SLUDGE WASHING AND DEMONSTRATION OF THE DWPF FLOWSHEET IN THE SRNL SHIELDED CELLS FOR SLUDGE BATCH 7a QUALIFICATION

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DISCLAIMER

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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 7a[*]) be completed in the Shielded Cells Facility of the Savannah River National Laboratory. 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). Sludge Batch 7a (SB7a) is composed of portions of Tanks 4, 7, and 12; the Sludge Batch 6 heel in Tank 51; and a plutonium stream from H Canyon. SRNL received the Tank 51 qualification sample (sample ID HTF-51-10-125) following sludge additions to Tank 51; SRNL simulated the addition of the plutonium stream with a sample from H Canyon during washing.

This report documents:

- The washing (addition of water to dilute the sludge supernate) and concentration (decanting of supernate) of the SB7a - Tank 51 qualification sample to adjust sodium content and weight percent insoluble solids to Tank Farm projections.

- The performance of a DWPF Chemical Process Cell (CPC) simulation using the washed Tank 51 sample. The simulation included a Sludge Receipt and Adjustment Tank (SRAT) cycle and a Slurry Mix Evaporator (SME) cycle.

- 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 initial slurry samples and samples after each phase of CPC processing.

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

- There were no issues with sludge washing. The sludge settled as needed for timely planned decants. SRNL was able to produce a washed sample comparable to the Tank Farm target endpoint with fewer washes. Rheological properties were acceptable at the targeted washing endpoint.

- The SB7a qualification sample as washed by SRNL met the processing constraints imposed by the DWPF. The acid addition and boiling time used by SRNL in the SRAT cycle destroyed nitrite and removed mercury to DWPF target levels. Hydrogen generation rates were below the DWPF design bases.

- Foaming was not problematic during SRAT and SME processing, and antifoam was effective when added.

- The SRNL SB7a qualification SRAT product had acceptable rheological properties at a total solids of 25.4 wt% (targeted 25 wt%). It is recommended that a SRAT product solids endpoint of 25% be used for initial SB7a operation at DWPF. The rheological properties of the SRAT product should be monitored in DWPF during initial SB7a processing.

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[*] Note that at the time this task was initiated, the sludge batch was designated as Sludge Batch 7. Due to changes in the SRS Tank Farm, Sludge Bath 7 has been divided into 7a and 7b. This report documents qualification of Sludge Batch 7a only.

- The SRNL SB7a qualification SME product yield stress at 42.9 wt% total solids was approximately twice the DWPF design basis upper limit of 15 Pa, and the consistency was close to the upper limit of 40 cP. A SME solids target of 40 to 45 wt% should be used for initial SB7a processing. The rheological properties of the SME product should be monitored in DWPF during initial SB7a processing to determine a nominal solids endpoint.

- It is recommended that DWPF adopt an acid digestion method for oxalate analysis. In the SME product, SRNL saw noticeable differences between slurry water dilution and acid digestion results for oxalate.

- The SB7a SME product (SB7a Qualification sludge plus Frit 418) 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 SB7a glass had a normalized boron release of 0.65 g/L, while the EA glass had a normalized release of 17.43 g/L. The PCT response was also predictable by the current durability models of the DWPF PCCS.

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LIST OF ABBREVIATIONS

AD	Analytical Development
AR	Aqua Regia digestion
ARG-1	Analytical Reference Glass – 1
ARM	Approved Reference Material
CPC	Chemical Process Cell
CVAA	Cold Vapor Atomic Absorption
C-	Contained X-Ray Diffraction
DI	De-ionized
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
FAVC	Formic Acid Vent Condenser
GC	gas chromatograph
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
MA	Mixed Acid
MAR	Measurement Acceptability Region
MWWT	Mercury Water Wash Tank
NIST	National Institute of Standards and Testing
PCCS	Product Composition Control System
PCT	Product Consistency Test
PF	Peroxide Fusion digestion
R&D	Research and Development
REDOX	Reduction/Oxidation ($Fe^{2+}/\Sigma Fe$)
SB7a	Sludge Batch 7a
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TIC	Total Inorganic Carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAPS	Waste Acceptance Product Specification
WSE	Waste Solidification Engineering

1.0 Introduction

Waste Solidification Engineering (WSE) has requested that characterization and a radioactive demonstration of the next batch of sludge slurry (Sludge Batch 7a[*]) 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 simulates the Tank Farm and DWPF processes with a Tank 51 sample (referred to as the qualification sample).

Sludge Batch 7a (SB7a) is composed of portions of Tanks 4, 7, and 12; the Sludge Batch 6 heel in Tank 51; and a plutonium stream from H Canyon. SRNL received the Tank 51 qualification sample (sample ID HTF-51-10-125) following sludge additions to Tank 51.

This report documents:

- The washing (addition of water to dilute the sludge supernate) and concentration (decanting of supernate) of the SB7a - Tank 51 qualification sample to adjust sodium content and weight percent insoluble solids to Tank Farm projections.

- The performance of a DWPF Chemical Process Cell (CPC) simulation using the washed Tank 51 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.[2]

- 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 initial slurry samples and samples after each phase of CPC processing.

This program was controlled by a Task Technical and Quality Assurance Plan (TTQAP)[3], and analyses were guided by an Analytical Study Plan[4]. 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.[5-7] The intent of this technical report is bring all of the SB7a related data together in a single permanent record and to discuss the overall aspects of SB7a processing.

2.0 Qualification Sample Washing and Characterization

A 3-L sample from Tank 51, the SB7a qualification sample, was received by SRNL on September 18, 2010. The Tank Farm sample ID was HTF-51-10-125. The sample was characterized, washed, and then used in a DWPF simulation (including glass fabrication and chemical durability measurements). This

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[*] Note that at the time this task was initiated, the sludge batch was designated as Sludge Batch 7. Due to changes in the SRS Tank Farm, Sludge Bath 7 has been divided into 7a and 7b. This report documents qualification of Sludge Batch 7a only.

section describes the washing process and characterization results (as received, during washing, and washed).

2.1 <u>Washing</u>

The 3-L sample from Tank 51 was pumped into a 4-L glass bottle with graduations to estimate volume and track settling throughout washing. A 500 mL subsample was taken from the larger sample and was used for the as-received characterization. The remaining sample was then washed to the Tank Farm endpoint projection, as of October 13, 2010, as given in Reference 8. Tank Farm washing was not simulated by SRNL; SRNL instead combined twelve Tank Farm washes into five Cells' washes. Fewer SRNL washes were required to allow the sludge batch readiness date to be met. In summary, from the time the SB7a qualification sample was pulled, the Tank Farm planned 12 additions (Wash C to Wash N) and 13 decants (Decant A/B to Decant N). SRNL, on the other hand, performed five washes with six decants. SRNL wash and decant amounts were calculated to obtain a similar post Decant N supernate composition, slurry oxalate content, and wt% insoluble solids. Most washes (Tank Farm and SRNL) consisted of inhibited water (0.01 M NaOH, 0.011 M $NaNO_2$), with the following exceptions. The first addition (in both the Tank Farm and SRNL washing schemes) included H Canyon Pu solution. One SRNL and Tank Farm wash included extra sodium nitrite. Note that as hydroxide concentration in a waste tank drops during washing, the molar nitrite to nitrate ratio must be greater than 1.6 to meet requirements of the Tank Farm corrosion control program.

Samples of each decant were submitted for elemental and anion analysis (see Table 2-1) throughout washing. SRNL decant designations do not correspond directly to Tank Farm decants except for Decant A/B and Decant N. For example, SRNL's Decant L composition does not correspond to the Tank Farm's Decant L composition. The sodium nitrite addition was made following SRNL Decant C. The Tank Farm washing endpoint is included in the table. As expected, oxalate concentration in the supernate increased as sodium concentration decreased. Also, there was good agreement between the Tank Farm oxalate projection and Decant N measurement, suggesting that the model for predicting soluble oxalate is adequate.

Table 2-1. Select Elemental and Anion Results of SRNL SB7a Decants

Element or Anion (M)	As-Received (Decant A/B)	Decant C	Decant D-K	Decant L	Decant M	Decant N	Tank Farm Washing Endpoint
Na	3.80	2.66	2.16	1.51	1.21	1.0	0.97
NO_2^-	0.66	0.40	0.72	0.47	0.32	0.26	0.24
NO_3^-	0.78	0.53	0.43	0.27	0.16	0.13	0.13
S	0.14	0.099	0.065	0.047	0.034	0.029	0.022
Al	0.21	0.14	0.091	0.062	0.045	0.039	0.033
$C_2O_4^{2-}$	0.012	0.027	0.040	0.056	0.071	0.10	0.12

Presented in Table 2-2 are the weight percent solids and density measurements of the as-received Tank 51 qualification sample and the SRNL-washed sample. As expected, slurry and supernate densities decreased as soluble solids were removed during the washing process.

