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Demonstration of Sulfur Solubility Determinations in High Waste Loading, Low-Activity Waste Glasses

K. M. Fox

April 2016

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REVIEWS AND APPROVALS

AUTHORS:

K. M. Fox, Hanford Mission Programs	Date
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TECHNICAL REVIEW:

D. L. McClane, Engineering Process Development, Reviewed per E7 2.60	Date
--	------

APPROVAL:

C. C. Herman, Director, Hanford Mission Programs	Date
--	------

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EXECUTIVE SUMMARY

A method recommended by Pacific Northwest National Laboratory (PNNL) for sulfate solubility determinations in simulated low-activity waste glasses was demonstrated using three compositions from a recent Hanford high waste loading glass study. Sodium and sulfate concentrations in the glasses increased after each re-melting step. Visual observations of the glasses during the re-melting process reflected the changes in composition. The measured compositions showed that the glasses met the targeted values. The amount of SO_3 retained in the glasses after washing was relatively high, ranging from 1.6 to 2.6 weight percent (wt %). Measured SnO_2 concentrations were notably low in all of the study glasses. The composition of the wash solutions should be measured in future work to determine whether SnO_2 is present with the excess sulfate washed from the glass. Increases in batch size and the amount of sodium sulfate added did not have a measureable impact on the amount of sulfate retained in the glass, although this was tested for only a single glass composition. A batch size of 250 g and a sodium sulfate addition targeting 7 wt %, as recommended by PNNL, will be used in future experiments.

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LIST OF ABBREVIATIONS

DI	De-ionized
DOE	U.S. Department of Energy
HLW	High-Level Waste
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
KH	Potassium hydroxide fusion
LAW	Low-Activity Waste
LM	Lithium Metaborate fusion
ORP	U.S. Department of Energy, Office of River Protection
PF	Sodium Peroxide Fusion
PNNL	Pacific Northwest National Laboratory
SRNL	Savannah River National Laboratory
wt %	Weight Percent
WTP	Hanford Tank Waste Treatment and Immobilization Plant

1.0 Introduction

The U.S. Department of Energy (DOE) Office of River Protection (ORP) is building the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to remediate defense radioactive waste that is temporarily stored in 177 underground tanks. The low-activity waste (LAW) fraction will be partitioned from the high-level waste (HLW). Both the LAW and HLW will then be vitrified in borosilicate glass with Joule-heated ceramic-lined melters.

Efforts are being made to increase the loading of Hanford tank wastes in glass while maintaining the ability to meet processing, regulatory compliance, and product quality requirements. Improved retention of sulfate in LAW glass is critical to achieving higher waste loadings, increasing waste throughput, and reducing the demands on off-gas systems and off-gas condensate recycling. Data are needed on the solubility of sulfate in simulated LAW glass to support the development of advanced models to predict sulfate incorporation as a function of glass composition. Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) are collaborating to develop the needed data in support of the ORP Enhanced Waste Glass Program.^{1,a}

In this report, SRNL provides a demonstration of sulfate solubility determinations following a methodology recommended by PNNL and characterization of the glasses. This work was executed in compliance with the Task Technical and Quality Assurance Plan.³

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Site Manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Laboratory data for this study were recorded in the SRNL Electronic Laboratory Notebook system, experiment C3489-00079-12.

2.0 Experimental Procedure

PNNL recommended three simulated LAW glass compositions for SRNL to use in demonstrating the methodology for sulfur solubility determination. These compositions were selected as part of a larger, statistically designed matrix.⁴ Identifiers and targeted compositions of the glasses are given in Table 2-1.

^a Note that recent ORP research and development plans¹⁻² inadvertently used the term “advanced” instead of “enhanced”.

Table 2-1. Identifiers and Targeted Compositions of the Study Glasses

Glass ID	EWG-LAW-Centroid	New-OL-17130	New-IL-1721
Al ₂ O ₃	9.00	3.50	6.25
B ₂ O ₃	10.00	13.75	11.75
CaO	5.50	1.65	2.75
Cl	0.21	0.47	0.31
Cr ₂ O ₃	0.14	0.31	0.21
F	0.32	0.71	0.47
Fe ₂ O ₃	1.00	1.50	1.25
K ₂ O	0.40	0.00	1.00
Li ₂ O	2.00	5.00	3.50
MgO	1.50	0.00	0.50
Na ₂ O	19.00	16.50	16.45
P ₂ O ₅	0.68	1.51	1.01
SiO ₂	39.55	47.00	43.25
SO ₃	0.70	0.10	1.30
SnO ₂	2.00	3.00	3.50
V ₂ O ₅	2.00	4.00	3.00
ZnO	3.00	1.00	2.00
ZrO ₂	3.00	0.00	1.50

