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Revision 0

Analysis of DWPF Sludge Batch 7a (Macrobatch 8) Pour Stream Samples

F.C. Johnson
J.M. Pareizs

May 2012

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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EXECUTIVE SUMMARY

The Defense Waste Processing Facility (DWPF) began processing Sludge Batch 7a (SB7a), also referred to as Macrobatch 8 (MB8), in June 2011. SB7a is a blend of the heel of Tank 40 from Sludge Batch 6 (SB6) and the SB7a material that was transferred to Tank 40 from Tank 51. SB7a was processed using Frit 418.

During processing of each sludge batch, the DWPF is required to take at least one glass sample to meet the objectives of the Glass Product Control Program (GPCP), which is governed by the DWPF Waste Compliance Plan, and to complete the necessary Production Records so that the final glass product may be disposed of at a Federal Repository. Three pour stream glass samples and two Melter Feed Tank (MFT) slurry samples were collected while processing SB7a. These additional samples were taken during SB7a to understand the impact of antifoam and the melter bubblers on glass redox chemistry. The samples were transferred to the Savannah River National Laboratory (SRNL) where they were analyzed. The following conclusions were drawn from the analytical results provided in this report:

- The sum of oxides for the official SB7a pour stream glass is within the Product Composition Control System (PCCS) limits (95-105 wt%).

- The average calculated Waste Dilution Factor (WDF) for SB7a is 2.3. In general, the measured radionuclide content of the official SB7a pour stream glass is in good agreement with the calculated values from the Tank 40 dried sludge results from the SB7a Waste Acceptance Program Specification (WAPS) sample.

- As in previous pour stream samples, ruthenium and rhodium inclusions were detected by Scanning Electron Microscopy-Electron Dispersive Spectroscopy (SEM-EDS) in the official SB7a pour stream sample.

- The Product Consistency Test (PCT) results indicate that the official SB7a pour stream glass meets the waste acceptance criteria for durability with a normalized boron release of 0.64 g/L, which is an order of magnitude less than the Environmental Assessment (EA) glass.

- The measured density of the SB7a pour stream glass was 2.7 g/cm^3.

- The $Fe^{2+}/\sum Fe$ ratios of the SB7a pour stream samples were in the range of 0.04 – 0.13, while the MFT sample glasses prepared by SRNL were in the range of 0.02 – 0.04.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ARG-1	Analytical Reference Glass 1
ARM	Approved Reference Material
ASP	Analytical Study Plan
CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EDS	Electron Dispersive Spectroscopy
GPCP	Glass Product Control Program
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
MB8	Macrobatch 8
MFT	Melter Feed Tank
PCCS	Product Composition Control System
PCT	Product Consistency Test
PF	Peroxide Fusion
PS	Pour Stream
REDOX	REDuction/OXidation
RSD	Relative Standard Deviation
SB	Sludge Batch
SEM	Scanning Electron Microscopy
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
St. Dev.	Standard Deviation
THERMO	Thermodynamic Hydration Energy Reaction MOdel
TTQAP	Task Technical and Quality Assurance Plan
WAPS	Waste Acceptance Product Specifications
WDF	Waste Dilution Factor
XRD	X-ray Diffraction

1.0 Introduction

The Defense Waste Processing Facility (DWPF) began processing Sludge Batch 7a (SB7a), also referred to as Macrobatch 8 (MB8), in June 2011. SB7a is a blend of portions of material from Tanks 4, 7 and 12; the Sludge Batch 6 (SB6) heel in Tank 51; and a plutonium stream from H canyon.[1,2] SB7a was processed using Frit 418.[3,4]

Sludge is received into the DWPF Chemical Process Cell (CPC) and is processed through the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) tank. The treated sludge slurry is then transferred to the Melter Feed Tank (MFT) and fed to the melter. During processing of each sludge batch, the DWPF is required to take at least one glass sample to meet the objectives of the Glass Product Control Program[5] (GPCP), which is governed by the DWPF Waste Form Compliance Plan, and to complete the necessary Production Records so that the final glass product may be disposed of at a Federal Repository.

The DWPF requested various analyses of radioactive glass samples obtained from the melter pour stream during processing of SB7a, as well as reduction/oxidation (REDOX) analysis of MFT samples to determine the impact of Argon bubbling and antifoam.[6] Sample analysis followed the Task Technical and Quality Assurance Plan (TTQAP)[7] and an Analytical Study Plan (ASP).[8] Three Pour Stream (PS) glass samples and two MFT slurry samples[a] were delivered to the Savannah River National Laboratory (SRNL) from the DWPF. Table 1-1 lists the sample information for each pour stream glass sample. SB7a PS#1 was selected as the official pour stream sample for SB7a and full analysis was requested. This report details the visual observations of the as-received SB7a PS#1 glass sample as well as results for the chemical composition, Product Consistency Test (PCT), radionuclide content, noble metals, and glass density. REDOX results will be provided for pour stream samples SB7a PS#1 and #3 and vitrified samples of MFT-580 and MFT-592. SB7a PS#2 was designated as the archive sample and will be placed in Primary Container 118 (PC0117).

Table 1-1. DWPF Pour Stream Glass Sample Information

Glass Canister	Sample Date	MFT Batch	Sample ID	Notes
S03619	Aug-11	580	SB7a PS#1	Official & REDOX
S03623	Aug-11	581	SB7a PS#2	Archive
S03677	Oct-11	592	SB7a PS#3	REDOX only

2.0 Experimental Procedure

2.1 Visual Examination, Extraction and Washing

Upon arrival at SRNL, pour stream samples SB7a PS#1 and PS#3 were inspected, removed from the Pt/Au collection boats and washed according to procedure prior to analysis.[9]

2.2 Chemical Composition

A sample of SB7a PS#1 was ground and then sieved to -200 mesh. Quadruplicate samples of the pour stream glass were digested by two separate methods: mixed acid[10] (MA) and sodium peroxide fusion[11] (PF). Three Analytical Reference Glass (ARG-1) standards were also digested by each method and submitted along with the samples. All of the prepared samples were submitted to Analytical Development (AD) and analyzed by Inductively Coupled Plasma-Atomic

[a] MFT Batch 580 and MFT Batch 592, which will be denoted as MFT-580 and MFT-592 in the text.