Table 2-2. Densities and Weight Percent Solids for the Tank 51 SB7a Qualification Sample (As-Received and Post SRNL-Washing)

Property	As-Received	SRNL-Washed
Slurry Density (g/mL)	1.25[†]	1.15[‡]
Supernate Density (g/mL)	1.18[†]	1.05[‡]
Wt% Total Solids (Slurry Basis)	26.9	18.1
Wt% Calcined Solids (Slurry Basis)	17.6	13.3
Wt% Dissolved Solids (Supernate Basis)	21.2	6.5
Wt% Soluble Solids (Slurry Basis)	19.7	5.8
Wt% Insoluble Solids (Slurry Basis)	7.2	12.3

[†] Temperature at time of slurry density measurements was 24 °C.
[‡] Temperature at time of slurry density measurements was 18 °C.

Given in Table 2-3 are more complete supernate compositions for the as-received and SRNL-washed Tank 51 qualification samples, as compared to Table 2-1. As expected, soluble analyte concentrations dropped due to removal during the washing process. Supernate oxalate concentration, however, increased as sodium oxalate dissolved during washing.

Table 2-3. Tank 51 SB7a Qualification Sample Supernate Constituents

Analyte	As-Received (M)	SRNL-Washed (M)
Sodium	3.8	1.0
Aluminum	0.21	0.039
Fluoride	<0.008	<0.02
Formate	<0.004	<0.005
Nitrite	0.66	0.26
Nitrate	0.78	0.13
Phosphate	<0.008	<0.003
Chloride	0.004 [a]	<0.007
Sulfur	0.14 [b]	0.029 [b]
Oxalate	0.012	0.10
Carbonate	0.27 [c]	0.072 [c]
Free OH	1.3	0.16

[a] Chloride was detected, in the as-received sample, but not on the IC calibration curve; a value is reported here only to show Cl is present.
[b] Sulfate by IC = 0.11 M for the as-received sample and 0.023 for the SRNL-washed sample.
[c] Carbonate is calculated from a total inorganic carbon result, assuming all inorganic carbon is carbonate.

2.2 Oxalate Analysis

The as-received SB7a sample contained significant quantities of sodium oxalate. At high sodium concentrations, the sodium oxalate is primarily insoluble. As sodium concentration dropped during washing, sodium oxalate dissolved and was removed in the washing process. Note the increases in oxalate in the decanted supernate during washing in Table 2-3. Total slurry oxalate in the as-received sample and the SRNL-washed sample were as follows:

    As-Received Sample   11,600 mg/kg of slurry
    SRNL-Washed Sample   8,200 mg/kg of slurry

The decreased concentration of oxalate does show that some oxalate was washed from the slurry. The actual percentage of oxalate removed can be calculated by comparison of oxalate to iron, which is essentially inert in the washing process. For each gram of iron in the as-received slurry there was 0.86 g of oxalate. In the washed sample, there was 0.34 g of oxalate per g of iron, indicating that approximately 60% of the oxalate was removed. Calculations are shown in Appendix C.

2.3 Composition of Total Solids and Slurry

Elemental compositions of the total solids for the as-received and the SRNL-washed samples are given in the following tables. Presented in Table 2-4 are the major elements in the as-received and washed samples on a total solids basis. Major elements are defined as those elements detected at greater than 0.1 wt% of total solids in either the as-received or SRNL-washed sample. In comparing the two samples, as one would expect, concentrations of soluble elements (Na, K, and S) decreased as they were washed from the sludge, while concentrations of insoluble (e.g., Fe and Ni) and partially soluble (e.g., Al) elementals increased.

Table 2-4. Major Elements in the SB7a Qualification Sample Total Solids

Element	As-Received Wt % of Total Solids	SRNL-Washed wt% of Total Solids
Al	5.4	10.6
Ca	0.20	0.56
Ce	0.042	0.12
Fe	5.0	13.2
Hg	0.67	1.5
K	0.17	0.067
Mg	0.099	0.28
Mn	1.2	3.13
Na	27	14.0
Ni	0.85	2.30
S	1.2	0.38
Si	0.60	1.48
Th	0.34	0.92
U	1.8	5.30
Zr	0.078	0.12

Presented in Table 2-5 are noble metals concentrations in the as-received and SRNL-washed qualification sample. The increase in concentration between the two samples confirmed that the noble metals other than palladium were primarily insoluble.

Table 2-5. Noble Metals in the Tank 51 SB7a Qualification Sample Total Solids

Element	As-Received Wt % of Total Solids	SRNL-Washed Wt % of Total Solids
Ru	3.3E-02	9.02E-02
Rh	7.3E-03	1.88E-02
Pd	1.3E-03	2.59E-03
Ag	5.4E-03	1.32E-02

Noble metal results for the washed sample are very similar to those for the SB6 qualification SRAT receipt sample[9] indicating that the SB7a-SB6 blend should have a similar sized region of suitable acid stoichiometries to what DWPF has found for SB6. Ru and Rh concentrations, though high, are below the HM-basis values of 0.217 and 0.038 wt% respectively.[10]

Several other elements in the SRNL-washed sample were specifically requested by DWPF.[1] These elements are presented in Table 2-6.

Table 2-6. Minor Elements in the SRNL-Washed SB7a Qualification Sample Total Solids

Element	SRNL-Washed Wt % of Total Solids
As	<0.002
Ba	0.085
Be	0.0004
Cd	0.036
Cl	<0.2 [a]
Co	0.012
Cr	0.043
Cu	0.039
F	<0.2 [a]
P	0.064
Pb	0.028
Sb	<0.05
Se	<0.003
Ti	0.017

[a] Calculated from IC analysis of slurry dilutions (Table 2-7).

Given in Table 2-7 are results of anion and total base analyses of slurry dilutions. Slurry samples were diluted with water. Filtered samples were submitted for Ion Chromatography (IC) analysis. Unfiltered samples were submitted for total base and total inorganic carbon analysis. Carbonate was calculated from the total inorganic carbon result. Additional analytical details are given in Appendix A.

Table 2-7. SRNL-Washed SB7a Qualification Sample Slurry Anions

Analyte	Result
Fluoride (mg/kg slurry)	<400
Formate (mg/kg slurry)	<400
Chloride (mg/kg slurry)	<400
Nitrite (mg/kg slurry)	9,900
Nitrate (mg/kg slurry)	7,900
Phosphate (mg/kg slurry)	<400
Sulfate (mg/kg slurry)	2,100
Oxalate (mg/kg slurry)	8,200
Carbonate (mg/kg slurry)	4,550 [a]
Total Base (mol/L slurry)	0.38

[a] Carbonate is calculated from a total inorganic carbon result, assuming all inorganic carbon is carbonate.

2.4 Rheology

Rheology results of the as-received and washed SB7a qualification sample are presented in Table 2-8. The yield stress and consistency of the SRNL washed sample were within the design basis. It should be noted that the SRNL washed sample had a wt% insoluble solids of 12.3, while the Tank Farm projection/target is below 11%. Therefore, if the Tank Farm washes/decants as planned (with a final wt% solids of below 11%), no rheological issues are expected.

Table 2-8. SB7a Rheology Data

Sample	Wt% Total Solids	Wt% Insoluble Solids	Consistency (cP)	Yield Stress (Pa)
Washed Sludge Slurry (Design Basis) [†]	*13 – 19*	*NA*	*4 – 12*	*2.5 – 10*
SB7a Qualification Sample – As-Received	26.9	7.2	7.3	1.8
SRNL Washed SB7a Qualification Sample (SRAT Receipt)	18.1	12.3	10	8.1

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

2.5 Settling During Washing

The interface location between clear supernate and settled solids was recorded during gravity settling. These results are presented graphically in Figure 2-1. Observations (time, sludge interface level) are shown in Appendix B. Settled solids volume is shown on the left axis and sludge interface position in cm is shown on the right axis. Visual comparisons of the settling rate (slope of each line) suggest that settling rate was nearly constant throughout washing with the possible exception of the as-received sample.
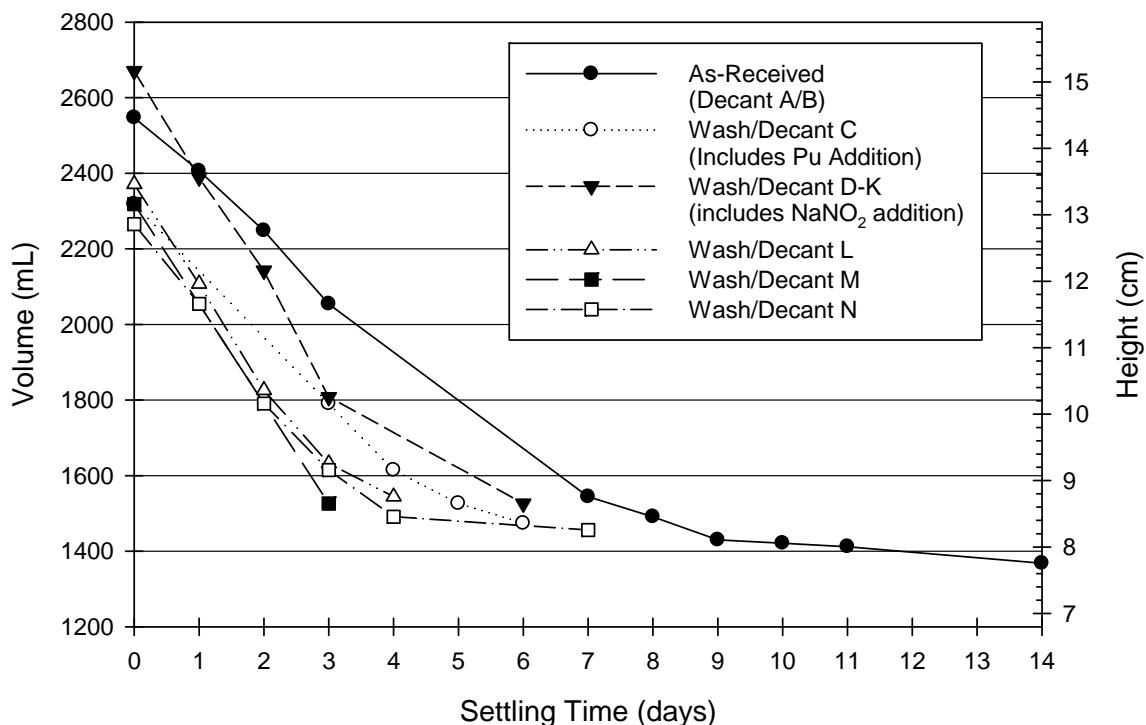
Figure 2-1. Settling During Washing.

