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**Sulfur, molybdenum, solubility,**  
**high level waste glass**

**Retention:**  
**Permanent**

**COMBINED RETENTION OF MOLYBDENUM AND SULFUR IN  
SIMULATED HIGH LEVEL WASTE GLASS**

**W.T. Shoulders**  
**K.M. Fox**

**SEPTEMBER 2009**

Savannah River National Laboratory  
Savannah River Nuclear Solutions  
Aiken, SC 29808

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**Prepared for the U.S. Department of Energy Under  
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## LIST OF ACRONYMS

CCC	canister centerline cooled
DI water	de-ionized water
DWPF	Defense Waste Processing Facility
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
PCCS	Product Composition Control System
PSAL	Process Science Analytical Laboratory
SB4	Sludge Batch 4
SB6	Sludge Batch 5
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

## 1.0 EXECUTIVE SUMMARY

This study was undertaken to investigate the effect of elevated sulfate and molybdenum concentrations in nuclear waste glasses. A matrix of 24 glasses was developed and the glasses were tested for acceptability based on visual observations, canister centerline-cooled heat treatments, and chemical composition analysis. Results from the chemical analysis of the rinse water from each sample were used to confirm the presence of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  on the surface of glasses as well as other components which might form water soluble compounds with the excess sulfur and molybdenum.

A simple, linear model was developed to show acceptable concentrations of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  in an example waste glass composition. This model was constructed for scoping studies only and is not ready for implementation in support of actual waste vitrification. Several other factors must be considered in determining the limits of sulfate and molybdenum concentrations in the waste vitrification process, including but not limited to, impacts on refractory and melter component corrosion, effects on the melter off-gas system, and impacts on the chemical durability and crystallization of the glass product.



## 2.0 INTRODUCTION

Composition projections of Sludge Batch 6 (SB6), to be vitrified at the Defense Waste Processing Facility (DWPF), predict relatively high concentrations of sulfate ( $\text{SO}_4^{2-}$ ) in the sludge.<sup>1</sup> Increased concentrations of molybdenum oxide ( $\text{MoO}_3$ ) are an issue at other waste vitrification plants, such as Sellafield in the U.K. Elevated sulfate concentrations in particular raise several issues with the processing of sludge and frit mixtures and performance of the final glass product. Should a need arise to vitrify a waste stream containing both sulfur and molybdenum, an understanding of the combined solubility of these components and the potential for formation of insoluble molybdenum sulfates would need to be better understood.

A high sulfate concentration is a concern as it can lead to the formation of sulfate inclusions in the glass and the formation of a molten, sulfate-rich phase atop the melt pool. The presence of this low viscosity melt phase on the surface of the melt pool increases corrosion rates of the materials of construction, including the off-gas system and refractories (primarily at the melt line), as well as melter top head components (e.g., thermowells, level dip tube and upper electrodes). The molten salt layer is purported to enhance the potential for steam explosions in waste glass melters that are slurry fed.<sup>2</sup> In addition, there is the potential for undesirable current paths to develop that could deplete energy delivered to the melter due to the high electrical conductivity of the molten salt layer. For example, the DWPF avoids these issues through the implementation of a sulfate concentration limit, originally set in the Product Composition Control System (PCCS) at 0.4 wt %  $\text{SO}_4^{2-}$  in glass,<sup>3-5</sup> and later 0.6 wt %  $\text{SO}_4^{2-}$  in glass for Sludge Batch 4 (SB4).<sup>6</sup>

As another example, waste containing relatively high molybdenum concentrations has been processed at the Sellafield, U.K. vitrification plant. Studies in support of Sellafield have shown that molybdenum accelerated corrosion of melters in its liquid state and was highly soluble in water as a solid.<sup>7</sup> When the solubility limit in glass is exceeded, Mo ions in various oxidation states have the capability of bonding to radioactive ions in a solid salt on the surface of a glass.

This work is designed as a scoping study of the combined solubility limits of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  in a simulated high level waste glass. The goal is to produce a plot of  $\text{SO}_4^{2-}$  retention versus  $\text{MoO}_3$  retention that can be used as a simple model to predict the retention of these components, using SB6 as a model system. It should be noted that the retention limits of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  are very likely dependent on the overall glass composition; therefore the results of this study may not be applicable to other waste compositions. The data presented in this report are not sufficient to provide guidelines for actual waste vitrification, but merely insight into the combined retention of these components in a borosilicate glass.

### 3.0 EXPERIMENTAL PROCEDURE

#### 3.1 GLASS MATRIX SELECTION

Initially, 12 glass compositions were designed for this study. The sludge composition chosen as an example for this study originated from a March 2009 SB6 projection.<sup>a</sup> Sulfate and the radioactive components (ThO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub>) were removed from the projection with the remaining components normalized to 100 wt %. Frit 418 (Table 1) was selected as a likely candidate for vitrification of SB6. A waste loading of 35% was arbitrarily chosen based on processing of previous sludge batches at the DWPF. A base glass composition, designated N3-01 was calculated using these conditions. Finally, SO<sub>4</sub><sup>2-</sup> and MoO<sub>3</sub> were added to the base glass composition at fixed concentrations as described below, with the glass compositions then being normalized to 100 wt %.

**Table 1. Composition of Frit 418 (wt %).**

B <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	Na <sub>2</sub> O	SiO <sub>2</sub>
8.0	8.0	8.0	76.0

The first 12 test glass compositions were designed around the current sulfate solubility limit. Sulfate concentrations were chosen at, below, and above the concentration limit of 0.6 wt % set for SB5,<sup>9</sup> specifically 0.0, 0.6 and 1.2 wt % SO<sub>4</sub><sup>2-</sup>.<sup>10</sup> Molybdenum was added at concentrations of 0, 2, 4 and 6 wt % MoO<sub>3</sub>. The resulting glass compositions are given in Table 2.

