

Iron Phosphate Glass for Vitriifying Hanford AZ102 LAW in Joule Heated and Cold Crucible Induction Melters – 12240

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ABSTRACT

An iron phosphate composition for vitrifying a high sulfate (~17 wt%) and high alkali (~80 wt%) Hanford low activity waste (LAW), known as AZ-102 LAW, has been developed for processing in a Joule Heated Melter (JHM) or a Cold Crucible Induction Melter (CCIM). This composition produced a glass waste form, designated as MS26AZ102F-2, with a waste loading of 26 wt% of the AZ-102 which corresponded to a total alkali and sulfate (represented as SO₃) content of 21 and 4.4 wt%, respectively. A slurry (7M Na⁺) of MS26AZ102F-2 simulant was melted continuously at temperatures between 1030 and 1090°C for 10 days in a small JHM at PNNL and for 70 hours in a CCIM at INL. The as-cast glasses produced in both melters and in trial laboratory experiments along with their canister centerline cooled (CCC) counterparts met the requirements for the Product Consistency Test (PCT) and the Vapor Hydration Test (VHT) responses in the Hanford Tank Waste Treatment and Immobilization Plant (WTP) Contract. These glass waste forms retained up to 77 % of the SO₃ (3.3 wt%), 100% of the Cesium, and 33 to 44% of the rhenium (used as a surrogate for Tc) all of which either exceeded or were comparable to the retention limit for these species in borosilicate glass nuclear waste form. Analyses of commercial K-3 refractory lining and the Inconel 693 metal electrodes used in JHM indicated only minimum corrosion of these components by the iron phosphate glass. This is the first time that an iron phosphate composition was melted continuously in a slurry fed JHM and in the US, thereby, demonstrating that iron phosphate glasses can be used as alternative hosts for vitrifying nuclear waste.

INTRODUCTION

Vitrification is the process chosen for treatment of high-level nuclear wastes worldwide. Vitrification of lower level nuclear wastes was chosen for several facilities including Hanford in the U.S., SAI Radon in the Russian Federation, and the Ulchin site in the Republic Of Korea. The U.S. Department of Energy (DOE) currently uses only borosilicate (BS) glasses [1, 2] for such purposes. However, many nuclear wastes presently awaiting disposal have complex and diverse chemical compositions and often contain components such as phosphates, sulfates, chromates and heavy metals that have low solubilities in BS glasses. Such wastes can be pre-processed and/or diluted to compensate for their incompatibility with a BS glass matrix, but this limits the waste loadings, and increases the waste form volume and overall cost for waste vitrification. These shortcomings create a need to develop alternative glass matrices such as the iron phosphate glasses [3] which can accommodate a higher waste loading while retaining the required chemical durability.

Compared to BS glasses, phosphate glasses readily dissolve larger amounts of many of these problematic components, including S, Fe, halides, heavy metals (Cr, Bi, Mo, etc), etc., at concentrations much higher than those in BS glasses. Conventional phosphate glasses are known to have a poor chemical durability that precludes their use in many practical applications including waste vitrification. However, numerous studies have clearly shown that iron phosphate (FeP) glasses are an exception [4-12]. They have shown promise for vitrifying a large variety of wastes such as high-chromium HLW (Hanford) [4-6], high-alkali/sulfate LAW (Hanford) [7-9], sodium bearing waste (SBW at INL) [10,11], and high molybdenum-containing HLW from spent nuclear fuel [12], with waste loading ranging from 30 to 70 wt%, which equals to or exceeds that of borosilicate glasses, while retaining a chemical durability that exceeds existing DOE requirements for glassy waste forms. FeP glasses have also been shown in laboratory tests to have a lower melting temperature ($< 950^{\circ}\text{C}$) and lower viscosity (between 200 and 400 cP at the melting temperature) than borosilicate glasses [1, 8, 10]. Thus, FeP glasses may melt faster and mix rapidly without a need for mechanical stirring or bubbling the fluid melt. A lower melting temperature and shorter melting time usually increases the retention of volatile components (S, Cl, F, Cs, Tc) and other long-lived radioactive elements in the glass waste form.

Most of the data for FeP glasses for nuclear waste disposal have been generated from small, laboratory scale tests. To assess their practical potential for nuclear waste vitrification, further data is needed to determine the suitability of the FeP compositions for industrial scale melting and processing. The general objective of the present research was to develop an iron phosphate glass composition for the high sulfate (~ 17 wt%)/high alkali (~ 80 wt%) Hanford AZ-102 LAW and which could be melted and processed in an existing Research Scale Melter (RSM) based on Joule Heated Melting (JHM) at PNNL and the Cold Crucible Induction Melter (CCIM) at INL. While an FeP glass has not been melted in a JHM prior to the present work, limited data for melting of an iron phosphate glass containing 45 wt% SBW in a CCIM are available [9, 10].

The factors of primary interest for the glass development work in the present study included: (1) designing iron phosphate glass compositions having high waste loadings, (2) selection of appropriate raw materials, (3) developing melting procedures compatible with the selected raw materials, (4) preparing glass waste forms containing simulated wastes, and (5) evaluating key properties to identify the appropriate compositions for the melter tests. The properties of the glass waste forms and their crystallized CCC counterparts were tailored through compositional adjustments to meet the DOE requirements for nuclear waste disposal. The CCC-treatment was accomplished according to time/temperature cooling profile recommended for WTP LAW glasses [13]. A composition, designated as MS26AZ102F-2, that contained 26 wt% of the Hanford AZ-102 LAW and which could be melted at 1050°C , was developed following the above criteria. The specific melt and glass properties of the MS26AZ102F-2 composition that were measured in the present work included: (1) the corrosion of Inconel 693 metal electrode and glass-contact refractory (Monofrax K-3) materials, (2) the melt viscosity and electrical conductivity as functions of temperature, (3) the chemical durability of the FeP glass waste form and its CCC-counterpart by PCT and VHT, (4) identification of crystalline phases formed in the as-prepared (quenched) and CCC-treated samples using x-ray diffraction (XRD) and scanning electron microscopy (SEM), and (5) chemical analysis of the quenched and CCC-samples by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

In addition, the percent retention of volatile components such as S, Cs, and Re (a surrogate for Tc-99) in the as-made glass and CCC-samples was measured as a function of melting temperature, melting time, redox state of the melt and the time the melt was bubbled with dry air. These measurements were important to identifying the appropriate processing conditions to increase the retention of these volatile

components in the melt, if needed. The effect of adding a reducing agent such as sugar on the behavior (foaming, off-gas composition, especially, NO_x) of the melt, and on the redox state of the iron ions that can potentially affect the waste form properties, was also investigated.

