius temperature dependence. The electrical conductivity increased from ~70 at 800°C to ~135 S/m at 1200°C for the iron phosphate melts. This conductivity is 3 to 4 times higher than that of a borosilicate melt (SBW-22-20 [36]) which contains 20 wt% of INEEL sodium bearing waste (SBW-composition is similar to LAW composition). The activation energy (Q) of ~20 kJ/mol, determined from the slope of the curves in Figure 6, for the iron phosphate melts is significantly less than that (~57 kJ/mol) for the borosilicate melt.

The higher electrical conductivity for the iron phosphate melts suggests that iron phosphate glass wasteforms can be easily processed in a Cold Crucible Induction Melter (CCIM), which has been of interest and has been confirmed by a previous melting experience [37]. This technique eliminates many materials and operating constraints, such as the chemical corrosion of the melter refractories and metal electrodes, which is unavoidable in a Joule-Heated Melter (JHM) like that now in use to vitrify nuclear waste in the DWPF at Savannah River Site. The smaller temperature dependence of the electrical conductivity of iron phosphate should be an operational advantage since the electrical resistance and, therefore, the current will not change so much with small changes in temperature.

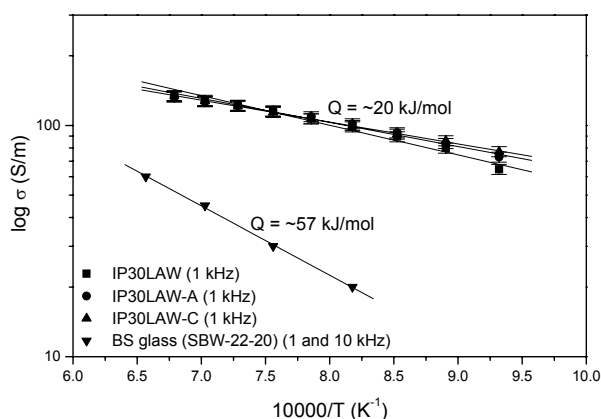


Figure 6. Electrical conductivity (σ) of IP30LAW, IP30LAW-A, and IP30LAW-C melts over their melting temperature range. Data [36] for borosilicate glass (SBW-22-20) containing 20 wt% of INEEL sodium bearing waste (SBW-composition is similar to LAW composition) is given for comparison. Activation energy (Q) for electrical conductivity was calculated from the slope $\log \sigma$ vs. $1/T$.

2.2. Hanford High Chrome Waste (HCW)

It has been estimated [2] that there is 12.3 million kilogram (Mkg) of High-Level nuclear Waste (HLW) at Hanford, WA which is to be treated for permanent disposal. This HLW has been divided into 17 compositional groups (called clusters) which contain varying amounts of chrome oxide, 4.25 wt% Cr_2O_3 being the highest. Cr_2O_3 is a refractory oxide, melting point of 2330°C, that is only slightly soluble in most silicate-type melts. Because of its low solubility, Cr_2O_3 is often a component of the refractory used to contain high temperature silicate and borosilicate melts.

The solubility of Cr_2O_3 in borosilicate glass is about 0.5 wt% [38]. If precipitation of Cr_2O_3 in the melt is to be avoided (with the potential to short circuit the electrodes in a joule-heated melter), then the waste content is limited by the Cr_2O_3 solubility. If the chrome oxide content of the waste exceeds its solubility limit in the melt, then extensive dilution of the wastes (from 3 to 9 times) may be necessary. In certain borosilicate glass compositions, the solubility of Cr_2O_3 can reach 1 wt%. Feng et al. [39] reported that when the melt becomes saturated in Cr_2O_3 , then crystalline Cr_2O_3 precipitates and the chemical durability of the borosilicate wasteform is decreased.

Vitrification of the high chrome waste at Hanford in borosilicate glasses has been estimated to produce 26.5 to 32.3 Mkg of wasteform [2], which will require about 9,720

to 12,110 m³ of space (volume) for permanent disposal, assuming a Cr₂O₃ solubility limit of 0.5 to 1.0 wt%. The volume of vitrified waste can be reduced by using alternative glasses, which have a higher solubility limit for Cr₂O₃ and offer, therefore, higher waste loadings.

The HLW at Hanford also contains oxides, such as P₂O₅, Fe₂O₃, Bi₂O₃, rare earth oxides like La₂O₃, and heavy metal oxides like U₃O₈, which are also difficult to dissolve uniformly in borosilicate glasses, but which are more soluble in phosphate glasses [3-24]. Because of the inherently higher solubility of these oxides in phosphate glasses, chemically durable iron phosphate glasses could potentially reduce the volume of the final wasteform.

2.2.1. Simulated Waste Composition. The HLW at Hanford [2] has 17 compositional clusters, which contain from 0.11 to 4.25 wt% Cr₂O₃ and whose combined mass is estimated to be 12.3 Mkg. The clusters #3, 4, 6, 7, 8, 10, and 14 are the seven highest Cr₂O₃-containing wastes and their combined mass is estimated to be 5.6 Mkg (about 45 wt% of total Hanford HLW). Rather than investigate each waste separately, it was decided to use a simplified waste composition (Table 7) that was a blend of the waste in clusters #3, 4, 6, 7, 8, 10, and 14. The blended composition was simplified by neglecting components present in quantities less than 1.0 wt% and contained 4 wt% Cr₂O₃, which is just slightly less than the maximum Cr₂O₃ content (4.25 wt%) of the waste in cluster #14 at Hanford.

Table 7. Composition (wt%) of blended waste from the high chrome nuclear waste for clusters #3, 4, 6, 7, 8, 10, and 14 at Hanford.

Component	Blended waste (wt%)
Al ₂ O ₃	21
Bi ₂ O ₃	4
CaO (CaF ₂)	5
Cr ₂ O ₃	4
Fe ₂ O ₃	12
La ₂ O ₃	1
Na ₂ O	24
P ₂ O ₅	3
SiO ₂	10
U ₃ O ₈	10
ZrO ₂	6
Total	100

2.2.2. Glass Preparation. The IP65HCW, IP70HCW, and IP75HCW glasses (Table 8) contained 65, 70, and 75 wt% of the simulated high chrome waste (HCW) at Hanford. Only one additional component was added to the waste, namely P_2O_5 (or some other material providing P_2O_5). These iron phosphate glasses were melted in a refractory crucible at 1200-1250°C for 2-3 hours in air. Each melt was stirred 3 to 4 times with a silica glass rod to aid homogenization. After melting, the glass was cast into a steel mold to form rectangular bars. The bars were annealed between 520 and 540°C for 4 hours and slowly cooled (overnight) in the annealing furnace to room temperature.

