Glass Formulation Development For INEEL Sodium-Bearing Waste (FY2001 WM-180)

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July 2001

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Summary

A systematic study was undertaken to develop a glass composition to demonstrate the vitrification flowsheet of the Idaho National Engineering and Environmental Laboratory's sodium bearing waste (SBW) using the latest WM-180 tank composition. Although the previous study did not restrict waste loadings (WLs) based on the potential to form a segregated salt layer, avoiding its development in a melter is beneficial and was the primary focus from the glass-formulation perspective. The testing results described in this report were aimed at providing a candidate glass composition for use in a scaled melter demonstration of direct vitrification of WM-180 in the Research Scale Melter (RSM) at Pacific Northwest National Laboratory and the EV-16 melter at the Clemson Environmental Technology Laboratory. 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).

The initial batch chemical tests suggested that the addition of CaO increased the solubility of SO_3 in these multi-component systems, which compares favorably with the findings from the literature survey. It was also observed that at higher WLs (> 40 mass%), if the salt formation could be avoided, the loading of SBW in glass would be limited by Product Consistency Test release or the formation of nepheline on cooling. Crucible tests with liquid SBW simulant were performed to gain a cursory understanding of the impacts of frit composition, HNO_3 concentration, WL, sugar concentration, and test method on the properties of simulated waste glasses. In particular, these tests identified a frit and WL that were likely to form a glass with acceptable properties without the formation of a salt layer. It was found that, to first order, the influence of HNO_3 and sugar concentrations had a minimal impact on salt formation, while the effects of frit composition and WL strongly influenced the amount of salt formed. Adding CaO at the expense of TiO_2 was found to help prevent a salt layer from forming while replacing CaO with BaO did not. Increasing WL and decreasing gas flow generally increased the likelihood of salt formation.

Based on the results of this study, the authors recommend that a glass made of 30 mass% of the 2000 SBW simulant (on a dry oxide and halogen basis) and 70 mass% of the additive mix (SBW-9) be used in the upcoming RSM and EV-16 melter demonstrations. This glass meets all the process and product performance criteria as specified. The SBW-9 additive (frit) composition is shown in Table S-1.

Table S-1. Recommended Additive Composition for Subsequent Melter Tests

Oxide	SBW-9
SiO_2	65.00
B_2O_3	15.00
Li_2O	5.00
Fe_2O_3	10.00
CaO	5.00
Total	100.00

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Glossary

ARM	Approved Reference Material (ARM-1)
ASTM	American Society for Testing and Materials
BDAT	best demonstrated available technology
CCC	centerline canister cooling
CETL	Clemson Environmental Technology Laboratory
CVS	composition variation study
DOE	U.S. Department of Energy
DIW	deionized water
DTA	differential thermal analysis
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EDS	energy dispersive spectroscopy
GC	gas chromatography
HLW	high-level waste
IC	ion chromatography
ICP	inductively coupled plasma
ICPP	Idaho Chemical Processing Plant
INEEL	Idaho National Environmental and Engineering Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
MS	mass spectrometry
NGLW	newly generated liquid waste
OES	optical emission spectroscopy
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
PUREX	plutonium uranium extraction
RSM	research scaled melter
SBW	sodium-bearing waste
SEM	scanning electron microscopy
SRS	Savannah River Site
SRTC	Savannah River Technology Center
T	temperature
TFA	Tanks Focus Area
TGA	thermogravimetric analysis
T_L	liquidus temperature
UDS	undissolved solids
η	viscosity
WAPS	Waste Acceptance Product Specification
WC	tungsten carbide

WL	waste loading
WVDP	West Valley Demonstration Project
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

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1.0 Introduction

For about four decades (beginning in the early 1960s), 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).[1] 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 3.8M L (1M gal) of these wastes are temporarily stored in stainless steel tanks at the Idaho National Engineering and Environmental Laboratory (INEEL). In addition to the SBW, roughly 4400 m^3 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).

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 1995). One of the requirements per this agreement is to remove liquid wastes (e.g., SBW) from the storage tanks by the end of 2013. More immediately, the technology must be applied to provide information required to initiate the design of the SBW treatment facility in year 2002. Hence, direct vitrification (no or minimal feed conditioning before vitrification) is being considered as an immobilization step for SBW, which is the focus of this report.

Vitrification is considered the "Best Demonstrated Available Technology" for immobilizing HLW. Precedents for vitrifying INTEC HLW into borosilicate glass have been established by the production-scale operation of the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS), the West Valley Demonstration Project (WVDP) at West Valley, New York, and certain European facilities. Production-scale technologies exist for the waste chemistries at these plants. However, it is unlikely that the frit formulations developed for immobilizing waste compositions at these sites could be applied to the INTEC wastes in a cost-effective manner. The composition of SBW differs significantly from the INEEL calcine as well as those wastes being vitrified at the DWPF and the WVDP. Therefore, efforts are underway at INEEL to develop integrated flowsheets and identify glass-composition regions for vitrifying SBW.

The DOE Office of Science and Technology (through the Tanks Focus Area [TFA]) and the Office of Waste Management (through the INEEL High-Level Waste Program) are sponsoring a joint effort by INEEL, Pacific Northwest National Laboratory (PNNL), and the Savannah River Technology Center (SRTC) to investigate processes and formulations for vitrifying INTEC HLWs. The overall strategy of this integrated task includes developing glass-property data and glass-composition/property models that cover the composition region expected from individual and/or blended INEEL wastes. The strategy, in terms of glass-formulation activities, has focused on two primary tasks: 1) collaborative (phased) glass composition variation studies (CVS) that "bound" the composition regions of interest to proposed pretreatment/separation and direct-vitrification flowsheets and 2) preliminary glass-form development aimed at specific waste streams to demonstrate feasibility via melter demonstration. Both tasks are focused on providing data required to establish a baseline flowsheet for both SBW and calcine vitrification.

Piepel et al. (1999), Staples et al. (1999), and Edwards et al. (1999) described efforts related to the development of glass-property data and models. Most of the glass-formulation activities supporting

[1] The Idaho National Engineering and Environmental Laboratory, located in Eastern Idaho, consists of an 890-square-mile reservation located 32 miles west of Idaho Falls, Idaho.

melter demonstrations have focused on various calcine waste streams. Peeler et al. (1998), Vienna et al. (2000), Musick et al. (2000), and Crum et al. (2001) reported on previous glass-formulation activities, focusing on blended INEEL calcine wastes and zirconia calcine waste. However, Vienna et al. (1999) discussed a systematic study that was undertaken to develop a glass composition to demonstrate direct vitrification of INEEL's SBW. The objective of that study was to demonstrate the feasibility of SBW vitrification, not the development of an optimum formulation for any given process. The 1998 SBW composition used by Vienna et al. (1999) is shown in Table 1. Only those components that are present in concentrations greater than 0.01 mass% and the components that were expected to remain in glass after vitrification are shown. A cursory examination of the composition suggested that the waste components critical for glass formulation were Al_2O_3, Na_2O, SO_3, and the anions (Cl^-, F^-, I^-, and PO_4^{2-}). The SBW is an HNO_3 solution with approximately 5 to 7 M NO_3^{2-}, which could have a significant impact on melt rate and off-gas-related issues.

Table 1. 1998 SBW Composition Used by Vienna et al. (1999) for Glass-Formulation Efforts

Oxide	Mass%
Al_2O_3	27.34
B_2O_3	0.65
CaO	2.23
Cl	1.04
Cr_2O_3	0.25
F	0.98
Fe_2O_3	1.55
I	0.02
K_2O	7.92
MgO	0.05
MnO_2	0.78
MoO_3	0.13
Na_2O	50.05
NiO	0.55
PbO	0.31
RuO_2	0.04
P_2O_5	1.19
SiO_2	0.18
SnO	0.02
SO_3	3.73
ZrO_2	1.00
Total	100.00

Calculations based on first-order models relating selected glass properties to 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 met all property restrictions when melted with 35 mass% of SBW on an oxide basis. Typically, a constraint on SO_3 concentration[2] 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 would tolerate salt separation. Therefore, no constraint on salt separation from glass was used for SBW

[2] Approximately 1 mass% of SO_3 is soluble in typical alkali-alumino-borosilicate waste glasses.

glass formulation (i.e., salt formation did not restrict waste loading [WL]). This glass (referred to as SBW-1) was ultimately recommended to INEEL and successfully processed in a pilot-scale melter at the Clemson Environmental Technology Laboratory (CETL). Although a glass was developed and processed that met specifications and demonstrated the feasibility of direct vitrification of SBW, this glass was not optimized.

2.0 Waste-Stream Basis for Current Testing

Feed streams to the SBW treatment facility are expected to come from existing tanks at the INTEC Tank Farm and from additional surge capacity that will be in use before facility start-up. The direct-vitrification treatment process for SBW would process all existing and new Tank Farm waste, including liquids, liquids with small concentrations of solids, and possibly tank heel sludges. Current INEEL Tank Farm management plans (Palmer et al. 2000)[3] show that the treatment facility would be required to treat six feed streams. Three of these feed streams are SBW: acidic, radioactive, and hazardous liquid wastes containing small amounts of undissolved solids (UDS) from three tanks, WM-180, WM-188, and WM-189. The INEEL HLW program decided to focus on subsequent SBW vitrification testing and design data collection using the WM-180 tank composition. The composition of this tank is not expected to significantly change between now and the time tank-waste treatment begins. The liquid, along with entrained solids referred to as UDS, was recently sampled and analyzed (Barnes 2000).

Table 2 summarizes the targeted WM-180 composition used as the basis for glass-formulation efforts in this report. These values were supplied by INEEL[4] as a guideline to assist glass-formulation efforts and to provide preliminary make-up procedures. These values are based on preliminary results of updating the projected WM-180 composition based on the revised Tank Farm planning with consideration of the recent WM-180 sample analysis (Barnes 2000). 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.

[3] T. G. Garn, "Sampling and Characterization of WM-180," INEEL Interoffice Memorandum, TGG-01-01, January 11, 2001.

[4] J. Christian, transmittal to "Users of WM-180 simulant makeup," November 5, 2000.

Table 2. Comparison of Estimated SBW Tank Compositions – Major Chemical Species (mass %)

Oxide	1998 SBW	2000 SBW
Al_2O_3	27.34	27.96
B_2O_3	0.65	0.35
BaO	0.00	0.01
CaO	2.23	2.22
CdO	0.00	0.08
CeO_2	0.00	0.01
Cl	1.04	0.88
CoO	0.00	0.21
Cr_2O_3	0.25	0.00
CuO	0.00	0.05
F	0.98	0.57
Fe_2O_3	1.55	1.43
Gd_2O_3	0.00	0.03
I	0.02	0.01
K_2O	7.92	7.62
MgO	0.05	0.40
MnO_2	0.78	0.82
MoO_3	0.13	0.02
Na_2O	50.05	52.54
NiO	0.55	0.09
P_2O_5	1.19	0.80
PbO	0.31	0.24
RuO_2	0.04	0.01
SO_3	3.73	3.57
SiO_2	0.18	0.00
SnO	0.02	0.00
ZnO	0.00	0.07
ZrO_2	1.00	0.01

The most striking differences between the SBW composition used by Vienna et al. (1999) and the new preliminary estimates of WM-180 provided by Christian (based on Barnes 2000) are the slight decrease in SO_3 and slight increase in Na_2O concentrations. Although the previous study did not restrict WLs based on the potential to form a segregated salt layer, avoiding its development in a melter is beneficial and should be a primary focus from the glass-formulation perspective. Based on the 2000 WM-180 compositional estimate (see Table 2), glass formulations will be SO_3 limited unless an integrated flowsheet can be developed that increases SO_3 solubility to over 1 mass% in glass, or S is separated by chemical or physical means (e.g., to the off-gas). The use of high-temperature or advanced melters may be beneficial as partitioning of S to the off-gas system could be increased and thus minimize the potential impacts of a salt layer forming on the glass surface in the melter. If successful, this may allow for WL increases for SBW, assuming that SO_3 recycle back to the melter is minimal.

If the SO_3 issue could be resolved, durability is expected to be the next constraint to limit WLs for SBW. That is, as WLs increase, the concentration of Na_2O in glass increases. Glasses with ~20 mass% Na_2O can be fabricated to meet current product specifications or constraints (e.g., durability criterion); however,

higher concentrations generally lead to decreased durability. Although not necessarily a WL limitation, the high levels of NO_3 in the waste may have a significant impact on melt rate and, ultimately, throughput.

The results described in this report were aimed at providing a candidate glass composition for use in a scaled-melter demonstration of direct vitrification of WM-180 simulant in the Research Scaled Melter (RSM) at PNNL and the EV-16 melter at CETL. We 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 RSM demonstration using the recommended additive (frit) composition were reported by Goles et al. (2001), while results from the EV-16 demonstration will be published in a subsequent report.

3.0 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 allow for adequate melter processability. The product-property requirements for acceptance in the federal repository are dictated by the Waste Acceptance Product Specification (WAPS) (DOE 1996). The WAPS imposes limitations on the performance of glass in the product consistency test (PCT) (ASTM 1998) and requires that chemical and phase-stability information be reported. The specific limit set is that the release of boron, sodium, and lithium, normalized to glass composition, must be significantly less than those of the 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 the 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), Musick et al. (2000), and Vienna et al. (2000). An additional concern is the formation of secondary phases during cooling, which may detract from the durability of glass. Specifically, glasses formed from wastes high in Na and Al are susceptible to nepheline crystallization during cooling, which has been shown to increase the normalized releases of some glasses subjected to the PCT (Li et al. 1997 and Li et al. 1998).

We let the HLW vitrification experience at the DWPF and WVDP be our guide for processing constraints. For these 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 least 100°C below the operating temperature (i.e., T_L nominally $\leq$ 1050°C). These restrictions were adopted for this study. Two additional processing concerns are related to corrosion and SO_3 partitioning. No specific constraint was used to avoid melts that are excessively corrosive to melter construction material other than the lower η constraint. The formation of a salt layer on the glass surface was deemed unacceptable for this study. However, it should be mentioned that the sole use of laboratory-scale tests to predict the formation of a salt layer during actual melter processing adds risk. Table 3 summarizes the glass property and composition constraints used to develop a glass to demonstrate the SBW (WM-180) vitrification flowsheet.

Table 3. Constraints Used in SBW Glass Formulation

Property	Property Limit
η at 1150°C	$2<\eta<10$ Pa·s
Liquidus Temperature (T_L)	$T_L \leq 1050$°C
PCT boron release (r_B)	$r_B < 1$ g/m^2
PCT sodium release (r_{Na})	$r_{Na} < 1$ g/m^2
PCT lithium release (r_{Li})	$r_{Li} < 1$ g/m^2
Salt Layer Presence or Accumulation	Unacceptable
Homogeneity	Homogeneous[(a)]

(a) Homogeneity was judged by the lack of second-phase identification by X-ray diffraction [XRD] (as described above) and by optical microscopy at magnifications of ≥ 100×.

