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Chemical Composition Analysis of Simulated Waste Glass T10-G-16A

K. M. Fox

August 2015

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EXECUTIVE SUMMARY

In this report, SRNL provides chemical composition analyses of a simulated LAW glass designated T10-G-16A. The measured chemical composition data are reported and compared with the targeted values for each component. No issues were identified in reviewing the analytical data.

The measured concentrations of Al_2O_3, CaO, Na_2O, and SiO_2 in T10-G-16A deviated from the targeted composition. It is of potential interest to note that these deviations result in a glass composition that is shifted toward the SiO_2 corner of the Al_2O_3-Na_2O-SiO_2 phase diagram, away from the nepheline phase field. The results of these analyses will be used in developing a better understanding of the properties and performance of this glass.

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LIST OF ABBREVIATIONS

DOE	U.S. Department of Energy
HLW	High Level Waste
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
KH	Potassium hydroxide digestion
LAW	Low Activity Waste
LM	Lithium Metaborate/tetraborate fusion
LRM	Low-level Reference Material
ORP	Office of River Protection
PF	Peroxide Fusion
PNNL	Pacific Northwest National Laboratory
SRNL	Savannah River National Laboratory
TTQAP	Task Technical and Quality Assurance Plan
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) has requested that the Savannah River National Laboratory (SRNL) provide expert evaluation and experimental work in support of the River Protection Project vitrification technology development. DOE is building the Hanford Tank Waste Treatment and Immobilization Plant (WTP) at the Hanford Site in Washington to remediate ~55 million gallons of 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 into borosilicate glass using Joule-heated ceramic melters.

Efforts are being made to increase the loading of Hanford tank wastes in the glass while conforming to processing requirements and product quality specifications. DOE-ORP has requested that SRNL support the advancement of glass formulations and process control strategies in key technical areas, as defined in the Task Technical and Quality Assurance Plan (TTQAP).[1]

In this report, SRNL provides chemical composition analysis of a simulated LAW glass supplied by the Pacific Northwest National Laboratory (PNNL). The results of these analyses will be used in developing a better understanding of the properties and performance of this glass.

2.0 Experimental Procedure

2.1 Glass Selected for Study

The glass sample provided by PNNL was designated T10-G-16A. The sample was fabricated by the Vitreous State Laboratory at the Catholic University of America. Details of the fabrication and heat treatment of this glass were not provided as part of the request for analysis. The targeted composition in weight percent (wt %) of the T10-G-16A glass is the same as that of the glasses designated LAW-ORP-LD1 described in earlier reports,[2,3] and is shown in Table 2-1.

Table 2-1. Targeted Composition of Glass T10-G-16A (LAW-ORP-LD1)

Oxide	wt %
Al_2O_3	10.15
B_2O_3	12.04
CaO	8.01
Cl	0.33
Cr_2O_3	0.50
Cs_2O	0.13
F	0.17
Fe_2O_3	1.00
K_2O	0.16
Li_2O	0.00
MgO	1.00
Na_2O	20.98
NiO	0.04
P_2O_5	0.29
PbO	0.01
SiO_2	37.14
SnO_2	0.00
SO_3	1.06
V_2O_5	1.00
ZnO	3.00
ZrO_2	3.00

In the sections that follow, the methods used for measuring the chemical composition of the glass are described and reviews of the resulting data are provided. Detailed data from these analyses are included as an appendix.

2.2 Compositional Analysis

Chemical analysis was performed on representative samples of the T10-G-16A glass to allow for comparisons with the targeted compositions. Three preparation techniques, including sodium peroxide fusion (PF), lithium metaborate (60%) / lithium tetraborate (40%) fusion (LM), and potassium hydroxide digestion (KH) were used to prepare the glass samples, in duplicate, for analysis. Each of the duplicate samples was analyzed twice for each element of interest by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) or ion chromatography (IC), for a total of four measurements per element. Samples of the Low-level Reference Material (LRM)[4] glass standard were included in the analyses to assess the performance of the ICP-AES and IC instruments over the course of these measurements. The preparation and measurement methods used for each of the reported glass components are listed in Table 2-2. Note that Cs was not included in the analyses since measurement of Cs requires the use of a separate analysis method and the targeted concentration of Cs_2O in the glass was small (0.13 wt %).