Emission Spectroscopy (ICP-AES). A multi-element standard and blank were also included in the analyses in order to assess the performance of the instrument over the course of the analyses.

2.3 Radionuclide Composition

The SB7a PS#1 glass sample was prepared in quadruplicate using a PF digestion and was analyzed by AD using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) to determine actinide and fission product content. Aliquots of the PF digestions were analyzed by counting methods and alpha spectroscopy to calculate the radionuclide concentration.[b] The reportable radionuclides for the GPCP and WCP[12] not measured in this study were calculated from the SB7a total dried solids results using a calculated Waste Dilution Factor (WDF).

2.4 Noble Metals

Noble metal concentrations were analyzed in the SB7a PS#1 sample using ICP-MS from the peroxide fusion dissolution. The total silver concentration is calculated using the measured concentration of ^{109}Ag and the calculated concentration of ^{107}Ag.[13] Due to interference from Cd, the palladium concentration is calculated using the sum of the measured concentration of ^{105}Pd and the calculated concentrations of ^{106}Pd, ^{107}Pd, ^{108}Pd, and ^{110}Pd using their fission yields.[13] The total concentration of ruthenium is calculated from the sum of the measured concentrations of three isotopes: ^{101}Ru, ^{102}Ru, and ^{104}Ru. The reported concentration of rhodium is from the measured concentration of a single isotope, ^{103}Rh.

In addition, a sample of SB7a PS#1 (-200 mesh) was analyzed using Scanning Electron Microscopy (SEM) along with Energy Dispersive Spectroscopy (EDS) to image and analyze any inhomogeneities in the glass.

2.5 PCT

The PCT was performed on quadruplicate samples of SB7a PS#1 to assess chemical durability using Method A of the procedure.[14] Also included was the Environmental Assessment (EA) glass, the Approved Reference Material (ARM) glass and blanks from the sample cleaning batch. Samples were ground, washed and prepared according to standard procedure. ARM and EA were only prepared in triplicate. The resulting solutions were sampled (filtered and acidified) and analyzed by AD. Samples of a multi-element standard were also included with the glass samples as a check of the accuracy of the ICP-AES. Normalized release rates were calculated based on the measured composition using the average of the leachate concentrations.

2.6 Density

The density of SB7a PS#1 was measured with a Hubbard-Carmick specific gravity bottle. By using the masses of the empty bottle (m_0), bottle and sample (m_1), bottle, sample and water (m_2) and bottle and water (m_3), the density of the sample (ρ_s) is calculated by

$$\rho_s = \frac{\rho_{H2O}(m_1 - m_0)}{(m_3 - m_0) - (m_2 - m_1)}$$

where ρ_{H2O}[c] is the density of water at the measurement temperature. A reference glass[d] was included in the set of measurements as an internal check of the measurement technique in the shielded cells.

[b] The sample used for Tc-99 determination was prepared in quadruplicate using both the PF and MA digestions.
[c] The density of H_2O was assumed to be 1 g/cm^3 for all measurements.

2.7 REDOX

2.7.1 *Pour Stream Samples*

A sample of SB7a PS#1 and #3 were ground and then sieved to -200 mesh. Both samples were prepared for REDOX measurement and analyzed via UV-Vis spectroscopy according to procedure.[15] In addition to the pour stream samples, the EA glass was included in each set of measurements as an internal check of the measured REDOX value.

2.7.2 *MFT Samples*

Both of the MFT slurry samples were prepared in triplicate and vitrified via the sealed crucible method according to procedure.[16] All of the samples were removed from the alumina crucibles, ground and sieved to -200 mesh. The samples were then prepared and analyzed in a similar manner as the pour stream samples (Section 2.7.1).

3.0 Results and Discussion

3.1 Visual Examination

Upon receipt inspection, small regions on the surface of the SB7a PS#1 appeared to be covered by a surface film; however, the bulk of the sample was black and shiny. Similar surface films have been observed on the surfaces of previous pour stream samples[17,18] and have been attributed to salt deposits. There did not appear to be a surface film on the SB7a PS#3 sample and the bulk of the sample was black and shiny.

3.2 Chemical Composition

Table 5-1 and Table 5-2 in Appendix A provide the measured elemental data from glasses prepared using mixed acid and peroxide fusion, respectively.

3.2.1 *ARG-1*

Table 3-1 shows a comparison of the published[19] and measured composition of the ARG-1 glass. The measured value is the average of three replicates from either the mixed acid or peroxide fusion data as noted in the table. In general, the measured values are consistent with the published values; however, there was some variation in the measurement of SiO_2 as shown by the Relative Standard Deviation (%RSD). In addition, the average measured value of SiO_2 is approximately 1.5 wt% higher than the target value. The sum of oxides is within the Product Composition Control System (PCCS) acceptance limits (the interval of 95 to 105 wt%).

3.2.2 *SB7a PS#1*

Table 3-2 lists the oxide composition of the SB7a PS#1 glass. The measured value is the average of three replicates from either the mixed acid or peroxide fusion data as noted in the table. Some of the analytes were below the detection limit of the instrument and are noted by a result preceded by a "<." The %RSD values for the major glass components (> 0.5 wt%) are less than 10%, indicating good precision in the results.