4.0 Functions to Relate Glass Properties to Composition

Glass compositions for immobilizing SBW waste can be formulated based on models that relate glass properties to linear functions of composition. This approach was successfully used by Vienna et al. (1999) in the development of SBW-1, which targeted a 35 mass% loaded glass; thus it provides the starting point for glass-formulation activities using the latest WM-180 composition. To calculate a glass composition for SBW waste that meets the criteria listed in Table 3, 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 modeled as linear functions of composition:

$$P = \sum_{i=1}^{n} a_i g_i \tag{1}$$

where P is the transformed property, a_i is the ith component coefficient, g_i is the ith component mass fraction in glass, and n is the number of components in glass (thus $\Sigma g_i=1$).[5] 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 4 lists the a_i values used to model glass properties in this study.

The first-order approximations for the properties listed in Table 4 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 (i.e., the a_i values) and 2) no data set sufficient to model T_L, homogeneity, or 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 ($Na_2O+Li_2O+K_2O$) be less than or equal to 23 mass% was used to ensure that the glass remains in a composition region where the preliminary PCT models were thought to be applicable. At a high concentration of alkali oxides, the glass durability may drop precipitously because a continuous network of non-bridging oxygen sites is generated in the glass.

[5] See Hrma et al. (1994) for details on property models.

Table 4. Property-Composition Coefficients (a_i values)

	ln [h (Pa×s)]	A[(a)]	B (K)[(a)]	ln [r_{Na} (g/m^2)]	ln [r_B (g/m^2)]
Al_2O_3	11.3	-4.1	21186.0	-25.6	-25.4
B_2O_3	-6.2	-13.7	10868.0	9.4	11.8
CaO	-7.5	-22.8	21522.0	-2.0	-9.0
Fe_2O_3	0.0	-6.4	8774.0	-4.1	-3.1
K_2O	-4.3[(b)]	-10.4[(b)]	9671.1[(b)]	8.0[(c)]	8.0[(b)]
Li_2O	-34.2	-4.5	-42288.0	19.8	23.0
Na_2O	-11.0	-9.6	-1217.1	19.7	17.8
P_2O_5	1.5[(b)]	--[(e)]	--[(e)]	-13.4[(c)]	-13.4[(b)]
SiO_2	9.0	-11.1	28539.0	-4.5	-4.3
TiO_2[(d)]	0.0	-6.4	8774.0	-4.1	-3.1
ZrO_2	7.4	-31.3	54574.0	-11.6	-10.6
Others[(e)]	-0.2	-17.1	19543.9	-0.8	0.2

(a) A and B are η parameters given later in Equation (2).
(b) a_i values were fitted to the database of Staples et al. (1999).
(c) a_i values for ln r_B were used for ln r_{Na}.
(d) $a_{Fe_2O_3}$ values were used for a_{TiO_2} .
(e) All components in the glass without a_i values listed were grouped into a pseudo-component called Others.

Based on the initial review of the 2000 WM-180 composition, SO_3 would probably be the limiting component in terms of WL. Although previous glass formulation for SBW (Vienna et al. 1999) did not place a constraint on SO_3 concentration[6] to avoid sulfate accumulation in the melter (Li et al. 1995; Lambert et al. 1996), accumulation of SO_3 in the melter is unacceptable for the current application. To minimize the potential development and accumulation of a salt layer in the melter, components thought to increase SO_3 solubility in glass were evaluated as potential frit components (e.g., CaO and BaO). It is recognized that SO_3 partitioning among the glass, salt layer, and off-gas is a complex process that depends on factors other than glass composition (e.g., use of a reductant as well as dynamic conditions and kinetic factors within the melter, etc). Components were selected (based on an initial literature survey) to potentially increase SO_3 retention in glass.

Insufficient data were available to predict the T_L or primary crystalline phase for the SBW glass since the T_L of such high Na waste glasses has generally been low and was not systematically studied. Although no first-order approximation was made for the r_{Li} by PCT, it is assumed that the glass will dissolve 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}.

Glass composition/property relationships can be used to: 1) estimate the properties of a glass (with unknown properties but known composition) or 2) estimate the effect of composition changes on the properties of a glass with known properties. The latter is generally more accurate for small composition changes. Therefore, the models were used to assess potential compositional effects on glass properties of

[6] Approximately 1 mass % of SO_3 is soluble in typical alkali-alumino-borosilicate waste glasses.

the baseline glass (SBW-1 frit with 35 mass% of 1998 SBW composition [see Table 1]). Table 5 summarizes the frits that were evaluated in this study.

Table 5. Candidate Frit Compositions Tested in This Study

Oxide	SBW-1	SBW-2	SBW-3	SBW-4	SBW-5	SBW-6	SBW-7	SBW-8	SBW-9	SBW-10
SiO_2	68.69	69.61	66.11	70.00	65.00	67.00	66.00	63.00	65.00	70.00
B_2O_3	14.26	12.00	15.00	12.00	15.00	15.00	10.00	15.00	15.00	12.00
Li_2O	2.67	4.00	4.50	4.00	4.00	4.00	5.00	5.00	5.00	4.00
Fe_2O_3	11.31	11.31	11.31	12.00	12.00	12.00	15.00	15.00	10.00	12.00
TiO_2	3.08	3.08	3.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.00	0.00	2.00	4.00	2.00	4.00	2.00	5.00	0.00
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

5.0 Batch-Chemical Testing

A series of crucible tests was performed using reagent-grade oxides, carbonates, and boric acid prior to the WM-180 liquid simulant being prepared. Glasses produced in this series coupled the 2000 SBW simulant composition (see Table 2) with the candidate frit compositions (see Table 5). This section discusses the experimental procedures and results of these preliminary or scoping tests using batch chemicals as the SBW simulant. The objective of these tests was to assess various frit additives and their effects on sulfate solubility and glass properties of interest.

5.1 Experimental

Each batch was prepared (to produce 100 g of glass) from the proper proportions of reagent-grade chemicals using standard batching and melting procedures. In general, the raw materials were thoroughly mixed and placed into a Platinum/5% Gold 250-mL crucible. The batch was subsequently placed into a high-temperature furnace, and the temperature was increased at ~10°C/min to 1150°C. After an isothermal hold at 1150°C for 1 h, the crucible was removed, and the glass was poured onto a clean stainless steel plate and allowed to air cool. The glass was ground in a tungsten carbide (WC) mill and remelted for 1 h at 1150°C. Visual observations of homogeneity (in particular the presence of a salt layer on the melt surface) were recorded after each pour.

Approximately 90 g of glass were removed (poured) from the crucible while ~10 g remained in the crucible along the walls. The pour patty was used as a sampling stock for the various heat treatments and property measurements (e.g., homogeneity, T_L, viscosity, and durability).

To bound the effects of thermal history on the product performance, ~ 25 g of each glass were heat treated to simulate cooling along the centerline of a DWPF-type canister (Marra and Jantzen 1993). This cooling regime is commonly referred to as the centerline canister cooling (CCC) curve. This terminology will be used in this report to differentiate samples from different cooling regimes (quenched versus CCC). It should be noted that for those glasses that were characterized by the presence of a salt layer on the surface of the melt after quenching, the salt layer was removed before performing the CCC treatment.

Although observations (visual and optical microscopy [minimum of 100×]) for crystallization were performed and documented, a representative sample from select glasses (both quenched and CCC versions) was analyzed using XRD. This analysis was used to confirm visual observations of homogeneity within a given detection limit based on the run conditions of the diffractometer. Samples were run under conditions allowing an approximate 1.0 vol% total crystallinity detection limit. That is, if crystals (or undissolved solids) are present at 1.0 vol% (or greater), the diffractometer will not only be able to detect these crystals, but will also allow a qualitative measure (i.e., determine the type of crystal present). Otherwise, a characteristic high background devoid of crystalline spectral lines indicates that the glass product contains less than 1 vol% of crystalline inclusions.

The PCT was performed on each glass to assess chemical durability using the technical procedure "Nuclear Waste Glass Product Consistency Test (PCT) Method – GTOP-3-025" (SRTC 1998), which is compliant with the ASTM C1285-97 (ASTM 1998). The PCT was conducted in triplicate for each glass (both quenched and CCC versions). Also included in this experimental test matrix were the EA glass, the Approved Reference Material (ARM-1) glass, and blanks. Samples were ground, washed, and prepared according to procedure. Fifteen mL of Type I ASTM water was added to 1.5 g of glass in stainless steel vessels. The vessels were closed, sealed, and placed in an oven at 90 ± 2°C. Samples were left at 90°C ± 2°C for 7 days. The resulting solutions (once cooled) were sampled (filtered and acidified), labeled, and analyzed. Normalized release rates were calculated based on target compositions using the average of the logs of the leachate concentrations.

High-temperature η was measured as a function of temperature (T) using a spindle viscometer for selected SBW glasses. The measurements were obtained using Glass Technology Operating Procedure (GTOP) 3-111 "Determination of Glass Viscosity" (SRTC 1999 and Schumacher and Peeler 1998), which is compliant with the (ASTM C 965-81 [ASTM 1990]). High-temperature η data were measured over the maximum temperature range allowable for each glass. The low-temperature limit was based on the effects of crystallization on the melt pool. The high-temperature limit was based on limiting the effects of volatilization. To validate the glass-η data, the η of the Batch 1 standard glass (Schumacher and Peeler 1998) was measured at the beginning and end of this study. Viscosity at 1150°C ($\eta_{1150°C}$) for each glass was calculated from a Vogel-Tamman-Fulcher fit of the measured data.

5.2 Results

5.2.1 Homogeneity

Table 6 summarizes the visual observations of homogeneity (for quenched and CCC) for the candidate frit compositions at various WLs. Again, it should be noted that these glasses were produced using reagent-grade oxides, carbonates, and boric acid (not using the liquid simulant). This evaluation provides an indication of the potential advantages of the frit-composition changes in terms of SO_3 retention in glass. It is recognized that potential differences may exist between the use of reagent-grade chemicals and the liquid feed in terms of S partitioning. It is also recognized that differences between the crucible-scale tests and the melter demonstrations may also exist; therefore, the crucible-scale tests only lower the risk of salt formation and/or accumulation in the melter, not eliminate it.

SBW-2 and SBW-3 compositions were developed to evaluate the effect of changes of Li_2O and/or B_2O_3 concentrations on SO_3 solubility. As shown in Table 6, a salt layer was observed on the surface of each SBW-2 and SBW-3 melt at all WLs evaluated. Visual observations of the salt-layer characteristics were consistent with that reported by Vienna et al. (1999) (see Figure 1).

Figure 1. SBW Glass with Sulfate Salt Formation on Melt Surface (from Vienna et al. 1999)

A sample of the salt layer that formed on the surface of the SBW-2-40[7] was analyzed using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and XRD. The highly crystalline structure of the salt layer is shown in Figure 2 and Figure 3. EDS analysis of the salt layer (see Figure 4) indicates that the primary elements associated with the salt layer are S, Na, and O with minor traces of P and perhaps Mo.

[7] The nomenclature SBW-2-40 corresponds to the use of the SBW-2 frit (see Section 4.0) with the 2000 SBW simulant at 40 mass% loading. This nomenclature is used throughout this report for convenience.

Table 6. Visual Observations of Homogeneity (quenched and CCC) as a Function of WL for Candidate Frit Compositions

Frit	Loading (Mass%)	Quenched	CCC
SBW-2	25	Salt	n/a
SBW-2	30	Salt	n/a
SBW-2	35	Salt	n/a
SBW-2	40	Salt	n/a
SBW-2	45	Salt	n/a
SBW-3	25	Salt	n/a
SBW-3	35	Salt	n/a
SBW-4	25	Homogeneous	Homogeneous
SBW-4	25	Homogeneous	Homogeneous
SBW-4	30	Homogeneous	Homogeneous
SBW-4	35	Salt on crucible wall questionable	n/a
SBW-4	35	Salt around melt line	5 spots on surface, 1.6 mm ($^{1}/_{16}$ in.) diameter, < 1% surface covered
SBW-5	35	Salt on surface, thin white layer	7 spots on surface, 1.6 mm ($^{1}/_{16}$ in.) diameter, < 1% surface covered
SBW-6	35	Salt on surface, thin white layer	~ 15 spots on surface, 1.6 mm ($^{1}/_{16}$ in.) diameter, thin layer covering ~¼ of melt surface
SBW-7	35	Salt on surface, thin white layer	~ 20 spots on surface, 3.2 mm ($^{1}/_{8}$ in.) diameter
SBW-8	35	Salt on surface, thin white layer	~ 10 spots on surface, 3.2 mm ($^{1}/_{8}$ in.) diameter, thin layer covering ~¼ of melt surface
SBW-9	35	Homogeneous	~ 15 spots on surface, 1.6 mm ($^{1}/_{16}$ in.) diameter, thin layer covers entire surface

