Characterization of Radioactive Macrobatch Four Glass being Produced by the Defense Waste Processing Facility at the Savannah River Site

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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 nine years. Currently the DWPF is immobilizing HLW sludge in Macrobatch 4 (MB4). Each macrobatch is nominally five hundred thousand gallons of HLW and produces nominally five hundred stainless steel canisters two feet in diameter ten feet tall filled with the borosilicate glass. This paper presents results of the characterization of a sample of MB4 glass taken directly from the pour stream of the DWPF melter during the filling of the canister S02312. This canister was the 275th canister filled during immobilizing MB4. The purpose of the sample was to confirm that the leachability of the glass in a standard ASTM test was less than the leachability criterion set forth in the Waste Acceptance Product Specifications (WAPS) for vitrified waste forms for permanent disposal in a Federal geologic repository. The sample was sent to the Savannah River National Laboratory (SRNL) for characterization.

The characterization of the glass sample includes measuring both its radioactive and nonradioactive composition, measuring its leachability in the standard ASTM leach test, and examining glass by scanning electron microscopy (SEM) to determine if any melt insolubles are present. Results of the compositional analysis indicate that the glass has a composition expected from measurements in the DWPF Analytical Laboratory and measurements at SRNL of MB4 HLW sludge. Results of the standard ASTM leach test indicate that the leachability of the glass is more than 10X less than the criterion stated in the WAPS and thus acceptable for permanent storage in a Federal geologic repository. Results of the SEM examination indicated that there were melt insolubles present. These were microcrystallites (≤ 2 µm in width) of U-235 fission product noble metals, Ru, Rh, and Pd in the glass. However, these did not cause the glass to fail leachability criterion.

INTRODUCTION

The radioactive high-level waste (HLW) at Savannah River Site (SRS) is stored as caustic slurries in million gallon tanks in the SRS Tank Farm. The Defense Waste Processing Facility (DWPF) is part of the program at SRS to empty these tanks. Currently the DWPF is immobilizing HLW sludge in Macrobatch 4 (MB4). Each macrobatch is nominally nineteen hundred cubic meters of HLW and produces nominally five hundred stainless steel canisters ~ 0.6 meters in diameter and ~ 3 meters tall filled with the borosilicate glass. Thus far during radioactive operations in the DWPF more than 2000 canisters have been produced with each canister containing nominally ~1800 kg. of glass. More than ten million Curies of radioactivity have been removed from the SRS HLW tanks. The DWPF began processing Macrobatch 4 (MB4), also called Sludge Batch 3, in March 2004. This macrobatch is in Tank 40, one of the two feed tanks to the DWPF. Macrobatch 4 is a blend of the heel of Macrobatch 3 left in Tank 40 after that campaign, the sludge that was transferred to Tank 40 from Tank 51, and direct additions to Tank 40 of waste solutions of Np-237 from one of the Separation Canyons at SRS. This is the first radioactive waste solution from a facility at SRS other than the HLW Tanks to be added to a Macrobatch to be immobilized into borosilicate glass for permanent disposal. The sludge transferred from Tank 51 contained sludges from HLW Tanks 7, 18 and 19 along with precipitated solutions of U, Pu/Gd and Am/Cm from the F and H Canyons at SRS.

For processing in the DWPF ~2E04 liters of MB4 sludge slurry are pumped from Tank 40 to the Sludge Receipt and Adjustment Tank (SRAT) in the DWPF. There are two treatment steps prior to feeding the slurry to the melter. The first is the addition of nitric and formic acid to the SRAT. This reduces the Hg in the HLW to metallic Hg so it can stream stripped from the slurry. This also adjusts the rheology of the slurry to enhance pumping within the DWPF. The second treatment step prior to making glass is in the Slurry Feed Evaporator (SME). Here, based on an analysis of the material in the SRAT, a prescribed amount of glass forming frit is added to the slurry. After addition of the frit and evaporation of water to adjust the weight percent solids of the slurry, a sample of the slurry is taken from the SME and vitrified in the DWPF Analytical Laboratory as it would be in the melter. This sample is then analyzed to confirm that the proper amount of frit had been added and the correct weight percent solids had been obtained. If so, then that SME batch is ready to be sent to the Melter Feed Tank and then to the melter. Each SME batch is sufficient to fill nominally six canisters of glass. The glass sample discussed in this paper was taken on 4/28/05 from the pour stream of the DWPF melter while filling Canister S02312 of SME Batch 319 of MB4.

