Qualification of a Radioactive High Aluminum Glass for Processing in the Defense Waste Processing Facility at the Savannah River Site - 8410

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ABSTRACT

At the Savannah River Site (SRS) the Defense Waste Processing Facility (DWPF) has been immobilizing SRS's radioactive high level waste (HLW) sludge into a borosilicate glass for approximately eleven years. Currently the DWPF is immobilizing HLW sludge in Sludge Batch 4 (SB4). Each sludge batch is nominally two million liters of HLW and produces nominally five hundred stainless steel canisters 0.6 meters in diameter and 3 meters tall filled with the borosilicate glass. In SB4 and earlier sludge batches, the Al concentration has always been rather low, (less than 9.5 weight percent based on total dried solids). It is expected that in the future the Al concentrations will increase due to the changing composition of the HLW. Higher Al concentrations could introduce problems because of its known effect on the viscosity of glass melts and increase the possibility of the precipitation of nepheline in the final glass and decrease its durability. In 2006 Savannah River National Laboratory (SRNL) used DWPF processes to immobilize a radioactive HLW slurry containing 14 weight percent Al to ensure that this waste is viable for future DWPF processing. This paper presents results of the characterization of the high Al glass prepared in that demonstration.

At SRNL, a sample of the processed high Al HLW slurry was mixed with an appropriate glass frit as performed in the DWPF to make a waste glass containing nominally 30% waste oxides. The glass was prepared by melting the frit and waste remotely at 1150ºC. The glass was then characterized by

- determining the chemical composition of the glass including the concentrations of several actinide and U-235 fission products,
- calculating the oxide waste loading of the glass based on the chemical composition and comparing it to that of the target
- determining if the glass composition met the DWPF processing constraints such as glass melt viscosity and liquidus temperature along with a waste form affecting constraint that prevents the precipitation of nepheline ($NaAlSiO_4$) crystals in the glass melt
- measuring the durability of the glass using the ASTM Standard Product Consistency Test (PCT) leach test to determine if the durability of the glass based on B, Li, and Na releases met the requirements for acceptance in a US geologic repository
- measuring the leachability of several radionuclides using the ASTM Standard PCT leach test and comparing them to the B, Li, and Na releases
- examining the glass by scanning electron microscopy and energy dispersive X-ray spectrometry to determine if any crystals had formed in the glass melt.

Results indicate that the high Al glass met all the requirements for processing and product quality in the DWPF.

INTRODUCTION

The radioactive high level wastes (HLW) generated at Savannah River Site (SRS) from more than 30 years of producing nuclear materials for the defense of the U.S. are stored as caustic slurries in 49 underground mild steel tanks in the SRS Tank Farm. The slurries are a mixture of hydrous oxide solids and an aqueous supernate containing primarily dissolved nitrate, nitrite, and hydroxide salts. Each tank can hold nominally 3.5E+06 liters (9.2E+05 gallons) of caustic HLW. Personnel at the Defense Waste Processing Facility (DWPF) at SRS have been immobilizing the HLW sludge slurries from the Tank Farm into a borosilicate glass for approximately eleven years. Two of the tanks, Tanks 51 and 40, are used as a feed preparation tanks for the DWPF. Tank 51 is used to blend sludge slurries from selected storage tanks for processing in the DWPF. Here, the slurry is washed to remove excess sodium salts. Tank 40 is the feed tank to the DWPF. Prior to sending a washed sludge batch from Tank 51 to Tank 40 to be processed in the DWPF, an aliquot of the Tank 51 slurry is sent to Savannah River National Laboratory (SRNL) to process in their Shielded Cells using the DWPF processes. Part of the demonstration at SRNL is to confirm that the DWPF can successfully immobilize the solids of the sludge batch into a borosilicate glass and that the glass meets the durability criterion for acceptance of a glass into a Federal geologic repository in the United States. The purpose of the demonstration at SRNL is to confirm that the sludge batch can be successfully processed in the DWPF.

Each batch of sludge slurry prepared in the SRS Tank Farm is nominally two million liters (five hundred thousand gallons). The DWPF can process nominally twenty three thousand liters (~six thousand gallons) at a time from Tank 40 so each sludge batch represents about 670 transfers to the DWPF. In the DWPF, a combination of nitric and formic acids is added to the slurry to perform the necessary chemical reactions and adjust slurry rheology. Formic acid is added to reduce Hg in the slurry so it can be steam stripped from the slurry. Then a frit containing primarily glass forming oxides is added to the slurry. It is then fed to a joule heated melter at 1150 ºC and the resulting molten glass is poured into stainless steel canisters. Depending on the waste loading used for processing, each sludge batch will produce nominally five hundred stainless steel canisters ~0.6 meters (2 feet) in diameter and ~3 meters (10 feet) tall filled with the borosilicate glass. The canisters will go to a geologic repository for permanent disposal.