The demonstration of sulfate solubility determinations was completed in three stages. In the first stage, the three glass compositions were fabricated in batches targeting 110 g of glass (prior to sodium sulfate addition). Sodium and sulfur concentrations were measured after each of the first three re-melting steps with sodium sulfate added (but without grinding and rinsing of excess sulfate), and after the fourth (final) re-melting step when the glass was crushed and excess sulfate was washed out. The full compositions of the glasses were also measured for comparisons with the targeted values. In the second stage, the impact of batch size was briefly investigated using a batch targeting 250 g of the EWG-LAW-Centroid glass. In the third stage, the impact of a slightly higher sodium sulfate addition was briefly investigated using a batch targeting 250 g of the EWG-LAW-Centroid glass. Fabrication and characterization of the glasses is described in the following sections.

2.1 Glass Fabrication

Each of the study glasses was prepared from the proper proportions of reagent-grade metal oxides, carbonates, and boric acid. The batches targeted 110 g of glass for the first stage of testing, and 250 g of glass for the second and third stages. The raw materials were mixed by hand in a plastic bag and placed into a platinum/gold crucible with a lid. The crucible was placed into a furnace at the melt temperature of 1150 °C. The crucible was removed from the furnace after an isothermal hold for about 60 minutes. The glass was poured onto a clean, stainless steel plate and allowed to air cool (quench). The cooled glass, along with the glass that remained adhered to the crucible, was collected and then ground in a tungsten carbide ring pulverizer^a for approximately 60 seconds.

The powdered glass was placed back in the crucible, covered, and melted in the furnace at 1150 °C for about 45 minutes. The crucible was then removed from the furnace and the glass was poured onto a clean stainless steel plate to quench.

^a Angstrom, Inc., Belleville, Michigan

A small amount of unincorporated batch material was observed at the bottom of the crucible after the first melt of each glass. The glasses appeared homogeneous after the second melt cycle (Figure 2-1).

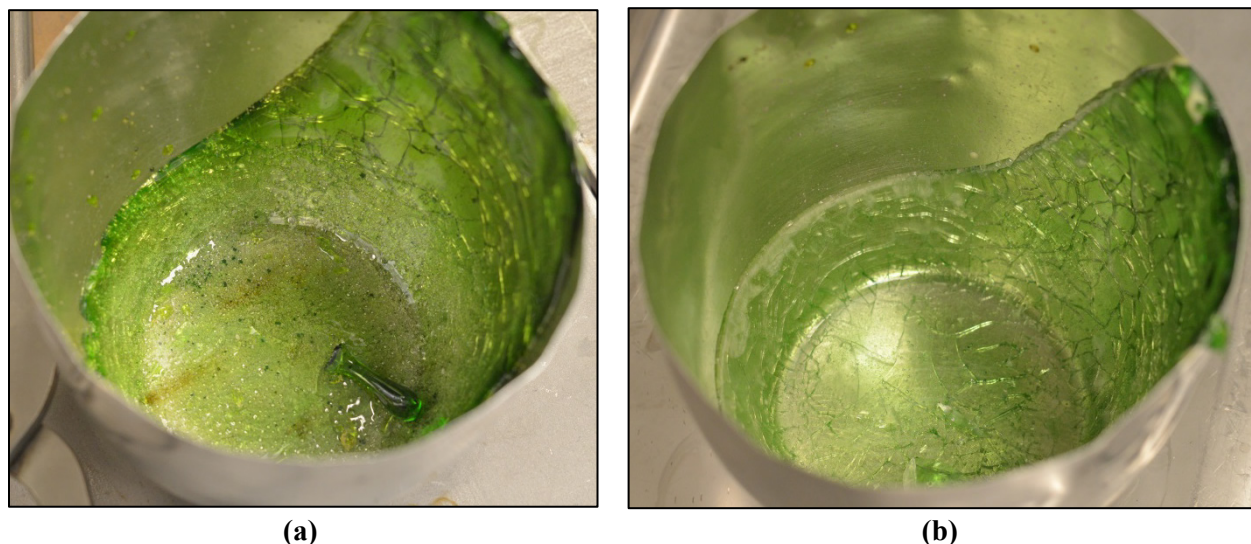


Figure 2-1. Glass EWG-LAW-Centroid with unincorporated batch material after first melt (a) and with homogeneous appearance after second melt (b)

2.2 Sulfate Incorporation

After the second melt cycle, the cooled glass and the glass that remained adhered to the crucible was collected and ground in the ring pulverizer for approximately 60 seconds. The mass of the glass powder was measured, and an amount of reagent grade sodium sulfate appropriate to target 6.5 wt % Na_2SO_4 in the glass was measured and added. This value was increased to 7 wt % Na_2SO_4 in stage three. The glass and sodium sulfate were blended in the ring pulverizer for approximately 30 seconds.