In the final stage of the present work, a MS26AZ102F-2 slurry (7M Na) simulant was continuously melted for 10 days at 1030°C to 1090°C in the RSM at PNNL and for 7 days in a CCIM at INL. The operational performance of both melters and melter components (refractory linings, and metal electrodes and tubes) was monitored and evaluated to determine the feasibility of melting FeP glasses in JHM and CCIM. The glass produced in these melters was sampled at regular intervals during the continuous melting process. These glass samples, as well as their CCC-treated counterparts, were analyzed using the same criteria as used for the small scale, laboratory glasses, i.e., their composition (ICP-AES), chemical durability (PCT, VHT), retention of volatile components (SO_3 , Cs, Re), and crystal phase identification (XRD).

EXPERIMENTAL METHODS

Composition Formulation

The composition for the high sulfate (~ 18 wt%)/high alkali (~ 80 wt%) containing AZ-102 LAW provided by Hanford for the glass formulation work is given in Table 1, column 2. Twenty-four iron phosphate compositions that contained minor amounts of other glass forming chemicals (GFC) and which were compatible with the AZ-102 LAW composition were initially formulated and used for laboratory scale (300 to 500 g) glass melting experiments. The guiding rationale for the compositional development was to identify a composition that produced a glass with the highest waste loading while achieving a low melting temperature ($\leq 1100^\circ\text{C}$), a melt viscosity of 25 to 100 poise and a melt whose electrical conductivity was between 10 and 100 S/m. The melt should not be corrosive toward the metal and refractory components to be used in the melter tests. The chemical durability of the iron phosphate glass waste form obtained by ordinary cooling of the melt and when cooled according to the CCC schedule, needed to meet the PCT and VHT requirements in the WTP Contract [14].

Based on the test results, five promising compositions were subjected to more rigorous tests, including the reproducibility of melting behavior and chemical composition of the glass when melted at a 2 to 5 kg scale. Finally, a baseline composition, designated as MS26AZ102F-2, which contained 26 wt% of the AZ-102 LAW (Table 1, column 2) and which could be melted between 1030°C and 1050°C in 3 to 5 h was selected as the candidate for conducting the JHM and CCIM tests. The glass forming chemicals (GFC), the final composition of MS26AZ102F-2, and the raw materials used to prepare the glass batch are also included in columns 3, 4, and 5, respectively, of Table 1. Additional tests such as the feasibility of melting a slurry-feed for longer times, up to 10 days, and the retention of volatile components like SO_3 , Cs and Re for reducing/oxidizing melting conditions were investigated for the MS26AZ102F-2 composition.

Simulated Joule Heated Melter (JHM) Experiment using Slurry (Liquid) Feed Batch at Missouri S&T/MO-SCI Corp.

A melting experiment for the MS26AZ102F-2 composition using a slurry (liquid) feed similar to what is used in the RSM (JHM) melter tests at PNNL was conducted using a 99.6% silica crucible, 127 mm ID, 178 mm tall, (~ 2.26 L capacity) in a resistance heated furnace at 1050°C. This experiment was performed to gain a broader understanding of the melting process and product performance, including glass composition and properties, and corrosion of the Inconel 693 electrode and K-3 refractory materials

under simulated melting conditions. The slurry feed was prepared by mixing the dry batch (including waste components) with de-ionized water and adding phosphoric acid (85% concentration H_3PO_4) as the primary source of P_2O_5 . The amount of water was adjusted to produce a feed volume of 8L which upon melting produced 4 kg of glass. The pH of the slurry was 2.7 and 0.5 before and after adding H_3PO_4 , respectively. The Na molarity in the slurry feed was 4.7M, and the viscosity of the slurry ranged between 5 and 10 centipoise.

Table 1: Iron phosphate glass forming composition (GFC), composition for Hanford AZ102 LAW, and raw materials for MS26AZ102F-2 for RSM and CCIM melter experiments.

Oxides	Hanford (AZ102) LAW, wt%	GFC wt%	Target Composition wt%	Raw Materials
Al_2O_3	0.27	17.76	13.21	$\text{Al}(\text{PO}_3)_3$
				AlPO_4
B_2O_3	0.1	0	0.03	H_3BO_3^*
Cl	0.14	0	0.04	NaCl^*
Cr_2O_3	0.81	3.36	2.7	Cr_2O_3
Cs_2O	0.5	0	0.13	CsNO_3^*
F	0.6	0	0.16	NaF^*
K_2O	3.01	0	0.78	KNO_3^*
Na_2O	77.04	0	20.03	NaNO_3^*
P_2O_5	0.22	51.35	38.06	Other GFC's
Re_2O_7	0.1	0	0.03	Re_2O_7^*
SiO_2	0.43	7.39	5.58	SiO_2
SO_3	16.79	0	4.37	Na_2SO_4^*
Bi_2O_3	0	2.39	1.77	$\text{Bi}(\text{OH})_3$
CaO	0	1.43	1.06	CaHPO_4
Fe_2O_3	0	9.59	7.1	Fe_2O_3
La_2O_3	0	0.96	0.71	La_2O_3
ZnO	0	4.8	3.55	ZnO
ZrO_2	0	0.96	0.71	ZrO_2
Total	100.01	100	100	

*

Raw materials used for glass formulation work, but these oxide components would be supplied by the waste stream. The contents of the critical oxides are shown in red.

Other GFC's: All P_2O_5 is available from $\text{Al}(\text{PO}_3)_3$ and AlPO_4 .

The silica crucible was located inside a furnace at 1050°C. The liquid slurry was fed from a reservoir through a flexible polyethylene tube which was connected to an alumina tube through which the slurry entered the hot crucible. The slurry was fed at 24h intervals, feeding 1L each for days 1 and 2, and 2L each for days 3, 4 and 5 at a feed rate of 0.33 L/min, thus completing the slurry feeding on day 5. The melt was held at 1050°C for another 5 days, for a total melting time of 10 days, whereupon, the melt was cast into a stainless steel mold. The melt was stirred periodically with a silica rod during the 5-day period. A steady melting temperature of 1030°C was recorded by a separate thermocouple located just above the melt surface inside the furnace.

An Inconel 693 coupon, of approximate dimensions 27.8 cm (long) x 3.4 cm (wide) x 0.8 cm (thick), was placed inside the crucible at the beginning of the 10 day melting experiment. Inconel 693 has been chosen as the electrode material for use in the RSM (JHM) melter test at PNNL. The 693 coupon and the interior walls of the silica crucible were analyzed before and after the 10 days of glass melting at 1030°C were analyzed by optical microscopy, scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDS) to evaluate the compatibility of these materials with the iron phosphate melt.