Portions of the iron phosphate melts were cooled from their melting temperature to their crystallization temperature at 2°C/min, held for 2 hours and then cooled to room temperature at 2°C/min in order to simulate the slower cooling a melt experiences in a metal canister. Both annealed and slowly cooled (partially crystallized) samples were examined for chemical durability.

Table 8. Batch composition (wt%) of iron phosphate glasses containing 65, 70, and 75 wt% HCW (IP65HCW, IP70HCW, and IP75HCW, respectively).

Component	IP65HCW (wt%)	IP70HCW (wt%)	IP75HCW (wt%)
Al_2O_3	13.6	14.7	15.7
Bi_2O_3	2.6	2.8	3.0
CaO (CaF_2)	3.3	3.5	3.8
Cr_2O_3	2.6	2.8	3.0
Fe_2O_3	7.8	8.4	9.0
La_2O_3	0.7	0.7	0.8
Na_2O	15.6	16.8	18.0
P_2O_5	36.9	32.1	27.2
SiO_2	6.5	7.0	7.5
U_3O_8	6.5	7.0	7.5
ZrO_2	3.9	4.2	4.5
Total	100.0	100.0	100.0

2.2.3. Glass Formation. The annealed samples of IP70HCW and IP75HCW contained trace amounts (< 1%) of crystalline Cr_2O_3 as identified by XRD, but no crystalline phase was found in the annealed IP65HCW sample (Figure 7). The slowly cooled samples of the three wasteforms contained crystalline Cr_2O_3 and other phases such as $NaFe_3P_3O_{12}$ and $Na_3Cr_2P_3O_{12}$. The presence of these crystalline phases in the iron phosphate wasteforms did not significantly affect their chemical durability, see section 2.2.4. The

solubility limit of Cr_2O_3 in these iron phosphate glasses was found to be about 2.6 wt% from XRD analyses of samples containing known amounts of Cr_2O_3 , compared to < 1 wt% [38] in common borosilicate glasses.

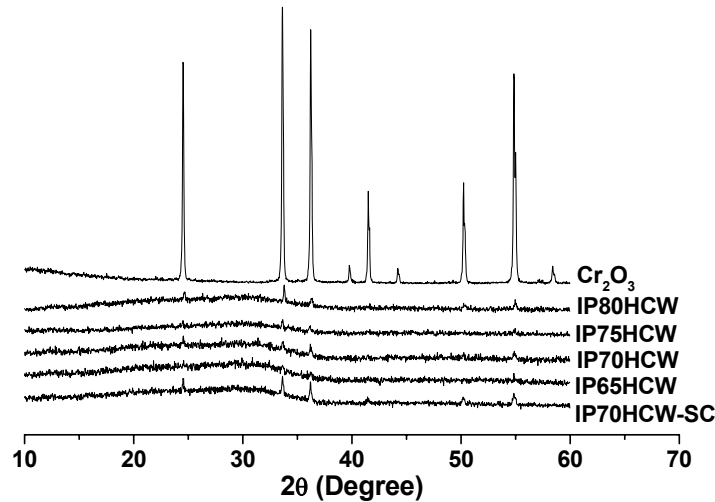


Figure 7. XRD pattern for Cr_2O_3 containing iron phosphate wasteforms, annealed. Trace amounts of crystalline Cr_2O_3 are evident in the samples with ≥ 70 wt% waste loading. The curve IP70HCW-SC is for a sample slowly cooled at $2^\circ\text{C}/\text{min}$ from its melting temperature.

2.2.4. Chemical Durability. The iron phosphate glasses with a waste loading of up to 75 wt% had an extremely good chemical durability as determined by PCT and VHT. The excellent chemical durability was still retained when the glasses were cooled slowly (partially crystallized). As shown in Table 9, the values of the normalized elemental mass release (r_{Na}) for sodium for the annealed and slowly cooled IP65HCW, IP70HCW, and IP75HCW wasteforms after PCT at 90°C for 7 days are well below the current DOE specification for HLW EA borosilicate glass ($r_{\text{Na}} = 6.67$).

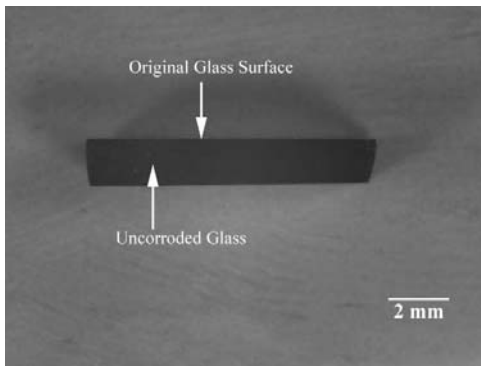
Table 9. PCT release (g/m^2) and VHT corrosion rates ($\text{g}/\text{m}^2/\text{day}$) for iron phosphate wasteforms containing up to 75 wt% HCW.

Chemical durability	IP65HCW		IP70HCW		IP75HCW		EA glass**
	Annealed	SC*	Annealed	SC*	Annealed	SC*	
PCT (r_{Na} , g/m^2) at 90°C	0.20	0.37	0.28	0.67	0.34	0.70	6.67 [32]
VHT ($\text{g}/\text{m}^2/\text{day}$) at 200°C	< ~1	< ~1	< ~1	12.5	8.6	20.9	NA

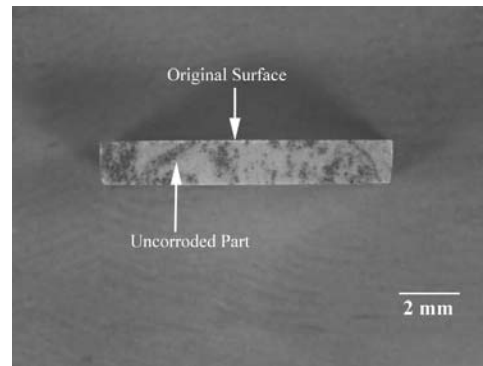
* Slowly Cooled sample.