A series of four melting and grinding cycles was used to incorporate sulfur into the glass. Each melt was performed at 1150 °C for approximately 50 minutes in a covered platinum/gold crucible. After each melt, the glass was quenched by pouring onto a stainless steel plate. The cooled glass and the glass that remained adhered to the crucible was collected and ground in a ring pulverizer for approximately 60 seconds. The appearances of the glasses changed after each melt, likely as a result of further incorporation of sulfate. As shown in Figure 2-2, the most obvious changes in appearance occurred between the first and second melts with sodium sulfate added, where the glasses became either less translucent (EWG-LAW-Centroid) or opaque (LAW-New-OL-17130 and LAW-New-IL-1721).

2.3 Washing of Excess Sulfate

After the fourth melting cycle, the glass was ground in a ring pulverizer and then washed repeatedly with deionized (DI) water to remove excess sulfate salts that were not incorporated into the glass. The quenched glass and the glass that remained adhered to the crucible was collected and ground in a ring pulverizer until all of the powder passed through a 75 micron screen. The powdered glass was placed in a beaker with DI water, and the beaker was placed in an ultrasonic bath for approximately 60 seconds. The solution was allowed to settle and was then decanted. The washing cycle was repeated until the water remained clear. The number of cycles used and the total volume of water used for each of the glasses are summarized in Table 2-2. The washed glass powders were dried overnight at 90 °C in beakers with aluminum foil covers.

Table 2-2. Summary of Excess Sulfate Washing Steps

Experimental Stage	Glass ID	Number of Washing Cycles Needed	Total Volume of Wash Water Used
1	EWG-LAW-Centroid	6	2.1 L
	LAW-New-OL-17130	8	2.8 L
	LAW-New-IL-1721	6	2.1 L
2	EWG-LAW-Centroid	5	3.9 L
3	EWG-LAW-Centroid	6	4.9 L