RSM (JHM) Test at PNNL

The continuously operated JHM test was conducted in the RSM at PNNL from 30 November to 09 December 2010 using a 7M Na⁺ liquid (slurry) feed of MS26AZ102F-2 iron phosphate composition (Table 1). The melter was equipped with Inconel 693 electrodes, Monofrax K-3 refractory, Inconel 690 pour spout and an Inconel 625 bubbler tube. An electric kiln surrounding the melter body minimized heat loss from the melter body during operation. The melter was also equipped with an off-gas treatment system that employed quenching, wet scrubbing, and high efficiency mist elimination. The glass discharge section was heated to facilitate pouring of the glass. The melter cavity was 15 cm in diameter with a nominal glass depth of 7.6 cm. The melter was operated at an average temperature of 1030°C and a plenum temperature between 300 and 600°C with a batch (slurry) feed rate ranging between 0.54 and 1.07 L/h. Prior to feeding the slurry to the melter it was loaded with 2.27 kg of start-up glass (MS26AZ102F-2 composition) prepared at Missouri S&T/MO-SCI Corp. to initiate the melting.

The test was conducted at varying melting conditions such as with or without air bubbling, or sugar addition (50 g/L as a reducing agent in the slurry feed to control foaming). The bubbling (air) was maintained at an average rate of 1.5 L/min. During the operation, small amounts of the melt were drained at regular intervals to provide samples for analysis. These tests included glass homogeneity (chemical analysis by ICP-AES, and XRD), chemical durability (PCT, VHT), density, and iron redox. Some of these samples were heat treated per CCC protocol, and analyzed for their chemical durability. The Inconel 693 metal electrodes were examined at the conclusion of these tests by optical microscopy and scanning electron microscopy to assess the extent of corrosion of the metal by the MS26AZ102F-2 melt.

Cold Crucible Induction Melter (CCIM) Test at INL

The CCIM test was conducted at INL also using a slurry feed as was used in the RSM experiment. The CCIM experiment was conducted continuously for 70 h between December 13-16, 2010 at temperatures between 1030 and 1100°C and at power levels up to 40 kW using a slurry-batch (normalized to 7M Na) feed rate between 0.86 and 2.0 L/h. A water cooled 316 stainless steel tubing with a water-cooled bottom plate and an un-cooled Inconel 625 melter lid constituted the melting crucible. As was done in the JHM experiment, pre-melted MS26AZ102F-2 frit was used to start the CCIM experiment. The melt was bubbled with air, and sugar (25 g/L) was added to the slurry feed. Samples of the melt were drained periodically to provide samples for analysis.

Glass Characterization

Depending upon the availability of equipment and facilities, the analysis and characterization of the glass and CCC-treated samples prepared from small scale laboratory melts, and from the RSM and CCIM tests were performed either at MO-SCI Corp./Missouri S&T or SRNL (Savannah River National Laboratory), or both. The chemical analysis for the glass samples was performed using ICP-AES primarily

at SRNL. The chemical durability of the samples was measured at SRNL using two methods: PCT per ASTM C 1285-02 (method A) [15] and VHT per ASTM C 1663-09 (method B) [16]. The VHT was performed at MO-SCI Corp. The high temperature viscosity of the MS26AZ102F-2 melt was measured at MO-SCI Corp. per ASTM C 965-96 [17], while the high temperature electrical conductivity of this melt was measured at the Catholic University of America (CUA) using VSL-08R1370-1, Rev. 0 procedures.

RESULTS AND DISCUSSION

General—Glass Formation

The MS26AZ102F-2 iron phosphate composition, containing 26 wt% of the simulated Hanford AZ-102 LAW, formed a homogeneous black glass when melted in a laboratory furnace between 1000 and 1050°C in air at various melting conditions such as dry and wet (slurry) batches, and small scale/short duration (~300 g/3 to 5 hrs) to large scale/long duration (4 to 80 kg/48 hrs to 10 days) melting protocols. Other melting conditions included bubbling the melt with air, adding sugar to the batch as a reducing agent, melting in the small scale JHM at PNNL and CCIM at INL. Except for the presence of a small amount (< 10 wt%) of crystalline material that, depending upon melting and cooling conditions consisted two or more of the compounds Na_2SO_4 , $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_3$, CaF_2 and Cr_2O_3 , glasses from all the as-quenched melts were x-ray amorphous. The density for the glasses prepared from the different melts including those from the JHM and CCIM tests was consistent, and ranged from 2.77 to 2.84 g/cm³.

The CCC samples of this glass, as well as a glass deliberately crystallized by heating it at 620°C for 48 h, contained an additional crystalline compound, $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$, but no Na_2SO_4 . The color of the CCC-treated or crystallized samples was greenish-yellow.

The JHM (PNNL) and CCIM (INL) tests for melting the MS26AZ102F-2 iron phosphate glass were completed successfully. In these trials, the JHM test operated continuously for 10 days and CCIM for 70 hrs. The specific melting rate reached 1010 kg/m²/day in the JHM and 664 kg/m²/day in the CCIM, producing about 125 kg of glass in the JHM in 10 days and 35 kg of glass in the CCIM in 70 hrs.

Chemical Analysis (ICP-AES)

The average composition (ICP-AES) for the MS26AZ102F-2 glasses prepared from different melts is shown in Table 2. The results in Table 2 indicate that the composition of all of the independently melted glasses is in excellent agreement with the target composition, even though the melting times ranged from 3 h (laboratory scale trial melts) to 10 days (slurry-fed simulated JHM tests) at temperatures between 1030 and 1050°C. The total Na_2O content in the analyzed glasses varied between 19.30 and 20.70 wt%, which agrees well with the target composition of 20.03 wt%.

A noteworthy result for this iron phosphate glass waste form is the high retention of volatile components, like SO_3 , Cs_2O , and Re_2O_7 , after melting at 1050°C. The concentration of these volatile components varied somewhat with the melting time, as expected. For glasses prepared from the laboratory scale melts, which melted rather quickly (average melting time 4 h), the retention of SO_3 ranged from 74 to 98% (average 86%), and that for Cs_2O and Re_2O_7 was 100% and 67%, respectively. For the larger 80 kg melt (starter glass), the retention of SO_3 was 65% due to the longer (48 h) melting time. The Cs_2O and Re_2O_7 contents in the starter glass were nearly the same as that for the glasses melted only for 4 h, with the retention being 92 and 67%, respectively. The retention for the glass prepared by

Table 2. Chemical composition (ICP-AES) for the MS26AZ102F-2 glasses prepared from different laboratory melting.

