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# Production and Performance of High Sulfur Concentration Waste Glasses - FY21


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# REVIEWS AND APPROVALS

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# EXECUTIVE SUMMARY

In FY21 Savannah River National Laboratory (SRNL) was tasked to investigate the practical aspects of low activity waste (LAW) glass production with high sulfur loading for the Office of River Protection (ORP). Relationships between sulfur solubility, retention, and melter resonance need to be evaluated to refine waste loading limits and the super saturated melting (triple melt, grind, and wash) methodology. The impact of high sulfur concentration on durability and phase stability (crystallization and liquid-liquid immiscibility) during slow cooling also needs to be further evaluated. To accomplish this, SRNL proposed scaled melter testing using simulants with matched physicochemical properties to melter feed, as opposed to laboratory reagents. This type of testing is expected to validate applicability to design parameters and functional criteria expected during unit operations.

This work was expected to commence in FY21, with the first melter tests being performed near the end of the FY. However, reduced access to Savannah River Site and personnel availability during the COVID-19 pandemic significantly reduced the amount of time and resources available to perform the task. This report documents the experimental plan and progress towards this task. The following is a summarized list of scheduled testing that will be performed on feed, condensate, cold cap and glass:

- Melter runs
- Product consistency test (PCT)
- Inductively coupled plasma optical emission spectroscopy (ICP-OES)
- Optical (OM) and scanning electron microscopy (SEM)

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| DAS | Data Acquisition System |
| DFLAW | Direct-Feed Low Activity Waste |
| FTIR | Fourier-Transform Infrared Spectroscopy |
| GFC | Glass Forming Chemical |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectroscopy |
| LAW | Low Activity Waste |
| MS | Mass Spectrometer |
| OM | Optical Microscopy |
| ORP | Office of River Protection |
| PCT | Product Consistency Test |
| QMRF | Quartz Melt Rate Furnace |
| SEM | Scanning Electron Microscopy |
| SRNL | Savannah River National Laboratory |
| TOC | Total Organic Carbon |
| WTP | Waste Treatment and Immobilization Plant |

## 1.0 Introduction

Due to the high corrosivity of sulfate salts, models have been developed to mitigate sulfate segregation in Hanford Tank Waste Treatment and Immobilization Plant (WTP) melters[1-3]. Several studies at Savannah River National Laboratory (SRNL) and the Vitreous State Laboratory (VSL) have also investigated the solubility of sulfur in waste glass in order to validate these models and create a validation method at a laboratory scale[4]. Thus far there has been a disparity between the thermodynamic solubility limit in laboratory crucible testing and the measured retained sulfur content in large scale test reactors, with larger retention values corresponding to larger scale testing. This work will investigate the sulfur retention in waste glasses and elucidate the cause of the difference between crucible and melter testing.

## 2.0 Experimental Plan

This study is investigating the total sulfur content of simulated low activity waste (LAW) glasses produced under operating conditions at an intermediate scale. To do this, a semi-closed system utilizing the quartz melt rate furnace (QMRF) was built which melts LAW simulant and glass forming chemicals (GFCs) in a quartz vessel. The vessel is connected to the feed, purge air, off-gas, and temperature monitoring systems by ground glass joints located at the top of the vessel. Off-gas sampling monitors for sulfur species, and sulfur retained in the melt and cold cap are characterized post-test. This will give a more accurate retained sulfur content and provide a quantitative analysis of any off-gassing sulfur species. A detailed schematic is shown in Figure 2-1.