** DOE requirement for HLW.

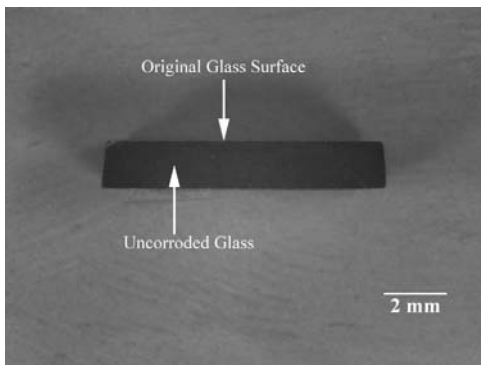
(a) IP65HCW (annealed)



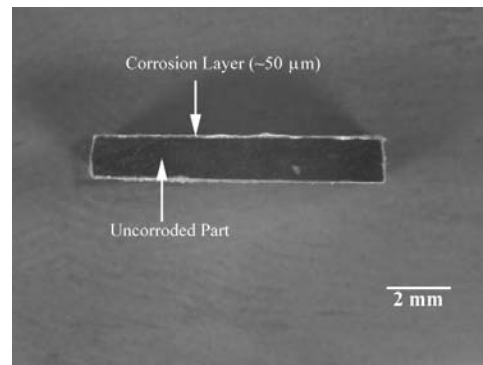
(a') IP65HCW-SC



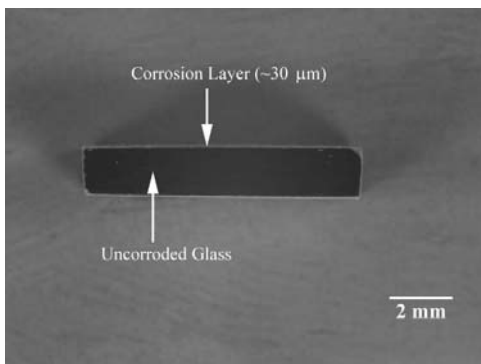
(b) IP70HCW (annealed)



(b') IP70HCW-SC



(C) IP75HCW (annealed)



(C') IP75HCW-SC

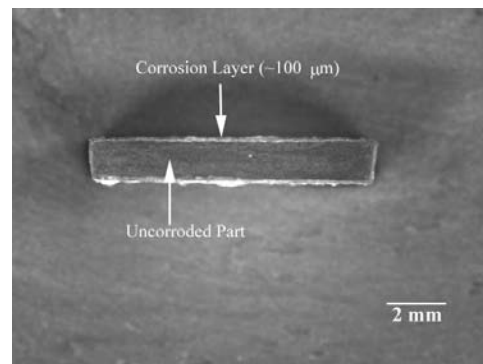


Figure 8. Optical micrographs of the cross section of iron phosphate wastefoms containing 65, 70, and 75 wt% HCW after VHT at 200°C for 7 days.

In Figure 8(a,a'), both glassy (annealed) and partially crystallized (slowly cooled) iron phosphate wastefoms containing 65 wt% HCW (IP65HCW and IP65HCW-SC,

respectively) did not have any visible or detectable corrosion layer on their surface after VHT at 200°C for 7 days. No corrosion layer was detectable on the surface of the glassy IP70HCW, but a thin corrosion layer (~50 µm) was observed on the surface of the partially crystallized IP70HCW-SC (Figure 8(b,b')). A corrosion layer of ~30 and ~100 µm thick was observed on the surface of the IP75HCW and IP75HCW-SC samples, respectively (Figure 8(c,c')). Based on this corrosion layer, the VHT corrosion rate for the iron phosphate wasteforms was calculated to vary from only < ~1 to 20.9 g/m²/day (Table 9). Currently, there is no DOE specification for VHT for High-Level Waste (HLW), but these values can be compared to the VHT specification (50 g/m²/day [31]) for Low-Activity Waste (LAW).

The simulated blend of the seven High Chrome Wastes (HCW) at Hanford used in the present study is about 45 wt% of the total HLW at Hanford. With a waste loading of 65 to 75 wt% HCW, the iron phosphate glasses offer the potential to greatly reduce the volume of vitrified high chrome HLW, and thus, significantly reduce the overall disposal cost.

2.3. INEEL Sodium Bearing Waste (SBW)

The Idaho National Engineering and Environmental Laboratory (INEEL) stores approximately 5.7 million liters of Sodium Bearing Waste (SBW) and plans for its disposal between 2007 and 2012 [2]. The SBW composition is relatively high in sodium, aluminum, and sulfate (Table 10). The poor solubility (< 1 wt%) of sulfate in the borosilicate glasses limits the waste loading to a maximum of only 20 wt% [40], which would result in an increased cost and a high wasteform volume. These are possibly the reasons that the plans for disposing of the SBW using vitrification have been discontinued at INEEL. However, our present work demonstrates that vitrification of the SBW in iron phosphate glasses could substantially reduce the cost and wasteform volume.

Table 10. Nominal composition and raw materials used to prepare INEEL simulated SBW.

Oxide	wt%	Raw Material	wt%
Na ₂ O	52.3	NaNO ₃	68.3
Al ₂ O ₃	27.8	Al ₂ O ₃	14.4
K ₂ O	7.6	KNO ₃	8.4
CaO	2.2	CaO	0.6
Fe ₂ O ₃	1.4	Fe ₂ O ₃	0.7
MnO	0.8	MnO	0.4
P ₂ O ₅	1.6	NaPO ₃ ·3H ₂ O	1.8
B ₂ O ₃	0.4	H ₃ BO ₃	0.3
MgO	0.4	MgO	0.2
Cr ₂ O ₃	0.2	Cr ₂ O ₃	0.1
SO ₃	3.6	Na ₂ SO ₄	3.3
Cl	0.9	NaCl	0.7
F	0.8	CaF ₂	0.8
Total	100.0	Total	100.0

2.3.1. Glass Preparation and Formation. The mixture of simulated SBW, along with the two additives Fe₂O₃ and P₂O₅, was thoroughly dry mixed and then melted in a high purity alumina crucible in an electric furnace. A total of 600 g of iron phosphate glass containing 40 wt% of the SBW (denoted as IP40SBW) was prepared by melting the batch at 1000°C for 3 hours. After melting, the glass was cast into bars that were annealed at 420°C for 4 hours and cooled to room temperature overnight in the annealing furnace.

