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Glass Formulation Development For INEEL Sodium-Bearing Waste

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July 1999

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Summary

For about four decades, radioactive wastes have been collected and calcined from nuclear fuels reprocessing at the Idaho Nuclear Technology and Engineering Center (INTEC), formerly Idaho Chemical Processing Plant (ICPP). Over this time span, secondary radioactive wastes have also been collected and stored as liquid from decontamination, laboratory activities, and fuel-storage activities. These liquid wastes are collectively called sodium-bearing wastes (SBW). About 5.7 million liters of these wastes are temporarily stored in stainless steel tanks at the Idaho National Engineering and Environmental Laboratory (INEEL). Vitrification is being considered as an immobilization step for SBW with a number of treatment and disposal options.

A systematic study was undertaken to develop a glass composition to demonstrate direct vitrification of INEEL's SBW. The objectives of this study were to show the feasibility of SBW vitrification, not a development of an optimum formulation. The waste composition is relatively high in sodium, aluminum, and sulfur. A specific composition and glass property restrictions, discussed in Section 2, were used as a basis for the development. Calculations based on first-order expansions of selected glass properties in composition and some general tenets of glass chemistry led to an additive (frit) composition (68.69 mass % SiO_2 , 14.26 mass % B_2O_3 , 11.31 mass % Fe_2O_3 , 3.08 mass % TiO_2 , and 2.67 mass % Li_2O) that meets all property restrictions when melted with 35 mass % of SBW on an oxide basis. The glass was prepared using oxides, carbonates, and boric acid and tested to confirm the acceptability of its properties. Glass was then made using waste simulant at three facilities, and limited testing was performed to test and optimize processing-related properties and confirm results of glass property testing.

The measured glass properties are given in Section 4. The viscosity at 1150°C, 5 Pa·s, is nearly ideal for waste-glass processing in a standard liquid-fed joule-heated melter. The normalized elemental releases by 7-day PCT are all well below 1 g/m², which is a very conservative set point used in this study. The T_L , ignoring sulfate formation, is less than the 1050°C limit. Based on these observations and the reasonable waste loading of 35 mass %, the SBW glass was a prime candidate for further testing.

Sulfate salt segregation was observed in all test melts formed from oxide and carbonate precursors. Melts fabricated using SBW simulants suggest that the sulfate-salt segregation seen in oxide and carbonate melts was much less of a problem. The cause for the difference is likely H_2SO_4 fuming during the boil-down stage of wet-slurry processing. Additionally, some crucible tests with SBW simulant were conducted at higher temperatures (1250°C), which could increase the volatility of sulfate salts. The fate of sulfate during the melting process is still uncertain and should be the topic of future studies. The properties of the simulant glass confirmed those of the oxide and carbonate glass. Corrosion tests on Inconel 690 electrodes and K-3 refractory blocks conducted at INEEL suggest that the glass is not excessively corrosive.

Based on the results of this study, the authors recommend that a glass made of 35% SBW simulant (on a mass oxide and halide basis) and 65 % of the additive mix (either fritted or raw chemical) be used in demonstrating the direct vitrification of INEEL SBW. It is further recommended that a study be conducted to determine the fate of sulfate during glass processing and the tolerance of the chosen melter technology to sulfate salt segregation and corrosivity of the melt.

Glossary

η	viscosity
AES	atomic emission spectroscopy
ASTM	American Society for Testing and Materials
CETL	Clemson Environmental Technology Laboratory
CH-TRU	contact-handled transuranic (wastes)
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EDS	energy dispersive spectroscopy
FY99	Fiscal Year 1999
HAW	high-activity waste
HLW	high-level waste
IC	ion chromatography
ICP	inductively coupled plasma
ICPP	Idaho Chemical Processing Plant
INEEL	Idaho National Environmental and Engineering Laboratory
INT	initial
INTEC	Idaho Nuclear Technology and Engineering Center
LAW	low-activity waste
LSM	laboratory-scale glass melter
OES	optical emission spectroscopy
PCT	product consistency test
RCRA	Resource Conservation and Recovery Act
RH-TRU	remote-handled transuranic (waste)
SBW	sodium-bearing waste
SEM	scanning electron microscopy
SRTC-ML	Savannah River Technology Center Mobile Laboratory
T	temperature
TFA	Tanks Focus Area
T_L	liquidus temperature
UDS	undissolved solids
WAPS	Waste Acceptance Product Specification
WIPP	Waste Isolation Pilot Plant
WVDP	West Valley Demonstration Project
XRD	X-ray diffraction

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1.0 Introduction

For about four decades, radioactive wastes have been collected and calcined from nuclear fuels reprocessing at the Idaho Nuclear Technology and Engineering Center (INTEC), formerly Idaho Chemical Processing Plant (ICPP). Over this time span, secondary radioactive wastes have also been collected and stored as liquid from decontamination, laboratory activities, and fuel-storage activities. These liquid wastes are collectively called sodium-bearing wastes (SBW). About 5.7 million liters of these wastes are temporarily stored in stainless steel tanks at the Idaho National Engineering and Environmental Laboratory (INEEL). Vitrification is being considered as an immobilization step for SBW with the following treatment options:

- 1) Direct vitrification of the liquid SBW with no pretreatment and send the final waste form to the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico, as remote-handled transuranic waste (RH-TRU).
- 2) Direct vitrification of the SBW after calcination and send resultant waste form to the federal geologic repository currently planned at Yucca Mountain, Nevada, for final disposal.
- 3) Fully separate the liquid SBW into high activity waste (HAW) and low activity waste (LAW) streams. The HAW fraction would be vitrified and sent to a repository as either RH-TRU or HLW, and the LAW fraction would be grouted and disposed of as either Class A or Class C waste.
- 4) Remove the cesium only from the liquid SBW and grout the remaining SBW and send to WIPP as contact handled TRU (CH-TRU) for final disposal.
- 5) Remove the cesium and strontium from the liquid SBW and either grout or vitrify the remaining SBW and send to WIPP as CH-TRU.
- 6) Calcine the liquid SBW and fully separate the SBW calcine into LAW and HAW fractions. The HAW fraction would be vitrified and sent to the federal geological repository, and the LAW fraction would be grouted and disposed of as either Class A or Class C waste.

Definitions of Waste Types. Class B waste is defined the same as Class C, but it is not referred to in this report.

Class A: The waste form requirements for Class A waste are minimal conjointly with the minimal radiological hazard of the waste. The minimal requirements for Class A waste are that the waste must be packaged; pyrophoric, explosive, toxic and infectious materials are banned; and liquid waste must be packaged with absorber or solidified to remove free liquid.

Class C: More rigorous waste form requirements are established for Class C waste as compared to Class A. In addition to the packaging requirements and prohibitions against pyrophoric, explosive, toxic and infectious materials, and free liquids, Class C waste must have structural stability. Structural stability means that the waste maintains its structural integrity under the expected disposal conditions. Stability prevents trench subsidence and water infiltration, prevents radionuclide release due to disintegration of the waste form, and minimizes the likelihood of intrusion into the waste; overall disposal site performance is improved by waste stabilization.

Reference

INTEC WASTE TREATMENT FACILITIES NRC LICENSING ASSESSMENT, December 17, 1998, Duke Engineering and Services, Inc., Subcontract NO. C95-175000.

In addition to the SBW, roughly 4,000 m³ of calcined high-level wastes (HLWs) are stored at INEEL in stainless steel bin sets. These calcined HLWs and liquid SBWs may be vitrified, either with or without a dissolution and separation process, and sent to the federal geologic repository for final disposal (Staples et al. 1999). This report focuses on direct vitrification of SBW (Options 1 and 2 listed above).