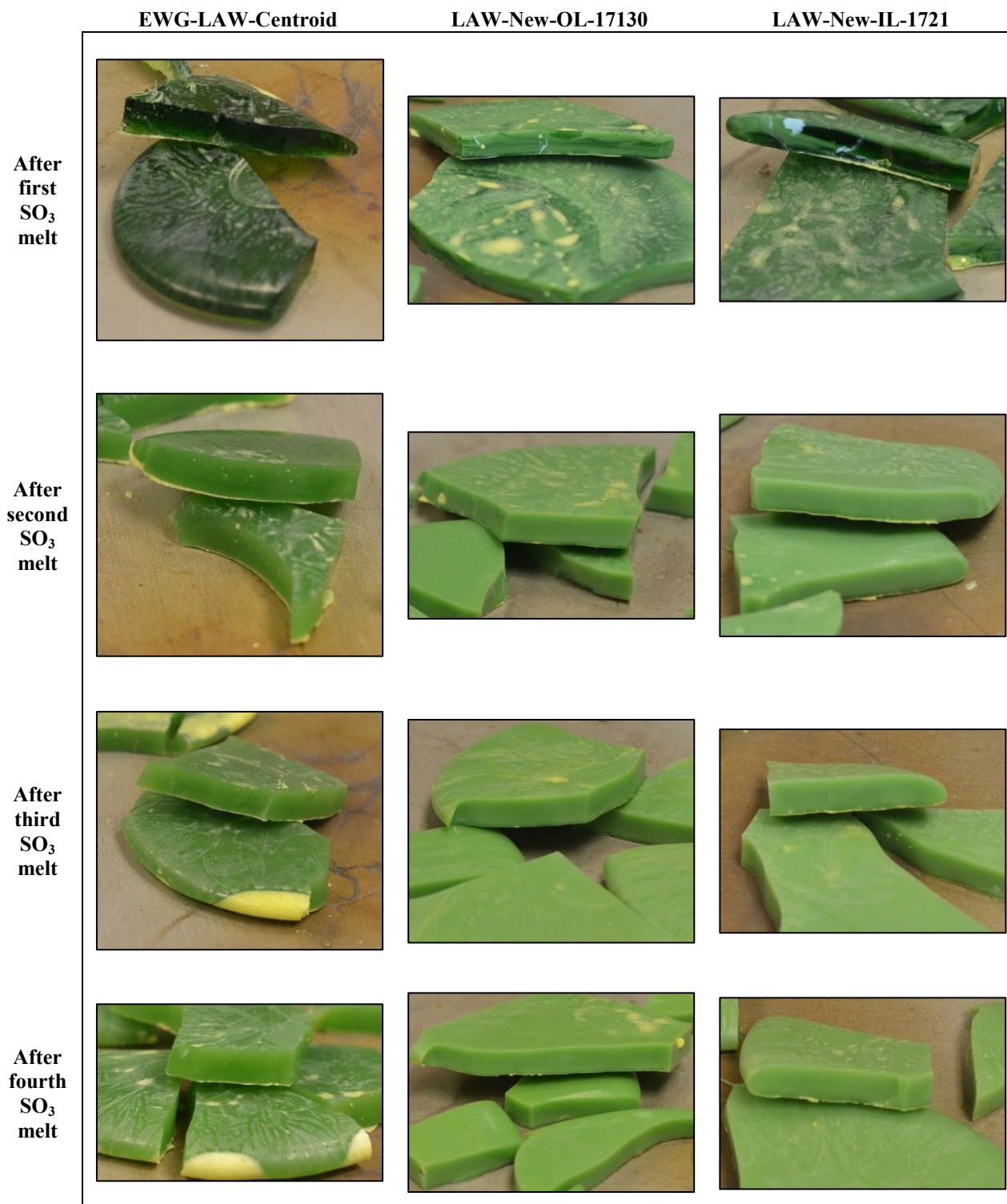


Figure 2-2. Photographs of the stage one study glasses (110 g batches) after each of the four sulfate incorporation melting cycles

2.4 Chemical Composition Analysis

Chemical analysis was performed on a representative sample of each of the study glasses to allow for determination of sodium and sulfate concentrations, and for comparisons with the targeted compositions. Three preparation techniques, sodium peroxide fusion (PF), lithium metaborate fusion (LM), and potassium hydroxide fusion (KH), were used to prepare the glass samples for analysis. The preparation methods used for each of the reported glass components are summarized in Table 2-3.

Each of the samples prepared by PF and LM was analyzed, twice for each element of interest, by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The samples prepared by KH were analyzed, twice for each element of interest, by Ion Chromatography (IC). Samples of the Batch-1 and LRM glasses were included as reference materials in the analysis of the study glasses.^{5,6} The LRM glass was selected mainly as a reference for sodium and sulfur concentration measurements, and the Batch-1 glass was selected as a secondary reference to check for potential bias in sodium concentration measurements.

Table 2-3. Preparation Methods Used in Reporting the Concentrations of Each of the Elements of the Study Glasses

Element	Preparation Method
Al	PF
B	PF
Ca	LM
Cl	KH
Cr	LM
F	KH
Fe	PF
K	LM
Li	PF
Mg	LM
Na	LM
P	LM
S	LM
Si	PF
Sn	LM
V	LM
Zn	LM
Zr	LM

3.0 Results and Discussion

3.1 Stage One – Sulfate Incorporation Over Multiple Melting Cycles

Samples of each of the three Stage One study glasses were collected after each of the first three sulfate incorporation re-melts. These samples were prepared and measured for sodium and sulfur concentrations. Note that these samples were not crushed and rinsed to remove excess sulfate. The results are presented as weight percent (wt %) oxides in Table 3-1. The values are the averages of the two duplicate measurements for each component. The individual, elemental measurements are provided in Table A-1 of Appendix A for reference. Both the sodium and sulfur concentrations in the three glasses increased after each of the three re-melts, indicating increased incorporation of the added sodium sulfate. The measurements are in agreement with the observed changes in appearance of the glasses (Figure 2-2).

As described in Sections 2.2 and 2.3, a fourth SO₃ re-melt was performed followed by grinding and washing of the excess sulfate salts. The three glasses were again sampled and analyzed after these steps, and the resulting sodium and sulfur concentrations are presented as wt % oxides in Table 3-2. The values are the averages of the two duplicate measurements for each component. The individual, elemental measurements are provided in Table A-2 of Appendix A for reference. These measurements in Table 3-2 are somewhat lower than those in Table 3-1, indicating as expected that not all of the sulfate measured prior to washing was actually incorporated into the glass structure.

