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Measurements of Sulfur Concentration with Lower Detection Limits in Simulated LAW Glasses

K. M. Fox

W. T. Riley

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REVIEWS AND APPROVALS

AUTHORS:

_____

K. M. Fox, Waste Form Processing Technologies Date

_____

W. T. Riley, Environmental Stewardship Directorate Operations Date

TECHNICAL REVIEW:

_____

D. L. McClane, Immobilization Technology, Reviewed per E7 2.60 Date

APPROVAL:

_____

C. C. Herman, Director, Waste Form Processing Technologies Date

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EXECUTIVE SUMMARY

This report provides sulfur concentration measurements for several simulated low-activity waste glass compositions. The Pacific Northwest National Laboratory (PNNL) selected and fabricated these glasses as part of a study on sulfur retention in glass. Methods were selected to achieve a lower detection limit for SO_3 than previously reported. The measured SO_3 concentrations of the glasses range from 0.036 to 0.130 wt %. These results will be used by PNNL in the development of improved property/composition models for LAW glass production at Hanford.

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LIST OF ABBREVIATIONS

DOE	U.S. Department of Energy
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
HLW	High-Level Waste
LAW	Low-Activity Waste
LRM	Low-level Reference Material
ORP	Office of River Protection
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 program. 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 regulations. 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] Two of these areas are enhancing waste glass property/composition models and broadening the compositional regions over which those models are applicable.

In this report, SRNL provides chemical analysis for several simulated LAW glass compositions with the intent of measuring lower concentrations of sulfur than previously reported for these glasses. The Pacific Northwest National Laboratory (PNNL) selected and fabricated these glasses as part of a study on sulfur retention. The resulting data will be used in the development of improved property/composition models for LAW glass production at Hanford.

2.0 Experimental Procedure

2.1 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. Laboratory data for this study were recorded in the SRNL Electronic Laboratory Notebook system, experiment C3489-00079-21.

2.2 Glasses Selected for Study

The glass compositions in this study were selected and fabricated at PNNL. Identifiers for each of the 12 glasses are listed in Table 2-1. The suffix "Q" indicates that these glasses were quenched after melting. Each of these glasses targeted a relatively low concentration of SO_3 (0.10 to 0.61 wt %). In previous analyses at SRNL, the sulfur concentrations of these glasses were reported to be below detection limits.[2,3] This limits the utility of these data in sulfur solubility modeling efforts. Therefore, it was of interest to modify the analysis approach to achieve lower detection limits for sulfur.

In the sections that follow, the methods used for measuring the sulfur concentrations (with reduced detection limits) of the glasses are described and brief reviews of the resulting data are provided.

Table 2-1. Glass Identifiers Included in This Study

Glass ID
EWG-LAW-New-OL-8445Q
EWG-LAW-New-OL-8788ModQ
EWG-LAW-New-OL-14844Q
EWG-LAW-New-OL-15493Q
EWG-LAW-New-OL-17130Q
EWG-LAW-New-OL-45748Q
EWG-LAW-New-OL-54017Q
EWG-LAW-New-OL-57284Q
EWG-LAW-New-OL-62380Q
EWG-LAW-New-OL-62909ModQ
EWG-LAW-New-OL-65959ModQ
EWG-LAW-New-OL-127708ModQ

2.3 Glass Composition Analysis

Chemical analysis was performed on a representative sample of each of the glasses listed in Table 2-1 to allow for comparisons with the targeted sulfur concentrations. Each sample was prepared for analysis via an Aqua Regia digestion. Briefly, hydrochloric acid and nitric acid were added to a small amount of finely ground glass sample. The mixture was heated to 90 °C for about 1 hour, and then diluted with deionized water. Use of this method minimized the needed dilutions, allowing for lower detection limits. Each of the prepared samples was analyzed twice for sulfur concentration by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).[4]

