Chemical Analysis of Simulated High Level Waste Glasses to Support Sulfate Solubility Modeling

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EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE), Office of Environmental Management (EM) is sponsoring an international, collaborative project to develop a fundamental model for sulfate solubility in nuclear waste glass. The solubility of sulfate has a significant impact on the achievable waste loading for nuclear waste forms both within the DOE complex and to some extent at U.K. sites. The development of enhanced borosilicate glass compositions with improved sulfate solubility will allow for higher waste loadings and accelerated cleanup missions.

Much of the previous work on improving sulfate retention in waste glasses has been done on an empirical basis, making it difficult to apply the findings to future waste compositions despite the large number of glass systems studied. A more fundamental, rather than empirical, model of sulfate solubility in glass, under development at Sheffield Hallam University (SHU), could provide a solution to the issues of sulfate solubility. The model uses the normalized cation field strength index as a function of glass composition to predict sulfate capacity, and has shown early success for some glass systems.

The objective of the current scope is to mature the sulfate solubility model to the point where it can be used to guide glass composition development for DOE waste vitrification efforts, allowing for enhanced waste loadings and waste throughput. A series of targeted glass compositions was selected to resolve data gaps in the current model. SHU fabricated these glasses and sent samples to the Savannah River National Laboratory (SRNL) for chemical composition analysis. SHU will use the resulting data to enhance the sulfate solubility model and resolve any deficiencies. In this report, SRNL provides chemical analyses for simulated waste glasses fabricated SHU in support of sulfate solubility model development.

A review of the measured compositions revealed that there are issues with the B_2O_3 and Fe_2O_3 concentrations missing their targeted values by a significant amount for several of the study glasses. SHU is reviewing the fabrication of these glasses and the chemicals used in batching them to identify the source of these issues. The measured sulfate concentrations were all below their targeted values. This is expected, as the targeted concentrations likely exceeded the solubility limit for sulfate in these glass compositions. Some volatilization of sulfate may also have occurred during fabrication of the glasses. Measurements of the other oxides in the study glasses were reasonably close to their targeted values.

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LIST OF ABBREVIATIONS

EM	Environmental Management
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
LAW	Low Activity Waste
LRM	Low-level Reference Material
SHU	Sheffield Hallam University
PNNL	Pacific Northwest National Laboratory
SRNL	Savannah River National Laboratory
WTP	Hanford Waste Treatment and Immobilization Plant

1.0 Introduction

The U.S. Department of Energy (DOE), Office of Environmental Management (EM) is sponsoring an international, collaborative project to develop a fundamental model for sulfate solubility in nuclear waste glass. The solubility of sulfate has a significant impact on the achievable waste loading for nuclear waste forms within the DOE complex. These wastes can contain relatively high concentrations of sulfate, which has low solubility in borosilicate glass.[1] This is a significant issue for low activity waste (LAW) at Hanford and is projected to have a major impact on Waste Treatment Plant (WTP) throughput. Sulfate solubility has also been a limiting factor for recent high level waste (HLW) sludge processed at the Savannah River Site's Defense Waste Processing Facility (DWPF).[2-5] The low solubility of sulfate in glass dictates that the waste be blended with lower sulfate concentration waste sources or heavily washed to remove sulfate prior to vitrification. The development of enhanced borosilicate glass compositions with improved sulfate solubility will allow for higher waste loadings and accelerated cleanup missions.

Studies at SRNL in support of the DWPF have identified frit additives that can be used to marginally improve sulfate solubility in simulated waste glasses.[6] However, due to the complexity of Savannah River waste compositions, much of this work has been done on an empirical basis,[2,5] making it difficult to apply the findings to future waste compositions despite the large number of glass systems studied.[7] Researchers at the Pacific Northwest National Laboratory (PNNL) have completed extensive glass formulation studies to evaluate the solubility of sulfate in glass compositions for Hanford wastes, although the empirical nature of these studies makes it difficult to apply the results to anticipated compositions to be processed in the WTP. A more fundamental, rather than empirical, model of sulfate solubility in glass, under development at Sheffield Hallam University (SHU), could provide a solution to the issues of sulfate solubility. The model uses the normalized cation field strength index as a function of glass composition to predict sulfate capacity, and has shown early success for some glass systems.[8]

Through previous DOE-EM International Program funding, the combination of this model with the data collected at SRNL resulted in positive model correlations for sulfate solubility in borosilicate waste glasses.[9] Utilizing funding obtained in late FY12, an extensive data set covering LAW and HLW glasses developed at PNNL and the Vitreous State Laboratory at Catholic University was compiled and transmitted to SHU for incorporation into the model. These data will significantly expand the coverage of the model given the compositional differences between HLW and LAW glasses.