The Batt Settlement Agreement was established in August 1995 between the U.S. Navy, the State of Idaho, and the U.S. Department of Energy (DOE) (DOE 1995). Section E.6 of the Agreement states that all HLW stored at INEEL will be rendered ready (immobilized) for transport to a suitable repository by the end of Year 2035. More immediately, the technology must be applied to provide information required to initiate design of the HLW treatment facility in Year 2007. This design supports the Settlement Agreement milestone of submitting a Resource Conservation and Recovery Act (RCRA) Part B permit application in Year 2012 and the Site Treatment Plan operational date of September 30, 2019.

The DOE's Tanks Focus Area (TFA) is supporting technology development for immobilization of these wastes. The overall strategy of this TFA Technical Task is twofold: (1) develop glass-property data and glass-composition property models that cover the composition region expected from individual and/or blended INEEL HLWs and (2) support INEEL with glass formulation and testing expertise to assist in flowsheet optimization and melter demonstrations. Efforts related to the development of glass-property data and models are described by Piepel et al. (1999), Staples et al. (1999), and Edwards et al. (1999). Peeler et al. (1998), Vienna et al. (1999), and Vienna et al. (in press) reported on previous glass-formulation activities, focusing on blended INEEL wastes and zirconia calcine waste. The fiscal year 1999 (FY99) glass-formulation activities for INEEL SBW are the focus of this report. The results of testing described in this report are aimed at providing a candidate glass composition for use in scaled melter demonstration of the SBW direct-vitrification flowsheet. We have made no attempt to optimize the composition of SBW glass, so this effort should be considered as preliminary (i.e., glasses formulated to show feasibility, not optimization, of direct vitrification). Results of the scaled melter demonstration will be published in a subsequent report. Previous scaled melter demonstrations of INEEL vitrification flowsheets were reported by Musick et al. (1998).

2.0 Formulation

To develop a waste glass composition, we have followed a sequence described by Piepel et al. (1998):

- 1) determine the waste composition
- 2) determine the property and composition constraints
- 3) develop functions that relate glass composition to the properties of interest
- 4) calculate a glass composition that meets the property and composition constraints
- 5) fabricate and test the glass to ensure that property and composition constraints are met.

Our applications of these steps are described in the following sections.

2.1 Sodium Bearing Waste Composition (wt%)

Roughly, 5.7 million liters or 276 tons of SBW is currently stored at INEEL. It is a HNO_3 solution with approximately 7 M NO_3^{2-} . The composition of SBW is listed in Table 2.1. Only those components that are present in concentrations greater than 0.01 mass % and the components that are expected to remain in glass after vitrification were considered for this study. The minor components will be added once the characterization results of SBW are better defined. A cursory examination of the composition suggests that the waste components critical for glass formulation are Al, Na, and the anions (Cl^- , F^- , I^- , PO_4^{2-} , and SO_4^{2-}).

Table 2.1. Composition of Sodium-Bearing Waste

Component	Mass %	Component	Mass %	Component	Mass %
Al	20.202	Fe	1.509	Pb	0.401
B	0.281	I	0.025	Ru	0.046
Ca	2.223	K	9.175	PO_4	2.226
Cd + Ni	0.602	Mg	0.046	Si	0.116
Cl	1.445	Mn	0.844	Sn	0.023
Cr	0.243	Mo	0.123	SO_4	6.242
F	1.363	Na	51.837	Zr	1.030

2.2 Glass Property/Composition Constraints

With the goal of developing an acceptable glass to demonstrate the feasibility of direct vitrification of INEEL SBW, we must first establish a definition of an acceptable glass. Two types of glass-property limitations must be considered: (1) those product properties required for waste-form acceptance and (2) those processing properties required to ensure adequate melter processability. The product property requirements for acceptance in the federal repository are dictated by the Waste Acceptance Product Specification (WAPS) (DOE 1995). The WAPS imposes limitations on the performance of glass in the product consistency test (PCT) (ASTM 1994) and requires that chemical and phase-stability information be reported. The specific limit set is that the releases of boron, sodium, and lithium, normalized to glass composition, must be less than those of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) glass. The normalized releases of boron (r_B), sodium (r_{Na}), and lithium (r_{Li}) for the DWPF-EA glass are 8.35 g/m^2 , 6.67 g/m^2 , and 4.78 g/m^2 , respectively

(Jantzen et al. 1993). For the purposes of this study, we took a conservative upper release limit of 1 g/m^2 for r_B , r_{Na} , and r_{Li} to account for uncertainty in PCT measurement and/or glass composition in the proposed INEEL vitrification plant. This limit is consistent with that used by Peeler et al. (1998), Vienna et al. (1999), and Vienna et al. (in press). An additional concern is regarding the formation of secondary phases during cooling, which can detract from the durability of glass. Specifically, glasses formed from wastes high in Na and Al are susceptible to nepheline crystallization, which has been shown to lower the durability of some glasses.

We let the HLW vitrification experience at the DWPF and West Valley Demonstration Project (WVDP) be our guide for processing constraints. For these operating HLW vitrification plants, the nominal melter operating temperature is maintained at or close to 1150°C . The viscosity (η) at the operating temperature is maintained between 2 and 10 Pa-s. Finally, the liquidus temperature (T_L) of glass in the melter is maintained at 100°C below the operating temperature (i.e., T_L nominally $\leq 1050^\circ\text{C}$). These restrictions were adopted for this study. An additional processing-related concern is that the glass will corrode the melter materials during processing. No specific constraint was used to ensure that the melt is not excessively corrosive to melter construction material. Table 2.3 in Section 2.3 summarizes the glass property and composition constraints used to develop a glass for demonstration of the SBW vitrification flowsheet.

2.3 Functions to Relate Glass Properties to Composition

To calculate a glass composition for SBW waste that meets the criteria described in Section 2.2, we first must describe the glass properties as functions of composition or waste and additive concentrations. For the purposes of these scoping tests, selected glass properties were expanded as linear functions of composition:

$$P = \sum_{i=1}^n a_i g_i \quad (1)$$

where P is the transformed property, a_i is the i^{th} component coefficient, g_i is the i^{th} component mass fraction in glass, and n is the number of components in glass (thus $\sum g_i = 1$).^a The database used to obtain the a_i values was primarily that of Hrma et al. (1994) with a_{K_2O} and $a_{P_2O_5}$ obtained from Staples et al. (1999). Table 2.2 lists the a_i values used to estimate glass properties in this study.

The first-order approximations for the properties listed in Table 2.2 will provide a good foundation for initial glass-formulation efforts. However, two significant shortcomings must be pointed out: (1) the use of these approximations is recommended only within the composition region covered by the experimental data used to fit component coefficients and (2) no data set sufficient to predict T_L , homogeneity, and melter corrosion properties was found for this specific composition range. To address these issues, additional constraints in the form of ad hoc multi-component concentration limits were added. A constraint that the total alkali oxide concentration ($\text{Na}_2\text{O} + \text{Li}_2\text{O} + \text{K}_2\text{O}$) be less than or equal to 22 mass % was used to ensure that the glass remains in a composition region where the preliminary PCT models were thought to be applicable. At high concentration of alkali oxides, the glass durability drops precipitously because a continuous network of non-bridging oxygen sites is generated in the glass. A constraint that the SiO_2 concentration in a SiO_2 - Al_2O_3 - Na_2O sub-mixture in glass be greater than or equal

^a See Hrma et al. (1994) for details on property expansion.

to 60 mass % was added to avoid nepheline precipitation in the glass.^b Typically, a constraint on SO₃ concentration^c would be used to avoid sulfate accumulation in the melter (Li et al. 1995; Lambert et al. 1996). However, the tests planned to demonstrate SBW processability include the use of a melter with a salt drain that will tolerate salt separation.^d Therefore, no constraint on salt separation from glass was used for SBW glass formulation (i.e., salt formation will not limit waste loading).