Table 2-2. Preparation and Measurement Methods Used in Reporting the Concentrations of Each of the Components of the T10-G-16A Glass

Analyte	Preparation Method	Measurement Method
Al	PF	ICP-AES
B	PF	ICP-AES
Ca	LM	ICP-AES
Cl	KH	IC
Cr	LM	ICP-AES
F	KH	IC
Fe	PF	ICP-AES
K	LM	ICP-AES
Li	PF	ICP-AES
Mg	LM	ICP-AES
Na	LM	ICP-AES
Ni	LM	ICP-AES
P	LM	ICP-AES
Pb	LM	ICP-AES
S	LM	ICP-AES
Si	PF	ICP-AES
Sn	LM	ICP-AES
V	LM	ICP-AES
Zn	LM	ICP-AES
Zr	LM	ICP-AES

2.3 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Site Manual E7, Procedure 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 Review and Evaluation of Chemical Composition Measurements

Table A-1 in Appendix A provides the elemental concentration measurements in wt % for the study glasses as prepared by the LM method. Table A-2 in Appendix A provides the elemental concentration measurements in wt % for the study glasses as prepared by the PF method. Table A-3 in Appendix A provides the elemental concentration measurements in wt % for the study glasses as prepared by the KH method. Elemental measurements for samples of the LRM standard glass are also provided in the tables of Appendix A. A review of these data showed that there were no obvious outliers among the four measurements of each component for each glass. These unprocessed data are provided as appendices to this report so that the values are readily available should they be of interest for future reviews.

In the sections that follow, the measurements of the LRM standard glass are investigated, the average chemical composition of the T10-G-16A glass is determined, and comparisons are made between the measured and the targeted composition. JMP™ Pro Version 11.2.1 (SAS Institute, Inc.)[5] was used to support these analyses.

3.1.1 Treatment of Detection Limits

The elemental concentrations in Table A-1 through Table A-3 of Appendix A were converted to oxide concentrations by multiplying the values for each element by the gravimetric factor for the corresponding oxide. During the process of converting to oxide concentrations, an elemental concentration that was reported to be below the detection limit of the analytical process used was set to the detection limit as the oxide concentration was determined for the purposes of review and calculating a sum of oxides for each glass. Those oxides with measured concentrations that were below the associated detection limit will be denoted with a less than symbol (<) as the measured compositions are reported.

3.1.2 Results for the LRM Standard

Table A-4 in Appendix A provides a comparison of the LRM results to their acceptability limits utilized by SRNL.[6] The table includes the upper and lower acceptability limits for the concentrations of each of the major elements in the reference glass, as well as each of the measured values from this study. The results show that all of the measurements for the elements present in the LRM standard glass were within the acceptability limits utilized by SRNL in conducting instrument and procedure assessments during the execution of these analyses.

3.1.3 Measured versus Targeted Compositions

All of the measurements for each oxide of the LRM and T10-G-16A glasses (i.e., all of the measurements in Appendix A, Table A-1 through Table A-3), were averaged to determine a representative chemical composition for each glass. A sum of oxides was also computed for each glass based upon the averaged, measured values. Table 4-1 provides a summary of the average compositions as well as the targeted compositions and some associated differences and relative differences. The measured sums of oxides for the study glasses fall within the interval of 95 to 105 wt %, which is considered to indicate recovery of all components. Entries in Table 4-1 show the relative differences between the measured values and the targeted values for the oxides with targeted values above 5 wt %. The relative differences are shaded if they are 10% or more.[a]

The concentrations of some of the major oxide constituents of glass T10-G-16A deviate from the targeted composition. The concentrations of Al_2O_3, CaO, and Na_2O are below their targeted values by about 10-15%. The concentration of SiO_2 is about 9% higher than the targeted value.

