

Sludge Batch 7b Qualification Activities With SRS Tank Farm Sludge

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November 2011

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Savannah River Nuclear Solutions, LLC
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EXECUTIVE SUMMARY

Waste Solidification Engineering (WSE) has requested that characterization and a radioactive demonstration of the next batch of sludge slurry – Sludge Batch 7b (SB7b) – be completed in the Shielded Cells Facility of the Savannah River National Laboratory (SRNL). This characterization and demonstration, or sludge batch qualification process, is required prior to transfer of the sludge from Tank 51 to the Defense Waste Processing Facility (DWPF) feed tank (Tank 40). Typically, SRNL receives a qualification sample from Tank 51 and washes that sample per Tank Farm plans and projections. With the tight schedule constraints for Sludge Batch 7b (SB7b) and the potential need for caustic addition to allow for an acceptable glass processing window, the qualification for SB7b was approached differently than past batches. For SB7b, SRNL prepared a Tank 51 and a Tank 40 sample for qualification. Due to schedule constraints, SRNL did not receive the qualification sample from Tank 51 nor did it simulate all of the Tank Farm washing and decanting operations. Instead, SRNL prepared a Tank 51 SB7b sample from samples of Tank 7 and Tank 51, along with a wash solution to adjust the supernatant composition to the final SB7b Tank 51 Tank Farm projections. SRNL then prepared a sample to represent SB7b in Tank 40 by combining portions of the SRNL-prepared Tank 51 SB7b sample and a Tank 40 Sludge Batch 7a (SB7a) sample. The blended sample was 71% Tank 40 (SB7a) and 29% Tank 7/Tank 51 on an insoluble solids basis. This sample is referred to as the SB7b Qualification Sample. The blend represented the highest projected Tank 40 heel (as of May 25, 2011), and thus, the highest projected noble metals content for SB7b. Characterization was performed on the Tank 51 SB7b samples and SRNL performed DWPF simulations using the Tank 40 SB7b material.

This report documents:

- The preparation and characterization of the Tank 51 SB7b and Tank 40 SB7b samples.
- The performance of a DWPF Chemical Process Cell (CPC) simulation using the SB7b Tank 40 sample. The simulation included a Sludge Receipt and Adjustment Tank (SRAT) cycle, where acid was added to the sludge to destroy nitrite and reduce mercury, and a Slurry Mix Evaporator (SME) cycle, where glass frit was added to the sludge in preparation for vitrification. The SME cycle also included replication of five canister decontamination additions and concentrations. Processing parameters were based on work with a non-radioactive simulant.
- Vitrification of a portion of the SME product and characterization and durability testing (as measured by the Product Consistency Test (PCT)) of the resulting glass.
- Rheology measurements of the SRAT receipt, SRAT product, and SME product.

Key observations, conclusions, and recommendations from this work include:

- Characterization of the Tank 51 SB7b did not identify any new reportable elements or radionuclides.
- Rheological properties were acceptable for SRAT receipt and SRAT product. However, the measured yield stresses were near the upper operating limits for DWPF processing and the material appeared to be very tacky/sticky. At >46 wt % total solids, the SME product had a very high consistency. It is recommended that DWPF not concentrate to this level.

- Potential error in the analytical inputs resulted in the need to add additional acid and re-boil the SRAT to meet the nitrite destruction limit. After the third addition and boiling cycle, the SB7b Tank 40 qualification sample as prepared by SRNL met the processing constraints imposed by the DWPF. Mercury was removed to DWPF target levels after the first addition and boiling cycle (nominally 12 hours). Hydrogen generation rates were below the DWPF design bases throughout the SRAT and SME cycles.
- Foaming was not problematic during SRAT and SME processing, and antifoam was effective when added. The antifoam was from Siovation Lot#111128-0613. 300 ppm antifoam was added prior to acid addition; 100 ppm antifoam was added after the initial nitric acid addition; 500 ppm antifoam was added prior to boiling in Stage 1; 100 ppm additions were made at the start of each additional stage of acid addition; and a 100 ppm addition was made prior to the first frit/formic acid addition.
- The SB7b SME product (SB7b Tank 40 Qualification sludge plus Frit 702) was used to fabricate a glass with a targeted waste loading of 36%. The glass was acceptable with respect to chemical durability as measured by the PCT. Specifically, the SB7b glass had a normalized boron release of 0.77 g/L, while the Environmental Assessment (EA) glass had a normalized release of 16.6 g/L. The PCT response was also predictable by the current durability models of the DWPF Product Composition Control System (PCCS).

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LIST OF ABBREVIATIONS

AD	SRNL Analytical Development
AR	aqua regia
ARG-1	Analytical Reference Glass-1
ARM	Analytical Reference Material
CPC	Chemical Process Cell
CVAA	cold vapor-atomic absorption
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
FAVC	Formic Acid Vent Condenser
GC	micro gas chromatograph
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectroscopy
LEPS	low energy photon spectroscopy
LSC	liquid scintillation counting
MAR	Measurement Acceptability Region
MWWT	Mercury Water Wash Tank
NA	not applicable
NM	not measured
PCCS	Product Consistency Control System
PCT	Product Consistency Test
PF	peroxide fusion
R&D	research and development
REDOX	reduction-oxidation ($Fe^2/\Sigma Fe$ in this document)
SB7a	Sludge Batch 7a
SB7b	Sludge Batch 7b
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TIC	total inorganic carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAPS	Waste Acceptance Product Specification
WSE	Waste Solidification Engineering
α -PHA	alpha pulse height analysis
γ -PHA	gamma pulse height analysis

1.0 Introduction

Waste Solidification Engineering (WSE) has requested that characterization and a radioactive demonstration of the next batch of sludge slurry – Sludge Batch 7b (SB7b) – be completed in the Shielded Cells Facility of the Savannah River National Laboratory (SRNL) via a Technical Task Request (TTR).¹ This characterization and demonstration, or sludge batch qualification process, is required prior to transfer of the sludge from Tank 51 to the Defense Waste Processing Facility (DWPF) feed tank (Tank 40). The current WSE practice is to prepare sludge batches in Tank 51 by transferring sludge from other tanks. Discharges of nuclear materials from H Canyon are often added to Tank 51 during sludge batch preparation. The sludge is washed and transferred to Tank 40, the current DWPF feed tank. Prior to transfer of Tank 51 to Tank 40, SRNL typically simulates the Tank Farm and DWPF processes with a Tank 51 sample (referred to as the qualification sample). With the tight schedule constraints for SB7b and the potential need for caustic addition to allow for an acceptable glass processing window, the qualification for SB7b was approached differently than past batches. For SB7b, SRNL prepared a Tank 51 and a Tank 40 sample for qualification. SRNL did not receive the qualification sample from Tank 51 nor did it simulate all of the Tank Farm washing and decanting operations. Instead, SRNL prepared a Tank 51 SB7b sample from samples of Tank 7 and Tank 51, along with a wash solution to adjust the supernatant composition to the final SB7b Tank 51 Tank Farm projections. SRNL then prepared a sample to represent SB7b in Tank 40 by combining portions of the SRNL-prepared Tank 51 SB7b sample and a Tank 40 Sludge Batch 7a (SB7a) sample. The blended sample was 71% Tank 40 (SB7a) and 29% Tank 7/Tank 51 on an insoluble solids basis. This sample is referred to as the SB7b Qualification Sample. The blend represented the highest projected Tank 40 heel (as of May 25, 2011), and thus, the highest projected noble metals content for SB7b. Characterization was performed on the Tank 51 SB7b samples and SRNL performed DWPF simulations using the Tank 40 SB7b material.

This report documents:

- The preparation and characterization of the Tank 51 SB7b and Tank 40 SB7b samples.
- The performance of a DWPF Chemical Process Cell (CPC) simulation using the SB7b Tank 40 sample. The simulation included a Sludge Receipt and Adjustment Tank (SRAT) cycle, where acid was added to the sludge to destroy nitrite and reduce mercury, and a Slurry Mix Evaporator (SME) cycle, where glass frit was added to the sludge in preparation for vitrification. The SME cycle also included replication of five canister decontamination additions and concentrations. Processing parameters were based on work with a non-radioactive simulant.
- Vitrification of a portion of the SME product and characterization and durability testing (as measured by the Product Consistency Test (PCT)) of the resulting glass.
- Rheology measurements of the SRAT receipt, SRAT product, and SME product.

This program was controlled by a Task Technical and Quality Assurance Plan (TTQAP)², and analyses were guided by an Analytical Study Plan³. This work is Technical Baseline Research and Development (R&D) for the DWPF.

It should be noted that much of the data in this document has been published in interoffice memoranda. The intent of this technical report is bring all of the SB7b related data together in a single permanent record and to discuss the overall aspects of SB7b processing.

2.0 Sample Preparation and Characterization

SRNL utilized portions of three tank samples for SB7b qualification:

- Tank 7: Tank Farm sample ID FTF-07-11-3. This sample was received specifically for SB7b qualification activities. The sample contained transfers from Tanks 4 and 12 and a heel from oxalic acid cleaning of Tanks 5 and 6.
- Tank 51: Tank Farm sample ID HTF-11-51-28. This sample was received as the Tank 51 SB7a confirmation sample. The sample underwent additional washing and decanting before blending with the SB7b sample to more closely match the heel in Tank 51 after the SB7a transfer.
- Tank 40: Tank Farm sample ID HTF-11-40-66. This sample was received for SB7a Waste Acceptance Product Specification characterization.

SB7b samples were then produced from the above samples. This section describes characterization methods and results for the above as-received samples. Descriptions of the SRNL-made SB7b samples along with characterization results are also included.

2.1 Description of Analytical Methods

Density measurements were conducted at a temperature of ~25 °C. This temperature was governed by the Shielded Cells conditions at the time of the measurements. Densities were measured using weight-calibrated balances and 8-9 mL volume-calibrated plastic test tubes.⁴ Four individual slurry aliquots and four individual supernatant aliquots were utilized in the measurements. Supernatant was generated by passing slurry through a 0.45 µm filtration membrane.

Total solids and dissolved solids determinations were performed by driving water from slurry and supernatant aliquots (respectively) at a nominal temperature of ~115 °C.⁴ Four individual slurry aliquots and four individual supernatant aliquots were utilized in the measurements. The mass of each aliquot was ~3.0 g. Insoluble and soluble solids concentrations were calculated based on the total solids and dissolved solids measurements. Calcined solids were then generated by heating the dried slurry aliquots (from the total solids measurements) to a temperature of ~1100 °C.

In preparation for elemental analyses, sludge solids aliquots were digested by both aqua regia (AR) and sodium peroxide fusion (PF) methods. Four individual sludge aliquots were utilized in each method. The total solids mass of each aliquot was ~0.25 g, and the volume of each final digest solution was 100 mL. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed on both the AR and PF digest solutions. Cold vapor atomic absorption (CVAA) and inductively coupled plasma mass spectroscopy (ICP-MS) measurements were performed only on the AR digest solutions. ICP-AES measurements of AR digest solutions were used to quantify a majority of the elements. ICP-AES measurements of PF digest solutions were used to quantify Al and Si. CVAA measurements were used to quantify As, Hg, and Se. The concentration of Nd was calculated from ICP-MS measurements by the sum of masses 143 to 146, 148, and 150. Noble metals (Ag, Rh, Ru, and Pd) were calculated from ICP-MS analysis using the methodology given in Reference⁵.