Figure 2. Secondary Electron Micrograph of Salt from SBW-2-40

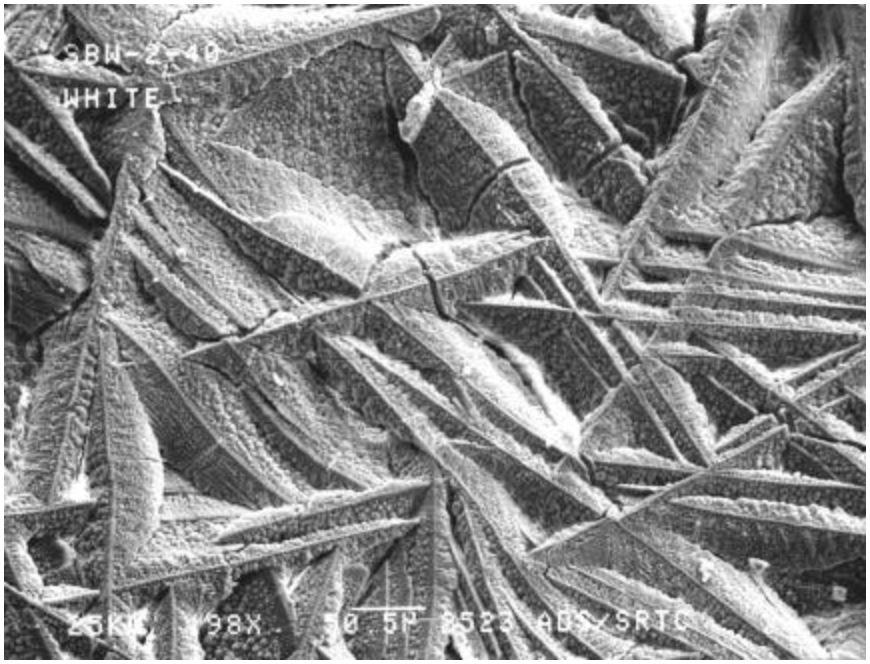

Figure 3. Secondary Electron Micrograph of Salt from SBW-2-40

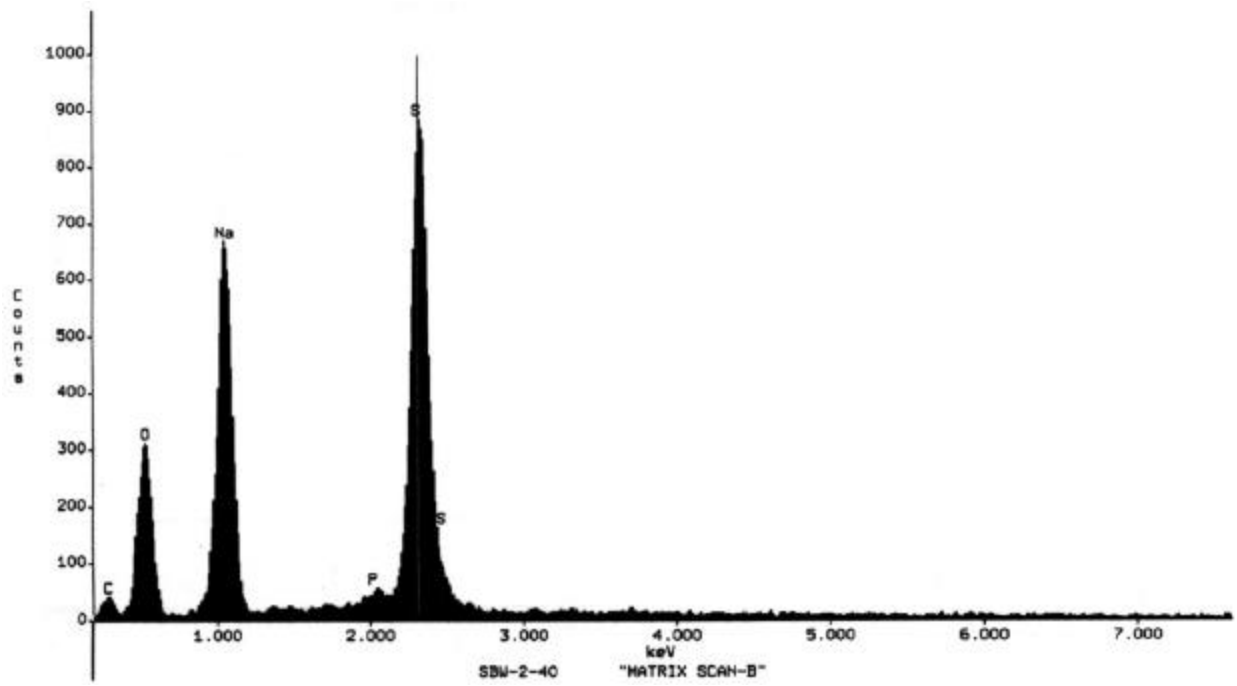

Figure 4. EDS Spectra of the Salt Layer Observed on the Surface of SBW-2-40

The XRD results shown in Figure 5, indicate sodium sulfate (Na_2SO_4 [JCPDS file: 83-1570 and 74-1738]) was the major phase. This result is consistent with the SEM/EDS spectra (see Figure 2 through Figure 4) as well as analysis performed by Vienna et al. (1999).

Frits SBW-4 through SBW-9 (see Table 5) were focused on additions of CaO to evaluate the potential to increase SO_3 solubility. Given the unknown effects of BaO on glass properties (i.e., property coefficients for BaO were not known), the primary focus was on CaO additions. However, SBW-10 was formulated to evaluate the addition of BaO (the same composition as SBW-9 with BaO replacing CaO on an equal mass basis).

Visual observations of the melt series using SBW-4 indicated that homogenous glasses were produced at WLs of 25 (duplicate tests) and 30 mass%. The formation of a salt layer was observed at a 35 mass% WL. Given that these melts were produced from oxides and carbonates and recognizing that differences between raw materials and the liquid simulant may exist, no further analysis was performed to understand S partitioning. The intent of these initial tests was to provide direction in terms of frit additives, which would support tests with the liquid feed. For WLs of 30 mass% or less with SBW-4, homogeneous glasses resulted after CCC (refer to Table 6).

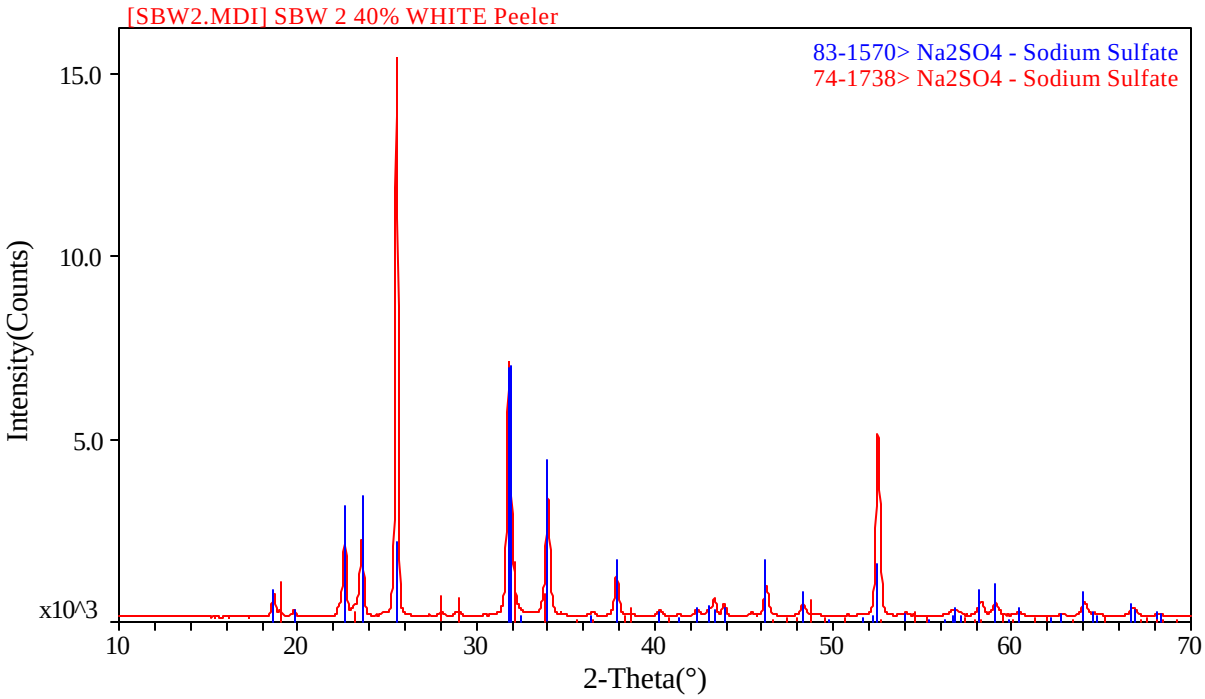

Figure 5. XRD Results of the SBW-2-40 Salt Layer

Given that a salt layer did not form during fabrication of adding CaO in SBW-4-30, systematic compositional changes from SBW-4 were made (resulting in SBW-5 through SBW-10), and glasses were produced at WLs of 35 mass%. These glasses were produced using reagent-grade chemicals targeting the original SBW composition. A salt layer was observed on the glasses produced with SBW-5, -6, -7, and -8 additives. However, the use of SBW-9 produced a homogeneous glass at 35 mass% WL upon initial fabrication. Showing that by increasing CaO, B_2O_3 and Li_2O at the expense of Fe_2O_3 and SiO_2 a salt layer could be avoided at 35% waste loading for this glass. After CCC, several isolated islands of salt (assumed to be sodium sulfate) and a thin pale layer were observed on the surface of the glass. Figure 6 and Figure 7 show a representative "island" found on the surface of SBW-9-35 after CCC. EDS analyses (Figure 8 through Figure 10) indicate that the S concentration increases as one transitions from the thin layer (Spot #1 in Figure 7) to the interior of the "island" (Spot #3 in Figure 7).

With homogeneous glasses being produced at 30 and 35 mass% for SBW-4 and SBW-9, respectively, these glasses became the two leading candidates to be evaluated during SBW liquid-simulant tests. Although data are reported for the other frits in the following sections, the primary discussion will revolve around the observations and measured properties of glasses produced using SBW-4 and SBW-9. Results associated with other frits will be discussed when appropriate.

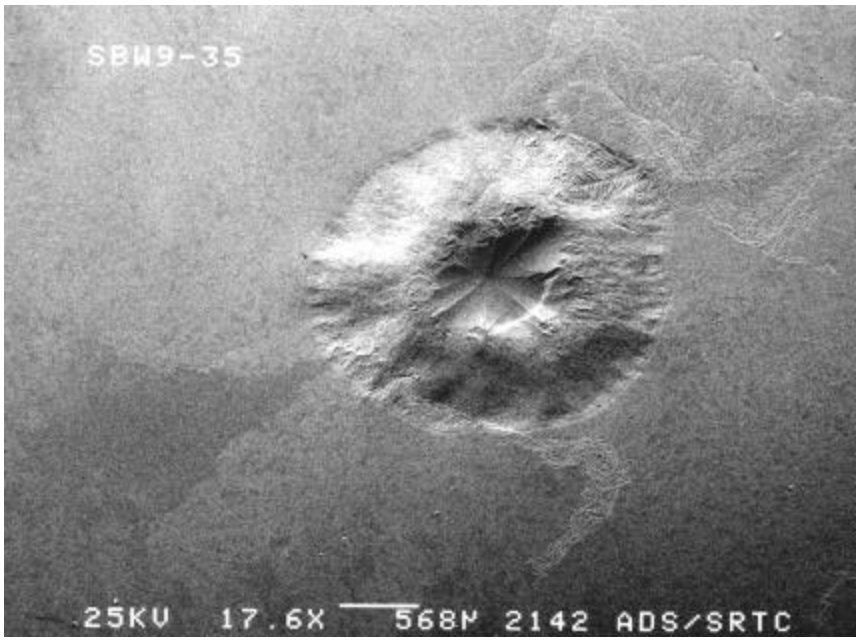

Figure 6. Representative "Salt Island" Observed on the Surface of SBW-9-35 after CCC

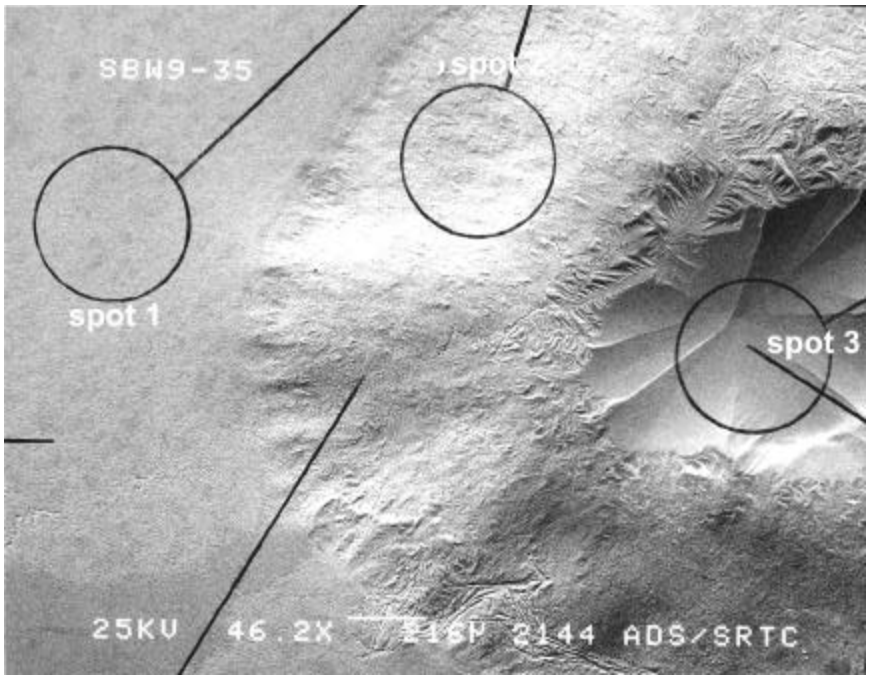

Figure 7. Representative "Salt Island" Observed on the Surface of SBW-9-35 after CCC

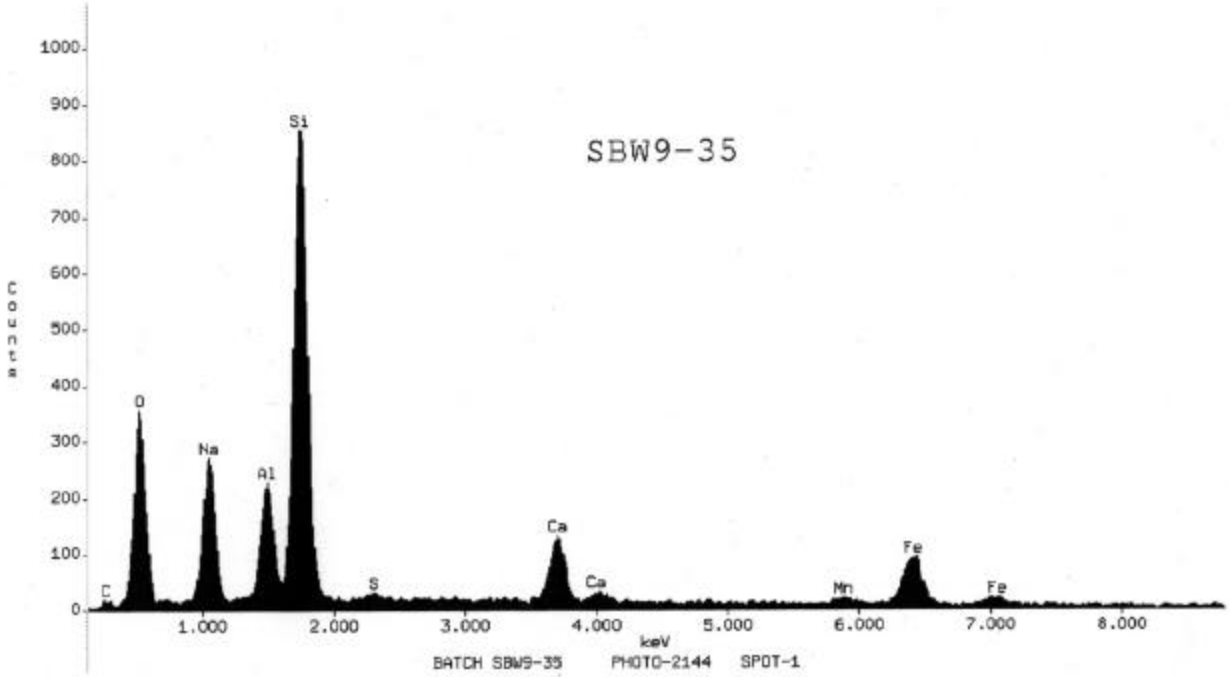

Figure 8. EDS Analysis of Spot #1 (exterior)