Currently the DWPF is immobilizing HLW sludge in Sludge Batch 4 (SB4). A portion of SB4 contains sludge solids whose Al concentration is ~2X greater than in previous sludge batches. For example, the sludge solids in SB1A contained 7.7 wt.% Al [1] in terms of weight percent of total dried solids. As shown in this paper, the Al in the high Al solids (called High Al HLW Slurry in this paper) was 14 wt. %. It is known that high concentrations of Al, a network former in glass, can increase the viscosity of the glass melt [2] and potentially decrease the durability of the final glass by causing nepheline ($NaAlSiO_4$) to precipitate in the glass [3]. This paper presents results of the characterization of a sample of the high Al HLW solids and the glass prepared from these slurry. In this paper, the glass is called the High Al Qualification Glass.

The first part of the characterization effort was to determine the composition of the High Al HLW Slurry (called the High Al Waste Slurry in this paper). Then the High Al Qualification Glass was prepared and its composition determined to see if its composition met the processing and product constraints in the models that are in the DWPF's Product Composition Control System (PCCS) [4]. The final part of the characterization was to confirm whether the glass met the durability criterion set forth in the Waste Acceptance Product Specifications (WAPS) [5] for vitrified waste forms for permanent disposal in a Federal geologic repository. This criterion is that the normalized releases based on B, Li, and Na (plus two times their respective standard deviations) in the ASTM 1285 standard nuclear waste glass leach test [6] must at least be lower than their respective releases from the Environmental Glass (EA glass) [7]. This leach test is commonly referred to as the Product Consistency Test (PCT). The final part of the characterization is to examine the glass for crystal inclusions by scanning electron microscopy (SEM).

EXPERIMENTAL

Analysis of the High Al HLW Slurry

A three liter sample of the High Al HLW Slurry was received into to the Shielded Cells of SRNL for the characterization and qualification. To determine the compositions of the solids they first had to be dissolved. For the dissolutions, aliquots of known masses of the mixed slurry were taken, dried at 110 ºC, and dissolved remotely by two different methods that are used in the DWPF process control analytical laboratory. One method was a sodium peroxide fusion at 675°C followed by a HNO_3 uptake. Triplicate samples were dissolved by this method. The other method was dissolution by cold chemical method. This method uses a mixture of concentrated HNO_3 and HF at ambient temperature. Boric acid was added to complex the excess HF. Quadruplicate samples were dissolved by this method. The solutions of the dissolved sludge from both methods were then diluted to known volumes (nominally 250 mL) so that ~15 mL aliquots could be safely removed from the Shielded Cells without exposing personnel to excess radiation. These aliquots were analyzed by Analytical Development (AD) using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). These dissolutions and analytical methods gave the concentrations in the total dried solids in the slurry. In order to know how much frit to add to make glass, the calcined composition of the sludge slurry had to be known. To determine this, quadruplicate aliquots of known masses of the mixed slurry were then taken and calcined at a temperature of 1150 ºC to determine metallic oxide composition of the sludge solids. Calcining converts the nitrate, nitrite, hydroxide salts and other salts to oxides. The calcine solids factor was 0.668 grams of oxides per gram of dried sludge solids.

Preparation the High Al Qualification Glass

Based on the calcined oxide composition of the High Al HLW Slurry, the frit recommended for the High Al Qualification Glass was SRNL Frit 507 [8]. The measured composition of Frit 507 is 67.5% SiO_2, 14.1% B_2O_3, 9.6% Li_2O, 4.2% Na_2O and 4.1% Fe_2O_3 [8]. To fabricate the glass, a known mass of the High Al HLW Slurry was mixed with sufficient Frit 507 to make a glass that would have a waste loading (WL) of 30 wt.% on an oxide basis. The frit and slurry were mixed in a 95% platinum/5% gold crucible and dried overnight at 110 °C. It was then heated at 5 °C per minute to 1150 °C and held at 1150 °C for four hours. It was then cooled to ambient temperature by placing the crucible in a shallow pan of water. No water contacted the glass during cooling. Approximately 35.6 grams of glass were made. The glass was black and shiny with no visible salt crystals or other inhomogeneities.