All supernatant analyses were performed on dilutions of nominally 1.5 g of supernatant diluted to 50 mL of de-ionized water. Four diluted supernatant aliquots were analyzed by each measurement technique. ICP-AES was used to quantify sodium, aluminum (assumed to be aluminate), and sulfur (assumed to be sulfate); ion chromatography was used to quantify nitrite,

nitrate, and oxalate; base titration was used to quantify free hydroxide; and total inorganic carbon analysis was used to quantify carbonate.

The analytical methods for radionuclide analyses are presented in Table 2-1. For each radionuclide, this table identifies: a) whether the analysis was performed on supernatant or on slurry; b) the type of slurry digestion that was performed (if applicable); c) whether a chemical separation was performed prior to measurements; d) the measurement technique utilized; and e) any other pertinent information applicable to the result.

Table 2-1. Summary of Analytical Methods

Radionuclides	Supernatant	Slurry	PF Digestion	AR Digestion	Other Digestion	Chemical Separation	Measurement Technique	Other Information
H-3	X					X	LSC	
C-14							n/a	SRR projection (Ref. 6)
Co-60, Ru-106, Sb-125, Ce-144, Eu-154, Eu-155, Am-241		X	X			X	γ -PHA	
Sr-90		X	X			X	LSC	
Tc-99, Th-232, U-233, U-234, U-235, U-236, U-238, Np-237, Pu-239, Pu-240, Pu-242		X		X			ICP-MS	
Y-90, Rh-106, Te-125m, Ba-137m, Pr-144							n/a	Calculated based on parent activity
I-129		X			X	X	LEPS	
Cs-134, Cs-137		X	X				γ -PHA	
Pm-147		X	X			X	LSC	
Pu-238		X	X			X	α -PHA	
Pu-241		X	X			X	LSC	
Am-242m, Cm-245		X	X		X	X	ICP-MS	
Am-243, Cm-244		X	X		X	X	α -PHA	
Total alpha		X	X				LSC	
Nonvolatile beta		X	X				LSC	
Total gamma							n/a	Sum of primary detectable γ -emitters (Ba-137m + Am-241 + Eu-154 + Eu-155 + Co-60)

PF = peroxide fusion; AR = aqua regia; LSC = liquid scintillation counting; γ -PHA = gamma pulse height analysis; ICP-MS = inductively coupled plasma mass spectroscopy; LEPS = low energy photon spectroscopy; α -PHA = alpha pulse height analysis.

Rheological properties of radioactive samples were determined using a Haake M5/RV30 rotoviscometer. The M5/RV30 is a Searle sensor system, where the bob rotates, and the cup is fixed. The torque and rotational speed of the bob are measured. Heating/cooling of the cup/sample/bob is through the holder for the cup. The shear stress is determined from the torque measurement and is independent of the rheological properties. Conditions that impact the

measured torque are; slip (material does not properly adhere to the rotor or cup), phase separation (buildup of liquid layer on rotor), sedimentation (particles settling out of the shearing zone), homogeneous sample (void of air), lack of sample (gap not filled), excess sample (primarily impacts rheologically thin fluids), completely filling up the void below the bob (air buffer that is now filled with fluid) and Taylor vortices. The first five items yield lower stresses and the last three add additional stresses. The shear rate is geometrically determined using the equations of change (continuity and motion) and is that for a Newtonian fluid. This assumption also assumes that the flow field is fully developed and the flow is laminar. The shear rate can be calculated for non-Newtonian fluids using the measured data and fitting this data to the rheological model or corrected as recommended by Darby.⁷ In either case, for shear thinning non-Newtonian fluids typical of Savannah River Site (SRS) sludge wastes, the corrected shear rates are greater than their corresponding Newtonian shear rates, resulting in a mathematically thinner fluid. Correcting the flow curves will not be performed in this task, resulting in calculations giving a slightly more viscous fluid.

The bob typically used for measuring tank sludge or SRAT product is the MV I rotor. For SME product, the MV II rotor is used to perform the measurements, due to the larger frit particles that are present in the SME product. The MV II has a larger gap to accommodate the larger frit particles. The shape, dimensions, and geometric constants for the MV I and MV II rotors are provided in Table 2-2.

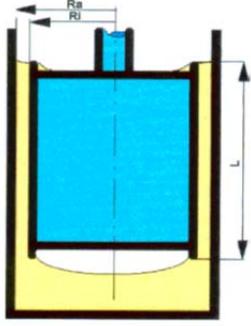
Prior to performing the measurements, the rotors and cups are inspected for physical damage. The torque/speed sensors and temperature bath are verified for functional operability using a bob/cup combination with a National Institute of Standards and Technology (NIST) traceable Newtonian oil standard, using the MV I rotor. The resulting flow curves are then fitted as a Newtonian fluid and this calculated viscosity must be within $\pm 10\%$ of the reported NIST viscosity at a given temperature for the system to be considered functionally operable. An N10 oil standard was used to verify system operability prior to the sludge measurements.

The flow curves for the sludge were fitted to the down curves using the Bingham Plastic rheological model, Equation 1, where τ is the measured stress (Pa), τ_o is the Bingham Plastic yield stress (Pa), μ_∞ is the plastic viscosity (Pa-sec), and $\dot{\gamma}$ is the measured shear rate (sec^{-1}). During all these measurements, the sample remained in the cup for the 2nd measurement, due to the limited sample availability.

Equation 1

$$\tau = \tau_o + \mu_\infty \dot{\gamma}$$

Table 2-2. MV I and MV II Rotor Specifications and Flow Curve Program

Rotor Design	Dimensions and Flow Curve Program		
	Rotor Type	MV I	MV II
	Rotor radius - R_i (mm)	20.04	18.40
	Cup Radius - R_a (mm)	21.0	21.0
	Height of rotor - L (mm)	60	60
	Sample Volume (cm^3) minimum	40	55
	A factor ($\text{Pa}/\% \text{torque}$)	3.22	3.76
	M factor ($\text{s}^{-1}/\% \text{RPM}$)	11.7	4.51
	Shear rate range (s^{-1})	0 – 600	0 – 300
	Ramp up time (min)	5	5
	Hold time (min)	1	1
	Ramp down time (min)	5	5

2.2 As-Received Characterization Results

Characterization results of the as-received Tank 7, Tank 40, and Tank 51 samples are given in the following tables. It should be noted that a large portion of these results has been published previously via memorandums.⁸⁻¹⁰ Density and solids distribution are given in Table 2-3; total solids composition is given in Table 2-5, and supernatant composition is given in Table 2-4.

Slight variation is expected in each tank composition due to differences in sludges; however, the results also illustrate changes in composition and properties as sludge is washed. Tank 7 was in the early stages of washing, Tank 51 was nearing the end of washing, and Tank 40 was a washed sludge being fed to DWPF. Supernatant density, wt % dissolved solids, sodium in the total solids, and most ion concentrations decrease as sludge is washed. This is indeed the case when comparing the characterization results of these three tanks. It should be noted that the high nitrite in the Tank 51 sample is the result of nitrite addition for corrosion control.

Table 2-3. As-Received Tank 7, Tank 40, and Tank 51 Density and Wt % Solids Results

Analysis	Tank 7	Tank 51	Tank 40
Slurry Density (g/mL)	1.15	1.15	1.14
Supernatant Density (g/mL)	1.13	1.08	1.05
Wt % Total Solids	18.5	19.3	17.2
Wt % Dissolved Solids	15.5	10.2	5.4
Wt % Insoluble Solids	3.6	10.1	12.5
Wt % Soluble Solids	14.9	9.2	4.7
Wt % Calcined Solids	NM	14.9	13.5

Table 2-4. As-Received Supernatant Results (M)

Ion	Tank 7	Tank 51	Tank 40
Na ⁺	3.3	1.8	1.0
NO ₂ ⁻	0.48	0.56	0.25
NO ₃ ⁻	0.43	0.27	0.098
Free OH ⁻	1.0	0.34	0.20
CO ₃ ²⁻	0.28	0.12	0.10
Al(OH) ₄ ⁻	0.14	0.065	0.037
C ₂ O ₄ ²⁻	0.019	0.046	0.050
SO ₄ ²⁻	0.15	0.045	0.019

Table 2-5. As-Received Elemental Composition Results (wt % in Total Solids)

Element	Tank 7	Tank 51	Tank 40
Ag	4.6E-03	NM	1.8E-02
Al	2.9E+00	NM	1.0E+01
B	8.0E-03	3.6E-03	<1.5E-02
Ba	4.2E-02	6.8E-02	1.0E-01
Be	1.2E-04	1.9E-04	3.4E-04
Ca	2.0E-01	4.3E-01	7.2E-01
Cd	< 1.0E-03	1.4E-02	3.6E-02
Ce	6.0E-02	8.2E-02	1.3E-01
Co	7.8E-03	1.0E-02	1.2E-02
Cr	5.9E-02	4.9E-02	4.6E-02
Cu	1.8E-02	2.8E-02	1.2E-01
Fe	5.9E+00	9.6E+00	1.4E+01
Gd	8.1E-03	8.2E-02	1.1E-01
Hg	1.8E-01	NM	1.9E+00
K	1.3E-01	8.8E-02	5.4E-02
La	3.5E-02	4.9E-02	7.8E-02
Li	6.9E-03	2.2E-02	2.9E-02
Mg	4.6E-02	2.2E-01	3.7E-01
Mn	5.5E-01	2.4E+00	3.9E+00
Mo	1.0E-02	6.5E-03	<9.7E-03
Na	3.2E+01	2.2E+01	1.3E+01
Nd	1.2E-01	NM	2.3E-01
Ni	1.7E+00	1.8E+00	2.4E+00
P	7.2E-02	3.8E-02	6.0E-02
Pb	1.4E-02	2.3E-02	2.7E-02
Pd	1.5E-03	NM	2.6E-03
Rh	9.6E-03	NM	1.9E-02
Ru	4.6E-02	NM	9.4E-02
S	1.9E+00	6.0E-01	2.3E-01
Sb	8.6E-03	1.7E-02	<2.0E-02
Si	2.4E-01	ND	1.2E+00
Sn	< 3.4E-03	< 3.4E-03	<8.9E-03
Sr	1.7E-02	3.2E-02	4.8E-02
Th	1.3E-01	8.2E-01	1.5E+00
Ti	5.5E-03	1.2E-02	1.8E-02
U	1.9E+00	3.7E+00	4.7E+00
V	< 4.2E-04	< 4.1E-04	<7.4E-04
Zn	2.0E-02	3.5E-02	4.3E-02
Zr	1.0E-01	1.5E-01	1.4E-01