After the first twelve glasses were melted and observed, twelve new compositions were devised to more closely determine the SO<sub>4</sub><sup>2-</sup> to MoO<sub>3</sub> solubility relationship. A more narrow range of molybdenum concentrations was used, covering 1.0 to 3.5 wt % MoO<sub>3</sub> in 0.5 wt % increments. These were combined with sulfate concentrations of 0.0, 0.2, 0.4, 0.5 and 0.6 wt % SO<sub>4</sub><sup>2-</sup>, as shown in Table 3.

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<sup>a</sup> An SB6 composition projection was received from the Liquid Waste Organization Planning Group via email in March 2009, and was closely based on the SB6 Variation 8 composition suggested by SRNL.<sup>8</sup>

Table 2. Target Compositions of Glasses N3-01 through N3-12 (wt %)

Oxide	N3-01	N3-02	N3-03	N3-04	N3-05	N3-06	N3-07	N3-08	N3-09	N3-10	N3-11	N3-12
Al <sub>2</sub> O <sub>3</sub>	8.323	8.156	7.990	7.823	8.273	8.106	7.940	7.773	8.223	8.056	7.890	7.724
B <sub>2</sub> O <sub>3</sub>	5.335	5.228	5.122	5.015	5.303	5.196	5.090	4.983	5.271	5.164	5.058	4.951
BaO	0.057	0.056	0.055	0.054	0.057	0.056	0.055	0.054	0.057	0.056	0.054	0.053
CaO	0.901	0.883	0.865	0.847	0.896	0.878	0.860	0.842	0.890	0.872	0.854	0.836
Ce <sub>2</sub> O <sub>3</sub>	0.050	0.049	0.048	0.047	0.050	0.049	0.048	0.047	0.050	0.049	0.048	0.047
Cr <sub>2</sub> O <sub>3</sub>	0.108	0.106	0.103	0.101	0.107	0.105	0.103	0.101	0.106	0.104	0.102	0.100
CuO	0.029	0.028	0.028	0.027	0.029	0.028	0.027	0.027	0.028	0.028	0.027	0.027
Fe <sub>2</sub> O <sub>3</sub>	8.775	8.600	8.424	8.249	8.723	8.547	8.372	8.196	8.670	8.494	8.319	8.143
K <sub>2</sub> O	0.011	0.011	0.010	0.010	0.011	0.010	0.010	0.010	0.011	0.010	0.010	0.010
La <sub>2</sub> O <sub>3</sub>	0.025	0.025	0.024	0.024	0.025	0.024	0.024	0.023	0.025	0.024	0.024	0.023
Li <sub>2</sub> O	5.335	5.228	5.122	5.015	5.303	5.196	5.090	4.983	5.271	5.164	5.058	4.951
MgO	0.707	0.693	0.679	0.665	0.703	0.689	0.675	0.661	0.699	0.685	0.671	0.656
MnO	2.546	2.495	2.444	2.393	2.530	2.479	2.429	2.378	2.515	2.464	2.413	2.362
MoO <sub>3</sub>	0.000	2.000	4.000	6.000	0.000	2.000	4.000	6.000	0.000	2.000	4.000	6.000
Na <sub>2</sub> O	14.975	14.676	14.376	14.077	14.885	14.586	14.286	13.987	14.795	14.496	14.196	13.897
NiO	1.397	1.369	1.341	1.313	1.388	1.360	1.332	1.305	1.380	1.352	1.324	1.296
PbO	0.036	0.035	0.034	0.034	0.036	0.035	0.034	0.034	0.035	0.035	0.034	0.033
SO <sub>4</sub> <sup>2-</sup>	0.000	0.000	0.000	0.000	0.600	0.600	0.600	0.600	1.200	1.200	1.200	1.200
SiO <sub>2</sub>	51.232	50.207	49.183	48.158	50.925	49.900	48.875	47.851	50.617	49.593	48.568	47.543
TiO <sub>2</sub>	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007
ZnO	0.036	0.035	0.034	0.034	0.036	0.035	0.034	0.034	0.035	0.035	0.034	0.033
ZrO <sub>2</sub>	0.115	0.113	0.110	0.108	0.114	0.112	0.110	0.107	0.114	0.111	0.109	0.107

Table 3. Target Compositions for Glasses N3-13 through N3-24 (wt %).