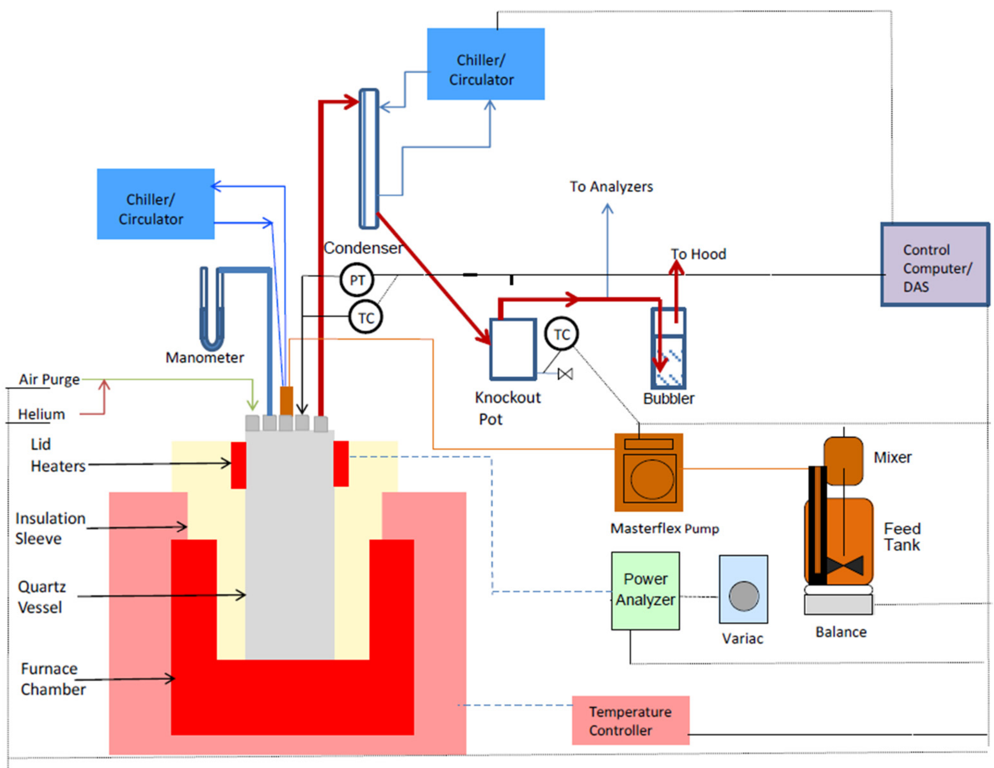


**Figure 2-1. Schematic of the Quartz Melt Rate Furnace**

### 2.1 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[5].

# 3.0 Results

3.1 <u>Composition selection</u>

LAW feed simulants and GFCs were selected from composition matrices developed for the Hanford Direct-Feed Low Activity Waste (DFLAW) program with the combined predicted oxide composition evaluated against LAW glasses previously studied at SRNL and VSL[3,4,6,7]. LAWA187 was selected as a primary target composition of interest as the sulfur retention in this composition has been calculated or measured by several methods[4]. LAW-1 and GFC-6 were selected on this criteria, and LAW-6, GFC-9, and GFC-11 were chosen as additional feed compositions representative of Hanford LAW glasses. By combining these selected LAW simulants and GFCs at least 10 Hanford LAW glasses can be studied. Compositions are contained in Appendix A.

3.2 <u>Furnace Assembly</u>

QMRF assembly was completed and passed SRNL's Final Acceptance Inspection (OSR 20-22). Figure 3-1 is an overview of the QMRF.