Table 3-1. Soda and Sulfate Concentrations of the Stage One Glasses Over the Course of Three Melting Cycles

Glass ID	Melt Cycles	Na ₂ O (wt %)	SO ₃ (wt %)
EWG-LAW-Centroid	1	20.5	2.01
	2	20.5	2.06
	3	20.6	2.43
LAW-New-IL-1721	1	16.9	1.97
	2	18.0	2.70
	3	18.4	3.01
LAW-New-OL-17130	1	18.0	2.83
	2	18.2	3.21
	3	18.4	3.56

Table 3-2. Soda and Sulfate Concentrations of the Stage One Glasses After Four Melting Cycles and Washing

Glass ID	Na ₂ O (wt %)	SO ₃ (wt %)
EWG-LAW-Centroid	20.0	1.55
LAW-New-IL-1721	17.7	1.87
LAW-New-OL-17130	17.6	2.61

Additional samples of each of the three Stage One study glasses, after the fourth SO₃ re-melt and washing steps, were prepared and analyzed for complete composition measurements for comparison with the targeted values. The results of these analyses are shown in Table 3-3 and Table 3-4 on an oxide basis. Again, the measured values are the averages of the duplicate measurements for each component. The individual, elemental measurements are provided in Table A-3 and Table A-4 of Appendix A for reference. Measurements that were below the analytical detection limit were taken as that detection limit in calculating a sum of oxides for each glass. The measured sums of oxides for the Stage One glasses range from 97.3 to 100.9 wt %, indicating good recovery of all components. Comparisons of the targeted and measured values for the Batch-1 and LRM reference glasses indicate no significant issues with the analytical process.^a

A review of the measured composition data shows that the study glasses generally met their targeted compositions. The measured concentrations are within 10% of the targeted values for those components with concentrations of at least 2 wt %, with the exception of SnO₂, which was consistently low. SnO₂ may have partitioned to the unincorporated sulfate phase that was washed from the glasses. The composition of the wash solution should be measured in future work to determine whether SnO₂ is

^a Note that the reference glasses include other components that are not included in the study glasses and were therefore not measured. Thus, the targeted sums of oxides for the reference glasses are less than 100 wt %.

present. The measured Na_2O concentrations are higher than the targeted values, which is expected due to the addition of excess sodium sulfate. The measured SO_3 concentrations of the Stage One glasses are well above the targeted values, demonstrating that greater incorporation of sulfate is possible for these compositions.

The measured values for Na_2O and SO_3 reported in Table 3-2 and Table 3-4 resulted from separate sampling and analysis of the Stage One glasses. Comparison of these values shows only minor differences in the measurements, and provides an indication of homogeneity of the glasses.

Table 3-3. Measured and Targeted Compositions of the Stage One Study Glasses (wt %) and Associated Differences, Part 1

Glass ID	Al₂O₃	B₂O₃	CaO	Cl	Cr₂O₃	F	Fe₂O₃	K₂O	Li₂O	MgO
LRM (Targeted) Relative Difference	9.87 (9.51) 3.8%	7.93 (7.85) 1.0%	0.56 (0.54) 4.2%	<0.01 (0) --	0.22 (0.19) 15.0%	0.88 (0.86) 1.9%	1.54 (1.38) 11.7%	1.63 (1.48) 10.0%	<0.22 (0.11) --	0.11 (0.10) 10.0%
Batch-1 (Targeted) Relative Difference	4.86 (4.88) -0.3%	8.08 (7.78) 3.9%	1.21 (1.22) -1.0%	0.01 (0) --	0.15 (0.11) 38.0%	<0.01 (0) --	13.1 (12.8) 1.8%	3.37 (3.33) 1.4%	4.38 (4.43) -1.2%	1.36 (1.42) -4.5%
EWG-LAW-Centroid (Targeted) Relative Difference	9.07 (9.00) 0.8%	10.0 (10.0) 0.3%	5.52 (5.50) 0.3%	0.10 (0.21) -54.4%	0.16 (0.14) 16.0%	0.24 (0.32) -24.7%	1.16 (1.00) 15.8%	0.43 (0.40) 8.7%	1.88 (2.00) -6.2%	1.47 (1.50) -2.0%
LAW-New-IL-1721 (Targeted) Relative Difference	6.31 (6.25) 0.9%	11.5 (11.8) -1.8%	2.78 (2.75) 1.0%	0.13 (0.31) -56.8%	0.20 (0.21) -6.6%	0.34 (0.47) -27.7%	1.22 (1.25) -2.8%	1.03 (1.00) 3.5%	3.27 (3.50) -6.6%	0.51 (0.50) 1.6%
LAW-New-OL-17130 (Targeted) Relative Difference	3.46 (3.50) -1.0%	13.1 (13.8) -4.8%	1.64 (1.65) -0.9%	0.24 (0.47) -48.0%	0.31 (0.31) -1.4%	0.49 (0.71) -30.5%	1.43 (1.50) -4.5%	<0.12 (0) --	4.56 (5.00) -8.8%	<0.02 (0) --

Table 3-4. Measured and Targeted Compositions of the Stage One Study Glasses (wt %) and Associated Differences, Part 2