Oxide	N3-13	N3-14	N3-15	N3-16	N3-17	N3-18	N3-19	N3-20	N3-21	N3-22	N3-23	N3-24
Al <sub>2</sub> O <sub>3</sub>	8.223	8.206	8.190	8.181	8.165	8.156	8.140	8.123	8.115	8.115	8.073	8.031
B <sub>2</sub> O <sub>3</sub>	5.271	5.260	5.250	5.244	5.234	5.228	5.218	5.207	5.202	5.202	5.175	5.148
BaO	0.057	0.057	0.057	0.056	0.056	0.056	0.056	0.056	0.056	0.056	0.056	0.055
CaO	0.890	0.889	0.887	0.886	0.884	0.883	0.881	0.880	0.879	0.879	0.874	0.870
Ce <sub>2</sub> O <sub>3</sub>	0.050	0.050	0.049	0.049	0.049	0.049	0.049	0.049	0.049	0.049	0.049	0.049
Cr <sub>2</sub> O <sub>3</sub>	0.106	0.106	0.106	0.106	0.106	0.106	0.105	0.105	0.105	0.105	0.104	0.104
CuO	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
Fe <sub>2</sub> O <sub>3</sub>	8.670	8.652	8.635	8.626	8.608	8.600	8.582	8.565	8.556	8.556	8.512	8.468
K <sub>2</sub> O	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.010	0.010
La <sub>2</sub> O <sub>3</sub>	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.024	0.024
Li <sub>2</sub> O	5.271	5.260	5.250	5.244	5.234	5.228	5.218	5.207	5.202	5.202	5.175	5.148
MgO	0.699	0.697	0.696	0.695	0.694	0.693	0.692	0.690	0.690	0.690	0.686	0.683
MnO	2.515	2.510	2.505	2.502	2.497	2.495	2.490	2.485	2.482	2.482	2.469	2.457
MoO <sub>3</sub>	1.000	1.000	1.000	1.500	1.500	1.500	2.000	2.000	2.000	2.500	3.000	3.500
Na <sub>2</sub> O	14.795	14.765	14.735	14.720	14.690	14.676	14.646	14.616	14.601	14.601	14.526	14.451
NiO	1.380	1.377	1.374	1.373	1.370	1.369	1.366	1.363	1.362	1.362	1.355	1.348
PbO	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035
SO <sub>4</sub> <sup>2-</sup>	0.200	0.400	0.600	0.200	0.400	0.500	0.200	0.400	0.500	0.000	0.000	0.000
SiO <sub>2</sub>	50.617	50.515	50.412	50.361	50.259	50.207	50.105	50.002	49.951	49.951	49.695	49.439
TiO <sub>2</sub>	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007
ZnO	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035	0.035
ZrO <sub>2</sub>	0.114	0.113	0.113	0.113	0.113	0.113	0.112	0.112	0.112	0.112	0.111	0.111

### 3.2 GLASS FABRICATION

Each sulfate and molybdenum doped glass was prepared from the proper proportions of reagent-grade metal oxides, carbonates, boric acid, and salts in 150 g batches. The raw materials were thoroughly mixed and placed into a 95% Pt/5% Au, 250 mL crucible and covered with a platinum/gold lid. The crucibles were placed into a high-temperature furnace at the melt temperature of 1150 °C. After an isothermal hold at 1150 °C for 1.0 h, the crucibles were removed from the furnace and placed on a steel plate to cool. Visual observations of the cooled glasses and of the crucibles after removing the glass were documented. Rinse tests and chemical composition determinations were completed for each of the glasses as described below.

### 3.3 GLASS COMPOSITION ANALYSIS

Rinse tests for N3-01 through N3-24 were prepared by pouring 10 mL of de-ionized water (DI water) into the crucible then sloshing and pouring into a labeled scintillation vial. The samples were submitted to the Process Science Analytical Laboratory (PSAL) for analysis of the concentration of dissolved solids, including Ca, Cr, Li, Mo, Na, and S. In addition, samples of about 5g of each glass were submitted to PSAL for chemical composition analysis. The glass samples were dissolved using a lithium metaborate fusion and the resulting liquids were analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

### 3.4 CANISTER CENTERLINE COOLING (CCC)

Samples of glasses N3-01 through N3-12 were heat treated to simulate slow cooling along the centerline of a DWPF canister to visually identify any crystallization that may occur during more kinetically favorable, slow cooling conditions. About 30 g of each glass was placed in a 100 mL 95% Pt/ 5% Au crucible. All twelve crucibles were placed in a furnace at 1150 °C. A program was then started to slowly cool the furnace following a schedule developed based on actual cooling data of an instrumented canister.<sup>11</sup> The crucibles were removed from the furnace after the program had finished. Visual observations were recorded.

## 4.0 RESULTS AND DISCUSSION

### 4.1 VISUAL OBSERVATIONS

Before presenting visual observations of each glass as it appeared upon cooling, it is fit to explain the terminology used in describing the appearance of the glasses. The terms ‘clean’ and ‘clean with bubbles’ as used here mean that there were no undissolved solids visible on the surface of the cooled glass and no visible crystallization. ‘Residue’ means there was some undissolved chemical left on the surface of the glass. A few pictures are given as examples of clean glasses and glasses with residue. Visual observations of all the quickly cooled glasses are summarized in Table 4.



**Figure 1. Example of a clean glass, N3-13.**



**Figure 2. Example of tan residue on glass N3-23.**

**Table 4. Visual observations of glasses after cooling in crucibles.**

<b>Glass ID</b>	<b>Observations</b>
N3-01	clean with few bubbles
N3-02	clean with few bubbles
N3-03	ring of tan residue on glass patty extending to edges of crucible
N3-04	residue ring + spots of tan residue in middle of glass patty surface
N3-05	clean
N3-06	bright yellow residue on edges of crucible
N3-07	thick ring of tan residue on patty
N3-08	thick ring of tan residue on patty
N3-09	clean
N3-10	large spots of yellowish residue all over surface
N3-11	large spots of tan residue all over surface
N3-12	large spots of tan residue all over surface
N3-13	clean
N3-14	clean
N3-15	clean
N3-16	clean
N3-17	clean
N3-18	clean
N3-19	clean
N3-20	light residue on edges of crucible
N3-21	yellowish residue on edges on crucible + large splotch of residue on patty
N3-22	clean
N3-23	ring of tan residue on glass patty extending to edges of crucible
N3-24	thick ring of tan residue on patty

Visual observations of glasses N3-01 through N3-12 after the CCC heat treatment were also recorded. None of these glasses showed any evidence of crystallization on any outside surface of the patty. Only three of the glasses exhibited an appearance different than that of their quickly cooled counterparts described in Table 4. Glasses N3-10, N3-11, and N3-12 had a marbled appearance, characteristic of surface crystallization.

#### 4.2 CHEMICAL COMPOSITION RESULTS

The chemical composition analyses focused mainly on determining the concentrations of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  retained in the glasses after melting. This is referred to as retention of these components in the glass, rather than solubility, as it is unlikely that true equilibrium conditions were reached during melting in the crucibles. Table 5 summarizes the target versus measured concentrations of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  in the study glasses. Note that the measured concentration of  $\text{MoO}_3$  in glass N3-19 is higher than the target value. This is likely due to a batching error when the glass was prepared.