The chemical composition of the glass IP40SBW was calculated from the batch composition and measured by ICP-ES and Leco (Table 11). The calculated and analyzed compositions were in satisfactory agreement with each other. The molar ratio of oxygen to phosphorus (O/P) calculated from the batch as well as measured compositions was 3.9. This value is slightly higher than the previously reported [4,8,11,16,17,20] range of O/P values, from 3.4 to 3.7, that yield the best glass forming tendency and chemical durability. SEM and powder XRD did not reveal any sulfate salt segregation, inclusions, nodules, or crystalline phases in the sample IP40SBW, suggesting that this glass was chemically homogeneous. Leco analysis indicated that about 43% of the sulfate originally present in the waste was retained in the glass (Table 11).

Table 11. Batch and analyzed (ICP-ES) compositions (wt%) of iron phosphate glass containing 40 wt% SBW.

Oxide (wt%)	IP40SBW	
	Batch	ICP-ES
Na ₂ O	20.5	23.2
Al ₂ O ₃	10.9	12.7
K ₂ O	3.0	3.2
CaO	0.9	0.8
Fe ₂ O ₃	10.3	11.5
MnO	0.3	0.4
P ₂ O ₅	51.7	47.3
B ₂ O ₃	0.1	NM
MgO	0.2	0.1
Cr ₂ O ₃	0.1	0.1
SO ₃	1.4	0.6*
Cl	0.3	NM
F	0.3	NM
Total	100.0	99.9

* Analyzed by Leco.

NM = not measured.

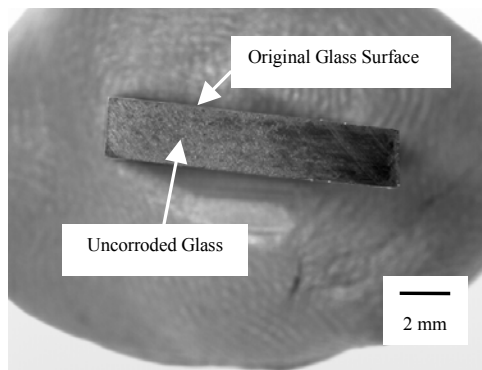
2.3.2. Chemical Durability. The normalized elemental mass release (r_{Na}) for sodium for the IP40SBW wasteform after PCT at 90°C for 7 days is well below the current DOE specification ($r_{\text{Na}} = 6.67$) for the EA borosilicate glass (Table 12). Figure 9 shows the appearance of the (a) cross section and (a') external surface of the IP40SBW wasteform after the 7-day VHT at 200°C. There was hardly any detectable corrosion on the surface of the IP40SBW sample. The polishing lines were still observable, and only a few corrosion products, heterogeneously distributed on the surface, were visible (Figure 9(a')). These small particles (corrosion products) were identified by XRD to be Na₃Al(PO₄)₂·1.5H₂O. The VHT corrosion rate was only $< \sim 1$ g/m²/day (Table 12) which was well below the DOE specification (50 g/m²/day [31]) for Low-Activity Waste (LAW). Currently, no VHT requirement has been specified for HLW such as SBW.

Table 12. PCT release (g/m²) and VHT corrosion rates (g/m²/day) for iron phosphate wasteform containing 40 wt% SBW.

Chemical durability	IP40SBW	EA glass*
PCT (r_{Na} , g/m ²) at 90°C	0.5	6.67 [32]
VHT (g/m ² /day) at 200°C	$< \sim 1$	NA

* DOE requirement for HLW.

(a) IP40SBW (cross section)



(a') IP40SBW (external surface)

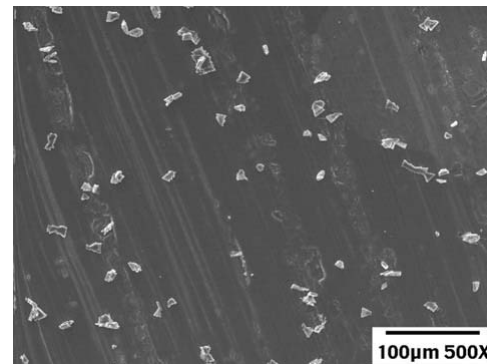


Figure 9. Optical micrographs of the (a) cross section and (a') external surface of iron phosphate wasteform containing 40 wt% SBW after VHT at 200°C for 7 days.

2.4. Corrosion of Refractory and Electrode Materials

Previous studies [15] have shown that iron phosphate glasses do not corrode commercial refractories to the degree normally expected for other phosphate glasses. The Russian experience [41] has also shown that processing of similar sodium-alumino-phosphate glasses is possible in AZS refractories with molybdenum electrodes.

Figure 10 shows the cross section of a dense high silica (DFC 83% silica 17% alumina) crucible after 14 days at 1250°C with the iron phosphate melt containing 27 wt% LAW (IP27LAW). No significant corrosion was evident on any of the crucibles examined. These results are encouraging since they suggest that the corrosion rate of common commercial refractories in iron phosphate melts should be comparable to the rate in borosilicate glasses now in use at DWPF. However, alternative processing technologies, such as cold crucible induction melting, could eliminate or minimize this issue as discussed in section 2.5.



Figure 10. Cross sectional view of a dense high silica crucible after 14 days at 1250°C with the iron phosphate melt containing 27 wt% LAW (IP27LAW).

A Joule-Heated Melter (JHM) is the melting technology that is now being used to vitrify nuclear waste at DWPF. Inconel 690 is the current electrode material being used in the JHM at DWPF. The weight loss of two metals, Inconel 690 and 693, in an iron phosphate melt containing 30 wt% Hanford LAW (IP30LAW) was measured as a function of time at 1025°C, the melting temperature for this glass. The weight loss for the submerged metal samples is shown in Figure 11. The weight loss at 155 days was 14 and 7.5% for the totally submerged Inconel 690 and 693 sample, respectively. Samples of these two metals that were only partially submerged were also examined in the same iron phosphate melt. Bars about 38 mm long and 5 mm square were stood on end so that the top one third of the metal bar extended out of the melt. In this more severe test, the Inconel 690 was rapidly corroded at the melt line, but the Inconel 693 was much more resistant, its weight loss being only 2.5% after 155 days at 1025°C, see Figure 11.

Based on these preliminary results, it appears that electrodes made of Inconel 693 could be a candidate for use in JHM. It should also be noted that molybdenum electrodes have been successfully used in JHM in Russia to melt sodium-alumino-phosphate glasses for long periods of time, up to six years [41]. The issue of electrode corrosion, however, can be eliminated with alternative melting technologies such as cold crucible induction melting, hot crucible induction melting, and microwave melting discussed in section 2.5.