Glass ID	Na ₂ O	P ₂ O ₅	SO ₃	SiO ₂	SnO ₂	V ₂ O ₅	ZnO	ZrO ₂	Sum
LRM (Targeted) Relative Difference	21.3 (20.0) 6.3%	0.48 (0.54) -11.6%	0.22 (0.30) -25.6%	57.1 (54.2) 5.4%	<0.13 (0) --	<0.18 (0) --	<0.12 (0) --	0.90 (0.93) -3.2%	103.4 (98.0) --
Batch-1 (Targeted) Relative Difference	8.82 (9.00) -2.0%	<0.23 (0) --	<0.12 (0) --	51.7 (50.2) 2.9%	<0.13 (0) --	<0.18 (0) --	<0.12 (0) --	0.09 (0.10) -8.3%	97.9 (95.3) --
EWG-LAW-Centroid (Targeted) Relative Difference	20.4 (19.0) 7.3%	0.48 (0.68) -29.0%	1.72 (0.70) 146%	39.3 (39.6) -0.5%	1.04 (2.00) -48.2%	1.95 (2.00) -2.5%	3.01 (3.00) 0.5%	2.88 (3.00) -3.9%	100.9 (100) --
LAW-New-IL-1721 (Targeted) Relative Difference	17.9 (16.5) 9.0%	0.72 (1.01) -29.0%	2.01 (1.30) 54.3%	42.1 (43.3) -2.8%	1.79 (3.50) -48.8%	2.86 (3.00) -4.6%	1.98 (2.00) -1.0%	1.39 (1.50) -7.5%	98.1 (100) --
LAW-New-OL-17130 (Targeted) Relative Difference	17.7 (16.5) 7.4%	1.14 (1.51) -24.3%	2.81 (0.10) 2706%	43.9 (47.0) -6.6%	1.64 (3.00) -45.3%	3.67 (4.00) -8.3%	0.94 (1.00) -5.9%	<0.14 (0) --	97.3 (100) --

3.2 Stages Two and Three – Influences of Batch Size and Sodium Sulfate Addition

PNNL recommended that the glass batch size be increased from 110 g to 250 g. Since the Stage One glasses had already been fabricated at the time this recommendation was made, an additional 250 g batch of glass EWG-LAW-Centroid was fabricated as a brief test to determine the influence of batch size on the retained sulfate concentration. This glass was referred to as the Stage Two test. Also, PNNL recommended that the addition of sodium sulfate should target 7 wt %. Since the Stage One glasses targeted a lower sodium sulfate addition (6.5 wt %), a third batch of glass EWG-LAW-Centroid was fabricated as a brief test to determine the influence of the sodium sulfate addition. This glass was referred to as the Stage Three test.

The Stage Two and Stage Three glasses were fabricated as described in Section 2.0. Samples of the glasses after the fourth re-melt and the grinding and washing steps were prepared and analyzed for their complete chemical compositions (Section 2.4). The results are shown in Table 3-5 on an oxide basis. The measured values are the averages of the duplicate measurements for each component. The individual, elemental measurements are provided in Table A-3 and Table A-4 of Appendix A for reference.

A review of Table 3-5 shows that the measured compositions of the glasses are similar, and close to the targeted values with the exception of SnO_2 . The measured sulfate concentrations are highlighted in Table 3-5. While these experiments present very little data, it appears that the size of the batch and the amount of excess sodium sulfate added did not have a strong effect on the amount of sulfate retained in glass EWG-LAW-Centroid after the re-melt cycles followed by grinding and washing. Therefore, the Stage One results are considered useful in demonstrating the acceptability of method. The larger batch size and higher sodium sulfate addition will be used as recommended for future experiments.

Table 3-5. Targeted and Measured Compositions for the EWG-LAW-Centroid Glasses, Stages One through Three

Glass ID	Targeted	EWG-LAW-Centroid, Stage One	EWG-LAW-Centroid, Stage Two	EWG-LAW-Centroid, Stage Three
Al_2O_3	9.00	9.07	9.20	8.95
B_2O_3	10.0	10.03	10.23	9.88
CaO	5.50	5.52	5.65	5.49
Cl	0.21	0.1	0.09	0.08
Cr_2O_3	0.14	0.16	0.13	0.18
F	0.32	0.24	0.24	0.24
Fe_2O_3	1.00	1.16	1.00	1.18
K_2O	0.40	0.43	0.43	0.42
Li_2O	2.00	1.88	1.90	1.84
MgO	1.50	1.47	1.52	1.52
Na_2O	19.0	20.38	20.08	20.15
P_2O_5	0.68	0.48	0.48	0.46
SO_3	0.70	1.72	1.71	1.73
SiO_2	39.6	39.33	38.89	38.11
SnO_2	2.00	1.04	1.03	0.99
V_2O_5	2.00	1.95	1.94	1.94
ZnO	3.00	3.01	3.07	2.98
ZrO_2	3.00	2.88	2.97	2.88
Sum	100	100.87	100.56	99.02