The objective of the current scope is to mature the sulfate solubility model to the point where it can be used to guide glass composition development for DWPF and WTP, allowing for enhanced waste loadings and waste throughput at these facilities. A series of targeted glass compositions was selected to resolve data gaps in the model that were identified during FY12 funded work. SHU fabricated these glasses and sent samples to SRNL for chemical composition analysis. SHU will use the resulting data to enhance the sulfate solubility model and resolve any deficiencies. In this report, SRNL provides chemical analyses for simulated HLW glasses fabricated SHU in support of the sulfate solubility model development.

2.0 Experimental Procedure

2.1 Chemical Composition Analysis

Chemical composition analysis was performed on a representative sample of each of the study glasses to allow for comparisons with the targeted compositions. Two preparation techniques, sodium peroxide fusion and lithium metaborate/tetraborate fusion, were used to prepare the glass samples, in duplicate, for analysis. Each of the prepared samples was analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). A reference glass, the low-level reference material (LRM),[10] was also measured to assess the performance of the ICP-OES instrument during these analyses.

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in 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.

3.0 Results and Discussion

3.1 Results for the LRM Reference Glass

The reference and measured concentrations of the oxides in the LRM glass are shown in Table 3-1. In general, the measured values for the LRM reference glass show no significant issues with the sample preparation and measurement methods. The measured Fe_2O_3 and Li_2O values are biased high, although the concentrations of Fe_2O_3 and Li_2O in the LRM glass are much lower than those in the study glasses. The measured sulfate concentration matched the reference value.

Table 3-1. Reference and Measured Values for LRM Reference Glass.

Oxide	Reference Value (wt %)	Measured Value (wt %)
Al_2O_3	10	9.54
B_2O_3	8	7.64
CaO	0.5	0.49
Fe_2O_3	1	1.42
Li_2O	0.1	0.18
Na_2O	20	21.35
SO_3	0.2	0.20
SiO_2	54	53.63
ZrO_2	1	1.22

3.2 Chemical Composition Measurements

The measurements for each sample as prepared and measured in duplicate are given in Table A-1 in Appendix A, as reported by the analytical laboratory in units of elemental wt %. The average of each pair of measured values was computed and multiplied by the appropriate gravimetric factor to arrive at the measured compositions for each of the study glasses, as oxides, reported in Table 3-2. All of the measured sums of oxides for the study glasses fall within the interval of 95 to 101 wt %, indicating good recovery of all components.

Table 3-2. Measured Compositions of the Sulfate Study Glasses

Identifier	Al_2O_3	B_2O_3	CaO	Fe_2O_3	Li_2O	Na_2O	SO_4	SiO_2	ZrO_2	Sum
A1	5.54	4.97	5.40	13.38	3.56	10.34	1.11	54.85	1.00	100.14
A2	5.77	7.70	5.83	14.09	3.98	11.07	1.15	48.65	0.98	99.20
A3=B3	5.97	7.56	7.16	15.43	4.84	12.87	1.25	42.10	1.16	98.34
A4	6.21	7.14	7.69	14.51	5.24	14.04	1.44	39.18	1.23	96.69
A5	7.56	8.26	8.79	13.79	5.71	15.21	1.35	34.72	1.21	96.59
A6	7.52	7.90	9.19	15.06	6.05	16.27	1.43	30.95	1.28	95.64
B1	6.15	7.82	4.44	10.85	4.48	5.71	0.95	55.20	1.12	96.71
B2	6.27	7.70	5.55	11.32	4.64	9.18	1.02	50.87	1.17	97.72
B4	6.35	7.96	9.12	11.61	4.72	16.06	1.48	37.81	1.19	96.31
B5	6.02	6.68	10.36	11.04	4.72	19.40	1.71	35.40	1.15	96.48
B6	6.23	8.28	11.90	11.04	4.64	22.18	1.71	29.66	1.16	96.81