This paper presents results of the characterization of the HLW glass sample from MB4. The primary purpose of the characterization was to confirm that the glass meets durability criterion in the Waste Acceptance Product Specifications (WAPS) for permanent disposal in a Federal geologic repository.[1] This criterion states that the normalized releases of the glass based an analysis of B, Li, and Na in the leachates of the standard ASTM 1285 Test [2], commonly referred to the Product Consistency Test or PCT, should be at least two standard deviations less than the respective releases for the Environmental Assessment (EA) glass.[3] In this paper the following topics are discussed.

- The major nonradioactive and radioactive composition of the sample is given.
- Its nonradioactive composition is compared to the sample vitrified in the DWPF from SME Batch 319.
- A waste dilution factor is calculated and used to predict the concentration of radionuclides in the glass which are compared to the measured concentrations.
- Results of the PCT are presented for several of the major elements and compared to PCT releases for several radionuclides.
- Finally results of examination of the glass by scanning electron microscopy (SEM) is presented. Evidence for insoluble fission product noble metals was found.

EXPERIMENTAL

Obtaining the DWPF Pour Stream Samples

Each canister in the DWPF is fitted with a throat protector while it is being filled with molten glass in the DWPF. Purpose of the protector is to ensure that if molten glass wicks from the pour stream it does not solidify on the throat of the canister itself and interfere with the welding of the permanent stainless steel (SS) plug into the throat. When the pour stream is to be sampled, a special throat protector is used. This protector contains a small Pt/Au cup that can be inserted remotely into the pour stream to collect the sample while the canister is being filled. After the sample cup is filled, it is remotely retracted while the remainder of the canister is filled. After the canister is filled and removed from under the melter, the throat protector is removed from the top of the canister and remotely taken to a table in the Melt Cell of the DWPF. Here the cup is removed from the sampler, placed in a labeled SS container. The container is placed in a shielded cask and shipped to SRNL. Nominally 40 grams of glass are obtained in the sample sent to SRNL.

Glass Sample Preparation at SRNL for Characterization

At SRNL the SS container is removed from the shielded cask and placed in the Shielded Cells. The Pt/Au cup is removed from the SS container and the glass is examined visually for variations or any striking features. The glass is then mechanically removed from the cup and weighed. As stated earlier, nominally 40 grams of glass are received. Approximately 20 grams are selected for characterization. The remaining glass is replaced in the labeled SS container for archival purposes should any characterization need to be repeated in future years.

Glass and Sludge Dissolution Methods

For analysis, the glass had to be dissolved. Prior to dissolution, a ~20 gram sample was crushed and ground to enhance dissolution. Weighed amounts of the crushed glass were then dissolved remotely by two different methods to ensure that all the elements were dissolved and could be analyzed. The two methods were a sodium peroxide fusion at 650°C followed by a HCl uptake and an acid dissolution in sealed vessels at 115°C using a combination of HF, HCl, and HNO_3 acids. Boric acid was then added to this latter dissolution method to complex excess fluoride. Samples of the MB4 sludge slurry were also dissolved and characterized at SRNL as part of the qualification of MB4 for processing in the DWPF. Aliquots of the dried sludge slurry were dissolved by the peroxide fusion method and by heated Aqua Regia dissolutions in sealed vessels at 110°C. The solutions of the dissolved glass and sludge were diluted to known volumes so that ~25 mL aliquots could be safely removed from the Shielded Cells without exposing personnel to excess radiation exposure. In all cases four aliquots of the crushed DWPF glass and dried sludge were dissolved by each technique. The aliquots were then taken to the Analytical Development Section (ADS) of SRNL where they were placed in radiological hoods. Here analyses could be performed by instruments especially designed for operation in the hoods using hands on techniques. Concurrent with each of sets of dissolutions in the Shielded Cells, a standard glass was dissolved to determine if the dissolutions were complete and the resulting analyses accurate. In all cases the results for the standard glass were acceptable confirming that dissolutions were complete and the analytical results accurate.

Analytical Methods

These analytical methods were used at SRNL to analyze the solutions of the dissolved glasses. The major nonradioactive elements in the dissolved glasses and dried sludges were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). Radioactive counting techniques were used to analyze for Cs-137 and Am-241 (gamma counting), Sr-90 and Pu-241 (beta counting), and Pu-238 (alpha counting). Other fission product radionuclides were determined by inductively coupled mass spectrometry (ICP-MS) along with noble metals and other actinides.