2.3 Preparation and Characterization of SRNL-Prepared Sludge Batch 7b Qualification Samples

Following the receipt and characterization of the Tank 51 SB7a confirmation sample (HTF-51-11-28, see Section 2.2 above), the sample was washed by SRNL per Tank Farm plans of April 27, 2011. Tank Farm washing plans included a Wash/Decant I, J, and K prior to transfer of Tank 51 to Tank 40. SRNL's washes and decants were proportional to the Tank Farm volumes. The washed material was then characterized with respect to densities, solids distribution, and primary supernatant ions (no dissolutions for elemental analyses were performed). Results are presented in Table 2-6. Note that these results have been published previously.¹¹

Table 2-6. Analytical Results of the SRNL-Washed Tank 51 SB7a Confirmation Sample

Analysis	Result
Slurry Density (g/mL)	1.12
Supernatant Density (g/mL)	1.05
Wt % Total Solids (slurry basis)	18.4
Wt % Dissolved Solids (supernatant basis)	6.5
Wt % Insoluble Solids (slurry basis)	12.7
Wt % Soluble Solids (slurry basis)	5.7
Wt % Calcined Solids	14.3
Na ⁺ (mol/L supernatant)	1.1
Al(OH) ₄ ⁻ (mol/L supernatant)	0.033
SO ₄ ²⁻ (mol/L supernatant)	0.023
CO ₃ ²⁻ (mol/L supernatant) †	0.055
NO ₂ ⁻ (mol/L supernatant)	0.22
NO ₃ ⁻ (mol/L supernatant)	0.11
C ₂ O ₄ ²⁻ (mol/L supernatant)	0.090
Free OH ⁻ (mol/L supernatant)	0.25

SRNL then prepared two SB7b samples based on Tank Farm projections: a Tank 51 SB7b sample, representing projected Tank 51 conditions at the conclusion of SB7b preparations, and a Tank 40 SB7b sample, representing Tank 40 following the transfer of Tank 51 SB7b to Tank 40.

The preparation of the Tank 51 SB7b sample is outlined below. Once again, significant time constraints and the fact that information on washing and settling times was not required resulted in a slightly different preparation and washing strategy for this sludge batch. Rather than performing several washes/decants to simulate Tank Farm washing, SRNL added a sodium solution to obtain the target supernatant composition with only one wash. The preparation of the Tank 51 SB7b sample is outlined below.

- Began with 2,850 mL of as-received Tank 7 slurry.
- Decanted 2,270 mL of Tank 7 supernatant.
- Added 350 mL of the SRNL-washed Tank 51 SB7a slurry.
- Added 10 mL of H Canyon Pu solution.
- Added 1,500 mL of wash water. The wash water had a composition of 0.44 M Na⁺, 0.14 M NO₂⁻, 0.018 M NO₃⁻, 0.30 M OH⁻, and 0.0068 SO₄²⁻.
- Decanted 1,200 mL of supernatant.

The Tank 40 SB7b sample was produced by combining 1,070 mL of Tank 40 slurry with 440 mL of the SRNL-produced Tank 51 SB7b slurry. Characterization results of these two samples are presented in Table 2-7, Table 2-8, and Table 2-9. A majority of these results has been previously published.¹²

Table 2-7. Density and Wt % Solids Results

Property	Tank 51 SB7b	Tank 40 SB7b
Slurry Density (g/mL)	1.14	1.12
Supernatant Density (g/mL)	1.05	1.06
Wt% Total Solids (Slurry Basis)	17.9	16.1
Wt% Calcined Solids (Slurry Basis)	14.4	11.8
Wt% Dissolved Solids (Supernatant Basis)	6.4	6.1
Wt% Insoluble Solids (Slurry Basis)	12.2	10.6
Wt% Soluble Solids (Slurry Basis)	5.7	5.5

Table 2-8. Elemental Composition Results (wt % in total solids)

Element	Tank 51 SB7b	Tank 40 SB7b
Ag	1.1E-02	1.1E-02
Al	6.7E+00	8.8E+00
As	<1.1E-03	NM
B	< 7E-03	< 8E-03
Ba	1.3E-01	1.0E-01
Be	2.7E-04	4.4E-04
Ca	6.6E-01	6.4E-01
Cd	2.3E-02	3.0E-02
Ce	1.9E-01	2.4E-01
Co	1.7E-02	1.3E-02
Cr	4.4E-02	4.3E-02
Cu	7.8E-02	8.0E-02
Fe	1.8E+01	1.4E+01
Gd	1.1E-01	1.0E-01
Hg	7.1E-01	1.3E+00
K	6.1E-02	< 3E-02
La	1.1E-01	8.3E-02
Li	2.6E-02	2.7E-02
Mg	2.0E-01	2.9E-01
Mn	2.4E+00	3.0E+00
Mo	< 5E-03	4.9E-03
Na	1.5E+01	1.4E+01
Nd	3.3E-01	2.5E-01
Ni	4.7E+00	2.9E+00
P	< 1E-01	1.0E-01
Pb	3.9E-02	< 5E-02
Pd	2.0E-03	2.4E-03
Rh	2.7E-02	2.1E-02
Ru	1.3E-01	1.0E-01
S	6.7E-01	4.6E-01
Sb	3.6E-02	2.2E-02
Se	<2E-03	NM
Si	1.0E+00	1.1E+00
Sn	7.2E-03	<4E-02
Sr	5.5E-02	4.5E-02
Th	6.4E-01	1.0E+00
Ti	1.8E-02	1.7E-02
U	6.0E+00	4.8E+00
V	< 3E-04	< 3E-04
Zn	3.7E-02	4.8E-02
Zr	1.6E-01	2.5E-01

Table 2-9. Tank 51 SB7b and Tank 40 SB7b Supernatant Results (M)

Ion	Tank 51 SB7b	Tank 40 SB7b
Na ⁺	1.0	1.0
NO ₂ ⁻	0.23	0.25
NO ₃ ⁻	0.11	0.11
Free OH ⁻	0.34	0.25
CO ₃ ²⁻	0.066 ^b	0.087
Al(OH) ₄ ⁻	0.034	0.036
C ₂ O ₄ ²⁻	0.018	0.043
SO ₄ ²⁻ (ICP-AES)	ND ^a	0.027
F ⁻	<0.01	<0.01
HCO ₂ ⁻	<0.005	<0.004
Cl ⁻	<0.006	<0.006
Phosphate	<0.002	<0.002
Sulfate (IC)	0.029	0.022

^a ND=Not Determined. The Quality Control check of sulfur for this set of samples was outside of specifications. Samples were not rerun since an estimate of sulfur can be obtained from IC analysis, and total sulfur was determined from a slurry digestion (see Table 2-8).

^b Carbonate is calculated from a total inorganic carbon result, assuming all inorganic carbon is carbonate.

2.4 Radionuclides in the Tank 51 SB7b Sample

Radionuclide concentrations in the SB7b Tank 51 sample are given below in Table 2-10. These results have been published in Reference 13. These are radionuclides necessary for the transfer of Tank 51 to Tank 40, as requested in the TTR.¹

Most of the radioactivity is due to beta-emitter Sr-90 and its short-lived beta-emitting daughter Y-90. Summing their concentrations with the next most dominant beta-emitter, Cs-137, gives a total beta activity concentration of 3.5E-2 Curies per gram of total solids. This value is about 10% lower than nonvolatile beta concentration determined via gross analysis (4.0E-2 Curies per gram of total solids). Given that the analytical uncertainties of the radiometric methods are typically 10-20%, the agreement between the two sets of results is considered very good.

The concentration of alpha activity is two orders of magnitude lower than the beta activity. Specifically, the sum of alpha activity due to the dominant alpha-emitters (Pu-238, Pu-239, Pu-240, Am-241, and Cm-244) is 1.7E-4 Curies per gram of total solids. This value is consistent with the total alpha concentration determined via gross analysis (<2.4E-4 Curies per gram of total solids).

The primary photon-emitter is Ba-137m (the short-lived daughter of Cs-137), with a concentration of 5.6E-4 Curies per gram of total solids. The next most dominant photon-emitters are Eu-154, Eu-155, and Co-60, with concentrations of 1.7E-5, 5.7E-6, and 4.5E-6 Curies per gram of total solids, respectively.

The RSD values provide an indication of measurement precision, which is helpful for identifying unusual analytical fluctuations. Although none of the RSD values are considered unacceptably large, it should be noted that those for Pu-240, Cm-244, and Cm-245 are on the order of 30-40%, while those for all other analytes are less than 15%. What this suggests is that the uncertainties for the Pu-240, Cm-244, and Cm-245 results may be higher than those for the other results.

Table 2-10. Mean Concentrations of Radionuclides in the SB7b Qualification Sample

Radionuclide	Ci per gram of total solids	Ci per gallon of slurry	wt% of total solids	%RSD
H-3	NA	<3.9E-05	NA	NA
C-14	1.4E-09 ^a	9.5E-07 ^a	3.2E-08	NA
Co-60	4.5E-06	3.5E-03	4.0E-07	1.3
Sr-90	1.7E-02	1.3E+01	1.3E-02	1.6
Y-90	1.7E-02	1.3E+01	3.2E-06	NA
Tc-99	9.2E-08	7.1E-05	5.4E-04	14 ^b
Ru-106	<6.4E-07	<5.0E-04	<1.9E-08	NA
Rh-106	<6.4E-07	<5.0E-04	<1.8E-14	NA
Sb-125	<1.8E-07	<1.4E-04	<1.8E-08	NA
Te-125m	<1.8E-07	<1.4E-04	<1.0E-09	NA
I-129	8.1E-10	6.3E-07	4.6E-04	8.6
Cs-134	<3.5E-06	<2.7E-03	<2.7E-07	NA
Cs-137	5.9E-04	4.6E-01	6.8E-04	2.2
Ba-137m	5.6E-04	4.3E-01	1.0E-10	NA
Ce-144	<9.9E-07	<7.7E-04	<3.1E-08	NA
Pr-144	<9.9E-07	<7.7E-04	<1.3E-12	NA
Pm-147	<2.3E-04	<1.8E-01	<2.5E-05	NA
Eu-154	1.7E-05	1.3E-02	6.2E-06	1.7
Eu-155	5.7E-06	4.4E-03	1.2E-06	10
Th-232	5.4E-10	4.2E-07	5.0E-01	4.5
U-233	<9.2E-08	<7.1E-05	<9.5E-04	NA
U-234	3.9E-08	3.0E-05	6.2E-04	13 ^c
U-235	6.2E-10	4.8E-07	2.8E-02	5.5
U-236	7.4E-10	5.7E-07	1.1E-03	4.8
U-238	1.9E-08	1.4E-05	5.5E+00	2.7
Np-237	2.2E-08	1.7E-05	3.1E-03	6.4
Pu-238	6.5E-05	5.0E-02	3.8E-04	3.5
Pu-239	8.5E-06	6.6E-03	1.4E-02	3.3
Pu-240	3.2E-06	2.4E-03	1.4E-03	27 ^d
Pu-241	~2.5E-05	~2.0E-02	~2.5E-05	NA ^e
Pu-242	<2.9E-08	<2.2E-05	<7.6E-04	NA
Am-241	6.0E-05	4.6E-02	1.7E-03	4.2
Am-242m	3.9E-08	3.0E-05	4.0E-07	12 ^f
Am-243	7.4E-07	5.7E-04	3.7E-04	7.9
Cm-244	3.1E-05	2.4E-02	3.8E-05	33
Cm-245	4.7E-09	3.6E-06	2.7E-06	36
Total alpha	<2.6E-04	<2.0E-01	NA	NA
Nonvolatile beta	4.0E-02	3.1E+01	NA	1.7
Total gamma	6.5E-04	5.0E-01	NA	NA

^aThe Ci/g and Ci/gal values for C-14 were taken from Reference 6. (The wt% value for C-14 was calculated from the Ci/g value).