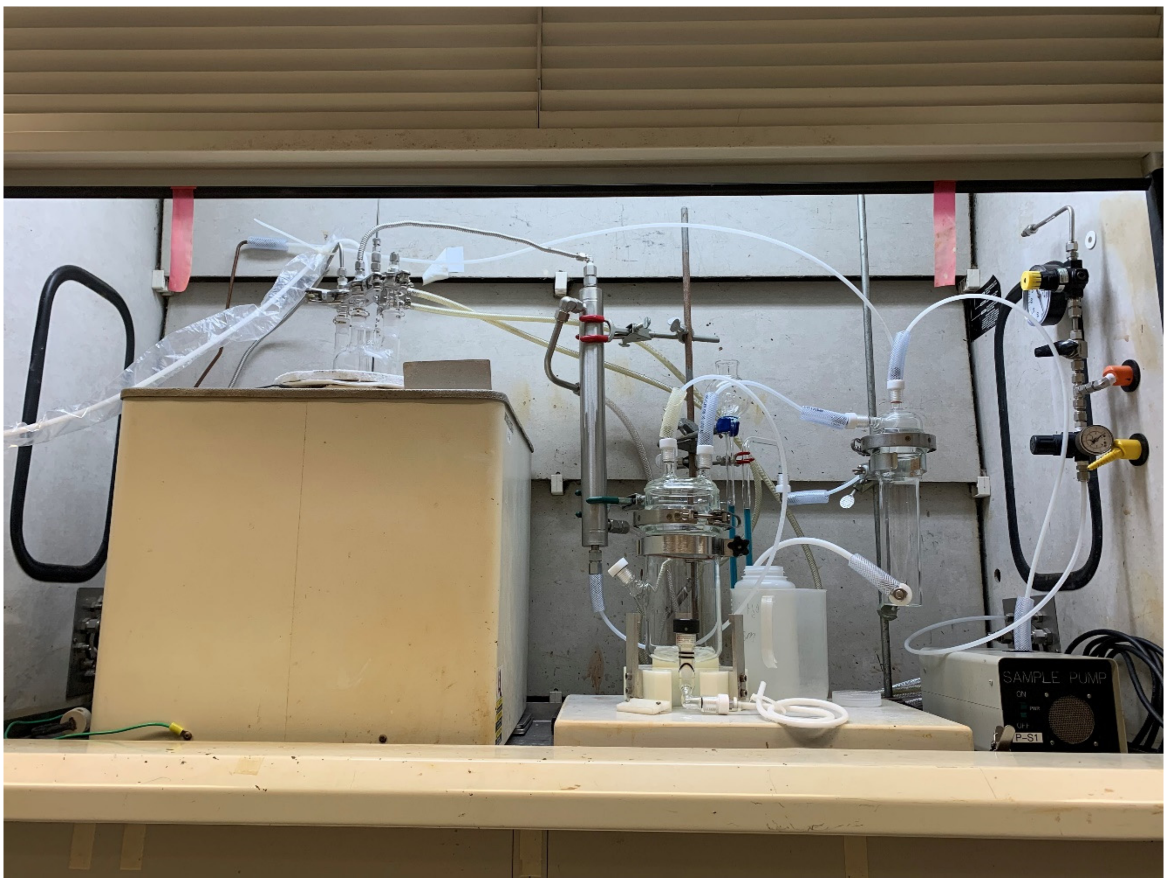


**Figure 3-1. Assembled Quartz Melt Rate Furnace**

*3.2.1 Quartz Vessel*

Six quartz vessels have been made by SRNL's glass shop. Figure 3-2 shows the top of the quartz vessel and ports for the feed system, purge air system, off-gas system, and vapor space thermocouple. There is an additional port that is capped in this design but is available if additional parameters are selected for *in situ* measurement such as redox or vessel pressure.

**Figure 3-2. Detail of the ports connecting the quartz vessel to each system.**

*3.2.2 Feed System*

The feed system (Figure 3-3) consists of a mixer, feed tank, digital scale, peristaltic pump, and water-cooled feed tube. Slurry is mixed in the feed tank atop the digital scale (Figure 3-3 A). A Data Acquisition System (DAS) controls the pump speed and records the mass change of the scale to determine feed rate. Slurry is pumped (Figure 3-3 B) into the quartz crucible through a water-cooled feed tube. This tube prevents the slurry from drying in the tube and creating a blockage.