3.0 Chemical Process Cell Simulation

This section describes the DWPF CPC simulations using the SRNL-washed Tank 51 Sludge Batch 7a sample. Simulations were performed in the SRNL Shielded Cells. 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 washed Tank 51 SB7a qualification sample were conducted following procedures in the Environmental and Chemical Process Technology Research Programs Section procedure manual.[11] A summary of each cycle is given in Table 3-1.

Table 3-1. Summary of SB7a Qualification CPC Processing

SRAT Cycle	SME Cycle
• Acid Calculation • Heating to 93 ºC • 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 14 hours at a DWPF boil-up rate of 5,000 lb steam/h	• 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 SB7a 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 two 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.
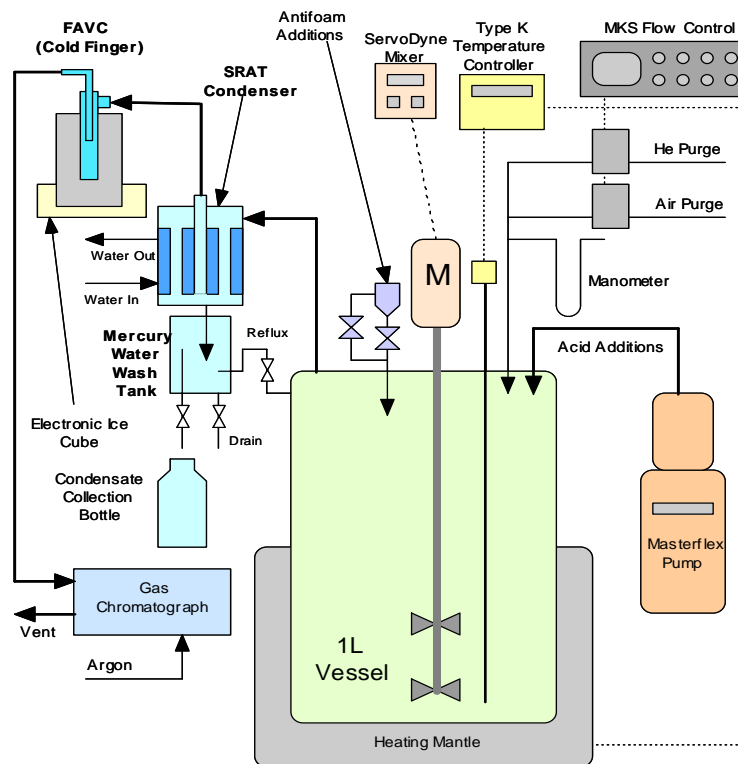
Figure 3-1. Schematic of SRAT Equipment Set-Up

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. 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 were recorded in Reference 12 and 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.[13] 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 SB7a simulant CPC testing. Acid stoichiometry and reflux time were also based on CPC processing of SB7a simulant sludge slurry.[2]

3.2 SRAT Cycle Results and Discussion

Following washing of the Tank 51 SB7a qualification sample, the material was used in DWPF CPC simulations. The initial step of the SB7a qualification SRAT simulations was the acid calculation to estimate the required acid necessary to complete reactions. This calculation used measured analytical inputs. Errors in these measurements can result in too little acid being added resulting in incomplete

reactions or too much acid being added resulting in excess formic acid that potentially leads to high hydrogen generation rates. Analytical results of the SRAT receipt sample are given in Section 2.0. All inputs for the acid calculation are presented in Table 3-2. The non-measured inputs (for example, Percent Acid in Excess Stoichiometric Ratio, Destruction of Formic acid charged in SRAT, etc.) were based on simulant tests.[2]

The primary results of the acid calculation (the acid requirements) are also included in Table 3-2. The actual acid amount added was 1.05 mol/L, or 118% of the calculated acid requirement based on the Hsu stoichiometric acid equation, the acid equation currently used by DWPF.[14]

Table 3-2. SB7a Qualification Acid Calculation Inputs and Outputs

Parameter	Result	Units
Sludge Mass	1,099	g slurry
Sludge Weight % Total Solids	18.1	wt%
Sludge Weight % Calcined Solids	13.3	wt%
Sludge Weight % Insoluble Solids	12.3	wt%
Sludge Density	1.15	kg / L slurry
Sludge Supernate density	1.05	kg / L supernate
Sludge Nitrite	9,850	mg/kg slurry
Sludge Nitrate	7,900	mg/kg slurry
Sludge Oxalate	8,200	mg/kg slurry
Sludge Slurry Total Inorganic Carbon (TIC)	912	mg/kg slurry
Supernate TIC	867	mg/L supernate
Sludge Hydroxide (Base Equivalents) pH = 7	0.38	Equiv Moles Base/L slurry
Sludge Manganese	4.12	wt % calcined basis
Sludge Mercury	1.50	wt% dry basis
Sludge Magnesium	0.36	wt % calcined basis
Sludge Sodium	18.4	wt % calcined basis
Sludge Potassium	0.088	wt % calcined basis
Sludge Calcium	0.73	wt % calcined basis
Sludge Strontium	0.050	wt % calcined basis
Sludge Nickel	3.03	wt % calcined basis
Conversion of Nitrite to Nitrate in SRAT Cycle	14	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	26	% formate converted to CO_2 etc.
Destruction of Oxalate charged	10	% of total oxalate destroyed
Percent Acid in Excess Stoichiometric Ratio	110	% of Koop. min. stoic. acid req.
Percent Acid in Excess Stoichiometric Ratio	118	% of Hsu equ. stoic. acid req.
SRAT Product Target Solids	25	%
Nitric Acid Molarity	10.534	Molar
Formic Acid Molarity	23.800	Molar
REDOX Target	0.200	Fe^{+2} / ΣFe
SRAT Steam Stripping Factor	750	(g steam/g mercury)
Hsu Total Stoichiometric Acid required	0.89	mol/L
Koopman Minimum Stoichiometric Acid required	0.96	mol/L
Actual acid to add to SRAT	1.05	mol/L
Nitric Acid Added	11.1	mL
Formic Acid Added	38.1	mL

The SRNL Tank 51 SB7a SRAT cycle (designated as SC-11 SRAT Cycle) was performed in December 2010. Antifoam (IIT747 from Siovation, Inc.) was added per the simulant run recommendation: 200 ppm at startup, 100 ppm after nitric acid addition, 100 ppm during formic acid addition, and 500 ppm after acid addition. As with past qualification runs, foaming was observed during formic acid addition. The planned 100 ppm antifoam addition was made when foam was observed on the sludge after approximately half of the formic acid was added. The foam did not immediately dissipate, so formic acid addition was stopped for approximately 10 minutes (until carbon dioxide concentration began to drop) to allow the antifoam to disperse and the foam to dissipate. Because of off-gas sampling issues as boiling began, the run was suspended nearly two days to troubleshoot and fix the problem (a leaking valve used to switch between calibration gas and processes gas). A further additional 200 ppm antifoam addition was made when the run resumed. No other incidents of foaming were observed.

No obvious indications of poor mixing were observed, although the contents of the SRAT/SME vessel could not easily be viewed. There were no issues with heat transfer; boil-up rate could be maintained without a need to increase heater output throughout reflux. Mercury was visible in the MMWT, indicating some mercury was being removed by steam stripping.

An analytical sample was taken at the conclusion of the SRAT cycle. The wt% solids, density, and detected anions were measured and are presented in Table 3-3 (First SRAT Sample). The values in Table 3-3 indicated that the SRAT processing criteria were just barely met (nitrite was at 1,000 mg/kg). Although the wt % solids were significantly lower than the target of 25%, SRNL proceeded with preparations for a SME cycle. However, prior to the SME cycle, slurry digestions were completed for elemental analyses and significant sodium was unaccounted for relative to the SRAT receipt sample. A second, smaller SRAT product sample was taken, and total solids were determined to be 25.4 wt%. This value was comparable to expectations (see Second SRAT Sample column in Table 3-3). The second sample was then digested for chemical composition, and sodium results were as expected. It is speculated that poor mixing and or poor positioning of the sample tube contributed to the unexpected and first sample results.