^bOne of the four replicate analysis results for Tc-99 was identified as having elevated uncertainty. ^cThree of the four replicate analysis results for U-234 were identified as having elevated uncertainties. ^dTwo of the four replicate analysis results for Pu-240 were identified as having elevated uncertainties. ^eThe Pu-241 concentration was the same order of magnitude as the minimum detection limit (MDL), and only one of the four replicate analyses yielded a result exceeding the MDL. This particular result was identified in the table with an approximation sign (see “~” symbol), since the value was based on a single analysis and the uncertainty may have been higher than normal, due to the result being close to the MDL. Because the reported value is based on a single analytical result, an RSD is not applicable. ^fOnly three of the four replicate analyses for Am-242m yielded results exceeding the MDL. The values in the table were based on these three results.

Table 2-11. Fissile Isotope Analytical Results for Each of the Four Replicates (Reported to Three Digits for Purposes of Comparison)

Isotope	Measured Concentration, wt% of total solids			
	#1	#2	#3	#4
U-233	<9.54E-04	<9.47E-04	<9.47E-04	<9.51E-04
U-235	2.90E-02	2.65E-02	3.02E-02	2.82E-02
Pu-239	1.35E-02	1.32E-02	1.40E-02	1.42E-02
Pu-241	<3.30E-05	<1.87E-05	<4.30E-05	2.47E-05

3.0 Chemical Process Cell Simulations

This section describes the DWPF CPC simulations using the SRNL-prepared Tank 40 SB7b sample, also designated as the SRAT receipt sample. Simulations were performed in the SRNL Shielded Cells. These simulations were designated as SC-12. The first subsection provides an overview of the simulations and an equipment description. The remaining subsections contain results and discussions of the SRAT and SME cycles.

3.1 CPC Simulations Overview and Equipment Description

DWPF simulations (SRAT and SME cycles) using the SRNL-prepared Tank 40 SB7b qualification sample were conducted following procedures in the Environmental and Chemical Process Technology Research Programs Section procedure manual.⁴ A summary of each cycle is given in Table 3-1.

Table 3-1. Planned SB7b Qualification CPC Processing

SRAT Cycle	SME Cycle
<ul style="list-style-type: none"> • Acid Calculation • Heating to 93 °C • Addition of nitric and formic acids per acid calculation • Heat to boiling • Concentration (water removal) to a target wt % total solids • Reflux to obtain a total time at boiling of 12 hours at a DWPF boil-up rate of 5,000 lb steam/h 	<ul style="list-style-type: none"> • Addition and removal of water to simulate addition and removal of water from the decontamination of 5 glass canisters • Addition of frit and dilute formic acid in two batches to target 36% waste loading • Concentration (water removal) to target 45-50 wt% total solids.

The SB7b qualification CPC processing was performed using a vessel designed to process one liter of sludge. This vessel is of the same design as used in the last three qualification runs. The SRAT rig was assembled and tested in the SRNL Shielded Cells Mockup area and placed into the Shielded Cells fully assembled. The intent of the equipment is to functionally replicate the DWPF processing vessels. The glass kettle is used to replicate both the SRAT and the SME, and it is connected to the SRAT Condenser and the Mercury Water Wash Tank (MWWT). Because the DWPF Formic Acid Vent Condenser (FAVC) does not directly impact SRAT and SME chemistry, it is not included in SRNL Shielded Cells CPC processing. Instead, a simple “cold finger” condenser is used to cool off-gas to approximately 20 °C below ambient to remove excess

water before the gas reaches the micro gas chromatograph (GC) for characterization. The Slurry Mix Evaporator Condensate Tank (SMECT) is represented by a sampling bottle that is used to remove condensate through the MWWT. For the purposes of this paper, the condensers and wash tank are referred to as the off-gas components. A sketch of the experimental setup is given as Figure 3-1.

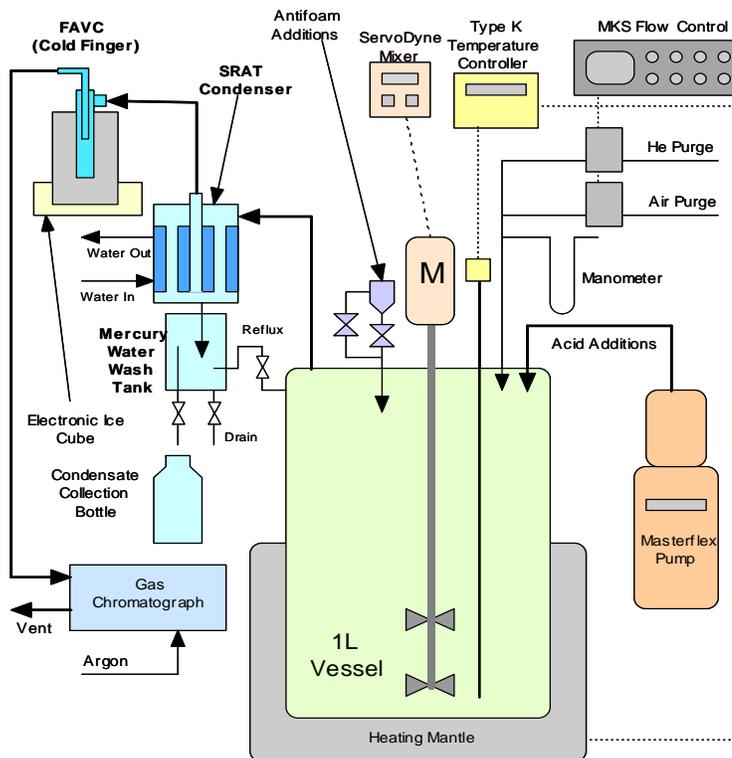


Figure 3-1. Schematic of SRAT Equipment Set-Up

Off-gas concentrations of hydrogen, oxygen, nitrogen, nitrous oxide, and carbon dioxide concentrations were measured during the experiments using in-line instrumentation (an Agilent 3000 series micro GC). Helium was introduced at a concentration of 0.5% of the total air purge as an inert tracer gas so that total amounts of generated gas and peak generation rates could be calculated. During the runs, the kettle was visually monitored to observe reactions that were occurring for signs of foaming, air entrainment, rheology changes, loss of heat transfer capabilities, and off-gas carryover. Observations are discussed in Sections 3.2 (SRAT cycle) and 3.3 (SME cycle).

Concentrated nitric acid (50-wt%) and formic acid (90-wt%) were used to acidify the sludge and perform neutralization and reduction reactions during processing. The amounts of acid to add were determined using the existing DWPF acid addition equation in the 3/12/2009 version of the SRNL acid calculation spreadsheet. The split of the acid was determined using the latest Reduction/Oxidation (REDOX) equation.¹⁴ To account for the reactions and anion destructions that occur during processing, assumptions about nitrite destruction, nitrite-to-nitrate conversion, and formate destruction were made based on results from SB7b simulant CPC testing. Acid stoichiometry and reflux time were also based on CPC processing of SB7b simulant sludge slurry.

3.2 SRAT Cycle

This section contains details of the SRAT cycle, including a discussion of a portion of the SRAT receipt characterization. It should be noted that the SRAT receipt sample is the Tank 40 SB7b sample described in the previous section. This section contains additional characterization results, specifically anions, carbonate, and total base on a slurry basis, rather than on a supernatant basis.

3.2.1 *SRAT Receipt Characterization and Acid Calculation*

SRAT cycle initiation was preceded by an acid calculation. Acid calculation inputs are presented in Table 3-2. Many of the inputs (e.g., density, wt % solids) have been presented in the previous section. Anions, total inorganic carbon (TIC), and total base for the acid calculation were determined from water dilutions of slurry samples, while these analytes are presented above from supernatant analysis.

Table 3-2 contains two analyses of the SRAT receipt material. Based on the original analysis, significantly more acid was needed than calculated to destroy nitrite. To determine if the need for more acid was a result of unexpected sludge behavior or errors in the acid calculation inputs, several inputs were remeasured – anions, total inorganic carbon, and total base. Slurry was diluted in the second analysis as in the original analysis with the exception of total base.

In the second analysis, the slurry total base was determined by an in-Cells titration, which allowed more sample to be used in the titration. When total base is determined by AD, nominally 1.5 g of slurry is diluted to 50 mL; 5 mL of diluted sample is submitted or approximately 0.15 g of slurry. Because of the small amount of actual slurry, there is also potential that a representative amount of solids is not submitted and titrated by AD. With an in-Cell titration, the total 1.5 g can be titrated.

Acid calculation results are presented in Table 3-3. Excess acid using both the original results and reanalyzed results are given. As discussed in Section 3.2.2 below, the SRAT cycle was completed in several stages, as more acid was added as it was determined that nitrite was not destroyed to below the target of 1,000 mg/kg SRAT product slurry. Based on the original analysis, analytical results (nitrite in SRAT product samples) suggest that the original analyses (specifically the total base) were in error. Excess acid was not significantly above 100%, using the second analyses, until the third stage of acid addition. It is important to note that in all stages, the split of nitric and formic acids was set to maintain a redox of 0.2.

Table 3-2. Acid Calculation Inputs

Input	Original SRAT Receipt Results	Reanalyzed SRAT Receipt Results	Units
SRAT Receipt Mass	1,120	*	g slurry
SRAT Receipt Weight % Total Solids	16.1	*	wt %
SRAT Receipt Weight % Calcined Solids	11.8	*	wt %
SRAT Receipt Weight % Insoluble Solids	10.6	*	wt %
SRAT Receipt Density	1.12	*	kg/L slurry
SRAT Receipt Supernatant Density	1.06	*	kg/L supernatant
SRAT Receipt Nitrite	9,060	10,300	mg/kg slurry
SRAT Receipt Nitrate	5,330	5,570	mg/kg slurry
SRAT Receipt Oxalate ‡	3,090	3,330	mg/kg slurry
SRAT Receipt Slurry TIC (treated as carbonate)	793	972	mg/kg slurry
Fresh Supernatant TIC (treated as carbonate)	1,050	*	mg/L supernatant
SRAT Receipt Hydroxide (Base Equivalents) pH = 7	0.38 †	0.49 †	Equiv Moles Base/L slurry
SRAT Receipt Manganese	4.11	*	wt % calcined basis
SRAT Receipt Mercury	1.35	*	wt % dry basis
SRAT Receipt Magnesium	0.39	*	wt % calcined basis
SRAT Receipt Calcium	0.87	*	wt % calcined basis
Conversion of Nitrite to Nitrate in SRAT Cycle	15	*	gmol NO ₃ ⁻ /100 gmol NO ₂ ⁻
Destruction of Nitrite in SRAT and SME cycle	100	*	% of starting nitrite destroyed
Destruction of Formic acid charged in SRAT	15	*	% formate converted to CO ₂ etc.
Destruction of Oxalate charged	2	*	% of total oxalate destroyed
Percent Acid in Excess Stoichiometric Ratio (Koop. Min Acid Eqn)	110	*	%
SRAT Product Target Solids	25	*	Wt %
REDOX Target	0.20	*	Fe ⁺² / ΣFe

* These analyses were not repeated, and these assumptions were not changed.