[d] The density of a sample of NIST 1830 glass was determined to be 2.48 g/cm^3 using the Archimedes method (ITS-0057) prior to its placement in the shielded cells.

Table 3-1. Published[19] and Measured Values of ARG-1

Oxide	Published (wt%)	Measured (wt%)	% RSD	Digestion Method
Al_2O_3	4.73	4.66	0.2	PF
B_2O_3	8.67	8.18	0.8	PF
BaO	0.09	0.09	1.6	PF
CaO	1.43	1.43	1.5	MA
Cr_2O_3	0.09	0.10	0.8	PF
Fe_2O_3	14.0	13.98	0.3	PF
K_2O	2.71	2.59	0.7	MA
Li_2O	3.21	3.18	0.4	PF
MgO	0.86	0.87	0.7	PF
MnO	1.88	1.89	0.7	PF
Na_2O	11.5	10.75	0.8	MA
NiO	1.05	1.05	0.8	PF
P_2O_5	0.22	0.41	9.7	PF
SiO_2	47.9	49.49	2.0	PF
TiO_2	1.15	1.14	0.4	PF
ZnO	0.02	0.02	1.1	PF
ZrO_2	0.13	0.12	0.8	MA
Total	99.64	99.94	---	---

Table 3-2. Average Measured Composition of SB7a PS#1

Oxide	Measured (wt%)	%RSD	Digestion Method	Oxide	Measured (wt%)	%RSD	Digestion Method
Al_2O_3	8.59	2.6	PF	MoO_3	<0.08	---	PF
B_2O_3	4.27	2.9	PF	Na_2O	12.45	5.9	MA
BaO	0.05	3.0	PF	NiO	1.22	4.1	PF
BeO	<0.004	---	PF	P_2O_5	<0.39	---	PF
CaO	0.46	6.2	MA	PbO	<0.15	---	PF
CdO	0.02	9.8	PF	SO_4	<0.45	---	MA
Ce_2O_3	<0.14	---	PF	Sb_2O_3	<0.25	---	PF
Cr_2O_3	0.07	9.5	PF	SiO_2	47.07	2.8	PF
CuO	0.40	3.9	PF	SnO_2	<0.14	---	PF
Fe_2O_3	8.37	2.9	PF	SrO	0.03	3.9	PF
Gd_2O_3	0.05	7.4	PF	ThO_2	0.69	5.4	PF
K_2O	<0.07	---	MA	TiO_2	0.66	2.7	PF
La_2O_3	0.04	1.5	PF	U_3O_8	2.43	4.1	PF
Li_2O	4.56	2.8	PF	ZnO	0.09	4.0	PF
MgO	0.27	3.4	PF	ZrO_2	0.15	5.3	MA
MnO	2.01	2.7	PF	Total	95.65	---	---

3.2.3 *WDF*

The WDF for a specific sludge batch is given by

$$WDF(i) = \frac{CS(i)}{CG(i)}$$

where *CS(i)* is the concentration of component *i* in the dried Tank 40 sludge[20] and *CG(i)* is the concentration of component *i* in the corresponding pour stream glass sample. Table 3-3 contains the calculated WDF values for Al, Ca, Fe and Mn for SB7a. The average WDF value will be used in Section 3.3 to calculate the concentration of radionuclides that were not directly measured in the glass.

Table 3-3. Waste Dilution Factor for the SB7a PS#1 Glass

Element	Concentration (wt%)		WDF
	Dried Sludge Slurry	Glass	
Al	10	4.55	2.2
Ca	0.72	0.33	2.2
Fe	14	5.86	2.4
Mn	3.9	1.56	2.5
Average	---	---	2.3
Std. Dev.	---	---	0.1

3.3 Radionuclide Composition

Based on measurements and analytical detection limits, twenty-five radionuclides were identified as reportable for DWPF SB7a (MB8) as specified by the Waste Acceptance Product Specification (WAPS).[1,21,e,f] Selected radionuclides were directly measured in quadruplicate either by gamma counting, beta counting, alpha spectroscopy or ICP-MS. Table 3-4 lists the average concentrations of these radionuclides.[g] Table 5-3 through Table 5-6 in Appendix A provide the actual measured radiological chemical data and ICP-MS data, respectively. Some of the analytes were below the detection limit of the instrument and are noted by a result preceded with a "<." The content of each radionuclide was also calculated from measured values of the Tank 40 dried SB7a sludge and the average WDF value shown in Table 3-3.[1]

3.4 Noble Metals

The average measured concentrations of the noble metals based on quadruplicate measurements of SB7a PS#1 are list in Table 3-5. Table 5-6 in Appendix A provides the actual measured ICP-MS data. The calculated noble metal concentration in the glass is determined from the concentration in the Tank 40 sludge[22] and the average WDF value (Table 3-3).

[e] Th-229 was identified as reportable for SB7a; however, there is no direct method for measuring its concentration, so its value will not be presented in this report. Based on the calculated values in SRNL-STI-2011-00720, Th-229 becomes reportable in the year 2515, which is of no practical significance to this study. Total ThO_2 is reported in Table 3-2.

[f] In addition to the twenty-five radionuclides identified above, U-235 and U-236 are also reportable per the requirements of the WAPS.

[g] Th-232 was also added to the list as it was measured at greater than 0.2 wt% by ICP-MS.