Analysis of the High Al Qualification Glass

The composition of the final glass was determined by dissolving samples of the glass by the sodium peroxide fusion method and by a mixed acid dissolution in sealed Teflon vessels at 115 °C using a combination of HF, HCl and HNO_3 acids. Boric acid was added to the latter dissolution method to complex excess fluoride. In order to enhance dissolution the samples of the glass were crushed and ground using agate cups, balls and caps in a mechanical pulverizing mixer mill. The glass was then sieved and only the portion that passed through a 200 mesh (75 µm) brass sieve was used for the dissolutions. Weighed amounts (nominally 0.25 grams) of the crushed glass were then dissolved remotely by the two methods to ensure that all the elements of interest were dissolved and could be analyzed. Three aliquots of the crushed High Al Qualification glass were dissolved by the fusion technique and four aliquots by the mixed acid technique. The dissolutions were diluted to a known volume and removed from the Shielded Cells for analyses by ICP-AES and ICP-MS. The dissolutions from the mixed acid method were also analyzed by gamma counting to determine the concentrations of Cs-137 (a U-235 fission product) and Am-241 (an actinide formed by the beta decay of Pu-241 in the waste) in the glass. They were also analyzed by ICP-MS to determine the concentrations of other U-235 fission products and actinides in the glass.

Check of Dissolution Methods and the ICP-AES Analytical Method

Concurrent with each set of dissolutions in the Shielded Cells, three samples of a standard glass were also dissolved to determine if the dissolutions were complete. Also with each set of samples sent to ADS for ICP-AES analysis, two samples of a certified multi-element standard containing known concentrations of Al, B, Fe, Li, Na, and Si were also submitted. Results of these efforts indicated that the dissolutions were complete and the calibration of the ICP-AES instrument was accurate.

Performance of the Standard ASTM 1285 Leach Test Procedure

The ASTM 1285 test [6] is a crushed glass (100 to 200 mesh, or 149 to 75 μm) leach test at 90°C for 7 days using deionized water in sealed stainless steel vessels. The test was performed in quadruplicate for each glass. Duplicate blanks and triplicate samples of a standard glass and triplicate samples of the EA glass were also tested with the samples. In the PCT, ten milliliters of deionized water are used for each gram of glass. Nominally 1.7 grams of glass and 17 mL of deionized water were used in stainless steel vessels that were sealed remotely. After 7 days at 90°C, the containers were removed from the oven, allowed to cool, weighed to determine water loss, and then opened. Due to the radioactivity of the glass, this portion of the test was performed remotely in a Shielded Cell using manipulators. The leachate from each vessel was decanted into a clean vessel and transported to a radiochemical hood where they could be handled and the analyses were completed. The pH of each leachate was measured and then it was filtered through a 0.45 micron filter and acidified to 1 volume percent HNO_3. Concentrations of B, Li, and Na were then determined using ICP-AES. These are the best elements to measure the durability of the glass because their concentrations in the final leachates are not affected by solubility constraints.

RESULTS AND DISCUSSION

Major Elements in High Al HLW Slurry and Qualification Glass

Table 1 shows the major elemental (excluding oxygen) compositions of the sludge solids in the High Al HLW Slurry and of the final High Al Qualification Glass. The Waste Dilution Factor (WDF) given in the final column of Table I is calculated from the following equation.

$$WDF_i = C_{is}/C_{ig}$$

where WDF_i = the waste dilution factor based on element i

C_{is} = the concentration of i in the dried sludge slurry

C_{ig} = the concentration of i in the glass.

Table I. Average of Elemental Concentrations Measured in the High Al HLW Slurry Solids and the Qualification Glass by ICP-AES[a]

Element	Weight % In Total Solids	Weight % In Calcined Solids	Weight % In Glass	Waste Dilution Factor
Al	13.7	20.5	6.67	2.1
B [b]	<0.01	<0.01	3.05	NA
Ca	0.824	1.23	0.41	2.0
Fe	7.01	10.5	5.14	NA
Li	0.008	0.012	3.62	NA
Mg	0.296	0.442	0.12	2.5
Mn	1.74	2.60	0.75	2.3
Na [c]	13.4	20.0	7.76	NA
Ni	0.63	0.941	0.27	2.3
S [c]	0.55	0.49	0.067	8.2
Si [b]	0.423	0.63	24.6	NA
U[d]	1.77	2.65	0.75	2.4

[a]Results are averages of seven determination unless noted. %RSD's range from 2 to 14%.
[b]Results of three samples dissolved by the peroxide fusion technique.
[c] Results of four samples dissolved by the mixed acid or cold chemical technique.
[d]Results of ICP-MS analysis of four samples dissolved by the mixed acid or cold chemical technique.

For the High Al HLW Slurry solids, the composition is given both in terms of weight percent in total dried solids (dried at 110 ºC) and in weight percent in calcined solids (calcined at 1150 ºC). All the results are for ICP-AES analysis except for U which was determined by ICP-MS. Essentially all of the B, Li, Si are from the glass frit added to the sludge in order to prepare the glass. The Fe and Na are from both the frit and the HLW sludge. The WDF is simply the factor by which an element in the total dried waste solids of the High Al HLW Slurry were diluted by addition of the frit. Consequently values for the WDF are not given for B, Li, Si Na and Fe. Of the remaining elements, except for S, that are exclusively from the waste, the WDF ranges from 2.0 to 2.5. However, the WDF for S is 3 to 4 times higher. This is due to volatilization of S from the glass melt at 1150 ºC. In fact, sulfate deposits have been observed in the off gas system of the first DWPF melter [9] and in off gas system of the current DWPF melter [10].

