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Vitrification of High-Level Waste at the Savannah River Site

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ABSTRACT

The objective of this study was to experimentally measure the properties and performance of a series of glasses with compositions that could represent high level waste Sludge Batch 5 (SB5) as vitrified at the Savannah River Site Defense Waste Processing Facility. These data were used to guide frit optimization efforts as the SB5 composition was finalized. Glass compositions for this study were developed by combining a series of SB5 composition projections with a group of candidate frits. The study glasses were fabricated using depleted uranium and their chemical compositions, crystalline contents and chemical durabilities were characterized. Trevorite was the only crystalline phase that was identified in a few of the study glasses after slow cooling, and is not of concern as spinels have been shown to have little impact on the durability of high level waste glasses. Chemical durability was quantified using the Product Consistency Test (PCT). All of the glasses had very acceptable durability performance. The results of this study indicate that a frit composition can be identified that will provide a processable and durable glass when combined with SB5.

INTRODUCTION

Cold War legacy, liquid, high level nuclear waste stored in underground tanks at the U.S. Department of Energy Savannah River Site is being vitrified into a glass waste form for safe immobilization and storage. The liquid (or sludge) waste is blended into batches to moderate its chemical composition prior to vitrification. The contents of Tank 51 have been blended with sludge from Tank 7 to constitute Sludge Batch 5 (SB5), the next batch to be vitrified at the Defense Waste Processing Facility (DWPF). The Savannah River Site (SRS) Liquid Waste Organization (LWO) performed low-temperature Al-dissolution in Tank 51 to reduce the total mass of sludge solids and Al being fed to the DWPF. A radioactive demonstration using a 3 L Tank 51 sludge slurry sample was performed to verify the Tank Farm processing parameters [1].

The aluminum dissolved sludge was used to determine potential downstream impacts so that technical issues could be identified before the start of SB5 processing. The potential downstream impacts assessed included the Tank Farm washing and concentration process and the DWPF Chemical Process Cell (CPC) and melter processing envelopes. The chemical composition of this 3 L Tank 51 sample was used to project potential compositions of SB5 as it will be processed by the DWPF. These projections were used by the Savannah River National Laboratory (SRNL) to develop frit compositions for SB5 that will produce glasses that will be acceptable for disposition to the federal repository. The objective of this study is to experimentally measure the properties and performance of a series of glasses with compositions that are anticipated to represent SB5 as processed at the DWPF. The data will be used to provide recommendations to the LWO regarding blending and washing strategies in preparing SB5 based on acceptability of the glass compositions. These data will also be used to guide frit optimization efforts as the SB5 composition is finalized.

EXPERIMENTAL PROCEDURE

Glass compositions for this study were developed by combining a series of SB5 composition projections with a group of frits. Three composition projections for SB5 were developed using a model-based approach at SRNL. These compositions, referred to as SB5 Cases B, C and D, project removal of 25, 50 and 75% (respectively) of the aluminum in Tank 51 through the low temperature aluminum dissolution process. The development of these SB5 composition projections is described in further detail in a previous report [2]. A fourth SB5 composition was provided later in the sludge batch preparation process. This composition, which will be referred to as 'LWO Al-Diss', represents 50% removal of aluminum from Tank 51 and a blend with the remnants of Sludge Batch 4 (SB4). The compositions of these four SB5 projections are given in Table I.

Table I. SB5 composition projections used in this study.

Oxide	SB5 Case B	SB5 Case C	SB5 Case D	LWO Al-Diss
Ag_2O	0.010	0.010	0.012	0.000
Al_2O_3	28.972	24.894	20.914	18.993
BaO	0.102	0.113	0.121	0.165
CaO	1.781	1.966	2.108	2.252
CdO	0.061	0.066	0.072	0.000
Ce_2O_3	0.371	0.409	0.439	0.266
CoO	0.024	0.026	0.028	0.000
Cr_2O_3	0.373	0.411	0.440	0.245
CuO	0.012	0.013	0.013	0.087
Fe_2O_3	23.246	25.644	27.491	27.641
K_2O	0.067	0.072	0.080	0.202
La_2O_3	0.163	0.180	0.193	0.046
MgO	1.178	1.299	1.393	1.228
MnO	4.861	5.362	5.748	6.094
Na_2O	24.832	24.194	24.500	27.206
NiO	2.730	3.011	3.228	3.154
P_2O_5	0.528	0.581	0.622	0.000
PbO	0.022	0.023	0.026	0.096
SO_4^{2-}	0.729	0.761	0.815	1.439
SiO_2	1.886	2.081	2.234	1.838
SrO	0.319	0.351	0.377	0.000
ThO_2	0.000	0.000	0.000	0.011
TiO_2	0.026	0.029	0.031	0.922
U_3O_8	7.436	8.203	8.794	7.696
ZnO	0.016	0.017	0.018	0.111
ZrO_2	0.258	0.285	0.306	0.307

