

**Contract No. and Disclaimer:**

**This manuscript has been authored by Savannah River Nuclear Solutions, LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.**

## **Retention of Sulfate in High Level Radioactive Waste Glass**

Amanda L. Billings\* and Kevin M. Fox\*†  
Savannah River National Laboratory  
Aiken, South Carolina 29808

### **Abstract**

High level radioactive wastes are being vitrified at the Savannah River Site for long term disposal. Many of the wastes contain sulfate at concentrations that can be difficult to retain in borosilicate glass. This study involves efforts to optimize the composition of a glass frit for combination with the waste to improve sulfate retention while meeting other process and product performance constraints. The fabrication and characterization of several series of simulated waste glasses are described. The experiments are detailed chronologically, to provide insight into part of the engineering studies used in developing frit compositions for an operating high level waste vitrification facility. The results lead to the recommendation of a specific frit composition and a concentration limit for sulfate in the glass for the next batch of sludge to be processed at Savannah River.

### **Introduction**

The production of nuclear material during the cold war has left a large volume of high-level radioactive waste (HLW) that must be safely treated for long term disposition. The U.S. Department of Energy is stabilizing this waste at the Savannah River Site (SRS) by combining it with an alkali-borosilicate glass frit and melting in a joule-heated melter to produce a durable glass waste form. The waste contains a broad array of elements resulting from fuel dissolution and separations operations, radioactive decay, and corrosion management. The major constituents of wastes at SRS are iron, aluminum and sodium. Several of the wastes also contain sulfate at concentrations that can be difficult to incorporate into a borosilicate glass.

The relatively low solubility of sulfur in the borosilicate glass system provides several challenges for waste vitrification. In particular, the potential formation of a low viscosity, sulfate-rich salt layer on top of the melt pool could result in volatility issues and impacts to off-gas systems, potential electrical shorting of a joule-heated melter, and accelerated corrosion of refractories at the melt line.<sup>1-3</sup> Precipitation of a high sulfate concentration phases may occur during cooling. Radioactive cesium may also partition to sulfate

---

\* Member, The American Ceramic Society

† kevin.fox@srl.doe.gov

salt surface layers on molten glass, leading to further volatility issues.<sup>4</sup> A sulfate concentration limit of 0.40 wt %  $\text{SO}_4^{2-}$  was originally imposed for HLW glass produced at SRS in order to avoid any segregation of sulfate to the surface of the melt.<sup>2, 5</sup> This limit has been increased to 0.60 wt %  $\text{SO}_4^{2-}$  for more recent sludge processing, with the recognition that the limit is composition dependent.<sup>6-8</sup> Projections of future waste compositions that will be vitrified at SRS indicate that this limit may need to be increased further (perhaps to 1.0 wt %  $\text{SO}_4^{2-}$  or greater) in order to meet waste loading and production rate goals.

The complex nature of HLW glasses makes it difficult to study the solubility of individual components. A typically HLW glass may contain 20 to 30 elements present in appreciable concentrations, several of which may have mixed influences on the retention of sulfate.<sup>9, 10</sup> The development of frit or glass compositions for waste vitrification provides the greatest opportunity to influence sulfate retention, along with several other properties of the glass waste form.<sup>11</sup> Frits used for SRS wastes typically consist of  $\text{B}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$  in varying ratios.<sup>12, 13</sup> While the work detailed here focuses on sulfate retention, other factors, such as anticipated rate of melting, ability to tolerate variation in the waste composition, manufacturability, avoidance of detrimental crystallization, and chemical durability are also part of the frit optimization process for each waste batch.<sup>11</sup>

This study consists of largely empirical investigations into the impact of frit composition on sulfate retention using crucible-scale, non-radioactive melts and observing the retention of sulfate via visual observations (a rapid screening method), chemical analysis, X-ray diffraction, and chemical durability testing. The work is presented chronologically to show the evolution of the technical and practical constraints that must be met in research efforts that are closely tied to implementation. The intent is to provide some perspective to the reader on one aspect (sulfate retention) of the engineering studies that are involved with frit development for the world's largest operating HLW vitrification facility.

## **Experimental Procedures and Observations**

This study was broken into several separate but related parts that will be described individually below. High level waste, in the form of a liquid and sludge slurry, is stored in large, underground steel tanks at the SRS. Various compositions of waste from these tanks are mixed and blended to form a uniform batch in preparation for vitrification. During the preparation of a sludge batch, which takes six to twelve months, a glass frit is designed that, when mixed with the waste and melted, will produce a glass waste form that is

acceptable for processing within the facility and for long term storage in a repository. The studies described below follow the progression of this process as waste composition projections are refined and other technical constraints are imposed.

#### *Influence of B<sub>2</sub>O<sub>3</sub> and CaO Using Factorial Designs*

Projected compositions for Sludge Batch 6 (SB6), the next waste batch to be vitrified at the Defense Waste Processing Facility (DWPF) at SRS were received in late 2009. An example composition is given in Table 1. Also included in the table is a version of the SB6 composition projection with uranium removed, the sulfate concentration forced to 3.0 wt % (to give a bounding concentration of 1.2 wt % SO<sub>4</sub><sup>2-</sup> in glass at 40 wt % waste loading), and the remaining components normalized to a total of 100 wt %. This modified projection formed the basis of the first series of experiments. Increased concentrations of alkaline earth oxides in the frit, including CaO, are thought to improve sulfate retention in HLW glass.<sup>9, 14, 15</sup> The first series of experiments used a 2<sup>3</sup> factorial design to determine how these influences extended to SB6 glasses, including the impacts of B<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O concentrations in the frit. A range of potential frit compositions were combined with the SB6 projection and evaluated using the DWPF Product Composition Control System (PCCS) models, which predict the properties and performance of a HLW glass based on its composition.<sup>16</sup> Nine candidate frit compositions were down-selected from the model prediction results and/or their ability to satisfactorily fill the 2<sup>3</sup> design, and their compositions are described in Table 2 (Frits A through I). Figure 2 provides a plot of these nine frits on the cube representing the 2<sup>3</sup> design. Glasses representing each of the frit and sludge compositions were fabricated by blending the appropriate masses of oxides, carbonates and boric acid, and melting in air at 1150 °C for one hour in platinum/gold crucibles with lids. The glasses were cooled in air in the crucibles. The formation of any sulfate-rich salt layer on top of the glasses was indicated by a white or yellow film. An example of this film on the surface of a glass is shown in Figure 1. Minor surface crystallization, typical of HLW glasses at higher waste loadings, was indicated by a mirror-like surface finish. The symbols in Figure 2(a) indicate the visual observations of each glass after cooling, and show that increased concentrations of B<sub>2</sub>O<sub>3</sub> and CaO in the frit, either individually or combined, appear to improve sulfate retention in this system. Higher Na<sub>2</sub>O concentrations in the frit generally decreased sulfur retention, unless both B<sub>2</sub>O<sub>3</sub> and CaO were included at higher concentrations. Figure 2(b) shows the results of the next set of experiments, where the same frit