Table 2.2. Property–Composition Coefficients (a_i values)

	$\ln [\eta \text{ (Pa}\cdot\text{s)}]$	$A^{(1)}$	$B \text{ (K)}^{(1)}$	$\ln [r_{Na} \text{ (g/m}^2\text{)}]$	$\ln [r_B \text{ (g/m}^2\text{)}]$
Al ₂ O ₃	11.3	-4.1	21186.0	-25.6	-25.4
B ₂ O ₃	-6.2	-13.7	10868.0	9.4	11.8
CaO	-7.5	-22.8	21522.0	-2.0	-9.0
Fe ₂ O ₃	0.0	-6.4	8774.0	-4.1	-3.1
K ₂ O	-4.3 ⁽²⁾	-10.4 ⁽²⁾	9671.1 ⁽²⁾	8.0 ⁽³⁾	8.0 ⁽²⁾
Li ₂ O	-34.2	-4.5	-42288.0	19.8	23.0
Na ₂ O	-11.0	-9.6	-1217.1	19.7	17.8
P ₂ O ₅	1.5 ⁽²⁾	-- ⁽⁵⁾	-- ⁽⁵⁾	-13.4 ⁽³⁾	-13.4 ⁽²⁾
SiO ₂	9.0	-11.1	28539.0	-4.5	-4.3
TiO ₂ ⁽⁴⁾	0.0	-6.4	8774.0	-4.1	-3.1
ZrO ₂	7.4	-31.3	54574.0	-11.6	-10.6
Others ⁽⁵⁾	-0.2	-17.1	19543.9	-0.8	0.2

⁽¹⁾ A and B are viscosity parameters given later in Equation (2).

⁽²⁾ a_i values were fitted to the database of Staples et al. (1999).

⁽³⁾ a_i values for $\ln r_B$ were used for $\ln r_{Na}$.

⁽⁴⁾ $a_{Fe_2O_3}$ values were used for a_{TiO_2} .

⁽⁵⁾ All components in the glass without a_i values listed were grouped into a pseudo-component called Others.

Insufficient data were available to predict the T_L or primary crystalline phase for the SBW glass since T_L of such high Na waste glasses have generally been low and were not systematically studied. However, constraints on the maximum concentration of Fe₂O₃ (8 mass %), TiO₂ (2 mass %), and Al₂O₃ (10 mass %) were used to avoid regions of glass composition known to have high T_L values. Although no first-order approximation was made for the normalized lithium release by PCT (r_{Li}), it is assumed that the glass will dissolve roughly congruently. If large differences between the predicted values for r_B and r_{Na} are found, then more effort will be made to predict r_{Li} . If not, it will be assumed that r_{Li} is roughly equal to r_B and r_{Na} . The corrosion-related properties are described by Sundaram et al. (1998). The database for predicting glass-composition effects on corrosion-related properties is inadequate to allow prediction of melter materials corrosion. The final set of property constraints for SBW formulation and methods for calculation are summarized in Table 2.3.

^b Li et al. (1997), Li et al. (1998), and Li et al. (in press) describe the origin of this constraint.

^c Approximately 1 mass % of SO₃ is soluble in typical alkali-alumino-borosilicate waste glasses.

^d Personal communication, Denny Bickford, Westinghouse Savannah River Company, to John Vienna Pacific Northwest National Laboratory, David Peeler, Westinghouse Savannah River Company, and Chris Musick, Idaho National Engineering and Environmental Laboratory, February 3, 1999.

Table 2.3. Constraints Used in SBW Glass Formulation

Property	Property limit	Method to address constraint in formulation
Viscosity (η) at 1150°C	$2 < \eta < 10$ Pa·s	Equation (1) used to target an η value of roughly 6.0 Pa·s at 1150°C with both sets of a_i values in Table 2.2
Liquidus Temperature (T_L)	$T_L \leq 1050^\circ\text{C}$	Restricted max. concentrations of Fe_2O_3 (8 mass %), TiO_2 (2 mass %), and Al_2O_3 (10 mass %)
PCT boron release (r_B)	$r_B < 8.35$ g/m ²	Equation (1) used with $r_B < 1$ g/m ² and sum of alkali oxide concentrations less than 22 mass %
PCT sodium release (r_{Na})	$r_{\text{Na}} < 6.67$ g/m ²	Equation (1) used with $r_{\text{Na}} < 1$ g/m ² and sum of alkali oxide concentrations less than 22 mass %
PCT lithium release (r_{Li})	$r_{\text{Li}} < 4.78$ g/m ²	Check to ensure that $r_B \cong r_{\text{Na}}$ then let $r_{\text{Li}} = r_B = r_{\text{Na}} < 1$ g/m ²
Homogeneity	Homogeneous	SiO_2 concentration in the SiO_2 - Al_2O_3 - Na_2O sub-mixture in glass >60 mass % to avoid nepheline formation

2.4 Glass Composition Calculation

A preliminary glass composition was formulated to immobilize the SBW stream. Table 2.4 shows the waste composition in Table 2.1 converted into mass fraction of oxides and halides. The proposed frit composition, generated using the glass property models discussed in Section 3.0, a simple mass balance, and the constraints found in Table 2.3, is shown in Table 2.4. Finally, the glass composition formed by melting 35 mass % of the SBW waste (on oxide basis) with 65 mass % of the calculated frit composition is listed in Table 2.4.

The properties of the SBW glass were predicted using Equation (1) and the coefficients in Table 2.2. The calculated η at 1150°C are 6.2 Pa·s using the 2nd column of Table 2.2 and 6.0 Pa·s using the 3rd and 4th columns of Table 2.2 and the equation

$$\ln[\eta \text{ (Pa·s)}] = A + B/T \quad (2)$$

The calculated r_{Na} and r_B values are 1.0 g/m² and 0.9 g/m², respectively. As the calculated r_B and r_{Na} values were within 0.1 g/m², and experience has shown that at calculated values of 1 g/m² and below, the measured values are likely over predicted,^c no further effort was made to calculate r_{Li} .

^c See Hrma et al. (1994) for discussion on over prediction of small PCT release values.

**Table 2.4. Waste, Frit, and Glass Composition in
Mass % Oxides and Halides**

Oxide	Waste	Frit	SBW Glass
Al ₂ O ₃	0.2734		0.0956
B ₂ O ₃	0.0065	0.1426	0.0950
CaO	0.0223		0.0078
Cl	0.0104		0.0036
Cr ₂ O ₃	0.0025		0.0009
Fe ₂ O ₃	0.0155	0.1131	0.0790
F	0.0098		0.0034
I	0.0002		0.0001
K ₂ O	0.0792		0.0277
Li ₂ O		0.0267	0.0173
MgO	0.0005		0.0002
MnO	0.0078		0.0027
MoO ₃	0.0013		0.0005
Na ₂ O	0.5005		0.1750
NiO	0.0055		0.0019
P ₂ O ₅	0.0119		0.0042
PbO	0.0031		0.0011
RuO ₂	0.0004		0.0002
SO ₃	0.0373		0.0130
SiO ₂	0.0018	0.6869	0.4474
SnO	0.0002		0.0001
TiO ₂		0.0308	0.0200
ZrO ₂	0.0100		0.0035
Total	1.0000	1.0000	1.0000
Loading	0.35	0.65	1.000

3.0 Glass Property Measurements

3.1 Glass Fabrication

Three SBW glasses (SBW, SBW-a, and SBW-b) were fabricated using oxides, carbonates, and boric acid precursors according to procedures described in Hrma et al. (1994). The glasses were melted for 1 h at 1150°C in a covered Pt/Rh crucible, quenched on a steel plate, ground in a WC mill, remelted for 1 h, and quenched on a steel plate. Differences among these three glasses were based on the presence or absence of sulfate and various halides (i.e., Cl, I, and F). The source materials for S, Cl, I, and F were Na₂SO₄, NaCl, NaI, and NaF, respectively, where applicable.