4.0 Summary

The method recommended by PNNL for sulfate solubility determinations in simulated LAW glasses was demonstrated using three compositions from a Hanford high waste loading glass study. Sodium and sulfate concentrations in the glasses increased after each re-melting step. Visual observations of the glasses during the re-melting process reflected the changes in composition. The measured compositions showed that the glasses met the targeted values. The amount of SO_3 retained in the glasses after washing was relatively high, ranging from 1.6 to 2.6 wt %. Measured SnO_2 concentrations were notably low in all of the study glasses. The composition of the wash solutions should be measured in future work to determine whether SnO_2 is present with the excess sulfate washed from the glass. Increases in batch size and the amount of sodium sulfate added did not have a measureable impact on the amount of sulfate retained in the glass, although this was tested for only a single glass composition. A batch size of 250 g and a sodium sulfate addition targeting 7 wt %, as recommended by PNNL, will be used in future experiments.

5.0 References

1. Peeler, D. K., D. S. Kim, J. D. Vienna, M. J. Schweiger, and G. F. Piepel, "Office of River Protection Advanced Low-Activity Waste Glass Research and Development Plan," *U.S. Department of Energy Report PNNL-24883, EWG-RPT-008*, Pacific Northwest National Laboratory, Richland, WA (2015).
2. Peeler, D. K., J. D. Vienna, M. J. Schweiger, and K. M. Fox, "Advanced High-Level Waste Glass Research and Development Plan," *U.S. Department of Energy Report PNNL-24450*, Pacific Northwest National Laboratory, Richland, WA (2015).
3. Fox, K. M. and D. K. Peeler, "Task Technical and Quality Assurance Plan for Hanford HLW Glass Development and Characterization," *U.S. Department of Energy Report SRNL-RP-2013-00692, Revision 0*, Savannah River National Laboratory, Aiken, SC (2013).
4. Piepel, G. F., S. K. Cooley, J. D. Vienna, and J. V. Crum, "Experimental Design for Hanford Low-Activity Waste Glasses with High Waste Loading," *U.S. Department of Energy Report PNNL-24391, EWG-RPT-006, Rev. 0*, Pacific Northwest National Laboratory, Richland, WA (2015).
5. Jantzen, C. M., J. B. Pickett, K. G. Brown, T. B. Edwards, and D. C. Beam, "Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability from Composition Using a Thermodynamic Hydration Energy Reaction Model (THERMOTM)," *U.S. Department of Energy Report WSRC-TR-93-673, Revision 1*, Westinghouse Savannah River Company, Aiken, South Carolina (1995).
6. Ebert, W. L. and S. F. Wolfe, "Round-robin Testing of a Reference Glass for Low-Activity Waste Forms," *U.S. Department of Energy Report ANL-99/22*, Argonne National Laboratory, Argonne, IL (1999).

Appendix A Tables Supporting the Chemical Composition Measurements

Table A-1. Measured, Elemental Data for the Stage One Glasses Over the Course of the First Three Melting Cycles with Sodium Sulfate Added (glasses were not washed prior to analysis)

Glass ID	Lab ID	Measurement	Na (wt %)	S (wt %)
LRM	S-5289	1	15.9	0.096
		2	16.0	0.098
Batch-1	S-5290	1	6.54	<0.050
		2	6.59	<0.050
EWG-LAW-Centroid-012116-1M	S-5291	1	15.1	0.808
		2	15.2	0.800
EWG-LAW-Centroid-012116-2M	S-5292	1	15.3	0.820
		2	15.1	0.831
EWG-LAW-Centroid-012116-3M	S-5293	1	15.2	0.955
		2	15.3	0.989
LAW-New-IL-1721-1M	S-5294	1	12.6	0.772
		2	12.4	0.806
LAW-New-IL-1721-2M	S-5295	1	13.4	1.09
		2	13.3	1.08
LAW-New-IL-1721-3M	S-5296	1	13.7	1.22
		2	13.6	1.19
LAW-New-OL-17130-1M	S-5297	1	13.3	1.10
		2	13.4	1.17
LAW-New-OL-17130-2M	S-5298	1	13.6	1.28
		2	13.5	1.29
LAW-New-OL-17130-3M	S-5299	1	13.6	1.44
		2	13.7	1.41