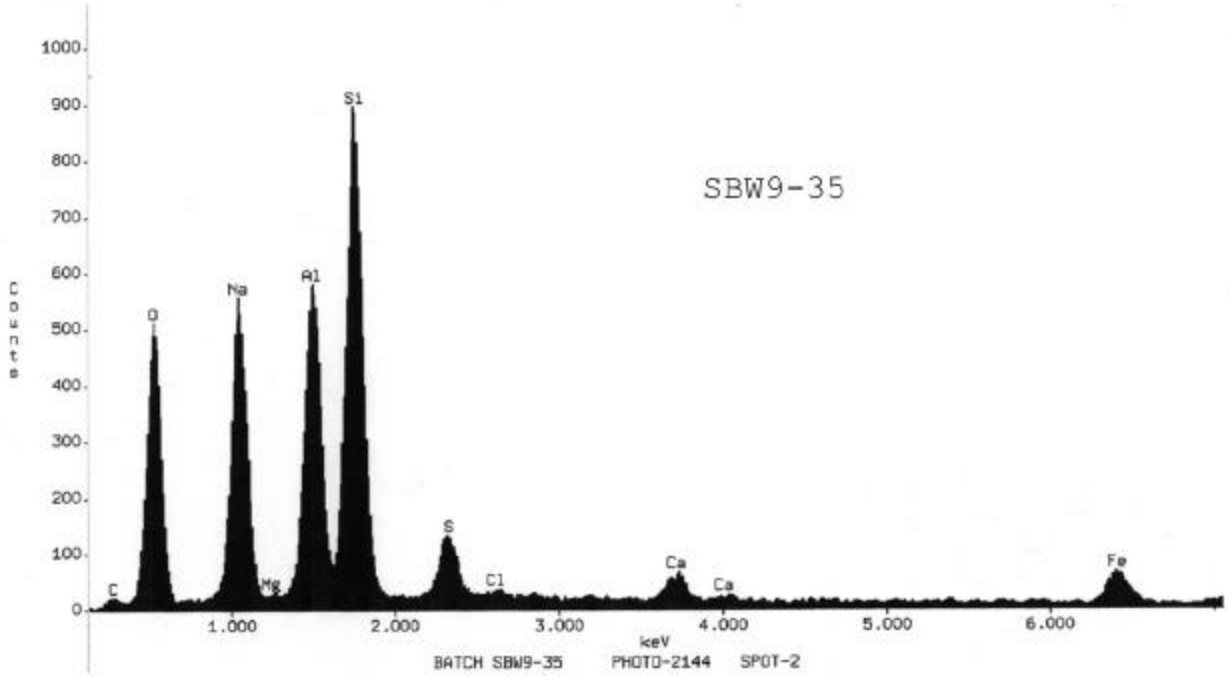

Figure 9. EDS Analysis of Spot #2

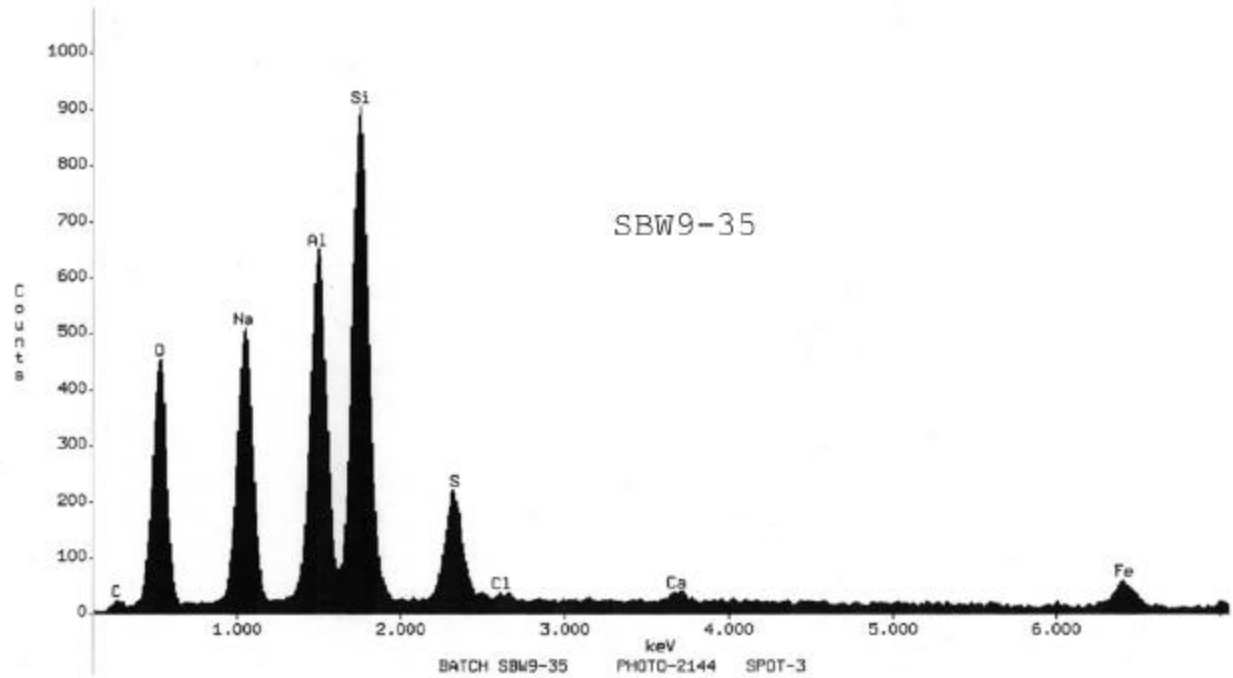

Figure 10. EDS Analysis of Spot #3 (interior of "island")

5.2.2 Liquidus Temperature

Roughly 5-g samples of selected as-fabricated (quenched) SBW glasses were heat treated at 1050°C for 24 h in a Pt/Rh crucible with a tight-fitting lid. Visual observations and optical microscopy analyses were made to assess the presence of crystallization or droplets of Na_2SO_4 (as observed by Vienna et al. 1999). Table 7 summarizes the visual and optical microscopy results of select glasses. All samples tested were homogeneous, indicating that the T_L is less than 1050°C (meeting one of the processing constraints as listed in Table 3). It should be noted that for those glasses on which a salt layer was observed after initial fabrication (e.g., those not italicized and bold in Table 7), the salt layer was removed before the 24-h heat treatment. The T_L results of these glasses should be viewed and used accordingly.

Table 7. Visual and Optical Microscopy Results of Select SBW Glasses after a 1050°C, 24-h Isothermal Heat Treatment

Frit	Loading (Mass%)	*Visual/Optical Observations*
SBW-2	25	Homogeneous
SBW-2	30	Homogeneous
SBW-2	35	Homogeneous
SBW-2	40	Homogeneous
SBW-2	45	Homogeneous
SBW-4	***25***	***Homogeneous***
SBW-4	***30***	***Homogeneous***
SBW-4	35	Homogeneous
SBW-5	35	Homogeneous
SBW-6	35	Homogeneous
SBW-7	35	Homogeneous
SBW-8	35	Homogeneous
SBW-9	***35***	***Homogeneous***

5.2.3 Viscosity

A standard technical procedure (SRTC 1999) was used to measure the η on select SBW pour patty glasses as a function of temperature (T) using a spindle viscometer. Glass η-T data were fitted to the Vogel-Tamman-Fulcher model:

$$\ln(\eta) = A + \frac{B}{(T - C)} \tag{2}$$

where η represents the η in Pascal seconds (Pa·s) and A, B, and C are temperature independent parameters whose values were estimated using the available data.

Figure 11 shows the η as a function of temperature for SBW-2 at various WLs. Note that a salt layer was removed before measuring η for each of these glasses. The data indicate that as waste loading increases, η is reduced. This is expected given the increasing concentration of Na_2O from the waste as loadings increase. Table 8 summarizes the estimated values for A, B, and C and the predicted η at 1150°C ($\eta_{1150°C}$) for the SBW-2 and SBW-4 glasses. It is also interesting to note that the predicted (based on the measured data) $\eta_{1150°C}$ of SBW-2-25 (i.e., 11.55 Pa·s) does not meet the η constraint as listed in Table 3 ($2 < \eta_{1150°C} < 10$ Pa·s). Figure 12 shows the η as a function of temperature for SBW-4-25. Although this glass was homogeneous upon initial fabrication (no salt layer), SBW-4-25 would be unacceptable with the $\eta_{1150°C}$ exceeding the 10 Pa·s upper limit (i.e., $\eta_{1150°C} = 11.37$ Pa·s). Higher WLs would be required for the η to be within the acceptable range. With SBW-4-35 producing a salt layer, concerns over the size of the operational window are raised.

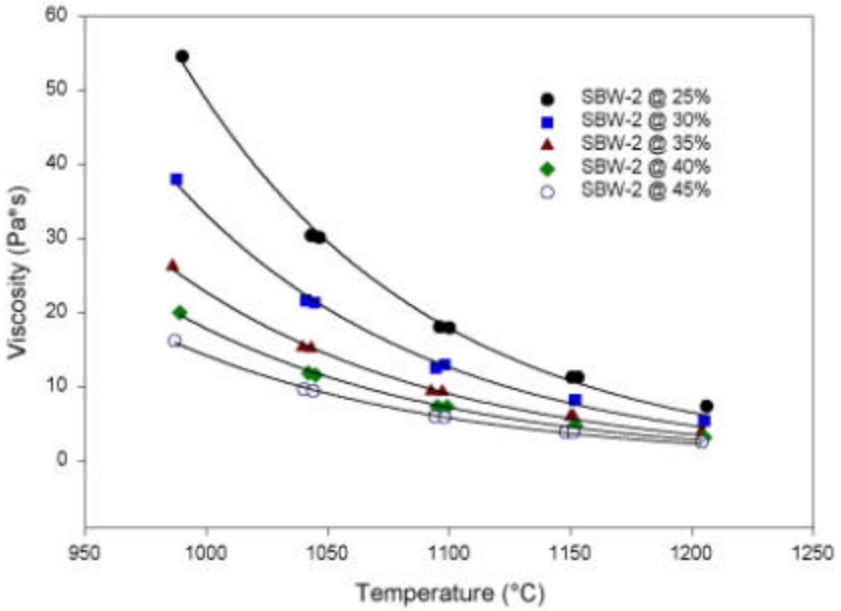

Figure 11. Viscosity-Temperature Relationships for SBW-2 as a Function of WL

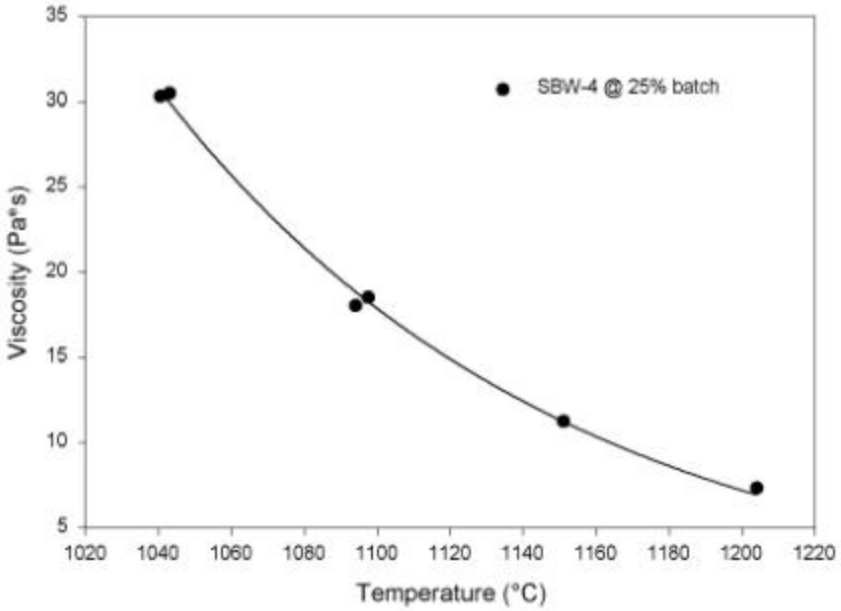

Figure 12. Viscosity-Temperature Relationships for SBW-4-25

Table 8. Estimated Values of A, B, and C, and Predicted $\eta_{1150°C}$ for Select SBW Glasses

Glass	A	B	C	$h_{1150°C}$ (Pa*s)
SBW-2-25	-6.27	9216.84	93.09	11.55
SBW-2-30	-5.85	8060.92	138.07	9.32
SBW-2-35	-7.04	10181.12	-1.47	6.07
SBW-2-40	-7.70	11240.79	-62.07	4.84
SBW-2-45	-7.99	11575.76	-86.47	3.93
SBW-4-25	-7.75	12321.48	-60.77	11.37

5.2.4 PCT Response

The PCT was performed on select SBW glasses to assess chemical durability. Again, these glasses were produced from batch chemicals using the 2000 WM-180 SBW simulant composition. If a salt layer was observed on the surface of the melt, the layer was removed before starting the PCT. To bound the effect of thermal history on durability, both quenched and CCC glasses were tested. Table 9 summarizes the results of these tests. The normalized elemental release values (r_i) are based on targeted glass compositions.

Table 9. PCT Results of SBW-2 and SBW-4 Quenched and CCC Glasses as a Function of WL

Glass	r_B (g/m^2)	r_{Li} (g/m^2)	r_{Na} (g/m^2)	r_{Si} (g/m^2)
SBW-2-25 (quenched)	0.227	0.277	0.207	0.185
SBW-2-25 (CCC)	0.241	0.274	0.215	0.191
SBW-2-30 (quenched)	0.234	0.230	0.250	0.185
SBW-2-30 (CCC)	0.261	0.259	0.266	0.202
SBW-2-35 (quenched)	0.264	0.197	0.321	0.199
SBW-2-35 (CCC)	0.293	0.242	0.337	0.220
SBW-2-40 (quenched)	0.400	0.203	0.520	0.270
SBW-2-40 (CCC)	0.368	0.232	0.468	0.265
SBW-2-45 (quenched)	0.707	0.221	0.876	0.362
SBW-2-45 (CCC)	5.345	3.868	3.353	1.163
SBW-4-25 (quenched)	0.207	0.268	0.226	0.159
SBW-4-25 (CCC)	0.200	0.254	0.212	0.157

Although no statistical analysis was performed, the SBW-2 data suggest that as WL increases r_i increases for both quenched and CCC versions. The PCT data for WLs from 25 to 40% indicate that the effect of CCC has essentially no practical impact relative to the quenched counterparts. However, when WL is increased to 45%, the quenched version of SBW-2-45 meets durability specifications, while the CCC version shows a dramatic increase in r_i
($r_B > 5$ g/m^2).