4.0 Summary

In this report, SRNL provides chemical composition analyses of a simulated LAW glass designated T10-G-16A. The measured chemical composition data are reported and compared with the targeted values for each component. No issues were identified in reviewing the analytical data.

The measured concentrations of Al_2O_3, CaO, Na_2O, and SiO_2 in T10-G-16A deviated from the targeted composition. It is of potential interest to note that these deviations result in a glass composition that is shifted toward the SiO_2 corner of the Al_2O_3-Na_2O-SiO_2 phase diagram, away from the nepheline phase field.

[a] These criteria were selected arbitrarily for the purpose of highlighting differences from targeted concentrations that may be of practical concern.

Table 4-1. Comparison of Measured and Targeted Glass Compositions

Identifier	Oxide	Measured (wt %)	Targeted (wt %)	% Difference?
T10-G-16A-1	Al_2O_3	9.13	10.15	-10.01%
T10-G-16A-1	B_2O_3	11.8	12.04	-2.04%
T10-G-16A-1	CaO	6.80	8.01	-15.13%
T10-G-16A-1	Cl	0.178	0.33	
T10-G-16A-1	Cr_2O_3	0.298	0.50	
T10-G-16A-1	Cs_2O	-	0.13	
T10-G-16A-1	F	0.123	0.17	
T10-G-16A-1	Fe_2O_3	0.936	1.00	
T10-G-16A-1	K_2O	0.352	0.16	
T10-G-16A-1	Li_2O	<0.215	0.00	
T10-G-16A-1	MgO	0.909	1.00	
T10-G-16A-1	Na_2O	18.5	20.98	-11.67%
T10-G-16A-1	NiO	<0.127	0.04	
T10-G-16A-1	P_2O_5	0.331	0.29	
T10-G-16A-1	PbO	<0.108	0.01	
T10-G-16A-1	SO_3	0.871	1.06	
T10-G-16A-1	SiO_2	40.4	37.14	8.90%
T10-G-16A-1	SnO_2	<0.127	0.00	
T10-G-16A-1	V_2O_5	0.881	1.00	
T10-G-16A-1	ZnO	2.74	3.00	
T10-G-16A-1	ZrO_2	2.71	3.00	
T10-G-16A-1	Sum	97.60	100.01	
LRM	Al_2O_3	9.46	9.51	-0.48%
LRM	B_2O_3	7.75	7.85	-1.27%
LRM	CaO	0.453	0.54	
LRM	Cl	<0.010	0.00	
LRM	Cr_2O_3	0.196	0.19	
LRM	F	0.835	0.86	
LRM	Fe_2O_3	1.39	1.38	
LRM	K_2O	1.48	1.48	
LRM	Li_2O	<0.215	0.11	
LRM	MgO	<0.166	0.10	
LRM	Na_2O	20.9	20.03	4.57%
LRM	NiO	0.175	0.19	
LRM	P_2O_5	0.462	0.54	
LRM	PbO	<0.108	0.10	
LRM	SO_3	<0.250	0.30	
LRM	SiO_2	54.3	54.20	0.22%
LRM	SnO_2	<0.127	0.00	
LRM	V_2O_5	<0.179	0.00	
LRM	ZnO	<0.124	0.00	
LRM	ZrO_2	0.803	0.93	
LRM	Sum	99.45	98.31	

5.0 References

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5. **JMP™ Pro, Ver. 11.2.1,** [Computer Software] SAS Institute Inc., Cary, NC (2014).

6. Best, D. R., "Inductively Coupled Plasma-Atomic Emission Spectrometer, Agilent 730 ES," *Manual L29, Procedure ITS-0079,* Savannah River National Laboratory, Aiken, SC (2014).