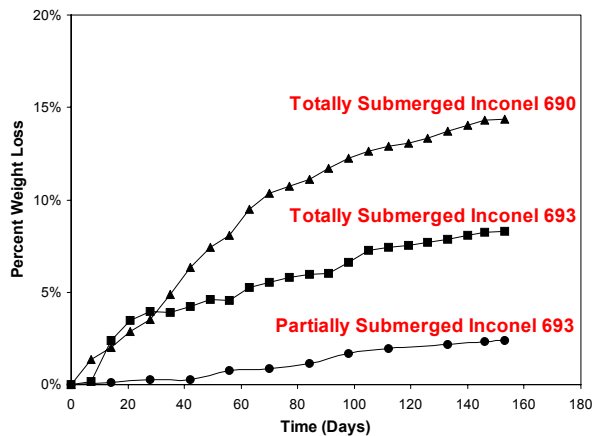


Figure 11. Weight loss of Inconel 690 and 693 samples submerged in iron phosphate melt containing 30 wt% LAW (IP30LAW) at 1025°C.

2.5. Alternative Melting Methods

2.5.1. Cold Crucible Induction Melter (CCIM). Melting iron phosphate glasses in a Cold Crucible Induction Melter (CCIM) has been of interest, since this technique eliminates many materials and operating constraints, such as the chemical corrosion of the melter refractories and metal electrodes, which is unavoidable in a Joule-Heated Melter (JHM) such as that now being used to vitrify nuclear waste at DWPF.

CCIM technology is based on heating a conductive melt in a high-frequency electromagnetic field. Frequencies of 0.44, 1.76, 5.28 MHz are commonly used. In CCIM, the crucible is formed by metal tubes with good heat conductivity (usually copper or stainless steel) placed within the inductor coils. The crucible tubes are water cooled so that their temperature does not exceed 200°C during melting. A protective layer of solid glass about 2-5 mm thick, called "skull", forms between melt and crucible. This protective layer prevents the melt from leaking between the crucible tubes and protects the crucible from chemical attack by the melt.

An iron phosphate glass containing 40 wt% simulated SBW (IP40SBW) was successfully melted in a CCIM. This was the first experimental melting of an iron phosphate wasteform in a CCIM and was conducted at the V.G. Khlopin Radium Institute (KRI) in St. Petersburg, Russia. A general view of the CCIM at KRI is shown in Figure 12. A detailed description of the CCIM technique is given in reference [40].



Figure 12. General view of CCIM in a shield box at KRI.

Raw batch (1 kg), phosphoric acid was used for the source of phosphate, was melted for 1 hour in a high frequency field (1.76 MHz) at a power level of 10 to 30 kW depending upon the stage of melting. A small amount (18 g) of a sacrificial conductive material (silicon carbide in this case) was added to the batch to initiate melting. The gases formed during the melting process were evacuated from the shield box through an aerosol filter to a special ventilation system. After melting, 800 g of iron phosphate glass was obtained indicating a 20% weight loss due to volatile components in the batch. The properties of the glasses melted in the CCIM were the same as those of the same glass composition conventionally melted in an electric furnace. These successful trials of melting iron phosphate glasses indicate that CCIM technology could be an attractive and practical method of melting iron phosphate glasses and avoid any potential problems of electrode or refractory corrosion.

2.5.2. Hot Crucible Induction Melter (HCIM). Small amounts (300 g) of an iron phosphate glass containing 35 wt% simulated LAW (IP35LAW) were successfully melted in a Hot Crucible Induction Melter (HCIM) (Figure 13). The batch was contained in a dense high silica crucible inside a graphite susceptor (Figure 13(a)) and melted at 1150°C for 2 hours at a power level of 12 to 18 kW, depending on the stage of melting. The chemical durability and other properties of the glasses melted in the HCIM were the same as those of the same glass conventionally melted in an electric furnace. The successful melting of the iron phosphate glass in the HCIM is encouraging since this method eliminates the need for metal electrodes in the melt, as in joule-heated melting and the stirring of the fluid melt by the magnetic field rapidly homogenizes the melt, thereby, reducing the melting time.

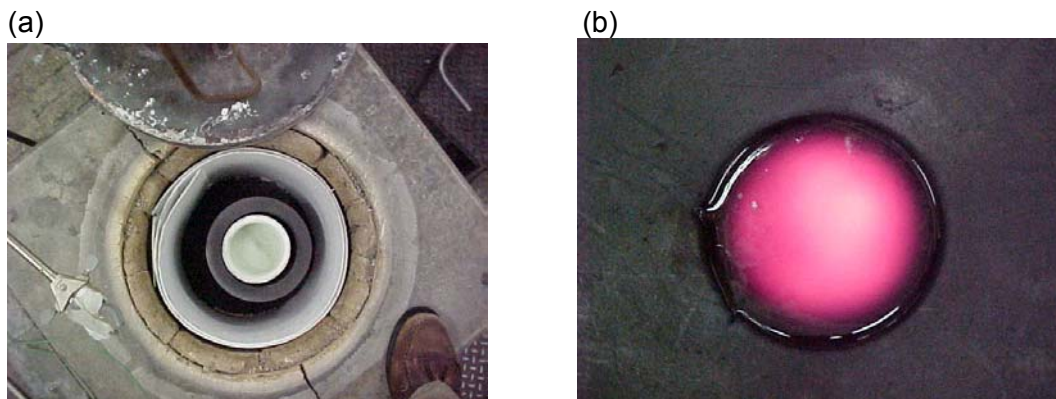


Figure 13. (a) Top view of HCIM and (b) iron phosphate glass wasteform (300 g) containing 35 wt% Hanford LAW that was melted at 1150°C for 2 hours.

2.5.3. Microwave Melting. Microwave melting is another alternative technology for vitrifying iron phosphate glass wasteforms. In collaboration with the Energy and Nuclear Research Institute, Brazil, small amounts (50 to 100 g) of the IP35LAW glass have been successfully melted, starting from a cold batch, in an ordinary microwave oven (1100 watts). Compositions containing significant amounts of alkalis, such as soda (~75 wt%) in the Hanford LAW, are an advantage since this improves the coupling of the microwave energy to the melt and promotes rapid melting. Microwave melting also eliminates the need for metal electrodes in the melt, but a refractory crucible is required (alumina and silica work well). The properties of the iron phosphate glasses prepared with microwave heating are the same as those of the same glass melted conventionally.