Figure 13 and Figure 14 show XRD results of the quenched and CCC versions of the SBW-2 glass (at 45 mass% WL). The XRD pattern of SBW-2-45 (quenched) is characterized by a high background devoid of crystalline spectral lines, indicating that less than 1 vol% of crystals is present in the sample. The XRD pattern of the CCC version of SBW-2-45 (shown in Figure 14) is characterized by distinct spectral lines, which indicate the presence of nepheline ($NaAlSiO_4$). The effect of CCC on HLW glass durability has been evaluated for more than 100 HLW glass compositions (Hrma et al. 1994; Kim et al. 1995), as shown in Figure 15. Kim et al. (1995) identified the crystalline phases that increased r_i and suggested that it was caused by an increase in the Na:Si+Al ratio in the residual glass by the extraction of nepheline.

Results of the SBW-4-25 quenched and CCC glasses indicate that each r_i is well below the stated limit or constraint of 1 g/m^2 (as defined in Table 3). There is essentially no practical difference between the quenched and CCC versions of this glass at 25 mass% WL.

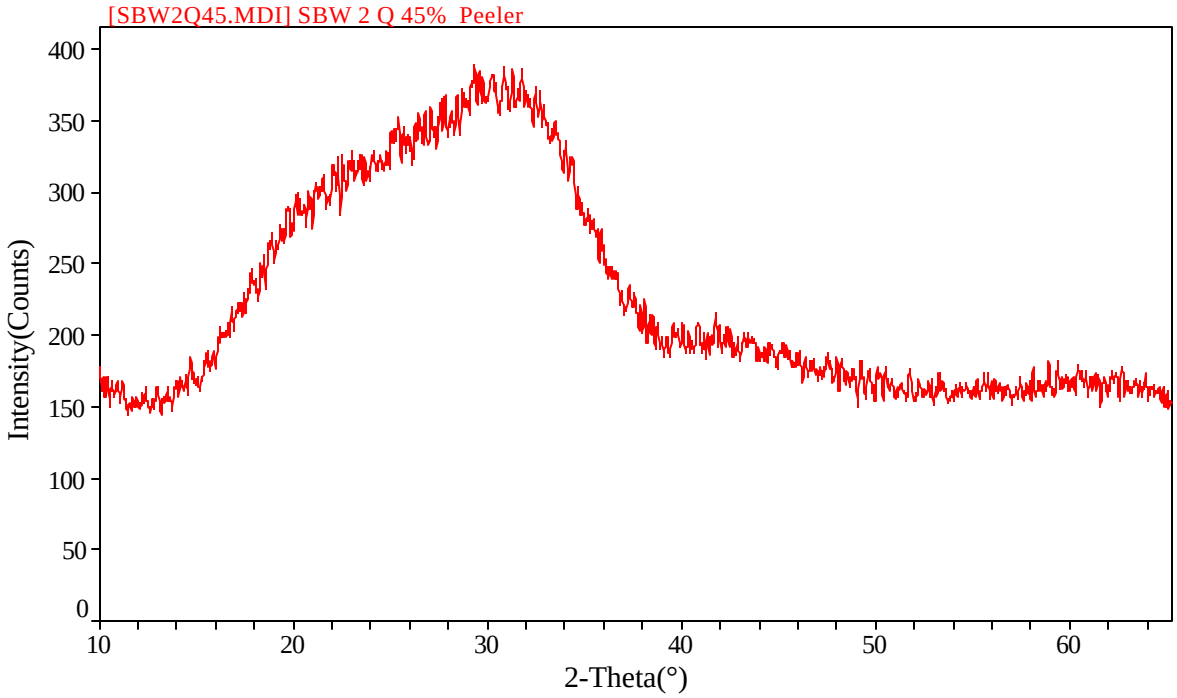

Figure 13. XRD Results of SBW-2-45 (Quenched)

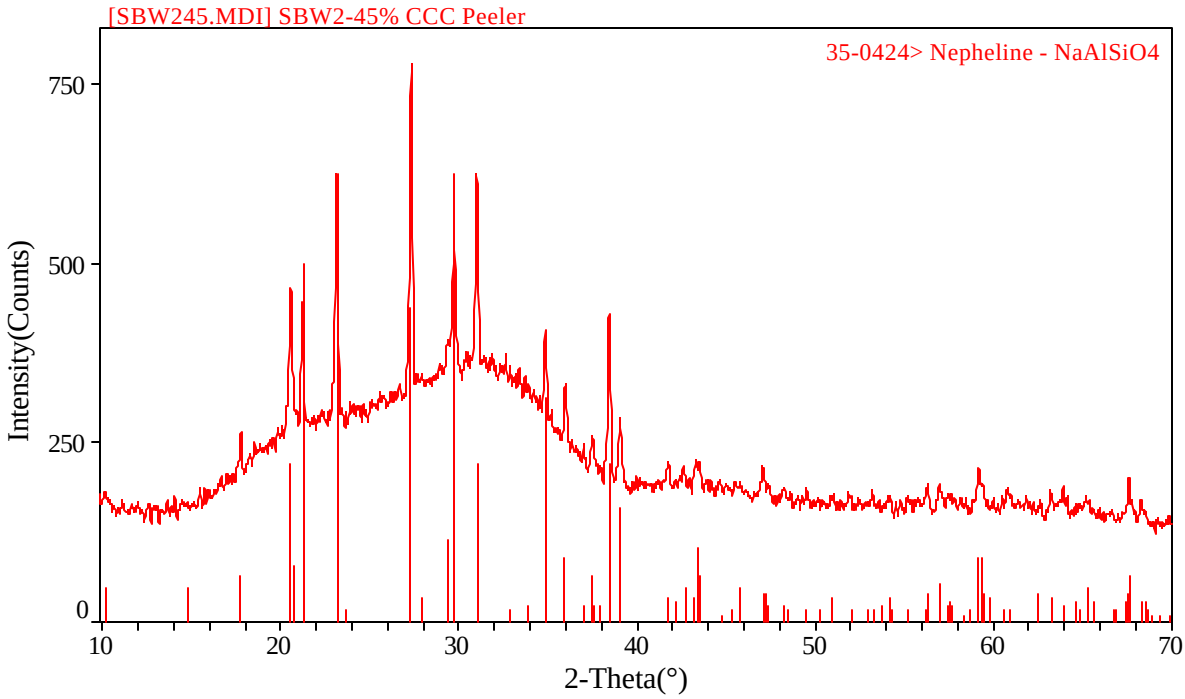

Figure 14. XRD Results of SBW-2-45 (CCC)

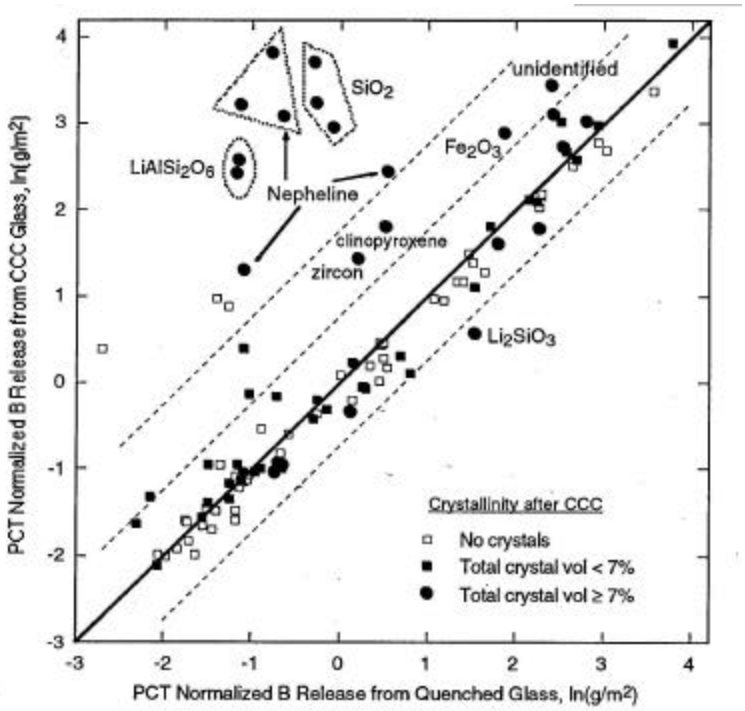

Figure 15. Natural logarithm of PCT r_B from CCC versus quenched glasses within Hanford composition region (Kim et al. 1995)

5.3 Summary of Batch Chemical Testing

Based on the initial scoping tests using batch chemicals, it appears that SBW-4 and SBW-9 are the primary candidates for tests using the liquid WM-180 SBW simulant. Homogeneous glasses have been produced with SBW-4 and SBW-9 with up to 30 and 35 mass% WLs, respectively. However, differences between the use of batch chemicals and the liquid feed may affect targeted WLs as S partitioning may vary. This could result in different targeted WLs in an effort to avoid salt-layer formation and/or accumulation.

The initial tests suggest that adding CaO increases the solubility of SO_3 in these multi-component systems, which compares favorably with the findings from the literature survey. It was also observed that at higher WLs (> 40 mass%), if the salt formation could be avoided, the loading of SBW in glass could be limited by PCT release or the formation of nepheline on cooling. That is, the r_i values of SBW-2-45 after CCC were much greater than acceptable values. This was due to the formation of nepheline in the CCC glass.

6.0 Liquid Simulant Testing

This section discusses the fabrication of the WM-180 simulant (Section 6.1), the experimental procedures used at SRTC and PNNL in support of the liquid simulant testing program (Section 6.2), and the results (Section 6.3). Section 6.4 summarizes the liquid-simulant tests. In Section 6.5, a recommendation on the glass formulation to be used to support the upcoming RSM and EV-16 melter demonstrations is provided.

6.1 Fabrication of WM-180 Simulant

Ten liters of SBW simulant were prepared to support laboratory testing. Table 10 summarizes the chemicals and amounts used to fabricate the WM-180 simulant. The simulant was prepared by mixing the dry salts in a beaker. Then just enough deionized water (DIW) was added to dissolve all of the salts with heating and stirring. The manganese nitrate and aluminum nitrate solutions were added to this solution. The resulting solution was continually heated and stirred as the boric acid was added. At this point, the heating and stirring were discontinued, and the solution was transferred to a plastic carboy. The hydrofluoric acid was then added to the slurry and stirred. Then the sulfuric acid was added to the slurry as it was stirred vigorously. About 500 mL of DIW was added to the slurry, and then the hydrochloric, phosphoric, nitric, and molybdic acids were added to the slurry. Finally, DIW was added to bring the final volume of the slurry to 10 L. The resulting slurry was then thoroughly mixed by stirring. The composition of the resulting solution was analyzed using inductively coupled plasma (ICP) and ion chromatography (IC). The average concentrations from four ICP measurements are listed in Table 11. The concentration of SO_4 in the solution as measured by IC was 4200 μg/mL. The measured concentrations of S in solution are both lower than target values; however, the precision of batch fabrication is expected to be higher than that of either measurement.

Table 10. Chemicals Used in the Preparation of WM-180 Simulant

Chemical Used	Amount Used (g)		Chemical Used	Amount Used	
$NaNO_3$	1650.60		$Mg(NO_3)_2\ 6H_2O$	29.13	g
KNO_3	187.22		$RuCl_3$	0.24	g
$Ca(NO_3)_2\ 4H_2O$	106.95		$Sr(NO_3)_2$	0.24	g
$Cd(NO_3)_2\ 4H_2O$	2.20		TiO_2	0.04	g
$Ni(NO_3)_2\ 6H_2O$	4.04		$Zn(NO_3)_2\ 6H_2O$	2.95	g
$Fe(NO_3)_3\ 9H_2O$	82.83		KI	0.21	g
ZrF_4	0.10		$Mn(NO_3)_2$ (50% soln)	47.64	g
$Cr(NO_3)_3\ 9H_2O$	12.66		2.2M $Al(NO_3)_3$ soln	2855	mL
$Ba(NO_3)_2$	0.14		H_3BO_3	7.18	g
$Ce(NO_3)_3\ 6H_2O$	0.19		28.9M HF	13.69	g
$Co(NO_3)_2\ 6H_2O$	0.05		18M H_2SO_4	52.07	g
$Cu(NO_3)_2\ 3H_2O$	1.59		12M HCl	27.38	g
$Gd(NO_3)_3\ 5H_2O$	0.73		14.6M H_3PO_4	15.13	g
$Pb(NO_3)_2$	4.08		15.4M HNO_3	804.4	g
$LiNO_3$	0.22		H_2MoO_4	0.295	g

Table 11. Chemical Analysis of SBW Simulant

Element	Moles	Target (g/mL)	Avg. ICP	Oxides	Mass% (target)
Al	0.6282	16950	17125	Al_2O_3	27.96
B	1.16E-02	126	122	B_2O_3	0.35
Ba	5.26E-05	7.22		BaO	0.01
Ca	4.53E-02	1815	2020	CaO	2.22
Cd	7.12E-04	80		CdO	0.08
Ce	4.46E-05	6.25		CeO_2	0.01
Co	1.82E-05	1.07	<0.050	CoO	0.21
Cr	3.16E-03	165		Cr_2O_3	0.00
Cu	6.58E-04	41.80	40.5	CuO	0.05
Fe	2.05E-02	1145	1200	Fe_2O_3	1.43
Gd	1.67E-04	26.31	22.0	Gd_2O_3	0.03
K	1.85E-01	7245	4010	K_2O	7.62
Li	3.20E-04	2.22		Li_2O	0.00
Mg	1.14E-02	276	273	MgO	0.40
Mn	1.33E-02	731	712	MnO_2	0.82
Mo	1.82E-04	17.45	13.5	MoO_3	0.02
Na	1.942	44646	46650	Na_2O	52.54
Ni	1.39E-03	81.53	58.4	NiO	0.09
P	1.29E-02	400	418	P_2O_5	0.80
Pb	1.23E-03	255	223	PbO	0.24
Ru	1.18E-04	11.89		RuO_2	0.01
Sr	1.12E-04	9.85		SrO	0.01
Ti	5.45E-05	2.61		TiO_2	0.00
Zn	9.90E-04	64.74	58.6	ZnO	0.07
Zr	5.97E-05	5.44	1.52	ZrO_2	0.01
I	1.27E-04	16.05		I	0.01
Cl	0.0284	1007	1455	Cl	0.88
SO_4	0.051	4899	3033	SO_3	3.57
NO_3	5.1125	317000		NO_3	0.00
F	0.0458	870	574	F	0.57

6.2 Experimental

A series of crucible tests was performed using the 2000 WM-180 simulant composition. The goal of these tests was to determine the appropriate WL, the need for any acid additions or adjustments, and additive compositions. A majority of the tests were performed using two basic test methods. In the first set of experiments (referred to as Method 1), all melts were made by mixing enough waste simulant and additives to obtain 50 g of glass (after loss of all H_2O, HNO_3, $C_6H_{12}O_6$, and other volatile components). The dry additives were slowly mixed into the waste simulant in either the melting crucible (~500-mL alumina crucibles) or Teflon beakers with a Teflon-coated stir bar. The sugar was added to the mixture along with other solid additives. In many cases, concentrated HNO_3 was added using a pipette to adjust the total pH after solids were added. The mixtures were heated on a hot plate with continued stirring using a hot-plate face temperature of roughly 140°C until nearly dry. The mixtures were transferred to

drying ovens to dry overnight (~16 h) at roughly 100°C. For samples dried directly in crucibles, the tight-fitting crucible lids were coated with a glass frit and placed on the crucible in the heat-treatment furnace. For samples dried in Teflon beakers, the sample was first transferred to a crucible. Heat treatments were performed by ramp heating from between room temperature and 150°C to 240°C at 3°C/min, from 240°C to 300 at 1°C/min, and then from 300°C to 1150°C at 6°C/min, held at 1150°C for 1 h, and quenched to room temperature. The lid was removed from the crucible (usually by breaking it off), and visual observations of the melt were made. A 20-mL sample of DIW was used to wash any salt off the top of the melt/crucible interior. The salt solutions were analyzed using ICP-OES and/or IC. Glass samples were broken from the crucible and ground to roughly 1-µm median particle diameter in a tungsten-carbide mill. Glass powder (and occasionally dry feed samples) were fused in Na_2O_2 and KOH, dissolved in HNO_3, and analyzed by ICP-OES. The S concentration of glass samples was also analyzed by XRF.

