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Sludge Washing and Demonstration of the DWPF Nitric/Formic Flowsheet in the SRNL Shielded Cells for Sludge Batch 9 Qualification

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) was requested by Savannah River Remediation (SRR) to qualify the next batch of sludge – Sludge Batch 9 (SB9). Current practice is to prepare sludge batches in Tank 51 by transferring sludge to Tank 51 from other tanks. The sludge is washed and transferred to Tank 40, the current Defense Waste Process Facility (DWPF) feed tank. Prior to sludge transfer from Tank 51 to Tank 40, the Tank 51 sludge must be qualified. SRNL qualifies the sludge in multiple steps. First, a Tank 51 sample is received, then characterized, washed, and again characterized. SRNL then demonstrates the DWPF Chemical Process Cell (CPC) flowsheet with the sludge. The final step of qualification involves chemical durability measurements of glass fabricated in the DWPF CPC demonstrations. In past sludge batches, SRNL had completed the DWPF demonstration with Tank 51 sludge. For SB9, SRNL has been requested to process a blend of Tank 51 and Tank 40 at a targeted ratio of 44% Tank 51 and 56% Tank 40 on an insoluble solids basis.

This report documents Task 4.1, items 3 and 6-10 in the Task Technical and Quality Assurance Plan[*]:

- Washing of the Tank 51 SB9 qualification sample. Compositions of the received sample and the washed sample have previously been documented.
- Demonstration of the CPC using a blend of SRNL-washed Tank 51 and Tank 40 Sludge Batch 8 (SB8) to show the sludge could be processed without exceeding hydrogen generation limits.
- Rheology measurements of the Sludge Receipt and Adjustment Tank (SRAT) receipt, SRAT product, and Slurry Mix Evaporator (SME) product.
- Vitrification of a portion of the SME product and subsequent characterization and durability testing (as measured by the Product Consistency Test (PCT)) of the resulting glass.

Based on the results, SRNL has qualified SB9 with the nitric acid/formic acid flowsheet. SRNL has demonstrated that SB9 can be processed using an acid addition strategy that has been shown to destroy nitrite without exceeding the DWPF hydrogen generation rates in the SRAT and SME. Also, the PCT responses from the Qualification Glass are acceptable relative to the chemical durability of the Environmental Assessment (EA) benchmark glass and predictable by current Product Composition Control System (PCCS) models for durability. All other PCCS Measurement Acceptability Region (MAR) criteria were met based on the measured glass composition.

Note the following:

- Specific recommendations for processing SB9 are based on the series of simulant tests and are published in a separate document.[†]
- During the execution of this work, SRR requested the evaluation of an additional blend composition. SRR is projecting a Tank 51/Tank 40 blend with more Tank 51 than what was tested at SRNL. SRNL has evaluated the impact of this change and concluded that no additional testing is necessary.[‡]

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[*] Pareizs, J. M. and Lambert, D. P. *Task Technical and Quality Assurance Plan for Sludge Batch 9 Shielded Cells Qualification Run – Nitric/Glycolic Flowsheet*; SRNL-RP-2015-00838, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2015.

[†] Pareizs, J. M. and smith, T. E. *Recommendations for Sludge Batch 9 Processing in the Defense Waste Processing Facility Chemical Process Cell*; SRNL-L3100-2016-00144, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2016.

[‡] Lambert, D. P. *February 2016 SB9 Projection Representing an SB8 Tank 40 Heel of 40 inches – CPC Nitric-Formic Acid Flowsheet Processing Assessment*; SRNL-L3100-2016-00061, Rev. 1; Savannah River National Laboratory: Aiken, SC, 2016.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption; SRNL-AD methods AAAS and AASE
AF	alkali fusion
AR	aqua regia
ARG-1	Analytical Reference Glass
ARM	Approved Reference Material
CI	confidence intervals
CPC	Chemical Process Cell
CQ	caustic quench
CVAA	cold vapor atomic absorption; SRNL-AD methods CVHG and CVHG DIGESTED
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
FAVC	Formic Acid Vent Condenser
GC	gas chromatograph
HMDSO	hexamethyldisiloxane
ICA	ion chromatography-anions; SRNL-AD method IC ANIONS
ICC	ion chromatography-cations; SRNL-AD method IC CATIONS
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy; SRNL-AD method RAD ICPES LEEMAN
ICP-ES-S	ICP-ES for S; SRNL-AD method RAD ICPES SULFUR AXIAL
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry; SRNL-AD method RAD ICPMS
MAR	Measurement Acceptability Region
MWWT	Mercury Water Wash Tank
NIST	National Institute of Standards and Technology
PCCS	Product Composition Control System
PCT	Product Consistency Test
R&D	Research and Development
REDOX	Reduction/Oxidation
RSD	Relative standard deviation
SB8	Sludge Batch 8
SB9	Sludge Batch 9
sccm	standard cubic centimeters per minute
scfm	standard cubic feet per minute
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRNL-AD	SRNL-Analytical Development
SRR	Savannah River Remediation
SRS	Savannah River Site
SVOA	semivolatile organic analysis; SRNL-AD method SVOA
TBP	tributyl phosphate
THERMO	Thermodynamic Hydration Energy Model
TIC	total inorganic carbon; SRNL-AD method TIC
Titr.	titration; SRNL-AD method T BASE/OH/OTHER BASE EXC CO_3^{2-}
TOC	total organic carbon; SRNL-AD method TOC
TTQAP	Task Technical and Quality Assurance Plan

TTR	Technical Task Request
VOA	volatile organic analysis; SRNL-AD method VOA
vol%	volume percent
WAPS	Waste Acceptance Product Specifications
wt%	weight percent
ΔG_P	Free energy of hydration

1.0 Introduction

Savannah River National Laboratory (SRNL) was requested by Savannah River Remediation (SRR) to qualify the next batch of sludge – Sludge Batch 9 (SB9).[1] Current practice is to prepare sludge batches in Tank 51 by transferring sludge to Tank 51 from other tanks. The sludge is washed and transferred to Tank 40, the current DWPF feed tank. Prior to sludge transfer from Tank 51 to Tank 40, the Tank 51 sludge must be qualified. SRNL qualifies the sludge in multiple steps. First, a Tank 51 sample is received, then characterized, washed, and again characterized. SRNL then demonstrates the DWPF Chemical Process Cell (CPC) flowsheet with the sludge. The final step of qualification involves chemical durability measurements of glass fabricated in the DWPF CPC demonstrations. In past sludge batches, SRNL had completed the DWPF demonstration with Tank 51 sludge. For SB9, SRNL has been requested to process a blend of Tank 51 and Tank 40.

This report documents Task 4.1, items 3 and 6-10 in the Task Technical and Quality Assurance Plan (TTQAP)[2]:

- Washing of the Tank 51 SB9 qualification sample. Compositions of the received sample and the washed sample have previously been documented.
- The performance of two DWPF CPC demonstrations using a blend of SRNL-washed Tank 51 and Tank 40 Sludge Batch 8 (SB8), designated as SC-16 and SC-17. Due to several issues with SC-16, the demonstration was repeated (SC-17). The demonstrations included a Sludge Receipt and Adjustment Tank (SRAT) cycle and a Slurry Mix Evaporator (SME) cycle. In the SRAT cycle, acid was added to the sludge to destroy nitrite and reduce Hg. In the SME cycle, glass frit was added to the sludge in preparation for vitrification. The SME cycle also included replication of five canister decontamination additions and concentrations. While some results from SC-16 are presented, the focus of this report is on SC-17.
- Rheology measurements of the SRAT receipt, SRAT product, and SME product.
- Vitrification of a portion of the SME product from the SC-17 SME cycle and subsequent characterization and durability testing (as measured by the Product Consistency Test (PCT)) of the resulting glass.

This work was requested via a Technical Task Request (TTR)[1] and was governed by a TTQAP[2]. This work is Technical Baseline Research and Development (R&D).

2.0 Experimental Procedure

2.1 Overview of Analytical Techniques

The following subsections describe general sample preparations and analytical techniques common to all aspects of this overall task.

2.1.1 Weight Percent Solids and Density

Aliquots of slurry and supernatant (nominally 3 g) are dried to a constant weight at 110 °C for weight percent (wt%) total solids and wt% dissolved solids, respectively. Weight percent insoluble and soluble solids are calculated from the total and dissolved solids measurements. Dried slurry samples are heated to 1100 °C, held at that temperature two hours, and then cooled and weighed to determine wt% calcined solids. All weights were obtained using M&TE balances.

Slurry and supernatant densities are determined gravimetrically from sample weights in vessels of known volume (plastic test tubes of nominally 8 mL capacity). The volume of each tube is determined individually.

2.1.2 Sample Preparations for Supernatant Characterization

The required results of supernatant characterization include various anions, free hydroxide, and several elemental constituents. Decanted supernatant was diluted by approximately 26X with deionized water to reduce personnel radioactivity exposure prior to submission to Savanah River National Laboratory-Analytical Development (SRNL-AD). Supernatant was diluted in quadruplicate, and the water used in the dilutions was submitted as a blank.

2.1.3 Sample Preparations for Oxalate Analysis (Slurry Dilutions)

Sodium oxalate was determined from a water dilution of slurry, by an acid strike, and by the relatively new caustic quench (CQ). For the water dilution, slurry was diluted with water by approximately 45X. Sodium oxalate solubility increases significantly as aqueous sodium concentration decreases.[3] Thus, a dilution of slurry to reduce the sodium concentration to less than 0.1 M should result in the dissolution of the majority of existing sodium oxalate.

The acid strike is a room temperature acid dissolution of slurry – 1 g of slurry is mixed with 2 mL concentrated HCl and 2 mL concentrated HNO_3 and diluted to 250 mL. This method dissolves oxalate present as calcium oxalate. A disadvantage of this method is the fact that the acids can destroy oxalate and samples must be analyzed as quickly as possible after sample preps to minimize analytical bias associated with the destruction of oxalate from the acids.

The CQ method[4] was utilized on the SC-17 SRAT product. This method involves adding 2 g of 50% sodium hydroxide to 10 g of slurry, followed by a 100X dilution.

2.1.4 Sample Preparations for Total Solids Characterization

To characterize the solids of the Tank 51 sample, aliquots of slurry were digested and submitted to SRNL-AD for analysis. (Slurry aliquot amount is chosen to target 0.25 g of solids in the digestions.[5]) Slurry samples were digested by two methods, aqua regia (AR) and alkali fusion (AF). For the AR digestions, aliquots of slurry were mixed with AR and heated in closed vessels for several hours at approximately 110 °C. The resulting liquids were diluted to 100 mL with water and submitted to SRNL-AD for analysis. For the AF digestions, aliquots of slurry were dried at approximately 110 °C and fused in a zirconium crucible at 675 °C with sodium peroxide. The fusions were then dissolved with nitric acid and water. The resulting liquids were diluted to 100 mL with water. The SRNL-AD results were then converted from a slurry basis to a wt% total solids basis using the measured wt% total solids. In general, AR results have lower detection limits compared to AF; AF utilizes a larger dilution prior to analysis due to the sodium used in the sample preparation. The AF is a more rigorous digestion and is better for some forms of aluminum (e.g., boehmite) and silicon. The AR digestion is necessary for Na, which is in the AF digestion reagent chemicals (along with potential trace amounts of K and Ca). In addition to slurry samples, reagent blanks and digested glass of known composition were processed. Results of these samples were used in evaluating AR and AF slurry digestion effectiveness.