† The first total base result (0.38 mol/L) was determined by a titration using a small amount of diluted slurry. The second result (0.49 mol/L) was determined by an in-Cell titration of 1.5 g of slurry diluted with 20 g of water.

‡ This result was obtained from a water dilution of slurry. It is comparable to an acid dissolution of SRAT receipt – 2,810 mg/kg (See Reference 15). Oxalate from water dilution of SME product was significantly less

Table 3-3. Acid Calculation Results Based on One Liter of SRAT Receipt Slurry

	Acid Calculation Results Based on Original SRAT Receipt Results	Acid Calculation Results Based on Reanalyzed SRAT Receipt Results
Hsu Total Stoichiometric Acid required (mol) *	0.824	0.990
Koopman Minimum Stoichiometric Acid required (mol) *	0.918	1.06
Stage 1		
Total Acid Added (mol)	1.01	
Stoichiometric Acid Hsu Eqn (%)	123	102
Stoichiometric Acid Koopman Minimum Eqn. (%)	110	95
Stage 2		
Acid added (mol)	1.06	
Stoichiometric Acid Hsu Eqn (%)	129	107
Stoichiometric Acid Koopman Minimum Eqn. (%)	115	100
Stage 3		
Acid added (mol)	1.15	
Stoichiometric Acid Hsu Eqn (%)	139	116
Stoichiometric Acid Koopman Minimum Eqn. (%)	125	108

* See Reference 16 for a description of the acid equations. Note that in the document, Equation 1 is the Hsu Total Stoichiometric Acid equation, and Equation 2 is the Koopman Minimum Stoichiometric Acid equation.

3.2.2 SRAT Cycle Discussion and Results

The SRAT cycle was completed in three stages. Stage 1 began with acid addition at 123% acid stoichiometry based on the Hsu acid equation and the original SRAT receipt analyses. Due to resource issues, Stage 1 was completed over two days. On day one, nitric and formic acids were added. On Day 2, the sludge was boiled (water was removed to concentrate the total solids followed by additional boiling to steam strip mercury). Total boiling time was 12 hours. The resulting SRAT product was characterized. Highlights follow:

- Mercury Removal - Mercury in the SRAT product total solids was 0.21 wt %. This is below the 0.8 wt % DWPF target for mercury.
- Nitrite destruction - Nitrite was not destroyed to below the DWPF limit of 1,000 mg/kg. The measured nitrite was 2,500 mg/kg slurry.
- Hydrogen generation peaked at 0.014 lb/h (DWPF scale), four hours into boiling.
- Antifoam Addition - 300 ppm antifoam was added prior to acid addition (200 ppm on the day of the planned start and 100 ppm the following day at the actual start). 100 ppm was added between nitric and formic acid additions. 500 ppm was added just prior to boiling. No evidence of foaming was observed. Antifoam was from Siovation Lot#111128-0613 (produced with new antifoam purchase specification).

Because nitrite was not destroyed, additional acid was added followed by eight hours of boiling (Stage 2). Total acid was equivalent to an increase from 123% to 128%, based on the Hsu acid equation and the original SRAT receipt characterization. Again, nitrite was still above 1,000 mg/kg slurry (approximately 1,800 mg/kg slurry). During this time of processing no hydrogen was detected (detection limit is approximately 0.01 vol %). No antifoam was added and foaming was not observed.

Again, because nitrite was still above the DWPF limit, additional acid was added to the SRAT followed by eight hours of boiling (Stage 3). Total acid was equivalent to an increase from 128% to 139%, based on the Hsu acid equation and the original SRAT receipt characterization. Nitrite concentration was finally reduced to below 1,000 mg/kg slurry (320 mg/kg slurry). During this time of processing, hydrogen peaked at 0.012 lb/h. 100 ppm antifoam was added prior to acid addition, and foaming was not observed.

It has not been necessary to add ~140% of the Hsu stoichiometric acid requirement to achieve nitrite destruction before SC-12 which led SRNL to suspect there might be errors in the acid calculation inputs. Reanalysis of the SRAT receipt sample resulted in small increases in the initial nitrite and TIC concentrations that increased the stoichiometric requirement by about 7%. The direct titration of diluted slurry, however, resulted in a significantly higher base equivalents value than had been determined for the original sample. Based on the reanalysis of the SRAT receipt sample, a stoichiometric factor of 116% was sufficient to destroy nitrite, consistent with simulant testing. Reanalysis and the acid calculation are discussed in 3.2.1 above, and a table showing acid stoichiometry using both the original and reanalyzed SRAT receipt analyses is given in Table 3-3.

SRAT product analytical results are given in Table 3-4. Samples were only measured for anions after Stage 2 and Stage 3. Acid stoichiometry based on both the original and reanalyzed SRAT receipt characterization is given in Table 3-2 above.

Table 3-4. SRAT Product Analytical Results

Analysis	SRAT Product Stage 1	SRAT Product Stage 2	SRAT Product Stage 3
Wt % Total Solids	23.6	NM	NM
Wt % Dissolved Solids	11.8	NM	NM
Wt % Insoluble Solids	13.3	NM	NM
Wt % Calcined Solids	17.7	NM	NM
Slurry Density (g/mL)	1.15	NM	NM
Supernatant Density (g/mL)	1.08	NM	NM
Formate (mg/kg slurry)	41,700	44,900	55,000
Nitrite (mg/kg slurry)	2,520	1,900	269
Nitrate (mg/kg slurry)	21,400	23,300	27,300
Oxalate (mg/kg slurry) *	1,100	NM	NM
Hg (wt % of total solids)	0.21	NM	NM

NM = not measured

* This result was obtained from an acid dissolution of SRAT product (See Reference 15). Oxalate from water dilution of SRAT product was significantly less – 1,100 mg/kg slurry.

3.3 SME Cycle

The SME cycle began with the simulation of the addition/removal of five canisters of frit decon water. This process corresponded to approximately ten hours of boiling. Frit and formic acid were then added, followed by dewatering. Hydrogen generation peaked at 0.022 lb/h at the conclusion of the cycle. 100 ppm antifoam was added prior to the addition of the frit and formic acid. Foaming was not observed. At the conclusion of the cycle, an analytical sample was taken. Results are presented in Table 3-5. A portion of the SME product was vitrified and characterized (see 4.0 below).

Table 3-5. SME Product Analytical Results

Analysis	Result
Wt % Total Solids	46.7
Wt % Dissolved Solids	13.9
Wt % Insoluble Solids	38.1
Slurry Density (g/mL)	1.45
Supernatant Density (g/mL)	1.10
Formate (mg/kg slurry)	30,700
Nitrite (mg/kg slurry)	<400
Nitrate (mg/kg slurry)	20,200
Oxalate (mg/kg slurry) *	3,600
Inorganic Carbon (mg/kg slurry)	749
Organic Carbon (mg/kg slurry)	10,200

* This result was obtained from an acid dissolution of SME product (See Reference 15). Oxalate from water dilution of SME product was significantly less – 390 mg/kg slurry).

3.4 Offgas Results

Peak hydrogen, carbon dioxide, and nitrous oxide concentrations and generation rates are presented in Table 3-6 (SRAT cycle) and Table 3-7 (SME cycle). Offgas data is presented graphically in Figure 3-2 and Figure 3-3. Only Stage 1 of the SRAT cycle (acid addition followed by twelve hours of reflux) is shown, as this was the stage with the maximum hydrogen, carbon dioxide, and nitrous oxide generation rates.

Table 3-6. SRAT Cycle Peak Gas Concentrations and Generation Rates

	Maximum Observed Concentration (mol%)	Maximum Observed DWPF-Scale Generation Rate (lb/h)
Hydrogen	0.017	0.012
Carbon Dioxide	18	366
Nitrous Oxide	1.6	30

Table 3-7. SME Cycle Peak Gas Concentrations and Generation Rates

	Maximum Observed Concentration (mol%)	Maximum Observed DWPF-Scale Generation Rate (lb/h)
Hydrogen	0.085	0.022
Carbon Dioxide	4.5	26
Nitrous Oxide	0.081	0.46

