PNNL-14649



Preliminary Investigation of Sulfur Loading in Hanford LAW Glass

J. D. Vienna P. Hrma W. C. Buchmiller J. S. Ricklefs

April 2004

Prepared for the U.S. Department of Energy under Contract DE-AC06-76RL01830



DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights**. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY operated by BATTELLE for the UNITED STATES DEPARTMENT OF ENERGY under Contract DE-AC06-76RL01830

 $\overset{\frown}{\simeq}\overset{\frown}{\simeq}$ This document was printed on recycled paper.

Preliminary Investigation of Sulfur Loading in Hanford LAW Glass

J. D. Vienna P. Hrma W. C. Buchmiller J. S. Ricklefs

April 2004

Prepared for the U.S. Department of Energy under Contract DE-AC06-76RL01830

Pacific Northwest National Laboratory Richland, Washington 99352

Summary

A preliminary estimate was developed for loading limits for high-sulfur low-activity waste (LAW) feeds that will be vitrified into borosilicate glass at the Hanford Site in the waste-cleanup effort. Previous studies reported in the literature were consulted to provide a basis for the estimate. The examination of previous studies led to questions about sulfur loading in Hanford LAW glass, and scoping tests were performed to help answer these questions. The results of these tests indicated that a formulation approach developed by Vienna and colleagues shows promise for maximizing LAW loading in glass. However, there is a clear need for follow-on work.

The approach taken by the Waste Treatment and Immobilization Plant (WTP) was based on a sulfur:sodium product. Specifically, the technical basis for WTP glass formulations was initially given by:

$$g_{Na_2O} \times g_{SO_3} \leq 5$$

where g_{Na_2O} and g_{SO_3} are the mass% of Na₂O and SO₃ in the target glass composition, respectively (Pegg et al. 2000). The range of applicability of the *rule-of-five*^(a) ranged from $g_{Na_2O} = 20$ (above which glass would be durability limited) to $g_{SO_3} = 1.0$ (above which salt accumulation occurred).^(b)

The approach taken in this study demonstrated increasing sulfur tolerance with increasing alkali and alkali-earth concentrations. Therefore, g_{SO_3} increases with g_{Na_2O} . The limits of applicability are $g_{Na_2O} = 20$ and $g_{SO_3} = 0.8$. Figure S1 compares the two approaches in a two-dimensional composition plot. The area to the bottom left of each curve is the acceptable processing range.

⁽a) The rule-of-five is shown in Figure 2.2.

⁽b) It should be noted that formulations that are more recent have reached higher loadings that those given by the rule-of-five in the region of $g_{SO3} < 0.7$ and have a lower g_{SO3} upper bound of rule applicability (due to refractory corrosion related issues); per a personal communication from E. V. Morrey to J. D. Vienna, 2003.



Figure S.1. Comparison of Formulation Constraints in Two-Dimensional Composition Plot

Abbreviations, Acronyms, and Symbols

AES	atomic emission spectroscopy
AO	alkaline earth
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EPA	U.S. Environmental Protection Agency
GFC	glass forming chemical
HEME	high-efficiency mist eliminator
HLW	high-level waste
ICP	inductively coupled plasma
IDF	Integrated Disposal Facility
INEEL	Idaho National Engineering and Environmental Laboratory
LAW	low-activity waste
LSM	laboratory-scale melter
MS	mass spectrometer
РСТ	product consistency test
PNNL	Pacific Northwest National Laboratory
RSM	research scale melter
SBW	sodium-bearing waste
TCLP	toxicity characteristic leaching procedure
TFA	Tanks Focus Area
VHT	vapor hydration test
WTP	waste treatment and immobilization plant
WVDP	West Valley Demonstration Project
XRF	X-ray fluorescence spectroscopy

Acknowledgments

The authors would like to acknowledge very useful conversations and suggestions from Hong Li (PPG, Inc.) Ian Pegg (Catholic University of America), and Dong-Sang Kim (Pacific Northwest National Laboratory). We are indebted to Wayne Cosby for his artful editing of the report. We thank Ron Sanders (KLM Analytical) for chemical analyses of samples. Bill Holtzscheiter (Tanks Focus Area) gave invaluable management support for this project.

We thank the Research and Technology staff at Hanford's Waste Treatment and Immobilization Plant project for useful conversation and information/data on baseline formulations and process information.

This study was funded by the U.S. Department of Energy's (DOE's) Office of Science and Technology, through the Tanks Focus Area, the Office of Waste Management through the Idaho National Environmental and Engineering Laboratory High-Level Waste Program, and the Office of River Protection through the River Protection Project. Pacific Northwest National Laboratory is operated for DOE by Battelle under Contract DE-AC06-76RL01830.

Contents

Sum	mary	iii
Abbi	reviations, Acronyms, and Symbols	v
Ackı	nowledgments	vii
1.0	Introduction	
2.0	Review of Previous Studies	
	2.1 WTP LAW Glass Studies	
	2.2 INEEL Glass Studies	
	2.2.1 Glass-Formulation Strategy	
	2.2.2 Melter Testing	
	2.2.3 Summary of SBW Formulation and Testing	
3.0	Scoping Tests for Hanford LAW	
	3.1 Experimental Approach	
	3.2 Testing Results and Discussion	
4.0	Conclusions and Recommendations	
5.0	References	
Арре	endix A. INEEL SBW Glass Compositions Tested	A.1

Figures

Figure S.1. C	Comparison of Formulation Constraints in Two-dimensional Composition Plotiii
Figure 2.1. S c_{BO} is th	O_3 Solubility as a Function of c_{NBO}^2/c_{BO} (c_{NBO} is the non-bridging oxygen concentration, and e bridging oxygen concentration as defined by Papadopoulos 1973) (from Li et al. 2001)2.2
Figure 2.2. N al. 2000	Measured Sulfur Solubility in Simulated Hanford LAW Glass Melts at 1200°C (from Pegg et)
Figure 2.3. S	chematic of the EV-16 Melter (after Musick et al. 2000)
Figure 2.4. S	chematic of the Research-Scale Melter System (after Goles et al. 2001)
Figure 3.1. L	aboratory-Scale Melter Schematic (from Darab et al. 2001)

Tables

Table 2.1.	Summary of Melter Test Segment Results with Various Simulated Hanford LAW Glasses	
Cont	aining 7.9 mass% Na ₂ O (after Pegg et al. 2000)	2.4
Table 2.2.	Various SBW Composition Estimates (Vienna et al. 2002)	2.6
Table 2.3.	Additive Compositions Tested with SBW (in mass% glass oxides)	2.7
Table 2.4.	Summary of RSM-01-1 Segments	.11
Table 2.5.	Summary of S Content in RSM-01-1 Glass	.11
Table 2.6.	Summary of S Content in EV-16-2001-1 Glass	.12
Table 2.7.	Summary of Test Segments for RSM-01-2	.13
Table 3.1.	Formulation Summary for Hanford LAW (From Muller et al. 2001)	3.2
Table 3.2.	Simulant Preparation Sheet with Chemicals in the Order of Addition	3.2
Table 3.3.	Comparison of LAWC22 and LAWN-1 Formulations (mass% glass oxides and halogens).	3.3
Table 3.4.	Example Batch Sheet for Feed for 85 g Glass AN107 Using Standard GFCs	3.5
Table 3.5.	Example WTP GFC Mix for C22 Glass	3.5
Table 3.6.	Observations from Laboratory Scale Melter Tests with AN-107 Waste Simulant	3.6
Table A.1.	Compositions of Tested INEEL SBW Glasses in mass%	A.1

1.0 Introduction and Objectives

Roughly 50-million gallons of high-level radioactive waste are stored in 177 underground tanks at the Hanford Site. These wastes were generated from over 4 decades of nuclear-fuel processing and heavyelement separations. The U.S. Department of Energy (DOE) has contracted for the design, construction, and demonstration of a waste treatment and immobilization plant (WTP) to treat these tank wastes (DOE 2000). The WTP will separate the tank wastes into low-activity waste (LAW) and high-level waste (HLW) fractions and vitrify them separately into borosilicate glasses. The LAW fraction of the tank waste is primarily composed of sodium salts (e.g., sodium-nitrate, -nitrite, -hydroxide, -sulfate, - phosphate, -chromate). The concentration of sulfur in many LAWs is sufficient to limit the loading of waste in borosilicate glass.

The loading of Hanford LAWs in borosilicate glasses produced in the baseline WTP process is limited by one of two factors: salt accumulation and chemical durability. To meet the performance assessment goals for the proposed Hanford site Integrated Disposal Facility (IDF), the LAW product must be of sufficient chemical durability to withstand corrosion in an aqueous environment. Chemical-durability constraints have been imposed on the LAW glass to lower the risk of obtaining a glass that does not meet the performance goals for the IDF. One such constraint is that the releases of sodium, boron, and silicon by the glass exposed to the product consistency test (PCT) after normalizing for concentrations in glass and surface area-to-solution volume ratio should be less than 2 g/m². Another is that the rate of alteration of glass exposed to the 200°C vapor hydration test (VHT) should be less than 50 g/(m²·d). These chemical-durability-related constraints can be consistently met with LAW glasses containing up to 20 mass% Na₂O (e.g., Muller et al. 2001; Vienna et al. 2001).

A molten sodium-sulfate-based salt will segregate from the glass melt phase during melter processing of LAWs with excessive sulfur concentrations. The salt phase is highly corrosive and can shorten the useful life of the melter. The sulfur concentration at which the salt phase accumulates is a function of key physical and chemical parameters of the glass-fabrication process. Key among these parameters is glass forming chemical (GFC) composition, redox, temperature, and feeding rate.

The objective of this study is to recommend a preliminary estimate of loading limits for high-sulfur LAW feeds processed beyond the current WTP program tanks (DOE 2000). The recommendation will rely heavily on results from previous studies reported in the literature. Much of the pertinent literature data are summarized in Section 2.0. Evaluating previous results led to questions about sulfur loading in Hanford LAW glass. Scoping tests, described in Section 3.1, were performed to help answer these questions. The results of this study are summarized and discussed in Section 3.2, and conclusions are presented in Section 4.0.

