DWPF VITRIFICATION - CHARACTERIZATION OF THE RADIOACTIVE GLASS BEING PRODUCED DURING IMMOBILIZATION OF THE SECOND BATCH OF HLW SLUDGE

N. E. Bibler and T. L. Fellinger
Savannah River Technology Center
Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

ABSTRACT

For approximately the last five years, the Defense Waste Processing Facility (DWPF) at Savannah River Site (SRS) has been immobilizing the radioactive high-level waste sludges at SRS into a borosilicate glass for permanent disposal in a geologic repository. Currently the DWPF is immobilizing sludge from Macro Batch 2. Macro Batch 1 took ~30 months to complete and resulted in 0.9 million kilograms of glass produced from immobilizing 1.6 million liters of waste. For every macro batch, SRS is required to take a least one glass sample from the pour stream of the melter for characterization at Savannah River Technology Center (SRTC). This characterization involves determining the density of the glass, its radioactive and nonradioactive composition, its durability in an ASTM 1285 leach test, and its microstructure. This paper reports the results of this characterization for a glass sample taken from the pour stream of the melter during processing Macro Batch 2. The nonradioactive composition is compared to that for glass samples prepared from the waste being fed to the melter when the Macro Batch 2 sample was taken. The agreement is excellent confirming that the composition of the glass coming from the melter can be predicted by analyzing samples from the melter feed tank. Also in this paper the composition (both radioactive and nonradioactive) of the Macro Batch 2 glass is compared to that for a glass taken from Macro Batch 1. The nonradioactive compositions are similar except that the concentration of Al is higher and that for Fe lower in the Macro Batch 2 glass. Analyses of the radioactive compositions indicate that the concentrations of U-235 fission products are ~6 times higher in the Macro Batch 2 glass while concentrations of actinides are similar in the two macro batches. Data is also presented in the paper based on a waste dilution factor indicating that a sizeable fraction of the radionuclide C-14 is not immobilized in the glass but is volatilized during processing in the DWPF. Finally, results of the ASTM leach test at SRTC indicated that the glass was more durable than the Environmental Assessment glass for the DWPF. This is one of the criteria for acceptance of the glass at a Federal geologic repository.

INTRODUCTION

The high level liquid waste generated at Savannah River Site (SRS) during many years of producing nuclear materials for the United States is stored in double walled underground steel tanks as caustic slurries. These slurries are either a sludge of hydrous oxides or a nitrate/nitrite salt slurry. Currently the Defense Waste Processing Facility (DWPF) is processing and immobilizing the sludge slurries into a durable borosilicate glass for permanent geological disposal. The DWPF has been immobilizing the sludge high level radioactive waste (HLW) for approximately five years, and has produced over four million pounds of radioactive glass. The DWPF is now processing a sludge called Macro Batch 2. A Macro Batch consists of ~500,000 gallons of caustic sludge slurry that is removed from selected tanks in the SRS Tank Farm and blended in a million gallon tank that supplies feed to the DWPF. Macro Batch 2

consists primarily of Tank 42 sludge slurry that was transferred to and mixed with the remaining small heel of the first Macro Batch remaining in Tank 51. Tank 51 is the feed tank for the DWPF.

After proper pretreatment of the sludge in the DWPF with nitric and formic acid to remove Hg and to adjust the rheology of the slurry, the slurry is pumped to an evaporator tank. Here glass formers are added and the slurry thoroughly mixed and concentrated to ~45 weight percent total solids. After sampling and confirming that the composition of the mixture meets process control requirements, the slurry is pumped to the melter feed tank (MFT). Here the slurry is sampled again, and then pumped to a melter operating at 1150°C. The MFT is an 11,000gallon (4.2E04 liters) tank and contains sufficient feed for eight canisters of glass. During the filling of canisters, molten glass samples can be taken from the pour stream using a specially designed sampler that is attached to the top of the canister. These glass samples are then transported to the Savannah River Technology Center (SRTC) where they are characterized.