The frits for this study were selected based on their predicted operating windows (i.e., the ranges of waste loadings over which the predicted properties of the glasses were acceptable according to the DWPF process control models [3]) and potential to provide acceptable melt rates for SB5. The selection process for the frits used in this study is described in further detail in a previous report [2]. The compositions of each frit are given in Table II.

Table II. Compositions of the candidate frits used in this study.

Frit ID	B_2O_3	CaO	Li_2O	Na_2O	SiO_2
530	10	4	7	7	72
531	11	2	7	7	73
532	14	2	6	7	71
533	16	0	5	8	71
534	15	0	9	4	72
535	14	0	7	8	71
536	15	0	5	10	70
537	16	0	4	7	73

Frits 530, 531, 532 and 533 were each combined with the four SB5 composition projections to form the first 16 glass compositions (glasses SB5-01 through SB5-16). All of the study glasses targeted 38 wt % waste loading (WL) in anticipation of higher WL targets for DWPF processing of SB5. Frits 534, 535, 536 and 537 were combined with SB5 Case B, SB5 Case C, SB5 Case D and LWO Al-diss, respectively, as these frits provided good predicted operating windows with these specific SB5 composition projections. That is, while the earlier frits provide good predicted operating windows with all four of the SB5 composition projections, these frits are tailored specifically for the individual composition projections that they are combined with. These combinations form glasses SB5-17 through SB5-20. The compositions of the 20 study glasses are given in Table III.

Table III. Target compositions of the study glasses.

Glass ID	SB5-01	SB5-02	SB5-03	SB5-04	SB5-05	SB5-06	SB5-07	SB5-08	SB5-09	SB5-10		
Frit ID	**530**	**531**	**532**	**533**	**530**	**531**	**532**	**533**	**530**	**531**		
Sludge Type	**Case B**	**Case B**	**Case B**	**Case B**	**Case C**	**Case C**	**Case C**	**Case C**	**Case D**	**Case D**		
Ag_2O	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004		
Al_2O_3	11.009	11.009	11.009	11.009	9.460	9.460	9.460	9.460	7.947	7.947		
B_2O_3	6.200	6.820	8.680	9.920	6.200	6.820	8.680	9.920	6.200	6.820		
BaO	0.039	0.039	0.039	0.039	0.043	0.043	0.043	0.043	0.046	0.046		
CaO	3.157	1.917	1.917	0.677	3.227	1.987	1.987	0.747	3.281	2.041		
CdO	0.023	0.023	0.023	0.023	0.025	0.025	0.025	0.025	0.027	0.027		
Ce_2O_3	0.141	0.141	0.141	0.141	0.155	0.155	0.155	0.155	0.167	0.167		
CoO	0.009	0.009	0.009	0.009	0.010	0.010	0.010	0.010	0.011	0.011		
Cr_2O_3	0.142	0.142	0.142	0.142	0.156	0.156	0.156	0.156	0.167	0.167		
CuO	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005		
Fe_2O_3	8.834	8.834	8.834	8.834	9.745	9.745	9.745	9.745	10.447	10.447		
HfO_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
K_2O	0.025	0.025	0.025	0.025	0.027	0.027	0.027	0.027	0.030	0.030		
La_2O_3	0.062	0.062	0.062	0.062	0.068	0.068	0.068	0.068	0.073	0.073		
Li_2O	4.340	4.340	3.720	3.100	4.340	4.340	3.720	3.100	4.340	4.340		
MgO	0.447	0.447	0.447	0.447	0.494	0.494	0.494	0.494	0.529	0.529		
MnO	1.847	1.847	1.847	1.847	2.038	2.038	2.038	2.038	2.184	2.184		
Na_2O	13.776	13.776	13.776	14.396	13.534	13.534	13.534	14.154	13.650	13.650		
Nd_2O_3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
NiO	1.037	1.037	1.037	1.037	1.144	1.144	1.144	1.144	1.227	1.227		
P_2O_5	0.201	0.201	0.201	0.201	0.221	0.221	0.221	0.221	0.236	0.236		
PbO	0.008	0.008	0.008	0.008	0.009	0.009	0.009	0.009	0.010	0.010		
SiO_2	45.357	45.977	44.737	44.737	45.431	46.051	44.811	44.811	45.489	46.109		
SO_4	0.277	0.277	0.277	0.277	0.289	0.289	0.289	0.289	0.310	0.310		
SrO	0.121	0.121	0.121	0.121	0.134	0.134	0.134	0.134	0.143	0.143		
ThO_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
TiO_2	0.010	0.010	0.010	0.010	0.011	0.011	0.011	0.011	0.012	0.012		
U_3O_8	2.826	2.826	2.826	2.826	3.117	3.117	3.117	3.117	3.342	3.342		
ZnO	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.007	0.007		
ZrO_2	0.098	0.098	0.098	0.098	0.108	0.108	0.108	0.108	0.116	0.116		