Oxides	Target Comp., wt%	Small Scale Melt* wt%	Starter Glass** Wt%	Slurry Melt*** Wt%
Al ₂ O ₃	13.21	13.18	13.00	13.55
B ₂ O ₃	0.03	NM	NM	NM
Cl	0.04	<0.50	NM	NM
Cr ₂ O ₃	2.7	2.57	2.47	0.40
Cs ₂ O	0.13	0.15	0.12	0.12
F	0.16	<0.5	NM	NM
K ₂ O	0.78	0.99	1.05	0.99
Na ₂ O	20.03	19.65	19.30	20.15
P ₂ O ₅	38.06	38.73	39.15	40.27
Re ₂ O ₇	0.03	0.02	0.02	0.01
SiO ₂	5.58	5.77	6.07	6.95
SO ₃	4.37	3.74	2.85	2.11
Bi ₂ O ₃	1.77	1.91	1.74	1.82
CaO	1.06	1.23	1.18	1.15
Fe ₂ O ₃	7.10	7.07	7.29	6.65
La ₂ O ₃	0.71	0.68	0.63	0.65
ZnO	3.55	3.64	3.57	3.73
ZrO ₂	0.71	0.62	0.61	0.64

*Average of 6 independent samples (melt size 300 to 500 g).

**Average of 2 independent samples (80 kgs of glass).

***Average of 2 independent samples (4 kgs of glass).

The contents of the critical oxides are shown in red.

slurry-feed melting, which lasted 10 days, was 48% for SO₃, 92% for Cs₂O, and 33% for Re₂O₇. However, an exception is noted for the retention of Cr₂O₃ in the glass prepared using a slurry feed, where Cr₂O₃ content was only 0.40 wt% compared to 2.70 wt% in the starting batch. This lower retention of Cr₂O₃ is believed due to the longer melting time (10 days) for the slurry feed experiment.

The average composition (ICP-AES) for the glasses prepared in the RSM (PNNL) and CCIM (INL) experiments is shown separately in Table 3. The composition for the RSM-PNNL glasses in Table 3 is the average of measurements on 17 independent samples that were collected periodically over 10 days. Likewise, the composition for the CCIM-INL glasses in Table 3 is the average for 8 independent samples collected over 4 days. In addition to sampling these glasses at different times, they were prepared under different melting conditions such as with and without bubbling or the addition of sugar to the slurry feed. Nevertheless, the standard deviation for all the measurements is low (< 0.9), and the average compositions for the glasses made in the RSM and CCIM are in excellent agreement with the target composition.

The concentration of Cs₂O appears to be unaffected (100% retention) by the melting conditions employed in these tests, whereas the retention of Re₂O₇ averaged about 33% in both tests. The average

concentration of SO₃ in Table 3 is dependent upon the melting conditions, as will be discussed separately in a later section.

Table 3: Chemical composition (ICP-AES) of the glasses prepared in the RSM at PNNL and CCIM at INL and measured at SRNL.

Oxides	Target Comp., wt%	RSM-PNNL*		CCIM-INL**	
		wt%	Sd. Dev.	wt%	Sd. Dev.
Al ₂ O ₃	13.21	14.2	0.5	13.15	0.27
B ₂ O ₃	0.03	<Det	---	<Det	---
Cl	0.04	<Det	---	<Det	---
Cr ₂ O ₃	2.70	2.73	0.19	2.24	0.14
Cs ₂ O	0.13	0.13	0.00	0.14	0.01
F	0.16	<Det	---	<Det	---
K ₂ O	0.78	1.18	0.07	0.92	0.04
Na ₂ O	20.03	20.5	0.5	19.83	0.26
P ₂ O ₅	38.06	38.5	0.9	38.82	0.44
Re ₂ O ₇	0.03	0.01	0.00	0.01	0.00
SiO ₂	5.58	6.15	0.14	5.66	0.15
SO ₃	4.37	1.78	0.75	3.32	0.23
Bi ₂ O ₃	1.77	1.91	0.11	1.77	0.05
CaO	1.06	1.20	0.03	1.10	0.02
Fe ₂ O ₃	7.10	7.25	0.27	7.16	0.13
La ₂ O ₃	0.71	0.62	0.02	0.601	0.04
ZnO	3.55	3.70	0.14	3.42	0.08
ZrO ₂	0.71	0.70	0.09	0.65	0.04

*Average for 17 separate samples.

**Average for 8 separate samples.

<Det: Below detection limit. The contents of critical oxides are shown in red.

Chemical Durability -Product Consistency Test (PCT)

The PCT results for the as-cast quenched glass (QG), and the CCC-treated MS26AZ102F-2 samples, prepared from many different melts (small scale trial melts, starter melt, simulated JHM slurry feed melt, and RSM and CCIM test melts), are given in Table 4 in terms of the normalized elemental mass release (g/L). The DOE limit for normalized mass release is specified only for B, Na, and Si for the Hanford LAW borosilicate glass, so these data are included in Table 4 (bottom row) for comparison. No value is given for B since only a negligible amount of B₂O₃ is present in the MS26AZ102F-2 composition.

All the PCT measurements were conducted in triplicate and the average of the three trials are shown in Table 4. The range of data in Table 4 includes the results for 10 QG and 14 CCC samples from RSM-PNNL, 8 samples each for QG and CCC from CCIM-INL, and 3 samples each from small trial melts. The average PCT results for all the samples from each melt are separately shown in Fig. 1 for two important elements, Na and Si, for which the DOE limit for Hanford LAW is specified. The results in Table 4 and Fig.

1 indicate that the PCT data for the quenched glasses as well as the CCC treated samples, prepared from entirely different melting conditions are remarkably similar. The normalized mass releases of Na and Si from both samples (QG and CCC) are well below the current DOE limit (~ 4 g/L) for LAW. The results in Table 4 and in Fig. 1 clearly show that both the glassy and CCC-treated MS26AZ102F-2 iron phosphate waste forms meet the DOE requirements for PCT response when melted in a continuously operated RSM or CCIM.

Table 4. PCT results (normalized mass release) for the glasses prepared under various melting conditions.