2.0 Review of Previous Studies

The solubility of sulfur in glasses has been studied for over 50 years (Fincham and Richardson 1954, for example). Sulfur was widely used in the commercial glass industry as a fining agent and for melting-rate enhancement. Generally, the solubility of sulfur increases with increasing alkali- and alkali-earth oxide concentrations in glass (Holmquist 1966; Papadopoulos 1973; Goldman 1985). In highly oxidizing conditions, the sulfur incorporation in silicate glass melts is largely a result of sulfate incorporation given by:

$$SO_{2}(g) + \frac{1}{2}O_{2}(g) = SO_{3}(g)$$

$$SO_{2}(g) + \frac{1}{2}O_{2}(g) + O^{2-}(melt) = SO_{4}^{2-}(melt)$$

$$SO_{3}(g) + O^{2-}(melt) = SO_{4}^{2-}(melt)$$
(2.1)

This relationship suggests that sulfate solubility increases with increasing oxygen activity in the melt or melt basicity. Papadopoulos (1973) found a linear relationship between the estimated ratio of nonbridging oxygen to bridging oxygen concentrations and sulfate solubility in soda-lime-silicate glasses. A similar relationship was found to adequately describe the sulfate retention in typical waste glasses melted in the presence of molten sulfate containing salts (see Figure 2.1). However, the solubility of sulfate represents only a portion of the challenge to increase the loading of high sulfur wastes in glass. Salt segregation has been found during waste glass melting at sulfur concentrations below the equilibrium solubility at the nominal melt composition and temperature. Therefore, the kinetics of salt segregation is an important practical consideration.

Studies of sulfur segregation during waste-glass melting have been performed in support of waste vitrification activities (for examples, see Perez et al. 1983; Bates et al. 1985; Fu et al. 1996; Li et al. 1996; Vienna et al. 1999; Pegg et al. 2000; Musick et al. 2000; Darab et al. 2001; Li et al. 2001; Goles et al. 2001; Muller et al. 2001; Peeler et al. 2001; Goles et al. 2002; Vienna et al. 2003; Hrma et al. 2003; and Hrma et al. 2004). The following subsections review a portion of that literature thought to be key to the understanding of sulfate-incorporation limits during Hanford LAW vitrification.

2.1 WTP LAW Glass Studies

In 1999, the sulfur-removal operation was eliminated from the WTP process. A study of sulfate loading limits was initiated in response to this flowsheet change (Pegg et al. 2000). In this study, a series of crucible melts and 13 melter test segments were performed. The authors report a quadratic relationship between soda content and sulfur solubility in equilibrium with a molten salt phase (see Figure 2.2). It is not yet clear why this relationship exists for these glasses rather than the monotonic increase in sulfate solubility with alkali content discussed above. However, it is possible that the difference is caused in part by other chemical differences between glasses. It is likely that the studied glasses were designed to have a similar viscosity at the fixed target melting temperature of the glass. Therefore, as soda content was decreased, increases in other flux-component concentrations offset the soda-content differences. Another possibility is a distribution of sulfur redox states in these glasses rather than sulfate ions only. Some evidence for this distribution in partially reduced melts was reported by McKeown et al. (2004).



Figure 2.1. SO₃ Solubility as a Function of c_{NBO}^2/c_{BO} (c_{NBO} is the non-bridging oxygen concentration, and c_{BO} is the bridging oxygen concentration as defined by Papadopoulos 1973) (from Li et al. 2001)

The results from 13 melter segments are compiled in Table 2.1. In these tests, three different glass compositions were used: LAWB37, LAWB39, and LAWB41. Each glass contained 7.9 mass% Na₂O and ranged in target SO₃ content from 1.02 to 2.04 mass%. Segments without the formation of a salt layer include 1a, 3c, and 4–6. Of these five test segments, three contained 1.02 mass% SO₃ and greater than 70% SO₃ retention in the glass: 1a, 4, and 5. These results indicated three possible compositions that can successfully immobilize up to 0.7 mass% SO₃.

The authors conclude that the allowable concentration of SO_3 in the glass that can be processed at an acceptable rate without the formation of a salt layer can be given by the product of SO_3 and Na_2O :

$$g_{Na_2O} \times g_{SO_3} \le 5 \tag{2.2}$$

where g_{SO3} and g_{Na2O} are the mass percents of SO₃ and Na₂O in the feed on a target-glass-composition basis. This product rule—the rule-of-five—is shown in Figure 2.2. The higher g_{Na2O} range of the solubility curve in Figure 2.2 is not thought to be kinetically favorable because local fluctuations in



 Na_2SO_4 within the melt may deplete the melt in Na_2O , reducing the SO_3 solubility, which promotes phase segregation (Pegg et al. 2000).

Figure 2.2. Measured Sulfur Solubility in Simulated Hanford LAW Glass Melts at 1200°C (from Pegg et al. 2000)

	Target SO ₃		SO ₃	Glass Rate		
Seg	in Feed (%)	Salt	Retention (%)	$(MT/d/m^2)$	Glass	Comments
1a	1.02	No	74	2.6	LAWB37	
1b	2.04	Yes	74	2.6	LAWB37	
2a	2.04	Yes	64	1.8	LAWB37	
2b	2.04	Yes	74	1.6	LAWB37	high water
2c	2.04	Yes	26	1.9	LAWB37	high sugar
2d	2.04	Yes	36	1.2	LAWB37	high water, high sugar
2e	2.04	No	41	1.5	LAWB37	high water, high sugar
3a	2.04	Yes	42	1.5	LAWB39	
3b	1.59	Yes	69	1.5	LAWB39	
3c	1.59	No	37	1.3	LAWB39	high sugar
4	1.02	No	84	1.6	LAWB39	
5	1.02	No	89	1.6	LAWB41	
6	1.02	No	Not Reported	2.7	LAWB41	

Table 2.1. Summary of Melter Test Segment Results with Various Simulated HanfordLAW Glasses Containing 7.9 mass% Na2O (after Pegg et al. 2000)

2.2 INEEL Glass Studies

Sodium-bearing waste (SBW) is a high soda, acidic, high-activity waste stored at the Idaho National Engineering and Environmental Laboratory (INEEL). Table 2.2 lists the SBW composition estimates on a glass-component basis. The composition of SBW falls within the region of expected Hanford LAWs with the exception of Al_2O_3 concentration, which is roughly 28% in SBW and up to roughly 20% in LAW. This difference may not be significant since Al_2O_3 is added as a glass former in Hanford LAW glasses (Muller et al. 2001).

Studies were performed to optimize the loading of SBW in glass to be produced in a liquid-fed, ceramiclined, Joule-heated melter similar to those used at the Defense Waste Processing Facility (DWPF) and West Valley Demonstration Project (WVDP) and those planned to be used at WTP. These studies began in 1999 and continued through 2002 with evolving waste-composition estimates and flowsheet assumptions. In the first phase, a glass was formulated to demonstrate the feasibility of direct vitrification of SBW using current melter technologies (Vienna et al. 1999). The second phase was aimed at developing a glass to demonstrate the direct vitrification process and determine the range of expected waste loadings, assuming that sulfur lost to the off-gas would be grouted (Peeler et al. 2001). The third phase of the study was aimed at formulating a baseline glass composition to be used in developing engineering data for vitrification plant design. The overriding assumption during the third phase was that salt accumulation in the melter would not be tolerated and that nearly all of the sulfur lost to the off-gas would be recycled back to the melter feed. Different SBW compositions were assumed for each phase of the study—1998 SBW, 2000 WM-180, and 2001 WM-180 in Phases 1, 2, and 3, respectively (shown in Table 2.2).

2.2.1 Glass-Formulation Strategy

The formulation work performed by Vienna, Peeler, and colleagues (Vienna et al. 1999; Peeler et al. 2001; Vienna et al. 2002; Vienna et al. 2003) was based primarily on years of research and production experience in commercial glass melts, which suggests that increasing the alkali- and alkali-earth content increases SO_3 solubility (see Section 2.0). To increase waste loading, it is necessary but insufficient to formulate a glass to have relatively high sulfate solubility. This is because many examples from studies with SBW, WVDP, and WTP glasses have shown that sulfate may segregate as a mixed alkali/alkaline earth oxyanionic salt during melter processing at concentrations below the equilibrium solubility of sulfate in the bulk melt at the nominal operating temperature. Tests were performed to determine the mechanism of sulfate segregation during melter processing and to mimic cold-cap processing conditions in the laboratory (Darab et al. 2001; Hrma et al. 2003; Vienna et al. 2002; and Hrma et al. 2004). These tests led to several key outcomes, including the determination of the primary phenomena responsible for salt segregation at seemingly sub-saturated conditions, the composition influences on sulfur-retention kinetics, and optimized glass formulations for treatment of SBW. It was found, as is intuitively logical, that the higher the sulfate solubility, the more that is incorporated into the melt before salt segregation. This led to formulations with increased alkali- and alkaline-earth concentrations. As general mixing thermodynamics would suggest, a combination of alkali- and alkaline-earth components is far more effective at increasing sulfur solubility than in higher concentrations of any single component. It was shown experimentally that no one alkali- or alkali-earth component was as effective as a mix of many alkali and alkali-earth components in increasing sulfur incorporation. Finally, the addition of V_2O_5 in the melt allowed for higher concentrations of sulfur in the feed before salt segregation. In addition to these simple rules, ZrO₂ was added to increase the chemical durability and viscosity of the waste glass/melt that was lowered by high alkali- and alkali-earth component concentrations. In early formulations, Fe₂O₃ was added to dilute the waste with a component that did not decrease durability and did not increase viscosity; later formulations added Fe₂O₃ only as a redox indicator. The overall blend of glass components was largely dictated by the need to meet a range of glass-property constraints.

The various additive compositions tested during this period of development are listed in Table 2.3. The glass compositions generated from mixing the additives with the waste simulants at various loadings are reported in Appendix A. Testing these additive compositions in a laboratory-scale melter (LSM) showed a consistent trend in that increased alkali (R₂O) and alkaline earth (AO) component concentrations, along with V₂O₅, allowed for higher sulfur incorporation. For example, a series of tests with SBW-22 through -27 with fixed waste loading at 20 mass% and excess SO₃^(a) showed salt formation in all samples with R₂O + AO < 20 mole% in frit and R₂O/(R₂O+AO) < 40 % in frit, while other samples showed no salt formation. One exception was SBW-24, which showed salt formation even with R₂O+AO = 21 mole% and R₂O/(R₂O+AO) = 64%. The major difference in this formulation is the lack of V₂O₅. Similar results were found with crucible melts as reported by Vienna et al. (2001).