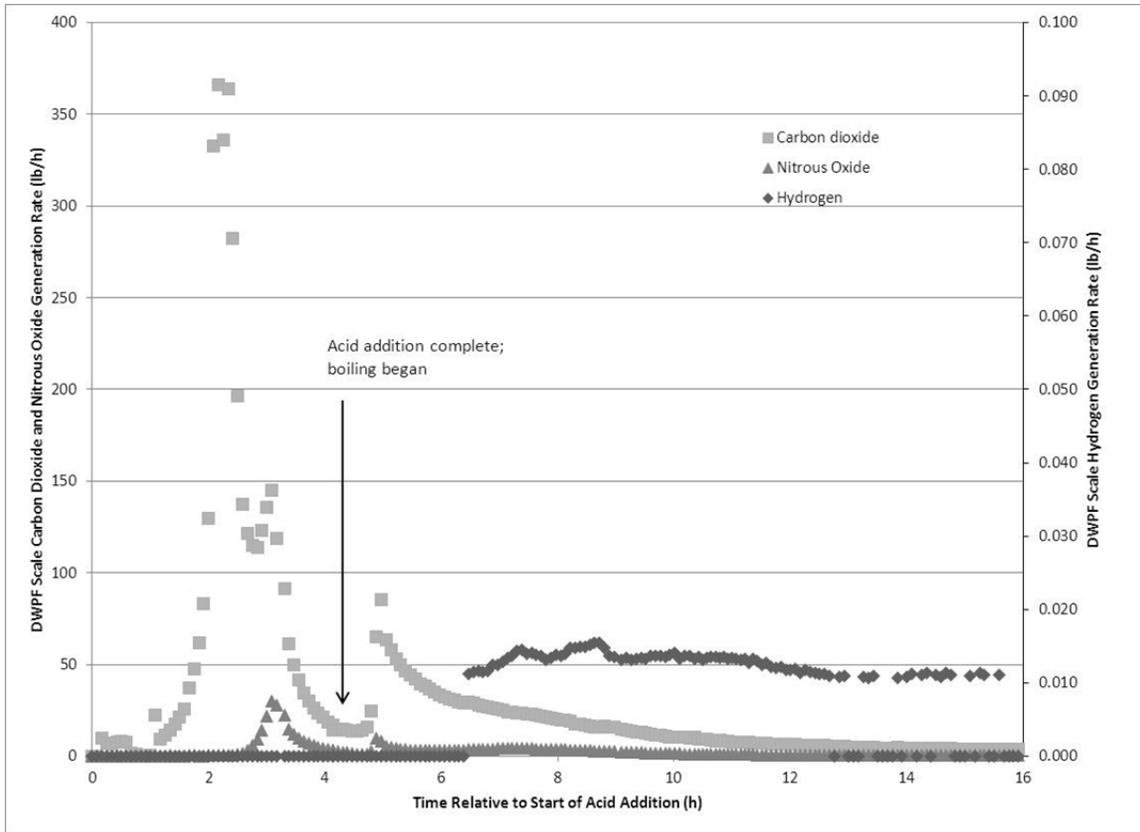


Figure 3-2. SRAT Cycle Offgas - Stage 1

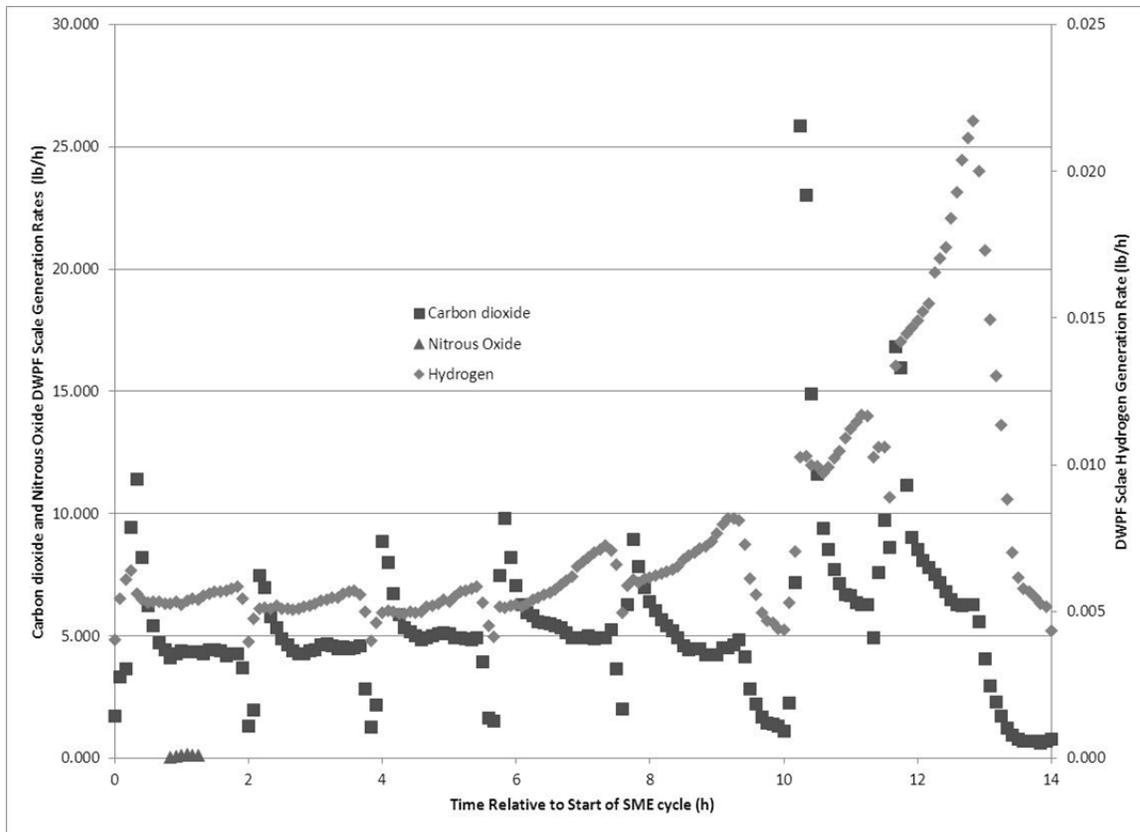


Figure 3-3. SME Cycle Offgas

3.5 Anion Destruction

Presented in Table 3-8 are cumulative anion destruction and conversion calculations based on analytical results following each stage of processing. Note that these calculations are approximate, as some of the inputs to the calculation are estimated (specifically the SRAT and SME product masses). As expected, overall nitrite destruction increased through each successive stage as more acid was added. It is interesting to note that formate destruction decreased during each stage of SRAT processing. Low formate destruction is consistent with the lack of hydrogen observed during SRAT processing. However, it is likely that at least some formate was destroyed and that no formate was created, as the decrease in formate destruction suggests. Nitrite to nitrate conversion exceeded the projected 15% used in the acid calculation.

Table 3-8. Cumulative Anion Destruction and Conversion

Product Sample	Nitrite Destruction (%)	Formate Destruction (%)	Nitrite to Nitrate Conversion (%)
Stage 1	81	7	22
Stage 2	86	6	29
Stage 3	98	0	42
SME Cycle	NA	35	20

3.6 Rheology

Rheological properties of the SRAT Receipt, SRAT Product, and SME Product were determined from analytical samples. It should be noted that the SRAT product results are based on the analytical sample taken after Stage 1, before all required acid was added. Results, along with DWPF design bases, are presented in Table 3-9. Flow curves are shown in Appendix B. The SRAT receipt and SRAT product results were determined from the average of two measurements. The SME product was determined from one measurement.

In comparing results to design bases, the SRAT receipt sample results are well within targets. SRAT product results exceed design bases, however, it is expected that the rheological properties would be improved with the appropriate amount of acid. With the high consistency of the SME product, concentration to beyond 46wt % total solids is not recommended.

Table 3-9. SRAT and SME SB7b Rheology Data

Sample	Wt% Total Solids	Wt% Insoluble Solids	Consistency (cP)	Yield Stress (Pa)
<i>Washed Sludge Slurry (Design Basis)</i> [†]	13 – 19	NA	4 – 12	2.5 – 10
SRNL Prepared SB7b SRAT Receipt	16.1	10.6	6.5	4.0
<i>SRAT Slurry (Design Basis)</i> [†]	18 – 25	NA	5 – 12	1.5 – 5
SB7b SRAT Product	22.6	13.3	13	6.7
<i>Melter Feed (Design Basis)</i> [‡]	40 – 50	NA	10 – 40	2.5 – 15
SB7b SME Product	46.7	38.1	56	21

[†] From *Basic Data Report: Defense Waste Processing Facility Sludge Plant; Savannah River Plant 200-S Area, DPSP-80-1033, Revision 10* (Ref. 17).

[‡] From *Preliminary Melter Feed Rheology Study, WSRC-RP-92-01240 Ref. 18)*.

4.0 Glass Fabrication and PCT

Presented in this section are observations and key results of the SRNL-prepared Tank 40 SB7b SME derived glass sample. Glass composition and Product Consistency Test (PCT) results, as well as predicted property information, are presented as requested by the DWPF via a TTR¹ and governed by a TTQAP.² A description of the glass fabrication is given below, followed by tables with analytical results.

The SB7b Qualification sample was subjected to the DWPF CPC simulations as reported in previous sections. Frit 702 was used during the SME cycle as was recommended for process simulations in a prior memo.¹⁹ The frit addition was based on a target waste loading of 36 wt % calcined sludge. A sample of the SME product was dried and vitrified, with the resulting glass characterized and evaluated using the PCT.

4.1 Glass Fabrication

Approximately 140 g of SME product was divided into nearly equal portions amongst 4 crucibles and dried overnight at 110 °C. After drying, the first portion was gradually heated to 1150 °C in a Pt/Au crucible in an electrically heated furnace. Upon reaching 1150 °C, the sample was held at temperature for approximately 30 minutes. The remaining portions were then added incrementally, allowing the crucible to return to temperature between each addition, resulting in a total time at 1150 °C of 4 hours. The crucible was removed from the furnace at temperature and bottom quenched (cooled) in a shallow pan of water, ensuring no water contacted the glass. The resulting glass appeared black and shiny, without the presence of a sulfate layer and was used for the glass chemical and PCT analyses.

4.2 Glass Dissolution Methods and Analyses

To support compositional analysis, a portion of the SB7b Qualification Glass had to be dissolved. In order to enhance dissolution, approximately 4 g of the glass was crushed and ground using agate cups, balls and caps in a mechanical pulverizing mixer mill. The glass was sieved and only the portion that passed through a 200 mesh (<75 µm) brass sieve was used for the dissolutions. Weighed amounts (nominally 0.25 g) of the crushed glass were then dissolved remotely by two different methods to ensure that all the elements of interest were dissolved and could be analyzed in at least one of the preparations. The two methods were a sodium peroxide fusion (PF) at 675 °C followed by a HNO₃ uptake, and a mixed acid dissolution (MA) in sealed vessels at 115 °C using a combination of HF, HCl, and HNO₃ acids. Boric acid was added to this latter dissolution method to complex excess fluoride. The solutions of the dissolved glass were diluted to known volumes so that approximately 15 mL aliquots could be safely removed from the Shielded Cells without exposing personnel to excess radiation.

The aliquots were then submitted to AD where they were analyzed by ICP-AES. Aliquots of the peroxide fusion dissolutions were also submitted for ICP-MS analysis and radioactive counting techniques. Concurrent with each set of dissolutions in the Shielded Cells, three samples of the Analytical Reference Glass (ARG-1) were also dissolved to determine if the dissolutions were complete and the resulting analyses accurate. A multi-element standard containing known concentrations of Al, Fe, Mn, Na, Ni, and S was also submitted with each set of samples sent to AD.

4.3 Standard ASTM 1285 Leach Test Procedure

The durability of the SB7b Qualification Glass was measured by following Test Method A of the ASTM 1285 standard nuclear waste glass leach test.²⁰ This test is commonly referred to as the PCT. The purpose of the PCT was to confirm that the SB7b Qualification Glass had a durability that met the criterion specified by the Waste Acceptance Product Specification (WAPS) for repository acceptance.²¹ WAPS 1.3 specifies that the mean concentrations of B, Li, and Na in the leachate, after normalizing for the concentrations in the glass, shall each be less than those of the Environmental Assessment (EA) glass.²² These normalized concentrations represent the concentration of leached glass in PCT solutions assuming all elements in the glass are soluble. DWPF complies with this criterion by demonstrating that the mean PCT results are at least two standard deviations below the mean PCT results of the EA glass.