Measured versus Targeted Oxide Composition of the High Al Qualification Glass

The measured and predicted composition of the High Al Qualification Glass in terms of oxides is presented in Table II.

Table II. Average Concentrations of the Major Oxides within the High Al Qualification Glass Measured by ICP-AES.[a]

Oxide	Measured Weight %	Predicted Weight %[b]	% Difference from Predicted
Al_2O_3	12.6	12.3	2.4
B_2O_3 [c]	9.81	9.80	0.1
CaO	0.57	0.55	3.6
Fe_2O_3	7.35	7.54	-2.5
Li_2O	7.80	7.01	11.
MgO	0.20	0.23	-13.
MnO	0.97	1.06	-8.5
Na_2O [d]	10.5	11.4	-7.9
NiO	0.34	0.38	-12.
$SO_4^{=}$ [d]	0.20	0.48	-58.5
SiO_2 [c]	52.5	48.0	9.4
U_3O_8 [e]	0.89	0.99	-10.

[a]Results are averages of seven determinations unless otherwise noted.
[b]Taken from Reference [8]
[c]Results of three samples dissolved by the peroxide fusion technique.
[d] Results of four samples dissolved by the mixed acid technique.
[e] Results of ICP-MS analysis of four samples dissolved by the mixed acid technique.

The measured values are simply the measured elemental calcined weight percents in Column 3 of Table I times the element to oxide conversion factor for that respective element The predicted values in the third column are taken from Reference 8. These were calculated in Reference 8 from the calcined composition of the High Al HLW Slurry given in Table I combined with Frit 507 at a 30% WL based on oxides. The last column shows the relative difference of the measured from the predicted calculated from the equation 100 × (Meas. – Pred.)/Pred. Note that the relative differences for the major elements in the waste oxides of Al, Ca, Mn, and U, along with oxides of Fe and Na from both the waste and the frit, and the oxides of B and Si from the frit itself are within 10% or better of the predicted. This agreement suggests that the waste loading of 30% based on oxides was indeed achieved. The reason for the slightly larger relative differences for the measured and predicted oxides of Li and Ni could be due to analytical uncertainties. The large negative difference for sulfate is due to volatilization of sulfur from the molten glass at 1150 ºC.

Predicted Processing Properties and Durability of the High Al Qualification Glass

The measured elemental concentrations in the High Al Qualification Glass presented in Column 4 of Table I were used to predict properties of the glass based on the PCCS models [4]. These predictions were then compared to DWPF acceptance values for the properties to see if this glass did indeed meet the processing and product quality constraints of the DWPF. As shown in Table III, based on the measured composition of the glass, all the predicted properties met the PCCS acceptable values.

Table III. Predicted Processing Properties and PCT Values forHigh Al Qualification Glass

Name of Constraint (unit)	Value	Acceptable Values
NL[B (g/L)]	0.412	< 16.7[a]
NL[Li (g/L)]	0.482	< 9.6 [a]
NL[Na (g/L)]	0.427	< 13.3 [a]
Del Gp Value (kcal/mol)	-8.37	>-13.9[b]
T_L Prediction (ºC)	857	< 1050[b]
Viscosity Prediction (P)	52	20 < 110[b]
Sum of Glass Oxides (%)	104	95 < 105[b]
Nepheline Constraint Value	0.695	>0.62[c]

[a]See Reference 7. [b]Presented in Reference 4. [c]See References 3 and 15.