Some general observations can be made regarding these data for the first twelve glasses (with the second 12 glasses being used to fill in the  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  concentration region of interest):

- Retention of  $\text{MoO}_3$  in this glass composition reached a maximum of about 3.0 wt % when no  $\text{SO}_4^{2-}$  was present.
- Retention of  $\text{MoO}_3$  was reduced when  $\text{SO}_4^{2-}$  was added at a target concentration of 0.60 wt %, and was further reduced when  $\text{SO}_4^{2-}$  was added at a target concentration of 1.20 wt %.

- Retention of slightly more than 1.0 wt %  $\text{SO}_4^{2-}$  without the formation of any visible surface layer was possible in this glass composition when no  $\text{MoO}_3$  was added (e.g., glass N3-09).
- The amount of  $\text{SO}_4^{2-}$  retained decreased significantly with increasing target concentrations of  $\text{MoO}_3$ .

**Table 5. Target and measured concentrations of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  in the study glasses.**

Glass ID	$\text{SO}_4^{2-}$ (wt %)		$\text{MoO}_3$ (wt %)	
	target	measured	target	measured
N3-01	0.00	0.00	0.00	0.00
N3-02	0.00	0.00	2.00	1.96
N3-03	0.00	0.00	4.00	3.05
N3-04	0.00	0.00	6.00	2.91
N3-05	0.60	0.582	0.00	0.00
N3-06	0.60	0.509	2.00	1.89
N3-07	0.60	0.384	4.00	2.54
N3-08	0.60	0.300	6.00	2.79
N3-09	1.20	1.062	0.00	0.00
N3-10	1.20	0.528	2.00	1.33
N3-11	1.20	0.410	4.00	2.05
N3-12	1.20	0.339	6.00	2.07
N3-13	0.20	0.00	1.00	0.89
N3-14	0.40	0.357	1.00	0.92
N3-15	0.60	0.513	1.00	0.90
N3-16	0.20	0.00	1.50	1.49
N3-17	0.40	0.361	1.50	1.37
N3-18	0.60	0.443	1.50	1.39
N3-19	0.20	0.00	2.00	2.95
N3-20	0.40	0.374	2.00	1.98
N3-21	0.50	0.467	2.00	2.00
N3-22	0.00	0.00	2.50	1.98
N3-23	0.00	0.00	3.00	2.76
N3-24	0.00	0.00	3.50	2.93

The complete chemical composition data, including the target and measured concentrations of each element for each of the study glasses, are included in the Appendix. A review of the data indicates little difficulty in meeting the target compositions for each glass. Four of the glasses with the lowest target  $\text{SO}_4^{2-}$  concentrations (glasses M3-13, N3-14, N3-16 and N3-19 targeted 0.20 wt %  $\text{SO}_4^{2-}$ ) had measured  $\text{SO}_4^{2-}$  concentrations that were below the detection limit of the instrument (indicated as 0.00 in Table 5). Note that the concentrations of  $\text{B}_2\text{O}_3$  and  $\text{Li}_2\text{O}$  were not measured since, due to the focus on sulfur and molybdenum concentrations, only a lithium metaborate dissolution was used to support the analyses in this study. A small number of discrepancies between the target and measured concentrations of some of the oxides for some of the study glasses are present (e.g.,  $\text{SiO}_2$  concentrations for glasses N3-08 and N3-12, and  $\text{NiO}$  concentrations for glasses N3-19, N3-20 and N3-21), although these are not expected to affect the outcome of the study.

Wash water samples from the surface of each glass were analyzed by ICP-AES, as summarized in Table 6. These data provide a qualitative measure of the composition of the water soluble surface layer observed on some of the cooled glasses (refer to the descriptions in Table 4). In general, those glasses that showed retention of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  that was lower than the target concentration had



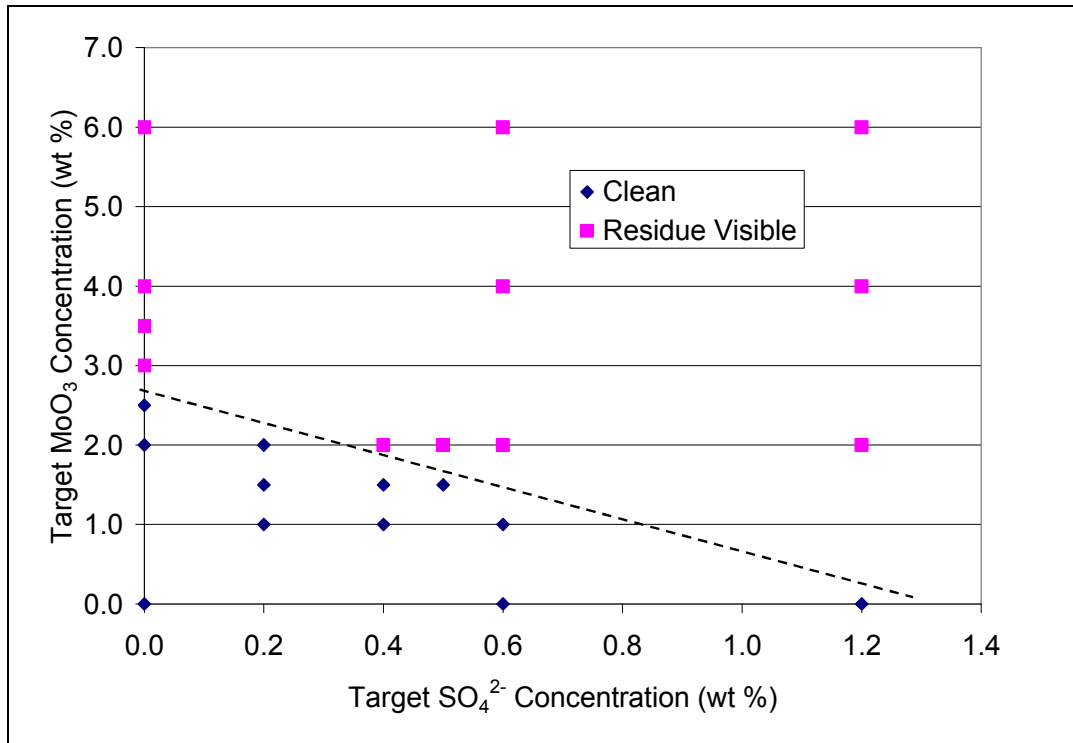
high concentrations of these cations on their surfaces after melting. The data also indicate that the alkali, and to some degree, the alkaline earth elements, are present in the surface layer in concentrations proportional to those of the excess sulfur and molybdenum. Note that some of the glasses (e.g., N3-03 and N3-04) had measurable amounts of sulfur in the wash water when no sulfur was batched into the glass. It may be that some sulfur is present as a contaminate in the MoO<sub>3</sub> batch chemical, since MoS<sub>2</sub> is the typical industrial source of this oxide.