In addition to ICP-MS, the SB7a PS#1 sample was also analyzed with SEM-EDS for noble metal inclusions. Examination of the glass with EDS indicated the presence of both Ru and Rh, which corresponds to the results of the ICP-MS noble metals analysis in Table 3-5.[h] Noble metal inclusions have been observed in previous pour stream samples, including SB4, SB5 and SB6.[17,23]

Table 3-4. Reportable Radionuclide Concentration in the SB7a PS#1 Glass

Radionuclide	Tank 40 SB7a Dried Sludge	Calculated SB7a Glass	Measured SB7a Glass
	(Ci/kg)		
Ni-59	1.5E-03	6.5E-04	---
Ni-63	2.5E-02	1.1E-02	---
Se-79	7.6E-06	3.3E-06	---
Sr-90	1.4E+01	6.1E+00	3.9E+00
Zr-93	5.3E-04	2.3E-04	5.4E-04
Nb-93m	4.6E-04	2.0E-04	---
Tc-99	1.0E-04	4.3E-05	1.8E-05
Sn-126	<6.4E-04	<2.8E-04	---
Cs-137	5.9E-01	2.6E-01	4.3E-01
Sm-151	2.3E-01	1.0E-01	---
Th-232	1.6E-06	7.0E-07	6.5E-07
U-233	1.3E-04	5.7E-05	<2.4E-04
U-234	4.8E-05	2.1E-05	<1.4E-04
U-235	6.4E-07	2.8E-07	2.9E-07
U-236	1.1E-06	4.8E-07	<7.9E-07
U-238	1.5E-05	6.5E-06	7.0E-06
Np-237	2.2E-05	9.6E-06	<1.9E-05
Pu-238	1.8E-01	7.8E-02	7.9E-02
Pu-239	1.3E-02	5.7E-03	6.1E-03
Pu-240	4.1E-03	1.8E-03	<4.5E-03
Pu-241	5.6E-02	2.4E-02	2.4E-02
Pu-242	<2.3E-05	<1.0E-05	<5.6E-05
Am-241	3.7E-02	1.6E-02	1.5E-02
Am-243	5.7E-04	2.5E-04	---
Cm-244	1.9E-02	8.3E-03	---
Cm-246	7.3E-06	3.2E-06	---
Cf-251	<9.2E-06	<4.0E-06	---

Alpha Spectroscopy:	Pu-238
Beta Counting:	Sr-90, Tc-99 and Pu-241
Gamma Counting:	Cs-137 and Am-241
ICP-MS:	Zr-93, Th-232, U-233, U-234, U-235, U-236, U-238, Np-237, Pu-239, Pu-240 and Pu-242

[h] More details can be found in notebook SRNL-NB-2011-00029 (pages 89-92).

Table 3-5. Noble Metal Concentration in the SB7a PS#1 Glass

Noble Metal	Tank 40 SB7a Dried Sludge	Calculated SB7a Glass	Measured SB7a Glass
	(wt%)		
Ag	0.02	0.008	0.01
Pd	0.003	0.001	0.003
Rh	0.02	0.008	0.005
Ru	0.09	0.04	0.03

3.5 PCT

The average normalized release values for ARM[i], EA (published[24] and measured) and SB7a PS#1 are shown in Table 3-6. No water loss issues were observed over the course of the test. Table 5-7 through Table 5-9[j] in Appendix A provides the as-received elemental leachate concentrations for the solutions samples generated by the PCTs. The normalized release values of the pour stream glass for B, Li, Na, Si and U are below 1 g/L, which is very acceptable with respect to the EA glass benchmark values provided in Table 3-6.

Table 3-6. Normalized PCT Results for the SB7a PS#1 Glass (g/L)

Glass ID	NL B	NL Li	NL Na	NL Si	NL U
ARM	0.47	0.55	0.49	0.28	---
St. Dev.	0.02	0.01	0.01	0.003	---
% RSD	3.2	1.9	2.2	1.1	---
EA - Measured	17.06	9.52	13.36	4.10	---
St. Dev.	0.10	0.13	0.04	0.01	---
% RSD	0.6	1.3	0.3	0.2	---
EA - Published	16.7	9.6	13.3	3.9	---
St. Dev.	1.2	0.7	0.9	0.4	---
% RSD	7	7	7	10	---
SB7a PS#1	0.64	0.71	0.97	0.48	0.15
St. Dev.	0.01	0.01	0.03	0.01	0.01
% RSD	2.2	2.0	3.4	2.1	5.0

3.6 Density

The density of the SB7a PS#1 glass was determined to be 2.7 g/cm^3. Data from the density measurements are shown in Table 5-10 in Appendix A.

3.7 REDOX

Summaries of the REDOX results of the pour stream samples and vitrified MFT samples were communicated to DWPF in a series of brief memoranda.[25-28] Table 3-7 and Table 3-8 list the average calculated values for $Fe^{2+}/\sum Fe$ and Fe^{2+}/Fe^{3+} for the pour stream samples and MFT samples, respectively. Complete sets of data for each of the replicates and EA samples included with the individual sets are shown in Table 5-11 and Table 5-12 in Appendix A.

[i] The concentrations of each element of interest for ARM were within the control limits stated in THERMO^{TM}.
[j] As-measured radionuclide data is shown in Tables 5-8 and 5-9.

Table 3-7. SB7a Pour Stream Glass REDOX Data

Sample ID	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
SB7a PS#1	0.13	0.15
SB7a PS#3	0.04	0.05

Table 3-8. SB7a MFT Glass REDOX Data

Sample ID	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
MFT-580	0.04	0.04
MFT-592	0.02	0.02

4.0 Conclusions

- The sum of oxides for the official SB7a pour stream glass is within the PCCS limits (95-105 wt%).
- The average calculated WDF for SB7a is 2.3. In general, the measured radionuclide content of the official SB7a pour stream glass is in good agreement with the calculated values from the Tank 40 dried sludge results from the SB7a WAPS sample.
- As in previous pour stream samples, ruthenium and rhodium inclusions were detected by SEM-EDS in the official SB7a pour stream sample.
- The PCT results indicate that the official SB7a pour stream glass meets the waste acceptance criteria for durability with a normalized boron release of 0.64 g/L, which is an order of magnitude less than the EA glass.
- The measured density of the SB7a pour stream glass was 2.7 g/cm^3.
- The $Fe^{2+}/\sum Fe$ ratios of the SB7a pour stream samples were in the range of 0.04 – 0.13, while the MFT sample glasses prepared by SRNL were in the range of 0.02 – 0.04.