compositions were used, but the waste composition was adjusted to give 1.4 wt %  $\text{SO}_4^{2-}$  in glass at 40 wt % waste loading. Only the four frit compositions that produced glasses free of a sulfate layer in Figure 2(a) were included in these experiments. The results in Figure 2(b) show that all of the glasses had a sulfate layer after cooling, potentially indicating that the limit for complete sulfate retention in this system had been exceeded.

Next, increases in the concentrations of the major waste components were used to further evaluate the impacts of potential variation in the waste composition on sulfate retention. The concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$  in the waste were increased by 7.5% (representative of the compositional and analytical uncertainty typically seen during processing of a waste batch at the DWPF), the uranium component was again removed, sulfate was forced to 3.0 wt % (to give 1.2 wt %  $\text{SO}_4^{2-}$  in glass at 40 wt % waste loading), and the remaining components were normalized to a total of 100 wt % (Table 1). The glasses at the base and along the diagonal of the  $2^3$  cube design were fabricated and observed after cooling, and the results are provided as Figure 3. All of these glasses had a visible sulfate layer on the surface after cooling except for those made with the higher CaO and lower  $\text{Na}_2\text{O}$  concentration frits. While individual component effects are difficult to establish using this technique, the increased  $\text{Na}_2\text{O}$  concentration from the waste in these glasses was considered to be the most likely cause of the reduced sulfate retention. Frit D in Table 2, which has the higher  $\text{B}_2\text{O}_3$  and CaO concentrations with the lower  $\text{Na}_2\text{O}$  concentration, was considered to be the best performer in terms of improving sulfate retention throughout the factorial design experiments and was carried forward into the next series of tests.

#### *Influence of Waste Composition Variation*

The influence of variation in the concentrations of the waste components was studied in further detail. Frit D, as described above, was used to vitrify the simulated waste in this portion of the study along with one additional frit, Frit D2, which contained additional  $\text{B}_2\text{O}_3$  in exchange for CaO (Table 2). Variation was applied to the SB6 composition projection given in Table 1 using +/- 7.5% around the concentrations of the major components ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , MnO,  $\text{Na}_2\text{O}$ , NiO, and  $\text{SiO}_2$ ), +/- 0.5 wt % around the concentrations of the minor components (CaO and MgO), and +/- 0.25 wt % around the sum of the remaining components (referred to as Others). These concentration intervals define a region for the potential waste composition that is intended to bound compositional variation during processing. The  $\text{U}_3\text{O}_8$  component was removed,

and the  $\text{SO}_4^{2-}$  concentration was fixed at 2.5 wt % (to give 1 wt %  $\text{SO}_4^{2-}$  in glass at 40 wt % waste loading). Individual waste compositions were then selected from this region to support the variation study. Initially, the Custom Design feature of the Design of Experiment platform in JMP Version 7.0.2 (SAS Institute, Cary, NC) was used to select ten waste compositions satisfying the concentration intervals described above. This JMP feature allows the user to specify the form of a model, such as a linear model consisting of a term for each of the nine oxides identified above and Others. Then the JMP coordinate exchange algorithm was used to optimally select a specified number of design points,  $n$  (where  $n \geq 10$ ), for this model from the region defined by the composition intervals, with the intervals being specified in JMP during the design activity. The optimality criterion used in this case was D-optimality, which has the goal of minimizing  $|(X^T X)^{-1}|$ , where  $X$  is the design matrix,  $X^T$  indicates the transpose of  $X$ ,  $(X^T X)^{-1}$  indicates the matrix inversion of the product of  $X^T$  and  $X$ , and  $|(X^T X)^{-1}|$  represents the determinant of the matrix  $(X^T X)^{-1}$ . In the task, the number of design points,  $n$ , was taken to be its smallest possible value, ten. The centroid, or average of the ten optimal points, was also included.

In total, 22 glasses were fabricated by combining the 11 waste compositions (10 optimally selected compositions from the variation region and the centroid) with the Frits D and D2, using the batching and melting methods described above. Samples of each of the glasses were heat treated to simulate slow cooling along the center of a DWPF-type stainless steel canister to evaluate any impacts that this may have on crystal formation and chemical durability.<sup>17</sup> Portions of each glass were dissolved using a lithium metaborate fusion and a sodium peroxide fusion. The resulting solutions were analyzed via ICP-AES (Perkin-Elmer 403, Waltham, MA) to confirm that the glass compositions met the targets. Samples of each of the glass were also subjected to the ASTM C-1285 Product Consistency Test (PCT) to determine whether the increased sulfate concentrations had an impact on their chemical durability.

No sulfate layer was visible on any of the glasses after melting and quenching. All of the glasses had a translucent, semi-reflective surface indicative of minor spinel crystallization. This type of crystallization is typically of no concern since spinels have little impact on the chemical durability of a HLW borosilicate glass.<sup>18</sup> X-ray diffraction detected no crystallization in the bulk glasses. Although not shown in detail here, the chemical composition measurements indicated no issues with meeting the target concentrations of each

component. The measured concentrations of sulfate in each glass are given in Table 3. The results show good retention of sulfate within the glasses, with minor losses likely due to volatility during melting.