Standard ASTM 1285 Leach Test Procedure

At SRNL the durability of the DWPF glass sample obtained from the pour stream was measured using the ASTM 1285 standard nuclear waste glass leach test.[3] This test is commonly referred to as the Product Consistency Test (PCT). Purpose of the PCT was to confirm that the DWPF was producing a glass that had a durability that met the criterion specified by the WAPS for repository acceptance.[1] The ASTM 1285 test[2] is a crushed glass (100 to 200 mesh) 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 the Environmental Assessment (EA) glass[3] are also tested with the samples. Purpose of the blanks is to measure impurities than may be in the water and or leached from the vessels. The standard glass is to determine that all the parameters in the test such as sieving were carefully controlled. The EA glass is necessary for the comparison prescribed by the waste acceptance criterion for DWPF glass.[1] In the PCT, ten milliliters of deionized water are used for each gram of glass. Nominally 1.7 grams of glass were used in stainless steel vessels that can be sealed remotely. After 7 days at 90°C, the containers are 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 steel container is decanted into a clean vessel. The radioactivities of the leachates are low enough so they can be transported to a radiochemical hood where they can be handled and the analyses are completed. The pH of each leachate is measured and then it is filtered through a 0.45 micron filter and acidified to 1 volume percent HNO_3. Concentrations of B, Li, and Na are then determined using ICP-AES. These are the best elements to measure to indicate the durability of the glass because their concentrations in the final leachates are not affected by solubility constraints. The concentrations of several radionuclides were also measured in the leachates in order to compare their releases with those of B, Li, and Na. The elements Si and S in the leachates were also measured to compare their normalized releases with those of B, Li, and Na.

RESULTS AND DISCUSSION

Major Composition of the Glass

Table I shows the major oxide composition of the MB4 glass sample. The oxides of B, Li, and Si are essentially all from the glass frit added to the sludge in the DWPF SME in order to dissolve the sludge in the melter at 1150°C and immobilize it into a borosilicate glass. The frit is 76% SiO_2, and 8% in B_2O_3, Li_2O, and Na_2O.

Table I. Oxides with Concentrations Greater than 0.2 Weight Percent in Macrobatch 4 Glass Measured by ICP-AES.[a]

Oxide	Weight %	% RSD
Al_2O_3	4.79	2.1
B_2O_3	4.44	2.0
CaO	1.03	1.6
Fe_2O_3	10.8	2.3
Li_2O	4.96	4.0
MgO	1.16	2.1
MnO	2.09	2.4
Na_2O [b]	11.9	1.4
NiO	0.55	4.3
P_2O_5	0.29 [b]	8.5
$SO_4^{=}$ [b]	0.39 [b]	12
SiO_2	51.0[c]	0.0
SrO	0.28 [b]	8.2
U_3O_8	3.51 [b]	1.1

[a] Results are averages of eight determinations unless otherwise noted.
[b] Results of four samples dissolved by the mixed acid technique.
[c] Results of four samples dissolved by the peroxide fusion technique.

As seen in Table I, these oxides account for more than 97.2 weight percent of the glass. The remaining oxides are fission products such as Tc-99, other actinides such as Am-241, and minor elements such as Cd and Ag that were used in the processes at SRS.

Comparison of the Composition measured at SRNL with the Composition Measured in the DWPF Analytical Laboratory

Table II provides a comparison of the major glass oxides measured at SRNL in the pour stream sample with those measured in the DWPF process control laboratory from a vitrified sample of SME Batch 319. Except for U, the agreement is better than 14% for all these elements. The relatively large discrepancy in U may be due to SRNL using ICP-MS to analyze for U while the DWPF uses ICP-AES. The ICP-MS measurement is considered better because element U has weak emission lines.

Table II. Concentration of Major Oxide (>0.5 Wt. %) for Glass Pour Stream Sample S02312 Compared to a Vitrified Sample of SME Batch 319

Oxide	Glass S02312 (Wt.%)	Vitrified SME Batch 319 (Wt.%)	Percent Difference (relative to SME)
Al_2O_3	4.79	5.22	-9.0
B_2O_3	4.44	4.9	-9.9
CaO	1.03	0.91	12
Fe_2O_3	10.8	10.5	2.9
Li_2O	4.96	4.8	2.4
MgO	1.16	0.99	14
MnO	2.09	1.8	14
Na_2O	11.9	11.2	5.6
NiO	0.55	0.53	3.3
SiO_2	51.0	54.3	-6.5
U_3O_8	3.51	2.7	22

Calculation of the Waste Dilution Factor (WDF) for the S02312 MB4 Glass

The WDF is the ratio of the concentration of the major components in the MB4 sludge to their concentrations in the glass. The WDF is simply the factor by which the elements or radionuclides specific to the waste are diluted by the addition of the nonradioactive frit. The following equation applies.