For each Macro Batch of sludge, the Waste Acceptance Product Specifications (WAPS) [1] require the characterization of at least one glass sample taken from pour stream of the melter. This characterization is part of the activities at SRS to demonstrate compliance for acceptance of the glass for permanent disposal in a geologic repository. To meet this requirement for Macro Batch 2, a glass sample was taken from the pour stream of the melter while the 222nd canister, Canister S01142, in Macro Batch 2 was being filled. (Each Macro Batch supplies feed for ~500 canisters.) This glass sample was then transported to Savannah River Technology Center's (SRTC) Shielded Cells Facility where it was characterized. The characterization includes determining the density of the glass, its nonradioactive and radioactive composition, its durability in a standard ASTM 1285 leach test, and its microstructure. This paper summarizes the results of that characterization. The paper also compares the composition of the glass to that of a glass sample from Macro Batch 1. Lastly the paper also compares the composition of the Macro Batch 2 glass sample to the composition of a sample prepared from the slurry in the MFT when sample was taken from the pour stream. Detailed results of the characterization are presented in three Department of Energy reports [2-4] that have been released and are available from either author.

PROCEDURES

Obtaining the DWPF Pour Stream Sample During Filling of Canister S01142

Each stainless steel (SS) canister in the DWPF is fitted with a throat protector prior to being filled with molten glass from the DWPF melter. The 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 SS plug into the throat. When the pour stream is to be sampled, a special throat protector is used. This protector contains a small SS cup with a platinum liner 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/sampler is removed from the top of the canister and the platinum liner containing the glass is removed from the SS cup. The platinum liner contains approximately 40 grams of glass. The platinum liner full of glass is sent in a shielded cask to SRTC.

Glass Sample Preparation at SRTC for Characterization

At SRTC, the platinum liner full of glass is removed from the shielded cask and placed into a remotely operated facility called the Shielded Cells. In the Shielded Cells, the glass is examined visually for color variations or any other striking features. The glass sample is then physically removed from the platinum liner. The resulting glass from the platinum liner is then weighed and a portion selected for characterization. The remainder is placed in a specially labeled SS container for storage. This container

also serves as an archival container for the glass not used in the characterization. This is to ensure that glass will be available should any characterization need to be repeated in future years.

Obtaining a Melter Feed Tank Sample at the DWPF of the Slurry Immobilized in Canister S01142

As stated earlier, the DWPF MFT contains enough slurry to fill approximately eight canisters with borosilicate glass. For each MFT batch, slurry samples are taken by a pneumatic sampling system. Several ~25 mL samples are remotely transferred to a shielded cell in the DWPF analytical facility. Here the samples are combined, dried, and vitrified at 1150°C. The final glass is then crushed, dissolved and analyzed for the major nonradioactive and radioactive elements (excluding oxygen) in the DWPF analytical laboratory.

Glass Dissolution Methods at SRTC

Prior to dissolution at SRTC, the glass sample is crushed and ground to enhance dissolution. Weighed amounts of the crushed samples were dissolved remotely by two different methods to ensure that all the elements were dissolved. The first method used was a sodium peroxide fusion at 650°C followed by a HCl dissolution. The second method was an acid dissolution in sealed vessels at 115°C using a combination of HF and HNO_3 acids and H_3BO_3 to complex excess fluoride. The dissolved samples were then diluted so that aliquots of the aqueous samples could be safely removed from the Shielded Cells facility for analyses without excess radiation exposure to personnel. These dissolution methods have been described in detail in Reference [5]. Concurrent with each of these dissolutions, a standard glass was dissolved to confirm that the dissolutions were complete and the resulting analyses accurate. The results of the glass standard indicated that the dissolution methods were performed correctly and the dissolutions were complete. In all cases, four aliquots of crushed glass were dissolved by the two methods.

Analytical Methods

The solutions of the dissolved glass were analyzed by several techniques. The major nonradioactive elements were determined by coupled plasma atomic emission spectrometry (ICP-AES). (This method was also used in the DWPF analytical laboratory for determining the nonradioactive composition of the vitrified sample from the MFT.) Counting techniques were used to determine several of the radionuclides. Gamma counting was used to analyze for Co-60, Cs-137 and Am-241. Beta counting was used for C-14, Sr-90, and Pu-241. Alpha counting was used for Pu-238. Inductively coupled plasma mass spectrometry (ICP-MS) was used for analysis of many of the U-235 fission products (both stable and long lived radionuclides) and actinides such as U-235 and Pu-239 in the solutions. Another publication describes the method of assigning ICP-MS results at mass numbers to specific U-235 fission products [6].