Table III. Target compositions of the study glasses. (continued)

Glass ID	SB5-13	SB5-14	SB5-15	SB5-16	SB5-17	SB5-18	SB5-19	
Frit ID	530	531	532	533	534	535	536	
Sludge Type	LWO Al-Diss	LWO Al-Diss	LWO Al-Diss	LWO Al-Diss	Case B	Case C	Case D	
Ag_2O	0.000	0.000	0.000	0.000	0.004	0.004	0.004	
Al_2O_3	7.217	7.217	7.217	7.217	11.009	9.460	7.947	
B_2O_3	6.200	6.820	8.680	9.920	9.300	8.680	9.300	
BaO	0.063	0.063	0.063	0.063	0.039	0.043	0.046	
CaO	3.336	2.096	2.096	0.856	0.677	0.747	0.801	
CdO	0.000	0.000	0.000	0.000	0.023	0.025	0.027	
Ce_2O_3	0.101	0.101	0.101	0.101	0.141	0.155	0.167	
CoO	0.000	0.000	0.000	0.000	0.009	0.010	0.011	
Cr_2O_3	0.093	0.093	0.093	0.093	0.142	0.156	0.167	
CuO	0.033	0.033	0.033	0.033	0.005	0.005	0.005	
Fe_2O_3	10.504	10.504	10.504	10.504	8.834	9.745	10.447	
HfO_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
K_2O	0.077	0.077	0.077	0.077	0.025	0.027	0.030	
La_2O_3	0.018	0.018	0.018	0.018	0.062	0.068	0.073	
Li_2O	4.340	4.340	3.720	3.100	5.580	4.340	3.100	
MgO	0.467	0.467	0.467	0.467	0.447	0.494	0.529	
MnO	2.316	2.316	2.316	2.316	1.847	2.038	2.184	
Na_2O	14.678	14.678	14.678	15.298	11.916	14.154	15.510	
Nd_2O_3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
NiO	1.198	1.198	1.198	1.198	1.037	1.144	1.227	
P_2O_5	0.000	0.000	0.000	0.000	0.201	0.221	0.236	
PbO	0.036	0.036	0.036	0.036	0.008	0.009	0.010	
SiO_2	45.338	45.958	44.718	44.718	45.357	44.811	44.249	
SO_4	0.547	0.547	0.547	0.547	0.277	0.289	0.310	
SrO	0.000	0.000	0.000	0.000	0.121	0.134	0.143	
ThO_2	0.004	0.004	0.004	0.004	0.000	0.000	0.000	
TiO_2	0.350	0.350	0.350	0.350	0.010	0.011	0.012	
U_3O_8	2.925	2.925	2.925	2.925	2.826	3.117	3.342	
ZnO	0.042	0.042	0.042	0.042	0.006	0.006	0.007	
ZrO_2	0.117	0.117	0.117	0.117	0.098	0.108	0.116	

Each of the study glasses 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 platinum/rhodium, 250 ml crucibles. The batch was placed into a high-temperature furnace at the melt temperature of 1150 °C. The crucible was removed from the furnace after a one hour isothermal hold. The glass was poured onto a clean, stainless steel plate and allowed to air cool (quench). The glass pour patty was used as a sampling stock for the various property measurements, including chemical composition and durability testing. Approximately 25 g of each glass was heat-treated to simulate cooling along the centerline of a DWPF-type canister [4] to gauge the effects of slow cooling on the product performance. This cooling schedule is referred to as the canister centerline cooling (ccc) heat treatment.