5.0 References

1. S.H. Reboul, D.P. DiPrete, D.R. Click, and C.J. Bannochie, "Reportable Radionuclides in DWPF Sludge Batch 7a (Macrobatch 8)," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2011-00720, 2011.

2. J.M. Pareizs, A.L. Billings, and D.R. Click, "Sludge Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells for Sludge Batch 7a Qualification," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2011-00226, 2011.

3. C.C. Herman, D.K. Peeler, D.R. Click, J.M. Pareizs, and M.E. Stone, "Summary of SRNL Sludge Batch 7a Testing and Recommendations for DWPF Processing," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00064, 2011.

4. D.K. Peeler, T.B. Edwards, and A.L. Billings, "SB7a Recommendation: Based on SB7a Compositional Projections from 12-8-10," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2010-00248, 2010.

5. J.W. Ray, B.H. Culbertson, S.L. Marra, and M.J. Plodinec, "DWPF Glass Product Control Program," Washington Savannah River Company, Aiken, SC, WSRC-IM-91-116-6, Rev. 6, 2006.

6. T.L. Fellinger, "Analysis of Sludge Batch 6 and 7 Pour Stream Samples," Savannah River Remediation, Aiken, SC, HLW-DWPF-TTR-2010-0047, 2010.

7. J.W. Amoroso and A.L. Billings, "Task Technical and Quality Assurance Plan for Analysis of Sludge Batch 6 and 7 Pour Stream Samples and Melter Feed Tank (MFT) Slurry Samples," Savannah River National Laboratory, Aiken, SC, SRNL-RP-2011-00104, 2011.

8. J.W. Amoroso and A.L. Billings, "Analytical Study Plan for Analysis of Sludge Batch 6 and 7 Pour Stream Samples and Melter Feed Tank (MFT) Slurry Samples," Savannah River National Laboratory, Aiken, SC, SRNL-RP-2011-00105, 2011.

9. C.J. Bannochie and N.E. Bibler, "Current and New Controls in the Shielded Cells for Handling DWPF Pour Stream Glasses and Comments Concerning S02244 and S02247 Glasses," Savannah River National Laboratory, Aiken, SC, SRNL-ITS-2005-00127, 2005.

10. "Acid Dissolution of Glass and Sludge for Elemental Analysis," Savannah River National Laboratory, Aiken, SC, ADS-2227, Latest Revision.

11. "Alkali Fusion Dissolutions of Sludge and Glass for Elemental and Anion Analysis," Savannah River National Laboratory, Aiken, SC, ADS-2502, Latest Revision.

12. "DWPF Waste Form Compliance Plan," Westinghouse Savannah River Company, Aiken, SC, WSRC-IM-91-116-0, Rev. 8, 2006.

13. N.E. Bibler, "Measuring and Predicting Fission Product Noble Metals in Savannah River Site High Level Waste Sludges," Westinghouse Savannah River Company, Aiken, SC, WSRC-TR-2005-0098, 2005.

14. "Nuclear Waste Glass and Glass-Ceramic Product Consistency Test (PCT) Methods (ASTM C1285 Latest Revision)," Savannah River National Laboratory, Aiken, SC, ITS-0009, Latest Revision.

15. "Determining Fe^{2+}/Fe^{3+} and Fe^{2+}/Fe(Total) Using UV VIS Spectrometer," Savannah River National Laboratory, Aiken, SC, ITS-0042, Latest Revision.

16. "Heat Treatment of Waste Slurries for REDOX (Fe^{2+}/Fe Total) and Chemical Composition Measurement," Savannah River National Laboratory, Aiken, SC, ITS-0052, Latest Revision.

17. M.M. Reigel and N.E. Bibler, "Analysis of Sludge Batch 4 (Macrobatch 5) for Canister S02902 and Sludge Batch 5 (Macrobatch 6) for Canister S03317 DWPF Pour Stream

Glass Samples," Savannah River National Laboratory, Aiken, SC SRNL-STI-2010-00435, 2010.

18. C.J. Bannochie and N.E. Bibler, "Analysis of Sludge Batch 3 (Macrobatch 4) DWPF Pour Stream Glass Sample for Canister S02312," Savannah River National Laboratory, Aiken, SC, WSRC-TR-2005-00354, 2005.

19. G.L. Smith, "Characterization of Analytical Reference Glass-1 (ARG-1)," Pacific Northwest National Laboratory, Richland, WA, PNL-8992, 1993.

20. S.H. Reboul and D.R. Click, "Stable Constituents in SB7a Tank 40 WAPS Sample," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00133, 2011.

21. "Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms," Department of Energy - Office of Environmental Management, Germantown, MD, DOE/EM-0093, Rev. 2, 1996.

22. C.J. Bannochie, "Tank 40 Final Chemical Characterization Results," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2012-00097, Draft.

23. F.C. Johnson, "Analysis of DWPF Sludge Batch 6 (Macrobatch 7) Pour Stream Glass Samples," Savannah River National Laboratory, Aiken, SC, SRNL-STI-2011-00555, 2012.

24. C.M. Jantzen, N.E. Bibler, D.C. Beam, C.L. Crawford, and M.A. Pickett, "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material," Westinghouse Savannah River Company, Aiken, SC, WSRC-TR-92-346, Rev. 1, 1993.