Standard ASTM 1285 Leach Test Procedure

At SRTC, the durability of the glass obtained from the pour stream was measured using the ASTM 1285 standard nuclear waste glass leach test [7]. This test is commonly referred to as the Product Consistency Test (PCT). The purpose of the test was to confirm that the DWPF was producing a glass that had a durability specified by the WAPS for repository acceptance [4]. This specification is that the normalized releases of B, Li, and Na in a PCT be less than two standard deviations the respective releases for the Environmental Assessment (EA) glass. This glass has been thoroughly characterized and it releases in a PCT been carefully determined [8]. The PCT 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 EA glass are also tested with the samples. The purpose of the blanks is to measure impurities than may be in the water and or leached from the vessels. The standard glass is used as a check to determine that all the parameters in the test such as sieving were carefully controlled. In the test, ten milliliters of deionized water are used for each gram of glass. 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 radioactivity of the leachate is low enough so it can be safely transported to a radiochemical hood where the analyses are completed. The pH of the leachate is measured. It is then filtered and acidified to 1 volume percent HNO_3. Concentrations of B, Li, and Na in the leachate are then determined using ICP-AES. These are the best elements to indicate the durability of the glass for their concentrations in the final leachate are not affected by solubility constraints.

RESULTS AND DISCUSSION

Initial Observations

The first tasks performed at SRTC on the Macro Batch 2 glass sample were to weigh it, inspect it visually, and then determine its density. Portions of it were then crushed for dissolutions and the PCT. After the glass was removed from the Pt boat, 38.86 grams of glass were obtained. Visual inspection by remotely operated magnifying periscope indicated that the glass was black and shiny with no visual indication of undissolved sludge. The density of the glass was 2.65±0.03 grams per milliliter. This density was determined by the volume displacement method.

Nonradioactive Composition

Table I presents the concentrations of the major oxides (those with concentrations greater than 0.1 weight percent) in the pour stream sample taken during filling of Canister S01142 in Macro Batch 2. The detailed composition including minor oxides is given in Reference 2. The results in Table I for Macro Batch 2 glass are averages from analyses of at least four aliquots from the crushed glass sample. Except for ZrO_2, the relative precisions of the averages are 6% or less. For ZrO_2 the results were not as precise (18%) possibly due to difficulty in dissolving the ZrO_2. Table I also presents the concentrations of oxides in a glass prepared from a slurry sample taken from the batch that was present in the MFT during filling of Canister S01142. This was MFT Batch 123 of the Macro Batch 2 campaign. This sample was dissolved and analyzed in the process support laboratory in the DWPF. Lastly, Table I presents the composition of a glass sample obtained during the Macro Batch 1 campaign in the DWPF. This sample was taken from the pour stream of the melter during filling of the 409th canister in Macro Batch 1 [4]. The sums of the concentrations of oxides for each glass are also shown in the table. If all the results were completely accurate, these sums would be exactly 100 %. The results for the two glass samples from Macro Batch 2 are very close to 100 %. The result for Macro Batch 1 glass is lower than 100%. This appears to be due to the low SiO_2 result for this glass.

The results in Table I for the Macro Batch 2 glass and the glass prepared from the slurry sample taken from the MFT batch for Canister S01142 are in excellent agreement. This confirms that the composition of the glass being poured from the melter can be accurately predicted from analysis of a vitrified slurry sample taken from the feed being transferred to the melter.

Table I. Concentrations (wt.%) of the Major Oxides (>0.1 wt.%) in DWPF Glass from Sludge Batch Two Compared to DWPF MFT Batch 123 and to a Glass from Sludge Batch One (a)

Oxide	Macro Batch 2 Glass Sample (b)	Macro Batch 2 Melter Feed Tank Sample (c)	Macro Batch 1 Glass (d)
Al_2O_3	5.4	5.3	4.3
B_2O_3	8.2	8.7	8.2
CaO	1.4	1.1	1.3
Fe_2O_3	10.5	9.1	12.6
Li2O	3.5	3.6	3.6
MgO	2.2	1.9	2.1
MnO	1.8	1.4	1.1
Na_2O	11.5	10.5	12.1
NiO	0.16	0.13	0.21
P_2O_5	0.63	(e)	0.39
SiO_2	52.4	55.5	48.1
ZrO_2	0.19	0.11	0.13
U_3O_8	1.1	1.2	1.0
Measured Oxide Sum	99.0	98.5	94.9

(a) Average of results from analyses of four or more samples. Except for ZrO_2 the relative standard deviations were 6 % or better. For ZrO_2 the precision 18%.
(b) Sample taken on 9/27/99 during pouring of the 222nd canister (Canister S01142) of the second sludge batch campaign.
(c) Composition of a vitrified feed taken from the melter feed tank (MFT Batch 123) prior to pouring the 222nd canister of the second sludge batch campaign.
(d) Sample taken on 6/30/98 during pouring of the 409th canister of the first sludge batch campaign. [4]
(e) n.m. - Indicates that the concentration of this oxide was not measured.