The predicted properties for the High Al Qualification Glass provided in Table III will now be discussed. The first three constraints in Table III are the predicted values from Reference 4 for the normalized releases of B, Li, and Na in the ASTM PCT test [6]. The accepted values for these in the third column of Table III are the consensus measured values for the reference EA glass [7]. The next constraint in Table III deals with the relative stability of the glass in kilocalories per mole (Del Gp Value) and is calculated based on the oxide composition of the glass [4]. Glasses with a Del Gp Value less than -13.9 kcal/mol will never be more durable than the EA glass in the PCT leach test. The fifth constraint is the liquidus temperature (T_L Prediction (ºC)) of the molten glass. This is the temperature below which crystals start to precipitate in the glass. Since crystals in the glass can decrease its durability and collect in the melter, it is desirable to prevent their formation within the glass. This constraint is based on models presented in References 11 and 12. The sixth constraint is the viscosity of the glass while it is molten at 1150 ºC. Clearly the viscosity has to be low enough so the glass can flow through the melter and into the final canister for disposal and high enough so there is sufficient retention in the melter to dissolve the sludge solids into the molten glass. The predicted viscosity has to be between 20 to 110 poise [4]. The model supporting this constraint is discussed in Reference 13. The seventh constraint on the sum of the measured oxides in the glass. This sum has to be between 95 to 105% [4]. This is an assessment of the reliability the dissolution and analytical methods used to analyze the glass. It is also an indication that all the elements of significant concentrations (>0.5 weight percent) in the glass were detected and analyzed. The basis for this constraint is discussed in Reference 14. The final constraint is associated with the possibility of the formation of nepheline ($NaAlSiO_4$) crystals in the glass. If these crystals form in the glass, the durability of the glass in a PCT can be decreased considerably. To prevent its formation, a study has shown that the ratio of the weight percent of SiO_2 to the sum of the weight percents of Na_2O, SiO_2 and Al_2O_3 must be greater than 0.62 [15]. Results of that study have been applied to DWPF type glasses and have confirmed that the constraint is still valid for use in PCCS [3].

As can be seen all the results in Table III meet the PCCS criteria for processing this glass in the DWPF and producing a glass durable enough to be accepted at the Federal repository being built in the USA. Results of the PCT will be discussed.

Results of the ASTM 1285 Leach Test (Product Consistency Test) for the B, Li, Na, Al and U in the High Al Qualification Glass

Quadruplicate samples of the ground glass were subjected to the PCT along with the appropriate blanks, a standard glass and the EA glass as prescribed by the procedure [6]. The results for the standard glass and the blanks indicated that the test was acceptable. Average normalized releases for the High Al Qualification glass were calculated from the following equation and are presented in Table IV along with measured and published values for the EA glass [7]. The normalized releases are based on the concentrations of B, Li, Na, Al and U given in Table I for the glass.

$NL_i = C_i/(F_i \cdot 1000)$

where i represents the elements B, Li, or Na

NL_i = the normalized release based on element i
C_i = the concentration (ppm) of i in the leachate measured by ICP-AES
and F_i = the weight fraction of element i in the glass.

The factor of 1000 is a result of the elemental concentration being given in parts per million.

The normalized release based on a specific element in the glass is a measure of the concentration of the glass (grams glass/liter) dissolved in the PCT leachate based on that specific element. The average pH value of the leachates is also presented. The leachate pH was measured as part of the PCT protocol and provides a secondary indication of glass durability. The greater the pH in the leachate, the higher the leachability of the glass due to ion exchange of the Na in the glass with hydronium ions in the water. Note that the average pH value for EA glass is larger than that for the High Al Qualification Glass and the leachability of the EA glass is higher. The last column in the Table presents the sum of averages for each of the measured normalized releases for B, Li, and Na plus twice their respective standard deviations.

Table IV Average PCT Results for High Al Qualification Glass Compared to EA Glass and Average pH Values for the Leachates

Element or pH	Measured g/L, (Std. Dev.,%RSD)	Measured EA Glass, g/L (Std. Dev., %RSD)	Published EA Glass,g/L (Std. Dev., %RSD)	Measured g/L plus Two Std. Dev.
B	0.564 (0.014,2.5)	14.9 (0.47, 5.6)	16.7 (1.2, 7)	0.592
Li	0.678 (0.014,3.5)	8.89 (0.31, 3.5)	9.6 (0.7, 7)	0.692
Na	0.542 (0.011,2.0)	12.7 (0.40, 3.2)	13.3 (0.9, 7)	0.564
Al	0.504 (0.015,3.0)	NA	NA	NA
U	0.388 (0..008,3.1)	NA	NA	NA
pH	10.4	11.7	11.9	NA

[a]NA = Not Applicable

As discussed previously, the WAPS criterion for durability is that the mean normalized releases for B, Li, and Na must be at least two standard deviations below the mean PCT results for the EA glass. The results in the last column of Table IV clearly indicate that this criterion is met. Also note that the measured releases for B, Na, and Li in Table IV are slightly higher than their respective predicted releases shown in Table III calculated by the PCCS. Results for Al and U are also presented in Table IV. In this glass the Al is leaching almost congruently with the B, Na, or Li while the normalized release for U is slightly lower.

Results of the ASTM 1285 Leach Test (Product Consistency Test) for Selected Radionuclides in the High Al Qualification Glass

The concentrations for several radionuclides were measured in the PCT leachates in order to compare the normalized releases based on the radionuclides to those based on B, Li, or Na. Results along with the analytical method used to measure the radionuclides in the glass and PCT leachates are presented in Table V.