2.1.5 Slurry Inorganic and Organic Analyses

Slurry samples diluted with water by a factor of approximately 45X were submitted for Total Inorganic Carbon (TIC), Total Organic Carbon (TOC), and Volatile Organic Analysis (VOA). VOA is designed to quantify organic materials boiling below 150 °C, including the specific analytes benzene, toluene, isopropanol, and butanol.

Slurry samples were extracted with methylene chloride to measure semivolatile organic compounds via SRNL-AD method semivolatile organic analysis (SVOA). Compounds quantified by this method generally include those organic materials boiling above 150 °C. Diluted slurry aliquots were mixed with a concentrated sodium nitrate solution and extracted. The extractant from this process yields the process chemicals tributyl phosphate (TBP), Isopar, and Norpar. A second set of diluted slurry aliquots was mixed with a buffer at pH 7. The extractant from this process yields n-paraffin, and phenol. Slurry was diluted by approximately 10X to reduce insoluble solids concentration; insoluble solids make it difficult to distinguish the aqueous and organic layers in the cells. 5 mL of diluted slurry was mixed with 5 mL of buffer and extracted with 10 mL of methylene chloride.

2.1.6 Savannah River National Lab Analytical Development Methods

Table 2-1 lists the SRNL-AD methods, the abbreviations for those methods used in this document, and the analytes reported from these methods. In the Results section, these methods are identified for each analysis.

Table 2-1. Analytes from SRNL-AD Methods

SRNL-AD Method	Abbreviation of Method in This Report	Expected Results to Satisfy Technical Task Request (TTR)[1] Requirements
RAD ICPES LEEMAN	ICP-ES	Ag, Al, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Gd, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sn, Sr, Th, Ti, U, V, Zn, Zr
RAD ICPES SULFUR AXIAL	ICP-ES-S	S
CVHG and CVHG DIGESTED	CVAA	Hg
AAAS and AASE	AA	As and Se
IC ANIONS	ICA	Bromide, Chloride, Fluoride, Formate, Nitrate, Nitrite, Oxalate, Phosphate, Sulfate
IC CATIONS	ICC	Ammonium
T BASE/OH/OTHER BASE EXC CO_3^{2-}	Titr.	Free OH^-
TIC	TIC	Total inorganic carbon (CO_3^{2-} is calculated from the TIC result)
TOC	TOC	Total organic carbon
RAD ICPMS	ICP-MS	Isotopic results are used to calculate Pd, Ru, Rh, Nd, Pd, Th, and U
VOA	VOA	Benzene, toluene, isopropanol, and butanol
SVOA	SVOA	TBP, Isopar, Norpar, n-paraffin, and phenol

2.1.7 Rheology Measurements

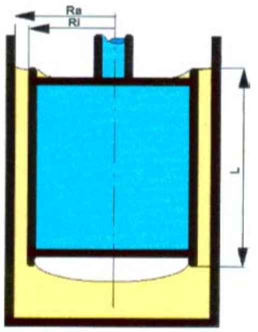
The rheological properties (consistency and yield stress) of the following samples were measured:

- The SRNL-washed SB9 qualification sample (sample HTF-51-15-81 washed to Tank Farm projections).
- A SRAT receipt sample (designated as SC-16). While this sample was not used in the SC-17 SRAT and SME demonstrations, it has the same composition as the SC-17 SRAT receipt.
- The SC-17 SRAT product.
- The SC-17 SME product.

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 provided 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 bob), sedimentation (particles settling out of the shearing zone), sample homogeneity (air voids), 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). 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.[6] 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 was not 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.

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 (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

Prior to performing the measurements, the rotors and cups were inspected for physical damage. The torque/speed sensors and temperature bath were 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 calculated viscosity, when the resulting flow curves are fitted as a Newtonian fluid, 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 (shear rate ramping down) using the Bingham Plastic rheological model, Equation 2-1, 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 these measurements, the sample remained in the cup for the 2nd measurement, due to the limited sample availability.

Equation 2-1 $$\tau = \tau_o + \mu_\infty \dot{\gamma}$$

2.2 Tank 51 Washing

Tank 51 was washed per Tank Farm plans as of October 20, 2015.[7] SRNL's planned volumes were calculated by scaling to Tank Farm volumes. For example, SRNL decant volume is calculated as:

$$SRNL\ Dec\ Vol = SRNL\ Pre\ Dec\ Vol \cdot \frac{Tank\ Farm\ Dec\ Vol}{Tank\ Farm\ Pre\ Dec\ Vol}$$

See Table 2-3 for planned Tank Farm and SRNL amounts.

SRNL washing methodology was as follows. For washes, the target water amount was added to the bulk slurry and mixed with an overhead mixer for approximately 30 minutes. The sludge was then allowed to settle to at least 1 cm below the target decant amount. Supernatant would then be pumped from the bulk sample vessel.

Table 2-3. Tank Farm and SRNL Planned Washing Volume

	Tank Farm (gal)	SRNL (mL)
SB9 Qual Sample	2.83E+05	2.02E+03
Wash L	1.96E+05	1.40E+03
After Wash L	4.79E+05	3.42E+03
Decant L	-1.72E+05	-1.23E+03
After Decant L	3.07E+05	2.20E+03
Wash M	1.33E+05	9.49E+02
After Wash M	4.40E+05	3.14E+03
Decant M	-1.34E+05	-9.59E+02
After Decant M	3.06E+05	2.18E+03
Wash N	1.31E+05	9.34E+02
After Wash N	4.36E+05	3.12E+03
Decant N	-1.97E+05	-1.41E+03
After Decant N	2.40E+05	1.71E+03

2.3 Making and Characterization of SRAT Receipt

The sludge slurry used in the SB9 SRAT and SME demonstrations was a blend of Tank 40-SB8 (HTF-40-13-119) and the SRNL-washed Tank 51 SB9 qualification sample. Tank 40 and Tank 51 were blended targeting a wt% insoluble solids ratio of 56% Tank 40 insoluble solids to 44% Tank 51 insoluble solids. This ratio was taken from the Tank Farm washing projections spreadsheet of 10/20/15 and correlates to Case 1 as recommended by SRR.[7, 8] The blend, in terms of insoluble solids is given in Table 2-4. The quantity of material blended was sufficient for all required characterization and for each SRAT cycle. The SC-16 SRAT receipt and the SC-17 SRAT receipts were created and characterized independently.

Table 2-4. Targeted Blend of Tank 40 and Tank 51

	Projected Insoluble Solids (kg)	Percent of Total
Tank 51	123,000	44.4%
Tank 40	154,000	55.6%
Total	277,000	100%

Full characterization of the SC-16 SRAT receipt was completed. Minimal characterization (analytical results for the SRAT cycle acid calculation) was done for the SC-17 SRAT receipt.

Characterization of the SC-16 material included wt% solids; density; supernatant Hg, S, and carbonate (total inorganic carbon – TIC); anions from water dilutions of slurry; and elemental composition of the total solids.

Characterization of the SC-17 SRAT receipt included weight percent solids; density; supernatant carbonate (TIC); anions from water dilutions of slurry; and Hg, Mn, Mg, and Ca in the total solids. For the SC-17 SRAT receipt, only elements in the total solids needed for the acid calculation (Hg, Mn, Mg, and Ca) were quantified.

2.4 Overview of SRAT and SME Cycles

Demonstrations of the DWPF nitric-formic flowsheet (SRAT and SME cycles) using the SRNL-prepared Tank 51 SB9 sample and Tank 40 SB8 sample were conducted following procedures in the Environmental and Chemical Process Technology Research Programs Section procedure manual.[9] A summary of each cycle is given in Table 2-5. A run plan, reviewed by the customer, was issued for each demonstration.[10-13]

Table 2-5. Planned SB9 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 target 25 wt % total solids • Reflux to steam strip Hg to less than 0.45 wt% of the total solids.	• 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 48 wt% total solids.

The SB9 qualification SRAT and SME processing was performed using a single rig, referred to as the SRAT rig, designed to process one liter of sludge. The intent of the SRAT rig is to functionally replicate the DWPF processing vessels. A glass kettle was used to replicate both the SRAT and the SME, and it was 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 was not included in SRNL Shielded Cells CPC processing. Instead, a cold finger condenser was used to cool offgas to approximately 20 °C below the ambient temperature to remove excess water before the gas reached the micro gas chromatograph (GC) for offgas characterization. The Slurry Mix Evaporator

Condensate Tank (SMECT) was represented by a sampling bottle that was used to remove condensate through the MWWT. For the purposes of this paper, the condensers and wash tank are referred to as the offgas components.

The SRAT rig was a new design for shielded cells processing. This new design is similar to the design utilized for simulant testing. The main difference between this apparatus and previous apparatuses is the use of heating rods instead of a heating mantle. See Figure 2-1 for a schematic. Similar to previous shielded Cells rigs, the nominal SRAT receipt volume is 1-L. Current plans are to utilize 4-L rig (nominal SRAT receipt volume of 2.6 L); this new sized rig was utilized in the SB9 nitric-glycolic acid demonstration.[14]

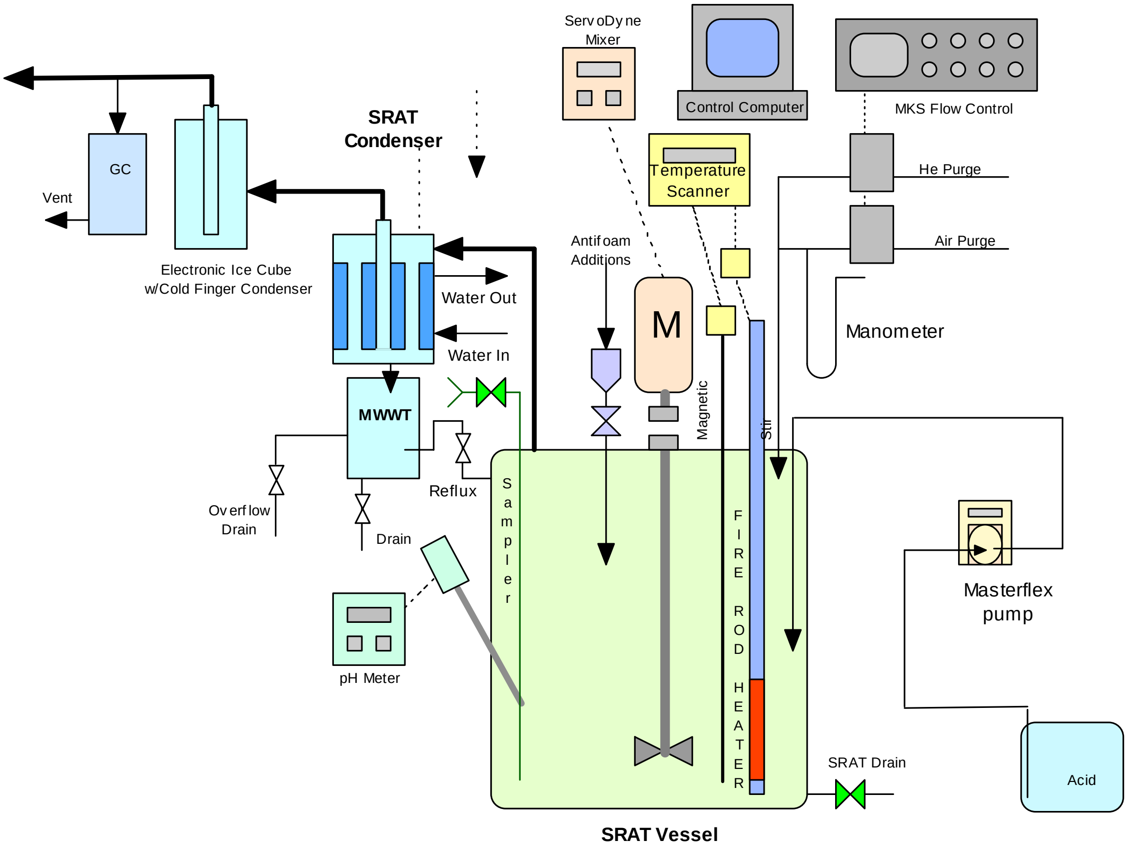


Figure 2-1. Schematic of SRAT Rig

Offgas concentrations of hydrogen, oxygen, nitrogen, nitrous oxide, and carbon dioxide were measured during the experiments using in-line instrumentation (an Agilent 3000 series micro GC). Helium was introduced at a concentration of 0.5 vol% 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 glass kettle was visually monitored to observe signs of foaming, air entrainment, rheology changes, and offgas carryover. Those observations are discussed in Section 3.2.