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

Where WDF_i = the waste dilution actor based on element i
C_{is} = the concentration of i in the dried sludge slurry
C_{ig} = the concentration of i in the dried sludge

The WDF was calculated from Al, Ca, Fe, Mg, Mn, Ni, and U and results are presented in Table III. The average WDF calculated from these elements is 2.19 with a relative standard deviation of 8%.

Table III. Waste Dilution Factor based on Seven Waste Elements in MB4 Glass and Dried Sludge

Element	Wt. % in Dried Slurry[a]	Wt. % in Glass[b]	WDF
Al	5.14	2.54	2.03
Ca	1.61	0.737	2.18
Fe	16.4	7.53	2.17
Mg	1.52	0.701	2.17
Mn	3.56	1.62	2.20
Ni	0.983	0.434	2.26
U	6.77	2.97	2.27

[a]Average of four or more samples of dried MB4 sludge at SRNL.
[c]Calculated from the respective oxide concentrations presented in Table I.

This waste dilution factor will be used to predict the concentrations of radionuclides and noble metals in the S02312 glass sample in order to compare them with their measured values.

Measured and Calculated Radionuclide Composition of S02312 MB4 Glass Sample

In the MB4 sludge the concentrations of 51 radionuclides were measured or estimated in order to satisfy one of the criterion of the WAPS. That criterion states that the glass producer shall report the concentration of any radionuclide that will contribute more than 0.05% of the Curies of the glass indexed to the years 2015 and 3115 after the glass is produced. A total of 30 radionuclides were identified as reportable. Of these, 18 were also measured in the glass. In Table IV the concentrations of these 18 in the glass are compared to their measured concentrations in dried sludge. The predicted concentrations in the glass were calculated by dividing the concentrations in the sludge by the WDF. Column 5 of Table IV gives the ratio of the predicted to the measured and Column 6 gives the method of analysis for each radionuclide. Note that the concentrations of all but four of the radionuclides are in the range of 0.3 to 25 ppm.

Table IV. Measured. Predicted, and Measured Radionuclide Composition of S02312 MB4 Glass Sample

Radionuclide	Conc. In MB4 Dried Sludge [a] (Wt. %)	Predicted Conc. In Glass [b] (Wt. %)	Measured Conc. In Glass (Wt. %)	Ratio Pred./Meas.	Analytical Method
Sr-90	3.56E-03	1.63E-03	1.38E-03	1.18	Counting
Zr-93	1.76E-03	8.07E-04	8.47E-03	0.10	ICP-MS
Tc-99	1.15E-03	5.28E-04	3.49E-04	1.51	ICP-MS
Cs-137	3.63E-04	1.66E-04	1.66E-04	1.00	Counting
Sm-151	7.44E-04	3.40E-04	3.38E-04	1.01	ICP-MS
U-233	1.61E-04	7.37E-05	4.44E-05	1.66	ICP-MS
U-234	4.84E-04	2.22E-04	2.17E-04	1.02	ICP-MS
U-235	3.38E-02	1.54E-02	1.69E-02	0.91	ICP-MS
U-236	1.31E-03	5.98E-04	6.44E-04	0.93	ICP-MS
Np-237	4.68E-03	2.14E-03	2.14E-03	1.00	ICP-MS
U-238	6.73	3.08	2.96	1.04	ICP-MS
Pu-238	1.51E-04	6.93E-05	7.72E-05	0.90	Counting
Pu-239	2.20E-02	1.01E-02	1.22E-02	0.83	ICP-MS
Pu-240	2.11E-03	9.64E-04	1.05E-03	0.92	ICP-MS
Pu-241	5.26E-05	2.41E-05	2.74E-05	0.88	Counting
Pu-242	1.43E-04	6.54E-05	4.49E-05	1.46	ICP-MS
Am-241	5.40E-04	2.47E-04	2.29E-04	1.08	Counting
Am-243	7.77E-04	3.56E-04	3.78E-04	0.94	ICP-MS

[a]Bannochie, C. J. and Bibler, N. E., *Determination of Reportable Radionuclides for Sludge Batch 3 (Macrobatch 4),* WSRC TR-2005-00157, Savannah River Site, Aiken, SC 29808 (2005).
[b]Predicted by dividing the concentration in the sludge by the WDF of 2.19.

The predicted and measured concentrations for 14 out of the 18 agree within 17% or better. The large discrepancy for the remaining 4 could be due to analytical error in the measurements. The agreement of the 14 does suggest that the radionuclides in MB4 are indeed being immobilized in the glass.