It should be noted that the cold chemical method was included as a digestion method which consumed significant SRAT product slurry sample mass. A rheology measurement was attempted on the remaining sample material although the volume was below the normal minimum used for the measurement. An estimate of yield stress was made based on this modified measurement. The post rheology slurry was then filtered for dissolved solids measurements and insoluble solids calculations.

Anions were not measured on the second SRAT sample. Instead, concentrations were calculated by a ratio of the weight fraction of supernate in the first SRAT sample to the weight fraction of supernate in the second sample[*]. The weight fraction of supernate is calculated by subtracting the weight fraction of insoluble solids from one. This calculation assumed that the anions are primarily soluble and that the supernates in the first and second SRAT samples were identical.

Mercury results are included in Table 3-3. Mercury was measured on both the first and second samples. Mercury was well below the SRAT product target of 0.8 wt% of the total solids.

It should be noted that the oxalate result includes only supernate oxalate and "water soluble" oxalate (presumably sodium oxalate). In the SRAT receipt sample, the oxalate result from a water dilution of the slurry was comparable to an acid strike (to dissolve all oxalate) of the slurry, suggesting insoluble oxalate was in the form of sodium oxalate. However, with the acid addition and complicated chemistry of the SRAT cycle, it cannot be assumed that the oxalate reported in Table 3-3 represents the total oxalate. Acid

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[*] $\frac{1-0.135}{1-0.158} = 1.03$

strike oxalate on the SME product indicated the presence of more oxalate mass in the SRAT product than was indicated by the water dilution result.

Table 3-3. SRAT Product Analytical Results

Analysis	First SRAT Sample	Second SRAT Sample
Wt% Total Solids	19.7	25.4
Wt% Dissolved Solids	4.6	13.7
Wt% Insoluble Solids	15.8	13.5
Wt% Calcined Solids	16.2	18.6
Slurry Density (g/mL)	1.1	NM
Supernate Density (g/mL)	1.02	NM
Formate (mg/kg slurry)	2.23E+04	2.30E+04*
Nitrite (mg/kg slurry)	9.9E+02	1.0E+03*
Nitrate (mg/kg slurry)	1.21E+04	1.24E+04*
Sulfate (mg/kg slurry)	1.2E+03	1.2E+03*
Oxalate (mg/kg slurry)	2.4E+03	2.4E+03*
Hg (wt% of total solids)	0.34	0.23
Yield Stress (Pa)	NM	>5 [†]

NM = not measured
*Values are calculated from results of the first SRAT sample.
[†] Estimated; measurement was attempted with too little material.

Presented in Table 3-4 are the major elements (>0.1 wt%) in the SRAT receipt and SRAT product total solids. Note that the SRAT receipt results were presented earlier in Table 2-4. Results of the SRAT product were obtained from analysis of the second SRAT product. SRAT product results are slightly lower than the SRAT receipt results, as expected, as the elementals are "diluted" by formate and nitrate in the SRAT process.

Table 3-4. Major Elements in the SB7a SRAT Slurry Total Sample Solids

Element	SRAT Receipt wt% of Total Solids	SRAT Product wt% of Total Solids
Al	10.6	8.92
Ca	0.56	0.47
Ce	0.12	0.14
Fe	13.2	11.03
Hg	1.5	0.23
Mg	0.28	0.21
Mn	3.13	2.33
Na	14.0	15.25
Ni	2.30	2.00
S	0.38	0.51
Si	1.48	1.21
Th	0.92	0.90
U	5.30	4.45
Zr	0.12	0.11

Table 3-5 shows a comparison of the projected nitrite and formate destruction and nitrite to nitrate conversion with comparison to the results (based on SRAT product analysis). Projections were based on simulant runs.[2] The most noteworthy differences between projections and measurements are the formate destruction and nitrite to nitrate conversion. Formate destruction was nearly 2x higher than projected. Nitrate was consumed in the SRAT cycle instead of increasing from conversion of nitrite to nitrate. It is possible nitrate is reacting further to produce ammonium. However, no ammonium was detected in the SRAT product (detection limit was 30 mg/L). Ammonium was detected in the MWWT at 180 mg/L.

Table 3-5. SB7a SRAT Cycle Anion Destruction/Conversion

	Projected	Measured
Conversion of Nitrite to Nitrate	14	-15
Destruction of Nitrite (%)	100	92.1
Destruction of Formic Acid (%)	26	50.7

Further analysis of the SRAT cycle, specifically the off-gas data, is given in Section 3.4

3.3 SME Cycle Results and Discussion

The SB7a qualification SME cycle using the remaining SRAT product was completed the week of January 10. The SME cycle was completed over several days because of two inclement weather days and an evacuation of the Shielded Cells area lasting several hours due to ventilation issues. It should be noted that it is not uncommon for DWPF SME cycles to occur over several days. Two frit decon water additions/removals were made on the first day. Three frit decon water additions/removals were made on the second day. On the final day, Frit 418 was added to target a waste loading of 36% calcined waste oxides as per the recommendation from the SRAT receipt analysis and MAR assessment documented in the memorandum SRNL-L3100-2011-00005.[15] Process frit was added in two batches, along with an equivalent mass of a 1.5 wt% formic acid solution (50 wt% frit, 50 wt% formic acid solution).

A 100 ppm antifoam addition was made at the start of SME processing (at the time of the first decon water addition). No foaming was observed during SME processing, and no additional antifoam was added during approximately 14 hours at boiling during the three day SME cycle.

Following frit addition, the SME contents were concentrated by boiling off water to a target of 47 wt% total solids. The resulting SME product was not pumpable using the equipment available in the Shielded Cells, a Masterflex peristaltic pump. The processing vessel was disassembled, and the contents were poured/manually transferred into a sample bottle. A sample was taken from the sample bottle to determine the total weight percent solids. This measurement indicated that the total solids retrieved from the sample bottle were approximately 50 wt%. Water was added until a somewhat fluid (pourable) SME product was obtained at ~43 wt% total solids. Physical property measurements of the SME product following dilution with water were completed. Results from the diluted SME product analyses are presented in Table 3-6. Note that the yield stress at 42.9 wt% total solids was approximately twice the DWPF design basis upper limit of 15 Pa, and the consistency was close to the upper limit of 40 cP.

Table 3-6. SME Product Physical Product Results

Analysis	Result
Wt% Total Solids	42.9
Wt% Dissolved Solids	11.5
Wt% Insoluble Solids	35.5
Wt% Calcined Solids	37.9
Slurry Density (g/mL)	1.37
Supernate Density (g/mL)	1.08
Yield Stress (Pa)	29
Consistency (cP)	37
pH	8.58

Table 3-7 gives analytical results of the SME product following dilution of the as-made material with water to 42.9% total solids. SME product samples were diluted with water for removal from the Shielded Cells. Filtered water dilutions were submitted for Ion Chromatography (IC) analysis. Unfiltered water dilutions were submitted for TIC and Total Organic Carbon (TOC). Note that the SME product nitrite is above the DWPF limit of 1,000 mg/kg. This may be a result of poor mixing (resulting in incomplete reactions or unrepresentative analytical samples) or an indication of ammonium side effect of the nitrate-to-ammonium reaction sequence.

For the oxalate analysis, the slurry was digested with nitric and hydrochloric acids followed by IC analysis. The water dilution of the slurry yielded an oxalate result of 5.13E+03, as compared to 6.0E+03 mg/kg from the acid digestion. There are several possibilities for this difference. 1) If all oxalate were in the form of sodium oxalate, there may not have been enough dilution to dissolve it completely in the analytical samples. 2) There may be insoluble forms of oxalate such as calcium or magnesium oxalate. 3) Because there is a 20% uncertainty in the acid strike oxalate analysis, there may be no difference between the waster dilution and acid digestion results. Because of uncertainties in analyses and in the form of oxalate, SRNL recommends an acid digestion for oxalate along with the normal water dilutions for sludge batches with significant quantities.

Table 3-7. SME Product Analytical Results

Analysis	Result (mg/kg SME Prod.)
Total Inorganic Carbon	8.44E+02
Total Organic Carbon	1.08E+04
Formate	2.95E+04
Nitrite	1.82E+03
Nitrate	1.45E+04
Sulfate	1.91E+03
Oxalate	6.0E+03[†]
Chloride	<4E+02
Fluoride	<4E+02

[†] The water dilution of the SME product yielded a result of 5.13E+03 mg/kg, suggesting that there was not enough dilution to dissolve all the sodium oxalate, or that there was a small amount of non-sodium oxalate. It should be noted, however, that the uncertainty on the "acid strike" oxalate method is ±20%.

3.4 <u>Off-gas Analysis Results</u>

Presented in Table 3-8, Figure 3-2, and Figure 3-3 are results from the analysis of the SRAT cycle off-gas data. As described in Section 3.2, the SRAT cycle was suspended shortly after the completion of acid addition. The time axis in Figure 3-3 only includes acid addition and the time the SRAT was heated. SRAT off-gas results are typical. Carbon dioxide production peaked during and immediately after acid addition. Nitrous oxide generation peaked after acid addition. Note that the nitrous oxide concentration and generation in the figures was multiplied by 00 to make it more "vissible". This is typical of a near-minimum acid addition test. Nevertheless, significant hydrogen generation began several hours after nitrous oxide generation peaked, indicating the destruction of a major portion of the nitrite. Hydrogen generation rates increased steadily from 9 hours after formic acid addition until the end of the SRAT cycle where the SRAT rate was above the DWPF SME cycle limit of 0.223 lb/h. The SRAT cycle was completed with hydrogen staying below 40% of the DWPF SRAT cycle limit of 0.65 lb/h.