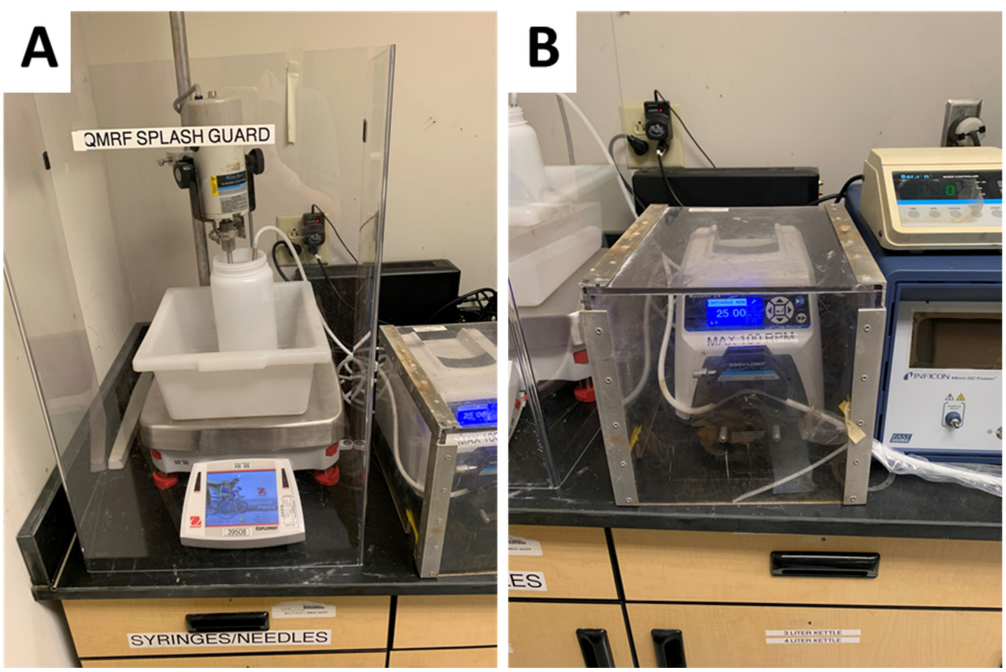


**Figure 3-3. (A) Feed mixer and (B) peristaltic pump.**

*3.2.3 Purge Air System*

The purge air system serves as a dilution air supply and pressure protection for the QMRF. Dry air (~1000 ppm $H_2O$) is supplied by metal tubing with an offshoot routed to a manometer to protect against over pressurization of the system. Helium is used as a tracer gas in the purge system at 5-10 sccm to calculate air flow.

*3.2.4 Furnace and Heaters*

The quartz vessel is primarily heated from the bottom by a Lindberg/BlueM CF56822C Crucible Furnace which is set to 1150 °C. The vapor space is heated by a clam shell heater which is controlled by a Variac potentiometer and monitored by a calibrated type K thermocouple inserted through a port at the top of the vessel. As most of the vessel sits above the furnace body, the area around the ports is packed with fiber insulation to minimize heat loss (not shown in Figures).

*3.2.5 Off-gas system*

The off-gas system connects the quartz vessel to the off-gas sampling system consisting of a mass spectrometer (MS) and Fourier-transform infrared spectrometer (FTIR). Off-gas is first routed through a water-cooled condenser to a knockout pot which retains condensate for analysis post-experiment. The off-gas sampling pump is connected to the line before the off-gas is vented through a bubbler. Figure 3-4 shows the assembled off-gas system.