**Table 6. Concentrations of elements measured in the wash water samples.**

Glass ID	Ca (mg/L)	Cr (mg/L)	Li (mg/L)	Mo (mg/L)	Na (mg/L)	S (mg/L)
N3-01	1.92	0.13	1.45	<0.100	17.55	<1.00
N3-02	1.95	1.18	1.50	5.78	22.17	<1.00
N3-03	5.13	81.7	476	8685	4103	53.3
N3-04	37.9	85.8	1365	28000	9340	134
N3-05	0.32	0.27	1.49	<0.100	2.57	2.20
N3-06	2.34	110	300	4870	2980	1040
N3-07	1.72	34.5	648	11650	5415	867
N3-08	6.34	31.3	657	11600	5010	647
N3-09	0.43	0.97	1.88	<0.100	23.4	17.3
N3-10	22.7	64.3	1.46	12000	13100	5195
N3-11	36.2	30.6	1.42	12750	10850	2905
N3-12	13.7	17.1	1.46	12000	10170	2090
N3-13	<0.100	1.23	2.12	15.49	17.22	7.85
N3-14	<0.100	0.45	1.62	3.50	3.88	1.55
N3-15	<0.100	<0.100	1.56	0.87	0.69	<1.00
N3-16	<0.100	1.03	1.61	6.60	5.49	<1.00
N3-17	<0.100	3.66	1.95	21.67	17.16	4.33
N3-18	<0.100	5.37	3.40	60.26	37.60	10.26
N3-19	0.704	2.96	2.06	22.3	13.7	1.27
N3-20	1.85	16.4	19.0	422	191	26.8
N3-21	3.34	101	213	4070	2140	565
N3-22	0.61	1.42	1.67	8.68	5.09	<1.00
N3-23	1.55	47.8	302	7740	2790	43.6
N3-24	6.05	95.1	734	17100	6030	84.1

#### 4.3 FITTING OF SULFUR AND MOLYBDENUM RETENTION MODEL

The tests and observations of the 24 glasses in this study have given some preliminary indications of the combined retention of SO<sub>4</sub><sup>2-</sup> and MoO<sub>3</sub> in this SB6 – Frit 418 glass system. A preliminary model shown in Figure 3 has been fitted based on visual observations of the cooled glasses.



**Figure 3. Preliminary model for sulfur and molybdenum retention in the SB6 – Frit 418 glass system studied.**

The model is constructed as a line of best fit between the acceptable glasses and the unacceptable glasses, with acceptability being determined using the visual observations. The relationship was assumed to be linear for simplicity. In general, the plot shows a significant decrease in the combined retention of  $\text{MoO}_3$  and  $\text{SO}_4^{2-}$  when they are both added to this glass composition. Concentrations of up to 2.5 wt %  $\text{MoO}_3$  were retained when no  $\text{SO}_4^{2-}$  was present, and concentrations of up to 1.2 wt %  $\text{SO}_4^{2-}$  were retained when no  $\text{MoO}_3$  was present. When both components were present, combined retention dropped to, as an example, 1.5 wt %  $\text{MoO}_3$  with 0.5 wt %  $\text{SO}_4^{2-}$ . The acceptable compositions line provides a basis for more testing and future refinement of the model.

## 5.0 SUMMARY

This study was undertaken to investigate the effect of potentially elevated sulfate and molybdenum concentrations in future nuclear waste glasses. Even low concentrations of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  that are not incorporated into the glass structure can cause significant problems in a high level waste melter. A matrix of 24 glasses was developed and the glasses were tested for acceptability based on visual observations. A glass was determined to be acceptable for the purposes of this study if it did not have any visible salt residue on its surface. Results from the chemical analysis of the rinse water from each sample were used to confirm the presence or absence of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  on the surface of glasses as well as other components which might form water soluble compounds with the excess sulfur and molybdenum.

A simple, linear model was developed to show acceptable concentrations of  $\text{SO}_4^{2-}$  and  $\text{MoO}_3$  in an example waste glass similar in composition to the SB6 projection used here. This model was constructed for scoping studies only and is not ready for implementation in support of actual waste vitrification. Several other factors must be considered in determining the limits of sulfate and molybdenum concentrations in the waste vitrification process, including but not limited to, impacts on refractory and melter component corrosion, effects on the melter off-gas system, and impacts on the chemical durability and crystallization of the glass product.