The results of the PCT for the quenched and slowly cooled glasses are given in Table 3. The values are presented as the normalized release for boron. Boron release is typically used as an indicator of expected radionuclide release in HLW borosilicate glasses. The values are all well below the benchmark value of 16.695 g/L developed for repository acceptance.<sup>19</sup> The results also indicate that the influence of the two frit compositions, heat treatment, the minor amount of spinels that formed, the variation of the waste composition, and the increased sulfate concentrations have little impact on the chemical durability of the glasses. Therefore, it appears that these frits, when combined with this projected SB6 composition including anticipated variation, are successful in producing glass that is free of a sulfate layer and has acceptable chemical durability (under the experimental conditions used). This represents the potential for a significant increase in the sulfate limit for SRS HLW glass over the previous 0.4 and 0.6 wt %  $\text{SO}_4^{2-}$  values. However, sulfate retention is likely to be strongly linked to glass composition, limiting the utility of this increased value to these specific waste and frit systems.

#### *Influence of Increased Sulfate Concentrations on Viscosity*

The viscosity of HLW glass is carefully controlled to ensure good pouring behavior and to prevent erosion of refractories over the temperature range experienced in the melter. A model has been developed for predicting the viscosity of HLW borosilicate glasses based on their composition.<sup>20</sup> A series of glasses was fabricated with multiple frits and at varying waste loadings to determine whether the higher sulfate concentrations projected for SB6 were likely to have any significant impacts on the ability of the model to correctly predict viscosity at the melt temperature of 1150 °C. The SB6 projection given in Table 1 was again used, this time with the only modification being the removal of the uranium component and normalization of the remaining components to 100 wt %. The predicted sulfate concentrations were used in this portion of the study, rather than forcing the concentration to a higher value. Frits D and D2 were combined with the simulated waste to produce glasses for viscosity testing. Frits 418 and 503 (Table 2), developed for previous vitrification of HLW at the DWPF<sup>13,21</sup> and of interest for continued use with SB6, were also included in this portion of the study. Waste loadings of 32, 36 and 40 wt % were used to bound the anticipated waste loading target at DWPF. A total of 12 glasses were fabricated, using the methods

described above, and as shown in Table 4. The target sulfate concentration for each glass, which is dependent upon waste loading, is given in Table 4. No sulfate layer was visible on the glasses after fabrication.

The viscosity of the test glasses was measured using a specially designed, rotating spindle viscometer (Harrop Industries, Inc., Columbus, OH).<sup>22</sup> Although used with non-radioactive glasses in this study, the instrument was developed for measuring radioactive glasses using a small volume platinum crucible (2.6 ml of glass) and platinum spindle, supported within a vertical tube furnace. The instrument was shown to produce accurate measurements through a round-robin study.<sup>‡</sup> The predicted range of viscosity (95% confidence interval) for each glass at 1150 °C, based on the target compositions, is given in Table 4. The measured viscosity values at 1150 °C are also given. The results indicated that for the waste and frit combinations studied, there appear to be no issues with the viscosity model predictions. Each of the measured values falls very close to or within the 95% confidence interval of the predicted values.

#### *Revised Waste Composition Projections*

As the sulfur retention study progressed, revised composition projections for SB6 were developed due to changes in waste tank blending and washing activities. Three revised projections are given in Table 5, which bound potential endpoints in the SB6 preparation process. Sulfur retention for these compositions was again evaluated by fabricating test glasses at the crucible scale and using visual observations as a fast screening technique. Ten frit compositions, named and described in Table 6, were selected to be combined with the simulated wastes using an approach based on the PCCS models. A large array of potential frit compositions (approximately 1,200) were combined with each of the three waste compositions in Table 5 over waste loadings of 25 to 60 wt %. Each of the resulting glass compositions (approximately 130,000) was then evaluated using the PCCS Measurement Acceptability Region to determine whether the models used at the DWPF predicted a given glass to be acceptable for processing and repository acceptance, with the exception of the sulfate concentration constraint. The results were reviewed in order to down-select frit compositions that produced glasses that were predicted to be acceptable over a useful range of waste loadings (typically 30-45 wt %) and that offered an opportunity to evaluate the impacts of varying B<sub>2</sub>O<sub>3</sub>,

---

<sup>‡</sup> J.D. Vienna, D.E. Smith, M.J. Schweiger, J.V. Crum, R. Russel, T.B. Edwards, D.K. Peeler, R.J. Workman and R. Schumacher, "DWPF Startup Frit Viscosity Measurement Round Robin Results," Pacific Northwest National Laboratory and Savannah River Technology Center, November 9, 2001, unpublished.



CaO, and Na<sub>2</sub>O concentrations on sulfur retention. The frits that met these criteria are those listed in Table 6. Frit 418 is also included since this frit was being used for vitrification of SB5, and it would be advantageous to the DWPF if this frit could continue to be used for SB6.

The three waste compositions listed in Table 5 were modified for the study by removing the uranium component and forcing the SO<sub>4</sub><sup>2-</sup> concentration to 2.0 or 2.5 wt %, to give 0.8 or 1.0 wt % in glass, respectively. The remaining components were normalized to a sum of 100 wt %. Glasses were fabricated from batch chemicals as described earlier, air quenched in the covered crucibles, and observed for the formation of any sulfate salt layer after cooling. The visual observations for the frit and sludge combinations studied are given in Table 6. The results show that all of the glasses fabricated with Frit 418 had a visible sulfate layer. Adding 3 wt % CaO to this frit at the expense of SiO<sub>2</sub> (W1) did not improve its performance with SB6-01. Frits with relatively low Na<sub>2</sub>O concentrations of 2 wt % (W3 and W4) appear to be most successful in improving sulfate retention for these waste compositions, although B<sub>2</sub>O<sub>3</sub> concentrations must be above 8 wt % or CaO must be included. The frits with 4 wt % Na<sub>2</sub>O did not retain sulfur as well as the 2 wt % Na<sub>2</sub>O frits for the SB6-03 projection, which may be due to the higher Na<sub>2</sub>O concentration in this waste (Table 5). The influence of Li<sub>2</sub>O in hindering sulfate retention does not appear to be as strong as that of Na<sub>2</sub>O, although there may be some effect of the total alkali concentration. In general, the trend of improved sulfate retention when the frit concentrations of B<sub>2</sub>O<sub>3</sub> and CaO are increased and the concentration of Na<sub>2</sub>O is decreased appears to hold true for these revised waste composition projections.