Table A-2. Measured, Elemental Data for the Stage One Glasses After Four Melting Cycles with Sodium Sulfate Added (glasses were crushed and washed to remove excess sulfate)

Glass ID	Lab ID	Measurement	Na (wt %)	S (wt %)
EWG-LAW-Centroid	S-5109	1	14.7	0.624
		2	14.9	0.618
LAW-New-IL-1721	S-5110	1	13.0	0.739
		2	13.2	0.755
LAW-New-OL-17130	S-5111	1	13.1	1.04
		2	13.0	1.05

Table A-3. Measured, Elemental Data for the Full Glass Compositions (wt %), Part 1
(glasses were crushed and washed to remove excess sulfate)

Glass ID	Lab ID	Measurement	Al	B	Ca	Cl	Cr	F	Fe	K
LRM	S-5280	1	5.23	2.46	0.411	<0.010	0.148	0.887	1.09	1.35
		2	5.22	2.46	0.394	<0.010	0.151	0.866	1.07	1.35
Batch-1	S-5281	1	2.57	2.57	0.863	0.014	0.101	<0.010	9.35	2.80
		2	2.57	2.44	0.863	0.013	0.101	<0.010	8.93	2.80
EWG-LAW-Centroid (Stage 1)	S-5282	1	4.80	3.12	3.96	0.094	0.110	0.241	0.823	0.360
		2	4.80	3.11	3.92	0.098	0.112	0.241	0.798	0.362
LAW-New-OL-17130 (Stage 1)	S-5288	1	1.84	4.07	1.16	0.247	0.207	0.497	1.00	<0.100
		2	1.83	4.06	1.18	0.242	0.212	0.490	1.00	<0.100
LAW-New-IL-1721 (Stage 1)	S-5287	1	3.32	3.58	1.95	0.135	0.135	0.339	0.850	0.866
		2	3.36	3.59	2.02	0.133	0.134	0.341	0.850	0.852
EWG-LAW-Centroid (Stage 2)	S-5283	1	4.84	3.17	3.99	0.085	0.088	0.241	0.695	0.358
		2	4.89	3.19	4.09	0.087	0.091	0.244	0.703	0.348
EWG-LAW-Centroid (Stage 3)	S-5284	1	4.77	3.08	3.96	0.079	0.125	0.237	0.829	0.344
		2	4.71	3.05	3.89	0.082	0.124	0.235	0.826	0.349

Table A-4. Analytical Data for the Full Glass Compositions (wt %), Part 2
(glasses were crushed and washed to remove excess sulfate)

Glass ID	Lab ID	Measurement	Li	Mg	Na	P	S	Si	Sn	V	Zn	Zr
LRM	S-5280	1	<0.100	0.065	15.7	0.202	0.090	26.7	<0.100	<0.100	<0.100	0.664
		2	<0.100	0.068	15.9	0.215	0.089	26.7	<0.100	<0.100	<0.100	0.669
Batch-1	S-5281	1	2.08	0.819	6.55	<0.100	<0.050	24.2	<0.100	<0.100	<0.100	0.067
		2	1.99	0.817	6.54	<0.100	<0.050	24.2	<0.100	<0.100	<0.100	0.067
EWG-LAW-Centroid (Stage 1)	S-5282	1	0.872	0.865	15.3	0.210	0.670	18.6	0.822	1.09	2.41	2.13
		2	0.872	0.908	15.0	0.212	0.709	18.2	0.811	1.09	2.43	2.14
LAW-New-OL-17130 (Stage 1)	S-5288	1	2.12	<0.010	13.2	0.461	1.11	20.1	1.18	2.05	0.757	<0.100
		2	2.11	<0.010	13.1	0.537	1.14	20.9	1.41	2.06	0.755	<0.100
LAW-New-IL-1721 (Stage 1)	S-5287	1	1.51	0.307	13.3	0.315	0.812	19.7	1.42	1.60	1.59	1.04
		2	1.53	0.305	13.3	0.311	0.794	19.6	1.41	1.60	1.60	1.02
EWG-LAW-Centroid (Stage 2)	S-5283	1	0.883	0.905	14.8	0.185	0.678	17.4	0.703	1.07	2.44	2.20
		2	0.886	0.927	15.0	0.237	0.688	18.9	0.916	1.10	2.49	2.20
EWG-LAW-Centroid (Stage 3)	S-5284	1	0.859	0.912	14.9	0.221	0.689	18.2	0.876	1.08	2.40	2.14
		2	0.849	0.920	15.0	0.179	0.701	17.5	0.687	1.08	2.39	2.12

Distribution:

J. W. Amoroso, 999-W
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