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**APPENDIX A.**

## Target and Measured Compositions of the Study Glasses

Oxide	Glass N3-01		N3-02	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.28	8.08	8.11	8.14
B <sub>2</sub> O <sub>3</sub>	5.30	not measured	5.20	not measured
BaO	0.06	0.046	0.06	0.078
CaO	0.90	0.838	0.88	0.858
CeO <sub>2</sub>	0.05	0.056	0.05	0.048
Cr <sub>2</sub> O <sub>3</sub>	0.11	0.082	0.10	0.105
CuO	0.03	0.031	0.03	0.036
Fe <sub>2</sub> O <sub>3</sub>	8.72	8.29	8.55	7.73
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.020	0.02	0.020
Li <sub>2</sub> O	5.30	not measured	5.20	not measured
MgO	0.70	0.679	0.69	0.669
MnO <sub>2</sub>	3.10	3.09	3.04	3.11
MoO <sub>3</sub>	0.00	0.00	1.99	1.96
Na <sub>2</sub> O	14.89	14.9	14.59	15.0
NiO	1.39	1.35	1.36	1.31
PbO	0.04	0.025	0.03	0.026
SO <sub>4</sub>	0.00	0.00	0.00	0.00
SiO <sub>2</sub>	50.94	50.4	49.93	49.4
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.04	0.033	0.03	0.032
ZrO <sub>2</sub>	0.11	0.111	0.11	0.117
Total	100.00	88.0	100.00	88.6

Oxide	Glass N3-03		N3-04	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	7.95	7.98	7.78	7.92
B <sub>2</sub> O <sub>3</sub>	5.09	not measured	4.99	not measured
BaO	0.05	0.049	0.05	0.06
CaO	0.86	0.832	0.84	0.89
CeO <sub>2</sub>	0.05	0.047	0.05	0.06
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.087	0.10	0.05
CuO	0.03	0.038	0.03	0.03
Fe <sub>2</sub> O <sub>3</sub>	8.38	8.97	8.20	7.16
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.018	0.02	0.02
Li <sub>2</sub> O	5.09	not measured	4.99	not measured
MgO	0.68	0.659	0.66	0.672
MnO <sub>2</sub>	2.98	3.01	2.92	2.86
MoO <sub>3</sub>	3.98	3.05	5.97	2.91
Na <sub>2</sub> O	14.30	14.3	14.00	12.2
NiO	1.33	1.33	1.31	1.23
PbO	0.03	0.029	0.03	0.028
SO <sub>4</sub>	0.00	0.00	0.00	0.000
SiO <sub>2</sub>	48.91	49.2	47.90	50.9
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.03	0.039	0.03	0.030
ZrO <sub>2</sub>	0.11	0.108	0.11	0.117
Total	100.00	89.7	100.00	87.2

Oxide	Glass N3-05		N3-06	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.23	7.92	8.06	8.08
B <sub>2</sub> O <sub>3</sub>	5.27	not measured	5.17	not measured
BaO	0.06	0.082	0.06	0.055
CaO	0.89	0.883	0.87	0.845
CeO <sub>2</sub>	0.05	0.049	0.05	0.047
Cr <sub>2</sub> O <sub>3</sub>	0.11	0.042	0.10	0.118
CuO	0.03	0.043	0.03	0.039
Fe <sub>2</sub> O <sub>3</sub>	8.67	8.14	8.50	9.28
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.023	0.02	0.019
Li <sub>2</sub> O	5.27	not measured	5.17	not measured
MgO	0.70	0.674	0.69	0.630
MnO <sub>2</sub>	3.08	2.89	3.02	3.00
MoO <sub>3</sub>	0.00	0.00	1.99	1.89
Na <sub>2</sub> O	14.80	13.6	14.50	14.4
NiO	1.38	1.22	1.35	1.31
PbO	0.04	0.024	0.03	0.029
SO <sub>4</sub>	0.60	0.582	0.60	0.509
SiO <sub>2</sub>	50.63	51.6	49.62	49.3
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.04	0.036	0.03	0.018
ZrO <sub>2</sub>	0.11	0.117	0.11	0.121
Total	100.00	87.9	100.00	89.7



Oxide	Glass N3-07		N3-08	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	7.90	8.09	7.73	8.35
B <sub>2</sub> O <sub>3</sub>	5.06	not measured	4.96	not measured
BaO	0.05	0.064	0.05	0.049
CaO	0.86	0.830	0.84	0.840
CeO <sub>2</sub>	0.05	0.123	0.05	0.054
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.091	0.10	0.099
CuO	0.03	0.037	0.03	0.032
Fe <sub>2</sub> O <sub>3</sub>	8.33	8.02	8.15	7.63
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.029	0.02	0.021
Li <sub>2</sub> O	5.06	not measured	4.96	not measured
MgO	0.67	0.653	0.66	0.663
MnO <sub>2</sub>	2.96	2.93	2.90	3.04
MoO <sub>3</sub>	3.98	2.54	5.97	2.79
Na <sub>2</sub> O	14.21	13.7	13.91	13.7
NiO	1.33	1.26	1.30	1.34
PbO	0.03	0.033	0.03	0.028
SO <sub>4</sub>	0.60	0.384	0.60	0.300
SiO <sub>2</sub>	48.61	48.2	47.59	50.3
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.03	0.047	0.03	0.036
ZrO <sub>2</sub>	0.11	0.122	0.11	0.109
Total	100.00	87.2	100.00	89.4