Results of the ASTM 1285 Leach Test (Product Consistency Test)

As mentioned before, 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[1]. The results for the standard glass and the blanks indicated that the test was acceptable. Average normalized releases for the S02312 MB4 glass were calculated from the following equation and are presented in Table V along with measured and published values for the EA glass. The normalized releases based specific elements in the glass were calculated from the following equation and the composition of the glass given in Table I.

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

Where NR_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 results from the elemental concentration given in parts per million.

The normalized release based on a specific elements in the glass is a measure of the concentration of glass (grams glass/liter) dissolved in the PCT leachate based on that specific element. Table V presents the results for the average normalized releases based on B, Na, Li, Si and S for the S02312 radioactive MB4 glass. The average measured values for the EA glass are also presented along with the published value[3]. The average pH values of the leachates are also presented. Silicon and S are not required by the WAPS. Silicon is provided because it is a major component of the glass. Sulfur was measured because of the additional sulfur that was brought into MB4 as sulfate with the SRS Canyon transfers of Np. 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.

Table V. Average Normalized PCT Results for S02312 MB 4 Glass and EA Glass

Element	Grams Glass per Liter Leachate[a] Std. Dev.,%RSD	Meas. EA, g/L, (Std. Dev.,%RSD)	Published EA, g/L, (Std. Dev.,%RSD)
B	1.09 (0.07, 6.4)	16.7 (0.2,. 1)	16.7 (1.2, 7)
Na	1.03 (0.02,3.2)	12.9(0.03,0.2)	16.7 (0.2,. 1)
Li	0.94 (0.02,2.3)	9.1 (0.0.03,0.3)	9.6 (0.7,7)
Si	0.58 (0.01,1.7)	3.9 (0.02,0.5))	3.9 (0.4,10)
S	1.1 (0.22,20)	NA	NA
pH	10.8	11.7	11.9

[a]Based on quadruplicate PCT tests.

The normalized elemental releases reported in Table V indicate that the glass sample taken during the filling of canister S02312 clearly meets the durability acceptance criterion as defined in the WAPS.[1] As mentioned before, this criterion states that the normalized releases based on B, Li, and Na must be at least two standard deviations lower than the respective releases for the EA glass. Results in Table V indicate that they are for DWPF glass S02312, the normalized releases for B, Na, and Li, are equal indicating that based on these elements there is congruent dissolution of the glass. This was also observed in the PCT of two pour stream samples from a previous macrobatch of HLW sludge.[4] All three of the elements are soluble in the leachate. Also in that macrobatch,[4] the normalized releases for B, Li , and Na were slightly less (10%) than the releases measured in MB4 glass. Note that sulfur has a normalized release equal to those for B, Li, and Na. Sulfur is probably present in the glass as sulfate which is probably in the leachate as soluble sulfate ions. Silicon indicates a lower dissolution rate for the glass presumably because silicon is not completely soluble in the leachate and is partially retained on the surface of the leached glass.[5] A lower release for Si has been observed in PCT tests at both SRS and at Argonne National Laboratory (ANL) of two radioactive glasses similar to DWPF glasses.[6] As shown in Table V this was also found for the EA 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 are presented in Table VI. Note that only the normalized release based on Tc-99 is equal within experimental error to the releases based on B, Li, or Na. This occurs probably because Tc-99 is soluble in the leachate as the pertechnetate anion. The other radionuclides except Cs-137 have limited solubilities in the leachates. The normalized release based on Cs-137 is lower possibly because Cs-137 is being retained in the altered layer of the glass perhaps as a cesium aluminum silicate. This lower normalized release based on Cs-137 has also been observed in PCT tests performed with two radioactive glasses similar to DWPF glass at both SRS and ANL.[6] Finally in Table V note that the normalized releases based on different isotopes of the same element are equal as they should be.

Table VI. Normalized PCT Results for Radionuclides in S02312 MB 4 Glass

Radionuclide	Grams Glass/Liter[a] (Std. Dev., %RSD)	Anal. Method For Leachate
Zr-93	0.036, (0.002, 6.3)	ICP-MS
Tc-99	0.87 (0.15, 17)	ICP-MS
Cs-137	0.23 (0.004, 1.8)	Counting
Sm-151	0.042 (0.003, 6.9)	ICP-MS
Np-237	0.025 (0.004, 16)	ICP-MS
U-235	0.14 (0.02, 16)	ICP-MS
U-238	0.12 (0.004, 3.8)	ICP-AES
Pu-239	0.068 (0.004, 5.8)	ICP-MS
Pu-240	0.071 (0.003, 4.8)	ICP-MS
Am-241	0.067 (0.005, 6.9)	Counting
Am-243	0.061 (0.008, 13)	ICP-MS

[a]Based on quadruplicate PCT tests.