3. SUMMARY AND PLANED WORK

Iron phosphate glasses containing simulated Hanford LAW up to 35 wt%, Hanford HCW up to 75 wt%, and INEEL SBW up to 40 wt% have been successfully vitrified. The chemical durability of these vitrified iron phosphate wasteforms satisfies all known DOE requirements (PCT and VHT). The glass becomes partially crystallized upon CCC or SC treatment, but this has only a minor effect on its chemical durability.

For the LAW and SBW wasteforms, there was no indication of sulfate salt segregation, as seen in most borosilicate glasses, so it is unlikely that the LAW and SBW waste loading in iron phosphate glasses will be limited by the SO_3 content of the waste. Furthermore, the iron phosphate glass retained a large percentage (up to 73%, depending on composition) of the sulfate originally present in the waste, which was equivalent to 2.4 wt% SO_3 on a target glass oxide basis. For the HCW wasteform, iron phosphate glasses appeared to have higher Cr_2O_3 solubility (2.6 wt%) than the solubility in common borosilicate glasses (< 1 wt%).

Iron phosphate glasses can be melted as low as 1000°C for LAW and SBW, and at 1250°C for HCW (75 wt% waste loading). Because these melts have a high fluidity and become rapidly homogeneous, melting times can be as short as a few hours (< 6 hours) compared to the ~48 hours needed for most borosilicate glasses. These iron phosphate glasses did not corroded commercial refractories and electrode materials (Inconel 693) to the degree normally expected for other phosphate glasses.

The successful melting of the iron phosphate glass in the Cold Crucible Induction Melter (CCIM), Hot Crucible Induction Melter (HCIM), and Microwave oven is

encouraging since these procedures avoid any potential corrosion problems associated with the refractories and metal electrodes needed for Joule-Heated Melting (JHM). These promising results combined with the high waste loading, low melting temperature, and rapid furnace throughput (short melting times) of iron phosphate glasses can offer significantly reduced costs of vitrifying the Hanford Low-Activity Waste (LAW) and High Chrome Waste (HCW), and INEEL Sodium Bearing Waste (SBW).

The investigation of the chemical, physical, structural, thermal, and electrical properties of iron phosphate wasteforms containing LAW, HCW, and SBW will continue. Melting experiments using CCIM (in collaboration with the V. G. Khlopin Radium Institute, Russia), HCIM, and Microwave Melting (in collaboration with Energy and Nuclear Research Institute, Brazilian Nuclear Energy Commission, Brazil) will continue during the next year. The work is on schedule and proceeding as planned. No problems are anticipated.

4. PUBLICATIONS

The following eight papers on iron phosphate glasses have either been published or were submitted for publication during the 12 month period covered by this progress report.

1. "Iron Phosphate Glass as an Alternative Waste-Form for Hanford LAW", D. S. Kim, W. C. Buchmiller, M. J. Schweiger, J. D. Vienna, D. E. Day, C. W. Kim, D. Zhu, T. E. Day, T. Neidt, D. K. Peeler, T. B. Edwards, I. A. Reamer, and R. J. Workman, PNNL-14251, Pacific Northwest National Laboratory, Richland, WA (2003).
2. "Chemically Durable Iron Phosphate Glasses for Vitrifying Sodium Bearing Waste (SBW) using Conventional and Cold Crucible Induction Melting (CCIM) Techniques", C. W. Kim, C. S. Ray, D. Zhu, D. E. Day, D. Gombert, A. Aloy, A. Moguš-Milanković, and M. Karabulut, J. Nucl. Mater. (in press).
3. "Iron Phosphate Glass for Immobilization of Hanford LAW", C. W. Kim, D. Zhu, D. E. Day, D. S. Kim, J. D. Vienna, D. K. Peeler, T. E. Day, and T. Neidt, Ceramic Transactions (in press).
4. "Vitrification of High Chrome Oxide Nuclear Waste in Iron Phosphate Glasses", W. Huang, D. E. Day, C. S. Ray, C. W. Kim, and A. Moguš-Milanković, J. Non-Cryst. Solids (in press).
5. "Iron Phosphate Glasses for Vitrifying Sodium Bearing Waste", C. W. Kim, D. Zhu, D. E. Day, and D. Gombert, Ceramic Transaction (in press).

6. "Solubility of High Chrome Nuclear Wastes in Iron Phosphate Glasses", W. Huang, C. W. Kim, C. S. Ray, and D. E. Day, *Ceramic Transaction* (in press).
7. "Iron Phosphate Glass (IPG) Waste Forms Produced using Induction Melter with Cold Crucible", A. S. Aloy, R. A. Soshnikov, A. V. Trofimenko, D. Gombert, D. E. Day, and C. W. Kim, *MRS 2003, Scientific Basis for Radioactive Waste Management XXVII*, Kalmar, Sweden, June 15-18, 2003 (accepted).
8. "Immobilization of Hanford LAW in Iron Phosphate Glasses", C. W. Kim and D. E. Day, *J. Non-Cryst. Solids* (submitted).

As of the date of this report, more than fifty technical papers on iron phosphate glasses have been published since EMSP started supporting this work in 1996.

5. PRESENTATIONS

1. "Iron Phosphate Glass for Immobilization of Hanford LAW", C. W. Kim, D. Zhu, D. E. Day, D. S. Kim, J. D. Vienna, D. K. Peeler, T. E. Day, and T. Neidt, *ACerS 2003 Annual Meeting*, Nashville, TN, April 27-30, 2003.
2. "Iron Phosphate Glass (IPG) Waste Forms Produced using Induction Melter with Cold Crucible", A. S. Aloy, R. A. Soshnikov, A. V. Trofimenko, D. Gombert, D. E. Day, and C. W. Kim, *MRS 2003, Scientific Basis for Radioactive Waste Management XXVII*, Kalmar, Sweden, June 15-18, 2003.

6. COLLABORATIONS

Pacific Northwest National Laboratory (PNNL) for studying the feasibility of vitrifying Hanford Low-Activity Waste (LAW) in the iron phosphate glasses.

Idaho National Engineering and Environmental Laboratory (INEEL) for investigating the feasibility of vitrifying Sodium Bearing Waste (SBW) in the iron phosphate glasses.

V. G. Khlopin Radium Institute, Russia for studying Cold Crucible Induction Melting (CCIM) technique for upscale melting.

Energy and Nuclear Research Institute, Brazilian Nuclear Energy Commission, Brazil for investigating Microwave melting technique as an alternative melting process.