#### *Fixed Frit Composition*

As the preparation of SB6 progressed, timing of activities at the DWPF dictated that Frit 418, in use for vitrification of SB5, would have to be used for at least the first few months of SB6 processing. However, the results described earlier showed that Frit 418 did not work well in retaining sulfate at concentrations above 0.6 wt % in glass with various SB6 composition projections. Therefore, the SB6 preparation process was further modified to reduce the concentration of sulfate by simply bringing less of the high sulfate concentration material into the batch. Note however that this sulfate remains in the wastes stored at SRS, and will eventually have to be vitrified.

A sulfate concentration limit of 0.6 wt % still represents an increase from the original limit of 0.4 wt %, and the ability to retain this increased concentration must be verified for each new sludge batch. For the SB6 and Frit 418 system, this verification was performed through additional laboratory studies. A series of additional SB6 composition projections were developed to account for the revised preparation method and reduced sulfate concentration. These compositions are not given in detail here for brevity, but are fairly similar to those in Table 5. For the verification testing, the uranium component was removed from each projection, the sulfate concentration was adjusted to give 0.6 wt %  $\text{SO}_4^{2-}$  in glass at a given waste loading, and the remaining components were normalized to a total of 100 wt %. The simulated wastes were combined with Frit 418 at a series of waste loadings from 32 to 40 wt %. The glasses were melted and quenched as described earlier. The formation of any sulfate salt layer was noted. Samples of each glass were also dissolved by lithium metaborate fusion and the concentrations of sulfate were measured by ICP-AES. A reference borosilicate glass containing sulfur<sup>23</sup> was included in the measurements to provide a measure of analytical error. Based on the measured results for the standard glass, the measurement uncertainty for  $\text{SO}_4^{2-}$  in the study glasses was determined to be +/- 0.01 wt %.

The results of this portion of the study are shown in Figure 4. None of the glasses had a visible sulfate layer after cooling. The glasses at waste loadings of 36 wt % and higher had a minor amount of surface crystallization, identified as spinels by XRD. The measured amounts of retained sulfate for each waste composition at each waste loading are indicated in the figure. The error bars represent the analytical error of +/- 0.01 wt %. Retention of the target 0.6 wt %  $\text{SO}_4^{2-}$  (indicated in Figure 4 by the dashed line) was fairly good for all of the glasses. Minor volatility during melting is likely the cause of the reduced sulfate concentrations for some of the glasses, since no sulfate layers were identified. Overall, the data indicate that Frit 418 is able to retain sulfate concentrations of 0.6 wt % over a range of composition projections and waste loadings.

Identification of an upper limit for the SB6 and Frit 418 system was also of interest, should the need arise to exceed 0.6 wt %  $\text{SO}_4^{2-}$  in glass (i.e., if the actual sulfate concentration in SB6 were found to be higher than the projected values). Additional glasses were fabricated to search for this limit, using a slightly modified version of the SB6-02 projection (Table 5) as a baseline for the SB6 composition. The uranium component was again removed, and sulfate concentrations were increased incrementally to

produce concentrations from 0.7 to 1.0 wt %  $\text{SO}_4^{2-}$  in glass. The resulting frit and simulated waste compositions were batched and melted as described earlier, with loose fitting platinum lids covering the crucibles. Visual observations of the glasses are given in Figure 5. None of the glasses fabricated with target sulfate concentrations of 0.6 or 0.7 wt % had any visible sulfate layer, indicating the potential to incorporate somewhat higher sulfate concentrations in this frit and sludge combination. Sulfate layers were visible on some of the glasses at target sulfate concentrations of 0.75 and 0.8 wt %. All of the glasses had sulfate layers at target sulfate concentrations of 0.9 and 1.0 wt %. The retained sulfate concentrations in each glass were measured using the method described earlier, and the results are given in Figure 6. The glasses were again generally successful in retaining close to the target concentrations of sulfate, with volatility likely accounting for the small losses. Note that one of the glasses at 38 wt % waste loading, indicated by the arrow in Figure 6, retained 0.7 wt %  $\text{SO}_4^{2-}$  when 0.75 wt % was targeted and also had a visible sulfur layer. This point indicates that there is little room available for extending the sulfate concentration limit for the SB6 and Frit 418 system beyond 0.6 wt %. If necessary, the limit could be extended slightly to 0.65 wt %  $\text{SO}_4^{2-}$ , as indicated by the dashed line in Figure 6.

#### *Influence of Glass REDOX*

The crucible scale experiments performed thus far in support of the sulfate retention evaluations were done in open or loosely covered crucibles, in air, in resistance heated furnaces. Batch chemicals (oxides, carbonates and boric acid) were used as raw materials, rather than the metal nitrates, oxides and glass frit that make up the actual radioactive feed. These conditions are obviously different from those in the full scale melter, and may have some influence on sulfate retention and volatility. To address these concerns, a small number of experiments were performed using simulated melter feed material and sealed crucibles. While still different from actual melter conditions, the experiments were intended to provide some insight into the impacts of a more representative feed material and semi-controlled reduction-oxidation (REDOX) conditions on sulfate retention.