These tests also showed a clear correlation between sugar concentration and sulfur retention, with the higher sugar concentrations leading to higher sulfur losses (Vienna et al. 2002). These losses were found to be caused by the formation of SO_2 gas in the reducing environment. Higher LSM feeding rates were found to increase the tendency for salt formation at fixed SO_3 concentrations (Darab et al. 2001).

⁽a) All other parameters in these tests were fixed, e.g., feed rate, reductant concentration.

Component	1998 SBW	2000 WM-180	2001 WM-180						
	Oxides (mass%	6 non-volatile oxid	les)						
Al ₂ O ₃	27.34	27.96	27.52						
As ₂ O ₃	0	0	0.04						
B ₂ O ₃	0.65	0.35	0.35						
BaO	0	0.01	0.01						
CaO	2.23	2.22	2.15						
CdO	0	0.08	0.08						
Ce ₂ O ₃	0	0.01	0.01						
CoO	0	0.21	0						
Cr ₂ O ₃	0.25	0	0.21						
CuO	0	0.05	0.05						
Fe ₂ O ₃	1.55	1.43	1.41						
Gd ₂ O ₃	0	0.03	0.03						
K ₂ O	7.92	7.62	7.53						
MgO	0.05	0.4	0.39						
MnO	0.78	0.82	0.81						
MoO ₃	0.13	0.02	0.02						
Na ₂ O	50.05	52.54	51.91						
NiO	0.55	0.09	0.09						
P ₂ O ₅	1.19	0.8	0.79						
PbO	0.31	0.24	0.24						
RuO ₂	0.04	0.01	0.01						
SO ₃	3.73	3.57	4.55						
Sb ₂ O ₅	0	0	0.01						
SeO ₂	0	0	0.01						
SiO ₂	0.18	0	0						
SnO	0.02	0	0						
SrO	0	0	0.01						
V_2O_5	0	0	0.07						
ZnO	0	0.07	0.07						
ZrO ₂	1	0.01	0.01						
	Halog	ens (mass%)	•						
Cl	1.04	0.88	0.87						
F	0.98	0.57	0.73						
Ι	0.02	0.01	0.01						
	Volatiles (moles/L)								
H^+	1.94	1.08	1.01						
NO ₃ ⁻	6.96	5.11	5.27						
	Oxide and Ha	logen Loading (g	/L)						
Solids	145.26	114.55	122.62						

 Table 2.2. Various SBW Composition Estimates (Vienna et al. 2002)

Mix ID	B ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Li ₂ O	MgO	Na ₂ O	SiO ₂	V_2O_5	ZrO ₂
SBW-1 ^(a)	14.26		11.31		2.67			68.69		
SBW-2 ^(a)	12.00		11.31		4.00			69.61		
SBW-3 ^(a)	15.00		11.31		4.50			66.11		
SBW-4	12.00	2.00	12.00		4.00			70.00		
SBW-5	15.00	4.00	12.00		4.00			65.00		
SBW-6	15.00	2.00	12.00		4.00			67.00		
SBW-7	10.00	4.00	15.00		5.00			66.00		
SBW-8	15.00	2.00	15.00		5.00			63.00		
SBW-9	15.00	5.00	10.00		5.00			65.00		
SBW-10 ^(a)	12.00		12.00		4.00			70.00		
SBW-11	12.15	5.02	1.52		6.11	1.75	1.90	64.23	4.88	2.44
SBW-12	6.03	5.02	1.52		6.11	1.75	6.98	65.27	4.88	2.44
SBW-13	12.15		1.52	8.15	6.11		1.90	62.85	4.88	2.44
SBW-14	14.45	5.02	1.52		6.11	1.75	1.90	66.81		2.44
SBW-15	7.00	8.00	8.00		6.00		7.00	64.00		
SBW-16	14.00	7.00			6.00		2.00	71.00		
SBW-17	12.00	2.00	12.00		4.00			70.00		
SBW-18	12.00	2.00	12.00		3.00		4.00	64.00	2.00	1.00
SBW-19	12.00	2.00	12.00		3.00		4.00	62.00	4.00	1.00
SBW-20	12.00	4.00	12.00		3.00		4.00	60.00	4.00	1.00
SBW-21	10.00	4.00	12.00		3.00		4.00	62.00	4.00	1.00
SBW-22	6.03	5.02	1.52		6.11	1.75	4.29	67.95	4.88	2.44
SBW-23	12.15		1.52	4.32	6.11		1.90	66.68	4.88	2.44
SBW-24	11.10	5.02	1.52		6.11	1.75	1.90	70.16		2.44
SBW-25	12.15	5.02	12.00		3.44	1.75		58.32	4.88	2.44
SBW-26	6.03	14.19	1.52		3.52	1.75	1.90	63.77	4.88	2.44
SBW-27	6.03	11.75	1.52		4.08	1.75	1.90	63.21	7.32	2.44
(a) SBW-1 t	hrough -3	contain (3.08 mass	% TiO ₂ ,	and SBV	<i>W</i> -10 con	tains 2 m	ass% Ba().	•

Table 2.3. Additive Compositions Tested with SBW (in mass% glass oxides)

2.2.2 Melter Testing

Melter testing was performed with:

- SBW-1 and 1998 SBW at a 35% waste loading in the first phase
- SBW-9 and 2000 WM-180 at loadings ranging from 20 to 35% in the second phase
- SBW-22 and 2001 WM-180 at 20% loading in the third phase

using the EV-16 melter at Clemson University and/or the research scale melter (RSM) at Pacific Northwest National Laboratory (PNNL). In addition, a number of tests were performed using a slurry-fed

melt-rate furnace operated by Savannah River Technology Center at Clemson University (Cozzi et al. 2002). The key points of these tests and their results are described below.

EV16-1999-1 Test

The initial formulation of SBW-1-35 (SBW-1 used to define the additive mix and -35 the waste loading used) was tested in a pilot-scale melter (EV-16). The EV-16 melter at Clemson University has a 45.7×45.7 -cm melt chamber, with a design depth of 40.6 cm and retrofit with a sloped bottom. A diagram of the melter (with the sloped bottom installed) is provided in Figure 2.3. The off-gas treatment system for the EV-16 is a multi-stage wet scrubber, designed to handle particulate matter and acid gases. The off-gas system is constructed of 304 stainless steel and PVC and consists of a quench chamber, steam/air atomizing scrubber, cyclonic separator, scrubbing column, demister, and rotary blower.



Figure 2.3. Schematic of the EV-16 Melter (after Musick et al. 2000)

The EV-16-1999-1 test was performed in April 1999 using the 1998 SBW simulant composition with glass-forming additives of SBW-1, and a target waste loading of 35 mass% based on crucible test results described in Vienna et al. 1999. Carbon in the form of powdered activated carbon was added to the feed at 87.4 g/L to ensure adequate reduction of transition elements to avoid undue corrosion of the melter electrodes and aid nitrate destruction for less problematic melting. The test was performed over a period of 3 days with a time-average feeding rate of 135 mL/min. Over the duration of the test, 450 L of feed were fed to the melter, producing 155 kg of glass. The target melt-pool temperature was 1150°C. However, temperature excursions of up to 1350°C occurred throughout the test because of a faulty temperature-control device.

Analyses of the resulting glass by X-ray fluorescence spectroscopy (XRF) and by inductively coupled plasma (ICP) atomic emission spectroscopy (AES) showed an SO₃ concentration of 0.49 mass% and 0.58 mass%, respectively. The target concentration of SO₃ in glass was 1.3 mass%, and ICP analyses of the melter feed suggest an *as-batched* SO₃ concentration of 1.07 mass%. This suggests that 54% of the S fed to the melter was in the glass (based on ICP measured results of the feed and the glass). No evidence of a salt layer was seen at the melt surface during or after the test.^(a) Insufficient data were collected to determine the amount and speciation of S in the off-gas. However, it is likely that the remaining fraction of the S fed to the melter partitioned to the off-gas as SO₂.

RSM-01-1 Test

The second formulation—SBW-9 with 30, 32, and 35% waste loading—was tested in an RSM. Peeler et al. (2001) reported the testing to support this formulation. The RSM is a 15.24-cm (6-in.) diameter, Joule-heated melter capable of continuous feeding and pouring that was specifically designed and built to evaluate various aspects of the vitrification process. The RSM consists of a 26-cm (10.25 in.) outside diameter \times 44.45-cm (17.5 in.) high Inconel 601 shell, lined with ceramic paper and Alfrax 66. A crucible of Monofrax K-3 high Cr₂O₃ refractory provided a melt cavity that measures 15.24 cm (6 in.) in diameter. The operating glass height of the RSM is nominally 7.6 cm (3 in.), resulting in a glass volume of 1.4 L. A view port in the lid allowed observations of the cold cap, observations of salt-layer formation, and sampling from the melt surface. The off-gas-system included a film cooler, venturi scrubber, high-efficiency mist eliminator (HEME), and scrub-solution tank. Emission rates of process off-gas effluents and equipment-abatement efficiencies were characterized using gaseous and particulate samplers operated according to applicable U.S. Environmental Protection Agency (EPA) protocols. In addition, an online quadrupole mass spectrometer (MS) allowed real-time analysis to be conducted for volatile and semivolatile effluents having mass numbers between 2 and 300 AMU. Figure 2.4 shows a schematic of the RSM.

The RSM-01-1 test was performed in January 2001 using the 2000 WM-180 simulant composition with glass-forming additives of SBW-9. The target waste loadings were increased from 30 to 35 mass% during the eight test segments to determine the loading at which a salt layer would accumulate (see Table 2.4). The amount of S was increased by 40% during the final segment to intentionally form a salt layer. Sugar was added as a reductant at concentrations ranging from 135 to 197 g/L of SBW to obtain an initial assessment of the impacts of reductant concentration on S loss and glass redox. The test was performed over a period of 120 hours with a feeding rate of 2.1 to 3.3 L/h and a glass pour rate of 35 to 54 Kg/h/m². The average oxide loading of the feed was 292 g/L. The melt-pool temperature was maintained between 1147 and 1162°C with a target nominal melt temperature of 1150°C.