25. F.C. Johnson and D.R. Click, "REDOX Analysis of a SB7a Pour Stream Sample from MFT Batch 592," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00233, 2011.

26. F.C. Johnson and D.R. Click, "REDOX Analysis of a Vitrified Sample from MFT Batch 592," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00224, 2011.

27. F.C. Johnson, "REDOX Analysis of a Vitrified Sample from MFT Batch 580," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00182, 2011.

28. F.C. Johnson, "REDOX Analysis of a SB7a Pour Stream Sample from MFT Batch 580," Savannah River National Laboratory, Aiken, SC, SRNL-L3100-2011-00181, 2011.

Appendix A. Supplemental Data Tables

Table 5-1. Measured Elemental Concentrations (µg/g) for Glasses Prepared Using a Mixed Acid Dissolution

Lab ID	Al	Ba	Be	Ca	Cd	Ce	Cr	Cu	Fe	Gd	K	La	Li	Mg	Mn
300293761	23300	778	24.2	10100	12.3	< 118	647	19.5	96700	< 42	21300	< 10.5	14900	5110	13800
300293766	23100	782	24	10200	13.5	< 118	646	18.2	96300	< 42	21500	< 10.5	15000	5130	13900
300294006	23200	794	24.2	10400	12.8	< 131	702	25.1	96300	< 46.5	21600	< 11.7	15100	5180	14000
300293762	42300	342	2.39	3410	174	374	553	3250	62800	365	< 599	244	20000	1620	16000
300293763	39900	257	2.39	3120	159	242	441	3050	59300	315	626	193	18800	1500	14800
300293764	38800	284	2.37	3060	168	306	454	2940	60400	325	< 594	212	19100	1510	15500
300293765	46000	187	2.4	3460	163	174	456	2950	59100	301	< 602	152	22200	1650	15400
300293760	< 66.4	4.2	< 1.6	27.6	7.6	< 121	< 20.4	< 12.6	116	< 43	< 602	< 10.8	< 29.2	8.5	< 10.6

Lab ID	Mo	Na	Ni	P	Pb	S	Sb	Si	Sn	Sr	Th	Ti	U	Zn	Zr
300293761	< 52.3	80400	7920	1040	< 140	< 1460	< 2080	212000	< 110	31.2	< 52.3	6590	< 6380	163	901
300293766	< 52.3	79200	7970	1060	< 140	< 1460	< 2080	218000	< 110	31.8	< 52.3	6640	< 6380	161	902
300294006	< 58	79700	8040	1040	< 155	< 1620	< 2310	214000	< 121	32	< 58	6680	< 7070	164	914
300293762	< 53.4	92000	10300	654	< 143	< 1490	< 2120	213000	< 112	174	4890	4240	22100	674	1220
300293763	< 53.4	87000	9460	527	< 143	< 1490	< 2120	203000	< 112	152	3670	3910	21000	629	1100
300293764	< 53	90400	9990	612	< 142	< 1480	< 2110	212000	< 111	153	4030	4100	21500	627	1160
300293765	< 53.6	99900	9720	606	< 143	< 1500	< 2130	214000	< 112	147	2540	4010	20500	623	1090
300293760	< 53.6	< 1480	< 91	< 173	< 143	< 1500	< 213	7170	< 112	< 1	< 53.6	< 7.6	< 653	< 18.4	< 11

Table 5-2. Measured Elemental Concentrations (µg/g) for Glasses Prepared Using a Peroxide Fusion Dissolution

Lab ID	Al	B	Ba	Be	Ca	Cd	Ce	Cr	Cu	Fe	Gd	K	La	Li
300293795	24700	25200	809	25	11600	< 59.6	< 1160	712	< 121	97500	< 150	21800	< 129	14700
300293800	24600	25400	815	23.4	11800	< 60.5	< 1180	711	< 123	98100	< 152	21500	< 131	14800
300294008	24700	25600	790	25.1	12100	< 70.8	< 1380	721	< 144	97700	< 178	21000	< 153	14800
300293796	43700	12700	413	< 15.7	4780	140	< 1190	431	3080	56100	388	< 5920	354	20300
300293797	45900	13400	436	< 15.9	4930	145	< 1200	498	3330	59000	417	< 5970	351	21400
300293798	45900	13500	438	< 15.2	4950	152	< 1150	542	3070	59100	447	< 5720	342	21400
300293799	46300	13500	441	< 16	5210	174	< 1210	476	3230	60100	458	< 6020	350	21600
300293794	1210	< 404	< 126	< 16	1800	< 62	< 1210	< 204	< 126	152	< 156	< 6020	< 134	< 292

Lab ID	Mg	Mn	Mo	Ni	P	Pb	S	Sb	Si	Sn	Sr	Th	Ti	U	Zn
300293795	5200	14600	< 515	8230	< 1670	< 1380	< 14400	< 2050	226000	< 1080	38.5	< 1050	6780	< 6280	163
300293800	5270	14700	< 523	8320	< 1690	< 1400	< 14600	< 2080	234000	< 1100	39.1	< 1070	6840	< 6380	160
300294008	5220	14500	< 612	8200	< 1980	< 1630	< 17100	< 2430	234000	< 1280	43.4	< 1250	6800	< 7450	160
300293796	1550	15000	< 528	9140	< 1700	< 1410	< 14800	< 2100	211000	< 1100	203	5620	3800	19700	654
300293797	1630	15700	< 532	9460	< 1720	< 1420	< 14900	< 2120	222000	< 1110	218	6220	3980	20000	694
300293798	1640	15700	< 510	9870	< 1650	< 1360	< 14300	< 2030	222000	< 1070	217	6210	3990	21300	719
300293799	1680	16000	< 536	10000	< 1730	< 1430	< 15000	< 2130	225000	< 1120	222	6360	4040	21300	704
300293794	< 30	< 106	< 536	< 910	< 1730	< 1430	< 15000	< 2130	< 878	< 1120	< 10	< 1100	< 26	< 6530	< 96