Except for the concentrations of Al_2O_3 and Fe_2O_3, the composition of the glass from the Macro Batch 2 is similar to that for Macro Batch 1 glass. This can be explained by considering the sources of the sludges used in each macro batch. Macro Batch 1 contained portions of the sludges from SRS Tanks 18, 21, and 22. These were blended in Tank 51 to form Macro Batch 1. Portions of these same three sludges were blended in Tank 42 in preparation of Macro Batch 2. However, sludge from Tank 15 was also blended with these in Tank 42. In preparation for processing Macro Batch 2, a glass was prepared from Tank 42 sludge since it would be the primary constituent of Macro Batch 2. The blended sludge in Tank 42 was then transferred to Tank 51 to make Macro Batch 2 and feed to the DWPF [9]. In the Tank 42 glass the concentrations of all the main nonradioactive elements were similar to Macro Batch 1 glass except Fe_2O_3 was lower, and that for Al_2O_3 was higher. In Tank 42 glass the ratio of the concentrations of Fe_2O_3 to Al_2O_3 was 1.9. This ratio in Macro Batch 1 glass is 2.9. Data in Table I indicate that in Macro Batch 2 glass this ratio is in the range 1.7 to 1.9. This agrees with that measured in the Tank 42 glass. This agreement indicates that the trend of higher aluminum and lower iron in Macro Batch 2 glass compared to Macro Batch 1 glass resulted from the large contribution of sludge from Tank 42 to the remaining heel of Macro Batch 1 sludge in Tank 51.

Radioactive Composition and the Waste Dilution Factor

During the characterization of the glass, the concentrations of 69 individual isotopes were measured and reported [3]. Examples of these isotopes are many of the U-235 fission products (both stable and radioactive) such as Ru-101 and Sr-90, actinides such as Pu-239 and Am-241, and neutron activation products such as C-14 and Co-60. Table II presents the concentrations of several of these radionuclides including the three major contributors to the radioactivity of the glass. These are Sr-90, Cs-137, and Pu-238. These radioactivity concentrations will be compared to those in Macro Batch 1 glass later in this paper. Table II also presents the concentrations of these radionuclides measured in the sludge prior to DWPF processing. These latter concentrations were measuring by drying and dissolving the sludge itself and are reported in Reference [3]. Except for C-14 in the glass where only an upper limit of its concentration could be made, all the concentrations presented in Table II for both the glass and the sludge are averages from analyses of four aliquots of the glass or dried sludge. The relative precisions of the averages are nominally 10% or better especially for those radionuclides with concentrations greater than 10 ppm in the glass or dried sludge. The last column of Table II presents values calculated for the waste dilution factor (WDF). This is the factor by which the concentration of each radionuclide in the waste is diluted by the addition of the nonradioactive Frit 200 in order to make glass out of the sludge presuming

Table II. Concentrations of Several Radionuclides in DWPF Glass from Macro Batch Two, their Concentrations in the HLW Sludge and the Calculated Waste Dilution Factor

Radionuclide	Radioactive Conc. In Batch 2 Glass, Bq/Kg (a)	Mass Conc. In Batch 2 Glass Wt. % (a)	Mass Conc. In Batch 2 Sludge Wt. % (b)	Waste Dilution Factor (c)
C-14 (d)	<2.7E03	<1.7E-09	9.9E-08(57)	>58
Co-60 (e)	7.5E06	1.8E-08(13)	6.2E-08(7.1)	3.4
Sr-90 (d)	5.2E10	1.1E-03(0.73)	3.1E-03(2.5)	2.8
Tc-99	2.6E06	4.1E-04(4.6)	1.1E-03(6.1)	2.7
Cs-137 (e)	1.9E09	5.7E-05(3.4)	1.8E-04(3.0)	3.2
Sm-151	7.8E08	7.1E-05(8.6)	2.4E-04(9.0)	3.4
U-233	6.3E05	1.7E-04(12)	4.5E-04(4.0)	2.6
U-234	4.8E05	2.1E-04(3.4)	4.7E-04(9.2)	2.2
U-235	4.4E03	5.3E-031.0)	1.3E-02(3.7)	2.5
U-236	1.5E04	6.4E-04(11)	1.1E-03(7.4)	1.7
U-238	1.1E05	9.0E-01(1.0)	1.9E00(4.1)	2.1
Pu-238 (f)	1.2E09	1.9E-04(5.1)	5.8E-04(8.3)	3.1
Pu-239	7.0E07	3.0E-03(6.7)	7.9E-03(3.3)	2.6
Pu-240	2.4E07	2.9E-04(23)	7.8E-04(9.5)	2.7
Pu-241 (d)	5.9E08	1.6E-05(29)	2.8E-05(11)	1.8
Pu-242	4.1E04	2.8E-05(10)	9.4E-05(18)	4.3
Am-241 (e)	8.5E07	6.7E-05(5.1)	1.9E-04(5.1)	2.9