Preparation of the simulated melter feed material is described in detail elsewhere.<sup>24</sup> Briefly, components are blended and prepared as the species that are present in the actual waste material as closely as possible, without the inclusion of radioactive elements. The measured composition of the simulated waste, referred to as SB6-11, is given in Table 7. The simulated feed is treated (at the bench scale) via the

same methods used at the DWPF in preparation for vitrification, and glass formers are added as a ground frit during the final stages of processing. Frit 418 was added for a target waste loading of 40 wt %. For the purposes of sulfate retention testing, additional sulfur was added to the feed as  $\text{Na}_2\text{SO}_4$  at concentrations targeting 0.6 wt % and 0.9 wt %  $\text{SO}_4^{2-}$  in glass. The simulated feed materials were dried overnight at 70 °C, resulting in a consistency similar to peanut butter. The material was placed into alumina crucibles with lids. The crucible lids were sealed using a nepheline gel, with the intent of maintaining REDOX conditions similar to those found in the DWPF melter, where a REDOX value of 0.2 ( $\text{Fe}^{2+}$  / total Fe) is targeted. The crucibles (three replicates for each of the two sulfate concentrations) were heated to 1150 °C and held for one hour. The crucibles were then removed from the furnace and allowed to cool quickly in air. All of the crucibles remained sealed after testing. In addition, a glass was prepared from batch chemicals with a composition targeted to match that of the glass made from the simulated waste material at 0.9 wt %  $\text{SO}_4^{2-}$  in glass. This glass was melted in air with a platinum crucible and loose-fitting lid, and used for comparison with the sealed crucible tests.

Samples of each of the glasses were dissolved and analyzed for sulfate concentration and REDOX. The results are given in Table 8. Despite the crucibles remaining sealed, the measured REDOX values varied between 0.17 and fully oxidized. However, no sulfate layers were visible on any of the glasses. The measured sulfate values show that some volatilization occurred during the REDOX testing as well. The glass prepared from batch chemicals to mimic the feed and frit composition was also free of any sulfate layer. While the REDOX testing was done only as a brief screening study, the results indicate that there is not a significant difference in sulfate retention between the two test methodologies (i.e., batch chemicals in open crucibles versus simulated feeds and frit in sealed crucibles) for this composition.

### **Summary and Discussion**

The sulfate retention study progressed in parallel with the waste batch preparation process at SRS. Because of this, the objectives and the methods used to meet these objectives evolved as the waste composition became better defined and as other technical constraints were put in place. The progression of this work describes one aspect of the engineering approach taken in support of a very unique, operating facility.

The first series of tests identified increased concentrations of  $B_2O_3$  and  $CaO$  in the frit as being beneficial for sulfate retention for SB6, while increased  $Na_2O$  in the frit had a negative effect. These trends continued for glasses made with the same frits when the concentrations of the major components of the waste ( $Al_2O_3$ ,  $Fe_2O_3$ , and  $Na_2O$ ) were varied. A more thorough variability study, where variation was applied to all of the waste components, showed that the frits with higher  $B_2O_3$  and  $CaO$  concentrations performed well. No sulfate-rich salt layers were formed on the variability study glasses, and measured composition data showed retention of sulfate at concentrations close to the targeted values. Chemical durability of the glasses, an important requirement for repository acceptability, was very acceptable.

The impact of elevated sulfate concentrations on the predictability of the glass viscosity using the DWPF process control model was briefly investigated using a series of glasses made with four different frits over a series of waste loadings. The results showed no significant differences between the predicted and measured viscosity values.

A new series of candidate frit compositions was developed when revised waste composition projections for SB6 were received. The frits were designed to further gauge the impacts of  $B_2O_3$ ,  $CaO$  and  $Na_2O$  concentrations in the frit on sulfate retention. In general, the trend of improved sulfate retention when the frit concentrations of  $B_2O_3$  and  $CaO$  are increased and the concentration of  $Na_2O$  is decreased appeared to hold true for these revised waste composition projections. The influence of  $Li_2O$  in hindering sulfate retention did not appear to be as strong as that of  $Na_2O$ , although there may be some effect of the total alkali concentration.

Later in the SB6 preparation process it became necessary to use a specific frit composition due to facility timing issues. The projected sulfate concentration in SB6 was somewhat reduced to meet this constraint by modifying the preparation process. Verification of retention of sulfate at a concentration of 0.6 wt % for SB6 with Frit 418 then became necessary. A series of glasses was fabricated using SB6 with further updated SB6 composition projections over a range of waste loadings. Visible observations and sulfate concentration measurements indicated that Frit 418 was able to retain sulfate concentrations of 0.6 wt % over a reasonable range of SB6 compositions and waste loadings. Similar glasses targeting higher sulfate concentrations showed that there was little room to increase the sulfate retention limit for the SB6

and Frit 418 system beyond 0.6 wt %  $\text{SO}_4^{2-}$  in glass. A limit of 0.65 wt %  $\text{SO}_4^{2-}$  could be set should the actual concentration be higher than the projected values.

Finally, a small number of glasses were melted in sealed crucibles to gauge the impacts of a more representative feed material and semi-controlled reduction-oxidation (REDOX) conditions on sulfate retention. After melting, the measured REDOX values varied between 0.17 and fully oxidized. No sulfate layers were visible on any of the glasses. The measured sulfate values showed that some volatilization occurred during the REDOX testing. The results indicated that there was not a significant difference in sulfate retention between the glasses prepared from batch chemicals in open crucibles versus those prepared using simulated feeds and frit in sealed crucibles.

Frit 418 was ultimately selected for vitrification of SB6,<sup>25</sup> and a limit of 0.6 wt %  $\text{SO}_4^{2-}$  in glass was set.<sup>26</sup> The sulfate limit assumes that there will be no volatilization during melting, which is considered to be a conservative approach since some volatilization is inevitable. The glasses fabricated and characterized to develop the limit were made under conditions that are generally different from those in the full scale melter. Non-radioactive simulants were used in place of actual radioactive waste. Despite these differences, this type of laboratory scale work has been shown to correlate very well with data from glass taken from the full scale melter.<sup>27, 28</sup> Future studies will focus on methods to develop a general sulfate limit for borosilicate waste glass produced at the DWPF that is not dependent upon the individual waste batch being processed, and further understanding of the impacts of  $\text{B}_2\text{O}_3$  and CaO in the frit on improved sulfate retention.