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 amount of each acid to add was determined using the existing DWPF acid addition equation in the 3/12/2009 version of the SRNL acid calculation spreadsheet and the most recent Reduction/Oxidation (REDOX) equation.[15] 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 simulant (non-rad) CPC testing.[16] Acid stoichiometry and reflux time were also based on CPC processing of SB9.[16]

2.5 Glass Fabrication, Analysis, and PCT

2.5.1 Glass Fabrication

In preparation for glass fabrication, approximately 120 g of SB9 SC-17 mixed SME product were divided into four portions, placed into high-purity alumina crucibles, and dried overnight in an oven at 110 °C. A single portion of dried SME product 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 added incrementally, allowing the crucible to return to temperature between each addition, resulting in a total time at the melting temperature of 3.5 hours at 1150 °C. The crucible was removed from the furnace while at temperature and bottom quenched (cooled) in a shallow pan of water, making sure that no water contacted the glass during the process. The resulting 52 g of glass appeared black and shiny, without any visible salt layer or crystals present. This fabricated glass is referred to as the SB9 SC17 Qualification Glass.

2.5.2 Compositional Analysis

The glass was crushed and ground using agate cups, balls, and caps in a mechanical pulverizing mixer mill, and then sieved to -200 mesh (<75 μm). Four replicate samples (nominally 0.25 g each) were digested remotely in a shielded cell by each of the following methods: an alkali fusion (AF)[17] at 675 °C followed by a HNO_3 uptake, and an aqua regia (AR) acid dissolution[18] in sealed vessels at 115 °C using a 3:1 by volume mixture of HCl and HNO_3 acids. A single sample of the Analytical Reference Glass (ARG-1)[19] was also prepared by both of these methods. 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. All of the prepared samples from both dissolution methods were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). A multi-element standard containing known concentrations of Al, Fe, Mn, Na, Ni, and S was also submitted with each set of samples.[**]

2.5.3 PCT

In order to meet the acceptance criterion stated in Section 1.3 of the Waste Acceptance Product Specifications (WAPS)[20], the durability of the SB9 SC17 Qualification Glass was determined by the PCT per Test Method A of ASTM International Standard C1285-14.[21] The test was performed on four replicates of the SB9 SC17 Qualification Glass. Duplicate blanks and triplicate samples of the Approved Reference Material (ARM)[22] and the EA[23] glass were also included. Samples were ground, washed, and prepared according to the standard procedure.[21] Fifteen milliliters of ASTM-type water were added to 1.5 g of glass per stainless steel vessel. The vessels were closed, tightly sealed, and placed in an oven for 7 days at 90 ± 2 °C. After 7 days, 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. The leachate from each vessel was then decanted into a clean 30 mL poly bottle. The radioactivity levels of the leachates were low enough that they could be transported to a radiochemical hood where they could be handled directly. The pH of each leachate

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[**] ICP multi-element custom solution, product number SM-744-063, High Purity Standards, Charleston, SC.

was measured, and then the leachates were filtered through a 0.45 µm filter and acidified to 1 volume percent (vol%) HNO_3. The leachates were then diluted and analyzed by ICP-AES. A multi-element standard containing known concentrations of Al, B, Fe, K, Li, Na, and Si was also submitted with the samples.[††]

2.6 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 Savannah River National Lab (SRNL) Washing Results

Following are results of the SRNL-washing and characterization of the Tank 51 SB9 qualification sample. Most of these results have previously been published.[24]

SRNL received the Tank 51 SB9 qualification sample on July 23, 2015. The sample was transferred from the Tank Farm sampler to a one gallon glass bottle. The slurry was subsampled and characterized.[25] Subsequently, the slurry was washed, mimicking Tank Farm washing; washing and decanting were volumetrically scaled to Tank Farm planned amounts. Actual SRNL-wash and decant amounts are presented in Table 3-1. SRNL was requested to track settling during washing. However, the sludge settled quickly; decants could be done in one to two days after a wash addition. SRNL-washing occurred at nearly the same time as Tank Farm washing, thus, SRNL settling rates were not needed or useful for Tank Farm washing.

Table 3-1. SRNL-Wash and Decant Volume

Initial Volume	**2.02E+03 mL**
Wash L	1.40E+03 mL
Decant L	–1.22E+03 mL
Wash M	9.49+02 mL
Decant M	– 9.59+02 mL
Wash N	9.34+02 mL
Decant N	– 1.41+03 mL
Final Volume	**1.72E+03 mL**

At the completion of washing, a subsample of the SRNL-washed slurry was then used for slurry and solids characterization. A portion of SRNL's final decant was utilized for supernatant analyses.

Presented in Table 3-2 are the density and wt% solids results. The wt% insoluble solids and soluble solids are calculated from the measured wt% total and dissolved solids.[26] Weight percent calcined solids were determined by heating dried slurry to 1100 °C, cooling, and weighing.

[††] ICP multi-element custom solution, product number SM-744-013, High Purity Standards, Charleston, SC.

Table 3-2. SRNL-Washed Tank 51 Density and wt% Solids

Property	Result	RSD, n*
Slurry Density (g/mL) T = 18 °C	1.15	5%, 4
Supernatant Density (g/mL) T = 22 °C	1.04	1%, 3
wt% Total Solids (Slurry Basis)	19.6	0.6%, 4
wt% Dissolved Solids (supernatant basis)	5.8	0.7%, 4
wt% Insoluble Solids (Slurry Basis)	14.6	NA
wt% Soluble Solids (Slurry Basis)	5.0	NA
wt% Calcined Solids (Slurry Basis)	15.3	0.7%, 4

* RSD = relative standard deviation, with n equal to the number of measurements. NA = not applicable, as result is calculated.

Presented in Table 3-3 are supernatant results. These results were determined from analysis of water-diluted supernatant (nominally 26X). Anions (with the exception of carbonate and hydroxide) were determined by Ion Chromatography (IC). Carbonate was determined from a TIC analysis by assuming all TIC was carbonate. Free hydroxide was determined from a titration. Hg was determined by a digestion technique performed by SRNL-AD followed by cold vapor atomic absorption (CVAA) (SRNL-AD method CVHG). The remaining elements were quantified by ICP-ES. The analytical methods for the various analytes are reiterated in Table 3-3.

As has been observed in previous Tank Farm supernatant samples, sulfate measured by IC is approximately 80% of the total S as measured by ICPES-S. This difference is likely due to non-sulfate species in the sludge slurry. Therefore, it is recommended that S be projected and tracked with S via ICPES-S instead of by IC, particularly if S content approaches DWPF limits in the final glass waste form.

Table 3-3. SRNL-Washed Tank 51 Supernatant Results

Analyte	Analytical Method*	Units	Result	RSD, n†
Bromide	ICA	M	<2E-02	NA
Chloride	ICA	M	<7E-03	NA
Fluoride	ICA	M	<1E-02	NA
Formate	ICA	M	<6E-03	NA
Nitrate	ICA	M	1.38E-01	0.4%, 4
Nitrite	ICA	M	2.96E-01	1%, 4
Oxalate	ICA	M	5.43E-02	0.3%, 4
Phosphate	ICA	M	<3E-03	NA
Sulfate	ICA	M	6.70E-03	3%, 4
Carbonate	TIC	M	9.87E-02	11%, 4
Free OH	Titr.	M	2.47E-01	3%, 4
Hg	CVAA	mg/L	8.78E+01	2%, 4
Na	ICP-ES	M	9.94E-01	0.4%, 4
Al	ICP-ES	M	4.89E-02	0.4%, 4
K	ICP-ES	M	2.99E-03	3%, 4
S	ICP-ES-S	M	8.49E-03	3%, 4

*ICA = ion chromatography-anions, SRNL-AD method IC ANIONS; TIC = total inorganic carbon (all inorganic carbon is assumed to be carbonate), SRNL-AD method TIC; Titr. = titration, SRNL-AD method T BASE/OH/OTHER BASE EXC CO_3^{2-}; ICP-ES = inductively coupled plasma-emission spectroscopy; ICPES-S = ICPES for S: CVAA = Cold Vapor Atomic Absorption, SRNL-AD method CVHG.
† RSD = relative standard deviation, with n equal to the number of measurements.

Oxalate in slurry was determined using both a water dilution and an acid strike, with both preparations followed by IC. Dilution by water decreases the sodium concentration, which increases the oxalate solubility, allowing sodium oxalate present in the slurry to dissolve. The acid strike method dissolves any calcium oxalate present in the slurry. However, the acids used in the method can destroy oxalate. SRNL analyzes these samples as quickly as possible to minimize analytical bias associated with acid-caused oxalate destruction. Results are presented in Table 3-4. The soluble oxalate in the supernatant (reported in Table 3-3) corresponds to 3,900 mg oxalate per kg slurry, suggesting all of the oxalate in the washed slurry was soluble.

Table 3-4. SRNL-Washed Tank 51 Slurry Oxalate Concentration

Sample Prep	Oxalate Concentration (mg/kg slurry)	RSD, n†
Water Dilution	3,880	5%, 4
Acid Dilution	3,660	1%, 3

† RSD = relative standard deviation with n = number of measurements.