Ruder Boskovic Institute, Croatia for studying the structure of iron phosphate glasses using Raman spectroscopy.

7. REFERENCES

1. "Tank Waste Remediation System High-Level Waste Feed Processability Assessment Report", S. L. Lambert and D. S. Kim, PNNL #WHC-SP-1143, Pacific Northwest National Laboratory, Hanford, WA (1994).

2. "High-Level Waste Melter Study Report", J. M. Perez, Jr., D. F. Bickford, D. E. Day, D. S. Kim, S. L. Lambert, S. L. Marra, D. K. Peeler, D. M. Strachan, M. B. Triplett, J. D. Vienna, and R. S. Wittman, PNNL-13582, Pacific Northwest National Laboratory, Hanford, WA (2001).
3. "Structural Features of Iron-Phosphate glasses," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, W. B. Yelon, C. H. Booth, P. G. Allen, and D. K. Shuh, *J. Non-Cryst. Solids* 222 (1997) 144.
4. "Immobilization of High-Level Radioactive Sludges in Iron Phosphate Glasses," M. Mesko, D. E. Day and B. C. Bunker, *Science and Technology for Disposal of Radioactive Tank Wastes*, Eds. W.W. Schulz and N.J. Lombardo, Plenum Publishing Corp., (1998) 379-90.
5. "Redox Characteristics and Structural Properties of Iron Phosphate Glasses: A Potential Host Matrix for Vitrifying of High Level Nuclear Waste," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, C. H. Booth, P. G. Allen, and D. K. Shuh, *Environment Issues and Waste Management Technologies III: Ceramic Transactions* 87 (1998) 261.
6. "On the Structure and Radiation Chemistry of Iron Phosphate Glasses: New Insights from Electron Spin Resonance, Mössbauer, and Evolved Gas Mass Spectroscopy," D. L. Griscom, C. I. Merzbacher, N. E. Bibler, H. Imagawa, S. Uchiyama, A. Namiki, G. K. Marasinghe, M. Mesko, and M. Karabulut, *Nucl. Instr. and Meth. B* 141 (1998) 600.
7. "Iron Redox and Crystallization of Iron Phosphate Glasses," C. S. Ray, X. Fang, M. Karabulut, G. K. Marasinghe, and D. E. Day, *Environment Issues and Waste Management Technologies IV: Ceramic Transactions*, 93 (1999) 187.
8. "Effects of Nuclear Waste Components on Redox Equilibria, Structural Features, and Crystallization Characteristics of Iron Phosphate Glasses," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, P. G. Allen, J. J. Bucher, D. K. Shuh, Y. Badyal, M. L. Saboungi, M. Grimsditch, S. Shastri, and D. Heaffner, *Environment Issues and Waste Management Technologies IV: Ceramic Transactions*, 93 (1999) 195.
9. "DC Conductivity and Polarization in Iron Phosphate Glasses," A. Mogus-Milankovic, D. E. Day and B. Santic, *Phys. Chem. Glasses* 40 (2) 69-74 (1999).
10. "Effects of Melting Temperature and Time on Iron Valence and Crystallization of Iron Phosphate Glasses," C. S. Ray, X. Fang, M. Karabulut, G. K. Marasinghe, and D. E. Day, *J. Non-Cryst. Solids* 249 (1999) 1.
11. "Immobilization of Spent Nuclear Fuel in Iron Phosphate Glass," M. G. Mesko and D. E. Day, *J. Nuclear Matls.* 273 27-36 (1999).
12. "X-Ray Photoelectron and Mössbauer Spectroscopic Studies of Iron Phosphate Glasses Containing U, Cs, and Bi," M. Karabulut G. K. Marasinghe,, C. S. Ray, D. E. Day, O. Ozturk, and G. D. Waddill, *J. Non-Cryst. Solids* 249 (1999) 106.
13. "TSC and DC Conductivity for Cesium Iron Phosphate Glasses," A. Mogus-Milankovic, B. Santic, B. Pivac and D. E. Day, *Phys. Chem. Glasses* 40 (6) 305-10 (1999).
14. "Oxygen and Phosphorus Coordination Around Iron in Iron-Phosphate Glasses With UO_2 or Na_2O and Crystalline Ferric Ferrous Pyrophosphate," C. S. Booth, P. G. Allen, J. J. Bucher, N. M. Edelstein, D. K. Shuh, G. K. Marasinghe, M. Karabulut, C. S. Ray, and D. E. Day, *J. Mat. Res.* 14 (1999) 2628.
15. "Corrosion of Selected Refractories by Iron Phosphate Melts," F. Chen and D. E. Day, *Environmental Issues and Waste Management Technologies IV: Ceramic Transaction*, 93 (1999) 213.