Table V. Normalized PCT Results for Selected Radionuclides for the High Al Qualification Glass

Radionuclide	Conc. in Glass, (wt. % unless noted)	Conc. in Leachate, ppb	Grams Glass/Liter[a] (%RSD)	Analytical Method
Zr-93	1.0E-02	2.48	0.025 (1.6)	ICP-MS
Tc-99	1.4E-04	0.547	0.41 (6.1)	ICP-MS
Cs-137	1.9E+08[b]	3.4E+04[c]	0.17 (3.5)	γ Counting
Sm-151	2.6E-04	0.75	0.029 (2.7)	ICP-MS
Np-237	5.1E-04	2.6	0.44 (3.4)	ICP-MS
U-235	5.9E-03	23.	0.40 (2.6)	ICP-MS
Pu-239	4.2E-03	13.	0.32 (3.8)	ICP-MS
Pu-240	6.1E-04	2.0	0.33 (2.4)	ICP-MS
Am-241	1.6E+07[b]	4.4E+03[c]	0.27 (10)	γ Counting
Am-243	7.3E-05	0.24	0.34 (6.1)	ICP-MS

[a]Based on quadruplicate PCT tests.
[b]Concentration in disintegrations per minute per gram of glass.
[c]Concentration in disintegrations per minute per milliliter of leachate.

In Table V note that none of the radionuclides have normalized releases greater than the releases based on B, Li, or Na. This is in agreement with the PCT results for the DWPF pour stream sample of SB3 where none of the radionuclides had releases greater than those for B, Li, or Na [16]. This again indicates that the normalized releases based on B, Li, or Na represent higher releases than any radionuclides from the glass in a PCT. In Table V the lower releases for the U-235 fission products Zr-93 and Sm-151 may be due to their limited solubilities in the leachates. The normalized release based on Cs-137, a U-235 fission product that is soluble in the leachate, is lower the releases of B, Li, and Na. This has also been observed in a DWPF glass taken from the pour stream of the DWPF melter during processing of SB3 [16]. A possible explanation is that Cs-137 is being retained in the altered layer of the glass perhaps as a cesium aluminum silicate. Finally in Table IV and V. note that except for Am-241 and Am-243 the normalized releases based on different isotopes of the same element are equal as they should be. These elements are Pu-239 and Pu-240 and also U-235 and the total U measured by ICP-ES as shown in Table IV. The 20% difference between the normalized releases for Am-241 and Am-243 may be due to measurement uncertainties associated with the two different analytical methods utilized to measure these radionuclides.

Examination by Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry Analysis

A portion of the glass that had been crushed, sieved (200 < mesh size < 100), and washed for the PCT was examined by SEM and by Energy Dispersive X-ray Spectrometry (EDS) analysis. Two representative SEM images are shown in Figures 1 and 2.

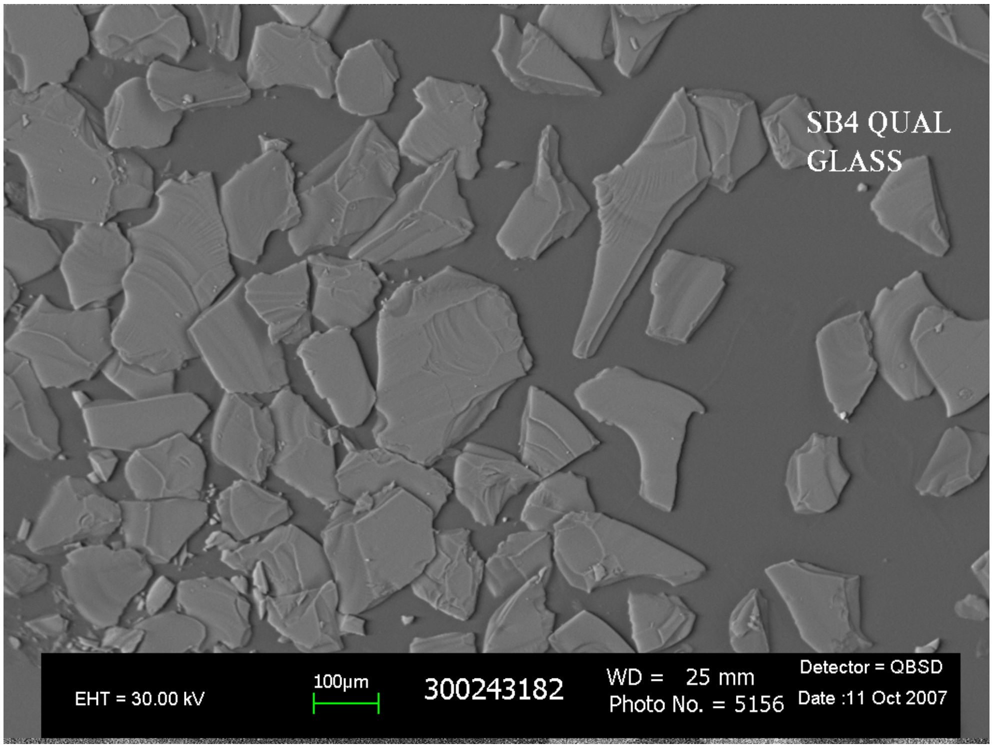

Figure 1. SEM image of a set of High Al Qualification Glass particles.