The second set of tests (Method 2) was also performed with the WM-180 simulant fabricated as described in Section 6.3.1, but differed slightly in the experimental procedure relative to Method 1. In this second set of tests, all melts were made by mixing 150 mL of waste simulant, which required varying quantities of frit additives to target between 40 to 60 g of glass. The dry additives were slowly mixed into the waste simulant in the melting crucible (~600 mL Pt/Au crucibles) for all tests. The sugar was added to the mixture along with other solid additives. In many cases, a predetermined quantity of concentrated HNO_3 was added using a pipette to adjust the total pH to that of the simulant before adding solids. The mixtures were heated on a hot plate with continued stirring using a hot-plate face temperature of roughly 140°C until nearly dry (during drying, a Pt/Au lid was placed on top of the crucible). The mixtures were transferred to a high-temperature furnace to dry. The furnace was then ramped at ~8°C/min to 150°C and held for 20 min, then to 225°C and held for 20 min. For select tests, a dry sample was obtained at this point for ICP and IC analysis. The furnace was then ramped at 8°C/min to 1150°C and then held for 1 h. The crucible was then removed and placed in a pan of water. No lid was used during vitrification. Visual observations of the melt were made during heating. Glass samples were broken from the crucible and analyzed by ICP. Other samples were taken for various property testing.

6.3 Results and Discussion

Table 12 summarizes the results of the liquid-simulant tests. The column headings provide critical information as to the combination of frit, WL, sugar addition, HNO_3 concentration, and the test method (1 and 2 as described above). Most of the tests were performed under what is referred to as "baseline" conditions: 1.1 M HNO_3 concentration and 141 g sugar per liter of waste addition (as reductant). Tests were performed where additional HNO_3 (up to 3 M HNO_3) was added to the WM-180 simulant to assess whether S partitioning would be affected (i.e., would adding free acid affect the partitioning of S between the off-gas, the glass, and a salt layer). Other tests used varying amounts of sugar as the reductant (from no sugar added up to 164 g/L). Also noted in Table 12 is a brief description of the presence of a salt layer (i.e., salt column) and observations regarding batch expansion or foam during drying and melting. For these latter columns a subjective scaling system was developed to minimize variations in observations between two laboratories performing the work. Although a system was developed and implemented, differences may exist as each site categorizes its observations. A brief description of the various classifications is provided in the footnote to Table 12.

Numerous comparisons could be made given the data presented in Table 12. However, discussions will focus on those tests with SBW-4 and SBW-9, given that they are the primary frit candidates. The tests performed with SBW-2 span a WL range from 20 to 35 mass% and were primarily focused on determining the amount of reductant to be added. These tests are discussed in Section 7.0. Tests with SBW-9 targeted WLs from 25 to 35 mass% using both the baseline HNO_3 and sugar additions as well as

various combinations. Caution should be used when making comparisons between the results of the liquid WM-180 SBW simulant tests with those using batch chemicals (see Section 5.0).

Table 12. Parameters, Visual Observations, and S Results for the Liquid SBW Tests

Frit	WL (mass%)	Sugar (g/L)	HNO_3 (M)	Test	Salt[a]	Foam (dry) [b]	Foam (melt)[c]	S in salt (g)	S in glass (%)	Comments
SBW-1	25	141	1.1	2	3	2	3			
SBW-4	20	141	1.1	2	No	2	3			
SBW-4	25	141	1.1	2	No	2	3			
SBW-4	25	141	2	2	No	2	3			
SBW-4	30	141	1.1	2	4	2	3			XRD and SEM/EDS results
SBW-4	30	141	2	2	4	2	3			
SBW-4	30	141	3	2	4	2	3			
SBW-4	35	0	1.1	2	2	2	1			
SBW-4	35	141	2	2	4	2	3			original SBW simulant
SBW-9	25	141	1.1	2	No	2	3			
SBW-9	25	141	1.1	2	No	2	3			
SBW-9	30	141	1.1	2	No	2	3			
SBW-9	30	141	2	2	1	2	3			
SBW-10	30	141	2	2	3	2	1			SBW-4 with BaO for CaO
SBW-2	35	77	1.1	1	4	1	4	.082		Sugar test FeII/Fe=7.07E-4
SBW-2	35	109	1.1	1	4	2	3	.093		Sugar test FeII/Fe=3.86E-4
SBW-2	35	131	1.1	1	4	3	3	.094		Sugar test FeII/Fe=1.32E-3
SBW-2	35	164	1.1	1	3	3	1	.093		Sugar test FeII/Fe=2.71E-1
SBW-4Q	35	141	1.1	other	n/a	2	n/a	.002	0.32	2.5 g Q-furnace test
SBW-4D	35	141	1.1	other	4	n/a	1			Dryout test
SBW-4D	35	141	3	other	2	n/a	1			Dryout test
SBW-4	35	141	2	1	3	3	4	.048	0.39	Acid adjustment
SBW-4	35	141	3	1	3	3	4	.038	0.39	Acid adjustment
SBW-9	30	141	2.1	1	1	3	3	.003	0.44	
SBW-9	30	141	2.1	1	1	3	3			
SBW-9	30	141	1.1	1	1	3	1	.025	0.34	
SBW-9	25	141	1.1	1	2	3	1	.019	0.31	
SBW-9	25	141	1.1	1	3	3	1			
SBW-9	28	141	1.1	1	3	3	1			
SBW-9	32	141	1.1	1	3	3	1			
SBW-9	32	135	1.1	other	No	n/a	1	n/a	0.17	oven dried in Al_2O_3 cruc, 5 cf/h N_2 sweep gas
SBW-9	32	135	1.1	other	No	2	1	n/a	0.09	5 cf/h N_2 sweep gas
SBW-9	32	135	1.1	other	No	2	1	n/a	0.06	Pt cruc, 5 cf/h N_2 sweep gas fast/exothermic reaction near completion of drying

(a) Salt – 1) faint patterns on surface, 2) hazy patterns cover surface, 3) accumulation of salt in areas, 4) gross accumulation of salt.

(b) Foaming during drying – 1) little or no foaming, 2) foaming requiring some manual stirring, 3) lots of foaming requiring lots of manual stirring.

(c) Foaming during melting – 1) none, 2) foaming but remains in crucible, 3) foaming slightly outside of crucible, 4) significant glass outside of crucible due to foaming.

6.3.1 Salt Formation

As mentioned several times, the avoidance of salt formation is a critical parameter for formulating a glass for SBW. In this section, we consider the impact of several parameters on the propensity to form a salt layer in crucible tests.

Frit Composition

At 25 mass% WL, SBW-1 accumulated salt in the second test method while SBW-4-25 and SBW-9-25 showed no signs of salt formation. At 30 mass% WL, SBW-4 showed salt formation while SBW-9-30 formed only slight patterns on the surface or no salt at all. This confirms the results of the "batch chemical" tests and literature data that adding calcium in place of titanium is beneficial for avoiding salt formation whereas replacing barium with calcium (going from SBW-9 to SBW-10) was found to increase the amount of salt formed. Of the 10 frits, only numbers 1, 2, 4, 9, and 10 were used to fabricate and test glasses with the liquid SBW simulant. Of these compositions, SBW-9 showed the most promise for fabrication of salt-free glass melts.

Sugar Concentration

The concentration of sugar was systematically varied from 77 to 164 grams per liter (g/L) of SBW at 35 mass% WL with the SBW-2 composition. The results suggest that although sugar concentration greatly influenced glass redox, little change was seen in salt formation.

HNO_3 Concentration

The concentration of HNO_3 was increased from 1 to 3 M during simulant tests with SBW-4-30, SBW-4-35, and SBW-9-30. The data suggest that the effect of nitric acid concentration on salt formation is minimal.

Test Method

Two major test methods (Methods 1 and 2) were used to fabricate glasses with the SBW simulant as described above. For SBW-9-25, a light haze of salt was seen by test Method 1, but not by test Method 2. For SBW-9-30, faint patterns of salt were observed on all glasses by Method 1 and by Method 2 with 2 M HNO_3, but no salt was found by Method 2 with 1.1 M HNO_3. Similar results were obtained by both methods with SBW-4-35. Although these two major test methods gave similar results, there were slight differences. The factors that most likely contributed to the differences include the crucible type, the drying method, and the gas flow in the crucible during heating. Therefore, a set of tests was performed to see the influence of these parameters with SBW-9-35. The type of crucible and the drying method were varied, and a significant gas flow was introduced during heat treatment. In this set of tests, no salt layer formed in any sample, whereas a salt accumulation was seen by test Method 1 that did not allow gas flow in the crucible. The concentration of S in all three samples was lower than any other test performed in this study, suggesting that the gas flow in the crucible significantly changed the S partitioning in the test. Since these test methods cannot easily mimic the gas-flow behavior in an operating melter, it was decided to use the two major methods consistently to compare other effects on salt formation (rather than gas flow).

Waste Loading

As S is introduced from waste, the influence of WL is obviously to increase the likelihood of salt formation if all other parameters are held constant. For the selected frit composition (SBW-9), generally the amount of salt formed increased with increasing WL. However, salt was generally not seen at WLs below 30%, and either no salt or faint patterns on the glass surface were seen at 30% WL. More significant salt formation occurred at higher WLs. This led to the conclusion that 30% WL was at the edge of acceptability for the crucible tests. Knowing that there would be significantly higher gas flow in operating glass melters, this would be the recommended WL to begin melter testing.

A sample of the salt layer observed on the surface of SBW-4-30 (using Method 2) was analyzed using XRD and SEM/EDS. Figure 16 and Figure 17 show SEM micrographs of the salt layer. Figure 18 through Figure 20 are EDS spectra of various "spots" as shown in Figure 17.