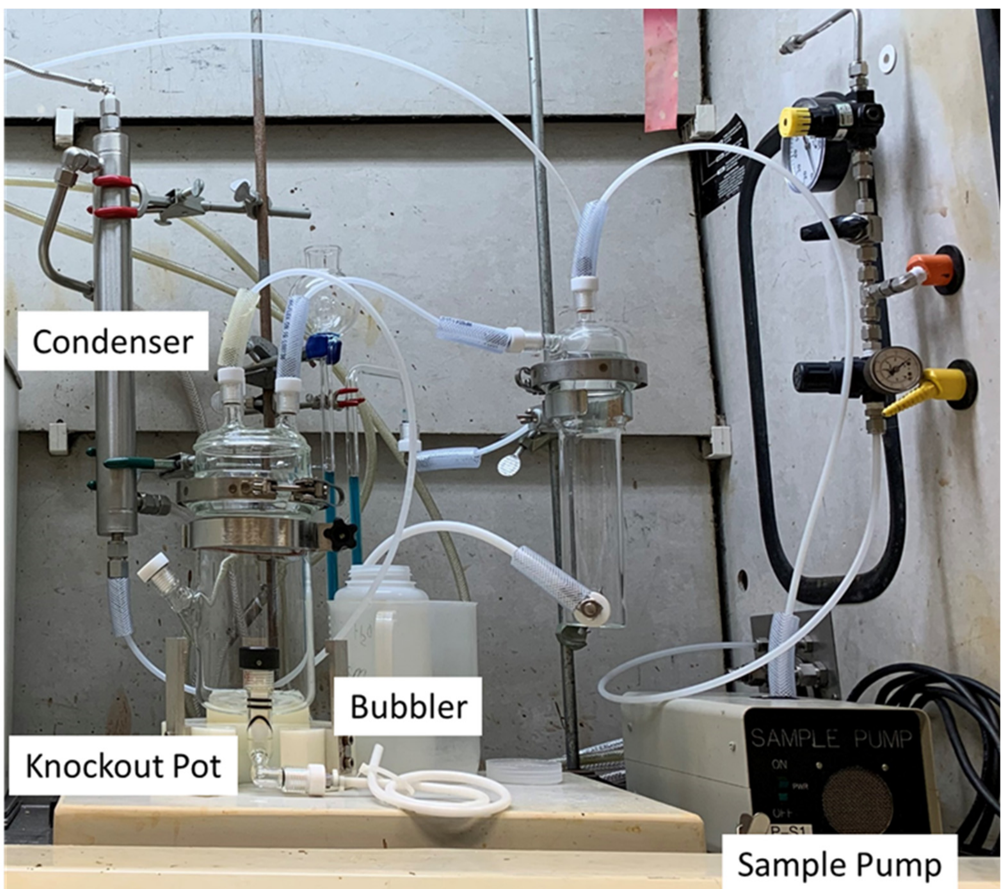


**Figure 3-4. Assembled off-gas system.**

## 4.0 Conclusions

Furnace assembly is complete and Final Acceptance Inspection (OSR 20-22) has been complete per Procedure 8Q,51. Initial QMRF operation is scheduled for early October 2021 beginning with a water run followed by 5 compositions which will be completed by the end of the month. Characterization of feed, condensate, cold cap, and glass will follow in late October and be completed in November. The techniques planned are ICP-OES, PCT, OM, and SEM. Glass samples will be washed to dissolve segregated sulfate salts and distinguish between present sulfur species.

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## Appendix A. Composition Tables

### Table A-1. Targeted GFC Compositions (wt%)

| | $Al_2O_3$ | $B_2O_3$ | CaO | $Li_2O$ | MgO | $SiO_2$ | $SnO_2$ | $V_2O_3$ | ZnO | $ZrO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **GFC-6** | 16.4% | 13.2% | 12.6% | 6.1% | 0.0% | 51.7% | 0.0% | 0.0% | 0.0% | 0.0% |
| **GFC-9** | 5.5% | 11.9% | 13.6% | 0.0% | 0.0% | 53.4% | 0.0% | 0.0% | 6.9% | 8.6% |
| **GFC-11** | 10.4% | 8.5% | 5.2% | 2.8% | 3.2% | 56.9% | 2.3% | 4.6% | 2.5% | 3.6% |

### Table A-2. LAW Feed Simulant Compositions (Molar)

| | TOC | Na | $NO_3$ | $NO_2$ | $CO_3$ | OH | $AlOH_4$ | K | $SO_4$ | Cl | $PO_4$ | $CrO_4$ | $C_2O_4$ | F |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **LAW-1** | 0.123 | 5.432 | 2.187 | 0.962 | 0.471 | 1.161 | 0.117 | 0.195 | 0.043 | 0.076 | 0.018 | 0.006 | 0.004 | 0.021 |
| **LAW-6** | 0.123 | 5.32 | 1.938 | 1.055 | 0.394 | 1.331 | 0.124 | 0.179 | 0.051 | 0.069 | 0.018 | 0.007 | 0.003 | 0.02 |

**Distribution:**

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