During fabrication of the SBW glass (targeting the composition shown in Table 2.4), a yellow salt layer was found on top of both the initial and final melts; see Figure 3.1 for an example. Optical microscopy was performed on the steel quenched glass (pour patty) and the glass that remained in the crucible (crucible wall glass). With the exception of the yellow salt phase, no crystalline material was found in either the crucible wall glass or the pour patty.

With the formation of a salt layer in the SBW glass, two glasses (SBW-a and SBW-b) were fabricated to evaluate the impact of SO₃, Cl, F, and I, not only on the formation of the salt layer, but also on potential impacts to product performance. The SBW-a glass was formulated targeting the SBW glass composition with the exception that Cl, F, I and SO₃ were omitted. The SBW-b glass included all components of the SBW glass with the exception of Cl and I. Table 3.1 shows the targeted compositions for all three glasses.

The SBW-a glass was homogeneous with no undissolved solids or crystallization observed in the pour patty or residual crucible glass via optical microscopy. A yellow salt layer was not observed for SBW-a, primarily a result of SO₃ being absent from the batch. The one distinguishing characteristic of SBW-a was recorded during pouring. This glass had a relatively high viscosity (i.e., it poured relatively slowly from the crucible). However, the viscosity was not formally measured. The difference is attributed to the lack of halides and sulfur in the glass.

The results of SBW-b were consistent with those found with the SBW glass. After both the initial and final melt at 1150°C, yellow swirls (due to SO₃) were observed on the surface of the glass. Although viscosity was not formally measured, observations during pouring of the SBW-b glass resulted in a much more fluid glass relative to SBW-a. The presence of F in the glass is thought to be the primary reason for the lower viscosity of SBW-b (relative to SBW-a).

3.2 Salt Formation

As previously mentioned, a bright yellow salt layer formed on the top of both the SBW and SBW-b melts. Based on the waste composition, it was assumed to be a sulfate salt. The glass and crucible from the SBW melt were washed using approximately 250 mL of warm deionized water in an ultrasonic bath. The resulting solution composition was measured using inductively coupled plasma/optical emission spectroscopy (ICP/OES) and by ion chromatography (IC). Table 3.2 lists the composition of this solution. The results from ICP/OES are consistent with those from IC (i.e., within 6%) once oxygen from IC is taken into account.

Table 3.1. Target Compositions of Different SBW Waste Simulants in Mass Fractions of Oxides and Halides

Oxide	SBW	SBW-a	SBW-b
Al ₂ O ₃	0.0956	0.0975	0.0959
B ₂ O ₃	0.0950	0.0969	0.0953
CaO	0.0078	0.0079	0.0078
Cl	0.0036	0.0000	0.0000
Cr ₂ O ₃	0.0009	0.00092	0.0009
Fe ₂ O ₃	0.0790	0.0806	0.0793
F	0.0034	0.0000	0.0034
I	0.0001	0.0000	0.0000
K ₂ O	0.0277	0.0283	0.0278
Li ₂ O	0.0173	0.0177	0.0174
MgO	0.0002	0.0002	0.0002
MnO	0.0027	0.0028	0.0027
MoO ₃	0.0005	0.0005	0.0005
Na ₂ O	0.1750	0.1786	0.1756
NiO	0.0019	0.0019	0.0019
P ₂ O ₅	0.0042	0.0042	0.0042
PbO	0.0011	0.0011	0.0011
RuO ₂	0.0002	0.0002	0.0002
SO ₃	0.0130	0.0000	0.0130
SiO ₂	0.4474	0.4564	0.4490
SnO	0.0001	0.0001	0.0001
TiO ₂	0.0200	0.0204	0.0200
ZrO ₂	0.0035	0.0036	0.0035
Total	1.0000	1.0000	1.0000

Figure 3.1. SBW Glass with Sulfate Salt Swirls on Top

Table 3.2. Composition of Salt Wash Solution

Element	Concentration (mg/L)
ICP/OES Method	
Cr	9.1
Fe	0.1
Na	440
P	4.5
S	270
K	57
IC Method	
F ⁻	6
Cl ⁻	17
PO ₄	13
SO ₄	846

The composition of the salt is given in Table 3.3. The salt is primarily Na₂SO₄ with small amounts of alkali-chromate, -phosphate, and -halide salts. The percent of the salt components batched in the initial melt were compared to those found in the salt layer in Table 3.4. Only small fractions (less than two mass %) of the salt material separated into the salt layer after two melts at 1150°C. The remaining salt components are either in the glass or volatilized during melting.

Table 3.3. Composition of Salt (excluding oxygen)

Element	Concentration (mol% element)
Cr	1.13
Fe	0.01
Na	54.75
P	0.56
S	33.59
K	7.09
F	0.75
Cl	2.12

Table 3.4. Fraction of "as Batched" Salt Components in the Salt Layer

	Mass in salt (g)	Mass batched (g)	Mass % of salt in salt layer
NaPO ₃	0.0022	2.71	0.082
Na ₂ SO ₄	0.1329	8.65	1.536
NaF	0.0012	3.38	0.036
NaCl	0.0048	2.67	0.180

3.3 Viscosity

A standard technical procedure (ASTM C 965 [ASTM 1990]) was used to measure the viscosity (η) on SBW pour patty glass (after removal of the salt layer) as a function of temperature (T) using a spindle viscometer. Glass η -T data were fitted to the Arrhenius model (Equation 2). Figure 3.2 shows the viscosity as a function of temperature. The measured values for A, B, and η at 1150°C are -9.9, 16409.5 (K), and 5.0 Pa·s, respectively. These values differ slightly from those values calculated using Equation (1) and columns 3 and 4 of Table 2.2: -10.2, 16994.6 (K), and 6.0 (Pa·s), respectively. The difference is likely due to the effects of halides and SO_3 , which were not considered in the calculation. However, the glass is well within the acceptable range of viscosity values (i.e., 2 to 10 Pa·s at 1150°C).

Figure 3.2. Viscosity-Temperature Relationship for SBW Glass

3.4 Product Consistency Test

The PCT was performed in triplicate for the SBW, SBW-a, and SBW-b glasses (see Table 3.1 for targeted compositions). Also included in the test matrix were the EA glass and blanks for control purposes. Samples were ground, washed, and prepared according to the procedure (ASTM 1994). Fifteen mL of American Society for Testing and Materials (ASTM) Type I water was added to 1.5 g of glass in stainless steel vessels. The vessels were closed, sealed, and placed into an oven at 90°C. After 7 days, vessels were allowed to cool to room temperature, and the final weight of each vessel and the solution pH were recorded. Leachate solutions were then filtered through a 0.45- μm pore size filter. Six mL of each leachate solution was then acidified with 4 mL of 0.4 M HNO_3 to ensure that the cations remain in solution. Leachate solutions and blanks were then analyzed for Si, B, Na, and Li concentration by the Savannah River Technology Center-Mobile Laboratory (SRTC-ML), using ICP/atomic emission spectroscopy (ICP/AES). A multi-element solution standard was also submitted with the PCT leachates for control purposes. Concentrations of Si, B, Na, and Li in acidified test solutions are reported in Appendix A. Averaged normalized release rates were calculated based on targeted compositions and reported in Table 3.5.

Table 3.5. PCT Results for the SBW Glasses and EA Glass

Glass	r_B	r_{Si}	r_{Na}	r_{Li}	pH
SBW	0.735	0.216	0.689	0.496	11.16
SBW-a	0.390	0.185	0.395	0.255	10.98
SBW-b	0.520	0.195	0.540	0.335	11.13
EA	8.937	2.156	7.314	4.940	11.84

The measured values are all below the stated limit of 1 g/m^2 and, as expected, were under-predicted by the calculation using Table 2.2 a_i values. The calculated PCT sodium and boron normalized releases for the SBW glass were 1.0 g/m^2 and 0.9 g/m^2 , respectively.