(a) Average of concentrations measured by ICP-MS (unless otherwise noted) in four dissolved glass and dissolved waste samples (unless otherwise noted).
(b) Values published in Reference [4].
(c) Waste Dilution Factor = Conc. in sludge/Conc. in glass
(d) Measured by beta counting after special separation.
(e) Measured by gamma counting.
(f) Measured by alpha counting.

that the radionuclide is not volatilized during processing in the DWPF. In Macro Batch 1, this factor was used to estimate if a significant fraction of the Tc-99 and Cs-137 was volatilized from the DWPF melter and not immobilized in the glass [10].

All the values for the WDF in column five of Table II would be the equal if the measured concentrations in the sludge and glass were completely accurate, and if the concentration of a radionuclide was not lowered by DWPF processing. As can be seen, all the values, except that for C-14, range from 1.7 to 4.3 with the average being 2.8±0.7. This range is due primarily to experimental errors in measuring the concentrations of the radionuclides in the dried sludge of Macro Batch 2 and in measuring their respective concentrations in the glass. This is clearly demonstrated by considering the WDF values calculated for the elements uranium and plutonium using the five isotopes of each that were measured. The average values are 2.2±0.4 for uranium and 2.9±0.9 for plutonium. These ranges can only be due to experimental error since there is no mechanism for an isotope effect in the processing radioactive sludge.

The WDF can also be calculated based on the major nonradioactive elements in the waste that are not present in the frit. These elements are Fe, Al, Ca, and Mn. Since these elements are detected only in the waste, they should be diluted by the same factor as the radionuclides. Table III gives the concentrations of these elements in the glass, in the dried sludge, and the values calculated for the WDF. The average WDF calculated from these elements is 2.6±0.3. This value is in agreement with the average value based on the radionuclides.

As mentioned earlier, the WDF has been used to estimate the amounts of Tc-99 and Cs-137 that could have volatilized from the DWPF melter during processing Macro Batch 1[10]. The melter operates at 1150°C and both these radionuclides have chemical species that have appreciable volatility at 1150°C. Based on the analysis of three samples of glass taken from the melter pour stream at different times during the two year period of processing Macro Batch 1, the data indicated that very little of these radionuclides volatilized from the melter. Since the values for the WDF for Tc-99 and Cs-137 in this work are similar and within the experimental error of the average value for the WDF, there is no significant evidence for extensive volatilization of these during the processing of Macro Batch 2. For C-14, however, this is not the case.

Table III. Concentrations (Wt.%) of Major Nonradioactive Elements Specific to the Waste in Macro Batch 2 Glass along with Concentrations Determined in the Dried Sludge Slurry and the Calculated Waste Dilution Factor (WDF)

Element	Conc. In Batch 2 Glass, Wt. % (a)	Conc. in Batch 2 Sludge, Wt. % (b)	Waste Dilution Factor (c)
Al	2.8	7.7	2.7
Fe	7.3	21.	2.9
Ca	0.99	2.2	2.2
Mn	1.4	3.3	2.4

(a) Calculated from oxide compositions given in Table I.
(b) Values published in Reference 3.
(c) Waste Dilution Factor = Conc. in dried sludge/Conc. in glass