Sample		Normalized Mass Release*, g/L					
		Na	Si	P	Al	Cr	Fe
RSM-PNNL**	QG	1.28-1.94	0.41-0.66	0.63-1.05	0.44-0.74	< Detect	< Detect
	CCC	1.56-2.51	0.94-1.17	0.60-1.33	0.77-1.48	< Detect	< Detect
INL-CCIM**	QG	1.39-1.70	0.59-0.91	0.60-0.84	0.54-0.71	< Detect	0.003-0.019
	CCC	1.46-1.69	0.94-1.02	0.56-0.66	0.71-1.11	< Detect	< Detect
Small trial melt**	QG	1.35-1.60	0.63-0.64	0.69-0.74	0.47-0.50	0.05	0.01
	CCC	1.30-1.43	1.03-1.17	0.60-0.62	0.76-0.79	0.05	0.01
Large starter melt	QG	1.36	0.68	0.67	0.49	0.00	0.00
	CCC	1.36	0.94	0.58	0.73	0.00	0.00
Slurry fed melt	QG	1.50	0.58	0.80	0.56	0.03	0.00
	CCC	1.19	0.96	0.51	0.73	0.03	0.00
DOE LAW limit		4	4	n/a	n/a	n/a	n/a

*Normalized as function of measured composition in Tables 2 and 3. All results are average of triplicate measurements.

<Detect: Below detectable limit; n/a: not available.

**The ranges in the mass release values are for 10 QG and 14 CCC samples from RSM-PNNL, 8 samples each for QG and CCC from CCIM-INL, and 3 samples each from small trial melts. One sample each for QG and CCC from starter and slurry fed melts.

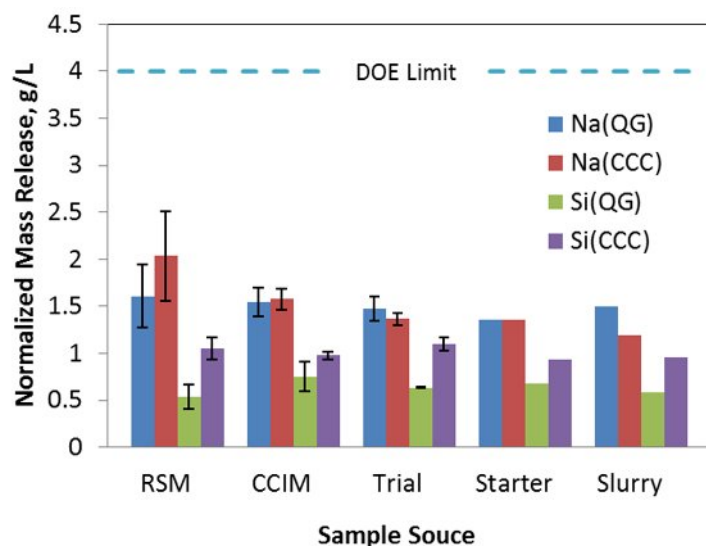


Fig. 1. PCT release for Na and Si for the glassy (QG) and CCC-treated samples from different melts.

Chemical Durability-Vapor Hydration Test (VHT)

Examples of both glassy and CCC-treated MS26AZ102F-2 samples after the VHT test are shown in Fig. 2 for two sets of representative samples: (a) sample prepared from a laboratory size melt at Missouri S&T/MO-SCI Corp. and (b) a sample melted in the RSM-PNNL test. No visible corrosion layer was observed in either glassy sample. The thickness for the alteration layer was small, and the corrosion rate was estimated to be $<5 \text{ g/m}^2/\text{day}$ for the small scale trial glass and $<8 \text{ g/m}^2/\text{day}$ for the RSM glass. A corrosion layer associated with a change in color is clearly visible in the CCC-treated samples, whose corrosion rate was calculated to be $21 \text{ g/m}^2/\text{day}$ (CCC-small scale trial melt, viz., Fig 2a) and $24 \text{ g/m}^2/\text{day}$ (CCC, RSM-PNNL melt, viz., Fig. 2b), which are well below the current DOE limit of $50 \text{ g/m}^2/\text{day}$ [16].

The VHT data listed in Table 5 are for selected glassy and CCC-treated samples prepared from different melts. All of the VHT values in Table 5, including those for the CCC-samples, were below the $50 \text{ g/m}^2/\text{day}$ DOE limit for LAW, except for three CCC-treated samples from the RSM test melts measured at PNNL (marked in red).

Table 5. VHT corrosion rate for the MS26AZ102F-2 quenched and CCC-treated samples.

Sample Origin	VHT Corrosion Rate, $\text{g/m}^2/\text{day}$		
	QG	CCC	DOE Limit
RSM-PNNL*	5.3, 6.2 (2 samples)	24, 42 (2 samples)	50
RSM-PNNL**	$<6-8$ (4 samples)	32-47 (3 samples)	
		60-116 (3 samples)	
CCIM-INL*	10.1-15.6 (3 samples)	22.6, 37.1 (2 samples)	
Trial Melt-MO-SCI*	<5 (one sample)	21 (one sample)	

*Measured at MO-SCI Corp.; **Measured at PNNL

Volatility/Retention of SO_3

The volatilization of SO_3 from the MS26AZ102F-2 melt depended upon the melting condition, such as the melting temperature and time, oxidizing/reducing state of the melt and melter atmosphere, and the gas used to bubble the melt. Iron oxide is a key component in this glass and the redox state of iron is expected to depend upon the oxidizing/reducing conditions of the melt. The iron redox for the glasses melted in the RSM under different conditions was measured using a calorimetric technique with UV-Vis spectroscopy according to procedure ITS-0042 developed at SRNL and is shown in Table 6 (column 3), along with the SO_3 concentration (column 2), measured by ICP-AES, for these glasses. These results are also separately shown in Fig. 3(a). Clearly, the retention of SO_3 decreases (volatilization of SO_3 increases) when the slurry contains a reductant (sugar). Addition of sugar provided a more reducing condition as evidenced by the larger Fe^{2+} fraction in these glasses, Fig. 3(a). Thus, an oxidizing melting condition appears more favorable for retaining a larger concentration of SO_3 in this iron phosphate glass.

The CCIM test was conducted with only one melting condition, namely, using sugar in the slurry and bubbling the melt with air for the entire 70 hrs experiment. The amount of sugar in the batch for the CCIM test was half (25 g/L) of that used in the PNNL-RSM test (50 g/L), thus providing a less reducing

condition for melting. This explains why the Fe^{2+} fraction for all of the INL-CCIM glasses (Table 6, column 4) is smaller than that for the PNNL-RSM glasses. The SO_3 content in the 8 INL-CCIM glasses as measured by ICP-AES ranged between 2.98 wt% to 3.53 wt% (retention between 68 and 81%), which is consistent with the lower fraction of Fe^{2+} .