Table 3-8. SRAT Cycle Peak Gas Concentrations and Generation Rates

	Maximum Observed Concentration (vol%)	Maximum Observed DWPF-Scale Generation Rate (lb/h)
Hydrogen	0.32	0.24
Carbon Dioxide	15	300
Nitrous Oxide	1.01	19
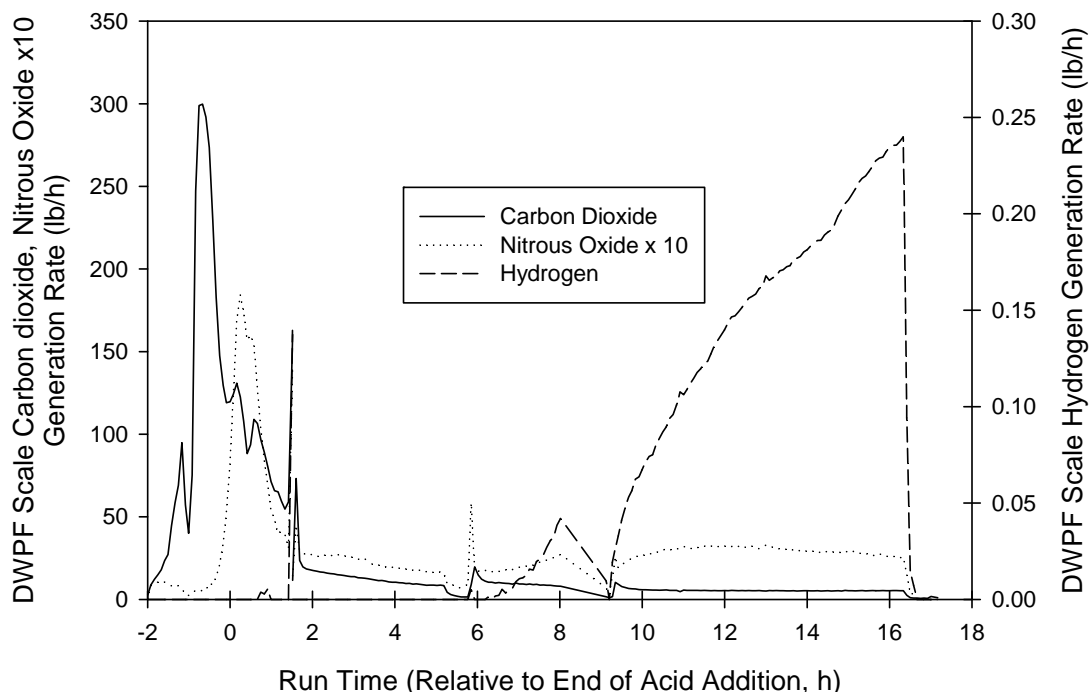
Figure 3-2. Off-gas Data From the SB7a Qualification SRAT Cycle – Gas Generation Rates

15
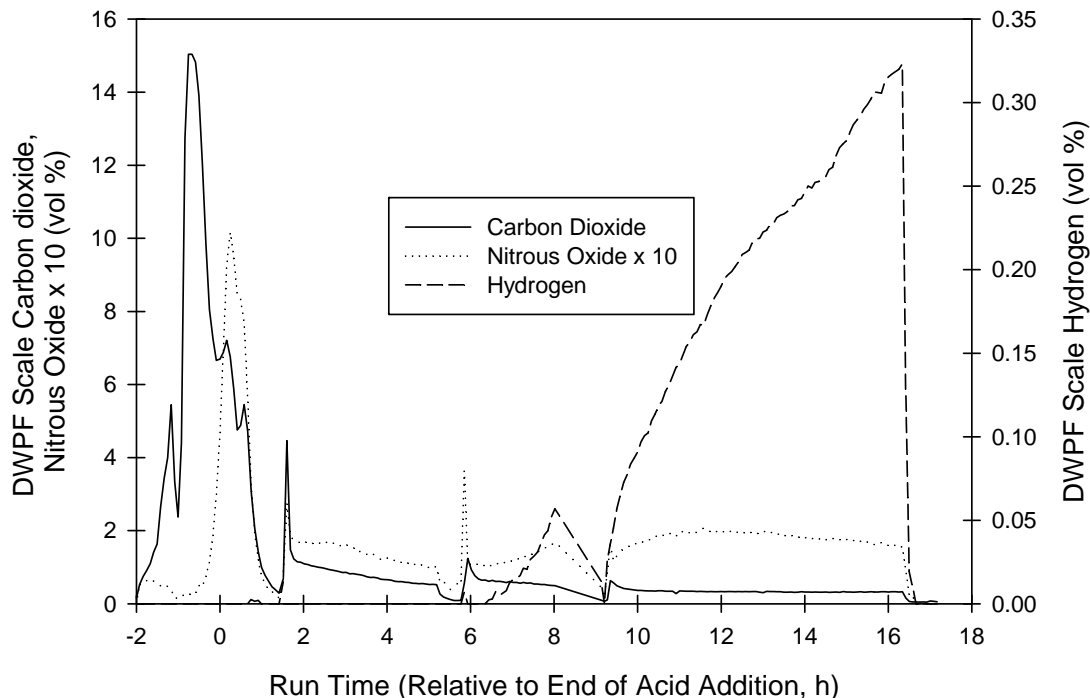
Figure 3-3. Off-gas Data From the SB7a Qualification SRAT Cycle – Gas Concentrations

Table 3-9, Figure 3-4, and Figure 3-5 show SME cycle off-gas results. The time axis reflects actual processing, i.e., time when the SME contents were being mixed and heated. In the SME cycle, hydrogen and nitrous oxide generation peaked at the end of the cycle. Carbon dioxide, however, had several spikes in generation and concentration. The first and second spikes occurred after start-up of mixing and heating and can be attributed to carbon dioxide retained in the sludge. The third spike occurred after making the second frit/formic acid addition. This spike may also be the result of releasing retained carbon dioxide as the sludge was thinned with the formic acid addition. Therefore, the reported maximum carbon dioxide is taken from near the end of the SME cycle.

Table 3-9. SME Cycle Peak Gas Concentrations and Generation Rates

|	Maximum Observed Concentration (vol%)	Maximum Observed DWPF-Scale Generation Rate (lb/h)
Hydrogen	0.18	0.044
Carbon Dioxide	1.3	7.2
Nitrous Oxide	0.29	1.6

Figure 3-4. Off-gas Data From the SB7a Qualification SME Cycle – Plot of Gas Generation Rates