C-14 is a radionuclide that was formed in the SRS reactors by a neutron induced proton displacement reaction on N-14 present as an impurity in the aluminum cladding of the reactor fuels. Prior to reprocessing these fuels to recover the uranium and any plutonium that was formed, the fuels were treated

by a caustic dissolution to remove the aluminum cladding. Any C-14 formed in the aluminum would also be dissolved by the caustic and be present in the decladding solution, probably as carbonate. Carbon-14 was indeed detected and measured in the dried sludge by a specially developed process. That C-14 concentration is presented in Table II. The value of the average concentration measured in the sludge was very imprecise (%RSD=57); however, it was definitely detected in the sludge by separating the C-14 from the dissolved sludge and measuring the characteristic C-14 beta particles. Carbon-14 could not detected in the glass by using the same technique even though extreme care was used not to lose the CO_2 formed in the separation process. Thus, only an upper limit is presented in Table II for its concentration in the glass. This leads to a lower limit for the WDF. The estimate for the WDF value for C-14 is definitely much larger than the average of the values based on the other radionuclides or on the major nonradioactive elements in the waste. This large value strongly indicates that some fraction of the C-14 was lost during DWPF processing. The C-14 concentration in the glass can be predicted using the average WDF. The predicted concentration is the measured concentration in the sludge divided by the average WDF. In this case the predicted concentration in the glass is 3.8E-08 weight percent. The upper limit in the glass is only 4% of this predicted concentration. Even though the measured concentration in the sludge is very imprecise, it is apparent that a sizeable fraction of the C-14 is not being immobilized in the glass. There are three steps in the DWPF process where C-14 could volatilize. If the C-14 is present as carbonate anion, which is very likely, it could volatilize as carbon dioxide during acid addition and evaporation processes in the DWPF. The third place is the melter where it could volatilize as carbon dioxide, even if some of the C-14 is incorporated as an organic compound in the waste.

Comparison of Isotopic Concentrations in Macro Batch 2 Glass with Macro Batch 1 Glass

Table IV compares the concentrations of several radionuclides and several stable U-235 fission products measured in Macro Batch 2 glass with those in Macro Batch 1 glass. Based on the concentrations of eight of the U-235 fission products that are insoluble in caustic, the concentration of these U-235 fission products is 6.0±0.6 times higher in Macro Batch 2 than in Macro Batch 1. This includes two of the noble metals formed as fission products of U-235. (In the glass prepared from the sludge in Tank 42 the concentration of Sr-90 was nominally 8X higher than in the Macro Batch 1 glass [9]; thus, the higher Sr-90 content of Macro Batch 2 can be attributed to the presence of Tank 42 sludge in Macro Batch 2.) Since Sr-90, Ru and Rh are insoluble in caustic, a relative measure of the concentration of Ru and Rh in two macro batches can be attained by simply determining the relative Sr-90 concentrations in the macro batches. Knowledge of these noble metal concentrations furnishes information on H2 production in the DWPF during processing. (Hydrogen is produced by noble metal catalyzed decomposition of formic acid during DWPF processing [11].) As seen in column 4 of Table IV, the relative concentrations of the fission products Tc-99 and Cs-137 in the two batches do not differ by a factor of 6. Each of these radionuclides can be soluble in the caustic supernate of the sludge (Cs as a cation and Tc as the pertechnatate anion). Thus, during the processing of the waste in the SRS Tank Farm, their concentrations relative to the fission products that are insoluble in caustic do not remain constant. The radionuclide Co-60 is a neutron activation product; thus, there is no reason to expect its concentration to be 6X higher in Macro Batch 2 than in Macro Batch 1unless one knew something of the neutron fluences to which each macro batch was exposed. The respective actinides have similar concentrations in Macro Batch 1 and 2. The actinides in the waste result from the inefficiencies of the separation processes that were performed at SRS, thus, there is no reason to expect their concentrations to be 6X higher in Macro Batch 2 than in Macro Batch 1.

Table IV. Concentrations of Several Isotopes in DWPF Glass from Macro Batch Two Compared to Concentrations in a DWPF Glass from Macro Batch One (a)

Isotope	Concentration in Macro Batch 2 Glass Sample, Wt. %	Concentration in a Macro Batch 1 Glass Sample, Wt.% (b)	Ratio of Concentration in Macro Batch 2 to Macro Batch 1
Co-60 (c)	1.8E-08	2.1E-08	0.86
Sr-90 (d)	1.0E-03	1.5E-04	6.7
Tc-99 (d)	4.1E-04	4.7E-04	0.92
Ru-101 (e)	2.7E-03	4.3E-04	6.3
Ru-102 (e)	2.5E-03	4.0E-04	6.3
Rh-103 (e)	1.5E-03	3.0E-04	5.0
Cs-137 (d)	5.7E-05	2.4E-05	2.4
La-139 (e)	7.2E-03	1.1E-03	6.5
Pr-141 (e)	4.7E-03	8.9E-04	5.3
Nd-143 (e)	4.5E-03	7.7E-04	5.8
Nd-146 (e)	3.1E-03	5.1E-04	6.1
U-235	5.3E-03	5.1E-03	1.0
U-238	9.0E-01	8.7E-01	1.1
Pu-238	1.9E-04	1.7E-04	1.1
Pu-239	3.0E-03	3.1E-03	1.0
Am-241	6.7E-05	7.0E-05	0.96