Presented in Table 3-5 are elemental analyses of the total dried solids of the SRNL-washed Tank 51 sample. As described above, slurry material was digested by both AR and AF. Both digestions were submitted for ICP-ES; AR digestions were submitted for AA, CVAA, and ICP-MS. In addition to the slurry samples, reagent blanks and digestions of a reference glass of known composition were analyzed by RAD ICPES.[19] The results of the blanks and reference glass digestions were used in evaluating the slurry results:

- The element Hg was determined from AR digestions and CVAA.
- For the elements Al, Ba, Cr, Fe, Gd, Mn, Ni, and Zn, both ICP-ES measurements from AR and AF were used, because there was no significant difference between respective analytical results.
- For Ca, results from the AR digestion were used solely because the AF results were high in the reference glass digestion (likely due to a Ca impurity in the reagent chemicals).
- For Ce, the AF results were used. The results from the AF were 7X higher than the result from the AR results. No Ce was detected in the reagent blank or the reference glass, thus, this high result, compared to the AR result, is likely not due to reagent impurities. It is possible that the AR digestion did not completely digest the Ce in the sludge.
- For Na and Zr, the AR digestion results were used; alkali fusions utilize Na as a reagent and they are performed in Zr crucibles.
- For Si, results from the alkali fusion digestion were used because the AR results were low in the reference glass digestion.
- Several elements were determined from ICP-MS results from AR digestions. Nd was calculated from the sum of masses 143-146, 148, and 150. Note that Nd may be biased low; mass 142 is not included in the calculation because both Ce and Nd contribute to mass 142. Pb was calculated from the sum of masses 206 to 208. Pd was calculated from mass 105 and fission yield values from masses 105-108 and 110.[27] Rh was determined from mass 103. Ru was calculated from the sum of masses 101, 102, and 104. Th was determined from mass 232. U was calculated from the sum of masses 233-236 and 238.
- Aqua regia digestions were submitted for As and Se measurements by atomic absorption (AA). These elements were not detected.
- Supernatant results (Table 3-3) were used for Cl and F. The detection limits in the supernatant were placed on a total solids basis by utilizing the supernatant density, the slurry wt% insoluble solids, and the slurry wt% total solids. This calculation assumes that Cl and F are soluble in the slurry.
- For the remaining elements, results (or detection limits for elements not detected) were obtained from measurements performed on AR digestions.

All replicates for Fe are reported in Table 3-6 in the event that replicates are needed for fissile uncertainty analyses.

Table 3-5. SRNL-Washed Tank 51: Elemental Composition of Total (Dried) Solids

Element	Digestion, Analytical Method*	wt% of Total Solids	RSD, n[‡]
Ag	AR, ES	1.11E-02	1%, 4
Al	AR/AF, ES	6.95E+00	4%, 8
As	AR, AA	<1E-03	NA
B	AR, ES	3.64E-02	6%, 4
Ba	AR/AF, ES	6.03E-02	3%, 8
Be	AR, ES	2.20E-03	1%, 4
Ca	AR, ES	1.03E+00	0.4%, 4
Cd	AR, ES	1.73E-02	3%, 4
Ce	AF, ES	1.86E-01	5%, 4
Cl	SUP, ICA	<1E-01	NA
Co	AR, ES	8.37E-03	3%, 4
Cr	AR/AF, ES	1.20E-01	2%, 7
Cu	AR, ES	4.12E-02	0.5%, 4
F	SUP, ICA	<1E-01	NA
Fe	AR/AF, ES	1.80E+01	3%, 8
Gd	AR/AF, ES	7.32E-02	5%, 8
Hg	AR, CVAA	3.12E+00	1%, 4
K	AR, ES	1.69E-01	10%, 4
La	AR, ES	2.30E-02	1%, 4
Li	AR, ES	7.32E-02	0.4%, 4
Mg	AR, ES	2.30E-01	0.5% 4
Mn	AR/AF, ES	6.03E+00	3%, 8

Element	Digestion, Analytical Method*	wt% of Total Solids	RSD, n[‡]
Mo	AR, ES	1.42E-02	11%, 4
Na	AR, ES	1.22E+01	0.8%, 4
Nd	AR, MS[†]	1.04E-01	0.7%, 4
Ni	AR/AF, ES	7.68E-01	4%, 8
P	AR, ES	2.03E-01	9%, 4
Pb	AR, MS[†]	2.85E-02	0.9%, 4
Pd	AR, MS[†]	2.02E-03	2%, 4
Rh	AR, MS[†]	8.87E-03	0.2%, 4
Ru	AR, MS[†]	4.60E-02	3%, 4
S	AR, ES-S	1.76E-01	11%, 4
Sb	AR, ES	<7E-02	NA
Se	AR, AA	<2E-03	NA
Si	AF, ES	1.73E+00	2%, 4
Sn	AR, ES	<4E-02	NA
Sr	AR, ES	2.21E-02	0.3%, 4
Th	AR, MS[†]	8.01E-01	0.7%, 4
Ti	AR, ES	3.26E-02	0.5%, 4
U	AR, MS[†]	3.09E+00	1%, 4
V	AR, ES	<2E-03	NA
Zn	AR/AF, ES	3.10E-02	1%, 8
Zr	AR, ES	5.87E-02	32%, 4

[*] Digestion, Analytical Method: AR=Aqua Regia; AF=Alkali Fusion; ES=SRNL-AD method RAD ICPES; ES-S=SRNL-AD method RAD ICPES SULFUR AXIAL; MS=SRNL-AD method RAD ICPMS; CVHG=SRNL-AD method CVHG; AA=atomic absorption – SRNL AD methods AAAS and AASE. For Cl and F, supernatant (SUP) IC results were used; it is assumed that any F or Cl present in the slurry would be soluble.

[†] For the elements quantified by RAD ICPMS: Nd is calculated from the sum of masses 143-146, 148, and 150; Pb is calculated from the sum of masses 206 to 208; Rh is determined from mass 103; Ru is calculated by summing masses 101, 102, and 104; Pd is calculated from mass 105 and fission yields from masses 105-108 and 110; Th is determined from mass 232; and U is calculated from the sum of masses 233-236 and 238.

[‡] RSD = relative standard deviation; n = number of replicates. NA = not applicable

Table 3-6. SRNL-Washed Tank 51 Total Solids Iron Replicates

Aqua Regia Digestions	Alkali Fusion Digestions
18.1	17.3
18.4	17.4
18.5	17.7
18.5	18.1

Presented in Table 3-7 are results of various carbon measurements. Inorganic and organic carbon was detected in the slurry. No specific volatile or semivolatile compounds were identified.

Table 3-7. SRNL-Washed Tank 51 Carbon Analysis

Analysis	Result (mg/kg slurry)	RSD, n[‡]
TIC	1.04E+03	4%, 4
TOC	9.31E+02	14%, 4
VOA	<4E+01	NA
SVOA	<3E+01	NA

[‡] RSD = relative standard deviation; n = number of replicates. NA = not applicable

Presented in Table 3-8 is a comparison between projections from October 20, 2015[7] measurements of the SRNL-washed Tank 51 sample, and measurements from the Tank Farm-washed Tank 51 sample[28]. When washing, SRNL targeted sodium, wt % total solids, and wt% insoluble solids. Washing consisted only of adding water and decanting, therefore, other constituents such as nitrite, nitrate, and free hydroxide were not intentionally adjusted. As can be seen in Table 3-8, the SRNL-washed sample was comparable to both projections and the Tank Farm-washed sample with the exception of carbonate and mercury. These differences have been discussed previously.[28] In summary, the higher supernatant carbonate concentration in the SRNL-washed sample is likely due to additional absorbed carbon dioxide that reacted with the sodium hydroxide in solution to form additional carbonate during SRNL washing. The exact source of the higher mercury in the SRNL sample is more difficult to pinpoint. The increase is likely due to processing differences and the complex distribution of mercury compounds within high level waste sludge slurries.

Table 3-8. Comparison Between Projections, Measurements for SRNL-Washed Tank 51, and Tank Farm-Washed Tank 51 Supernatant

Analysis	Unit	Projection	SRNL-Washed Tank 51	Tank Farm-Washed Tank 51
Insol. Solids	wt%	13.74	14.6	13.7
Total Solids	wt%	18.97	19.6	18.9
Supernatant Density	g/mL	1.049	1.04	1.05
Sodium	M	1.006	0.994	0.956
Nitrite	M	0.320	0.296	0.342
Nitrate	M	0.139	0.138	0.140
Free OH	M	0.300	0.247	0.252
Chloride	M	0.001	<0.007	<0.007
Sulfur	M	0.007	0.00849	0.00855
Fluoride	M	0.001	<0.01	<0.01
Carbonate	M	0.033	0.0987	0.0544
Aluminum	M	0.059	0.0489	0.0532
Oxalate	M	0.048	0.0543	0.0527
Phosphate	M	0.000	<0.003	<0.003
Potassium	M	0.003	0.00299	0.00251
Hg	mg/L	52	87.8	38.8

3.2 SRAT and SME Cycle Results

3.2.1 SRAT Receipt Preparation and Characterization

Two DWPF demonstrations were completed for SB9, designated as SC-16 and SC-17. SRAT receipt material for each was independently produced and characterized, but both were created with the same source material, a blend of SRNL-washed Tank 51 and SB8 Tank 40 samples. The sample material used was HTF-51-15-81 (with subsequent washing in SRNL) and HTF-40-13-119 blended at a target ratio of 44% Tank 51 to 56% Tank 40 on an insoluble solids basis. Actual amounts of each tank used in the SRAT receipts are given in Table 3-9. Actual amounts were within 1% of targets.

Table 3-9. SC-16 and SC-17 SRAT Receipts Makeup

	SC-16		SC-17	
	Slurry Mass (g)	Insoluble Solids Basis (%)	Slurry Mass (g)	Insoluble Solids Basis (%)
SRNL-Washed Tank 51	609.5	44.7	658.43	45.0
Tank 40	926.8	55.3	987.43	55.0
Total	1536.3	100	1645.86	100

For the SRAT receipts, a full characterization, per the TTR[1], of the SC-16 SRAT receipt was completed, while only analyses needed for SRAT processing was completed for the SC-17 SRAT receipt Note that there are additional comparisons between SC-16 and SC-17 SRAT products. See for example Table 3-19 and Table 3-20.

Presented in Table 3-10 are density and weight percent solids results of the two SRAT receipt samples.

Table 3-10. SC-16 and SC-17 SRAT Receipt Density and wt% Solids

Property	SC-16 Average (RSD, n)	SC-17 Average (RSD, n)*
Slurry Density (g/mL) 17	1.11 (0.8%, 4)	1.13 (0.8%, 4)
Supernatant Density (g/mL)	1.05 (0.3%, 4)	1.05 (0.2%, 4)
wt% Total Solids (Slurry Basis)	18.5 (0.1%, 3)	18.7 (0.2%, 4)
wt% Dissolved Solids (Supernatant Basis)	6.1, (4.2%, 3)	6.6 (0.2%, 4)
wt% Insoluble Solids (Slurry Basis)	13.2 (NA)	13.0 (NA)
wt% Soluble Solids (Slurry Basis)	5.3 (NA)	5.7 (NA)
wt% Calcined Solids (Slurry Basis)	14.4 (0.6%, 2)	14.7 (0.5%, 4)

* RSD = relative standard deviation, with n equal to the number of measurements. NA = not applicable, as result is calculated.

Table 3-11 shows requested supernatant results. Because supernatant Hg and S concentrations are not needed for acid calculations, these analytes were not quantified for the SC-17 SRAT receipt supernatant. However, Hg and S are expected to be similar between SC-16 and SC-17 SRAT receipt since they were prepared at the same Tank 40/Tank 51 ratio with the same source material. See Table 3-9, Table 3-10,

Table 3-12, Table 3-15, and Table 3-16 for comparisons between the SC-16 and SC-17 SRAT receipt make-up and composition.

Table 3-11. SC-16 and SC-17 SRAT Receipt Supernatant Results

		SC-16		SC-17	
Analyte	**Analytical Method**	**Average**	**RSD, n**[*]	**Average**	**RSD, n**[*]
S (mg/L)	ICP-ES-S	5.02E+02	2%, 4	NM	NA
Hg (mg/L)	CVAA	2.32E+01	11%, 4	NM	NA
Inorganic Carbon (mg/L)	TIC	1.79E+03	8%, 4	1.70E+03	3%, 4
Organic Carbon (mg/L)	TOC	1.14E+03	4%, 4	9.37E+02	11%, 4
Free OH (mg/L)	Titr	3.10E-01	NA, 1	NM	NA

[*] RSD = relative standard deviation; n = number of measurements. NM = not measured; NA = not applicable.