Oxide	Glass N3-09		N3-10	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.18	8.25	8.01	8.56
B <sub>2</sub> O <sub>3</sub>	5.24	not measured	5.14	not measured
BaO	0.06	0.053	0.06	0.050
CaO	0.89	0.867	0.87	0.876
CeO <sub>2</sub>	0.05	0.048	0.05	0.054
Cr <sub>2</sub> O <sub>3</sub>	0.11	0.102	0.10	0.157
CuO	0.03	0.035	0.03	0.035
Fe <sub>2</sub> O <sub>3</sub>	8.62	7.84	8.45	8.73
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.021	0.02	0.020
Li <sub>2</sub> O	5.24	not measured	5.14	not measured
MgO	0.69	0.669	0.68	0.699
MnO <sub>2</sub>	3.06	3.04	3.00	3.19
MoO <sub>3</sub>	0.00	0.00	1.99	1.33
Na <sub>2</sub> O	14.71	14.7	14.42	14.7
NiO	1.37	1.33	1.34	1.38
PbO	0.04	0.031	0.03	0.032
SO <sub>4</sub>	1.19	1.062	1.19	0.528
SiO <sub>2</sub>	50.33	49.8	49.32	51.9
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.04	0.033	0.03	0.040
ZrO <sub>2</sub>	0.11	0.106	0.11	0.116
Total	100.00	88.0	100.00	92.4

Oxide	Glass N3-11		N3-12	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	7.85	8.65	7.68	8.60
B <sub>2</sub> O <sub>3</sub>	5.03	not measured	4.92	not measured
BaO	0.05	0.046	0.05	0.037
CaO	0.85	0.852	0.83	0.883
CeO <sub>2</sub>	0.05	0.051	0.05	0.050
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.097	0.10	0.034
CuO	0.03	0.033	0.03	0.036
Fe <sub>2</sub> O <sub>3</sub>	8.27	9.30	8.10	7.69
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.020	0.02	0.026
Li <sub>2</sub> O	5.03	not measured	4.92	not measured
MgO	0.67	0.694	0.65	0.714
MnO <sub>2</sub>	2.94	3.12	2.88	3.11
MoO <sub>3</sub>	3.98	2.05	5.97	2.07
Na <sub>2</sub> O	14.12	13.8	13.82	12.4
NiO	1.32	1.36	1.29	1.33
PbO	0.03	0.041	0.03	0.018
SO <sub>4</sub>	1.19	0.410	1.19	0.339
SiO <sub>2</sub>	48.30	51.9	47.29	56.5
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.03	0.028	0.03	0.029
ZrO <sub>2</sub>	0.11	0.111	0.11	0.126
Total	100.00	92.6	100.00	94.0

Oxide	Glass N3-13		N3-14	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.18	8.05	8.16	8.11
B <sub>2</sub> O <sub>3</sub>	5.24	not measured	5.23	not measured
BaO	0.06	0.078	0.06	0.058
CaO	0.89	0.860	0.88	0.856
CeO <sub>2</sub>	0.05	0.055	0.05	0.061
Cr <sub>2</sub> O <sub>3</sub>	0.11	0.104	0.11	0.142
CuO	0.03	0.041	0.03	0.036
Fe <sub>2</sub> O <sub>3</sub>	8.62	8.94	8.60	9.07
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.019	0.02	0.023
Li <sub>2</sub> O	5.24	not measured	5.23	not measured
MgO	0.69	0.646	0.69	0.670
MnO <sub>2</sub>	3.06	3.02	3.06	3.05
MoO <sub>3</sub>	0.99	0.89	0.99	0.92
Na <sub>2</sub> O	14.71	14.6	14.68	14.5
NiO	1.37	1.31	1.37	1.31
PbO	0.04	0.027	0.04	0.034
SO <sub>4</sub>	0.20	0.00	0.40	0.357
SiO <sub>2</sub>	50.33	49.2	50.23	49.7
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.04	0.035	0.04	0.033
ZrO <sub>2</sub>	0.11	0.111	0.11	0.114
Total	100.00	88.0	100.00	89.1

Oxide	Glass N3-15		N3-16	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.14	8.08	8.14	8.21
B <sub>2</sub> O <sub>3</sub>	5.22	not measured	5.21	not measured
BaO	0.06	0.042	0.06	0.035
CaO	0.88	0.886	0.88	0.846
CeO <sub>2</sub>	0.05	0.047	0.05	0.052
Cr <sub>2</sub> O <sub>3</sub>	0.11	0.234	0.11	0.087
CuO	0.03	0.036	0.03	0.039
Fe <sub>2</sub> O <sub>3</sub>	8.59	9.28	8.58	8.37
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.019	0.02	0.021
Li <sub>2</sub> O	5.22	not measured	5.21	not measured
MgO	0.69	0.650	0.69	0.678
MnO <sub>2</sub>	3.05	2.99	3.05	3.05
MoO <sub>3</sub>	0.99	0.90	1.49	1.49
Na <sub>2</sub> O	14.65	14.6	14.64	14.6
NiO	1.37	1.31	1.37	1.33
PbO	0.04	0.023	0.04	0.036
SO <sub>4</sub>	0.60	0.513	0.20	0.00
SiO <sub>2</sub>	50.13	49.5	50.08	49.9
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.04	0.022	0.04	0.026
ZrO <sub>2</sub>	0.11	0.113	0.11	0.111
Total	100.00	89.2	100.00	88.9

Oxide	Glass N3-17		N3-18	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.12	7.89	8.11	7.86
B <sub>2</sub> O <sub>3</sub>	5.20	not measured	5.20	not measured
BaO	0.06	0.048	0.06	0.049
CaO	0.88	0.835	0.88	0.822
CeO <sub>2</sub>	0.05	0.051	0.05	0.055
Cr <sub>2</sub> O <sub>3</sub>	0.11	0.126	0.10	0.125
CuO	0.03	0.034	0.03	0.036
Fe <sub>2</sub> O <sub>3</sub>	8.56	9.12	8.55	9.90
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.020	0.02	0.020
Li <sub>2</sub> O	5.20	not measured	5.20	not measured
MgO	0.69	0.676	0.69	0.658
MnO <sub>2</sub>	3.04	2.98	3.04	2.98
MoO <sub>3</sub>	1.49	1.39	1.49	1.37
Na <sub>2</sub> O	14.61	14.3	14.59	14.2
NiO	1.36	1.31	1.36	1.28
PbO	0.04	0.033	0.03	0.030
SO <sub>4</sub>	0.40	0.361	0.50	0.443
SiO <sub>2</sub>	49.98	48.5	49.93	48.4
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.04	0.027	0.03	0.031
ZrO <sub>2</sub>	0.11	0.109	0.11	0.109
Total	100.00	87.8	100.00	88.4