Table 5-3. As-Measured Radionuclide Concentrations (dpm/g) via Gamma and Beta Counting and Alpha Spectroscopy

Replicate	Glass ID	Lab ID	Am-241	Cs-137	Pu-238	Pu-241	Sr-90
1	SB7a PS#1	300294028	3.55E+07	1.07E+09	1.81E+08	4.56E+07	7.55E+09
2		300294029	3.39E+07	8.30E+08	1.87E+08	6.25E+07	8.19E+09
3		300294030	3.19E+07	9.50E+08	1.61E+08	5.39E+07	7.61E+09
4		300294031	3.50E+07	9.70E+08	1.69E+08	5.54E+07	1.17E+10
1	Blank	300294027	3.42E+04	<1.05E+07	2.26E+06	<1.74E+05	<1.15E+08

Table 5-4. As-Measured Tc-99 Concentrations (dpm/g) via Beta Counting Prepared Using a Peroxide Fusion Dissolution

Replicate	Glass ID	Lab ID	Tc-99
1	SB7a PS#1	300297002	3.90E+04
2		300297003	3.92E+04
3		300297004	4.30E+04
4		300297005	3.97E+04
1	Blank	300297001	<1.79E+03

Table 5-5. Measured Tc-99 Concentrations (dpm/g) via Beta Counting Prepared Using a Mixed Acid Dissolution

Replicate	Glass ID	Lab ID	Tc-99
1	SB7a PS#1	300297132	4.71E+04
2		300297133	4.28E+04
3		300297134	3.73E+04
4		300297135	3.64E+04
1	Blank	300297131	<1.73E+03

Table 5-6. As-Measured Concentrations of m/z (µg/g) via ICP-MS

Replicate	Glass ID	Lab ID	m/z						
			93	101	102	103	104	105	106
1	SB7a PS#1	300293796	2.11E+02	1.38E+02	1.21E+02	4.88E+01	7.05E+01	< 1.97E+01	1.12E+02
2		300293797	2.27E+02	1.34E+02	1.30E+02	7.36E+01	7.66E+01	< 1.98E+01	7.60E+01
3		300293798	2.12E+02	1.30E+02	1.13E+02	3.57E+01	7.54E+01	< 1.90E+01	5.18E+01
4		300293799	2.14E+02	1.30E+02	1.28E+02	3.64E+01	6.15E+01	< 2.00E+01	7.80E+01
1	Blank	300293794	2.72E+01	< 1.50E+01	< 5.00E+00	< 5.17E+00	< 5.00E+00	< 2.00E+01	3.37E+02

Replicate	Glass ID	Lab ID	m/z						
			107	108	109	110	232	233	234
1	SB7a PS#1	300293796	5.12E+01	4.87E+01	1.94E+01	5.37E+01	5.39E+03	< 2.46E+01	< 2.21E+01
2		300293797	4.61E+01	< 3.22E+01	2.09E+01	4.26E+01	5.77E+03	< 2.48E+01	< 2.23E+01
3		300293798	2.60E+01	3.15E+01	< 1.43E+01	3.95E+01	6.19E+03	< 2.38E+01	< 2.14E+01
4		300293799	3.79E+01	< 3.25E+01	2.06E+01	4.60E+01	6.20E+03	< 2.50E+01	< 2.25E+01
1	Blank	300293794	1.14E+02	1.15E+02	1.50E+01	1.39E+02	< 1.75E+01	< 2.50E+01	< 2.25E+01

Replicate	Glass ID	Lab ID	m/z						
			235	236	237	238	239	240	242
1	SB7a PS#1	300293796	1.23E+02	< 1.23E+01	< 2.71E+01	1.95E+04	9.57E+01	< 1.97E+01	< 1.48E+01
2		300293797	1.40E+02	< 1.24E+01	< 2.73E+01	2.05E+04	9.66E+01	< 1.98E+01	< 1.49E+01
3		300293798	1.42E+02	< 1.19E+01	< 2.61E+01	2.15E+04	1.05E+02	< 1.90E+01	< 1.43E+01
4		300293799	1.39E+02	< 1.25E+01	< 2.75E+01	2.20E+04	9.70E+01	< 2.00E+01	< 1.50E+01
1	Blank	300293794	< 1.00E+01	< 1.25E+01	< 2.75E+01	1.75E+01	< 1.75E+01	< 2.00E+01	< 1.50E+01

Table 5-7. As-Received Measurements of the PCT Solutions

Replicate	Glass ID	Lab ID	As Received (mg/L)			
			B	Li	Na	Si
1	ARM	300296634	9.4	7.51	20.5	36.1
2		300296635	10.5	8.01	22.1	37.5
3		300296636	9.79	7.73	21.3	36.7
1	EA	300296631	36.6	11.7	101	56.7
2		300296632	35.9	11.3	100	56.3
3		300296633	36.1	11.2	101	56.3
1	SB7a PS#1	300296637	5.09	9.16	54.5	64.4
2		300296638	5	8.97	53.3	62.5
3		300296639	4.9	8.72	51.6	61.6
4		300296640	5.3	9.32	55.9	66.1
1	Soln Std	300296641	19.8	9.67	82.2	51.9
1	Blank	300296629	<0.381	<0.0584	<2.95	<0.391
2		300296630	<0.381	<0.0584	<2.95	<0.391

Table 5-8. As-Measured Concentrations of m/z (µg/L) via ICP-MS for the PCT Solutions