(a) Average of results from analyses of four samples. Relative standard deviations were 10% or better.
(b) Sample taken on 6/30/98 during pouring of the 409th canister of the first Macro Batch campaign. [4]
(c) Formed in the reactors as a neutron activation product of Co-59.
(d) Radioactive U-235 fission product.
(e) Stable U-235 fission product.

ASTM 1285 (PCT) Durability Results

At SRTC, quadruplicate samples of the ground glass were subjected to the PCT along with the appropriate blanks, standard glass and EA glass as prescribed by the procedure. The results for the standard and blanks indicated that the test was acceptable. Average normalized releases for B, Li, and Na are presented in Table V along with values measured in a Macro Batch 1 glass and the Environmental Assessment glass. The normalized releases were calculated from the following equation and are a measure of the concentration of glass in grams per liter dissolved in the PCT based on that respective element.

$$NR_i = C_i/(F_i \cdot 1000) \qquad \text{(Eq. 1)}$$

where NR_i = the normalized release (grams glass per liter) based on element i
C_i = the concentration (ppm) of i in the leachate measured by ICP-AES
F_i = the weight fraction of i in the glass.

Table V. Normalized PCT Releases (grams glass/L) for DWPF Glass from Macro Batch Two Compared to a Glass from Macro Batch One and Values for the Environmental Assessment (EA) Glass (a)

Element	Macrobatch 2 Glass	Macrobatch 1 Glass	EA Glass (b)
B	0.63±0.01(1.6)	0.78±0.03(3.8)	16.7±1.2(7.3)
Li	0.78±0.02(2.6)	0.77±0.02(2.6)	9.6±0.7(7.7)
Na	0.59±0.01(1.7)	0.75±0.01(1.3)	13.3±0.9(6.8)

(a) Average of the results from quadruplicate tests. For each glass the standard deviation is given along with the percent relative standard deviation in parentheses.
(b) Values published in Reference 8.

The standard deviations obtained in the quadruplicate tests, and the percent relative standard deviations are also reported in Table V. The normalized releases for both Macro Batch 2 and Macro Batch 1 glass are similar as would be expected because of their similar compositions. The normalized releases reported in Table V indicate that both glasses meet the WAPS acceptance criterion which states that the normalized releases for B, Li, and Na for the glass produced must be at least two standard deviations less than the respective releases for the EA glass [1]. Both glasses are nominally 10 to 20 times more durable than the EA glass.

MICROSTRUCTURAL EXAMINATION

Samples of the crushed and ground glass from the pour stream sample were examined by scanning electron microscopy (SEM) and by x-ray diffraction. The results of both methods showed that there were no crystals in the glass indicating that it was amorphous. The SEM examination also indicated that there was no undissolved HLW sludge in the glass.

CONCLUSIONS

The results presented in this paper support the following conclusions:

- The nonradioactive composition of radioactive glass being poured from the production melter in the DWPF can be accurately predicted by vitrification and analysis of slurry samples from the melter feed tank.
- The composition of Macro Batch 2 glass is similar to that for Macro Batch 1 glass except that the concentration of the waste element Fe is lower and that for Al higher.
- A sizeable fraction of the C-14 in the waste is volatilized during DWPF processing. Only a small fraction of the Cs-137 and Tc-99 are.
- The U-235 fission products that are insoluble in caustic have concentrations that are 6.4±0.6 times larger than those in Macro Batch 1 glass.
- Macro Batch 2 glass meets the criterion for durability in the ASTM 1285 standard leach test. The normalized releases plus two standard deviations for triplicate tests for B, Li, and Na are 10-20 times less than the respective releases from the Environmental Assessment glass.
- Scanning electron microscopy and x-ray diffraction indicated no crystals in the glass samples examined. Also the SEM analysis indicated no undissolved HLW sludge.

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This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy.