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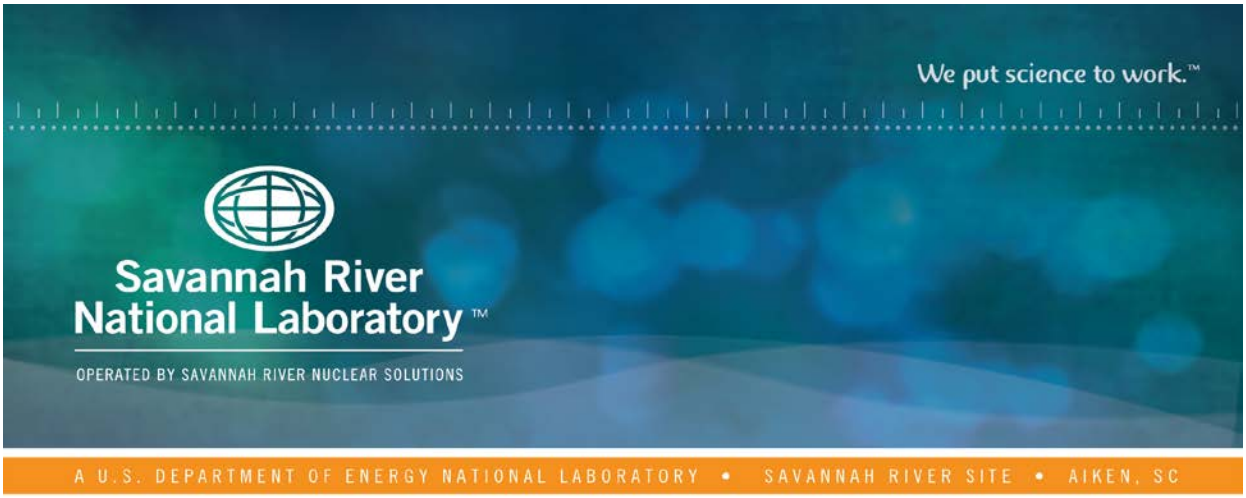

Reduced Sample Masses for Characterization of Simulated Hanford Low-Activity Waste Glasses

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

In this report, a method for preparing a smaller mass of simulated low-activity waste glass for anion measurements is demonstrated. The required mass of sample was reduced from 1.0 g to 0.2 g. This method will be used in future studies to reduce the amount of time and effort needed to produce sulfur saturated glasses for characterization.

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LIST OF ABBREVIATIONS

DOE	U.S. Department of Energy
IC	Ion Chromatography
HLW	High Level Waste
KH	Potassium hydroxide digestion
LAW	Low Activity Waste
LRM	Low-level Reference Material
ORP	Office of River Protection
PNNL	Pacific Northwest National Laboratory
ppm	Parts Per Million
PSAL	Process Science Analytical Laboratory
Q	Quenched
SRNL	Savannah River National Laboratory
SSM	Sulfur Saturated Melt
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 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.

More specifically, SRNL is supporting the Pacific Northwest National Laboratory (PNNL) in gathering composition data for simulated LAW glasses to develop the basis for improved sulfur solubility models.[2-8] Fabrication of glasses for this effort, referred to as sulfur saturated melts (SSMs), includes grinding, washing, and vacuum filtering steps that are relatively labor intensive and time consuming. About 4 g of glass are produced in each iteration of the grinding, washing, and filtering process.[4,9] The process is typically performed twice for each glass composition to ensure that sufficient glass is available for characterization. Fabrication of smaller masses of the glasses would be advantageous from a cost and schedule perspective, but requires that subsequent characterization methods be viable with smaller quantities of glass. Anion concentration measurements at SRNL have used a potassium hydroxide fusion preparation method (referred to as KH) followed by ion chromatography (IC) measurements.[10,11] This method consumes at least 1 g of glass sample per preparation, and samples are typically prepared in duplicate. In this report, an alternative preparation method is demonstrated that reduces the mass of glass sample needed to 0.2 g per preparation.

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 C3489-00079-22. The glasses provided by PNNL were fabricated following Test Instructions EWG-TI-0056, EWG-TI-0057, and EWG-TI-0060.

2.2 Glasses Selected for Study

Two baseline (air quenched, abbreviated as Q) glass compositions fabricated at PNNL were selected from a concurrent task to support the study described in this report.[8] These glasses were selected because their targeted compositions include Cl and F concentrations that should be above detection limits. The identifiers of the glasses selected are LP2-OL-07-1Q and LP2-OL-12Q.

2.3 Sample Preparation and Measurement

The KH preparation method[10] was modified by the SRNL Process Science Analytical Laboratory (PSAL) to reduce the required mass of sample from 1.0 g to 0.2 g. The amount of potassium hydroxide was reduced

to obtain the same ratio of sample to KOH as in the original method. The mixtures were heated to 375 °C for at least 15 minutes, then dissolved in water and diluted to 50 mL.

A sample of the low-level reference material (LRM)[12] was also prepared via the modified KH method to serve as a benchmark in the analyses. The LRM composition reported as the "Consensus Average" is used as the reference composition of this glass for the purposes of this study.[12]

Each prepared sample was measured twice by IC for Cl^- and F^- concentrations with the instrument being recalibrated between the duplicate measurements.[11] The instrument was calibrated between 0.1 ppm and 5 ppm and the samples were run at a 10x dilution.

3.0 Results and Discussion

The measured fluorine and chlorine anion concentrations for the study glasses prepared by the modified KH method are shown in Table 3-1. The two individual measurements for each glass are shown, along with the mean of the duplicate measurements. Measurements for the LRM glass are also included in the table. On the right side of Table 3-1, measured fluorine and chlorine anion concentrations reported earlier[8] for the same glasses prepared with the original KH method are shown. In the earlier study, each of these glasses was prepared twice and each of the prepared solutions was measured twice, for a total of four measurements. Each pair of measurements is shown in Table 3-1, along with the mean values of the four measurements. Multiple measurements of the LRM glass were made as part of the earlier study; the mean values from the two sets of measurements are shown in the table for simplicity.[a] Comparisons to the targeted concentrations of fluorine and chlorine for the study glasses are not made in this study due to the volatility of these constituents during the melting process.[b]

A review of the data in Table 3-1 shows that the duplicate measurements of fluorine and chlorine for the study glasses and LRM prepared by the modified KH method are reasonably consistent. The mean measured fluorine concentration for LRM is within 15% of the consensus average value of 0.86 weight percent (wt %),[12] and is also within the PSAL quality control range of 0 - 1.72 wt %.[13]

Given the relatively low targeted concentrations of these constituents in the glasses, differences among the measured values of 15% or less are considered to be within the limits of the measurement methodology. Comparisons of the mean measured values of fluorine and chlorine for the study glasses by the two preparation methods show no differences greater than 15%. Therefore, the modified KH method can be considered sufficient for preparing future simulated Hanford LAW glasses for fluorine and chlorine anion concentration measurements.

[a] Refer to SRNL-STI-2018-00150 for detail of the use of the LRM glass throughout the earlier study.
[b] Comparisons of the targeted and measured values of these analytes are provided in SRNL-STI-2018-00150.

Table 3-1. Measurements of Fluorine and Chlorine Concentrations in the Study Glasses

Glass ID	Modified KH Preparation Method (This study)		Original KH Preparation Method (Reported in SRNL-STI-2018-00150)	
	F^- (wt %)	Cl^- (wt %)	F^- (wt %)	Cl^- (wt %)
LP2-OL-07-1Q	0.125 0.126 0.126 (mean)	0.238 0.224 0.231 (mean)	0.124 0.126 0.107 0.130	0.196 0.208 0.210 0.203
			0.122 (mean)	0.204 (mean)
LP2-OL-12Q	0.669 0.679 0.674 (mean)	0.376 0.376 0.376 (mean)	0.573 0.592 0.574 0.604	0.339 0.349 0.338 0.367
			0.586 (mean)	0.348 (Mean)
LRM	0.971 0.970 0.971 (mean)	<0.025 <0.025 <0.025 (mean)	0.870 (mean, Set 1)	<0.05 (mean, Set 1)
			0.908 (mean, Set 2)	<0.05 (mean, Set 2)

4.0 Summary

Fabrication of sulfur saturated melts using simulated LAW glasses is relatively labor intensive and time consuming. Fabrication of smaller masses of the glasses would be advantageous from a cost and schedule perspective, but requires that subsequent characterization methods be viable with smaller quantities of glass. This study demonstrated that a modified potassium hydroxide fusion sample preparation method can produce results with 0.2 g of sample mass that are similar to those produced via an earlier method that consumed 1.0 g of sample. Measurements generated by the two preparation methods differed by less than 15%. These differences were considered to be within the limits of the measurement methodology given the relatively low targeted concentrations (typically less than 1 wt %) of the anions of interest in the study glasses. The modified preparation method can be considered sufficient for preparing future simulated Hanford LAW glasses for fluorine and chlorine anion concentration measurements and reduces the mass of sample needed.

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