⁽a) The absence of a salt phase during this test may have been influenced by the temperature excursions.



Figure 2.4. Schematic of the Research-Scale Melter System (after Goles et al. 2001)

	Waste Loading	Target SO ₃	Target Na₂O	Sugar Concentration	Average Feed Rate
Segment	(mass%)	Concentration	Concentration	(g/L of SBW)	(L/h)
А	30	1.07	15.8	135	2.1
В	30	1.07	15.8	135	2.3
С	32	1.14	16.8	135	3.0
D	32	1.14	16.8	135	2.8
Е	35	1.25	18.4	135	2.5
F	35	1.25	18.4	150	2.6
G	35	1.25	18.4	155	3.2
Н	35	1.75	18.4	178	3.3

Table 2.4. Summary of RSM-01-1 Segments

Goles et al. (2001) thoroughly described the results of the RSM-01-1 test. Table 2.5 compares the ICP analyses of SO₃ in glass with target values. Roughly, 50 to 60% of the S fed to the melter partitioned to the glass and is apparently relatively independent of waste loading in the range of 30 to 35 mass%. A mass balance over the entire 120-hour test found that roughly 25% of the S fed to the melter partitioned to the off-gas system, roughly 80% of which was found in the drainage from the HEME, and the remaining was in the scrub solution. More of the S could have been in the HEME since the entire HEME was not flushed after the test. Alternatively, if the remaining 15 to 25% of the S left the melter as SO₂, the concentration of SO₂ would have been below the detection limit of the MS used to monitor off-gas composition. Very small spots of molten salt could be found on the melt surface during nearly the entire test. Typically, the salt disappeared after feeding was stopped for some period. Salt accumulation was not seen until the waste loading was increased to 35%. Although no accurate data were taken to quantify the amount of salt accumulation, visual observations suggested that the amount of salt on the melt surface during the last test segment.

Waste Loading (mass%)	Target Na ₂ O in Glass (mass%)	Target SO ₃ in Glass (mass%)	Measured SO3 in Glass (mass%)	% of S in Glass
30	15.8	1.07	0.68	63
32	16.8	1.14	0.66	56
35	18.4	1.25	0.70	56
35 (1.40×S)	18.4	1.75	0.89	51

Table 2.5. Summary of S Content in RSM-01-1 Glass

EV-16-2001-1 Test

A second melter test was performed in the EV-16 pilot-scale melter in April of 2001 (Perry et al. 2001). The melter plenum was rebuilt before the test, and other melter modifications were made to simulate more closely the planned INEEL process. This test, EV-16-2001-1, processed a glass using the 2000 WM-180 waste simulant at 30 mass% loading with the SBW-9 additive mix (SBW-9-30). Sugar was added as a reductant to the feed at a concentration of 160 g/L of SBW. With the exception of the sugar concentration, the target feed composition was the same as that processed in the RSM-01-1 test during the first two segments. This test was performed over 175 hours with active feeding for approximately

120 hours. The average nominal feeding rate was 14.7 L/h. Approximately 1790 L of feed was fed during the test, and 538 kg of glass were produced. The empirical oxide loading of the feed was 21.9%. The melt pool temperature was maintained between 1100°C and 1175°C with a nominal target of 1150°C. Normalizing the feed rate to the melter surface area, the average RSM-01-1 feed rate was 120 L/h/m², and that for the EV-16-2001-1 was 70 L/h/m².^(a) With slower feeding, there is more opportunity for the melt to approach the equilibrium concentration of SO₃, which is estimated to be roughly 1 mass% for this melt composition in air.

A molten salt was found to form and possibly accumulate during the EV-16-2001-1 test, unlike the EV-16-1999-1 and RSM-01-1 tests. A method to measure the amount of salt at the melt-pool surface during the test was not available, but qualitative observations were made by probing the melt surface with an alumina tube. The amount of salt that remained on the glass surface when the melter was cooled after the test was estimated. This salt layer, which was found primarily on the melter refractory-glass interface, was estimated to contain 7.7% of the S fed to the melter.^(b) After completion of the test, melter-feed samples that had been systematically taken during feeding were analyzed using ICP-AES to find that a significantly higher sulfur content was in the feed than targeted in glass. Table 2.6 compares the concentrations of SO₃ in feed and in glass with the target values (all on a glass oxide composition basis). Therefore, these results correspond well with the result of the RSM-01-1 test.

Sample	Target SO ₃ (Mass%)	ICP SO ₃ in Feed on a Mass% in Glass Basis	XRF SO3 in Glass (mass%)	ICP SO ₃ in Glass (mass%)
Melter Bottom	1.07	1.35	0.74	0.79
General Melter Glass	1.07	1.35	0.75	0.77
Melter Top	1.07	1.35	0.76	0.76

 Table 2.6.
 Summary of S Content in EV-16-2001-1 Glass

RSM-01-2 Test

The third composition tested at melter scale was SBW-22 at 20% loading of the 2001 WM-180 simulant (SBW-22-20). This formulation differed from SBW-9 since the concentration of sulfur in the waste increased. The planned INEEL flowsheet changed from one in which the sulfur leaving the melter would be grouted to one in which a majority of sulfur leaving the melter would return as recycle. Vienna et al. (2002) described the formulation and testing activities for this feed.

This test was performed in much the same manner as RSM-01-1. The test was performed over a period of 120 hours with a feeding rate of 1.24 to 1.9 L/h and glass pour rates of 6.2 to 9.4 lb/h/ft². The melt-pool temperature was maintained at roughly 1150°C throughout the test. Details of this test are reported by Goles et al. (2002) and summarized in Table 2.7.

⁽a) The complexity of melter feed to glass-conversion processes does not allow the scaling of melter feed rates between different melters; the feed rate per unit melt pool surface area is often used as a very rough estimate for comparison purposes.

⁽b) The amount of salt on the melter surface after the test was roughly 575 g, and a total of 2594 g of S was fed to the melter. Assuming the salt was composed of 34.77 mass% S, 7.7% of the S fed to the melter would be in the salt.

			Reductant	Feed	Glass
	Feeding		Concentration	Rate,	Production
Segment	Time, h	Туре	g/L-SBW	L/h	Rate, lbs/h/ft ²
A1	16.0	sugar	200	1.89	9.42
A2	4.9	sugar	180	1.54	7.67
A3	4.7	sugar	46	1.34	6.65
A4	9.0	sugar	170	1.9	9.43
A5	1.5	sugar	175	1.61	8.03
B1	6.5	glycolic acid	280	1.76	8.77
B2	2.1	glycolic acid	280	1.77	8.82
B3	1.3	glycolic acid	340	1.46	7.28
B4	3.8	glycolic acid	392	1.4	6.95
C1	5.1	sugar	160	1.85	9.18
C2	3.5	sugar	160	1.83	9.08
D1	2.0	none	n/a	1.35	6.73
D2	1.0	none	n/a	1.39	6.89
D3	1.6	none	n/a	1.45	7.2
D4	1.7	none	n/a	1.24	6.16
Е	0.8	sugar	250	1.78	8.85

 Table 2.7.
 Summary of Test Segments for RSM-01-2

Analyses of the feed and glass suggest that the target SO_3 concentration was obtained in the feed and that 94.2% of the sulfur fed to the melter remained in the glass with 3.4% found in the off-gas scrub solution. The additional 2.4% of sulfur could not be accounted for by the mass balance, but no sign of salt formation existed. The sulfur retention in glass would likely be higher if not for the wide variations in reductant concentrations. These varied reductant concentrations were used to determine the impacts on mercury speciation in the off-gas rather than to control sulfur behavior.

EV16-2001-2 Test

A final EV-16 test with SBW simulant (2001 WM-180) was performed in September of 2001. This test was performed with the same feed composition of the RSM-01-2 test (SBW-22-20). The test was conducted over a 3-day period, stopped short by unrelated difficulties occurring on September 11, 2001. This test showed excellent agreement with the RSM-01-2 test. Analyses of the feed and glass suggest that the target SO₃ concentration was obtained in the feed and that 97.1% of the sulfur fed to the melter remained in the glass with 2.4% found in the off-gas scrub solution. The additional 0.5% of sulfur could not be accounted for by the mass balance. No indication of a salt layer on top of the melt was found.

2.2.3 Summary of SBW Formulation and Testing

Formulations were performed to develop high-loaded SBW glasses that would avoid salt formation during pilot-scale melter testing at prototypic plant operating conditions. Initial formulations showed that

concentrations of SO₃ in feed of >1 mass% (on a glass oxide basis) could be processed without salt formation/accumulation in the melter. A baseline glass, developed as a conservative formulation, contained 0.91 mass% of SO₃ (on a glass oxide basis). This formulation was shown to incorporate nearly completely to the glass phases during pilot testing (97.1%) at prototypic processing rates. These formulations were based on increased alkali, alkaline earth, and vanadium. Na₂O concentrations in melter tests ranged from 14 to 17.5% in glass. These correspond to Na₂O×SO₃ products between 12.6 and 19.2. Because the testing was performed on single-point compositions without accounting for variation in waste composition, waste loading, and process uncertainty, it was recommended that INEEL reduce the anticipated sulfate loading in the incoming feed to 0.8 mass% on a glass-oxide basis. This limit was to be combined with a limit of 20 mass% Na₂O for the purposes of durability control. These limits were independent of each other. In other words, the glass could contain up to 20% Na₂O and/or 0.8% SO₃, but neither should be higher than the limits.

3.0 Scoping Tests for Hanford LAW

The compositions of Hanford LAW are very similar to those of INEEL SBW. The SBW is higher in nitrates and aluminum, while the LAW is basic. These differences are considered minor so long as sugar concentration is adjusted for the nitrate concentration, and alumina is added as a glass former in LAW.