Examination by Scanning Electron Microscopy

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 X-ray fluorescence (XRF) analysis. A low magnification overview of the sample is shown in Fig. 1. Note that the grains are relatively uniform in size and because of the washing do not have fines associated with them. Upon careful examination of the sample at higher magnification, it was noted that many of the grains contained micro particles that were ~2μm in width or less. An example of these is shown in Fig. 2. Results of XRF examination are shown in Fig. 3 and Fig. 4. The spectrum in Fig. 3 of Spot 6 in Fig. 2 is a raster scan of the glass and is typical of DWPF glasses. The spectrum of Spots 4 and 5 were essentially identical and showed that they did indeed contain noble metals that were apparently insoluble in the molten glass. From this examination it could not be determined if these noble metals were present as oxides or metals. Insoluble noble metals were not unexpected, because it had already been shown that RuO_2 was a melt insoluble that enhanced devitrification of the glass [7] although no other types of crystals were detected in the sample of S02312 glass. Noble metal melt insolubles were not detected by SEM examination of two pour stream samples from a previous MB1 that was processed by the DWPF.[4]

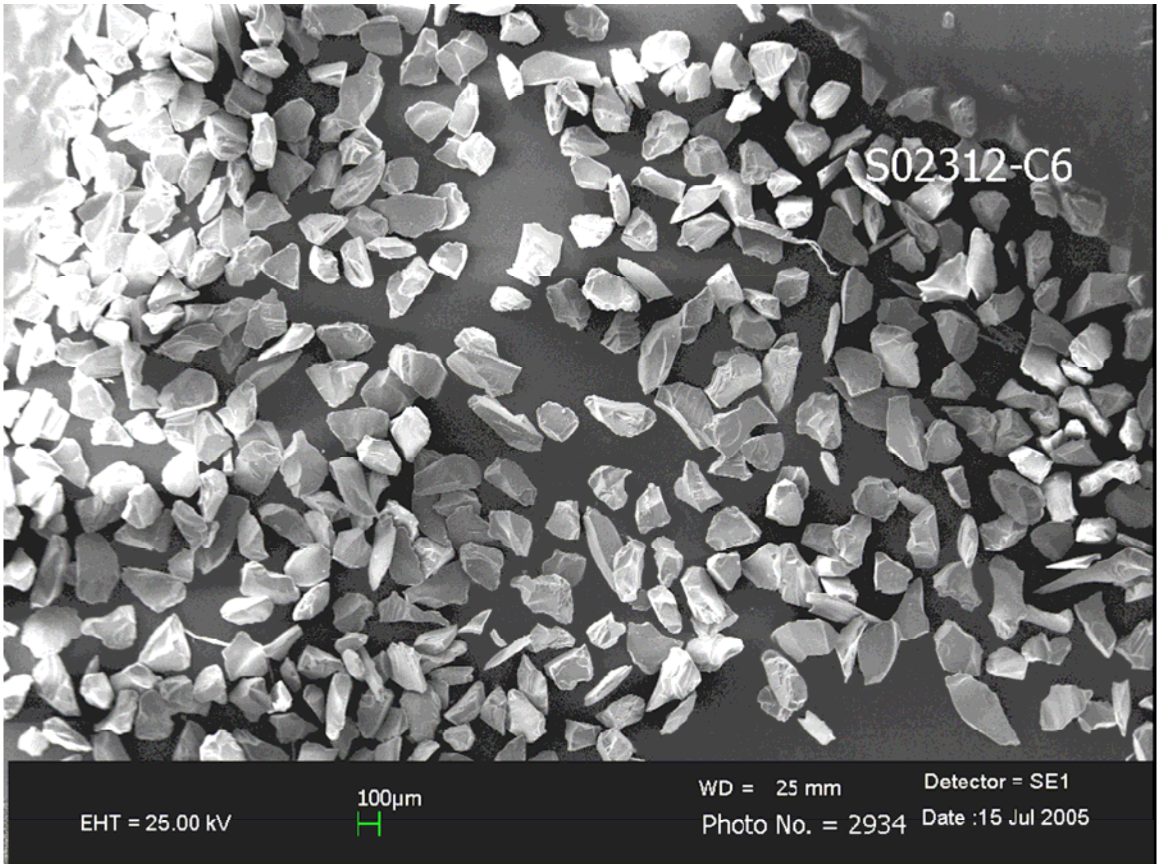

Fig. 1. SEM image of DWPF pour stream sample S02312 at low magnification

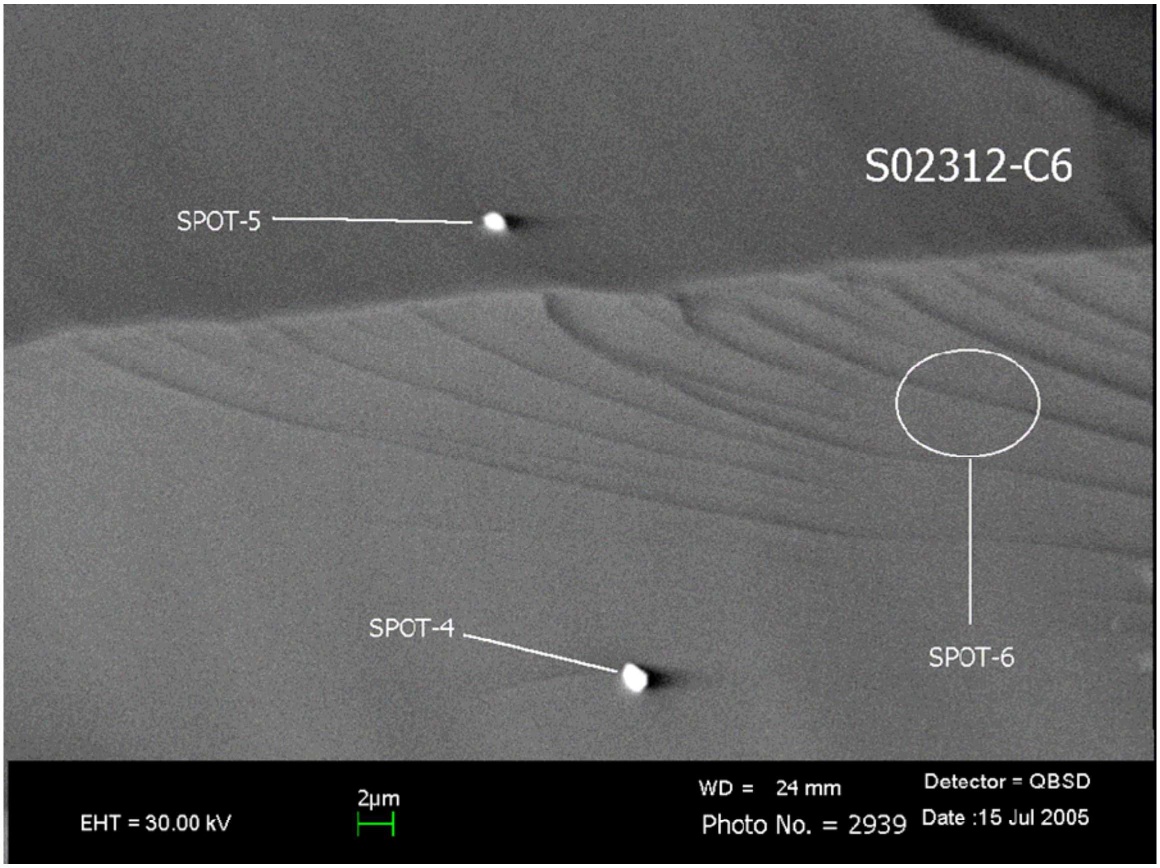

Fig. 2. SEM image of DWPF pour stream sample S02312 at higher magnification

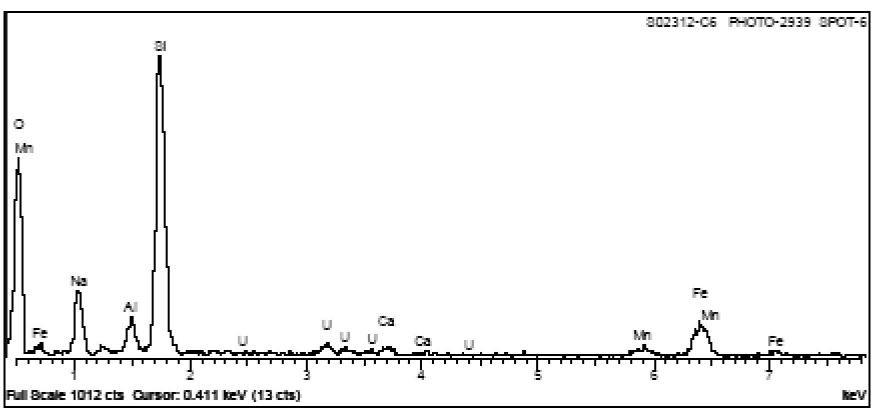

Fig. 3. X-Ray Fluorescence Spectra of Raster Scan of Spot 6 in Fig. 2 for DWPF Pour Stream Glass Sample S02312