### **Acknowledgements**

The authors would like to thank Irene Reamer, Phyllis Workman, Thomas Edwards, Pat Simmons, David Best, and David Missimer for their skilled assistance with glass fabrication, characterization, and interpretation. The Savannah River National Laboratory is operated for the U.S. Department of Energy by Savannah River Nuclear Solutions under contract number DE-AC09-08SR22470.

### **References**

1. Walker, D. D., "Sulfate Solubility in DWPF Glass," *U.S. Department of Energy Report DPST-86-546*, E.I. duPont deNemours & Co., Savannah River Laboratory, Aiken, SC (1986).

2. Bickford, D. F., A. Applewhite-Ramsey, C. M. Jantzen and K. G. Brown, "Control of Radioactive Waste Glass Melters: I, Preliminary General Limits at Savannah River," *Journal of the American Ceramic Society*, **73** [10] 2896-2902 (1990).
3. Jantzen, C. M. and M. E. Smith, "Revision of the Defense Waste Processing Facility (DWPF) Sulfate Solubility Limit," *U.S. Department of Energy Report WSRC-TR-2003-00518, Revision 0*, Westinghouse Savannah River Company, Aiken, SC (2003).
4. Plodinec, M. J. and J. R. Wiley, "Evaluation of Glass as a Matrix for Solidifying Savannah River Plant Waste: Properties of Glasses Containing  $\text{Li}_2\text{O}$ ," *U.S. Department of Energy Report DP-1498*, E.I. duPont deNemours & Co., Savannah River Laboratory, Aiken, SC (1979).
5. Bickford, D. F. and C. M. Jantzen, "Inhibitor Limits for Washed Precipitate Based on Glass Quality and Solubility Limits," *U.S. Department of Energy Report DPST-86-546*, E.I. DuPont deNemours & Co., Savannah River Laboratory, Aiken, SC (1986).
6. Peeler, D. K., C. C. Herman, M. E. Smith, T. H. Lorier, D. R. Best, T. B. Edwards and M. A. Baich, "An Assessment of the Sulfate Solubility Limit for the Frit 418 – Sludge Batch 2/3 System," *U.S. Department of Energy Report WSRC-TR-2004-00081, Revision 0*, Westinghouse Savannah River Company, Aiken, SC (2004).
7. Fox, K. M., T. B. Edwards and D. K. Peeler, "Sulfate Retention in High Level Waste (HLW) Sludge Batch 4 (SB4) Glasses: A Preliminary Assessment," *U.S. Department of Energy Report WSRC-STI-2006-00038, Revision 0*, Washington Savannah River Company, Aiken, SC (2006).
8. Raszewski, F. C., D. R. Best and D. K. Peeler, "An Assessment of the Applicability of the 0.6 wt%  $\text{SO}_4^{2-}$  PCCS Limit for the Frit 418-SB5 System," *U.S. Department of Energy Report SRNL-L3100-2008-00023*, Savannah River National Laboratory, Aiken, SC (2008).
9. Papadopoulos, K., "The Solubility of  $\text{SO}_3$  in Soda-Lime-Silica Melts," *Physics and Chemistry of Glasses*, **14** [3] 60-65 (1973).
10. Ooura, M. and T. Hanada, "Compositional Dependence of Solubility of Sulfate in Silicate Glasses," *Glass Technology*, **39** [2] 68-73 (1998).
11. Fox, K. M. and D. K. Peeler, "Vitrification of High Level Waste at the Savannah River Site"; pp. 229-237 in Materials Research Society Symposium Proceedings, Vol. 1193, *Scientific Basis for Nuclear Waste*

*Management XXXIII*. Edited by B. E. Burakov and A. S. Aloy. Materials Research Society, Warrendale, PA, 2009.

12. Fox, K. M., T. B. Edwards, D. K. Peeler, D. R. Best, I. A. Reamer and R. J. Workman, "High Level Waste (HLW) Sludge Batch 4 (SB4) with Frit 418: Results of a Phase II Variability Study," *U.S.*

*Department of Energy Report WSRC-STI-2006-00329, Revision 0*, Washington Savannah River Company, Aiken, SC (2006).

13. Fox, K. M., T. B. Edwards and D. K. Peeler, "Recommended Frit Composition for Initial Sludge Batch 5 Processing at the Defense Waste Processing Facility," *U.S. Department of Energy Report WSRC-STI-2008-00338, Revision 0*, Washington Savannah River Company, Aiken, SC (2008).

14. Manara, D., A. Grandjean, O. Pinet, J. L. Dussossoy and D. R. Neuville, "Sulfur Behavior in Silicate Glasses and Melts: Implications for Sulfate Incorporation in Nuclear Waste Glasses as a Function of Alkali Cation and V<sub>2</sub>O<sub>5</sub> Content," *Journal of Non-Crystalline Solids*, **353** [1] 12-23 (2007).

15. Youchak-Billings, A. L., "A Scoping Study Examining the Possibility of a Frit Additive to Increase Sulfur Solubility in DWPF Glass," *U.S. Department of Energy Report SRNL-PSE-2008-00173*, Savannah River National Laboratory, Aiken, SC (2008).

16. Brown, K. G., R. L. Postles and T. B. Edwards, "SME Acceptability Determination for DWPF Process Control," *U.S. Department of Energy Report WSRC-TR-95-00364, Revision 4*, Westinghouse Savannah River Company, Aiken, SC (2002).

17. Marra, S. L. and C. M. Jantzen, "Characterization of Projected DWPF Glass Heat Treated to Simulate Canister Centerline Cooling," *U.S. Department of Energy Report WSRC-TR-92-142, Revision 1*, Westinghouse Savannah River Company, Aiken, SC (1993).

18. Bickford, D. F. and C. M. Jantzen, "Devitrification of SRL Defense Waste Glass"; pp. 557-565 in *Scientific Basis for Nuclear Waste Management VII*. Edited by G. L. McVay. Elsevier, New York, 1984.