Other differences in the process may be more significant. For example, the concentration of water in SBW is significantly higher with a sodium molarity of 2 M rather than the molarity range from 1.15 to 10 that is currently planned for Hanford LAW. The planned INEEL flowsheet did not include the use of bubblers in their melter to increase the processing rate. The combined differences between the sodium concentration and the lack of bubbling gives a reduced processing rate for SBW (ranged between 0.38 and 1.3 MTg/d/m²). A final difference between the INEEL SBW and Hanford LAW glasses is the glassproperty constraints imposed on the glasses and thus on the formulations. For SBW glass, the entire melter operating time was planned to be less than 3 years while for Hanford LAW glass, the melter life was planned to be significantly longer; plus, it was not planned that the SBW melter would use bubblers. This translates to a difference in constraints on the corrosivity of the melt to glass-contact materials. The SBW glass was to be disposed of in the Federal Geologic Repository and so was required to meet durability constraints based on the product consistency test (PCT) and the toxicity characteristic leaching procedure (TCLP), much like Hanford LAW glasses. However, Hanford LAW glass must also meet constraints based on the VHT, which was not required for the SBW glasses. These added constraints further restrict the flexibility in glass composition that must be accounted for when formulating LAW glass.

With these similarities and differences in mind, a small task was performed by PNNL under the funding and guidance of the Tanks Focus Area (TFA) to evaluate the possibility of expanding the experience from glass formulation and testing for SBW to Hanford LAW.

3.1 Experimental Approach

To perform the study, a typical Hanford LAW was selected so that the current WTP formulation would give significantly lower waste loading than would a formulation based on the loading limits developed for INEEL (e.g., $Na_2O \le 20\%$ and $SO_3 \le 0.8\%$). The baseline formulations assumed in this comparison were those reported by Muller et al. (2001) and listed in Table 3.1. As Sub-Envelopes A1 and A2 were limited by 20% Na_2O , and Sub-Envelope B2 was limited by 1% SO₃, only Sub-Envelopes A3, C1, and C2 would have a substantially increased loading if the INEEL limits were used. Sub-Envelope C1 (AN-107) was found to have the greatest loading increase, so it was used in this study.

A simulant of AN-107 was prepared according to the procedures used in pilot melter testing of AN-107 with glass LAWC22 by the WTP. A number of salts (Table 3.2) were gradually added to H_2O .

A new formulation was developed for the waste using the approach described above for INEEL SBW. This new formulation is known as LAW-New-1 or LAWN-1. The waste, additives, and resulting glasses are compared in Table 3.3. The LAWN-1 composition was designed to meet the property constraints for the Hanford LAW melter while allowing for higher sulfur incorporation. The predicted VHT response of LAWN-1 is comparable to that of LAWC22 glass (fabricated from C22 additives and AN-107 waste)

using models reported by Vienna et al. (2001). The ZnO added to LAWC22 for corrosion resistance of glass-contact materials was not added to LAWN-1.

Current								
Envelope								
Designation	Envelope A			Envelo	ope B ^(a)	Env	Envelope C	
Sub- Envelope	A1	A2	A3	B1	B2	C1	C2	
Tanks applicable to this subset	AN-105 SY-101 AN-103	AP-101 AW-101	AN-104 possibly AP-108	Blended AZ-101 & AZ-102	AZ-102	AN-107	AN-102 possibly S-102	
Na ₂ O wt%	20%		14.8 % (recycled SO ₃ added)	6.5 %	5 %	~ 14%	11.2% (recycled SO ₃ added)	
K ₂ O wt%	0.3 to 0.7%	~ 2%	$\sim 0.3\%$	~0.2%	~0.2%	~0.3%	$\sim 0.2\%$	
SO ₃ wt%	0.1 to 0.2%	0.1 to 0.2%	~ 0.35 %	0.75 %	~1 %	~ 0.35 %	$\sim 0.45\%$	
Formulation Selected	LAWA44	LAWA88	LAWA102S	LAWB45 ^(a)	LAWB53S ^(a)	LAWC22	LAWC21S	
(a) The current selection of glasses for Envelope B may not apply to individual tank waste as most of the present study was based on blending of AZ-101 and AZ-102, now abandoned.								

 Table 3.1. Formulation Summary for Hanford LAW (From Muller et al. 2001)

 Table 3.2. Simulant Preparation Sheet with Chemicals in the Order of Addition

Source Chemical	Amount Added (g)	Source Chemical	Amount Added (g)
Water to be added	1040.00	РЬО	0.44
Sodium Acetate	16.77	La_2O_3	0.04
Sodium Oxalate	9.19	NaCl	3.42
Glycolic Acid	24.14	NaF	8.26
Citric Acid	30.17	Na ₃ PO ₄ ·12H ₂ O	16.25
Nitrilotriacetic Acid	10.26	Na_2SO_4	13.97
Iminodiacetic Acid	9.65	NaNO ₃	235.53
$Na_2 EDTA \cdot 2H_2O$	15.48	NaOH, 50% sol.	284.55
Na ₃ HEDTA·2H ₂ O	16.67	КОН	3.69
Sodium Gluconate	10.12	Na ₂ CrO ₄ ·4H ₂ O	1.51
Al(NO ₃) ₃ ·9H ₂ O, 60% sol.	178.21	HCOONa	18.23
$Ca(NO_3)_2 \cdot 4H_2O$	3.74	NaNO ₂	100.56
CsNO ₃	0.00	NH ₄ NO ₃	3.85
Fe(NO ₃) ₃ ·9H ₂ O	22.51	Na ₂ CO ₃	148.06
NiO	0.69	Total	2225.96

		C22	LAWC22	New	LAWN-1
Oxide	AN-107	Additives	Glass	Additives	Glass
Al ₂ O ₃	3.52	6.58	6.09	2.85	3.00
B_2O_3		11.99	10.05	7.71	6.00
CaO	0.22	6.04	5.10	5.07	4.00
Cl	0.50		0.08		0.11
Cr ₂ O ₃	0.12		0.02		0.03
F	0.91		0.15		0.20
Fe ₂ O ₃	1.08	6.43	5.57	1.62	1.50
K ₂ O			0.00	0.96	0.75
Li ₂ O		2.98	2.50	3.21	2.50
MgO		1.80	1.51	2.57	2.00
Na ₂ O	90.19		14.58		20.00
NiO	0.17		0.03		0.04
P ₂ O ₅	0.74		0.12	1.46	1.30
PbO	0.11		0.02		0.02
SO ₃	2.35		0.38		0.52
SiO ₂		55.58	46.60	67.48	52.53
TiO ₂		1.36	1.14		0.00
V_2O_5			0.00	4.50	3.50
ZnO		3.65	3.06		0.00
ZrO ₂		3.59	3.01	2.57	2.00
SUM	99.91	100.00	100.00	100.00	100.00
Loading		83.85	16.15	77.85	22.15

Table 3.3. Comparison of LAWC22 and LAWN-1 Formulations(mass% glass oxides and halogens)

The LSM described in Darab et al. (2001) was used to compare the allowable sulfur loading between the two compositions. In the LSM (see Figure 3.1), feed is pumped into a quartz-glass crucible through a stainless steel tube. Another stainless steel tube around the feed tube allows sweep gas to flow into the crucible. The quartz arm extending from the main tube allows off-gas to escape. The quartz-glass tube assembly is inserted in a box furnace. The furnace is brought to equilibrium at 1150°C, and the feed is pumped into the crucible. As the melt level increases with time, the quartz-glass tube assembly is gradually lowered into the furnace, which maintains heating from the bottom and a lower temperature plenum. When the run is finished, the quartz-glass tube assembly is removed from the furnace and allowed to cool. Glass samples are broken from the crucible and analyzed by XRF.

The source of GFCs used to fabricate the melter feeds was also varied to determine the impacts of the physical and chemical form of GFCs on salt formation. In particular, the particle size of the SiO₂ used in the melter feed was varied (S = small [\leq 37 µm], M = medium [75 to 150 µm], and L = large [200 to 500 µm]) because SiO₂ makes up a majority of the solids mass in the feed. In addition to the basic raw

materials used (see Table 3.4, for example), the current WTP GFCs were used in selective tests (see Table 3.5).

The two formulations were tested in the same LSM with all conditions held constant (e.g., feed rate, temperature, sweep gas, reductant type, and concentration) at those values expected for the WTP LAW melter. A series of tests was performed with increasing SO_3 concentrations in the simulant to determine the maximum concentration of SO_3 that could be added to the feed without the formation of an accumulated salt phase. The results from the LSM testing of the two feeds are reported in Section 3.2.



Figure 3.1. Laboratory-Scale Melter Schematic (from Darab et al. 2001)

Component	Mass (g)
Waste	87.13
Al_2O_3	4.61
H ₃ BO ₃	14.90
Ca(OH) ₂	5.59
Fe ₂ O ₃	4.51
LiOH·H ₂ O	5.87
MgO	1.26
SiO ₂	38.79
TiO ₂	0.95
ZnO	2.55
ZrO ₂	2.52
Na_2SO_4	0.87

Table 3.4. Example Batch Sheet for Feed for 85 gGlass AN107 Using Standard GFCs

Table 3.5. Example WTP GFC Mix for C22 Glass

Mineral	Formula	Mass (g)
Kyanite	Al ₂ SiO ₅	7.31
Boric acid	H_3BO_3	14.88
Wollanstonite	CaSiO ₃	8.75
Hematite	Fe ₂ O ₃	4.50
Lithium carbonate	Li ₂ CO ₃	10.32
Olivine	Mg ₂ SiO ₄	2.19
Silcosil	SiO ₂	29.34
Rutile	TiO ₂	0.95
Zinc oxide	ZnO	2.55
Zircon	ZrSiO ₄	3.74
Sulfate	Na_2SO_4	1.78
Sugar	Sugar	0.43

3.2 Testing Results and Discussion

The results from LSM testing are summarized in Table 3.6.

These results clearly demonstrate that in the LSM, the LAWN-1 glass can tolerate almost twice the SO₃ loading as the LAWC22 formulation before a salt forms. In addition, these results show that the allowable SO₃ concentration was higher in a glass with 20% Na₂O than one with 14.6% Na₂O. It should be noted that the LSM was found to show higher allowable sulfur concentrations before a salt forms than did the pilot melter. However, there was a consistent shift in allowable sulfur concentrations, so the LSM gives an excellent qualitative comparison between formulations.

The more efficient incorporation of sulfate achieved with minerals other than sand is probably caused by delays in the incorporation of those components into the glass melt that reduce sulfate solubility at temperatures below 900°C.