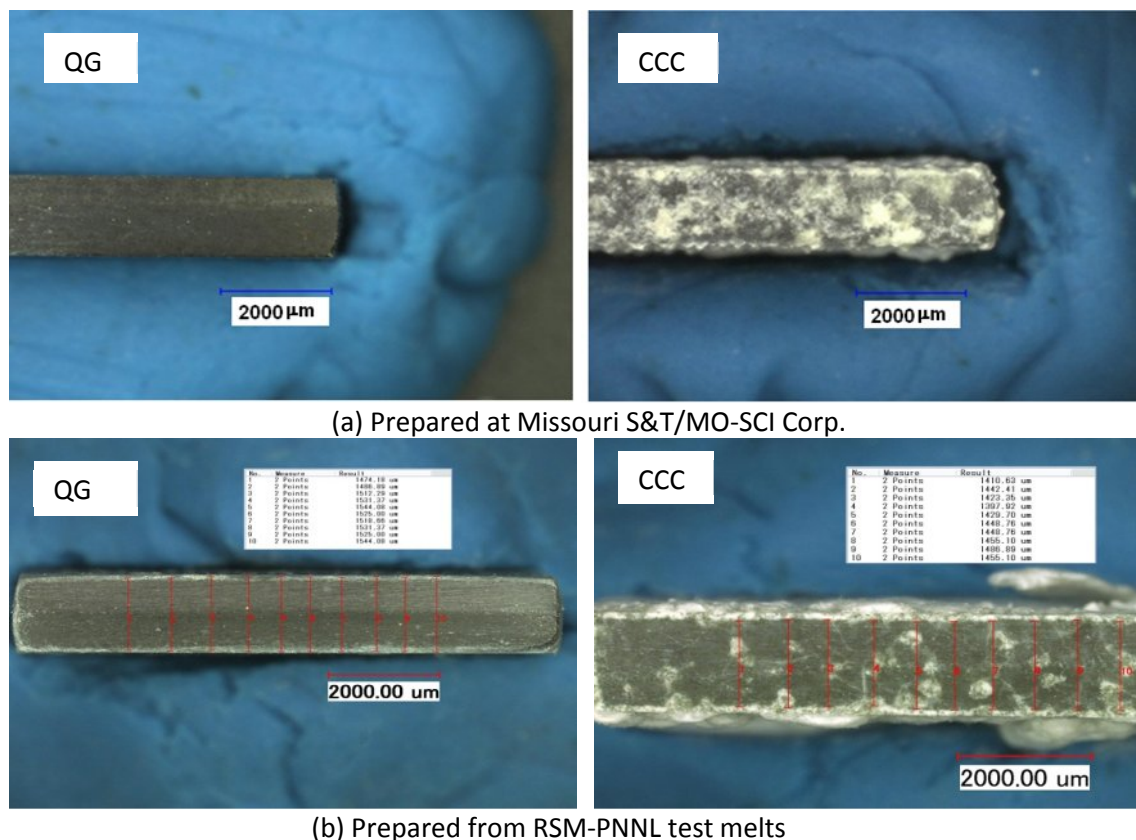


Fig. 2. Optical images for the post-VHT glassy (QG) and CCC-treated MS26AZ102F-2 samples prepared at (a) Missouri S&T/MO-SCI Corp. and (b) RSM-PNNL.

Table 6. Concentration of SO_3 and Fe^{2+} fraction in the glasses prepared in RSM-PNNL and CCIM-INL under various melting conditions.

Melting Condition	SO_3 Concentration, wt% (RSM-PNNL)*	Iron Redox, $\text{Fe}^{2+}/\Sigma\text{Fe}$	
		PNNL-RSM*	INL-CCIM**
Base Line	2.80, 3.43 (2 samples)	0.05, 0.06 (2 samples)	N/A
Bubbler Only	2.42 (1 sample)	0.04 (1 sample)	N/A
Sugar Only	0.99-1.32 (5 samples)	0.43-0.52 (5 samples)	N/A
Sugar plus Bubbler	1.16-1.47 (5 samples)	0.29-0.34 (5 samples)	0-0.09 (8 samples)
Bubbler Only	2.22-2.48 (5 samples)	0 – 0.06 (5 samples)	N/A

*sugar 50 g/L; **Sugar 25 g/L

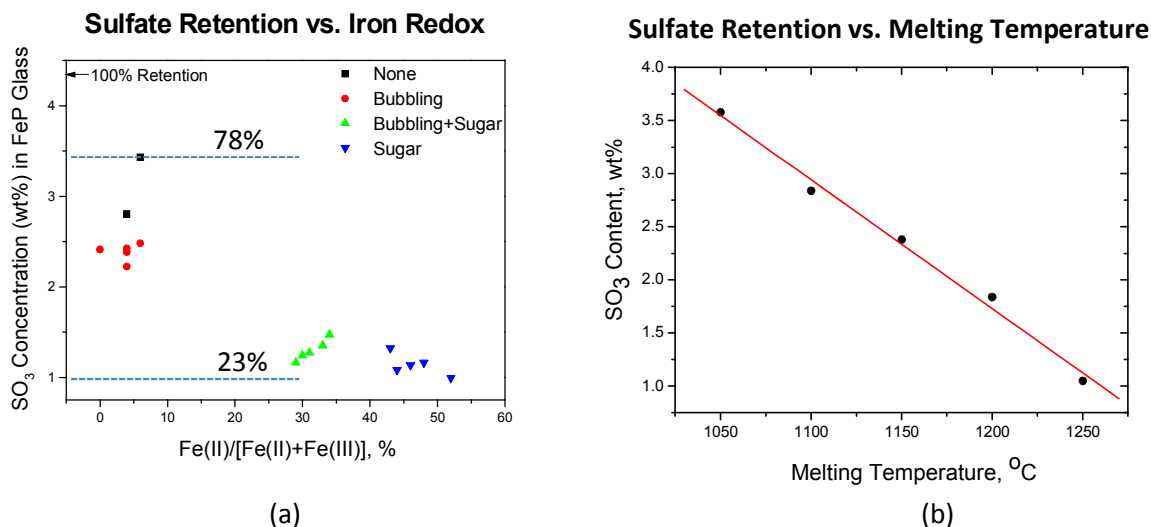


Fig. 3. Retention of SO₃ as a function of (a) Iron redox for the MS26AZ102F-2 glasses prepared at RSM-PNNL under different melting conditions, and (b) melting temperature for the same glasses prepared at Missouri S&T/MO-SCI.