The ASTM 1285 Test Method A is a crushed glass (-100 to +200 mesh or 75 to 149 µm) leach test at 90 °C for 7 days using deionized (DI) water in sealed stainless steel vessels. The test was performed in quadruplicate for the SB7a Qualification Glass. Duplicate blanks and triplicate samples of the standard glass [Approved Reference Material (ARM)] and triplicate samples of the EA glass were also tested with the SB7b Qualification glass samples. In the PCT, 10 mL of DI

water are used for each gram of glass. Nominally 1.7 g of glass and 17 mL of DI water were used in stainless steel vessels that were sealed tightly and weighed in order to ensure enough leachate was generated for analysis. After 7 days at 90 °C, the stainless steel vessels were removed from the oven, allowed to cool, weighed to determine water loss, and then opened. Due to the radioactivity of the glass, the initial portion of the test was performed remotely in a Shielded Cell using manipulators. The leachates from each vessel were then decanted into a clean scintillation vials. The radioactivity levels of the leachates were low enough so they could be transported to a radiochemical hood where they could be handled directly. The pH of each leachate was measured and then filtered through a 0.45 µm filter and acidified to 1 volume percent HNO₃. The leachates were then diluted and submitted to AD, where the concentrations of B, Na, Li, Si and U, were determined using ICP-AES.

4.4 Glass Fabrication and PCT Results and Discussion

Table 4-1 lists the oxide composition of the SB7b Qualification Glass on a wt % basis. All elements specifically requested in the TTR,¹ along with elements necessary for Product Composition Control System (PCCS) calculations (e.g., Cu and Nd), are reported in this table. Essentially all of the B, Li and Si and a portion of the Na are from the glass frit added to the SRAT product in order to prepare the glass. The frit used was Frit 702, which has a nominal composition of 76 wt % SiO₂, 8 wt % B₂O₃, 10 wt % Li₂O and 6 wt % Na₂O. This frit was recommended for use during the SME cycle based on a Measurement Acceptability Region (MAR) assessment completed on the analyzed SRAT Receipt material.¹⁹ Depending upon the element, the results in Table 4-1 represent an average of up to eight measurements (actual number of measurements noted in table) resulting from the glass dissolution and analysis techniques.

Table 4-1. Determined Oxide Concentrations Measured in SB7b Qualification Glass

Oxide	Wt %	Est. Std. Unc. (1-Sigma)	# Samples Averaged	Digestion Methods ^a	Detection Method
Ag ₂ O	0.008	0.0003	4	PF	ICP-MS
Al ₂ O ₃	7.284	0.0894	8	PF/MA	ICP-AES
B ₂ O ₃	4.870	0.0481	4	PF	ICP-AES
BaO	0.047	0.0004	8	PF/MA	ICP-AES
BeO	0.000	0.0000	4	MA	ICP-AES
CaO	0.417	0.0032	4	MA	ICP-AES
CdO	0.013	0.0002	8	PF/MA	ICP-AES
Ce ₂ O ₃	0.057	0.0020	4	PF	ICP-MS
CoO	0.008	0.0001	4	MA	ICP-AES
Cr ₂ O ₃	0.068	0.0005	8	PF/MA	ICP-AES
CuO	0.217	0.0022	8	PF/MA	ICP-AES
Fe ₂ O ₃	8.603	0.0599	8	PF/MA	ICP-AES
Gd ₂ O ₃	0.037	0.0005	8	PF/MA	ICP-AES
K ₂ O	0.031	0.0010	4	MA	ICP-AES
La ₂ O ₃	0.038	0.0010	8	PF/MA	ICP-AES
Li ₂ O	6.665	0.0395	8	PF/MA	ICP-AES
MgO	0.215	0.0028	8	PF/MA	ICP-AES
MnO	1.679	0.0142	8	PF/MA	ICP-AES
MoO ₃	0.006	0.0001	4	MA	ICP-AES
Na ₂ O	11.977	0.0862	4	MA	ICP-AES
Nd ₂ O ₃	0.110	0.0019	4	PF	ICP-MS
NiO	1.588	0.0131	8	PF/MA	ICP-AES
P ₂ O ₅	0.135	0.0029	4	MA	ICP-AES
PbO	0.013	0.0013	4	PF	ICP-MS
PdO	0.001	0.0000	4	PF	ICP-MS
Rh ₂ O ₃	0.008	0.0006	4	PF	ICP-MS
RuO ₂	0.013	0.0004	4	PF	ICP-MS
Sb ₂ O ₃	0.020	0.0009	4	MA	ICP-AES
SiO ₂	51.504	0.3534	4	PF	ICP-AES
SnO ₂	0.007	0.0003	4	MA	ICP-AES
SO ₄ ²⁻	0.345	0.0225	3	MA	ICP-AES
SrO	0.024	0.0003	8	PF/MA	ICP-AES
ThO ₂	0.480	0.0199	4	PF	ICP-AES
TiO ₂	0.021	0.0011	8	PF/MA	ICP-AES
U ₃ O ₈	2.410	0.0520	4	PF	ICP-MS
V ₂ O ₅	< 0.0007	N/A	4	MA	ICP-AES
Y ₂ O ₃	0.014	0.0006	4	PF	ICP-MS
ZnO	0.058	0.0009	8	PF/MA	ICP-AES
ZrO ₂	0.137	0.0015	4	MA	ICP-AES
Sum of Oxides	99.1				

^a PF = Peroxide Fusion dissolution method, MA = Mixed Acid dissolution method

The measured SB7b Qualification Glass composition reported in Table 4-1 was used to predict the properties of the glass based on the PCCS models. The results are listed in Table 4-2. The predicted properties from this composition were then compared to SME acceptability criteria to evaluate whether this glass did indeed meet the DWPF processing and product quality constraints. Based on the measured composition, all of the predicted properties met the PCCS MAR criteria and a list of selected predicted properties are found in Table 4-2.

Table 4-2. PCCS Results for SB7b Qualification Glass

PCCS Model	Predicted Value
B ΔG_p Value	-10.211
NL[B (g/L)]	0.889
T _L Prediction (°C)	903.4
Viscosity Prediction (P)	43.8
Nepheline Constraint Value	0.728
Al ₂ O ₃ (wt %)	7.28
All PCCS MAR Criteria Met	yes

For the SB7b Qualification Glass, the waste loading was calculated based on the analyzed glass Li₂O content and the targeted Li₂O content of the Frit 702 (10.0 wt %). Using these results yields a waste loading of 33.4wt % which is only slightly lower than the targeted 36 wt % WL and within the analytical error. Other calculations based upon the measured SRAT product composition and the measured SB7b Glass composition yield an average result of 33% WL. These results can be found in Table 4-3.

Table 4-3. Calculated Waste Loading

Oxide	SB7b Glass Measured Concentration (wt%)	Frit 702 Target Concentration (wt%)	SRAT Product Measured Concentration (wt%)	Calculated % Waste Loading
Al ₂ O ₃	7.284	0	22.135	32.9
Fe ₂ O ₃	8.603	0	27.016	31.8
Li ₂ O	6.665	10	N/A	33.4
U ₃ O ₈	2.410	0	7.113	33.9
Average % Waste Loading				33.0

Quadruplicate samples of the SB7b Qualification Glass were subjected to the PCT along with triplicate blanks, triplicate samples of the ARM and the EA²² reference glass as prescribed by the ASTM procedure.²⁰ The results for the reference glasses and the blanks indicated that the test was acceptable by ASTM standards. All vessels exhibited minimal to no water loss (< 5% relative water loss) during the course of the test. The blanks and leachates from the ARM reference glass all had elemental and normalized releases within the reference values.²³ One

replicate of EA exhibited anomalous results and was excluded from the calculation of normalized release rates as prescribed by the ASTM procedure. The remaining 2 EA leachates had elemental and normalized releases within the referenced value. Results for the averaged normalized releases, based on B, Na, Li, Si and U (grams of normalized element per liter of PCT leachate) are given in Table 4-4. A table listing the ppm releases of the leachates tested and the pH of the individual leachates can be found in Appendix A, Table A1. The normalized releases for the SB7b Qualification Glass based on B, Na, Li and Si are more than an order of magnitude less than those for the EA glass. These releases are also predictable by the current durability models of the DWPF PCCS. A representation of predictability for ARM, EA and the SB7b Qualification Glass are in the plots for log normalized B, Li, Na and Si release as a function of ΔG_p as can be found in Table 4-4.

Table 4-4. PCT Results for ARM, EA and the SB7b Qualification Glass

Glass ID	NL (B) g/L	NL (Na) g/L	NL (Li) g/L	NL (Si) g/L	NL (U) g/L
ARM ^a	0.46	0.48	0.54	0.27	N/A
Est. Std. Unc. (1-Sigma) ^b	0.0037	0.0027	0.0035	0.0017	N/A
EA ^c	16.60	13.36	9.56	3.96	N/A
Est. Std. Unc. (1-Sigma) ^b	0.0237	0	0.0421	0	N/A
SB7b-QUAL ^d	0.77	0.92	0.91	0.61	0.38
Est. Std. Unc. (1-Sigma) ^b	0.0115	0.0134	0.0136	0.0088	0.0107

^a Average of 3 PCT replicates

^b Est. Std. Unc. – Estimated Standard Uncertainty

^c Average of 2 PCT replicates

^d Average of 4 PCT replicates

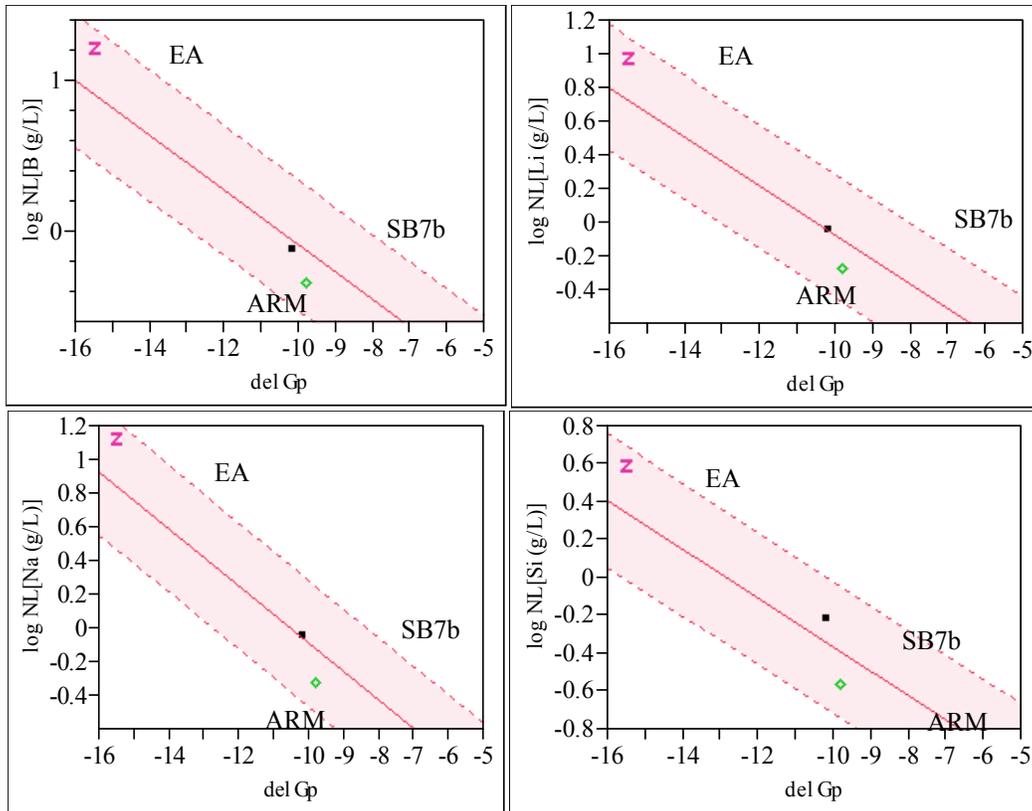


Figure 4-1. Fit of log Normalized Release of B, Li, Na and Si (g/L) vs. ΔG_p for the measured releases of ARM, EA and the SB7b Qualification glasses.