Representative samples of all the ccc glasses were analyzed using X-ray diffraction (XRD) to identify any crystalline phases present. Samples were run under conditions providing a detection limit of approximately 0.5 vol %. That is, if crystals (or undissolved batch material) were present at 0.5 vol % or greater, the diffractometer would not only be capable of detecting the crystals but would also allow for a qualitative determination of the type of crystal(s) present.

To confirm that the as-fabricated glasses met the target compositions, a representative sample from each quenched glass was prepared using the peroxide fusion and lithium metaborate fusion dissolution methods and analyzed with Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Glass standards were also intermittently measured to assess the performance of the analytical instrumentation over the course of these analyses.

The PCT Method-A [5] was performed in triplicate on each quenched and ccc glass to assess chemical durability. Also included in the experimental test matrix was the Environmental Assessment (EA) benchmark glass [6], the Approved Reference Material (ARM) glass, and blanks from the sample cleaning batch. Samples were ground, washed, and prepared following the standard procedure [5]. Fifteen milliliters of Type-I ASTM water were added to 1.5 g of glass in stainless steel vessels. The vessels were closed, sealed, and placed in an oven at 90 ± 2 °C where the samples were maintained at temperature for 7 days. Once cooled, the resulting solutions were sampled (filtered and acidified), then analyzed by ICP-AES. Samples of a multi-element, standard solution were also included in the analysis as a check on the accuracy of the analytical instrumentation used for these measurements. Normalized release rates were calculated based on measured, bias-corrected compositions using the average of the common logarithms of the leachate concentrations.

RESULTS AND DISCUSSION

Only the ccc version of each glass was submitted for XRD analysis as visual observations of the quenched glasses (and later the PCT performance) indicated that crystallization in the quenched glasses was unlikely. Trevorite (a spinel) was the only crystalline phase that was identified in a few of the study glasses (SB5-15, SB5-16, SB5-17 and SB5-18). See Figure 1 for an example. Spinels are not of concern as they have been shown to have little impact on the durability of high level waste glasses [7]. In some cases, crystallization was visible on the surface of a ccc glass but not detected by XRD. It is likely that the volume fraction of crystallization in these glasses was below the XRD detection limit of about 0.5 vol%.