It has been reported [19] previously that the Fe²⁺ fraction in an iron phosphate glass increases with increasing melting temperatures, which suggests that a melt gets more reduced as the melting temperature increases. According to the present work, therefore, the concentration of SO₃ should decrease in a sulfate containing iron phosphate glass when melted at increasing temperatures. The SO₃ content as measured by ICP-AES for the MS26AZ102F-2 iron phosphate glasses melted at temperatures between 1050 and 1250°C for 5 h in air is shown in Fig. 3(b), which clearly shows a decrease in SO₃ content with increasing melting temperature.

Corrosion of Inconel 693 Metal Electrode

The visual appearance (optical) of one of the Inconel 693 paddles used in the 10-day RSM experiment is shown in Fig. 4(a). This sample was subjected to an AC voltage between 10 and 35 V (current density between 1.6 and 3.5 A/cm²) in the MS26AZ102F-2 melt at temperatures between 1030 and 1050°C. Fig. 4(b) shows the SEM image of a small interior section that was cut from one side (marked by a red arrow in Fig. 4(a)) of the paddle located under the melt line. The sample was metallographically polished before the SEM examination.

As is evident in Fig. 4(a), the paddle does not show any visible sign of degradation and its edges appear sharp after being submerged in the iron phosphate melt for 10 days. The SEM image (Fig. 4(b)), shows some small void formation to a depth of ~300 μm from the surface of the electrode in this 10 day test. These results suggest that Inconel 693 metal can be used as an electrode for melting iron phosphate compositions such as MS26AZ102F-2.

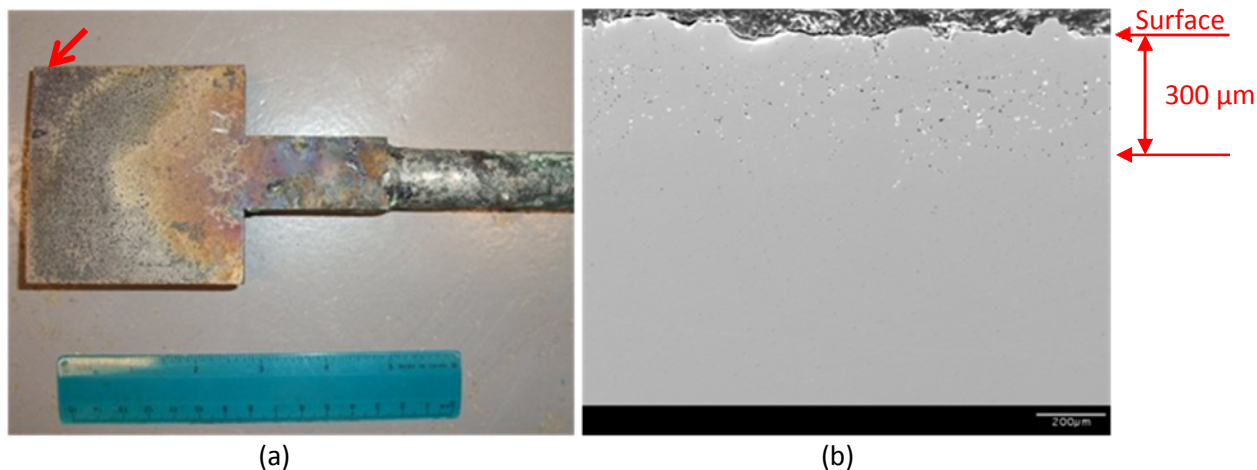


Fig. 4. (a) Inconel 693 metal electrode after 10 days in the MS26AZ102F-2 melt at 1030-1050°C in the RSM-PNNL test, (b) SEM picture on the polished interior section of a small part from the top left corner (marked by an arrow) of the electrode in (a).

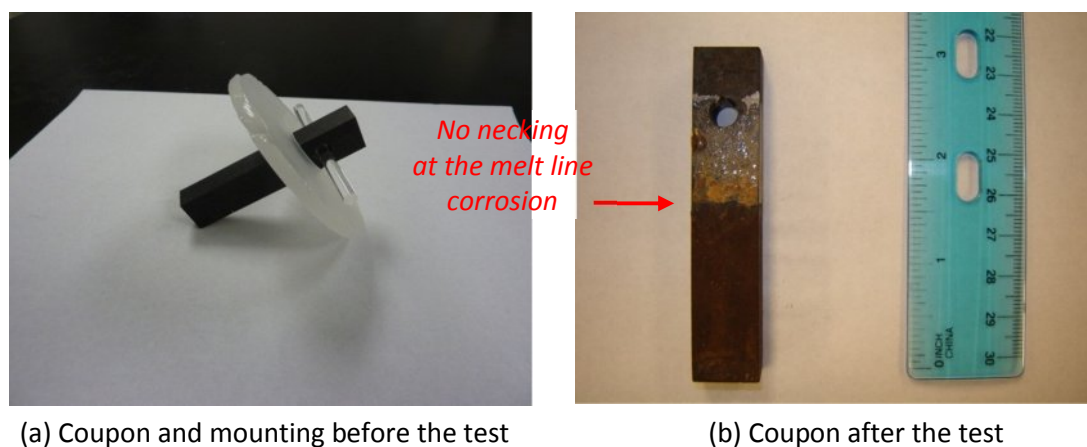


Fig. 5. Monofrax K-3 refractory coupon (a) before and (b) after the corrosion test in MS26AZ102F-2 melt at 1050°C for 7 days.

Other Studies-- Corrosion of Monofrax K-3 Refractory

The corrosion resistance of the Monofrax K-3 refractory in the MS26AZ102F-2 melt was measured per ASTM C621-09. This refractory was used in the JHM at PNNL, and would be in contact with the melt during glass processing. The optical images of a K-3 refractory coupon before and after partially immersion in the MS26AZ102F-2 melt at 1050°C for 7 days are shown in Fig. 5. No dimensional change or melt line necking of the coupon was observed after 7 days at 1050°C. These results indicate a high corrosion resistance of the K-3 refractory in the MS26AZ102F-2 melt, and suggest that this refractory should be acceptable for melting iron phosphate compositions similar to that of MS26AZ102F-2. The negligible corrosion of several commercial refractories by the iron phosphate melts that contained up to 16 wt% alkali, at temperatures ranging from 1000 to 1300°C has been reported previously [20].