Anions from slurry dilutions, particularly nitrite, nitrate, and total base, are key acid calculation inputs. Results are presented in Table 3-12.

Table 3-12. SC-16 and SC-17 SRAT Receipt Slurry Dilution Results (Slurry Basis)

		SC-16		SC-17	
Analyte	**Analytical Method**	**Average**	**RSD, n**[†]	**Average**	**RSD, n**[†]
Bromide (mg/kg)	ICA	<1.1E+03	NA	<1.2E+03	NA
Chloride (mg/kg)	ICA	<2.3E+02	NA	<2.3E+02	NA
Fluoride (mg/kg)	ICA	<2.3E+02	NA	<2.3E+02	NA
Formate (mg/kg)	ICA	<2.3E+02	NA	<2.3E+02	NA
Nitrate (mg/kg)	ICA	7.14E+03	0.8%, 4	7.32E+03	0.9%, 4
Nitrite (mg/kg)	ICA	1.30E+04	0.9%, 4	1.37E+04	0.7%, 4
Oxalate (mg/kg)	ICA	2.65E+03	0.5%, 4	2.61E+03	0.6%, 4
Phosphate (mg/kg)	ICA	<2.3E+02	NA	<2.3E+02	NA
Sulfate (mg/kg)	ICA	1.02E+03	1.1%, 4	1.09E+03	1%, 4
Ammonium (mg/kg)	ICC	<2.3E+01	NA	NM	NA
Inorganic Carbon (mg/kg)	TIC	1.36E+03	4%, 4	1.60E+03	1%, 4
Organic Carbon (mg/kg)	TOC	7.72E+02	18%, 4	7.71E+02	3%, 4
Free OH (mol/L)	Titr	3.08E-01	8%, 4	1.59E-01	6%, 4
Total Base (mol/L)	Titr-Cells[*]	4.39E-01	4%, 3	0.469	4%, 3

[*] Titr-Cells = in cells titration of slurry to pH 7.

[†] RSD = relative standard deviation; n = number of measurements. NM = not measured; NA = not applicable.

Presented in Table 3-13 are elemental analyses, on a total dried solids basis, of the SC-16 SRAT receipt. As described above, slurry material was digested by both AR and AF. Both digestions were submitted for ICP-ES; AR digestions were submitted for CVAA, ICP-MS, and AA. In addition to the slurry samples, reagent blanks and digestions of a reference glass of known composition were analyzed by ICP-ES.[19] The results of the blanks and reference glass digestions were used in evaluating the slurry results:

- The element Hg was determined from AR digestions and CVAA.
- For Al, results from the AF digestions were used. Results from this digestion were higher than results from AR, suggesting undigested aluminum compounds in the AR.
- For the elements Ba, Fe, Mn, Ni, Sr, and Zn, both ICP-ES measurements from AR and AF were used because there was no significant difference between respective analytical results.
- For Ca, results from the AR digestion were used because Ca was detected in the AF blank (likely due to a Ca impurity in the reagent chemicals).
- For Ce, the AF results were used. The results from the alkali fusions were 5X higher than the result from the AR results. No Ce was detected in the reagent blank or the reference glass, thus, this high result, compared to the AR result, is likely not due to reagent impurities. It is possible that the AR digestion did not completely digest the Ce in the sludge.
- For Na and Zr, the AR digestion results were used; AF utilize Na as a reagent and they are performed in Zr crucibles.
- For Si, results from the AF digestion were used because the AR results were low in the reference glass digestion.
- Several elements were determined from ICP-MS results from AR digestions. Nd was calculated from the sum of masses 143-146, 148, and 150. Note that Nd may be biased low; mass 142 is not included in the calculation because both Ce and Nd contribute to mass 142. Pd was calculated from mass 105 and fission yield values from masses 105-108 and 110.[27] Rh was determined from mass 103. Ru was calculated from the sum of masses 101, 102, and 104. Th was determined from mass 232. U was calculated from the sum of masses 233-236 and 238.
- AR digestions were submitted for As and Se measurements by AA. These elements were not detected.
- Slurry results (Table 3-12) were used for Cl and F. The detection limits in the slurry were placed on a total solids basis by dividing by the slurry wt% total solids. This calculation assumes that Cl and F are soluble in the slurry.
- For the remaining elements, results (or detection limits for elements not detected) were obtained from measurements performed on AR digestions.
- All replicates of Fe are presented in Table 3-14.

Table 3-13. SC-16 Elemental Composition of Total Solids (Dried)

Element	Digestion, Analytical Method*	Total Solids (wt%)	RSD, n[‡]
Ag	AR, ES	<2E-03	NA
Al	AF, ES	7.50E+00	3.5%, 4
As	AR, AA	<8.4E-03	NA
B	AR, ES	<1E-02	NA
Ba	AR/AF, ES	7.54E-02	5.1%, 8
Be	AF, ES	1.88E-03	4.4%, 4
Ca	AR, ES	1.00E+00	0.4%, 4
Cd	AR, ES	1.78E-02	1.9%, 4
Ce	AF, ES	1.83E-01	10.6%, 4
Cl	WD, IC	<1.2E-01	NA
Co	AR, ES	9.91E-03	4.7%, 4
Cr	AF, ES	1.17E-01	23.4%, 4
Cu	AF, ES	4.16E-02	3.8%, 4
F	WD, IC	<1.2E-01	NA
Fe	AR/AF, ES	1.73E+01	3.0%, 8
Gd	AR, ES	8.93E-02	0.3%, 4
Hg	AR, CVAA	1.97E+00	6.7%, 4
K	AR, ES	<1E-01	NA
La	AR, ES	4.36E-02	0.1%, 4
Li	AR, ES	5.36E-02	3.3%, 4
Mg	AR, ES	2.29E-01	0.3%, 4
Mn	AR/AF, ES	5.74E+00	2.7%, 8
Mo	AR, ES	6.72E-03	6.9%, 4
Na	AR, ES	1.37E+01	0.5%, 4
Nd	AR, MS[†]	1.49E-01	0.6%, 4
Ni	AR/AF, ES	1.30E+00	4.1%, 8
P	AR, ES	1.64E-01	4.7%, 4
Pb	AR, ES	3.73E-02	3.6%, 4
Pd	AR, MS[†]	2.53E-03	0.5%, 4
Rh	AR, MS[†]	1.25E-02	0.9%, 4
Ru	AR, MS[†]	5.63E-02	2.4%, 4
S	AR, ES-S	2.47E-01	4.2%, 4
Sb	AR, ES	<6E-02	NA
Se	AR, AA	<1.7E-02	NA
Si	AF, ES	1.39E+00	3.9%, 4
Sn	AR, ES	<4E-02	NA
Sr	AR/AF, ES	2.80E-02	3.2%, 8
Th	AR, MS[†]	8.28E-01	0.5%, 4
Ti	AR, ES	2.22E-02	0.3%, 4
U	AR, MS[†]	3.37E+00	1.0%, 4
V	AR, ES	<1E-03	NA
Zn	AR/AF, ES	2.98E-02	5.5%, 8
Zr	AR, ES	6.28E-02	21.6%, 4

[*] Digestion, Analytical Method: AR=Aqua Regia; AF=Alkali Fusion; ES=SRNL-AD method RAD ICPES; ES-S=SRNL-AD method RAD ICPES SULFUR AXIAL; MS=SRNL-AD method RAD ICPMS; CVHG=SRNL-AD method CVHG; AA=atomic absorption – SRNL AD methods AAAS and AASE. For Cl and F, slurry water dilution (WD) IC results were used; it is assumed that any F or Cl present in the slurry would be soluble.

[†] For the elements quantified by RAD ICPMS: Nd is calculated from the sum of masses 143-146, 148, and 150; Pb is calculated from the sum of masses 206 to 208; Rh is determined from mass 103; Ru is calculated by summing masses 101, 102, and 104; Pd is calculated from mass 105 and fission yields from masses 105-108 and 110; Th is determined from mass 232; and U is calculated from the sum of masses 233-236 and 238.

[‡] RSD = relative standard deviation; n = number of replicates. NA = not applicable

Table 3-14. SC-16 Total Solids Iron Replicates)

Aqua Regia Digestions	Alkali Fusion Digestions
17.1	17.2
17.1	17.2
17.1	18.6
17.0	17.4

As stated above, only analyses needed for acid calculation were completed for the SC-17 SRAT receipt, requiring only an AR digestion for Hg, Mn, Mg, and Ca. Several other elements are reported with the ICP-ES scan. Those detected at greater than 1% are listed in Table 3-15 below with comparison to the SC-16 results. As can be seen, the two samples are comparable with respect to elemental composition. The largest difference is Hg. It should be noted that the typical SRNL-AD one sigma uncertainty is 10% for Ca, Fe, Mg, Mn, Na, and Ni and 20% for Hg.

Table 3-15. Comparison of SC-16 and SC-17 Major Elements in Solids Digestions

	SC-16			SC-17		
Element	**Digestion, Analytical Method***	**Total Solids (wt%)**	**RSD, n[‡]**	**Digestion, Analytical Method***	**Total Solids (wt%)**	**RSD, n[‡]**
Ca	AR, ES	1.00E+00	0.4%, 4	AR, ES	9.89E-01	0.0%, 4
Fe	AR/AF, ES	1.73E+01	3.0%, 8	AR, ES	1.74E+01	0.4%, 4
Hg	AR, CVAA	1.97E+00	6.7%, 4	AR, CVAA	2.18E+00	11.8%, 4
Mg	AR, ES	2.29E-01	0.3%, 4	AR, ES	2.25E-01	0.3%, 4
Mn	AR/AF, ES	5.74E+00	2.7%, 8	AR, ES	5.68E+00	0.5%, 4
Na	AR, ES	1.37E+01	0.5%, 4	AR, ES	1.39E+01	0.5%, 4
Ni	AR/AF, ES	1.30E+00	4.1%, 8	AR, ES	1.67E+00	0.5%, 4

[*] Digestion, Analytical Method: AR=Aqua Regia; AF=Alkali Fusion; ES=SRNL-AD method RAD ICPES; CVAA=SRNL-AD method CVHG.

[‡] RSD = relative standard deviation; n = number of replicates.

3.2.2 Acid Calculation Inputs and Outputs

Using characterization results, acid demand for the SRAT cycles was calculated. SRNL calculates acid demand using the Koopman Minimum Acid Equation and then compares those results to the Hsu Acid Equation used by DWPF.[29, 30] Inputs such as excess acid and anion destruction/conversion were determined from experiments with simulated sludge.[16] The split between nitric and formic acids was determined using the latest REDOX equation.[15]

Table 3-16 presents acid calculation inputs for both SC-16 and SC-17, including composition of the SRAT receipt material. As can be seen, the two SRAT receipts are similar with respect to analytical results with the exception of slurry TIC (carbonate) and Hg. Table 3-17 shows the acid calculation outputs, including the equivalent Hsu (DWPF) excess acid. The differences in acid calculation inputs, particularly carbonate, result in an increase of approximately 5% in acid demand using the Koopman equation and 9% using the Hsu equation. The large difference in conflux times between the two runs is due to the larger measured Hg value in the SC-17 sample.