Appendix A Tables Supporting the Chemical Composition Measurements

Table A-1. Measurements of the Study Glasses Prepared by LM

Preparation	Measurement	Identifier	Ca (wt %)	Cr (wt %)	K (wt %)	Mg (wt %)	Na (wt %)	Ni (wt %)	P (wt %)
1	1	LRM	0.326	0.136	1.22	<0.100	15.4	0.140	0.197
1	2	LRM	0.326	0.135	1.18	<0.100	15.3	0.136	0.208
1	1	T10-G-16A-1	4.72	0.204	0.303	0.556	13.4	<0.100	0.147
1	2	T10-G-16A-1	4.61	0.208	0.294	0.553	13.0	<0.100	0.148
2	3	LRM	0.321	0.133	1.25	<0.100	15.6	0.138	0.197
2	4	LRM	0.321	0.132	1.27	<0.100	15.8	0.135	0.204
2	3	T10-G-16A-1	5.06	0.199	0.290	0.542	14.3	<0.100	0.140
2	4	T10-G-16A-1	5.04	0.203	0.283	0.543	14.3	<0.100	0.143

Preparation	Measurement	Identifier	Pb (wt %)	S (wt %)	Sn (wt %)	V (wt %)	Zn (wt %)	Zr (wt %)
1	1	LRM	<0.100	<0.100	<0.100	<0.100	<0.100	0.583
1	2	LRM	<0.100	<0.100	<0.100	<0.100	<0.100	0.609
1	1	T10-G-16A-1	<0.100	0.351	<0.100	0.495	2.17	1.96
1	2	T10-G-16A-1	<0.100	0.353	<0.100	0.501	2.10	1.92
2	3	LRM	<0.100	<0.100	<0.100	<0.100	<0.100	0.585
2	4	LRM	<0.100	<0.100	<0.100	<0.100	<0.100	0.602
2	3	T10-G-16A-1	<0.100	0.345	<0.100	0.485	2.26	2.07
2	4	T10-G-16A-1	<0.100	0.347	<0.100	0.492	2.26	2.06

Table A-2. Measurements of the Study Glasses Prepared by PF

Preparation	Measurement	Identifier	Al (wt %)	B (wt %)	Fe (wt %)	Li (wt %)	Si (wt %)
1	1	LRM	5.07	2.53	1.00	<0.100	25.4
1	2	LRM	5.05	2.43	0.982	<0.100	25.4
1	1	T10-G-16A-1	4.95	3.76	0.683	<0.100	19.3
1	2	T10-G-16A-1	4.95	3.77	0.683	<0.100	19.3
2	3	LRM	4.92	2.31	0.944	<0.100	25.1
2	4	LRM	4.99	2.36	0.955	<0.100	25.6
2	3	T10-G-16A-1	4.73	3.57	0.627	<0.100	18.5
2	4	T10-G-16A-1	4.71	3.55	0.626	<0.100	18.5

Table A-3. Measurements of the Study Glasses Prepared by KH

Preparation	Measurement	Identifier	Cl (wt %)	F (wt %)
1	1	LRM	<0.010	0.814
1	2	LRM	<0.010	0.811
1	1	T10-G-16A-1	0.178	0.123
1	2	T10-G-16A-1	0.179	0.122
2	3	LRM	<0.010	0.857
2	4	LRM	<0.010	0.859
2	3	T10-G-16A-1	0.178	0.123
2	4	T10-G-16A-1	0.178	0.123

Table A-4. Comparison of Measured Values for LRM Reference Glass with SRNL Acceptability Limits

Element	Lower Acceptability Limit (wt %)	Upper Acceptability Limit (wt %)	Measurement Number (values in wt %)			
			1	2	3	4
Al	4.53	5.54	5.07	5.05	4.92	4.99
B	1.83	3.05	2.53	2.43	2.31	2.36
F	0	1.72	0.81	0.81	0.86	0.86
Fe	0	1.93	1.00	0.98	0.94	0.96
K	0.92	1.54	1.22	1.18	1.25	1.27
Na	13.37	16.35	15.44	15.34	15.61	15.76
Si	22.80	27.87	25.38	25.42	25.11	25.65
Zr	0	1.38	0.58	0.61	0.59	0.60

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