19. Jantzen, C. M., N. E. Bibler, D. C. Beam, C. L. Crawford and M. A. Pickett, "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material," *U.S. Department of Energy Report WSRC-TR-92-346, Revision 1*, Westinghouse Savannah River Company, Aiken, SC (1993).



20. Jantzen, C. M., "The Impacts of Uranium and Thorium on the Defense Waste Processing Facility (DWPF) Viscosity Model," *U.S. Department of Energy Report WSRC-TR-2004-00311, Revision 0*, Westinghouse Savannah River Company, Aiken, SC (2005).
21. Peeler, D. K., T. B. Edwards and K. M. Fox, "Frit Recommendation for SB4," *U.S. Department of Energy Report SRNL-PSE-2006-00128*, Washington Savannah River Company, Aiken, SC (2006).
22. Schumacher, R. F. and D. K. Peeler, "Establishment of Harrop, High-Temperature Viscometer," *U.S. Department of Energy Report WSRC-RP-98-00737, Revision 0*, Westinghouse Savannah River Company, Aiken, SC (1998).
23. Ebert, W. L. and S. F. Wolfe, "Round-robin Testing of a Reference Glass for Low-Activity Waste Forms," *U.S. Department of Energy Report ANL-99/22*, Argonne National Laboratory, Argonne, IL (1999).
24. Koopman, D. C. and D. R. Best, "Sludge Batch 6 Phase II Flowsheet Simulations," *U.S. Department of Energy Report SRNL-STI-2010-00041, Revision 0*, Savannah River National Laboratory, Aiken, SC (2010).
25. Fox, K. M., T. B. Edwards and J. R. Zamecnik, "Frit Development for Sludge Batch 6," *U.S. Department of Energy Report SRNL-STI-2010-00137, Revision 0*, Savannah River National Laboratory, Aiken, SC (2010).
26. Billings, A. L., "DWPF Sulfate Limit Verification for SB6," *U.S. Department of Energy Report SRNL-STI-2010-00191, Revision 0*, Savannah River National Laboratory, Aiken, SC (2010).
27. Cozzi, A. D., N. E. Bibler and C. J. Bannochie, "Analytical Results of DWPF Glass Sample Taken During Filling of Canister S01913," *U.S. Department of Energy Report WSRC-TR-2004-00316, Revision 2*, Washington Savannah River Company, Aiken, SC (2005).
28. Bannochie, C. J. and N. E. Bibler, "Analysis of Sludge Batch 3 (Macrobatches 4) DWPF Pour Stream Glass Sample for Canister S02312," *U.S. Department of Energy Report WSRC-TR-2005-00354, Revision 0*, Washington Savannah River Company, Aiken, SC (2005).

**Figure 1. Top-Down View of a Sulfur-Rich Salt Layer Visible on Top of a Simulated HLW Glass in a Platinum Crucible After Melting and Cooling.**

**Figure 2. Results of Factorial Design Experiments with Varying Frit Compositions at Target Sulfate Concentrations in Glass of 1.2 wt %(a) and 1.4 wt %(b).**

**Figure 3. Results of Factorial Design Experiments with Varying Frit Compositions and Increased  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  in Waste.**

**Figure 4. Measured Sulfate Retention as a Function of Waste Composition and Loading.**

**Figure 5. Visual Observations of Glasses Fabricated with SB6-04 and Frit 418.**

**Figure 6. Measured Sulfate Retention in Glasses Fabricated with SB6-04 and Frit 418.**

**Table 1. Sludge Batch Composition Projections (wt %).**

Oxide	SB6 Projection	Non-radioactive SB6 Projection	Additional Al, Fe and Na Projection
Al <sub>2</sub> O <sub>3</sub>	28.78	29.98	30.59
BaO	0.11	0.12	0.11
CaO	1.51	1.57	1.42
Ce <sub>2</sub> O <sub>3</sub>	0.09	0.10	0.09
Cr <sub>2</sub> O <sub>3</sub>	0.37	0.38	0.34
CuO	0.10	0.10	0.09
Fe <sub>2</sub> O <sub>3</sub>	23.88	24.88	25.38
K <sub>2</sub> O	0.02	0.03	0.02
La <sub>2</sub> O <sub>3</sub>	0.08	0.09	0.08
MgO	0.86	0.90	0.81
MnO	7.27	7.57	6.83
Na <sub>2</sub> O	24.49	25.52	26.04
NiO	2.67	2.78	2.51
PbO	0.02	0.02	0.02
SO <sub>4</sub> <sup>2-</sup>	2.01	3.00	3.00
SiO <sub>2</sub>	2.48	2.59	2.33
U <sub>3</sub> O <sub>8</sub>	4.88	-	-
ZnO	0.06	0.07	0.06
ZrO <sub>2</sub>	0.30	0.31	0.30

**Table 2. Target Frit Compositions (wt %).**

Frit	B <sub>2</sub> O <sub>3</sub>	CaO	Li <sub>2</sub> O	Na <sub>2</sub> O	SiO <sub>2</sub>
A	8	-	11	2	79
B	8	5	12	2	73
C	12	-	12	2	74
D	12	5	11	2	70
E	10	2	10	4	74
F	8	-	11	6	75
G	8	5	09	5	73
H	12	-	10	5	73
I	12	5	09	5	69
D2	14	3	11	2	70
418	8	-	8	8	76
503	14	-	8	4	74

**Table 3. Chemical Durability Results for Variation Study.**

<b>Glass ID</b>	<b>Frit ID</b>	<b>Measured SO<sub>4</sub><sup>2-</sup> (wt %)</b>	<b>Normalized Release for Boron (g/L)</b>	<b>Normalized Release for Boron after Slow Cooling (g/L)</b>
GTS-01	D	0.93	0.65	0.63
GTS-02	D	0.91	0.89	0.66
GTS-03	D	0.96	0.75	0.73
GTS-04	D	0.94	0.84	0.63
GTS-05	D	0.93	0.69	0.62
GTS-06	D	0.92	0.66	0.77
GTS-07	D	0.96	0.80	0.71
GTS-08	D	0.96	0.63	0.61
GTS-09	D	0.96	0.61	0.48
GTS-10	D	0.93	0.66	0.51
GTS-11	D	0.95	0.68	0.66
GTS-12	D2	0.94	0.63	0.68
GTS-13	D2	0.94	0.78	0.76
GTS-14	D2	0.95	0.72	0.80
GTS-15	D2	0.97	0.82	0.83
GTS-16	D2	0.95	0.64	0.77
GTS-17	D2	0.94	0.73	0.77
GTS-18	D2	0.95	0.86	0.90
GTS-19	D2	0.94	0.71	0.75
GTS-20	D2	0.90	0.67	0.62
GTS-21	D2	0.95	0.73	0.61
GTS-22	D2	0.97	0.71	0.71