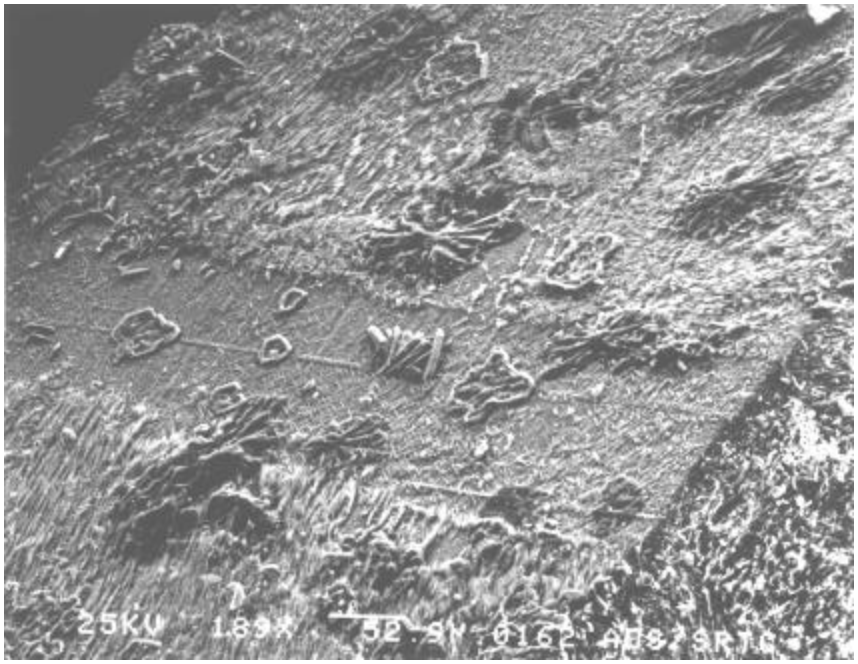

Figure 16. Secondary Electron Micrograph of Salt Layer Observed on SBW-4-30

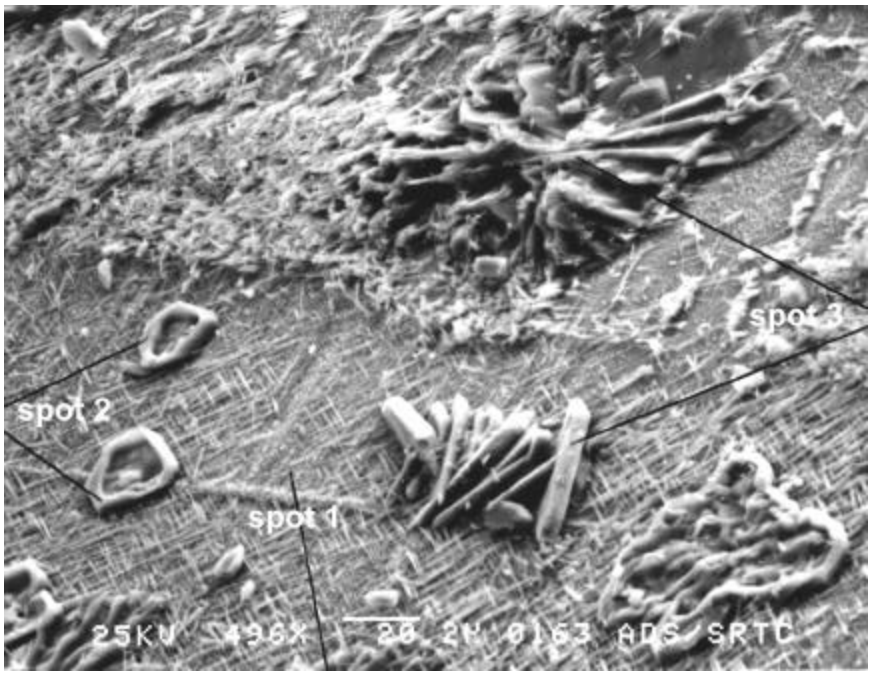

Figure 17. Secondary Electron Micrograph of Salt Layer Observed on SBW-4-30

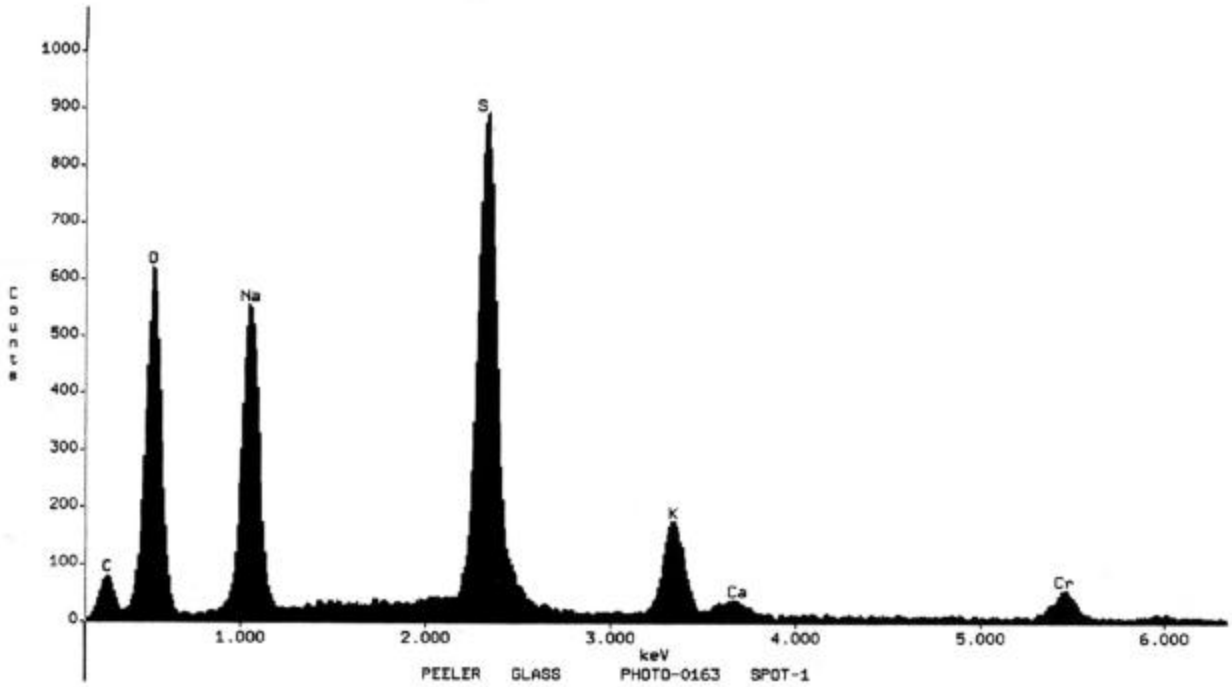

Figure 18. EDS Spectra of "Spot #1"

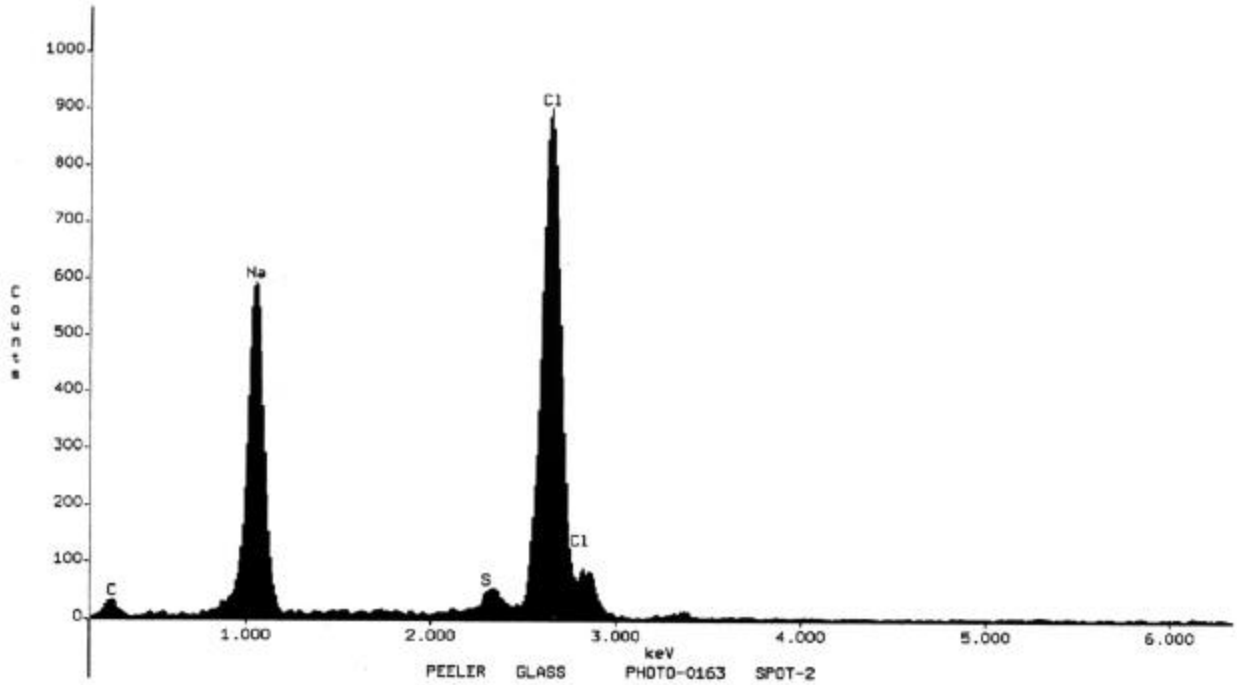

Figure 19. EDS Spectra of "Spot #2"

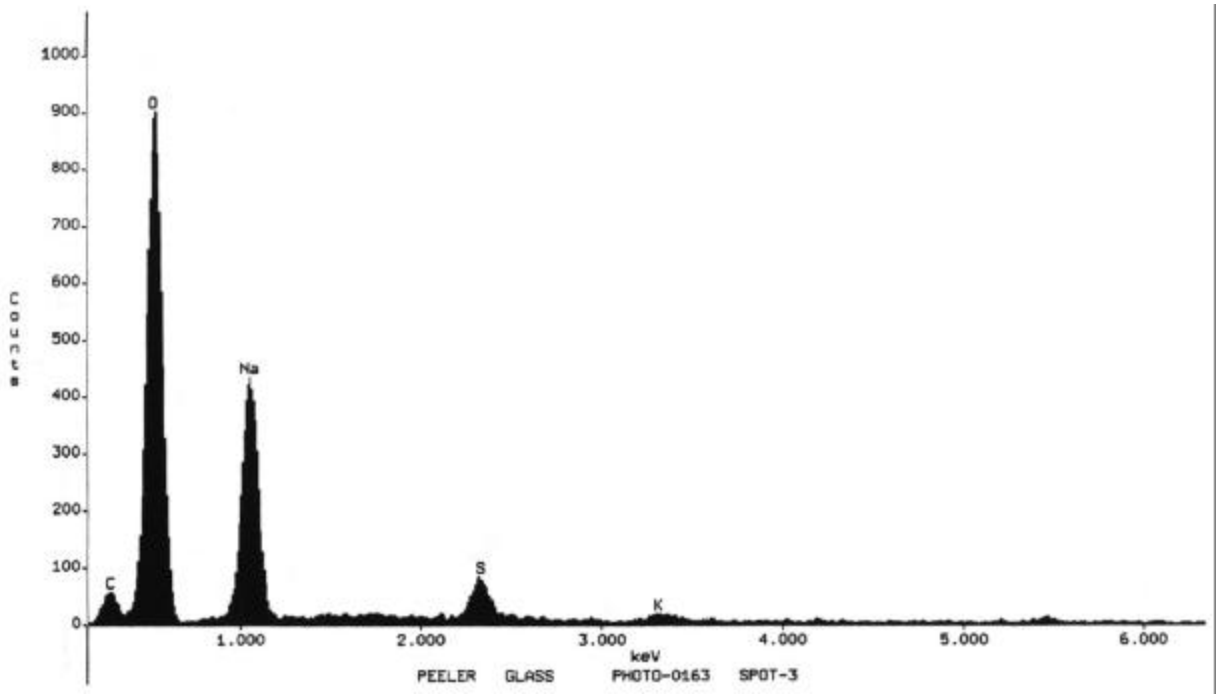

Figure 20. EDS Spectra of "Spot #3"

The XRD results (see Figure 21) indicate that the primary phase associated with the salt layer in SBW-4 at 30 mass% WL is sodium sulfate. This is consistent with the SEM/EDS analysis (Figure 16 through Figure 20) and with the salt layer observed in the batch chemical tests (see Figure 5).

6.3.2 Liquidus Temperature

Four samples of approximately 5-g each of SBW-9 based glasses (quenched) were heat treated at 1050°C for 24 h in a Pt/Rh crucible with a tight-fitting lid. Visual observations were made and optical microscopy was performed to assess the presence of crystallization or droplets of Na_2SO_4 (as observed by Vienna et al. 1999). Table 13 summarizes the visual and optical microscopy results. Three of the four glasses were homogeneous after initial fabrication (see Table 7). SBW-9 at 30% WL using 2M HNO_3 contained a salt layer. Before the 24-h heat treatment, the salt layer was removed from the surface, so the result should be appropriately considered. The results of the 24-h isothermal heat treatments indicate that T_Ls are less than 1050°C, meeting one of the processing constraints as listed in Table 3.

Table 13. Visual and Optical Microscopy Results of Select SBW-9 Glasses after a 1050°C, 24-h Isothermal Heat Treatment

Frit	Test Method	Loading (Mass%)	HNO_3	1050°C
SBW-9	2	30	1.1	Homogeneous
SBW-9	2	30	2	Homogeneous
SBW-9	2	25	1.1	Homogeneous
SBW-9	2	25	1.1	Homogeneous

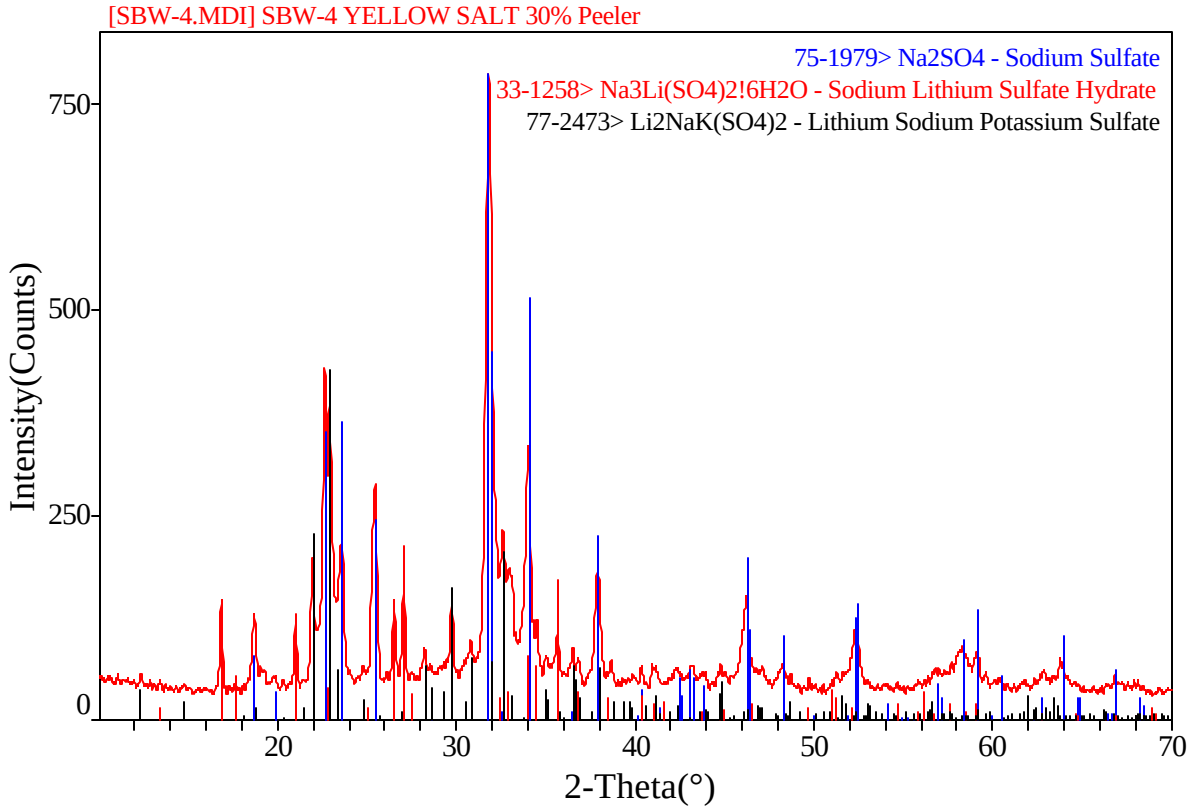

Figure 21. XRD Spectra of Salt Layer Observed on SBW-4 at 30 mass% WL

6.3.3 Viscosity

A standard technical procedure (ASTM C 965-81 [ASTM 1990]) was used to measure the η on select SBW-4 and SBW-9 glasses as a function of T using a spindle viscometer. Glass η-T data were fitted to the Vogel-Tamman-Fulcher model (Equation 2). Viscosity data for three SBW-4 based glasses were measured: SBW-4-25 and SBW-4-30 fabricated from both the 2M and 3M HNO_3 feeds. Viscosity data for SBW-9-25 and SBW-9-30 were also obtained.

Figure 22 summarizes the SBW-4 based data. As expected, as WL increases for the SBW-4 glasses, the η decreases. There appears to be no practical difference between the two SBW-4 glasses targeting 30% WL with each yielding $\eta_{1150°C}$, approximating 7.5 Pa·s. It should be noted that although SBW-4 at 25% loading produces a homogeneous glass, the η is outside the current specifications (i.e., > 10 Pa·s).