Oxide	Glass N3-19		N3-20	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.09	8.57	8.08	8.27
B <sub>2</sub> O <sub>3</sub>	5.19	not measured	5.18	not measured
BaO	0.06	0.044	0.06	0.058
CaO	0.88	0.896	0.87	0.921
CeO <sub>2</sub>	0.05	0.050	0.05	0.056
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.045	0.10	0.063
CuO	0.03	0.058	0.03	0.052
Fe <sub>2</sub> O <sub>3</sub>	8.53	7.92	8.52	7.89
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.022	0.02	0.025
Li <sub>2</sub> O	5.19	not measured	5.18	not measured
MgO	0.69	0.664	0.69	0.666
MnO <sub>2</sub>	3.03	3.15	3.03	3.08
MoO <sub>3</sub>	1.99	2.95	1.99	1.98
Na <sub>2</sub> O	14.56	14.8	14.53	14.6
NiO	1.36	0.00	1.36	0.00
PbO	0.03	0.031	0.03	0.033
SO <sub>4</sub>	0.20	0.00	0.40	0.374
SiO <sub>2</sub>	49.82	51.8	49.72	51.5
TiO <sub>2</sub>	0.01	0.017	0.01	0.016
ZnO	0.03	0.032	0.03	0.038
ZrO <sub>2</sub>	0.11	0.112	0.11	0.110
Total	100.00	91.2	100.00	89.8

Oxide	Glass N3-21		N3-22	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.07	8.54	8.07	8.41
B <sub>2</sub> O <sub>3</sub>	5.17	not measured	5.17	not measured
BaO	0.06	0.037	0.06	0.046
CaO	0.87	0.930	0.87	0.889
CeO <sub>2</sub>	0.05	0.051	0.05	0.048
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.050	0.10	0.054
CuO	0.03	0.057	0.03	0.052
Fe <sub>2</sub> O <sub>3</sub>	8.51	7.66	8.51	7.65
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.023	0.02	0.021
Li <sub>2</sub> O	5.17	not measured	5.17	not measured
MgO	0.69	0.665	0.69	0.658
MnO <sub>2</sub>	3.02	3.14	3.02	3.10
MoO <sub>3</sub>	1.99	1.98	2.49	2.00
Na <sub>2</sub> O	14.52	15.2	14.52	15.2
NiO	1.35	0.00	1.35	1.32
PbO	0.03	0.026	0.03	0.028
SO <sub>4</sub>	0.50	0.467	0.00	0.00
SiO <sub>2</sub>	49.67	52.1	49.67	50.8
TiO <sub>2</sub>	0.01	0.024	0.01	0.017
ZnO	0.03	0.041	0.03	0.026
ZrO <sub>2</sub>	0.11	0.115	0.11	0.106
Total	100.00	91.1	100.00	90.4



Oxide	Glass N3-23		N3-24	
	Target (wt %)	Measured (wt %)	Target (wt %)	Measured (wt %)
Al <sub>2</sub> O <sub>3</sub>	8.03	8.38	7.99	8.53
B <sub>2</sub> O <sub>3</sub>	5.15	not measured	5.12	not measured
BaO	0.06	0.065	0.06	0.071
CaO	0.87	0.882	0.86	0.879
CeO <sub>2</sub>	0.05	0.045	0.05	0.047
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.057	0.10	0.059
CuO	0.03	0.057	0.03	0.044
Fe <sub>2</sub> O <sub>3</sub>	8.46	8.25	8.42	7.56
K <sub>2</sub> O	0.01	0.00	0.01	0.00
La <sub>2</sub> O <sub>3</sub>	0.02	0.019	0.02	0.021
Li <sub>2</sub> O	5.15	not measured	5.12	not measured
MgO	0.68	0.646	0.68	0.654
MnO <sub>2</sub>	3.01	3.05	2.99	3.08
MoO <sub>3</sub>	2.98	2.76	3.48	2.93
Na <sub>2</sub> O	14.44	15.1	14.37	14.9
NiO	1.35	1.33	1.34	1.33
PbO	0.03	0.028	0.03	0.028
SO <sub>4</sub>	0.00	0.00	0.00	0.00
SiO <sub>2</sub>	49.42	50.4	49.17	51.4
TiO <sub>2</sub>	0.01	0.00	0.01	0.00
ZnO	0.03	0.039	0.03	0.035
ZrO <sub>2</sub>	0.11	0.107	0.11	0.108
Total	100.00	91.2	100.00	91.7

**Distribution:**

S. L. Marra, 773-A  
A. B. Barnes, 999-W  
D. A. Crowley, 773-43A  
S. D. Fink, 773-A  
C. W. Gardner, 773-A  
B. J. Giddings, 786-5A  
C. C. Herman, 999-W  
F. M. Pennebaker, 773-42A  
C. J. Bannochie, 773-42A  
D. K. Peeler, 999-W  
M. E. Stone, 999-W  
K. M. Fox, , 999-W  
F.C. Raszewski, 999-W  
A.L. Billings, 999-W  
J.C. Marra, 773-42A  
A.S. Choi, 999-W  
D.H. Miller, 999-W