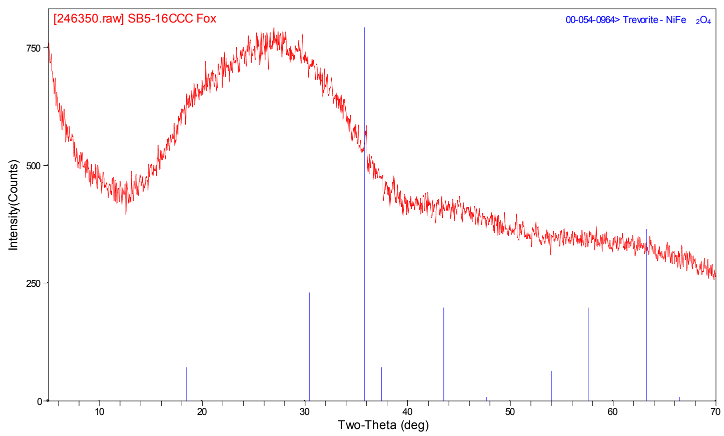


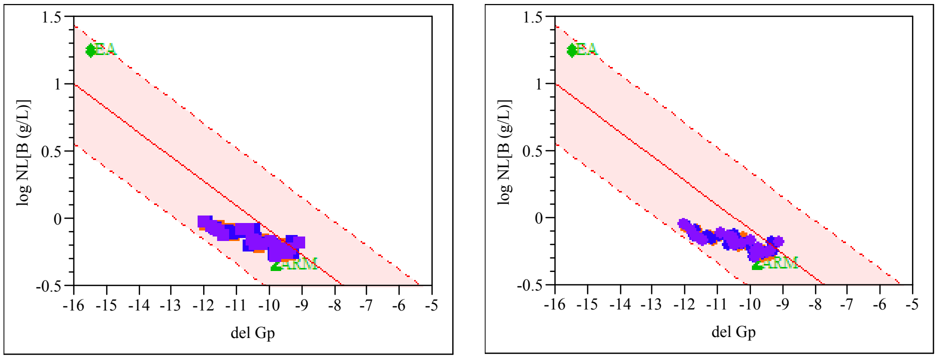
Figure 1. XRD results for glass composition SB5-16 after the ccc heat treatment showing a small amount of Trevorite ($NiFe_2O_4$).

All of the prepared samples were analyzed for chemical composition, twice for each element of interest, with the ICP-AES instrumentation being re-calibrated between the duplicate analyses. Some of the results from these analyses provided incentive for adjusting the measurements by the effects of the ICP-AES calibration. Therefore, the oxide measurements of the study glasses were bias corrected for the effect of the ICP-AES calibration. The measurements for each oxide for each glass were averaged to determine a representative chemical composition for each glass. These determinations were conducted both for the measured and for the bias-corrected data. Overall, comparisons between the measured and targeted compositions suggested only minor difficulties in meeting the targeted compositions for some of the oxides for some of the glasses, none of which were significant enough to affect the outcome of the study.

Chemical durability of the glasses was evaluated using the PCT [5]. The PCT leachate concentrations were normalized using the measured cation composition (expressed as a weight percent) in the glass to obtain a grams-per-liter (g/L) leachate concentration. The common logarithm of the normalized PCT (normalized leachate, NL) for each element of interest was determined and used for comparison.

The NL values for B, Li, Na and Si for all of the study glasses were well below those of the EA benchmark glass [6], regardless of heat treatment. The highest NL [B] for the study glasses was 0.914 g/L (the quenched version of glass SB5-13), as compared to 16.695 g/L for the EA glass. This indicates that all of the glasses have very acceptable durability performance. The complete PCT results are available in detail elsewhere [8].

The ability of the DWPF process control models to correctly predict the durability of glasses SB5-01 through SB5-20 was also investigated. Figure 1 provides plots of the measured and predicted PCT responses for boron (used as an indicator for the leaching rate of radioactive species [5]) as a function of heat treatment. Prediction limits at a 95% confidence for an individual PCT result are also plotted along with the linear fit. The EA and ARM results are indicated on these plots as well. The plots illustrate good predictability of the durability of study glasses SB5-01 through SB5-20 by the current free energy of hydration (ΔG_p) models [9].



Quenched **ccc**

Figure 2. Normalized Leachate for Boron versus ΔG_p Model Prediction with 95% Confidence Interval for Individual PCTs.

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CONCLUSIONS

The objective of this study was to experimentally measure the properties and performance of a series of glasses with compositions that could represent SB5 as processed at the DWPF. Glass compositions were developed by combining a series of SB5 composition projections with a group of frits. Three composition projections for SB5 were developed using a model-based approach at SRNL and represent various amount of aluminum removal. The frits for this study were selected based on their predicted operating windows and their potential (based on historical trends) to provide acceptable melt rates for SB5.

The study glasses were fabricated and characterized at SRNL. Chemical composition analyses suggested only minor difficulties in meeting the targeted compositions for some of the oxides for some of the glasses. No crystalline phases were identified that are expected to adversely impact chemical durability. The normalized leachate values for B, Li, Na and Si for all of the study glasses were well below those of the EA benchmark glass, regardless of heat treatment. This indicates that all of the glasses had very acceptable durability performance. The measured PCT responses were predictable by the current ΔG_p models.

The results of this study indicate that a frit composition can be identified that will provide a processable and durable glass when combined with SB5 at the DWPF. In particular, the frit compositions identified were capable of producing acceptable glasses over a fairly wide range of aluminum concentrations in the waste sludge. Additional studies are underway to recommend a frit that continues to meet process and performance requirements as well as to provide an enhanced melt rate for improved waste throughput.

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