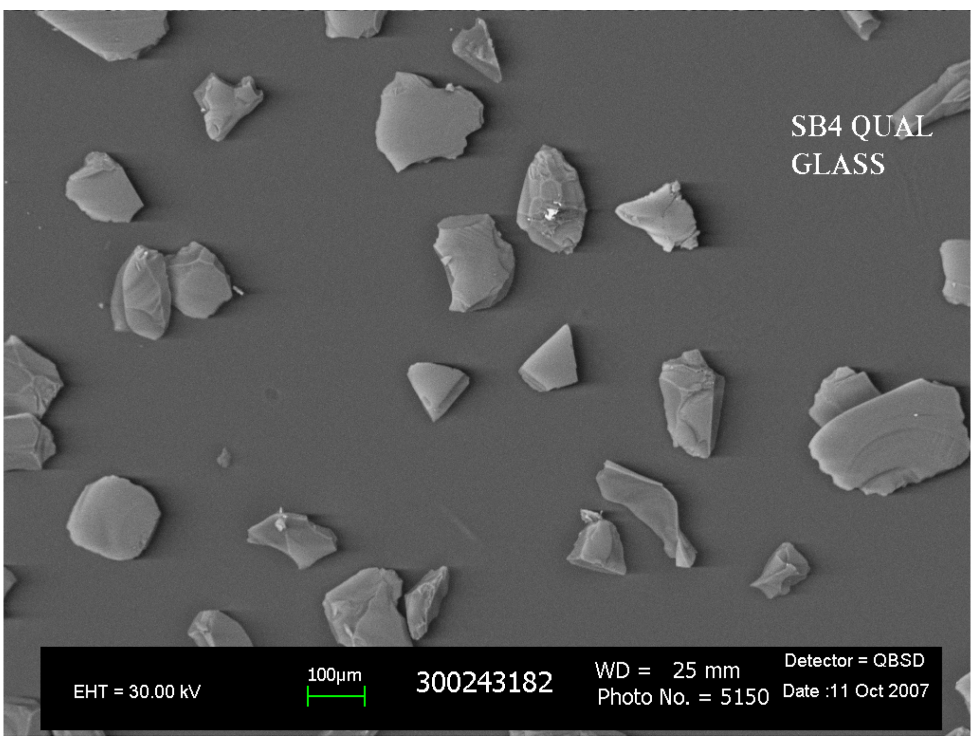

Figure 2. SEM image of a second set of High Al Qualification Glass particles.

Note that the particles are relatively uniform in size and because of the washing do not have any glass fines associated with them. Also at this magnification there is no evidence for crystals in the glass. (No crystals were observed at higher magnifications but micrographs were not included in the paper.) Note that in Figures 1 and 2 there were only two bright particles in both images. The brightness indicates that these particles have electron densities that are different from the glass itself. Figure 3 is an EDS spectrum that was representative of the glass particles in Figures 1 and 2. This spectrum is similar to that for the SB3 glass [16] and typical of DWPF glasses with Si, Al, Na, and Fe being the major elements.