16. "The Effects of Uranium Oxide High-Level Waste on the Structure of Iron Phosphate Glasses," Y. Badyal, M. Karabulut, G. K. Marasinghe, C. S. Ray, D. E. Day, M-L. Saboungi, D. Haefner, and S. Shastri, *MRS* 556 (2000) 297.
17. "Properties and Structure of Vitrified Iron Phosphate Nuclear Wasteforms," G. K. Marasinghe, M. Karabulut, C. S. Ray, D. E. Day, D. K. Shuh, P. G. Allen, M. L. Saboungi, and M. Grimsditch, *J. Non-Cryst. Solids* 263 (2000) 146.
18. "Properties of Mixed Na₂O and K₂O Iron Phosphate Glasses," Xiangyu Fang, C. S. Ray, G. K. Marasinghe, and D. E. Day, *J. Non-Cryst. Solids* 263 (2000) 293.
19. "A High Energy X-ray and Neutron Scattering Study of Iron Phosphate Glasses Containing Uranium," M. Karabulut, G. K. Marasinghe, C. S. Ray, G. D. Waddill, D. E. Day, Y. Badyal, M-L. Saboungi, D. Haefner, and S. Shastri, *J. Appl. Phys.* 87 (2000) 2185.
20. "Vitrified Iron Phosphate Nuclear Wasteforms Containing Multiple Waste Components," G. K. Marasinghe, M. Karabulut, X. Fang, C. S. Ray, D. E. Day, J. J. Bucher, N. M. Edelstein, D. K. Shuh, and P. G. Allen, *Environment Issues and Waste Management Technologies V: Ceramic Transactions* 107 (2000) 115.
21. "Immobilization of CsCl and SrF₂ in Iron Phosphate Glass," M. G. Mesko, D. E. Day, and B. C. Bunker, *Waste Management* 20 (2000) 271.
22. "Electrical Relaxation in Mixed Alkali Iron Phosphate Glasses," A. Mogus-Milankovic, B. Santic, C. S. Ray, and D. E. Day, *J. Non-Cryst. Solids* 263 (2000) 299.
23. "Properties of Mixed Na-K Iron Phosphate Glasses," X. Fang, C. S. Ray, G. K. Marasinghe, and D. E. Day, *Environmental Issues and Waste Management Technologies* 107 (2000) 207.
24. "Local Environment of Iron and Uranium Ions in Vitrified Iron Phosphate Glasses Studied by Fe K and U L_{III}-edge X-ray Absorption Fine Structure Spectroscopy," M. Karabulut, G. K. Marasinghe, C. S. Ray, D. E. Day, G. D. Waddill, P. G. Allen, C. H. Booth, J. J. Bucher, D. L. Caulder, D. K. Shuh, M. Grimsditch, and M-L. Saboungi, *J. Mater. Res.* 15 (2000) 1972.
25. "Summary Data on the Radioactive Waste, Spent Nuclear Fuel, and Contaminated Media Managed by the U.S. Department of Energy", U.S. Department of Energy, Washington D.C. (2001).
26. "Iron Phosphate Glass as an Alternative Waste-Form for Hanford LAW", D. S. Kim, W. C. Buchmiller, M. J. Schweiger, J. D. Vienna, D. E. Day, C. W. Kim, D. Zhu, T. E. Day, T. Neidt, D. K. Peeler, T. B. Edwards, I. A. Reamer, and R. J. Workman, PNNL-14251, Pacific Northwest National Laboratory, Richland, WA (2003).
27. "Vitrification and Product Testing of AW-101 and AN-107 Pretreated Waste", G. L. Smith, L. R. Greenwood, G. F. Piepel, M. J. Schweiger, H. D. Smith, M. W. Urie, and J. J. Wagner, PNNL-13372, Pacific Northwest National Laboratory, Richland, WA (2000).
28. "Sulfate Segregation in Vitrification of Simulated Hanford Nuclear Waste", G. K. Sullivan, M. H. Langowski, and P. H. Hama, *Ceramic Transactions* 61 (1995) 187-193.
29. "Standard Practices for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method", American Society for Testing and Materials (ASTM) C 829-81 (1995).
30. "Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT)", American Society for Testing and Materials (ASTM) C 1285-97 (1998).
31. "Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant", U.S. Department of Energy (DOE), Contract No.: DE-

- AC27-01RV14136, DOE Office of River Protection, Richland, WA; Contract with Bechtel National, Inc., San Francisco, CA (2001).
32. "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material (U)", C. M. Jantzen, N. E. Bibler, D. C. Beam, C. L. Crawford, and M. A. Pickett, WSRC-TR-92-346, Rev.1, Westinghouse Savannah River Company, Aiken, South Carolina (1993).
 33. "Hanford Immobilized LAW Product Acceptance Testing: Tanks Focus Area Results", J. D. Vienna, P. Hrma, A. Jiricka, D. E. Smith, T. H. Lorier, I. A. Reamer, and R. L. Schulz, PNNL-13744, Pacific Northwest National Laboratory, Richland, WA (2001).
 34. "Glass Science", R. Doremus, John Wiley & Sons Inc. (1994).
 35. Personal Communication with D. K. Peeler at Westinghouse Savannah River Company (2003).
 36. Personal Communication with J. D. Vienna at Pacific Northwest National Laboratory (2002).
 37. "Chemically Durable Iron Phosphate Glasses for Vitrifying Sodium Bearing Waste (SBW) using Conventional and Cold Crucible Induction Melting (CCIM) Techniques", C. W. Kim, C. S. Ray, D. Zhu, D. E. Day, D. Gombert, A. Aloy, A. Moguš-Milanković, and M. Karabulut, J. Nucl. Mater. (in press).
 38. "Tank Farm Contactor Operation and Utilization Plan (TWRS-OUT)", R. A. Kirkbride, HNF-SD-WM-SP-012, Rev.2, CH2M Hill Hanford Group, Inc., Richland, WA (2000).
 39. "Glass Optimization for Vitrification of Hanford Site Low-Level Tank Waste", X. Feng, P. R. Hrma, J. H. Westsik, Jr., N. R. Brown, M. T. Schweiger, H. Li et al., PNNL-10918, Pacific Northwest Laboratory, Richland, WA (1996).
 40. "Cold Crucible Induction Melter Technology: Results of Laboratory Directed Research and Development", D. Gombert, INEEL/EXT-01-01213, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID (2001).
 41. "JCCEM Workshop-US/Russian Experiences on Solidification Technologies-Record of Melting", Augusta, GA, September 4-5 (1997).

APPENDIX 1

Milestone Status Table

Task / Milestone Description	Planned Completion	Actual Completion	Comments
Identification of High Priority Candidate Wastes	6/15/02	6/15/02	
Evaluation of Candidate Refractories and Electrode Materials	6/15/03	6/15/03	Will continue to 5/31/04
Evaluation of Raw Materials/Use of Industrial Wastes	6/15/03	6/15/03	
Evaluation of Melting Conditions/Techniques	6/15/03	6/15/03	Will continue to 5/31/04
Wasteform Property and Characterization Measurements	6/15/03	6/15/03	Will continue to 5/31/04
Preparation of Final Report	9/15/03		New date 5/31/04

APPENDIX 2

Budget Data

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE	Cost Share	Total	DOE	Cost Share	Total
	From	To	Amount			Amount		
Year 1	10/1/00	9/31/01	173,000	-	173,000	82,746	-	82,746
Year 2	10/1/01	9/31/02	173,000	-	173,000	222,478	-	222,478
Year 3	10/1/02	5/31/03	174,000	-	174,000	63,337	-	63,337
Year 4	6/1/03	5/31/04	151,000	-	151,000	See below*		
Totals			671,000	-	671,000			

* A no cost time extension is being requested for the period from 9/31/03 (current ending date) to 5/31/04.

Spending Plan for the Next Year

Month	Estimated Spending
June 03	18,900
July 03	18,900
August 03	18,900
September 03	10,522
October 03	10,522
November 03	10,522
December 03	10,522
January 04	10,522
February 04	10,522
March 04	10,522
April 04	10,522
May 04	10,524