LAWN-1 has lower concentrations of the components that lower the melt basicity, such as B_2O_3 and Al_2O_3 . Some AN107 components are dropped entirely, such as TiO_2 and ZnO. Alkali- and alkali-earth oxides are in different proportions (K_2O is introduced) to benefit the effects of mixing that may enhance the SO₃ solubility. Also, P_2O_5 is added as an additive component. As reported by Sullivan et al. (1995) and Li et al. (1996), P_2O_5 increases sulfate retention. Finally, V_2O_5 is a mixture ingredient. V_2O_5 is a well-known surface-active component and is known to catalyze a reaction between SO₂ and SO₃ (Equation 1). How V_2O_5 may increase sulfate dissolution is not yet clear. It may improve the spreading of liquid sulfate over available internal surfaces of the melting feed and thus increase its chance of being dissolved at early stages of melting.

		Target	Measured	Average	
		SO ₃	SO ₃	SiO ₂ size	
Test ID	Additive	(mass%)	(mass%)	(mm)	Salts Observation
S6-1-1	C22	0.6	0.46	0.068	No salt visible
M6-1-1	C22	0.6	0.49	0.138	No salt visible
L6-1-2	C22	0.6	0.66	0.200	No salt visible
S9-1-1	C22	0.9	0.63	0.068	No salt visible
M9-1-1	C22	0.9	0.55	0.138	No salt visible
L9-1-2	C22	0.9	0.73	0.200	No salt visible
S12-1-1	C22	1.2	0.70	0.068	Trace salts
M12-1-1	C22	1.2	0.82	0.138	Specks of salt seen in broken glass sample
L12-1-2	C22	1.2	0.74	0.355	Salts observed at meniscus
C12 ^(b)	C22	1.2	0.84	0.038	No salt visible
C15 ^(b)	C22	1.5	1.10	0.038	Salt observed
NS12-2-1	New-1	1.2	0.85	0.068	No salt visible
NS15-1-1	New-1	1.5	1.15	0.068	No salt visible
NS18-1-1	New-1	1.8	1.26	0.068	No salt visible
NS21-1-1	New-1	2.1	1.26	0.068	No salt visible
NM12Sg ^(c)	New-1	1.2	0.82	0.138	No salt visible

 Table 3.6. Observations from Laboratory Scale Melter Tests with AN-107 Waste Simulant^(a)

(a) Note that the Na₂O content of C22-based glasses was roughly 14.6 mass% while that of New-1 based glasses was 20.0 mass%. As additional SO₃ was added as Na₂SO₃, the Na₂O concentrations were not fixed.

(b) WTP GFCs used.

(c) Higher sugar added.

4.0 Conclusions and Recommendations

This report presented a brief review of literature data and results of scoping studies for glass formulations considered for immobilization of INEEL SBW and Hanford LAW. These glass formulations are influenced by the presence of Na and sulfur in the waste composition. The literature data suggest that a difference in sulfur tolerance is possible with different glass-formulation approaches. The Hanford WTP baseline LAW glass-development approach yields lower sulfur loading with increasing Na (Na₂O) loading while the INEEL SBW formulation approach yields the opposite trend. Specifically, a Na₂O independent g_{SO3} limit of 0.8 mass% was developed and demonstrated for INEEL SBW. The g_{Na2O} limit of 20 mass% is the same for the WTP and INEEL glass-formulation approaches. Therefore, scoping studies were performed to determine if the INEEL SBW approach could be applicable to Hanford LAW.

These results show promise for the use of the formulation approach developed by Vienna and colleagues (Vienna et al. 1999; Peeler et al. 2001; Vienna et al. 2002; Vienna et al. 2003) for maximizing Hanford LAW loading in glass. Scoping studies indicated that approximately twice as much S can be incorporated in the glass as compared to current WTP glass formulations (e.g., up to 0.8 wt% SO₃ at 20 wt% Na₂O). These scoping studies suggest that the Hanford LAW glass development and formulation program could benefit from additional studies, including:

- testing and optimization for those properties key to Hanford LAW glasses that were not considered for INEEL SBW (VHT response, melter-component corrosion)
- scale-up testing to demonstrate the ability to incorporate higher LAW loadings while meeting required processing-rate constraints using the bubbled melters similar to those designed for WTP
- variation studies to ensure the robustness of the compositions to process uncertainties and wastecomposition variations
- additional waste-form qualification activities (to expand the current LAW composition region to include these compositions).

The benefit of adopting this glass-development approach would be to lower the amount of LAW glass produced (and costs) at the WTP during life-cycle operations due to higher sulfur tolerances.

5.0 References

Bates, S. O., D. S. Goldman, and W. C. Richey. 1985. *A Letter Report Summarizing the Sulfate/Redox Relationship to Glass Melting Chemistry and Behavior*. HWVP-020207A, Pacific Northwest Laboratory, Richland, WA.

Cozzi, A. D., D. F. Bickford, and M. E. Stone. 2002. *Slurry Fed Melt Rate Furnace Runs to Support Glass Formulation Development for INEEL Sodium-Bearing Waste*. WSRC-TR-2002-00192, Westinghouse Savannah River Company, Aiken, SC.

Darab, J. G., D. D. Graham, B. D. MacIsaac, R. L. Russell, D. K. Peeler, H. D. Smith, and J. D. Vienna. 2001. *Sulfur Partitioning During Vitrification of INEEL Sodium Bearing Waste: Status Report*, PNNL-13588, Pacific Northwest National Laboratory, Richland, WA.

Fincham, C.J.B., and F. D. Richardson. 1954. "The Behavior of Sulfur in Silicate and Aluminate Melts." In *Proc. Royal Soc.*, London, **223A**, 40-63.

Fu, S. S., K. S. Matlack, R. K. Mohr, W. Luo, E. Wang, M. Leontiev, H. Hojaji, M. Brandys, I. L. Pegg, and P. B. Macedo. 1996. "Minimelter Runs of Mixed Wastes High in Lead, Barium, Phosphorous, and Sulfur." In *Ceramic Transactions*, **72**, pp. 27-40, American Ceramic Society, Westerville, OH.

Goldman, D. S. 1985. "Redox and Sulfur Solubility in Glass Melts." In *Proc. Intl. Congress on Glass*, Charleroi, Belgium.

Goles, R. W., J. M. Perez, B. D. MacIsaac, D. D. Siemer, and J. A. McCray. 2001. *Test summary Report INEEL Sodium-Bearing Waste Vitrification Demonstration RSM-01-01*. PNNL-13522, Pacific Northwest National Laboratory, Richland, WA.

Goles, R. W., J. A. Del Debbio, R. J. Kirkham, B. D. MacIsaac, J. A. McCray, D. D. Siemer, and N. R. Soelberg. 2002. *Test Summary Report INEEL Sodium-Bearing Waste Vitrification Demonstration RSM-* 01-2. PNNL-13869, Pacific Northwest National Laboratory, Richland, WA.

Holmquist, S. 1966. "Oxygen Ion Activity and the Solubility of Sulfur Trioxide in Sodium Silicate Melts." In *J. Am. Ceram. Soc.* **49**(9):467:473.

Hrma, P., J. D. Vienna, and J. S. Ricklefs. 2003. "Mechanism of Sulfate Segregation during Glass Melting." In *Scientific Basis for Nuclear Waste Management XXVI*, pp 147-152, Materials Research Society, Warrendale, PA.

Hrma, P., J. D. Vienna, and J. S. Ricklefs. 2004. "Sulfate Retention During Waste Glass Melting." In *Ceramics Transactions*, **155**, American Ceramic Society, Westerville, OH.

Li, H., J. G. Darab, D. W. Matson, P. A. Smith, P. Hrma, Y. Chen, and J. Liu. 1996. "Phosphate-Sulfate Interaction in Simulated Low-Level Radioactive Waste Glasses." In *Scientific Basis for Nuclear Waste Management XIX*, pp 141-148, Materials Research Society, Pittsburgh, PA.

Li, H., P. Hrma, and J. D. Vienna. 2001. "Sulfate Retention and Segregation in Simulated Radioactive Waste Borosilicate Glass." In *Ceramic Transactions*, **119**, pp. 237-246, American Ceramic Society, Westerville, OH.

McKeown, D. A., I. S. Muller, H. Gan, I. L. Pegg, and W. C. Stolte. 2004. "Determination of sulfur environments in borosilicate waste glasses using X-ray absorption near-edge spectroscopy." In *J. Non-Cryst. Sol.* 333:74–84.

Muller, I. S., A. C. Buechele, and I. L. Pegg. 2001. *Glass Formulation and Testing with RPP-WTP LAW Simulants - Final Report*. VSL-01R3560-2, Vitreous State Laboratory, The Catholic University of America, Washington D.C.

Musick, C. A., B. A. Scholes, R. D. Tillotson, D. M. Bennert, J. D. Vienna, J. V. Crum, D. K. Peeler, I. A. Reamer, D. F. Bickford, J. C. Marra, and N. L. Waldo. 2000. *Technical Status Report: Vitrification Technology Development Using INEEL Run 78 Pilot Plant Calcine*. INEEL\EXT-2000-00110, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

Papadopoulos, K. 1973. "The Solubility of SO₃ in Soda-Lime-Silica Melts." In *Phys. Chem. Glasses* 14:60-65.

Peeler, D. K., T. B. Edwards, I. A. Reamer, R. J. Workman, J. D. Vienna, J. V. Crum, and M. J. Schweiger. 2001. *Glass Formulation Development for INEEL Sodium-Bearing Waste (WM-180) (U)*. WSRC-TR-2001-00295, Westinghouse Savannah River Company, Aiken, SC.

Pegg I. L., H. Gan, I. S. Muller, D. A. McKeown, and K. S. Matlack. 2000. *Summary of Preliminary Results on Enhanced Sulfate Incorporation During Vitrification of LAW Feeds*. VSL-00R3630-1, Rev. 1, Vitreous State Laboratory, The Catholic University of America, Washington, D.C.

Perez, J. M., L. J. Ethridge, D. S. Goldman, R. W. Goles, R. D. Peters, N. L. Scharnhorst, and G. J. Sevigny. 1983. *West Valley Vitrification Experiment PSCM-16 Summary*. Pacific Northwest Laboratory, Richland, WA.

Perry, K. J., R. R. Kimmitt, N. R. Soelberg, R. D. Tillotson, and A. N. Olson. 2001. *Test Results from* SBW-FY91-PS-01 Vitrification Demonstration of Sodium Bearing Waste Simulant using WM-180 Surrogate. INEEL/EXT-01-01073, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID.