Table 3-16. Acid Calculation Inputs

Input	SC-16	SC-17	Unit
SRAT Receipt Mass	1,212	1,420	g slurry
SRAT Receipt Volume	1,092	1,257	mL slurry
SRAT Receipt Total Solids	18.5	18.7	wt%
SRAT Receipt Calcined Solids	14.4	14.7	wt%
SRAT Receipt Insoluble Solids	13.2	13.0	wt%
SRAT Receipt Density	1.11	1.13	kg/L slurry
SRAT Receipt Supernatant Density	1.05	1.05	kg/L supernate
SRAT Receipt Nitrite	13,000	13,700	mg/kg slurry
SRAT Receipt Nitrate	7,140	7,320	mg/kg slurry
SRAT Receipt Oxalate	2,650	2,610	mg/kg slurry
SRAT Receipt Slurry TIC (treated as carbonate)	1,360	1,600	mg/kg slurry
Fresh Supernatant TIC (treated as carbonate)	1,785	1,700	mg/L supernate
SRAT Receipt Hydroxide (base equivalents) pH = 7	0.432	0.469	mol/L slurry
SRAT Receipt Manganese	7.38	7.26	wt% calcined basis
SRAT Receipt Hg	1.97	2.18	wt% dry basis
SRAT Receipt Magnesium	0.294	0.287	wt% calcined basis
SRAT Receipt Calcium	1.28	1.26	wt% calcined basis
Conversion of Nitrite to Nitrate in SRAT Cycle	25	25	gmol NO3-/100 gmol NO2-
Destruction of Nitrite in SRAT and SME Cycle	100	100	% of starting nitrite destroyed
Destruction of Formic Acid Charged in SRAT	25	25	% formate converted to CO2 etc.
Destruction of Oxalate	0	0	% of total oxalate destroyed
Percent Acid in Excess Stoichiometric Ratio (Koopman Min Acid Eq) – for Total Acid to Add Determination	120	120	%
Water to Rinse Sample Bottle	50	50	g
Total Water Added to Flush Nitric and Formic Acid Lines/Bottles	20	20	g
SRAT Product Target Solids	25	25	%
REDOX Target	0.15	0.15	Fe^{+2} /∑Fe
Antifoam Addition prior to Formic Acid Addition	1.5	1.5	gal (DWPF Scale)
Antifoam Addition prior to Initial SRAT Boiling	1.5	1.5	gal (DWPF Scale)
Antifoam Addition During SRAT Boiling	1	1	gal (DWPF Scale)
Water Flush Volume after each Antifoam Addition	100	100	gal (DWPF Scale)
SRAT Air Purge	186	186	scfm
DWPF Acid Addition Rate	2	2	gallons per minute
Nitric Acid Molarity	10.47	10.47	Molar
Formic Acid Molarity	23.57	23.57	Molar
SRAT Boil Up Rate	5000	5000	lbs/hr
SRAT Hg Product Target Concentration	0.45	0.45	wt% total solids basis
SRAT Steam Stripping Factor	750	750	(g steam/g Hg)

Table 3-17. Acid Calculation Outputs

Output	SC-16	SC-17	Unit
Hsu Total Stoichiometric Acid Required	1.20	1.31	mol/L
Koopman Minimum Stoichiometric Acid Required	1.33	1.40	mol/L
Total Acid to Add based on Koopman Equation Stoichiometric Factor	1.60	1.68	mol/L
Stoichiometric Hsu Acid Equation	133	128	%
Fraction of Formic Acid for REDOX Target	0.903	0.902	moles formic acid / mole total acid
Nitric Acid Volume Required	16	19.8	ml
Formic Acid Volume Required	67	80.7	ml
SRAT Dewater Mass	369	431	g
Prototypical Nitric Acid Feed Time	43	47	min
Prototypical Formic Acid Feed Time	176	193	min
Minimum SRAT Conflux Time	1,283	1,580	min

Table 3-18 shows DWPF processing parameters and the SRNL scaled values used in the demonstrations. The volume based scale factor was calculated by dividing a 6,000 gal DWPF SRAT receipt by the SRNL SRAT receipt volume and correcting for units.

Table 3-18. SRAT Cycle DWPF Processing and SRNL Scale Factors

	DWPF Scale	SC-16	SC-17
Volume Based Scale Factor	NA	20,800	18,070
SRAT Air Purge	186 scfm	253 sccm	291 sccm
Acid Addition Rate	2 gpm	0.36 mL/min	0.42 mL/min
Boil Up Rate	5,000 lb/hr	1.82 g/min	2.09 g/min
Antifoam Addition (prior to prior to Formic Acid Addition and prior to boiling)	1.5 gal	0.27 g	0.31 g
Antifoam Addition (during boiling)	1 gal	0.18 g	0.21 g
Antifoam Flush	100 gal	18.20 g	20.95 g

NA = not applicable.

3.2.3 SRAT Cycle

Two SRAT cycles were completed, designated as SC-16 and SC-17. Parameters used were as specified above (purge rates, acid addition amounts and rates, conflux time). In both runs, antifoam was added prior to formic acid addition and prior to boiling – 1.5 gal DWPF equivalent antifoam followed by 100 gal DWPF equivalent water after each antifoam addition.

For the SC-16 run, the vessel was initially mixed at a rate of 250 rpm. Torque as measured by the mixer controller increased dramatically if mixing rate was increased. During reflux, the mixer motor was adjusted, allowing an increase in mixing rate. Therefore, it is concluded that the high torque was not a result of thick material. When emptying the vessel after the cycle, it was discovered that the agitator shaft had broken. It is likely the shaft broke at the end of the run or during mixing while emptying the vessel. If mixing were lost during the cycle, the heating rods would likely have fouled and overheated. The relatively low mixing rate and lack of knowledge of the precise time when the agitator failed contributed to the decision to repeat the run.

As a result of the issues with the SRAT cycle mixing and agitator failure, the SB9 qualification SRAT run was repeated with SC-17. For run SC-17, a new vessel, including heating rods and agitator, was tested, installed, and used. Agitation rate was maintained at 700 rpm with no torque issues.

Table 3-19 includes density and Wt% solids results for SC-16 and SC-17. In both runs, Wt% solids were less than the target of 25%. For SC-16, there were some issues with sampling and the entire vessel was emptied to replace the agitator. For SC-17, an unplanned antifoam addition and flush was added due to observed foaming. The addition was equivalent to a DWPF antifoam volume of 1 gal., followed by a DWPF volume of 100 gal. of flush water. Per discussion with the customer, it was decided that the water from the flush did not need to be removed. Therefore, the additional water contributed to the lower-than-planned total solids.

Table 3-19. SC-16 and SC-17 SRAT Product Density and wt% Solids

	SC-16		**SC-17**	
Property	**Average**	**RSD, n**[*]	**Average**	**RSD, n**[*]
Slurry Density (g/mL)	1.13	0.8%, 4	1.15	1.3%, 4
Supernatant Density (g/mL)	1.09	0.4%, 4	1.09	0.1%, 4
wt% Total Solids (Slurry Basis)	21.5	2.5%, 4	22.9	0.5%, 4
wt% Dissolved Solids (Supernatant Basis)	13.1	0.1%, 4	13.2	0.4%, 4
wt% Soluble Solids (Slurry Basis)	11.8	NA	11.7	NA
wt% Insoluble Solids (Slurry Basis)	9.7	NA	11.2	NA
wt% Calcined Solids (Slurry Basis)	14.8	3.0%, 4	16.5	0.7%, 4

[*] RSD = relative standard deviation, with n equal to the number of measurements. NA = not applicable, as result is calculated.

Presented in Table 3-20 are anions, carbon, and pH of the SC-16 and SC-17 SRAT products. Anions and carbon were determined from water dilutions of slurry. The results of the two runs are very similar. In addition to a water dilution, the CQ method was done with the SC-17 SRAT product and results are shown in Table 3-21. As expected, the oxalate value from the CQ method was significantly higher than from water dilutions. The formate result from the CQ method was lower than the result from the water dilution. This was not seen during the method development. However, the method was specifically developed for the forthcoming nitric-glycolic acid DWPF flowsheet.[4] Therefore, SRNL only recommends use of the CQ method for oxalate in the current (nitric-formic acid) flowsheet.

Table 3-20. SC-16 and SC-17 SRAT Product Slurry Dilution Results

Analyte	Analytical Method	SC-16 Average (mg/kg)	SC-16 RSD, n*	SC-17 Average (mg/kg)	SC-17 RSD, n*
Fluoride	ICA	<2.2E+02	NA	<2.4E+02	NA
Formate	ICA	5.89E+04	0.8%, 4	6.03E+04	2%, 4
Chloride	ICA	<2.2E+02	NA	<2.4E+02	NA
Nitrite	ICA	<2.2E+02	NA	<2.4E+02	NA
Nitrate	ICA	2.59E+04	0.5%, 4	2.53E+04	1%, 4
Phosphate	ICA	<2.2E+02	NA	<2.4E+02	NA
Sulfate	ICA	1.10E+03	2%, 4	9.30E+02	1%, 4
Oxalate	ICA	4.50E+02	7%, 4	4.07E+02	4%, 4
Bromide	ICA	<1.1E+03	NA	<1.2E+03	NA
Ammonium	ICC	<2.2E+02	NA	<2.4E+02	NA
Total Carbon	TIC+TOC	1.78E+04	2%, 4	1.67E+04	0.3%, 4
Inorganic Carbon	TIC	1.73E+03	4%, 4	2.08E+03	2%, 4
Organic Carbon	TOC	1.60E+04	2%, 4	1.46E+04	0.6%, 4
S	ICP-ES-S	4.33E+02	4%, 4	5.05E+02	5%, 4

* RSD = relative standard deviation, with n equal to the number of measurements.

Table 3-21. SC-17 SRAT Product CQ Method Results

Analyte	Average (mg/kg)	RSD, n*
Fluoride	<1.2E+03	NA
Formate	4.98E+04	2%, 4
Chloride	<1.2E+03	NA
Nitrite	<1.2E+03	NA
Nitrate	2.43E+04	1%, 4
Phosphate	<1.2E+03	NA
Sulfate	1.23E+03	3%, 4
Oxalate	2.86E+03	2%, 4
Bromide	<6.0E+03	NA

* RSD = relative standard deviation, with n equal to the number of measurements.

Presented in Table 3-22 are elemental analyses, on a total dried solids basis, of the SC-17 SRAT product. As described above, slurry material was digested by both AR and AF. Both digestions were submitted for RAD ICPES; AR digestions were submitted for CVAA and RAD ICPMS. In addition to the slurry samples, reagent blanks were also submitted.

- The element Hg was determined from AR digestions and the SRNL-AD CVAA method.
- For the elements Al, Cr, Fe, La, Mg, Mn, Sr, and Zn, both RAD ICPES measurements from AR and AF were used because there was no significant difference between respective analytical results; percent difference was calculated to be less than 10%.
- For Ca, Ba, and V results from the AR digestion were used because these elements were detected in the AF blank.
- For K, Li, Na and Zr, the AR digestion results were used; AF utilize Na (which may have trace amounts of Li and K) as a reagent and they are performed in Zr crucibles.