3.5 Liquidus Temperature

A 5-g sample of the SBW glass was heat-treated at 1050°C for 24 h in a Pt/Rh crucible with a tight-fitting lid. Optical microscopy showed small (roughly 1 to $5 \mu\text{m}$) spherical droplets of material uniformly dispersed in the glass. Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) was used to identify the material in these droplets as Na_2SO_4 . Figure 3.3 shows an SEM image of the droplets. The EDS spectrum of the bulk glass is compared to that of a typical droplet in Figure 3.4. It is clear from EDS that the droplets contain Na, O, and S. The XRD trace of the heat-treated glass showed only an amorphous hump and no crystalline peaks. Therefore, no crystalline phase was present in quantities above the XRD detection limit. As discussed in Section 2.3, the formation of an immiscible salt phase does not restrict the formulation for SBW glass. Since no other phase was identified in the heat-treated SBW glass, the glass passes the $T_L \leq 1050^\circ\text{C}$ restriction.

Figure 3.3. SEM Image of Heat-Treated SBW Glass

Figure 3.4. EDS Spectra of (a) Glass Matrix and (b) a Typical Droplet in the Heat-Treated SBW Glass

4.0 Crucible Tests with Simulants

4.1 Composition and Property Prediction

An SBW simulant (SBW-sim) was fabricated at INEEL for use in vitrification flowsheet demonstrations. The composition of the simulant is slightly different from that used for glass formulation. Table 4.1 compares the compositions of the waste and waste simulant along with the SBW glass and SBW-sim glass. To estimate the impact of the composition differences on glass properties, Equation (1) was used to calculate the critical properties of the SBW-sim glass. A comparison of the calculated glass properties, shown in Table 4.2, suggests that the difference in composition should have little impact on viscosity and durability. The primary difference appears to be in the SO_3 concentration. This will impact the formation of a secondary salt phase since the solubility of SO_3 is expected to be roughly 1 mass % (Li et al. 1995, and Lambert et al. 1996).

Table 4.1. Compositions of SBW, SBW-Sim, Frit, SBW Glass, and SBW-Sim Glass in Mass Fractions of Oxides or Halide

Oxide/ Halide	SBW	SBW-sim	Frit	SBW glass	SBW-sim glass
Al_2O_3	0.2734	0.2634	-	0.0956	0.0922
B_2O_3	0.0065	0.0063	0.1426	0.0950	0.0949
CaO	0.0223	0.0215	-	0.0078	0.0075
Cl^-	0.0104	0.0100	-	0.0036	0.0035
Cr_2O_3	0.0025	0.0025	-	0.0009	0.0009
F^-	0.0098	0.0094	-	0.0034	0.0033
Fe_2O_3	0.0155	0.0149	0.1131	0.0790	0.0787
I^-	0.0002	0.0002	-	0.0001	0.0001
K_2O	0.0792	0.0762	-	0.0277	0.0267
Li_2O	-	-	0.0267	0.0173	0.0173
MgO	0.0005	0.0005	-	0.0002	0.0002
MnO	0.0078	0.0075	-	0.0027	0.0026
MoO_3	0.0013	0.0013	-	0.0005	0.0004
Na_2O	0.5005	0.4819	-	0.1750	0.1687
NiO	0.0055	0.0031	-	0.0019	0.0011
P_2O_5	0.0119	0.0218	-	0.0042	0.0076
PbO	0.0031	0.0030	-	0.0011	0.0010
RuO_2	0.0004	0.0004	-	0.0002	0.0001
SO_3	0.0373	0.0646	-	0.0130	0.0226
SiO_2	0.0018	0.0017	0.6869	0.4474	0.4471
SnO	0.0002	0.0002	-	0.0001	0.0001
TiO_2	-	-	0.0308	0.0200	0.0200
ZrO_2	0.0100	0.0096	-	0.0035	0.0034
Total	1.0000	1.0000	1.0000	1.0000	1.0000

Table 4.2. Calculated Property Values for the SBW and SBW-Sim. Glasses

Property	SBW glass	SBW-sim. Glass
η at 1150°C (using the 2 nd column of Table 2.2)	6.2 (Pa·s)	6.5 (Pa·s)
η at 1150°C (using the 3 rd and 4 th columns of Table 2.2)	6.0 (Pa·s)	5.9 (Pa·s)
r_{Na} (using the 5 th column of Table 2.2)	0.9 (g/m ²)	0.8 (g/m ²)
r_B (using 6 th column of Table 2.2)	1.0 (g/m ²)	1.0 (g/m ²)

4.2 Fabrication and Melting Observations

Undissolved solids (UDS) were observed on the bottom of the 4-L bottle of SBW simulant received from INEEL. An impeller was used to suspend particulates while the solution was pipetted from the container, added to a porcelain crucible, and weighed. Loss on ignition was performed, heating the sample from 100 to 1150°C, with mass loss of 89.63%.

Five small crucible melts were made in 50 to 100 cm³ porcelain crucibles to check melt characteristics and the effect of carbon on glass redox. To form a glass, SiO₂, H₃BO₃, Fe₂O₃, Li₂CO₃, and TiO₂ (weight % of chemical compounds: 68.7, 14.3, 11.3, 2.67, and 3.08 respectively) were used as glass former additives to the simulant SBW solution targeting the 35 wt% SBW-sim glass. The batch components for the five melts are summarized later in Table 4.3.

The dry components (glass additives, carbon, and NiO) that were used to form the melts were weighed, mixed in a plastic bag, and put in a porcelain crucible. Carbon was added to some of these melts to reduce multivalent components, and NiO was added to melts #3, 4, and 5 to determine if nickel would be reduced to the metallic state (i.e., as a redox indicator). The stirred SBW simulant was pipetted, weighed, and slowly added to the crucible while stirring the solution into the dry chemicals. A vigorous exothermic reaction with foaming occurred as the blending took place. Each melt was heated on a hot plate until dry, then added to a high temperature furnace at about 1000°C and heated to 1250°C. The drying process took approximately 4 hours, and the melting took between 1.5 to 2 hours.

During the drying process, it was observed that both boiling (spattering) and fuming occurred, and fine white dendrite growths formed on the wire mesh that covered the crucible. The crystals were analyzed by XRD (see scan in Figure 4.1) to include the phases: B₂O₃, NaNO₃, SiO₂, NaAlSi₃O₈, and CaSO₄. Temperatures during the drying process may ultimately approach the temperature of the hot plate surface (350°C to 400°C). Such temperatures, if attained, would not volatilize any of the crystalline phases identified by XRD, but would volatilize any free HNO₃ or H₂SO₄. (HNO₃ would come off with boiling water, and H₂SO₄ volatilizes at about 300°C.) We believe that both the silica and the sodium along with nitrate were probably transported to the screen as spatter or aerosol droplets, and the simplest explanation is that the dendrites crystallized from the spattered material. However, the potential for acid volatilization may have contributed to the development of the dendrite deposits, particularly the elevated sulfate levels in the dendrite deposits. No salt layers were formed in the crucible melts using the simulant.