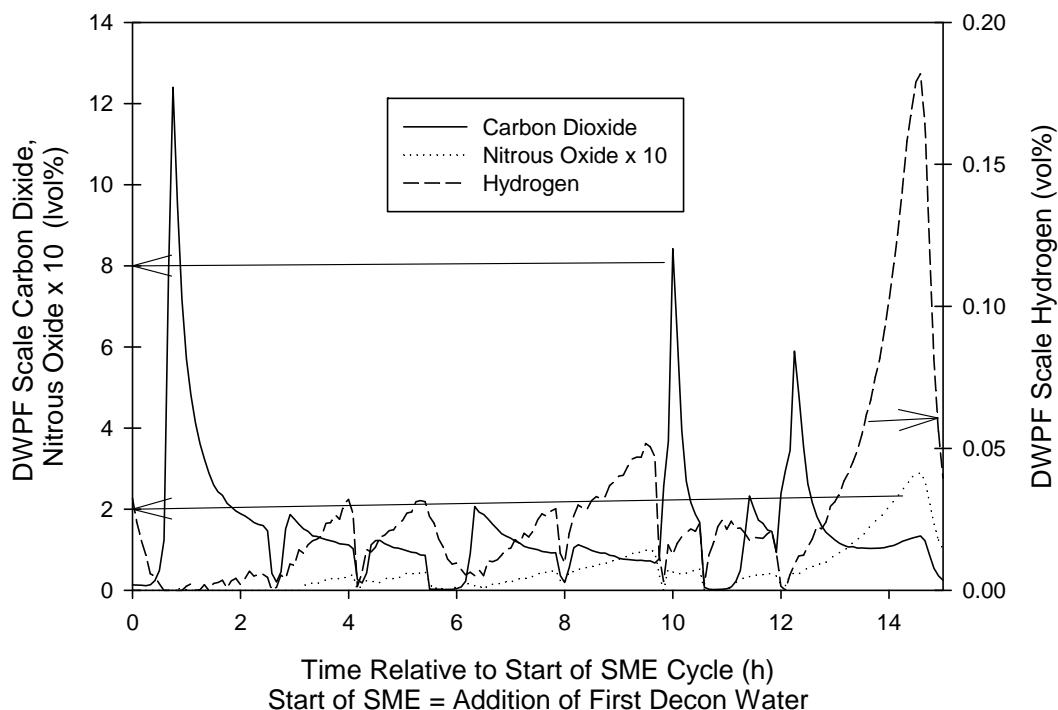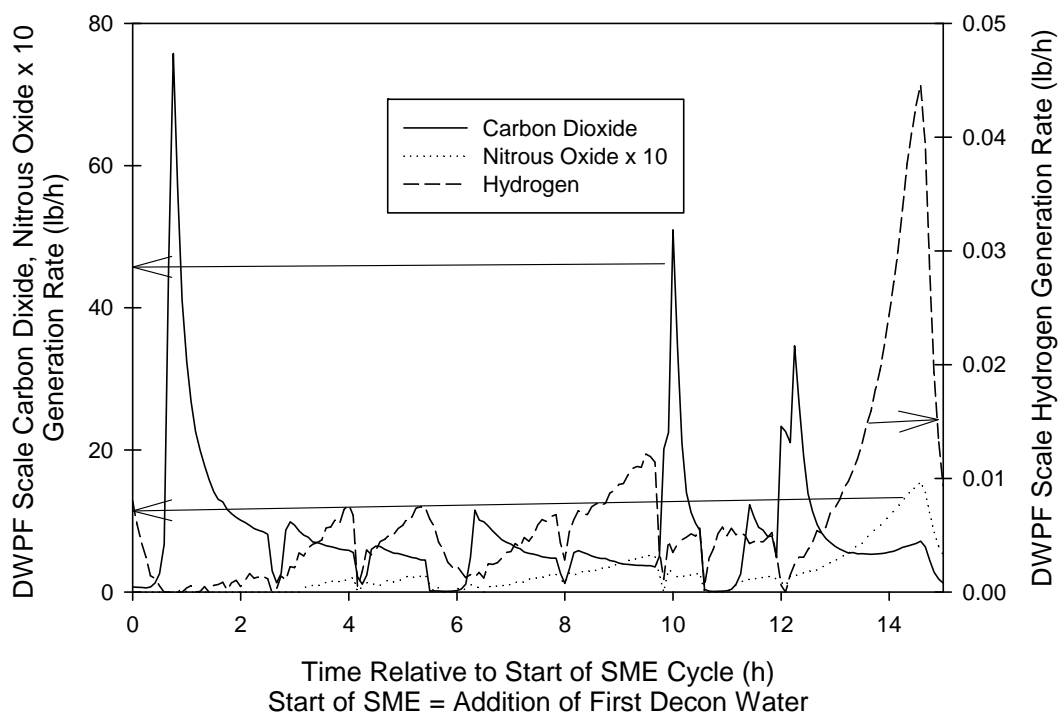**Figure 3-5. Off-gas Data From the SB7a Qualification SME Cycle – Plot of Gas Concentrations**

4.0 Glass Fabrication and PCT

4.1 Glass Fabrication

In preparation for glass fabrication, approximately 120 g of SB7a SME product was divided into four nearly equal portions and placed into crucibles and dried overnight at 110 °C. After thoroughly drying, the first portion was gradually heated to 1150 °C in an open 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 the melting temperature of 1150 °C of 3.5 hours. The crucible was removed from the furnace while at temperature and bottom quenched (cooled) in a shallow pan of water, making sure no water contacted the glass during the process. The resulting glass appeared black and shiny, without the presence of a visible salt layer, crystals or other inhomogeneities. This fabricated glass is referred to as the SB7a Qualification Glass 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 SB7a 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 HNO_3 uptake, and a mixed acid dissolution (MA) in sealed vessels at 115 °C using a combination of HF, HCl, and HNO_3 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 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Aliquots of the peroxide fusion dissolutions were also submitted for Inductively Coupled Plasma-Mass Spectroscopy (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 SB7a Qualification Glass was measured by following Test Method A of the ASTM 1285 standard nuclear waste glass leach test.[16] This test is commonly referred to as the PCT. The purpose of the PCT was to confirm that the SB7a Qualification Glass had a durability that met the criterion specified by the Waste Acceptance Product Specification (WAPS) for repository acceptance.[17] 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.[18] 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 SB7a 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 HNO_3. The leachates were then diluted and submitted to AD, where the concentrations of B, Na, Li, and Si, were determined using ICP-AES.

4.4 <u>Glass Fabrication and PCT Results and Discussion</u>

Table 4-1 shows the full measured composition of the SB7a Qualification Glass. Elements specifically requested in the TTR[1] (e.g., elements greater than 0.1 wt % in the sludge), along with elements necessary for Product Composition Control System (PCCS) calculations (e.g., Cu and Nd), are reported. 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 418, which has a nominal composition of 76 wt % SiO_2, 8 wt % B_2O_3, 8 wt % Li_2O and 8 wt % Na_2O. 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.[15] Depending upon the element, the results in Table 4-1 represent an average of up to eight measurements (actual number of measurements are noted in the table) resulting from the glass dissolution methods and analysis techniques mentioned in the experimental procedure. The dissolution method(s), analytical technique(s) used to determine the average composition, and calculated uncertainties are noted in Table 4-1 next to each element.

Table 4-1. Determined Oxide Concentrations Measured in SB7a Qualification Glass

Oxide	Wt %	Est. Std. Unc. (1-Sigma)	# Samples Averaged	Digestion Methods	Detection Method
Ag_2O	0.008	0.0002	4	PF	ICP-MS
Al_2O_3	8.772	0.0189	4	PF	ICP-AES
B_2O_3	4.588	0.0050	4	PF	ICP-AES
BaO	0.041	0.0006	8	MA/PF	ICP-AES
CaO	0.389	0.0044	4	MA	ICP-AES
CdO	0.016	0.0002	8	MA/PF	ICP-AES
Ce_2O_3	0.048	--	4	PF	ICP-MS
CoO	0.004	0.0000	3	MA	ICP-AES
Cr_2O_3	0.040	0.0003	8	MA/PF	ICP-AES
CuO	0.235	0.0029	8	MA/PF	ICP-AES
Fe_2O_3	8.087	0.0430	8	MA/PF	ICP-AES
Gd_2O_3	0.045	0.0007	8	MA/PF	ICP-AES
K_2O	0.056	0.0002	3	MA	ICP-AES
La_2O_3	0.028	0.0007	8	MA/PF	ICP-AES
Li_2O	5.104	0.0211	8	MA/PF	ICP-AES
MgO	0.219	0.0014	8	MA/PF	ICP-AES
MnO	1.803	0.0102	8	MA/PF	ICP-AES
MoO_3	0.009	0.0003	3	MA	ICP-AES
Na_2O	13.227	0.3202	4	MA	ICP-AES
Nd_2O_3	0.094	--	4	PF	ICP-MS
NiO	1.382	0.0081	8	MA/PF	ICP-AES
P_2O_5	0.149	0.0017	3	MA	ICP-AES
PbO	0.011	0.0001	3	MA	ICP-AES
PdO	0.002	0.0000	4	PF	ICP-MS
Rh_2O_3	0.007	0.0004	4	PF	ICP-MS
RuO_2	0.013	0.0001	4	PF	ICP-MS
Sb_2O_3	0.024	0.0006	3	MA	ICP-AES
SiO_2	50.328	0.0750	4	PF	ICP-AES
SnO_2	0.004	0.0003	2	MA	ICP-AES
SO_4^{2-}	0.242	0.0020	3	MA	ICP-AES
SrO	0.023	0.0002	8	MA/PF	ICP-AES
ThO_2	0.417	0.0121	8	MA/PF	ICP-AES
TiO_2	0.027	0.0002	8	MA/PF	ICP-AES
U_3O_8	2.574	0.0248	8	MA/PF	ICP-AES
Y_2O_3	0.014	--	4	PF	ICP-MS
ZnO	0.062	0.0006	8	MA/PF	ICP-AES
ZrO_2	0.145	0.0012	4	MA	ICP-AES
Sum of Oxides	98.237				

[a] PF = Peroxide Fusion dissolution method, MA = Mixed Acid dissolution method

The measured SB7a Qualification Glass composition reported in Table 4-1 was used to complete a another MAR assessment which verified the predictability of the process and durability requirements of

the fabricated glass based on the PCCS models. Based on the measured composition, all of the predicted properties met the PCCS MAR criteria. A list of the primary predicted properties is found in Table 4-2.

Table 4-2. PCCS Results for SB7a Qualification Glass

PCCS Model	Predicted Value
ΔG_p Value	-9.6249
NL[B (g/L)]	0.70
Liquidus Temperature (T_L) Prediction (ºC)	895
Viscosity Prediction (P) at 1150 °C	65
Nepheline Constraint Value	0.70
Al_2O_3 (wt %)	8.77
All PCCS MAR Criteria Met	yes

For the SB7a Qualification Glass, the waste loading of the fabricated glass was calculated based on the analyzed glass Li_2O content (Table 4-1) and the nominal Li_2O content of the Frit 418 (8.0 wt %) used for glass fabrication. Using these values yields a waste loading of 36.2 wt % which corresponds well to the targeted 36 wt % WL.

Quadruplicate samples of the SB7a Qualification Glass were subjected to the PCT along with triplicate blanks, triplicate samples of the ARM and the EA reference glass as prescribed by the ASTM procedure.[16] The results for the reference glasses and the blanks indicated that the test was acceptable. The vessels exhibited minimal to no negligible water losses (within the bounds allowed by the ASTM procedure) during the course of the test. The blanks and leachates from the ARM and EA references all had elemental and normalized releases within the reference values.[18, 19] Results for the averaged normalized releases (based on the measured composition), for B, Na, Li, and Si (grams of normalized element per liter of PCT leachate) are given in Table 4-3. A table listing the ppm releases of the leachates tested and the pH of the individual leachates can be found in Appendix D, Table D-1. The normalized releases for the SB7a 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 SB7a 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 Figure 4-6.