3.3 Measured versus Targeted Compositions

Targeted compositions for the study glasses were provided by SHU. Table 3-3 provides a comparison of the measured compositions to the targeted compositions with the relative percent differences. Upon review of this table, it is apparent that there are issues with the B_2O_3 and Fe_2O_3 concentrations missing their targeted values by a significant amount for several of the study glasses. SHU is reviewing the fabrication of these glasses and the chemicals used in batching them to identify the source of these issues. The measured sulfate concentrations are all below their targeted values. This is expected, as the targeted concentrations likely exceeded the solubility limit for sulfate in these glass compositions. Some volatilization of sulfate may also have occurred during fabrication of the glasses. Measurements of the other oxides in the study glasses were reasonably close to their targeted values.

Table 3-3. Comparison of Targeted and Measured Compositions (wt %) of the Study Glasses.

ID	**Type**	**Al_2O_3**	**B_2O_3**	**CaO**	**Fe_2O_3**	**Li_2O**	**Na_2O**	**SO_4**	**SiO_2**	**ZrO_2**
A1	Targeted	4.84	4.84	5.65	12.91	4.03	10.49	2.00	54.44	0.81
	Measured	5.54	4.97	5.40	13.38	3.56	10.34	1.11	54.85	1.00
	% Error	14%	3%	-4%	4%	-12%	-1%	-44%	1%	23%
A2	Targeted	5.39	5.39	6.29	14.37	4.49	11.68	2.00	49.49	0.90
	Measured	5.77	7.70	5.83	14.09	3.98	11.07	1.15	48.65	0.98
	% Error	7%	43%	-7%	-2%	-11%	-5%	-43%	-2%	9%
A3=B3	Targeted	5.94	5.94	6.93	15.84	4.95	12.87	2.00	44.55	0.99
	Measured	5.97	7.56	7.16	15.43	4.84	12.87	1.25	42.10	1.16
	% Error	1%	27%	3%	-3%	-2%	0%	-38%	-5%	18%
A4	Targeted	6.49	6.49	7.57	17.30	5.41	14.06	2.00	39.60	1.08
	Measured	6.21	7.14	7.69	14.51	5.24	14.04	1.44	39.18	1.23
	% Error	-4%	10%	2%	-16%	-3%	0%	-28%	-1%	14%
A5	Targeted	7.04	7.04	8.21	18.77	5.87	15.25	2.00	34.65	1.17
	Measured	7.56	8.26	8.79	13.79	5.71	15.21	1.35	34.72	1.21
	% Error	7%	17%	7%	-27%	-3%	0%	-33%	0%	3%
A6	Targeted	7.59	7.59	8.85	20.24	6.32	16.44	2.00	29.70	1.26
	Measured	7.52	7.90	9.19	15.06	6.05	16.27	1.43	30.95	1.28
	% Error	-1%	4%	4%	-26%	-4%	-1%	-28%	4%	1%
B1	Targeted	5.94	5.94	3.46	15.84	4.95	6.43	2.00	54.44	0.99
	Measured	6.15	7.82	4.44	10.85	4.48	5.71	0.95	55.20	1.12
	% Error	4%	32%	28%	-32%	-10%	-11%	-52%	1%	13%
B2	Targeted	5.94	5.94	5.20	15.84	4.95	9.65	2.00	49.49	0.99
	Measured	6.27	7.70	5.55	11.32	4.64	9.18	1.02	50.87	1.17
	% Error	5%	30%	7%	-29%	-6%	-5%	-49%	3%	18%
B4	Targeted	5.94	5.94	8.66	15.84	4.95	16.09	2.00	39.60	0.99
	Measured	6.35	7.96	9.12	11.61	4.72	16.06	1.48	37.81	1.19
	% Error	7%	34%	5%	-27%	-5%	0%	-26%	-5%	20%
B5	Targeted	5.94	5.94	10.39	15.84	4.95	19.30	2.00	34.65	0.99
	Measured	6.02	6.68	10.36	11.04	4.72	19.40	1.71	35.40	1.15
	% Error	1%	13%	0%	-30%	-5%	1%	-15%	2%	16%
B6	Targeted	5.94	5.94	12.13	15.84	4.95	22.52	2.00	29.70	0.99
	Measured	6.23	8.28	11.90	11.04	4.64	22.18	1.71	29.66	1.16
	% Error	5%	39%	-2%	-30%	-6%	-1%	-15%	0%	17%