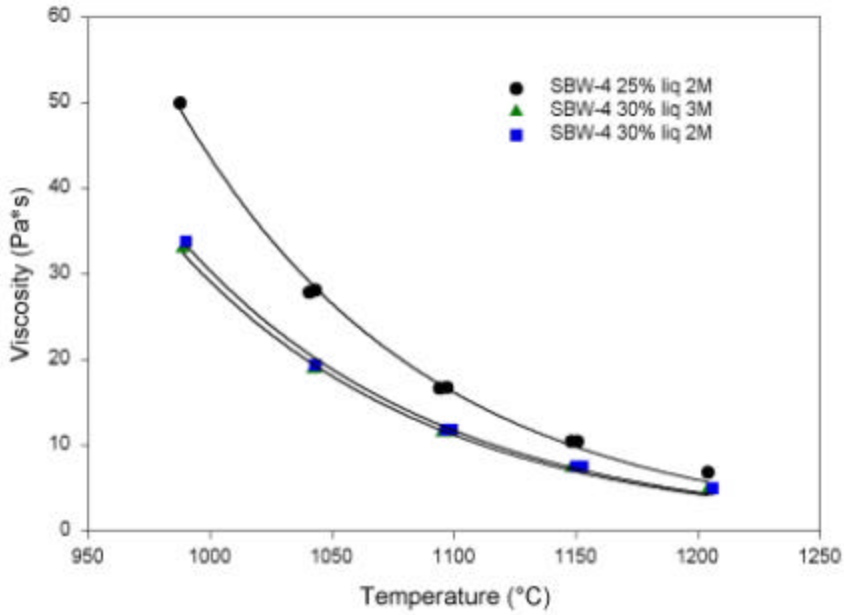

Figure 22. Viscosity-Temperature Relationships for SBW-4 as a Function of WL

Figure 23 shows a plot of η versus T for SBW-9 at 25% and 30% WL. As with previous SBW systems, as WL increases, the η decreases because of the high Na_2O concentration in the simulant. Although the η of both SBW-9 based glasses meets the current constraints, the lower limit (2 Pa·s at 1150°C) is challenged by the 30% loaded glass. Interpolated ηs at 1150°C for the 25% and 30% glasses are 3.90 and 2.54 Pa·s, respectively. Given that, η could ultimately limit WL, assuming that SO_3 formation and/or accumulation were not an issue. Table 14 summarizes the estimated values for A, B, and C and the predicted η at 1150°C ($\eta_{1150°C}$) for select SBW-4 and SBW-9 based glasses produced using the liquid simulant.

6.3.4 Durability

The PCT was performed on select SBW-4 and SBW-9 glasses to assess chemical durability. To bound the effect of thermal history on durability, both quenched and CCC glasses were tested. Table 15 summarizes the results of these tests. The normalized release values (r_i) are based on targeted glass compositions.

Although no statistical analysis was performed, the SBW-4 data suggest that as WL increases from 25 to 30 mass%, there is no practical difference in r_i with all values < 1 g/m^2. The SBW-9 data (note duplicate analysis for SBW-9 at 25% WL) indicate that r_i increases with increased WL. Again, the r_i values < 1 g/m^2 are well below the EA limits and the self-imposed limit of this study. For SBW-9-30, there does appear to be a slight decrease in r_i upon CCC, but it is of little practical difference. The effect of thermal history on r_i in the SBW-2 based glasses was not observed in either SBW-4 or SBW-9 based glasses.

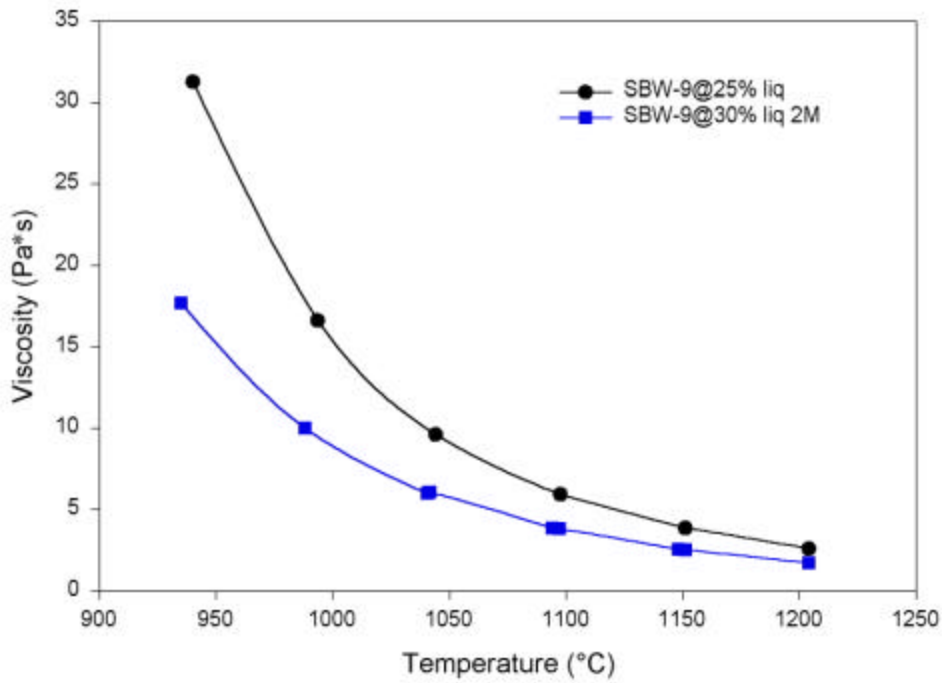

Figure 23. Viscosity-Temperature Relationships for SBW-9 as a Function of WL

Table 14. Estimated Values of A, B, and C and Predicted $\eta_{1150°C}$ for Select SBW Glasses (liquid feed)

Glass	A	B	C	$h_{1150°C}$ (Pa*s)
SBW-4-25 (2M)	-6.46	9480.48	73.70	10.45
SBW-4-30 (2M)	-6.56	9330.63	64.64	7.63
SBW-4 30 (3M)	-6.35	8831.11	90.90	7.33
SBW-9 25	-5.57	6295.19	241.705	3.90
SBW-9 30 (2M)	-6.61	7941.39	97.39	2.54

6.4 Summary of Liquid Simulant Testing

Crucible tests with liquid SBW simulant were performed to gain a cursory understanding of the impacts of frit composition, HNO_3 concentration, WL, sugar concentration, and test method on the properties of simulated waste glasses. In particular, these tests were used to identify a frit and WL that were likely to form a glass with acceptable properties without forming a salt layer. It was found that, to first order, the influence of HNO_3 and sugar concentrations had a minimal impact on salt formation, while the effects of frit composition and WL strongly influenced the amount of salt formed. Adding CaO at the expense of TiO_2 was found to help prevent a salt layer from forming while replacing CaO with BaO did not. Increasing WL and decreasing gas flow generally increased the likelihood of salt formation. A glass showing promising results in the liquid-feed tests was selected for further testing. The selected glass,

SBW-9-30, meets all the criteria listed in Table 3 and is expected to perform adequately in scaled melter tests.

Table 15. PCT Results of SBW-2 and SBW-4 Quenched and CCC Glasses as a Function of WL

Glass	r_B (g/m^2)	r_{Li} (g/m^2)	r_{Na} (g/m^2)	r_{Si} (g/m^2)
SBW-4 @ 25% loading (quenched)	0.221	0.264	0.245	0.159
SBW-4 @ 25% loading (CCC)	0.180	0.217	0.205	0.124
SBW-4 @ 30% loading (quenched)	0.212	0.219	0.279	0.162
SBW-4 @ 30% loading (CCC)	0.203	0.230	0.261	0.157
SBW-9a @ 25% loading (quenched)	0.249	0.336	0.305	0.140
SBW-9a @ 25% loading (CCC)	0.221	0.323	0.271	0.134
SBW-9b @ 25% loading (quenched)	0.242	0.332	0.331	0.143
SBW-9b @ 25% loading (CCC)	0.220	0.335	0.299	0.142
SBW-9 @ 30% loading (quenched)	0.522	0.481	0.770	0.222
SBW-9 @ 30% loading (CCC)	0.403	0.422	0.636	0.202

7.0 Sugar Concentration Tests

Recognizing that redox control was critical for processing SBW, a series of tests was performed to address the use of sugar as a potential reductant. This study was performed in parallel with frit-development activities (as discussed in Sections 5.0 and 6.0). Four concentrations of sugar (77, 109, 131, and 164 g/L) were initially tested using the SBW-2-35 targeted glass composition to determine the concentration of sugar needed to result in an 8% Fe^{II}/Fe^{total}. These levels of sugar addition were based on the required amount of sugar needed per sample for nitrate reduction.

7.1 Experimental

Glasses were batched using oxides, carbonates, and boric acid for the frit components with sugar and the SBW simulant targeting a 35 mass% loaded glass. The batches were placed into an alumina crucible and heated to a thick paste consistency using a hotplate. To maintain homogeneity, a stir bar was used during heating until the batch thickened beyond the stir bar's capability. The crucible was then moved into a drying oven at ~100°C until dry.

After drying, the batches were ramp heated up to 1150°C using two steps: 1) a rate of 3°C/min up to 400°C and 2) changing to 4°C/min up to 1150°C melting temperature. Melts were held at 1150°C for 1 h and then air quenched inside the crucible. To provide the best possible seal between the crucible and the lid, contact areas were polished and coated with a glass powder. During the melting process, the glass powder wets and seals the lid to the mating surfaces of the crucible. Excess gas pressure from the batch-to-glass conversion is released while minimizing the influx of air into the crucible atmosphere.

As the glass formulation work progressed and a candidate glass composition emerged to support upcoming melter runs (refer to Sections 5.0 and 6.0 for more details), these tests were repeated to determine the required sugar concentrations. More specifically, the SBW-9-30 glass was tested at 100, 120, and 141 g/L of sugar. The same procedure as discussed above was used with one exception: a Teflon beaker was used to dry the mixture, and the dried material was then transferred to an alumina crucible for ramp heating to the melting temperature instead of using an alumina crucible for drying.

7.2 Results

Visual observations of the drying and melting process along with the measured Fe^{II}/Fe^{total} ratio of the quenched glass are given in Table 16. During testing, it was observed that as the concentration of sugar increased, the intensity of foaming increased during the drying process, but the opposite behavior was observed during melting. A salt layer also formed at the top of the SBW-4 melts. The degree of salt formed also appeared to slightly decrease with the highest sugar concentration, providing some evidence that the higher sugar concentration assisted S partitioning.

Redox values for the SBW-9 test show that glasses were more oxidized at high-sugar levels. Based upon the melt observations, higher sugar-level tests were poorly sealed during melting, resulting in a more oxidizing atmosphere. Testing of SBW-9 at 30 mass% SBW simulant resulted in a change in sugar selection of 135 g/L of waste simulant, again targeting 8% Fe^{II}/Fe^{total}.

Based on these results, a ratio of 141 g of sugar per liter of liquid waste simulant was chosen for all of the simulant testing.

Table 16. Observations and Redox Results of Sugar Testing

Frit ID	WL	Sugar	HNO_3	Salt [(a)]	Foam (dry)[(b)]	Foam (melt)[(c)]	Comments
SBW-2	35	77	1.1	4	1	4	FeII/Fe=7.07E-4
SBW-2	35	109	1.1	4	2	3	FeII/Fe=3.86E-4
SBW-2	35	131	1.1	4	3	3	FeII/Fe=1.32E-3
SBW-2	35	164	1.1	3	3	1	FeII/Fe=2.71E-1
SBW-9	30	100	1.1	1	2	4	FeII/Fe=2.2E-3
SBW-9	30	120	1.1	1	3	4	FeII/Fe=1.8E-3
SBW-9	30	141	1.1	3	3	1	FeII/Fe=7.5E-4
SBW-9	32	141	1.1	3	3	1	FeII/Fe=7.5E-4

(a) Salt – 1) faint patterns on surface, 2) hazy patterns cover surface, 3) accumulation of salt in areas, 4) gross accumulation of salt.

(b) Foaming during drying – 1) little or no foaming, 2) foaming requiring some manual stirring, 3) lots of foaming requiring lots of manual stirring.

(c) Foaming during melting – 1) none, 2) foaming but remains in crucible, 3) foaming slightly outside of crucible, 4) significant glass outside of crucible due to foaming.

8.0 Conclusions and Recommendations

A systematic study was undertaken to develop a glass-composition to demonstrate the vitrification flowsheet of INEEL's SBW using the latest WM-180 tank composition. Although the previous study (Vienna et al. [1999]) did not restrict WLs based on the potential to form a segregated salt layer, avoiding its development in a melter is beneficial and was the primary focus from the glass-formulation perspective. The testing results described in this report were aimed at providing a candidate glass composition for use in a scaled melter demonstration of direct-vitrification of a WM-180 simulant in the RSM and the EV-16 melter. 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).

Glass composition/property relationships were used to assess potential compositional effects on glass properties of the baseline glass (SBW-1 frit with 35% of original SBW composition). A series of crucible tests was performed using reagent-grade oxides, carbonates, and boric acid targeting the 2000 WM-180 SBW simulant composition coupled with the candidate frit compositions prior to the fabrication of the WM-180 liquid simulant.

Based on the initial scoping tests using batch chemicals, Frits SBW-4 and SBW-9 were the primary candidates for tests using the liquid WM-180 SBW simulant. Homogeneous glasses were produced with SBW-4 and SBW-9 with up to 30 and 35 mass% WLs, respectively, of the original SBW simulant. However, it was anticipated that the SO_3 concentration in the WM-180 simulant may increase, which could result in lower targeted WLs in an effort to avoid salt-layer formation and/or accumulation. The differences between the use of batch chemicals and the liquid feed may also affect targeted WLs.

The initial batch chemical tests suggested that the addition of CaO increased the solubility of SO_3 in these multi-component systems, which compares favorably with the findings from the literature survey. It was also observed that at higher WLs (> 40 mass%), if the salt formation could be avoided, the loading of SBW in glass would be limited by PCT release or the formation of nepheline on cooling. That is, the r_i values of SBW-2-45 after CCC were much greater than acceptable values. This was due to the formation of nepheline in the CCC glass.

Crucible tests with liquid SBW simulant were performed to gain a cursory understanding of the impacts of frit composition, HNO_3 concentration, WL, sugar concentration, and test method on the properties of simulated waste glasses. In particular, these tests identified a frit and WL that were likely to form a glass with acceptable properties without the formation of a salt layer. It was found that, to first order, the influence of HNO_3 and sugar concentrations had a minimal impact on salt formation, while the effects of frit composition and WL strongly influenced the amount of salt formed. The addition of CaO at the expense of TiO_2 was found to help avoid the formation of a salt while replacing CaO with BaO did not. Increasing WL and decreasing gas flow generally increased the likelihood of salt formation.

Based on the results of this study, the authors recommend that a glass made of 30% SBW simulant (on an mass oxide and halogen basis) and 70 mass% of the additive mix (SBW-9) be used in the upcoming RSM and EV-16 melter demonstrations. This glass meets all the process and product performance criteria as specified.

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