Sullivan, G., M. H. Langowski, and P. Hrma. 1995. "Sulfate Segregation in Vitrification of Simulated Hanford Nuclear Waste Glasses." In *Ceramic Transactions* 61, pp 187-193, American Ceramic Society, Westerville, OH.

U.S. Department of Energy (DOE). 2000. *Design, Construction, and Commissioning of the Hanford Tank Waste Treatment and Immobilization Plant.* Contract Number: DE-AC27-01RV14136, as amended, U.S. Department of Energy, Office of River Protection, Richland, WA.

Vienna, J. D., M. J. Schweiger, D. E. Smith, H. D. Smith, J. V. Crum, D. K. Peeler, I. A. Reamer, C. A. Musick, and R. D. Tillotson. 1999. *Glass Formulation Development for INEEL Sodium-Bearing Waste*. PNNL-12234, Pacific Northwest National Laboratory, Richland, WA

Vienna, J. D., P. Hrma, A. Jiricka, D. E. Smith, T. H. Lorier, I. A. Reamer, and R. L. Schulz. 2001. *Hanford Immobilized LAW Product Acceptance Testing: Tanks Focus Area Results*. PNNL-13744, Pacific Northwest National Laboratory, Richland, WA.

Vienna, J. D., W. C. Buchmiller, J. V. Crum, D. D. Graham, D. S. Kim, B. D. MacIsaac, M. J. Schweiger, D. K. Peeler, T. B. Edwards, I. A. Reamer, and R. J. Workman. 2002. *Glass Formulation Development for INEEL Sodium-Bearing Waste*. PNNL-14050, Pacific Northwest National Laboratory, Richland, WA.

Vienna, J. D., D. S. Kim, and D. K. Peeler. 2003. "Glass Formulation for INEEL Sodium Bearing Waste." In *Ceramic Transactions* 143, pp. 169-176, American Ceramic Society, Westerville, OH.

Waste	1998	2000	2000	2000	2000	2000	2000	2000	2000	2000
Additive	SBW-1	SBW-1	SBW-2	SRW-2	SBW-2	SBW-2	SBW-2	SBW-3	SBW-3	SBW-4
Loading	35	25	25	30	35	40	45	25	35	20
Ag ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$A_{1_2O_3}$	9.56	7.00	7 00	8 40	9.80	11 20	12.60	7 00	9.80	5 60
As_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B_2O_2	9.50	10.78	9.09	8.51	7.92	7.34	6.76	11.34	9.87	9.67
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.78	0.56	0.56	0.67	0.78	0.89	1.00	0.56	0.78	2.04
CdO	0.00	0.02	0.02	0.02	0.03	0.03	0.04	0.02	0.03	0.02
Ce ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.36	0.22	0.22	0.26	0.31	0.35	0.40	0.22	0.31	0.18
CoO	0.00	0.05	0.05	0.06	0.07	0.08	0.09	0.05	0.07	0.04
Cr ₂ O ₃	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cs ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.00	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.01
F	0.34	0.14	0.14	0.17	0.20	0.23	0.26	0.14	0.20	0.11
Fe ₂ O ₃	7.90	8.84	8.84	8.35	7.85	7.36	6.86	8.84	7.85	9.89
Gd_2O_3	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
I	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	2.77	1.91	1.91	2.29	2.67	3.05	3.43	1.91	2.67	1.53
Li ₂ O	1.73	2.00	3.00	2.80	2.60	2.40	2.20	3.38	2.93	3.20
MgO	0.02	0.10	0.10	0.12	0.14	0.16	0.18	0.10	0.14	0.08
MnO	0.27	0.17	0.17	0.20	0.23	0.27	0.30	0.17	0.23	0.13
MoO ₃	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00
Na ₂ O	17.50	13.15	13.15	15.79	18.42	21.05	23.68	13.15	18.42	10.52
Nb ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.19	0.02	0.02	0.03	0.03	0.04	0.04	0.02	0.03	0.02
P_2O_5	0.42	0.20	0.20	0.24	0.28	0.32	0.36	0.20	0.28	0.16
PbO	0.11	0.06	0.06	0.07	0.08	0.10	0.11	0.06	0.08	0.05
PdO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO ₂	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SeO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	44.74	51.52	52.21	48.73	45.25	41.77	38.29	49.58	42.97	56.00
SnO_2	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_3	0.00	0.89	0.89	1.07	1.25	1.43	1.61	0.89	1.25	0.72
SrO	1.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	2.00	2.31	2.31	2.16	2.00	1.85	1.69	2.31	2.00	0.00
V_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZnO	0.00	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.02	0.01
ZrO ₂	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix A. INEEL SBW Glass Compositions

 Table A.1. Compositions of Tested INEEL SBW Glasses in mass%

Table A.1. Cont.

Waste	2000	2000	2000	2000	2000	2000	2000	2000	2000	2000
Additive	SBW-4	SBW-4	SBW-4	SBW-5	SBW-6	SBW-7	SBW-8	SBW-9	SBW-9	SBW-9
Loading	25	30	35	35	35	35	35	25	28	30
Ag ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	7.00	8.40	9.80	9.80	9.80	9.80	9.80	7.00	7.84	8.40
As ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B_2O_3	9.09	8.51	7.92	9.87	9.87	6.62	9.87	11.34	10.90	10.61
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	2.06	2.07	2.08	3.38	2.08	3.38	2.08	4.31	4.22	4.17
CdO	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.02	0.02	0.02
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.22	0.26	0.31	0.31	0.31	0.31	0.31	0.22	0.25	0.26
CoO	0.05	0.06	0.07	0.07	0.07	0.07	0.07	0.05	0.06	0.06
Cr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cs ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.02
F	0.14	0.17	0.20	0.20	0.20	0.20	0.20	0.14	0.16	0.17
Fe ₂ O ₃	9.36	8.83	8.30	8.30	8.30	10.25	10.25	7.86	7.60	7.43
Gd_2O_3	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ι	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	1.91	2.29	2.67	2.67	2.67	2.67	2.67	1.91	2.14	2.29
Li ₂ O	3.00	2.80	2.60	2.60	2.60	3.25	3.25	3.75	3.60	3.50
MgO	0.10	0.12	0.14	0.14	0.14	0.14	0.14	0.10	0.11	0.12
MnO	0.17	0.20	0.23	0.23	0.23	0.23	0.23	0.17	0.19	0.20
MoO ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na ₂ O	13.15	15.79	18.42	18.42	18.42	18.42	18.42	13.15	14.73	15.79
Nb_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03
P_2O_5	0.20	0.24	0.28	0.28	0.28	0.28	0.28	0.20	0.22	0.24
PbO	0.06	0.07	0.08	0.08	0.08	0.08	0.08	0.06	0.07	0.07
PdO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SeO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	52.50	49.00	45.50	42.25	43.55	42.90	40.95	48.75	46.80	45.50
SnO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_3	0.89	1.07	1.25	1.25	1.25	1.25	1.25	0.89	1.00	1.07
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ZnO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
ZrO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.1. Cont.

Waste	2000	2000	2000	2001	2001	2001	2001	2001	2001
Additive	SBW-9	SBW-9	SBW-10	SBW-9	SBW-11	SBW-11	SBW-11	SBW-11	SBW-11
Loading	32	35	30	18.5	15	18.5	20	25	30
Ag ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	8.96	9.80	8.40	5.09	4.13	5.09	5.50	6.88	8.26
As ₂ O ₃	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01
B_2O_3	10.31	9.87	8.51	12.29	5.18	4.98	4.90	4.61	4.33
BaO	0.00	0.00	1.40	0.00	0.00	0.00	0.00	0.00	0.00
CaO	4.11	4.03	0.67	4.47	4.59	4.49	4.45	4.30	4.16
CdO	0.03	0.03	0.02	0.01	0.01	0.01	0.02	0.02	0.02
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.28	0.31	0.26	0.16	0.13	0.16	0.17	0.22	0.26
CoO	0.07	0.07	0.06	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.00	0.00	0.00	0.04	0.03	0.04	0.04	0.05	0.06
Cs ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01
F	0.18	0.20	0.17	0.14	0.11	0.14	0.15	0.18	0.22
Fe ₂ O ₃	7.26	7.00	8.83	8.41	1.50	1.50	1.50	1.49	1.49
Gd_2O_3	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.01
Ι	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	2.44	2.67	2.29	1.39	1.13	1.39	1.51	1.88	2.26
Li ₂ O	3.40	3.25	2.80	4.08	5.19	4.98	4.89	4.58	4.28
MgO	0.13	0.14	0.12	0.07	1.55	1.50	1.48	1.41	1.34
MnO	0.21	0.23	0.20	0.15	0.12	0.15	0.16	0.20	0.24
MoO ₃	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01
Na ₂ O	16.84	18.42	15.79	9.60	11.44	13.10	13.82	16.20	18.58
Nb ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.03	0.03	0.03	0.02	0.01	0.02	0.02	0.02	0.03
P_2O_5	0.26	0.28	0.24	0.15	0.12	0.15	0.16	0.20	0.24
PbO	0.08	0.08	0.07	0.04	0.04	0.04	0.05	0.06	0.07
PdO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SeO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	44.20	42.25	49.00	52.98	57.76	55.38	54.36	50.96	47.57
SnO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO ₃	1.14	1.25	1.07	0.84	0.68	0.84	0.91	1.14	1.36
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V_2O_5	0.00	0.00	0.00	0.01	4.16	3.99	3.92	3.68	3.44
ZnO	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.02
ZrO ₂	0.00	0.00	0.00	0.00	2.07	1.99	1.95	1.83	1.71

Table A.1. Cont.

Waste	2001	2001	2001	2001	2001	2001	2001	2001	2001
Additive	SBW-12	SBW-13	SBW-14	SBW-15	SBW-16	SBW-17	SBW-18	SBW-19	SBW-20
Loading	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
Ag ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	5.09	5.09	5.09	5.09	5.09	5.09	5.09	5.09	5.09
As ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
B_2O_3	4.98	4.98	4.98	4.98	4.98	4.98	4.98	4.98	4.98
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49
CdO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
CoO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Cs ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
F	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
Fe ₂ O ₃	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Gd_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ι	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39
Li ₂ O	4.98	4.98	4.98	4.98	4.98	4.98	4.98	4.98	4.98
MgO	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
MnO	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
MoO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	13.10	13.10	13.10	13.10	13.10	13.10	13.10	13.10	13.10
Nb_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
P_2O_5	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
PbO	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
PdO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SeO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	55.38	55.38	55.38	55.38	55.38	55.38	55.38	55.38	55.38
SnO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_3	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.84
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V_2O_5	3.99	3.99	3.99	3.99	3.99	3.99	3.99	3.99	3.99
ZnO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ZrO ₂	1.99	1.99	1.99	1.99	1.99	1.99	1.99	1.99	1.99

Table A.1. Cont.