Replicate	Glass ID	Lab ID	m/z			
			99	233	234	235
1	SB7a PS#1	300296637	< 7.50E+00	< 5.00E+00	< 7.50E+00	< 1.75E+01
2		300296638	< 7.50E+00	< 5.00E+00	< 7.50E+00	< 1.75E+01
3		300296639	< 7.50E+00	< 5.00E+00	< 7.50E+00	< 1.75E+01
4		300296640	< 7.50E+00	< 5.00E+00	< 7.50E+00	< 1.75E+01
1	Blank	300296629	< 7.50E+00	< 5.00E+00	< 7.50E+00	< 1.75E+01

Replicate	Glass ID	Lab ID	m/z				
			236	238	239	240	242
1	SB7a PS#1	300296637	< 1.25E+01	1.84E+03	< 5.00E+00	< 1.25E+01	< 5.00E+00
2		300296638	< 1.25E+01	1.81E+03	6.70E+00	< 1.25E+01	< 5.00E+00
3		300296639	< 1.25E+01	1.66E+03	7.54E+00	< 1.25E+01	< 5.00E+00
4		300296640	< 1.25E+01	1.83E+03	1.03E+01	< 1.25E+01	< 5.00E+00
1	Blank	300296629	< 1.25E+01	< 5.00E+00	< 5.00E+00	< 1.25E+01	< 5.00E+00

Table 5-9. As-Measured Radionuclide Concentrations (dpm/mL) via Gamma and Beta Counting

Replicate	Glass ID	Lab ID	Cs-137	Sr-90
1	SB7a PS#1	300296637	1.36E+05	2.02E+05
2		300296638	1.40E+05	1.10E+05
3		300296639	1.38E+05	1.19E+05
4		300296640	1.61E+05	2.97E+05
1	Blank	300296629	<4.24E+03	<4.62E+03

Table 5-10. Density Measurement Data

Parameter	NIST 1830	SB7a PS#1
m0 (g)	38.347	38.346
m1 (g)	43.39	46.402
m2 (g)	67.29	69.319
m3 (g)	64.256	64.257
Density (g/cm^3)	2.51	2.69

Table 5-11. SB7a Pour Stream Glass REDOX Data

Sample ID	Replicate	Fe^{2+}	$\sum Fe$	Fe^{3+}	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
EA	---	0.093	0.526	0.433	0.177	0.215
SB7a PS#1	1	0.058	0.441	0.383	0.132	0.151
	2	0.055	0.375	0.320	0.147	0.172
	3	0.055	0.460	0.405	0.120	0.136
EA	---	0.1517	0.8235	0.6718	0.184	0.226
SB7a PS#3	1	0.0458	1.0664	1.0206	0.043	0.045
	2	0.0329	0.7584	0.7255	0.043	0.045
	3	0.0485	1.1006	1.0521	0.044	0.046

Table 5-12. SB7a Vitrified MFT REDOX Data

Sample ID	Replicate	Fe^{2+}	$\sum Fe$	Fe^{3+}	$Fe^{2+}/\sum Fe$	Fe^{2+}/Fe^{3+}
EA	---	0.094	0.497	0.403	0.189	0.233
MFT-580-A	1	0.011	0.396	0.385	0.028	0.029
	2	0.013	0.469	0.456	0.028	0.029
	3	0.012	0.379	0.367	0.032	0.033
MFT-580-B	1	0.022	0.607	0.585	0.036	0.038
	2	0.026	0.669	0.643	0.039	0.040
	3	0.02	0.409	0.389	0.049	0.051
MFT-580-C	1	0.025	0.547	0.522	0.046	0.048
	2	0.026	0.456	0.430	0.057	0.060
	3	0.018	0.384	0.366	0.047	0.049
EA	---	0.1729	0.9417	0.7688	0.184	0.225
MFT-592-A	1	0.0224	1.1181	1.0957	0.020	0.020
	2	0.0156	0.7576	0.7420	0.021	0.021
	3	0.0238	1.0321	1.0083	0.023	0.024
MFT-592-B	1	0.0207	1.0168	0.9961	0.020	0.021
	2	0.0244	0.9740	0.9496	0.025	0.026
	3	0.0209	0.9800	0.9591	0.021	0.022
MFT-592-C	1	0.0254	0.9999	0.9745	0.025	0.026
	2	0.0258	1.0246	0.9988	0.025	0.026
	3	0.0233	0.9028	0.8795	0.026	0.026

Distribution:

J.W. Amoroso, 999-W
C. J. Bannochie, 773-42A
J. M. Bricker, 704-27S
M. A. Broome, 704-29S
C.L. Crawford, 773-42A
T.B. Edwards, 999-W
H.H. Elder, 704-24S
T. L. Fellinger, 704-26S
S. D. Fink, 773-A
K.M. Fox, 999-W
B. J. Giddings, 786-5A
J. M. Gillam, 766-H
C. C. Herman, 999-W
R. N. Hinds, 704-S
E. W. Holtzscheiter, 704-15S
J. F. Iaukea, 704-30S
P. R. Jackson, DOE-SR, 703-46A
C.M. Jantzen, 773-A
F.C. Johnson, 999-W
M. T. Keefer, 766-H
D.P. Lambert, 999-W
S. L. Marra, 773-A
D.W. McIlmoyle, 766-H
J.D. Newell, 999-W
J. E. Occhipinti, 704-S
J.M. Pareizs, 773-A
D. K. Peeler, 999-W
F. M. Pennebaker, 773-42A
J. W. Ray, 704-S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
A. V. Staub, 704-27S
M. E. Stone, 999-W
K. H. Subramanian, 766-H
J. P. Vaughan, 773-41A
W. R. Wilmarth, 773-A
J.R. Zamecnik, 999-W