Figure 4.1. XRD Trace of Material on Crucible Lid (screen)

4.3 Redox Adjustment

A redox adjustment to the candidate glass formulation was investigated before conducting the pilot-scale melter tests. The target glass redox ($\text{Fe}^{\text{II}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$) for melter testing is 0.33, which is a function of the oxygen partial pressure in the melt. The reasons for controlling the redox of the glass were threefold: 1) reduce corrosion to the molybdenum electrodes and drain spout, 2) increase feed rates by providing a lower temperature reaction route for denitration, and 3) reduce NO_x emissions. In 1996, the INEEL Alternative Calcination Development Program conducted scoping tests that included sugar-additive SBW calcination.^f The objectives of those scoping tests were to increase calciner production flow-rates, reduce calcination product volume/mass, and reduce NO_x emissions. A review of these test results identified two runs (Run 27 and Run 28) as successful in fully denitrating the SBW and reduced NO_x emissions for 500°C calcination processing. It was recommended that between 1.24 to 1.53 moles of carbon per mole of nitrate should be used for scale-up testing. These data were considered in adjusting the redox of the glass and increasing melt rates in the pilot-scale melter tests at Clemson. Note that 1.25 moles of carbon are required per mole of nitrate present in the feed for the following reaction to go to completion:

^f J. Pao and J. A. McCray, "Laboratory-Scale Sugar-Additive and High-Temperature Denitration Calcination Test Results." Internal LMITCO Letter JHP-06-96/JAM-08-96 to D.V. Croson, September 30, 1996.

Laboratory tests were employed because of the complexity of the chemistry that occurs in a melter feed as it is heated to the melting temperature and because a larger number of conditions can be tested at a significantly lower cost. Since the crucible tests can only indicate approximate conditions because of the difference in scale, pilot scale tests are necessary for proof of principle. In this highly acid system, about two moles HNO_3 per liter of waste (Table 5.1, Section 5.1), which should distill from the feed in the 100°C to 150°C range, significantly reduces the amount of nitrate that needs to be reduced (Smith et al. 1999). This volatilized acid will condense in the off-gas system. With carbon as the reductant, reaction with the remaining nitrate, as in the "black powder" reaction, does not occur until about 400°C (Smith et al. 1999). The partial reduction of nitrate by other reactions, possibly induced catalytically by the waste oxides present, may occur.

The principal limitations of crucible tests relate to their size and the effect of atmospheric O_2 . It has been shown in past crucible testing that the surface-to-volume ratio can play a significant role in the resulting oxidation state of the glass (Maupin et al. 1988, p. 17). This is especially apparent when attempting to produce a more reduced glass in an environment containing O_2 . This is not surprising and relates to the rapid diffusion of molecular O_2 into the exposed surface of any material being heated and melted in an atmosphere containing O_2 . Other physical processes such as the redistribution of oxidation and reduction agents during the drying of the melter feed may cause incomplete reaction of these reactants on the time scale of the test. Crucible test results must, therefore, be interpreted carefully as well as carefully repeated to provide useful information for larger-scale testing.

Table 4.3 summarizes the carbon and nitrate composition of the laboratory melting runs performed to indicate a good oxidation-reduction chemistry to employ for the pilot-scale melting test. The Glass Former Additives column gives the dry weight (g) of the chemicals added to the SBW to produce the waste glass. To this glass feed, varying amounts of carbon reductant (g) were added to reduce the resulting glass melt. Nickel oxide was also added as an indication of reductant activity, producing reduced metal ahead of iron oxide. The $\text{M}_\text{C}:\text{M}_{\text{NO}_3}$ column relates the amount of carbon added relative to the amount of nitrate present in terms of the molar ratio in the initial (INT) mixture. The column headed Stoich (for stoichiometric) adjusts the molar ratio to the stoichiometric ratio, which takes into account the fact that it takes 1.25 moles of carbon to completely reduce 1.0 moles of nitrogen (as nitrate) in the INT mixture (see Equation 3). The Stoich (-volatile nitric) column takes into account the fact that two out of the seven moles of nitrate present in the feed are present as the free acid and are expected to volatilize when the feed dries. Hence, there will only be 5 moles of nitrate per liter of SBW that will be around for carbon to reduce.

Table 4.3. Additives to Crucible Melts with Simulant SBW Based Feed

Melt #	Glass Former Additives(g)	Simulant SBW(g)	Carbon (grams)	C (wt%)	NiO (grams)	$\text{M}_\text{C}:\text{M}_{\text{NO}_3}$ (INT)	Stoich (INT)	Stoich (-volatile nitric)
1	10.00	24.6	0	0	0	0	0	0
2	5.00	13.0	0.18	1	0	0.18	0.14	0.20
3	5.00	13.0	0.5	2.8	0.3	0.50	0.40	0.56
4	10.00	24.8	0.5	1.44	0.3	0.26	0.21	0.29
5	10.00	30.7	2.4	5.9	0.4	0.99	0.79	1.11

Crucible tests were performed with activated carbon and simulated SBW feed. They were conducted to indicate the $\text{C}:\text{NO}_3$ ratio appropriate for scaled melter demonstrations. Melt #1, with no

carbon, formed a film over the slurry while drying and had to be stirred into the slurry occasionally. Bubbling and volatilization also took place during the drying cycle. While melting, a rigid foam cap also developed and had to be forced back into the melt by pushing it down with a metal rod. At 1250°C, the melt viscosity was about 15 Pa·s, and the glass looked good, but there were indications from color variations on the crucible wall that iron and other transition metal oxidation states were not uniform in the melt. It is unclear why the viscosity is much higher than that calculated above.

Bubbling and foaming were minimal in melts that were produced from melter feeds that contained carbon. The carbon, however, added some problems to the melting process. In Melts #2 and #3, the batch size was small, and carbon was well oxidized by atmospheric O₂. These two feed batches produced a good glass product when the melting was complete. However, melts #4 and #5 were twice the size of the previous batches. Melt #5 appeared to have segregated part of the carbon, creating a carbon rich layer in the melt, and did not allow the carbon to uniformly react with the melter feed during the melting process. The trapped carbon formed a cake that floated above the molten glass, but remained encapsulated by the glass. This occurred, but was less evident in Melt #4. These melts were dominated by the mass of carbon in the melt and made evaluation of the glass melt characteristics more difficult.

Nickel oxide was spiked into melts #3, #4, and #5 to determine if nickel would be reduced to the metallic state by the presence of carbon. All but Melt #1 were quenched in a water bath to shatter the porcelain crucible and glass so that the melt could be examined by optical microscopy. Metal was not observed in any of the melts except Melt #5, which had metallic nodes incorporated in the carbon mass. Note that Melt #5 also had more than the stoichiometric amount of carbon to completely reduce all of the nitrate in the melter feed (Table 4.3). Based on the above results, it was recommended that the melter be run using a substoichiometric amount of carbon.

5.0 Laboratory Scale Melter Tests

Once the candidate glass frit was formulated and selected, crucible and laboratory-scale melter tests using liquid SBW, as opposed to oxides, were performed at INEEL to identify processability upsets, evaluate corrosivity of materials of construction, and compare PCT, viscosity, and homogeneity results to the glasses made from oxides. Homogeneity, viscosity, and PCT were determined using the identical procedures and laboratory practices as outlined earlier in the report.

5.1 Batching and Melting

Simulated liquid-sodium bearing waste and additive mix were batched per Table 5.1. The targeted total undissolved solids in the simulated SBW was 2.97 g/L. Two hours before operating the laboratory-scale glass melter (LSM), the frit material was added and blended with the simulated waste using a hot plate and stir bar.

The LSM was fabricated with Monofrax K-3 fire cast refractory and two Inconel 690 electrodes. Power supply for joule heating included a 120 volt Variac rheostat with a 0-140 volt AC / 22 amp output. Current and voltage of the melt were monitored with two Fluke 87 digital multimeters. A modified (1200°C) Blue M Furnace was used for initial heat-up. The slurry feed system consisted of the following: a 2-liter feed vessel located on a magnetic stir plate, a variable speed diaphragm transfer pump, and a 3/8-inch outside diameter quartz feed tube. Melt temperature was monitored using a Type R thermocouple located inside an alumina thermowell, which is located in the melt chamber. A schematic of the LSM is shown in Figure 5.1.