5.0 Conclusions

SRNL has completed qualification activities for SB7b. Characterization including radionuclide analyses was performed and reported. The CPC processes have been demonstrated and a glass has been fabricated and subjected to durability testing. The pertinent results of the testing were as follows:

- No new reportable elements or radionuclides were identified as part of the characterization.
- Rheological properties were acceptable for the SRNL prepared SRAT receipt and SRAT product. However, the measured yield stresses were near the upper operating limits for DWPF processing and the material appeared to be very tacky/sticky. At >46 wt % total solids, the SME product had a very high consistency. It is recommended that DWPF not concentrate to this level.
- After adjusting the acid addition levels and further boiling, the SB7b Tank 40 qualification sample as prepared by SRNL met the processing constraints imposed by the DWPF. Mercury was removed to DWPF target levels after the first addition and boiling cycle (nominally 12 hours). Hydrogen generation rates were below the DWPF design bases throughout the SRAT and SME cycles.

- Foaming was not problematic during SRAT and SME processing, and antifoam was effective when added. The antifoam was from Siovation Lot#111128-0613. 300 ppm antifoam was added prior to acid addition; 100 ppm antifoam was added after the initial nitric acid addition; 500 ppm antifoam was added prior to boiling in Stage 1; and 100 ppm additions were made at the start of each additional stage.
- The SB7b SME product (SB7b Tank 40 Qualification sludge plus Frit 702) was used to fabricate a glass with a targeted waste loading of 36%. The glass was acceptable with respect to chemical durability as measured by the PCT. Specifically, the SB7b glass had a normalized boron release of 0.77 g/L, while the EA glass had a normalized release of 16.6 g/L. The PCT response was also predictable by the current durability models of the DWPF PCCS.

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Appendix A. Supplemental PCT Data

Table A-1. PCT Elemental Releases and Measured pH for ARM, EA and the SB7b Qualification Glass

Glass ID	pH	Elemental Release - Dilution Factor Corrected (ppm)						
		Li	B	Na	Si	Fe	Al	U
ARM-1-199	9.95	12.80	16.47	34.67	60.17	N/A	4.85	N/A
ARM-2-200	9.93	12.57	16.25	34.33	59.17	N/A	4.77	N/A
ARM-3-215	9.88	12.53	16.02	34.00	59.00	N/A	4.83	N/A
EA-1-125	11.54	188.33	581.67	1665.00	901.67	<0.64	<2.22	N/A
EA-2-188	11.58	190.00	583.33	1665.00	901.67	<0.64	2.43	N/A
EA-3-195	11.59	12.78	17.00	<49.17	60.50	<0.64	5.77	N/A
SB7b-Qual-1-216	10.76	28.33	11.67	82.33	149.83	18.00	20.67	7.45
SB7b-Qual-2-220	10.74	28.17	11.70	81.67	143.50	17.00	20.33	8.20
SB7b-Qual-3-221	10.75	27.50	11.27	79.33	142.33	17.50	20.17	7.90
SB7b-Qual-4-222	10.71	29.33	11.88	84.33	148.83	17.33	20.50	7.23

Appendix B. Flow Curves

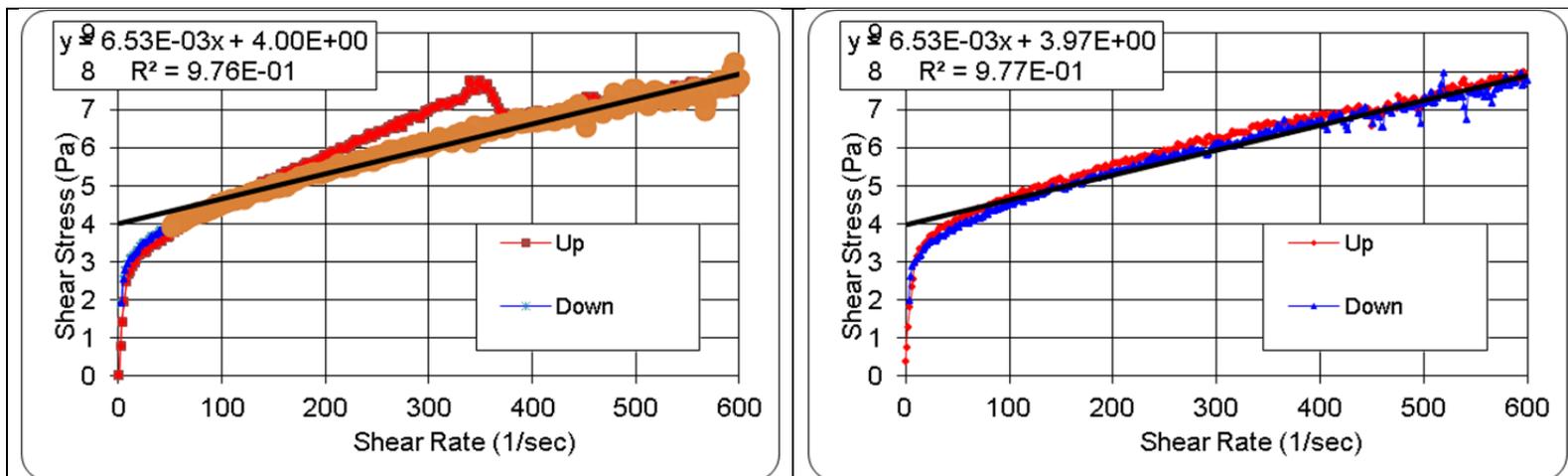


Figure B-1. SB7b SRAT Receipt Flow Curves

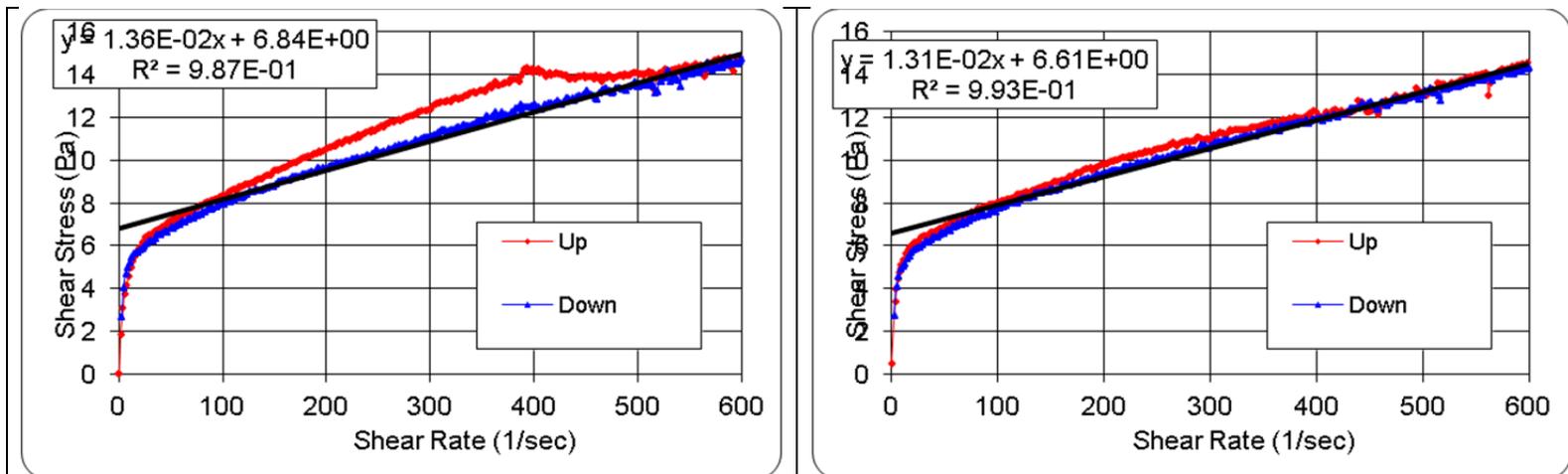


Figure B-2. SB7b SRAT Product Flow Curves

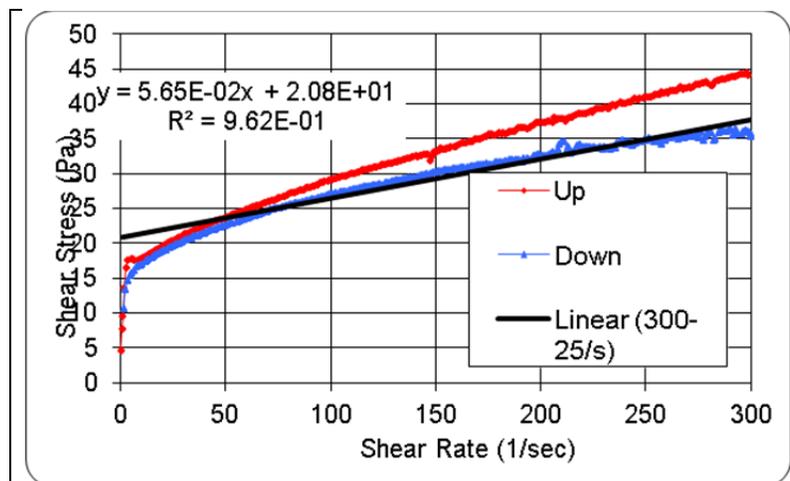


Figure B-3. SB7b SME Product Flow Curve

Distribution:

A. B. Barnes, 999-W
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
J. M. Bricker, 704-27S
T. L. Fellinger, 704-26S
J. M. Gillam, 766-H
E. W. Holtzscheiter, 704-15S
J. F. Iaukea, 704-30S
M. T. Keefer, 766-H
D. W. Mcilmoyle, 766-H
J. E. Occhipinti, 704-S
D. K. Peeler, 999-W
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

P. R. Jackson, DOE-SR, 703-46A
K. H. Subramanian, 766-H
M. A. Broome, 704-29S
R. N. Hinds, 704-S
J. P. Vaughan, 773-41A

C. E. Duffey, 704-61H
M. A. Rios-Armstrong, 773-66A
T. B. Edwards, 999-W
D. C. Koopman, 999-W
K. M. Fox, 999-W
J. W. Amoroso, 999-W
F. C. Johnson, 999-W
J. R. Zamecnik, 999-W
A. S. Choi, , 999-W
H. Bui, 704-61H
D. J. Martin, 241-152H
C. M. Gregory, 773-A