- For Si, results from the AF digestion were used.
- Several elements were determined from RAD ICPMS results from AR digestions. Nd was calculated from the sum of masses 143-146, 148, and 150. Note that Nd may be biased low; mass 142 is not included in the calculation because both Ce and Nd contribute to mass 142. Pd was calculated from mass 105 and fission yield values from masses 105-108 and 110.[27] Rh was determined from mass 103. Ru was calculated from the sum of masses 101, 102, and 104. Th was determined from mass 232. U was calculated from the sum of masses 233-236 and 238.
- Slurry results (Table 3-12) were used for Cl and F. The detection limits in the slurry were placed on a total solids basis by dividing by the slurry wt% total solids. This calculation assumes that Cl and F are soluble in the slurry.
- For the remaining elements, results (or detection limits for elements not detected) were obtained from measurements performed on AR digestions.

Table 3-22. SC-17 SRAT Product Elemental Composition of Total Solids (Dried)

Element	**Digestion, Analytical Method***	**Total Solids (wt%)**	**RSD, n[‡]**
Ag	AR, ES	<2E-03	NA
Al	AR/AF, ES	6.19E+00	2.5%, 8
B	AR, ES	7.11E-02	0.6%, 4
Ba	AR, ES	6.82E-02	0.6%, 4
Be	AR, ES	5.83E-04	2.6%, 4
Ca	AR, ES	9.57E-01	0.8%, 4
Cd	AR, ES	1.78E-02	3.5%, 4
Ce	AR, ES	<7.1E-03	NA
Co	AR, ES	8.53E-03	2.7%, 4
Cr	AR/AF, ES	8.74E-02	5.8%, 8
Cu	AR, ES	2.91E-02	0.9%, 4
Fe	AR/AF, ES	1.52E+01	2.8%, 8
Gd	AR, ES	5.61E-02	2.1%, 4
Hg	AR, CVAA	7.89E-01	0.8%, 4
K	AR, ES	1.01E-01	9.5%, 4
La	AR/AF, ES	4.09E-02	13.5%, 8
Li	AR, ES	3.74E-02	1.0%, 4
Mg	AR/AF, ES	2.03E-01	4.6%, 8
Mn	AR/AF, ES	5.22E+00	2.6%, 8
Mo	AR, ES	6.95E-03	17.4%, 4
Na	AR, ES	1.32E+01	0.3%, 4
Nd	AR, MS[†]	1.32E-01	0.5%, 4
Ni	AR, ES	1.37E+00	0.5%, 4
P	AR, ES	1.44E-01	4.5%, 4
Pb	AR, ES	3.76E-02	8.0%, 4
Pd	AR, MS[†]	2.27E-03	0.8%, 4
Rh	AR, MS[†]	1.07E-02	2.3%, 4
Ru	AR, MS[†]	5.28E-02	0.5%, 4
S	AR, ES-S	2.53E-01	6.5%, 4
Sb	AR, ES	<5E-02	NA
Si	AF, ES	1.21E+00	4.0%, 4
Sn	AR, ES	<3E-02	0.0%, 4
Sr	AR/AF, ES	2.62E-02	5.0%, 8
Th	AR, MS[†]	7.31E-01	0.6%, 4
Ti	AR, ES	<3E-02	NA
U	AR, MS[†]	2.97E+00	0.6%, 4
V	AR, ES	<1E-03	NA
Zn	AR/AF, ES	2.75E-02	6.7%, 4
Zr	AR, ES	3.52E-02	17.5%, 4

[*] Dig, Analytical Method: AR=Aqua Regia; AF=Alkali Fusion; ES= ICP-ES; ES-S=ICP-ES low sulfur method; MS=ICP-MS; AA=Atomic Absorption; WD=water dilution; IC=Ion Chromatography

[†] .For the elements quantified by MS: Nd is calculated from the sum of masses 143-146, 148, and 150; Ru is calculated by summing masses 101, 102, and 104; Rh is determined from mass 103; Pd is calculated from mass 105 and fission yields; Th is determined from mass 232; and U is calculated from the sum of masses 233 to 236 and 238.

[‡] RSD = relative standard deviation; n = number of replicates. NA = not applicable.

Figure 3-1 shows the pH profile during the SC-17 SRAT cycle. As expected, pH drops as the vessel is heated and continues to drop as nitric acid is added. During formic acid addition, pH continues to drop to a minimum of 4.2 and then slowly increases during boiling.

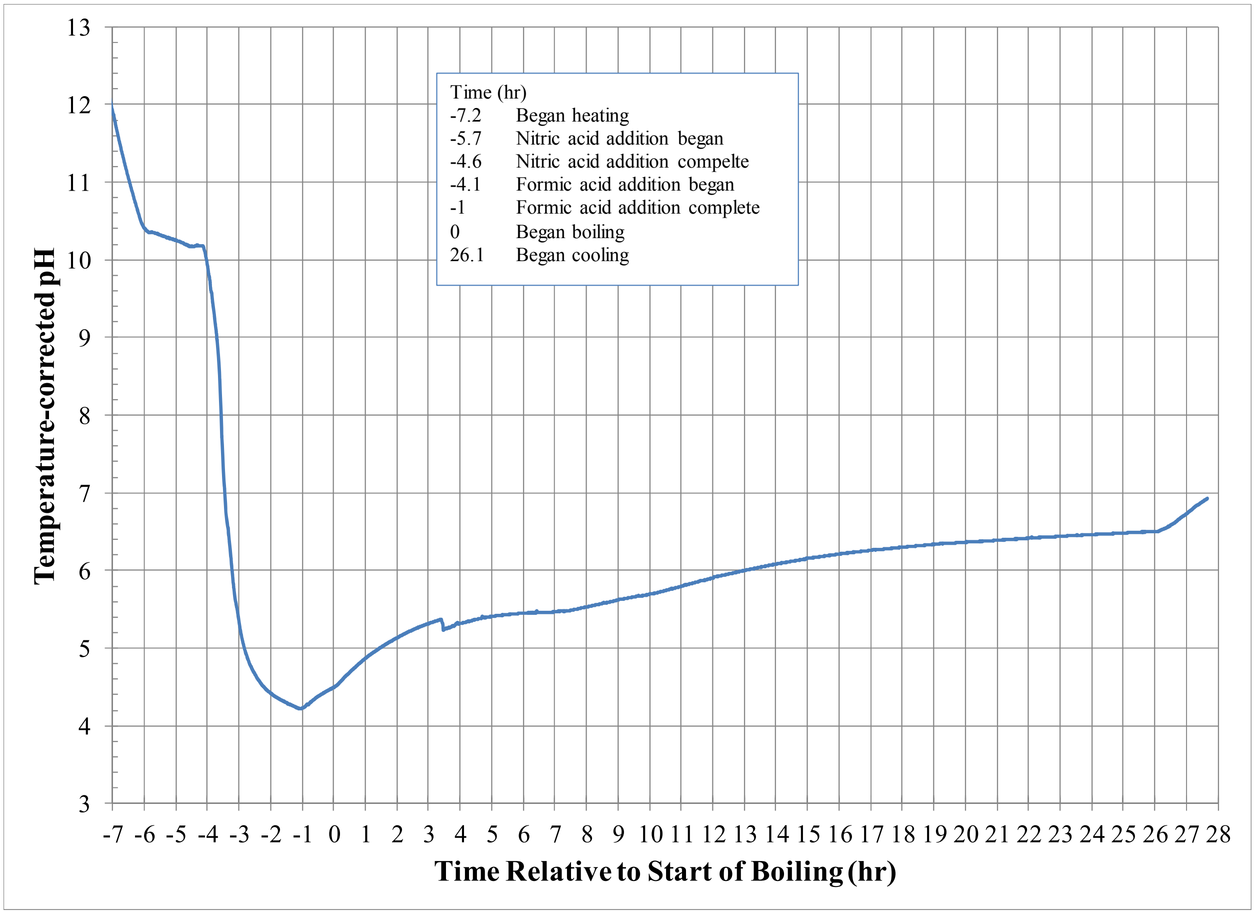

Figure 3-1. SC-17 SRAT Cycle pH Profile

3.2.4 SC-17 SRAT Cycle Anion Destruction and Conversion

Formate destruction and conversion of nitrite to nitrate are two inputs/assumptions to the acid calculation. These inputs are compared to actual results in Table 3-23. The measured results are based on analysis of water diluted slurry (Table 3-20).

Table 3-23. SC-17 SRAT Cycle Comparison of Predicted and Measured Anion Destruction and Conversion

Input	Predicted, used in acid calc (%)	Measured (%)
Conversion of Nitrite to Nitrate in SRAT Cycle	25	33
Destruction of Nitrite in SRAT and SME cycle	100	100
Destruction of Formic acid charged in SRAT	25	11

3.2.5 SME Cycles

The SC-16 SME cycle began with a new agitator and heating rods. The vessel bottom from the SRAT cycle was re-used. The amount of frit to be added was calculated based on the amount of SRAT material added to the vessel plus an estimate of material remaining in the vessel after emptying. Near the beginning of the SME cycle, a heating rod overheated, possibly due to fouling. The PC control software did not reduce power to the heating rods as expected (this issue was corrected prior to the SC-17 SRAT and SME cycles). A decision was made to continue the run with only one heating rod. As a result of running with only one heating rod, the target boil up rate was not attained. At the conclusion of the run, the wt% solids were measured to be 40 wt%, less than the target 48 wt%. The cause of under concentration was due to an error when transferring dewater calculations to the run directions. As a result of these issues, the SB9 qualification SME run was repeated with SC-17.

The SC-17 SME cycle was performed as planned. SME feed consisted of SRAT product minus SRAT product analytical samples. The same vessel, heating rods, agitator, etc., used in the SRAT cycle were used in the SME cycle. The SC-16 and SC-17 scale factors and processing parameters are given in Table 3-24. SRNL scaled to a 6,000 gallon DWPF SRAT product. As can be seen in the scale factors, there was significantly more SC-17 material than SC-16 material.

Table 3-24. SME Cycle DWPF Processing and SRNL Scale Factors

	DWPF Scale	SC-16	SC-17
Volume Based Scale Factor	NA	38,800	24,500
SME Air Purge	72 scfm	53 sccm	83.2 sccm
Boil Up Rate	5,000 lb/hr	0.97 g/min	1.54 g/min
Canister Decontamination Water	1000 gal	97.51 g	154 g
Antifoam Addition Prior to Decon Dewater	0.5 gal	0.05 g	0.077 g
Antifoam Addition Prior to Process Frit Addition	1 gal	0.1 g	0.154 g
Antifoam Flush (water added after any antifoam addition)	100 gal	9.75 g	15.4 g

NA = not applicable.

Presented in Table 3-25 are the SC-17 SME product density and wt% solids results. The target wt% total solids was 48%[11, 16] A result slightly higher than the target is likely due to loss of water from small leaks in the experimental apparatus and analytical uncertainty. The SC-17 SME product slurry anions, ammonium, and carbon results are given in Table 3-26.

Table 3-25. SC-17 SME Product Density and wt% Solids

Property	Result	RSD, n*
Slurry Density (g/mL)	1.47	0.3%, 4
Supernatant Density (g/mL)	1.12	0.1%, 4
wt% Total Solids (Slurry Basis)	49.6	0.2%, 4
wt% Dissolved Solids (supernatant basis)	18.6	0.5%, 4
wt% Insoluble Solids (Slurry Basis)	38.1	NA
wt% Soluble Solids (Slurry Basis)	11.5	NA
wt% Calcined Solids (Slurry Basis)	43.0	0.6%, 4

* RSD = relative standard deviation, with n equal to the number of measurements. NA = not applicable, as result is calculated.