Table 4-3. PCT Results for ARM, EA and the SB7a 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]	0.43	0.46	0.52	0.26	NA
Est. Std. Unc. (1-Sigma) [b]	0.0034	0.0036	0.0032	0.0022	NA
EA [a]	17.43	13.73	9.85	4.07	NA
Est. Std. Unc. (1-Sigma) [b]	0.1199	0.0447	0.1293	0.0307	NA
SB7a-QUAL [c]	0.65	0.87	0.74	0.52	0.36
Est. Std. Unc. (1-Sigma) [b]	0.0032	0.029	0.0010	0.0032	0.0079

[a] Average of 3 PCT replicates
[b] Est. Std. Unc. – Estimated Standard Uncertainty
[c] Average of 4 PCT replicates
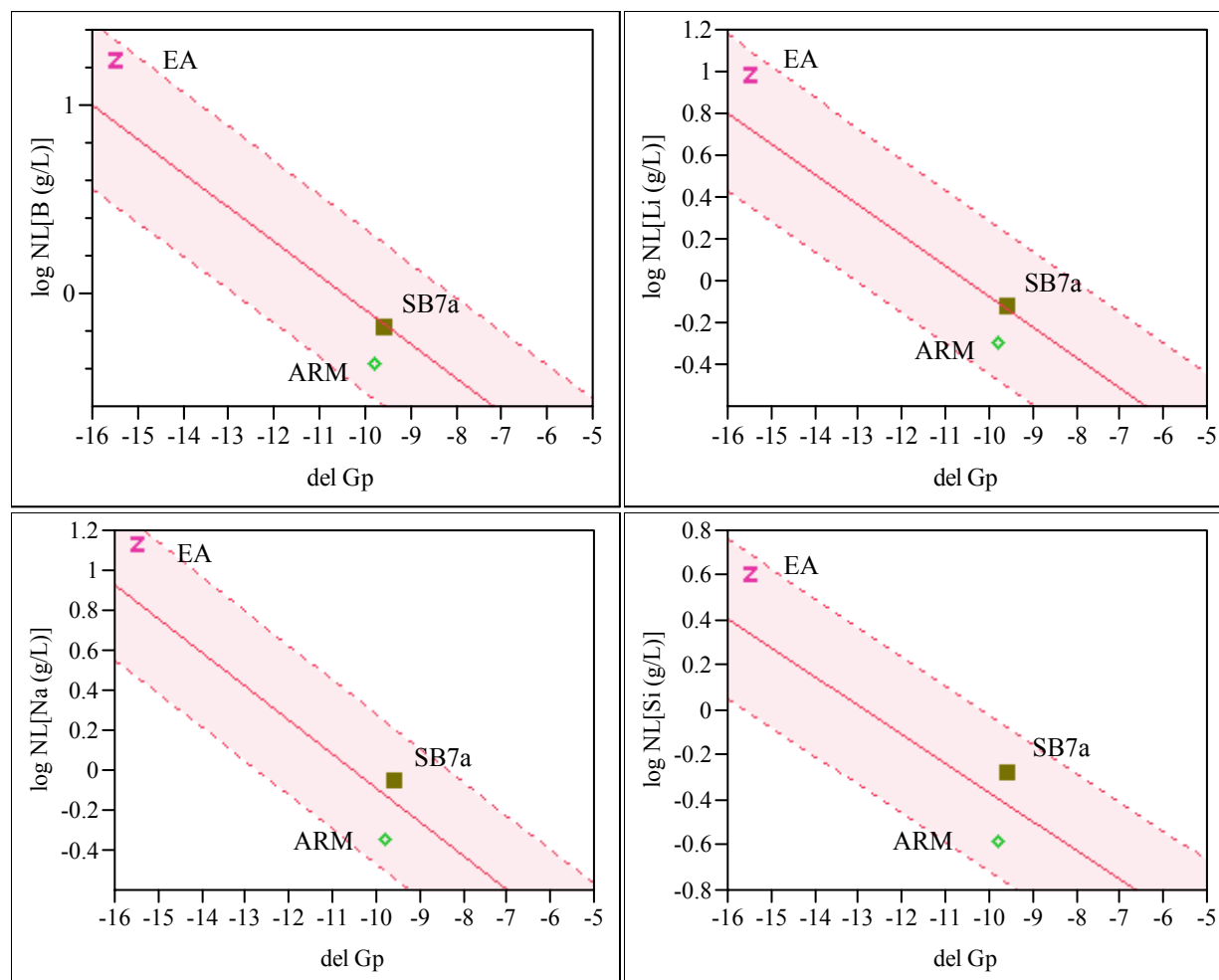
Figure 4-6. Fit of log Normalized Release of B, Li, Na and Si (g//L) vs. Δ G$_p$ for the measured releases of ARM, EA and the SB7a Qualification glasses.

5.0 Conclusions/Recommendations

- There were no issues with sludge washing. The sludge settled as needed (it settled fast enough and far enough to allow timely decants). SRNL was able to produce a washed sample comparable to the Tank Farm target endpoint of 1 M Na with fewer washes; SRNL combined twelve Tank Farm washes into five Cells' washes. Rheological properties were acceptable at the targeted washing endpoint. It is recommended that the Tank Farm wash as planned.

- The SB7a qualification sample as washed by SRNL met the processing constraints imposed by the DWPF. The acid addition and boiling time used by SRNL in the SRAT cycle destroyed nitrite and removed mercury to DWPF target levels. Hydrogen generation rates were below the DWPF design bases.

- Foaming was not problematic during SRAT and SME processing, and antifoam was effective when added.

- The SRNL SB7a qualification SRAT product had acceptable rheological properties at a total solids of 25.4 wt% (targeted 25 wt%). It is recommended that a SRAT product solids endpoint of 25% be used for initial SB7a operation at DWPF. The rheological properties of the SRAT product should be monitored in DWPF during initial SB7a processing.

- The SRNL SB7a qualification SME product yield stress at 42.9 wt% total solids was approximately twice the DWPF design basis upper limit of 15 Pa, and the consistency was close to the upper limit of 40 cP. A SME solids target of 40 to 45 wt% should be used for initial SB7a processing. The rheological properties of the SME product should be monitored in DWPF during initial SB7a processing to determine a nominal solids endpoint.

- It is recommended that DWPF adopt an acid digestion method for oxalate analysis. In the SME product, SRNL saw noticeable differences between slurry water dilution and acid digestion results for oxalate.

- The SB7a SME product (SB7a Qualification sludge plus Frit 418) was used to fabricate a glass with a targeted waste loading oft 36%. The glass was acceptable with respect to chemical durability as measured by the PCT. Specifically, the SB7a glass had a normalized boron release of 0.65 g/L, while the EA glass had a normalized release of 17.43 g/L. The PCT response was also predictable by the current durability models of the DWPF PCCS.

6.0 References

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Appendix A.   Analytical Methods

Described below are the methods and techniques used to generate the analytical data presented in this report.

Described below are the methods and techniques used to generate the analytical data presented in this report.

As-Received, SRAT Receipt and SRAT Product Characterization

Eight separate aliquots of the slurry for each type of sample were digested, four with HNO_3/HCl (aqua regia[*]) in sealed Teflon® vessels and four in Na_2O_2 (alkali or peroxide fusion[†]) using Zr crucibles. Due to the use of Zr crucibles and Na in the peroxide fusions, Na and Zr cannot be determined from this preparation. Additionally, other alkali metals, such as Li and K, and alkaline earth metals, such as Ca, that may be contaminants in the Na_2O_2 are not determined from this preparation. Three Analytical Reference Glass – 1[‡] (ARG-1) standards were digested along with a blank for each preparation. The ARG-1 glass allows for an assessment of the completeness of each digestion. Each aqua regia digestion and blank was diluted to either 100 mL or 250 mL with de-ionized water and submitted to AD for ICP-AES analysis, ICP-MS analysis of masses 81-209 and 230-252, and cold vapor atomic absorption (CVAA) analysis for Hg. Equivalent dilutions of the peroxide fusion digestions and blank were submitted to AD for ICP-AES analysis.

The elemental concentrations reported are either a combination of both digestion methods and an average of eight data points or an average of four data points from one digestion method.

Glass Dissolution Methods and Analyses

To support compositional analysis, a portion of the SB7a 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. The two methods were a sodium peroxide fusion at 675 °C followed by a HNO_3 uptake, and an acid dissolution in sealed vessels at 115 °C using a combination of HF, HCl, and HNO_3 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. Four aliquots of the crushed SB7a Qualification Glass were dissolved by each technique. The aliquots were then submitted to AD, where they were analyzed by ICP-AES, radioactive counting techniques, and by ICP-MS. Concurrent with each set of dissolutions in the Shielded Cells, three samples of ARG-1 were also dissolved to determine if the dissolutions were complete and the resulting analyses accurate. With each set of samples sent to AD, two samples of a multi-element standard containing known concentrations of Al, B, Fe, Li, Na, and Si were also submitted.