A sample of the low-level reference material (LRM)[5] glass was included as a check of the performance of the ICP-AES instrument. The LRM composition reported as the "Consensus Average" is used as the reference composition of this glass for the purposes of this study.[5]

3.0 Results and Discussion

Table 3-1 provides the elemental sulfur concentration measurements for the study glasses. The duplicate measurements for each prepared glass sample are shown. Elemental measurements for the LRM glass are also included in the table for reference. The duplicate sulfur measurements were converted to oxide concentrations using the appropriate gravimetric factor and averaged to determine a representative SO_3 concentration for each glass. The targeted concentrations of SO_3 are provided for comparison.

The preparation and measurement methods used provided a detection limit of about 0.001 wt % SO_3. All of the study glasses had measurable SO_3 concentrations via these methods. Five of the study glasses have measured SO_3 concentrations (0.077 to 0.101 wt % SO_3) that are near the targeted value of 0.1 wt %. Four of the study glasses have measured SO_3 concentrations (0.044 to 0.054 wt % SO_3) that are lower than the targeted value of 0.1 wt %. Measured SO_3 concentrations for two of the study glasses were above (0.127 to 0.130 wt % SO_3) the targeted value of 0.1 wt %. Glass EWG-LAW-New-OL-127708ModQ has a higher targeted SO_3 concentration of 0.610 wt %, yet its measured value was only 0.036 wt %. The lower measured values may be due to lack of sulfur solubility in those glass compositions, or volatility during melting.

Table 3-1. Measured and Targeted SO_3 Concentrations for the Study Glasses

Sample ID	Lab ID	Measured S (mg/kg)	Measured SO_3 (wt %)	Targeted SO_3 (wt %)
LRM	S-7571	909	0.226	0.300
	S-7571	904		
EWG-LAW-New-OL-8445Q	S-7572	399	0.099	0.100
	S-7572	397		
EWG-LAW-New-OL-8788ModQ	S-7573	382	0.095	0.100
	S-7573	382		
EWG-LAW-New-OL-14844Q	S-7574	539	0.130	0.100
	S-7574	502		
EWG-LAW-New-OL-15493Q	S-7575	517	0.127	0.100
	S-7575	500		
EWG-LAW-New-OL-17130Q	S-7576	403	0.101	0.100
	S-7576	405		
EWG-LAW-New-OL-45748Q	S-7577	216	0.054	0.100
	S-7577	217		
EWG-LAW-New-OL-54017Q	S-7578	353	0.087	0.100
	S-7578	347		
EWG-LAW-New-OL-57284Q	S-7579	310	0.077	0.100
	S-7579	311		
EWG-LAW-New-OL-62380Q	S-7580	175	0.044	0.100
	S-7580	180		
EWG-LAW-New-OL-62909ModQ	S-7581	207	0.051	0.100
	S-7581	203		
EWG-LAW-New-OL-65959ModQ	S-7582	238	0.060	0.100
	S-7582	243		
EWG-LAW-New-OL-127708ModQ	S-7583	144	0.036	0.610
	S-7583	147		

4.0 Summary

In this report, SRNL provides sulfur concentration measurements for several simulated LAW glass compositions with detection limits that are lower relative to those of previous analyses. PNNL selected and fabricated these glasses as part of a study on sulfur retention in LAW glasses. Chemical analyses were performed on a representative sample of each of the study glasses to allow for comparisons with the targeted compositions. Aqua Regia was used for preparing each of the glass samples for analysis. Each of the samples was analyzed twice for sulfur concentration by ICP-AES. A glass standard was also measured as a check of the performance of the analytical instruments. Average SO_3 concentrations for each of the glass compositions were determined and reported. Sulfur was detectable in each of the glass samples using these preparation and analysis methods. Most of the measured SO_3 concentrations agreed reasonably with the targeted values. These results will be used by PNNL in the development of improved property/composition models for LAW glass production at Hanford.

5.0 References

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