Other Properties—Viscosity

For processing in a JHM or CCIM, the melt should have a viscosity between 20 and 110 poise [21]. In order to ensure this requirement, the high temperature viscosity of the MS26AZ102F-2 melt was measured between 950 and 1250°C using a rotating spindle viscometer modified for high temperature use and following the procedures described in ASTM C965-96 (2007) [17]. The viscosity at each temperature between 900 and 1250°C was measured three times after equilibrating the melt at the desired temperature for 30 min. The average of the three values is shown in Fig. 6(a) for each temperature. For comparison, the viscosity profile in this temperature range for the DWPF EA borosilicate glass is also shown in Fig. 6(a). The WTP recommended viscosity range, between 20 and 110 poise, for waste form processing in RSM and CCIM is shown by the two horizontal dashed lines. As shown in Fig. 6(a), the viscosity of the MS26AZ102F-2 iron phosphate melt falls within the planned processing temperature range around 1050°C, well within the WTP recommended viscosity range.

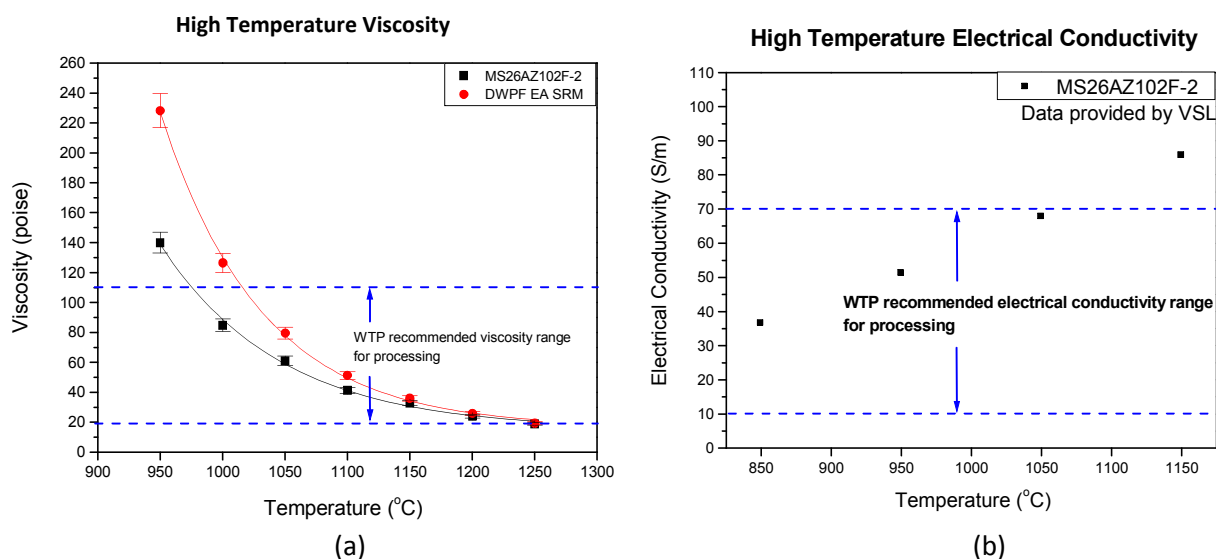


Fig. 6. (a) High temperature viscosity of MS26AZ102F-2 melt as a function of temperature between 900 and 1250°C using a rotating spindle viscometer, and (b) electrical conductivity of the same melt between 850 and 1150°C.

Other Properties—Electrical Conductivity

The WTP recommended electrical conductivity, at the frequency independent range, should be between 10 and 70 S/m for processing melts in a JHM. A higher electrical conductivity for a melt is preferred for CCIM processing. The electrical conductivity of the MS26AZ102F-2 melt was measured at several temperatures between 850 and 1150°C by VSL using VSL procedures (VSL-08R1370-1, Rev. 0) [18] and is shown in Fig. 6(b). The electrical conductivity of the MS26AZ102F-2 iron phosphate melt at the planned processing temperature of 1050°C is within, but close to the upper limit of the WTP recommended conductivity range (horizontal lines).

Summary/Conclusions

The following conclusions are drawn from the results of the present work.

- (1) An iron phosphate composition, designated as MS26AZ102F-2, containing 26 wt% of the simulated high sulfate (17 wt%), high alkali (80 wt%) Hanford AZ-102 LAW meets all the criteria for processing in a JHM and CCIM. This composition produces a homogeneous glass with a density of $2.80 \pm 0.04 \text{ g/cm}^3$ after melting between 1000 and 1050°C for 3 to 5 h.
- (2) This is the first time that an iron phosphate glass was melted in the JHM continuously for 10 days achieving a specific melting rate of 1010 kg/m²/day and in the CCIM for 70 hrs with a melting rate of 664 kg/m²/day.
- (3) The analyzed (ICP-AES) compositions for all the glasses prepared under several melting conditions are in excellent agreement with the target composition. The variation of melting conditions include: (i) use of small scale/short melting time to large scale/long melting time (300 g to 80 kg, 4 h to 10 days) operations including melting in the JHM and CCIM, (ii) use of dry or wet (slurry) melter feed, (iii) addition of reductant (sugar) in the batch, and (iv) bubbling the melt with air.
- (4) The chemical durability as measured by PCT and VHT for the quenched and CCC-treated waste forms prepared from laboratory, JHM or CCIM melting exceeds the DOE requirements for LAW.
- (5) Depending upon the melting time (4 h to 10 days), the average concentration of SO₃ in the MS26AZ102F-2 iron phosphate glass waste form varies from about 1.78 (RSM) to 3.74 (laboratory melt) wt% which corresponds to an SO₃ retention of 41 to 86% when melted between 1030 at 1050°C in air.
- (6) The retention of SO₃ in the glass was reduced when a reductant (sugar) was added to the slurry.
- (7) The retention of other problem components like Cesium and Rhenium/Tc-99 is also high; from 92 to 100% for Cs₂O under different melting conditions, and from 66 to 33% for Re₂O₇ for melts processed from 3 to 5 hours and up to 10 days.
- (8) Corrosion tests on Inconel 693 and K-3 refractory at temperatures between 1000 and 1050°C indicate that both materials should be suitable for melting iron phosphate glasses.
- (9) The viscosity and electrical conductivity of the MS26AZ102F-2 melt are within the acceptable limits for RSM and CCIM processing.
- (10) This work has shown that iron phosphate compositions are a potential alternative to borosilicate glasses for vitrifying problematic wastes such as Hanford AZ-102 LAW that contains high amounts sulfate and alkali oxides, and that iron phosphate melts such as MS26AZ102F-2 can be processed in the JHM or CCIM.

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