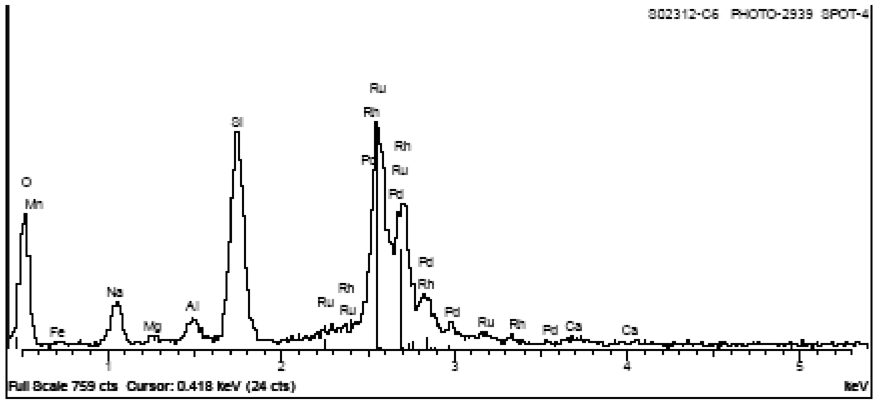

Fig. 4. X-Ray Fluorescence Spectra of Spot 4 in Fig. 2 for
DWPF Pour Stream Glass Sample S02312 Showing the Expected Ru, Rd, and Pd Lines.

Noble Metal Concentrations in the S02312 MB4 Glass Sample

Results for the measured concentrations of the noble metals in the glass are in Table VII along with the predicted concentrations using the WDF. The measured concentrations in Table VII were determined by ICP-MS analysis of the alkali fusion dissolutions of the glass. Results using the acid dissolution method were 10 to 100X lower indicating that the acid dissolution method did not completely dissolve the noble metals. The elemental concentration of each noble metal is the sum of the concentrations of the isotopes shown. The elements Pd, Rh, and Ru are fission products of U-235 and the element Ag is natural Ag that was used in one of the processes at SRS. The predicted concentrations are those obtained by dividing the weight percent of each noble metal in the dried sludge by the average value for the WDF (2.19). Although we did not estimate the concentration of the noble metal insolubles in the glass from the SEM micrographs, the ratios in Column 5 Table VII suggest that the noble metals are largely swept from the melter with the molten glass.

Table VII. Measured and Calculated Fission Product Noble Metal Concentrations in MB4 Radioactive Glass

Noble Metal	Wt. % Dried Sludge	Wt. % Glass (Calculated)	Wt. % Glass (Measured)	Ratio Measured to Calculated
Ag (-107, -109)	0.0159	0.00726	0.00478	0.66
Pd (-105, -106, -107, -108, -110)	0.00146	0.000667	0.000480	0.72
Rh (-103)	0.00729	0.00333	0.00231	0.69
Ru (-101, -102, -104)	0.0296	0.0135	0.0155	1.1

CONCLUSIONS

The results in this paper support the following conclusions at SRNL.

- The major nonradioactive composition of the glass agreed well with the composition measured in the DWPF Analytical Laboratory for the feed to the melter during the filling of canister S02312.

- Based on measurements at SRNL of the MB4 HLW sludge, the waste elements in the sludge were diluted by a factor of 2.19 by the addition of frit in the DWPF in order to make glass to immobilize the waste in a borosilicate glass.

- The concentrations of 14 of the 18 radionuclides measured in the glass agreed well with their predicted values using the waste dilution factor.

- Results of the ASTM PCT test indicated that the normalized releases of B, Li, and Na were 10 to 15X lower than their respective normalized releases in the EA glass. As a result the glass meets the leachability criterion in the WAPS for permanent storage in a Federal Repository. Also the normalized releases for these elements were equal indicating congruent dissolution of the glass in the PCT.

- In the ASTM PCT test, the normalized release of S from the glass was equal to those for B, Li, and Na.

- The only radionuclide that had normalized release equal to B, Li, Na, or S was Tc-99. Releases based on Zr-93, Cs-137, Sm-151, Np-237, and the U, Pu, and Am radionuclides were all lower.

- Based on SEM analysis, the glass contained microcrystallites of the U-235 fission product Ru, Rh, and Pd. Analysis of the concentration of these fission products in the glass however indicated that they were largely swept from the melter and were immobilized in the glass.

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