The LSM operating conditions were monitored and documented. The furnace resistance heaters were energized, and the heat-up rate was controlled at 50°C/h until the Type R thermocouple indicated a temperature of 650°C, where joule heating was initiated, and 300 mL of feed was then added to the crucible. Once the melt temperature reached 925°C, an additional 600 mL of feed was added to the melt chamber. Due to the increase in temperature, the feed in the quartz tube began to denitrate, resulting in several pieces of quartz falling into the melt. A new feed tube was fabricated from stainless steel tubing, and the addition of feed to the melt chamber continued. A cold cap was formed in the melt chamber, but the slurry feed began to puddle on top of the cold cap. It boiled rapidly until the vapor escaped, leaving a "domed" crust on top of the melt. NO_x release continued for several minutes following the crust formation. The crust would gradually recede, allowing for more feed to be fed to the melter chamber. Care was taken not to add too much feed at one time to prevent the feed from exiting the melt chamber. A steady feed rate was not reached. The feed continued to be added semi-continuously until 1250 mL was fed. Particulate from the liquid feed began to collect on one of the electrode leads. This caused oxidation of the lead, resulting in a loss of joule power to the glass. The K-3 refractory crucible containing the melt was transferred to a high-temperature furnace for the remainder of the test. The high-temperature furnace was heated to 1050°C, and the remaining feed was added manually to the crucible. A total of 1500 mL of feed was added to the LSM chamber. The furnace setpoint was then changed to 900°C until the following day. After 14 hours at 900°C, the furnace temperature was increased to 1150°C for 4 hours and 50 minutes.

Table 5.1. Feed Makeup for SBW Glass – Laboratory Scale Glass Melter

Total Batch Volume = 1.2 L			Stock Chemicals Added				
Dissolved Species	Desired Molarity		Liquid SBW Feed			Glass Additives	
			Chemical	M	Quantity	Chemical	Mass (g)
H ⁺	1.94E+00		All Acids	-----	-----	Al ₂ O ₃	0.00
Al ³⁺	7.84E-01		Al(NO ₃) ₃ sol'n.	2.16	4.51E-01 L	H ₃ BO ₃	85.79
B ³⁺	1.91E-02		H ₃ BO ₃		1.47E+00 g	CaCO ₃	0.00
Cd ²⁺			Cd(NO ₃) ₂ sol'n.	4.78	0.00E+00 mL	NaCl	0.00
Ca ²⁺	5.76E-02		Ca(NO ₃) ₂		1.51E+01 g	Cr ₂ O ₃	0.00
Cl ⁻	4.05E-02		HCl	12.00	4.19E+00 mL	NaF	0.00
Cr ³⁺	4.78E-03		Cr(NO ₃) ₃ • 9H ₂ O		2.38E+00 g	Fe ₂ O ₃	37.88
F ⁻	7.12E-02		HF	27.60	3.20E+00 mL	NaI	0.00
I ⁻	2.00E-04		KI		4.12E-02 g	K ₂ CO ₃	0.00
Fe ³⁺	2.71E-02		Fe(NO ₃) ₃ • 9H ₂ O		1.36E+01 g	Li ₂ CO ₃	22.12
Pb ²⁺	2.01E-03		Pb(NO ₃) ₂		8.27E-01 g	MgO	0.00
Mn ²⁺	1.59E-02		Mn(NO ₃) ₂ [50% soln.]		7.07E+00 g soln.	MnO ₂	0.00
Mo ⁶⁺	8.43E-04		H ₂ MoO ₄		1.70E-01 g	MoO ₃	0.00
Ni ²⁺	5.59E-03		Ni(NO ₃) ₂ • 6H ₂ O		2.02E+00 g	Na ₂ CO ₃	0.00
NO ₃ ⁻	6.95E+00		HNO ₃	13.10	1.63E-01 L	NiO	0.00
PO ₄ ³⁻	2.04E-02		H ₃ PO ₄	14.80	1.71E+00 mL	(NaPO ₃) ₁₃ * Na ₂ O	0.00
K ⁺	2.45E-01		KNO ₃		3.07E+01 g	PbO	0.00
Na ⁺	2.36E+00		NaNO ₃		2.49E+02 g	RuO ₂	0.00
SO ₄ ²⁻	6.37E-02		H ₂ SO ₄	18.00	4.40E+00 mL	SiO ₂	230.09
Zr ⁴⁺	7.31E-03		ZrO(NO ₃) ₂ • 3H ₂ O		2.59E+00 g	SnO ₂	0.00
						Na ₂ SO ₄	0.00
Actual NO ₃ =	6.96E+00	M				TiO ₂	10.32
TOTAL UDS =	2.97E+00	g/L					Total Grams 386.00

Figure 5.1. K-3 Refractory Crucibles

During continuous feeding of the LSM with surrogate liquid SBW, a significant amount of foaming was observed at operating temperatures above 600°C. This foaming was caused from the NO_x offgas venting from the melt. No molten salt was observed to form during continuous feeding or steady state. The fate of sulfur during LSM testing is still unclear. Further study into the sulfur behavior is recommended.

5.2 Composition

The composition of LSM produced glass is compared to the target glass compositions in Table 5.2. The measured SiO₂ content is significantly higher than the target value due to the dissolution of the broken feed tube into the melt.

5.3 Viscosity Comparison

Viscosity profiles of the LSM melt, a crucible melt made from SBW simulant, and two crucible melts from oxide and carbonate precursors were measured as a function of temperature over the range of 950°C to 1250°C as shown in Figure 5.2. Glass η and T data were fitted to the Arrhenius (2) model. Table 5.3 shows the calculated values for A, B, and η at 1150°C. Both crucible glasses are within the targeted range of viscosity values; however, the LSM glass viscosity was slightly high due to the added silica resulting from fragments of the broken quartz feed tube that dissolved in the LSM glass. Figure 5.2 illustrates the viscosity for each of the four glasses as a function of temperature.

Table 5.2. Target and Measured Compositions

	Target		Measured
	SBW Glass	SBW-Sim Glass	SBW-LSM
Al ₂ O ₃	0.0956	0.0922	0.0987
B ₂ O ₃	0.0950	0.0949	0.0875
CaO	0.0078	0.0075	0.0639
Cl ⁻	0.0036	0.0035	NM
Cr ₂ O ₃	0.0009	0.0009	0.0011
F ⁻	0.0034	0.0033	NM
Fe ₂ O ₃	0.0790	0.0787	0.0864
I ⁻	0.0001	0.0001	NM
K ₂ O	0.0277	0.0267	0.0228
Li ₂ O	0.0173	0.0173	NM
MgO	0.0002	0.0002	0.0015
MnO	0.0027	0.0026	0.0033
MoO ₃	0.0005	0.0004	NM
Na ₂ O	0.1750	0.1687	0.1530
NiO	0.0019	0.0011	0.0024
P ₂ O ₅	0.0042	0.0076	0.0046
PbO	0.0011	0.0010	0.0009
RuO ₂	0.0002	0.0001	NM
SO ₃	0.0130	0.0226	NM
SiO ₂	0.4474	0.4471	0.4820
SnO	0.0001	0.0001	NM
TiO ₂	0.0200	0.0200	0.0210
ZrO ₂	0.0035	0.0034	0.0025
Total	1.0000	1.0000	97.4

Table 5.3. Temperature Coefficients and Viscosity at 1150°C

Glass	A	B (K)	ln(η)	η (Pa.s)
Initial Crucible Melt From Oxides	-9.9	16409.5	1.79	6.0
Second Crucible Melt From Oxides	-10.22	17044	1.76	5.79
Crucible Melt From Simulant	-10.01	16950	1.90	6.70
LSM	-10.25	17940	2.36	10.55

Figure 5.2. Viscosity-Temperature Relationship for LSM and Crucible SBW Glasses

5.4 PCT Comparison

The increase in SiO_2 content in the LSM glass, as discussed in Section 5.3, should decrease the normalized release values from PCT. As expected, the PCT results, shown in Table 5.4, indicate that the laboratory-scale melter glass is more durable than the crucible glasses.