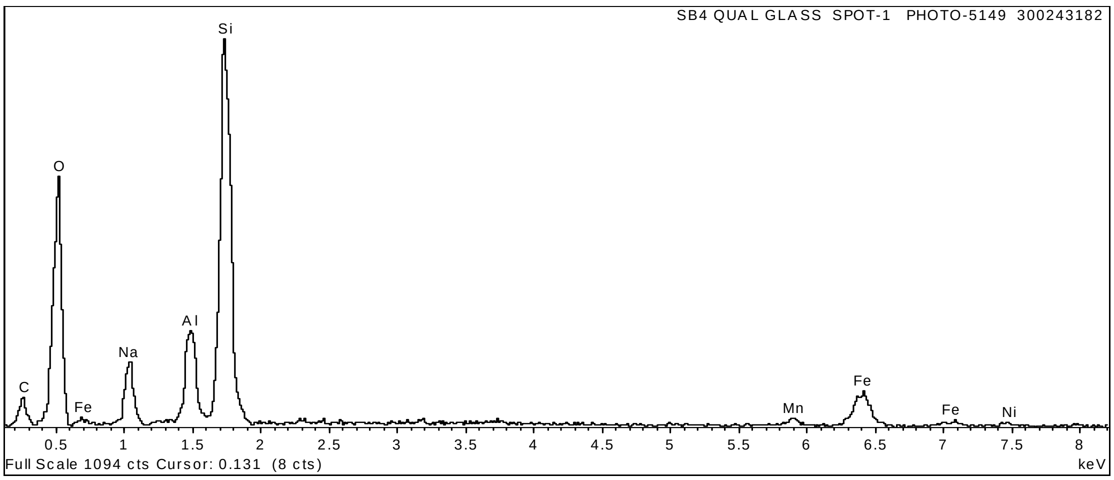

Fig. 3. Energy Dispersive X-ray Spectrum of the High Al Qualification Glass particles in Figures 1 and 2

The EDS spectra were then taken for the two bright particles in Figures 1 and 2. These spectra were identical and one is shown in Figure 4.

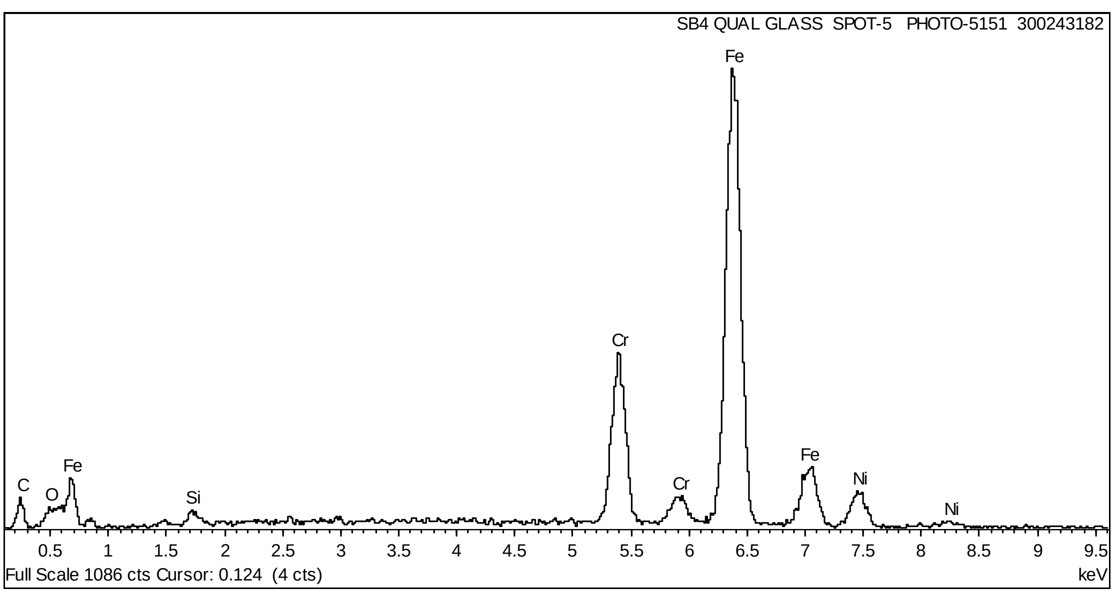

Fig 4. Energy Dispersive X-ray Spectrum of the two bright particles in Figures 1 and 2. Spectrum is typical of stainless steel.

The spectrum indicates that the major elements are Fe, Cr, and Ni and is typical of that for stainless steel (SS). Apparently the particles were abraded from the SS grinder used to prepare the glass for the PCT. However it has been shown that SS does not affect the results of the PCT [6]. Another metallic contaminant found by the SEM examination but less prevalent that the SS particles were traces of micron sized Cu particles from the brass sieves used to achieve the proper particle size for the PCT. Brass sieves are recommended for performance of the PCT [6].

CONCLUSIONS

A glass with a targeted WL of ~30% was made from a combination of Frit 507 and a High Al HLW Slurry in the SRNL Shielded Cells from a sample of the High Al HLW Slurry from Tank 51. The chemical composition of this High Al Qualification Glass was measured, and the results were found to meet the PCCS acceptance criteria for processing at the DWPF.

The measured PCT results for the High Al Qualification Glass yielded values for normalized releases of B, Li, and Na of 0.564, 0.678, and 0.542 g/L, respectively. These are well below the releases for EA glass. Thus, the High Al Qualification Glass satisfies the qualifications necessary for processing in the DWPF as well as the leaching criterion set forth in the WAPS for acceptance into a Federal geologic repository. Normalized releases for several radionuclides were also measured and all were found to be less than the releases for B, Li, and Na. indicating that these three elements represent the highest leach rate in the PCT. Finally examination of the glass by scanning electron microscopy and energy dispersive X-ray spectrometry indicated that the glass contained no crystals.

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