Waste	2001	2001	2001	2001	2001	2001	2001	2001	2001
Additive	SBW-21	SBW-22	SBW-22	SBW-22	SBW-22	SBW-23	SBW-23	SBW-23	SBW-23
Loading	18.5	15	18.5	20	25	15	18.5	20	25
Ag ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	5.09	4.13	5.09	5.50	6.88	4.13	5.09	5.50	6.88
As ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
B_2O_3	4.98	5.18	4.98	4.90	4.61	5.18	4.98	4.90	4.61
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	4.49	4.59	4.49	4.45	4.30	4.59	4.49	4.45	4.30
CdO	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.02
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C1	0.16	0.13	0.16	0.17	0.22	0.13	0.16	0.17	0.22
CoO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr_2O_3	0.04	0.03	0.04	0.04	0.05	0.03	0.04	0.04	0.05
Cs ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
F	0.14	0.11	0.14	0.15	0.18	0.11	0.14	0.15	0.18
Fe ₂ O ₃	1.50	1.50	1.50	1.50	1.49	1.50	1.50	1.50	1.49
Gd_2O_3	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01
Ι	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	1.39	1.13	1.39	1.51	1.88	1.13	1.39	1.51	1.88
Li ₂ O	4.98	5.19	4.98	4.89	4.58	5.19	4.98	4.89	4.58
MgO	1.50	1.55	1.50	1.48	1.41	1.55	1.50	1.48	1.41
MnO	0.15	0.12	0.15	0.16	0.20	0.12	0.15	0.16	0.20
MoO ₃	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01
Na ₂ O	13.10	11.44	13.10	13.82	16.20	11.44	13.10	13.82	16.20
Nb ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02
P_2O_5	0.15	0.12	0.15	0.16	0.20	0.12	0.15	0.16	0.20
PbO	0.04	0.04	0.04	0.05	0.06	0.04	0.04	0.05	0.06
PdO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SeO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	55.38	57.76	55.38	54.36	50.96	57.76	55.38	54.36	50.96
SnO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_3	0.84	0.68	0.84	0.91	1.14	0.68	0.84	0.91	1.14
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V_2O_5	3.99	4.16	3.99	3.92	3.68	4.16	3.99	3.92	3.68
ZnO	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02
ZrO_2	1.99	2.07	1.99	1.95	1.83	2.07	1.99	1.95	1.83

Table A.1. Cont.

Waste	2001	2001	2001	2001	2001	2001	2001	2001	2001
Additive	SBW-24	SBW-24	SBW-24	SBW-24	SBW-25	SBW-25	SBW-25	SBW-25	SBW-26
Loading	15	18.5	20	25	15	18.5	20	25	15
Ag ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	4.13	5.09	5.50	6.88	4.13	5.09	5.50	6.88	4.13
As ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
B_2O_3	5.18	4.98	4.90	4.61	5.18	4.98	4.90	4.61	5.18
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	4.59	4.49	4.45	4.30	4.59	4.49	4.45	4.30	4.59
CdO	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.02	0.01
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.13	0.16	0.17	0.22	0.13	0.16	0.17	0.22	0.13
CoO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr ₂ O ₃	0.03	0.04	0.04	0.05	0.03	0.04	0.04	0.05	0.03
Cs ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
F	0.11	0.14	0.15	0.18	0.11	0.14	0.15	0.18	0.11
Fe ₂ O ₃	1.50	1.50	1.50	1.49	1.50	1.50	1.50	1.49	1.50
Gd_2O_3	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.00
Ι	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	1.13	1.39	1.51	1.88	1.13	1.39	1.51	1.88	1.13
Li ₂ O	5.19	4.98	4.89	4.58	5.19	4.98	4.89	4.58	5.19
MgO	1.55	1.50	1.48	1.41	1.55	1.50	1.48	1.41	1.55
MnO	0.12	0.15	0.16	0.20	0.12	0.15	0.16	0.20	0.12
MoO ₃	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
Na ₂ O	11.44	13.10	13.82	16.20	11.44	13.10	13.82	16.20	11.44
Nb ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiO	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.01
P_2O_5	0.12	0.15	0.16	0.20	0.12	0.15	0.16	0.20	0.12
PbO	0.04	0.04	0.05	0.06	0.04	0.04	0.05	0.06	0.04
PdO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ReO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SeO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	57.76	55.38	54.36	50.96	57.76	55.38	54.36	50.96	57.76
SnO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_3	0.68	0.84	0.91	1.14	0.68	0.84	0.91	1.14	0.68
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V_2O_5	4.16	3.99	3.92	3.68	4.16	3.99	3.92	3.68	4.16
ZnO	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01
ZrO ₂	2.07	1.99	1.95	1.83	2.07	1.99	1.95	1.83	2.07

Waste 2001 2001 2001 2001 2001 2001 2001 Additive **SBW-26 SBW-26 SBW-26 SBW-27 SBW-27 SBW-27 SBW-27** Loading 18.5 20 25 15 18.5 20 25 Ag₂O 0.00 0.00 0.00 0.00 0.00 0.00 0.00 Al₂O₃ 5.09 5.50 4.13 5.09 5.50 6.88 6.88 0.01 0.01 0.01 0.01 0.01 As₂O₃ 0.01 0.01 B_2O_3 4.98 4.90 4.61 5.18 4.98 4.90 4.61 BaO 0.00 0.00 0.00 0.00 0.00 0.00 0.00 CaO 4.49 4.45 4.30 4.59 4.49 4.45 4.30 CdO 0.01 0.02 0.02 0.01 0.01 0.02 0.02 0.00 0.00 0.00 0.00 0.00 0.00 0.00 Ce_2O_3 Cl 0.16 0.17 0.22 0.13 0.16 0.17 0.22 CoO 0.00 0.00 0.00 0.00 0.00 0.00 0.00 Cr_2O_3 0.04 0.04 0.05 0.03 0.04 0.04 0.05 Cs_2O 0.00 0.00 0.00 0.00 0.00 0.00 0.00 CuO 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.14 0.15 0.18 0.11 0.14 0.15 0.18 1.50 1.50 1.49 1.50 1.50 1.50 1.49 Fe₂O₃ Gd_2O_3 0.00 0.01 0.01 0.00 0.00 0.01 0.01 0.00 0.00 0.00 0.00 0.00 0.00 0.00 1.39 1.39 1.51 K_2O 1.51 1.88 1.13 1.88 Li₂O 4.98 4.89 4.58 5.19 4.98 4.89 4.58 MgO 1.50 1.48 1.41 1.55 1.50 1.48 1.41 MnO 0.15 0.20 0.12 0.16 0.20 0.16 0.15 0.00 0.00 0.01 0.00 0.00 0.00 MoO₃ 0.01 Na₂O 13.10 13.82 16.20 11.44 13.10 13.82 16.20 Nb₂O₅ 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.02 NiO 0.02 0.02 0.01 0.02 0.02 0.02 P_2O_5 0.15 0.16 0.20 0.12 0.15 0.16 0.20 PbO 0.04 0.05 0.06 0.04 0.04 0.05 0.06 PdO 0.00 0.00 0.00 0.00 0.00 0.00 0.00 ReO₂ 0.00 0.00 0.00 0.00 0.00 0.00 0.00 RuO_2 0.00 0.00 0.00 0.00 0.00 0.00 0.00 Sb₂O₃ 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 SeO₂ 0.00 0.00 0.00 0.00 0.00 SiO₂ 55.38 54.36 50.96 57.76 55.38 54.36 50.96 SnO₂ 0.00 0.00 0.00 0.00 0.00 0.00 0.00 SO₃ 0.84 0.91 1.14 0.68 0.84 0.91 1.14 SrO 0.00 0.00 0.00 0.00 0.00 0.00 0.00 TiO₂ 0.00 0.00 0.00 0.00 0.00 0.00 0.00 V_2O_5 3.99 3.92 3.68 4.16 3.99 3.92 3.68 ZnO 0.01 0.01 0.02 0.01 0.01 0.01 0.02 1.99 1.95 2.07 1.99 1.95 ZrO₂ 1.83 1.83

Table A.1. Cont.

Distribution

No. of

No. of <u>Copies</u>

OFFSITE

<u>Copies</u> <u>ONSITE</u>

1	A. Aloy		2	DOE/Office of River Protection	
	V. G. Khlopin Radium Ir	stitute		W. F. Hamel	H6-60
	28, 2 nd Murinsky Pr.			B. Mauss	H6-60
	RF-194021 St. Petersbur	g, Russia			
			1	<u>Duratek</u>	
1	I. L. Pegg			C. C. Chapman	H1-11
	Catholic University of A	merica		-	
	Vitreous State Laborator	J	6	<u>RPP-WTP Program</u>	
	620 Michigan Ave., N. E			R. L. Gilchrist	H4-02
	Washington, D. C. 2006	4		E. V. Morrey	H4-02
	-			C. M. Musick	H4-02
3	Westinghouse Savannah	River Company		J. M. Perez	H4-02
	Aiken, SC 29808,			W. Tamosaitis	H4-02
	Attn:			J. H. Westsik	H4-02
	E. W. Holtzscheiter	773-A			
	C. M. Jantzen	773-A	22	Pacific Northwest National Laboration	atory
	D. K. Peeler	999-W		G. H. Beeman	K9-18

Tachie Northwest National Laboratory	
G. H. Beeman	K9-18
W. F. Bonner	K9-14
J. V. Crum	K6-24
M. L. Elliott	K6-28
R. W. Goles	K6-24
P. R. Hrma	K6-24
L. K. Holton	H6-61
E. O. Jones	K6-24
G. B. Josephson	K6-69
D. S. Kim	K6-24
L. K. Holton	H6-61
M. J. Schweiger	K6-24
J. D. Vienna (10)	K6-24