Supernate Sample Preparation For Analysis

A portion of the well-mixed sludge slurry was filtered through a 0.45 μm porosity filter. Portions of the filtered supernate were diluted with de-ionized distilled water or nitric acid to reduce the sample activity and to allow removal from the Shielded Cells for chemical analysis. All sample preparations of the filtered supernate samples were conducted in quadruplicate. A blank was prepared along with the sample dilutions.

[*] Coleman, C. J. *Aqua Regia Dissolution of Sludge for Elemental Analysis*; Manual L16.1, Procedure ADS-2226, Rev. 9; Savannah River National Laboratory: Aiken, SC, 2009.
[†] Coleman, C. J. *Alkali Fusion Dissolutions of Sludge and Glass for Elemental and Anion Analysis*; Manual L16.1, ADS-2502, Rev. 6; Savannah River National Laboratory: Aiken, SC, 2008.
[‡] Smith, G. L. *Characterization of Analytical Reference Glass – 1 (ARG-1)*; PNL-8992; Pacific Northwest National Laboratory: Richland, WA, 1993.

<u>Weight Percent Solids and Density Measurements</u>
The densities of the filtered supernate and the well-mixed slurry sample were measured in the Shielded Cells using calibrated plastic tubes with a nominal volume of ~8.25 mL. The density measurements were conducted in quadruplicate on each phase of the sample.

The weight percent total solids in the slurry sample were measured in the Shielded Cells using a conventional drying oven at 110 °C. The slurry sample was dried until repeated weights indicated no further loss of water. The weight percent dissolved solids in a sample of the filtered supernate were measured in the same manner. All weight percent solids measurements were made in quadruplicate. The weight percent insoluble solids and weight percent soluble solids in the slurry sample were calculated using the equations shown below.

Equation 1
$$W_{is} \frac{W_{ts} - W_{ds}}{1 - W_{ds}}$$

Equation 2
$$W_{ss} = W_{ts} - W_{is}$$

where:
    W_{is} = weight fraction of insoluble solids in the slurry
    W_{ss} = weight fraction of soluble solids in the slurry
    W_{ts} = weight fraction of total solids in the slurry
    W_{ds} = weight fraction of dissolved solids in the filtered supernate

Thus:
    Wt% dissolved solids = (wt dissolved solids/wt of supernate) x 100
    Wt% total solids = (wt total solids/wt of total slurry) x 100
    Wt% insoluble solids = (wt insoluble solids/wt of total slurry) x 100
    Wt% soluble solids = (wt of dissolved solids/wt of total slurry) x 100

Weight percent calcined solids were determined by heating the dried solids to 1100 °C for two hours. The calcined solids are then calculated from the initial slurry weight used for the total solids and the weight of material remaining after calcining:

<u>Rheology</u>
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.[*] In either case, for shear thinning non-Newtonian fluids typical of Savannah River Site (SRS)

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[*] Darby, R., *Chemical Engineering Fluid Mechanics, 2nd edition.* Marcel Dekker: 2001.

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 A-1.
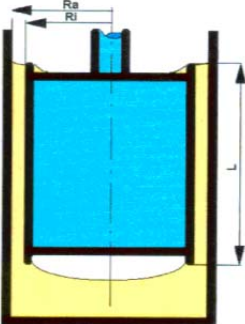
Prior to performing the measurements, the rotors and cups are inspected for physical damage. The torque/speed sensors and temperature bath are verified for functional operability using a bob/cup combination with a National Institute of Standards and Technology (NIST) traceable Newtonian oil standard, using the MV I rotor. The resulting flow curves are then fitted as a Newtonian fluid and this calculated viscosity must be within ± 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 3, 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 3 $$\tau = \tau_o + \mu_\infty \dot{\gamma}$$

Table A-1. 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 (Pa/%torque)	3.22	3.76
	M factor (s^{-1}/%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

Appendix B.   **Settling During Washing**

The settled level is read from a centimeter scale affixed to the side of the washing vessel. It is not exactly the height of the sludge. For example, zero sludge corresponds to 0.7 cm.

Volume (mL) = 176 x Level (cm) – 128

Date	Settling Time (days)	Level (cm)	Volume (mL)
Decant A/B			
9/20/2010	0	15.2	2,547
9/21/2010	1	14.4	2,406
9/22/2010	2	13.5	2,248
9/23/2010	3	12.4	2,054
9/27/2010	7	9.5	1,544
9/28/2010	8	9.2	1,491
9/29/2010	9	8.9	1,430
9/30/2010	10	8.8	1,421
10/1/2010	11	8.8	1,412
10/4/2010	14	8.5	1,368
10/13/2010	23	8.3	1,333
Decant C			
10/15/2010	0	13.9	2,318
10/18/2010	3	10.9	1,790
10/19/2010	4	9.9	1,614
10/20/2010	5	9.4	1,526
10/21/2010	6	9.1	1,474
Decant D-K			
10/26/2010	0	15.9	2,670
10/27/2010	1	14.3	2,389
10/28/2010	2	12.9	2,142
10/29/2010	3	11.0	1,808
11/1/2010	6	9.4	1,526
Decant L			
11/1/2010	0	14.2	2,371
11/2/2010	1	12.7	2,107
11/3/2010	2	11.1	1,826
11/4/2010	3	10.0	1,632
11/5/2010	4	9.5	1,544

Date	Settling Time (days)	Level (cm)	Volume (mL)
Decant M			
11/5/2010	0	13.9	2,318
11/8/2010	3	9.4	1,526
Decant N			
11/8/2010	0	13.6	2,266
11/9/2010	1	12.4	2,054
11/10/2010	2	10.9	1,790
11/11/2010	3	9.9	1,614
11/12/2010	4	9.2	1,491
11/15/2010	7	9.0	1,456

Appendix C.   **Calculation of Oxalate Removed During SRNL-Washing**

The amount of oxalate removed from the Tank 51 qualification sample during washing is calculated below. In the calculation, it is assumed that Fe is inert (and a constant) in the washing process. The amount of oxalate per gram of Fe is calculated for the As received and washed sludge. The difference is used to calculate the percent of total oxalate removed during washing.

	As received	Washed	
Fe wt% of total solids	5.0	13.2	See Table 2-4
Oxalate mg/kg slurry	11,600	8,200	See Section 2.2
wt% total solids	26.9	18.1	See Table 2-2
Fe mg/kg slurry	13,450	23,892	Fe wt% of total solids x wt% total solids x 100
Given 1 g of Fe,			
Oxalate g	0.86	0.34	Oxalate (mg/kg) / Fe (mg/kg)
% removed		60%	(Ox in as-rec - Ox in washed)/Ox in as-rec x 100

Appendix D.   **Supplemental PCT Data**

Table D-1. PCT Elemental Releases and Measured pH for ARM, EA and the SB7a Qualification Glass

Glass ID	pH	Elemental Release - Dilution Factor Corrected (ppm)						
		Li	B	Na	Si	Al	Fe	U
ARM-1-314	10.19	12.10	15.12	33.33	57.33	4.97	<0.04	NA
ARM-2-315	10.10	12.32	15.25	33.50	57.50	4.92	<0.04	NA
ARM-3-316	9.92	12.08	14.85	32.67	56.00	4.80	<0.04	NA
EA-1-306	11.74	190.00	603.33	1700.00	913.33	<3.13	<0.35	NA
EA-2-307	11.73	196.67	615.00	1716.67	933.33	<3.13	<0.35	NA
EA-3-313	11.72	198.33	616.67	1716.67	935.00	<3.13	<0.35	NA
SB7a-Qual-1-317	10.80	17.17	9.23	84.67	120.50	23.17	15.60	8.27
SB7a-Qual-2-318	10.87	17.67	9.33	85.83	123.00	23.67	17.00	8.10
SB7a-Qual-3-319	10.71	19.403	9.870	90.279	115.206	22.83	15.00	7.60
SB7a-Qual-4-320	10.71	20.311	10.442	94.312	120.584	23.67	16.67	7.90

Distribution:

A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
A. M. Murray, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
J. W. Amoroso, 999-W
K. M. Fox, 999-W
J. M. Gillam, 766-H
C. M. Gregory, 773-A
B. A. Hamm, 766-H
J. F. Iaukea, 704-30S
F. C. Johnson, 999-W
D. C. Koopman, 999-W
D. P. Lambert, 999-W
D. W. McIlmoyle, 766-H
J. E. Occhipinti, 704-S
D. K. Peeler, 999-W
B. R. Pickenheim, 999-W
J. W. Ray, 704-S
S. H. Reboul, 773-A
H. B. Shah, 766-H
D. C. Sherburne, 704-S
A. V. Staub, 704-27S
M. E. Stone, 999-W
J. R. Zamecnik, 999-W
P. R. Jackson, 703-46A
K. H. Subramanian, 766-H
M. A. Broome, 704-29S
R. N. Hinds, 704-S
J. P. Vaughan, 773-41A
J. M. Bricker, 704-27S
T. L. Fellinger, 704-26S
E. W. Holtzscheiter, 704-15S
M. T. Keefer, 766-H
H. M. Pittman, 704-27S
C. E. Duffey, 704-61H