**Table 4. Predicted and Measured Viscosity for GTS-series Glasses.**

<b>Glass ID</b>	<b>Frit</b>	<b>Waste Loading (wt %)</b>	<b>Target SO<sub>4</sub><sup>2-</sup> (wt %)</b>	<b>Predicted Viscosity Range at 1150 °C (poise)</b>	<b>Measured Viscosity at 1150 °C (poise)</b>
GTS-01	D	32	0.68	27-58	24
GTS-02	D	36	0.76	23-50	22
GTS-03	D	40	0.84	19-42	29
GTS-04	D2	32	0.68	24-53	25
GTS-05	D2	36	0.76	21-45	23
GTS-06	D2	40	0.84	18-38	28
GTS-07	418	32	0.68	45-96	65
GTS-08	418	36	0.76	39-83	59
GTS-09	418	40	0.84	33-71	69
GTS-10	503	32	0.68	47-100	54
GTS-11	503	36	0.76	40-86	50
GTS-12	503	40	0.84	34-73	49

**Table 5. Revised Composition Projections for SB6 (wt %).**

Oxide	SB6-01	SB6-02	SB6-03
Al <sub>2</sub> O <sub>3</sub>	25.55	26.92	27.50
BaO	0.15	0.13	0.13
CaO	1.55	1.84	1.89
CdO	0.00	0.10	0.11
Ce <sub>2</sub> O <sub>3</sub>	0.22	0.23	0.23
Cr <sub>2</sub> O <sub>3</sub>	0.38	0.15	0.16
CuO	0.12	0.11	0.11
Fe <sub>2</sub> O <sub>3</sub>	25.86	24.96	25.71
Gd <sub>2</sub> O <sub>3</sub>	0.00	0.05	0.05
K <sub>2</sub> O	0.02	0.08	0.07
La <sub>2</sub> O <sub>3</sub>	0.11	0.11	0.11
MgO	0.82	0.00	0.00
MnO	7.48	6.79	7.00
Na <sub>2</sub> O	25.07	26.13	24.33
NiO	3.20	3.14	3.23
PbO	0.03	0.03	0.03
SO <sub>4</sub> <sup>2-</sup>	1.30	1.50	1.38
SiO <sub>2</sub>	2.39	2.36	2.42
SrO	0.00	0.07	0.07
ThO <sub>2</sub>	0.02	0.00	0.00
TiO <sub>2</sub>	0.04	0.02	0.02
U <sub>3</sub> O <sub>8</sub>	5.23	4.90	5.05
ZnO	0.10	0.06	0.06
ZrO <sub>2</sub>	0.37	0.31	0.32

**Table 6. Visual Observation of Frit and Waste Combinations.**

Identifier	Frit					Waste and Sulfate Concentration (wt %)					
	Composition (wt %)					SB6-01		SB6-02		SB6-03	
	B <sub>2</sub> O <sub>3</sub>	CaO	Li <sub>2</sub> O	Na <sub>2</sub> O	SiO <sub>2</sub>	1.0	0.8	1.0	0.8	1.0	0.8
418	8	0	8	8	76	SL	SL	SL	SL	SL	SL
W1	8	3	8	8	73	SL	SL	-	-	-	-
W2	8	0	12	2	78	SL	SL	-	-	-	-
W3	8	3	12	2	75	SL	C	SL	C	C	C
W4	12	0	11	2	75	SL	C	SL	C	C	C
W5	10	3	11	2	74	SL	C	SL	C	PSL	C
W6	14	0	9	4	73	SL	C	SL	C	SL	PSL
W7	12	3	9	4	72	SL	C	SL	C	SL	C
W8	9	0	10	4	77	SL	SL	-	-	-	-
W9	9	3	10	4	74	SL	C	SL	C	SL	C

Visual Observations: SL – Sulfate salt layer; PSL – Partial Sulfate salt layer; C – Minor surface crystallization; (-) – Indicates combination that was not fabricated.

**Table 7. Simulated Waste Composition for REDOX Testing (wt %).**

Oxide	SB6-11 Simulated Sludge
Al <sub>2</sub> O <sub>3</sub>	30.43
B <sub>2</sub> O <sub>3</sub>	0.00
BaO	0.13
CaO	1.68
CeO <sub>2</sub>	0.10
Cr <sub>2</sub> O <sub>3</sub>	0.33
CuO	0.07
Fe <sub>2</sub> O <sub>3</sub>	24.91
K <sub>2</sub> O	0.09
La <sub>2</sub> O <sub>3</sub>	0.09
Li <sub>2</sub> O	0.00
MgO	0.89
MnO	10.45
Na <sub>2</sub> O	24.16
NiO	2.88
SO <sub>4</sub> <sup>2-</sup>	0.87
SiO <sub>2</sub>	2.81
ZnO	0.07
ZrO <sub>2</sub>	0.04

**Table 8. REDOX Testing Results.**

Glass ID	Measured SO <sub>4</sub> <sup>2-</sup> (wt %)	REDOX (Fe <sup>2+</sup> / Total Fe)	Visual Observations
0.6A	0.51	0.08	clean glass
0.6B	0.50	0.13	clean glass
0.6C	0.49	0.09	clean glass
0.9A	0.73	Fully oxidized	clean glass
0.9B	0.77	0.17	clean glass
0.9C	0.71	0.08	clean glass