4.0 Summary

DOE-EM is sponsoring an international, collaborative project to develop a fundamental model for sulfate solubility in nuclear waste glass. The solubility of sulfate has a significant impact on the achievable waste loading for nuclear waste forms within the DOE complex.

The objective of the current scope is to mature the SHU sulfate solubility model to the point where it can be used to guide glass composition development for DOE waste vitrification efforts, allowing for enhanced waste loadings and waste throughput. A series of targeted glass compositions was selected to resolve data gaps in the current model. SHU fabricated these glasses and sent samples to SRNL for chemical composition analysis.

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Appendix A. Tables Supporting the Chemical Composition Measurements

Table A-1. Measurements of the Study Glasses as Prepared and Measured in Duplicate (elemental wt %).

Sample ID	Lab ID	Al	B	Ca	Fe	Li	Na	S	Si	Zr
A1 (A)	14-0038a	2.88	1.51	3.95	9.59	1.62	7.86	0.361	25.3	0.723
A1 (B)	14-0038b	2.98	1.58	3.76	9.12	1.69	7.46	0.380	26.0	0.753
A2 (A)	14-0039a	3.05	2.37	4.19	9.90	1.85	8.24	0.388	22.9	0.731
A2 (B)	14-0039b	3.06	2.41	4.14	9.81	1.85	8.16	0.377	22.5	0.726
A3=B3 (A)	14-0040a	3.19	2.39	5.20	10.9	2.28	9.60	0.420	19.8	0.861
A3=B3 (B)	14-0040b	3.12	2.31	5.03	10.7	2.22	9.46	0.412	19.5	0.864
A4 (A)	14-0041a	3.28	2.22	5.42	10.0	2.44	10.2	0.489	18.2	0.915
A4 (B)	14-0041b	3.29	2.21	5.57	10.3	2.44	10.6	0.470	18.4	0.911
A5 (A)	14-0042a	3.99	2.58	6.43	9.85	2.66	11.5	0.457	16.2	0.892
A5 (B)	14-0042b	4.01	2.55	6.13	9.43	2.65	11.0	0.443	16.2	0.896
A6 (A)	14-0043a	3.96	2.43	6.57	10.5	2.80	12.1	0.478	14.4	0.950
A6 (B)	14-0043b	3.99	2.48	6.55	10.5	2.82	12.0	0.479	14.6	0.950
B1 (A)	14-0044a	3.18	2.33	3.57	7.58	2.02	4.23	0.315	26.0	0.817
B1 (B)	14-0044b	3.33	2.53	2.77	7.59	2.14	4.22	0.321	25.6	0.837
B2 (A)	14-0045a	3.31	2.38	3.96	7.93	2.16	6.78	0.339	23.8	0.865
B2 (B)	14-0045b	3.32	2.40	3.97	7.90	2.15	6.83	0.341	23.8	0.864
B4 (A)	14-0046a	3.40	2.53	6.43	8.03	2.23	11.8	0.493	17.7	0.891
B4 (B)	14-0046b	3.32	2.41	6.60	8.21	2.16	12.0	0.495	17.6	0.867
B5 (A)	14-0047a	3.09	1.99	7.46	7.80	2.13	14.4	0.571	16.6	0.832
B5 (B)	14-0047b	3.27	2.16	7.34	7.65	2.26	14.3	0.568	16.5	0.868
B6 (A)	14-0048a	3.31	2.58	8.49	7.70	2.17	16.3	0.564	13.7	0.864
B6 (B)	14-0048b	3.29	2.56	8.51	7.73	2.15	16.6	0.576	14.0	0.857
LRM standard	LRM	5.05	2.37	0.351	0.992	0.084	15.8	0.080	25.1	0.902

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