Table 5.4. Normalized PCT Releases for SBW Glass, EA Glass, and ARM-1

Glass	Average Normalized Release (g/m^2)			
	B	Si	Na	Li
EA	8.937	2.159	7.314	4.940
SBW ⁽¹⁾	0.735	0.216	0.689	0.496
SBW-1-LSM ⁽²⁾	0.224	0.157	0.270	0.173

(1) Crucible glass batched from oxides and carbonates.

(2) LSM glass batched from simulated liquid SBW.

5.5 Melter Corrosion Testing

One of the main objectives of performing the laboratory-scale glass melter test was to evaluate the compatibility of the SBW glass formulation and the refractory materials used for construction. After the melter testing, the electrodes were removed, quenched, cleaned, and submitted for analysis. Analysis included optical microscopy and mass loss. Corrosion of the K3 refractory and the Inconel 690 electrodes by SBW glass was minimal. Visual inspection of the refractory revealed no corrosion at either the melt line or chamber. The mass loss of the refractory could not be accurately determined due to the porosity of the K-3 refractory. Optical microscopy (70 $\times$) of the electrodes detected some pitting at the melt line on

both of the electrodes, but was judged as being minimal considering that the weight loss of each electrode was ~1%. This value is low, as expected from such a short-term test. It is recommended that a quantitative corrosion analysis be completed before operating a pilot-scale melter that utilizes Molybdenum electrodes for processing liquid SBW. Table 5.5 shows initial weight, final weight, and % change of both electrodes.

Table 5.5. Electrode Weight Comparison

Electrode	Initial Weight	Final Weight	% Change
4	74.8	74.2	0.8
5	74.2	73.4	1.1

This evaluation was conducted to obtain qualitative analysis of materials of construction for the melter at Clemson Environmental Technology Laboratory (CETL). The melter chosen to perform the pilot-scale testing at CETL was constructed from flux block refractory and molybdenum electrodes. As stated earlier, the LSM is fabricated from K-3 refractory and Inconel 690 electrodes. Therefore, the measured corrosion of K-3 brick and Inconel 690 electrode cannot yield conclusive evidence about the corrosivity of this melt in the CETL scaled-melter. However, there is also no indication that the melt may be excessively corrosive.

6.0 Conclusion and Recommendation

A systematic study was undertaken to develop a glass composition to demonstrate the vitrification flowsheet for INEEL's SBW. The waste composition listed in Table 2.1 and glass property restrictions listed in Table 2.3 were used as a basis for the development. Calculations based on first-order expansions of selected glass properties in composition and some general tenants of glass chemistry led to an additive composition (68.69 mass % SiO_2 , 14.26 mass % B_2O_3 , 11.31 mass % Fe_2O_3 , 3.08 mass % TiO_2 , and 2.67 mass % Li_2O) that meets all property restrictions when melted with 35 mass % of SBW on an oxide basis. The glass was prepared using oxides, carbonates, and boric acid and tested to confirm its acceptability. Glass was then made using waste simulant at three facilities, and limited testing was performed to test and optimize processing-related properties and confirm results of glass property testing.

The measured glass properties are given in Sections 4.0 and 5.0. The viscosity at 1150°C, 5 Pa-s, is nearly ideal for waste glass processing in a standard liquid-fed joule-heated melter. The normalized elemental releases by 7-day PCT are all well below 1 g/m², which is a very conservative set point used in this study. The T_L , ignoring sulfate formation, is less than the 1050°C limit. Based on these observations and the reasonable waste loading of 35 mass %, the SBW glass was a prime candidate for further testing.

Simulant melts suggest that the sulfate-salt segregation seen in oxide and carbonate melts was much less of a problem. One possible cause was identified as H_2SO_4 fuming during the boil-down stage of wet slurry processing. However, a systematic study on the fate of sulfur during processing and on the impacts sulfate salt separation on melter operation should be performed. The properties of the simulant glass confirmed those of the oxide and carbonate glass. Corrosion tests on Inconel 690 electrodes and K-3 refractory blocks conducted at INEEL were largely inconclusive, but suggest that the glass is not excessively corrosive.

Based on the results of this study, the authors recommend that a glass made of 35% SBW simulant (on a mass oxide and halide basis) and 65 % of the additive mix (either fritted or raw chemical) be used in demonstrations of the vitrification flowsheet for INEEL SBW.

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Appendix A

Raw PCT Solution Data

Appendix A. – Raw PCT Solution Data

Date: 2/24/99

Sample ID: PCT SBW, SBW-a, and SBW-b Glasses (90°C)

Elementals ⁽¹⁾ (µg/mL)					
	STD1	STD2	STD3	BLK1	BLK2
B	20.9	21.6	21.0	<0.180	<0.180
Si	50.1	49.9	48.7	<0.180	<0.180
Zr	<0.080	<0.080	<0.080	<0.080	<0.080
Na	78.4	82.5	82.3	0.842	<0.530
Li	9.81	9.93	9.99	<0.100	<0.100
	EA1	EA2	EA3		
B	376	362	391		
Si	591	572	607		
Zr	<0.800	<0.800	<0.800		
Na	1090	1050	1030		
Li	120	115	117		
	SBW-1	SBW-2	SBW-3		
B	27.2	26.3	24.5		
Si	56.3	53.4	52.8		
Zr	0.390	0.362	0.363		
Na	112	105	105		
Li	5.16	4.58	4.59		
	SBW-a-1	SBW-a-2	SBW-a-3		
B	12.8	17.8	12.0		
Si	47.6	48.6	47.9		
Zr	0.245	0.234	0.244		
Na	64.5	64.0	62.6		
Li	2.63	2.55	2.60		
	SBW-b-1	SBW-b-2	SBW-b-3		
B	18.3	19.0	18.4		
Si	49.1	50.1	49.3		
Zr	0.355	0.335	0.318		
Na	83.1	87.7	85.4		
Li	3.28	3.37	3.45		

(1) ppm values from each leachate solution, which was acidified with 4 mL of 0.4 M HNO₃.

Date: 3/11/99
Sample ID: PCT LSM Glass (90°C)

Elementals ⁽¹⁾ (µg/mL)					
	BLK1	BLK2	STD1	STD2	STD3
B	0.327	<0.180	22.4	20.5	20.8
Si	<0.180	<0.180	52.5	51.4	48.4
Zr	<0.080	<0.080	<0.080	<0.080	<0.080
Al	<0.200	<0.200	4.11	3.76	3.89
Na	<0.530	<0.530	83.8	83.1	83.1
Li	<0.100	<0.100	10.1	9.60	9.51
K	<0.530	<0.530	10.3	9.88	10.3
	EA1	EA2	EA3		
B	386	410	394		
Si	575	581	593		
Zr	<0.800	<0.800	<0.800		
Al	<2.00	<2.00	<2.00		
Na	1100	1140	1100		
Li	125	120	122		
K	<5.30	<5.30	<5.30		
	LSM-1	LSM-2	LSM-3		
B	7.97	7.12	6.81		
Si	42.1	42.4	42.5		
Zr	0.160	0.163	0.163		
Al	9.57	9.63	8.91		
Na	36.8	37.6	35.8		
Li	1.67	1.72	1.58		
K	3.46	3.68	3.70		

(1) ppm values from each leachate solution, which was acidified with 4 mL of 0.4 M HNO₃.

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