Table 3-26. SC-17 SME Product Slurry Dilution Results

Analyte	Analytical Method	Average (mg/kg)	RSD, n
Fluoride	ICA	<1.1E+02	NA
Formate	ICA	5.22E+04	5%, 4
Chloride	ICA	<1.1E+02	NA
Nitrite	ICA	<1.1E+02	NA
Nitrate	ICA	2.40E+04	3%, 4
Phosphate	ICA	<1.1E+02	NA
Sulfate	ICA	1.01E+03	2%, 4
Oxalate	ICA	3.96E+02	18%, 4
Bromide	ICA	<5.4E+02	NA
Ammonium	ICC	<1.1E+02	NA
Total Carbon	TIC+TOC	1.60E+04	NA-calculated
Inorganic Carbon	TIC	7.55E+02	20%, 4
Organic Carbon	TOC	1.52E+04	0.7%, 3

Figure 3-2 shows the pH profile during the SC-17 SME cycle. As expected, the pH dropped as the vessel was heated. The pH was nearly constant during decontamination water additions and removals. The pH dropped slightly with the addition of formic acid with the frit and then increased during concentration.

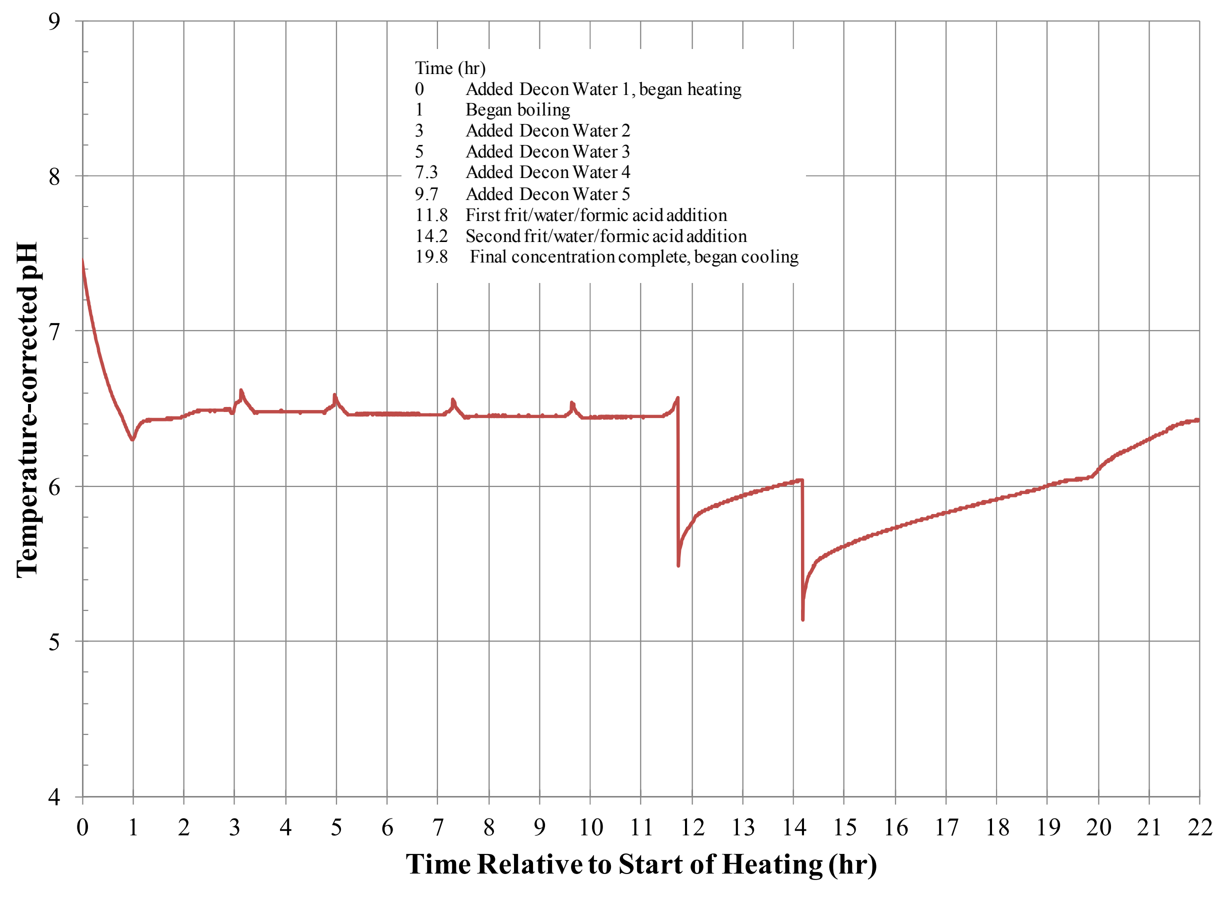

Figure 3-2. SC-17 SME Cycle pH Profile

3.2.6 *SRAT and SME Cycles Hg and S Solubility*

Presented in Table 3-27 are SRAT and SME product Hg and S results. The soluble Hg and S were determined from dilutions of supernatant and then placed on a slurry basis using the wt% insoluble solids. The total Hg and S were determined from AR digestions of slurry samples.

As seen in Table 3-27, S solubility was nearly the same between the SRAT and SME. Hg was not detected in either the SRAT or SME supernatant. Finally, the SRAT product Hg on a total solids basis is 0.79 wt% of the total solids, much higher than the target, indicating lower steam stripping than expected.

Table 3-27. SME Product Hg and S

	SRAT Product	SME Product
Soluble Hg (mg/kg slurry)	<2.3E-01	<1.4E-01
Total Hg (mg/kg slurry)	1.81E+03	4.32E+2
Percent Soluble	0%	0%
Soluble S (mg/kg slurry)	4.43E+02	4.17E+02
Total S (mg/kg slurry)	5.78E+02	5.72E+02
Percent Soluble	77%	73%

3.2.7 SRAT and SME Cycle Offgas Results

As discussed above, due to processing issues encountered during the first qualification effort for SB9 (designated as SC-16), SRNL repeated the DWPF SRAT SME cycles (designated as SC-17).[2] The offgas results of this second demonstration have previously been published[31, 32] and are repeated here with minor edits.

Figure 3-3 contains a plot of gasses produced during the SC-17 SRAT cycle and measured by GC: carbon dioxide (CO_2), N_2O, and H_2. Carbon dioxide and N_2O are reported in vol%. Hydrogen is adjusted to the DWPF scale and is reported in pounds per hour (lb/hr). The adjustment is based on scaling of the initial laboratory SRAT slurry volume to 6,000 gallons of DWPF scale SRAT receipt. See Table 3-18 for the volume based scale factor.

Hydrogen was not measured above the limit of quantification of the GC until after boiling was achieved. There was a delay after the completion of acid addition of about 45 minutes to correct an issue with the antifoam addition port. Thus, boiling was achieved at approximately 1 hour from the end of acid addition. A first peak in H_2 concentration (typically attributed to rhodium catalysis) was noted approximately 1.7 hours after completion of acid addition. A second, larger peak in H_2 concentration (typically attributed to ruthenium catalysis) occurred in the later portion of the SRAT cycle reflux period and may not have attained a crest prior to the endpoint of the SRAT cycle. The measured peak H_2 concentration in the SRAT of 0.0539 lb/hr on the DWPF scale (prior to application of analytical uncertainty) was far below the DWPF limit of 0.65 lb/hr.[33]

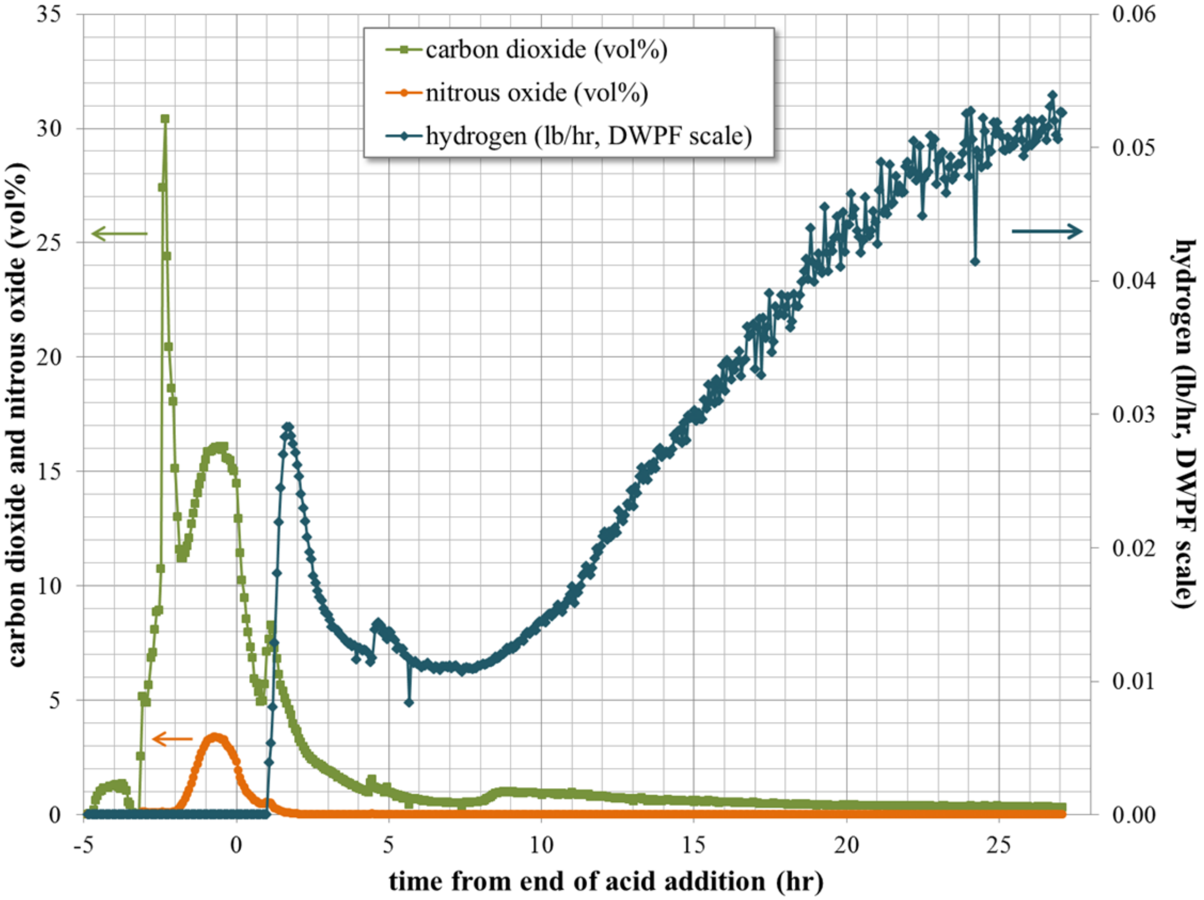

Figure 3-3. SC-17 SRAT Cycle Offgas Quantified by GC

The peak production and release of CO_2 and N_2O occurred during formic acid addition. Prior to the application of uncertainty, the measured peak concentrations of CO_2 and N_2O were 30.4 vol% and 3.39 vol%, respectively. The measured peak N_2O concentration was below the DWPF limit of 15 vol%.[33]

Figure 3-4 and Figure 3-5 contain plots of gasses produced during the SME cycle and measured by GC: CO_2, N_2O, and H_2. Carbon dioxide and N_2O are reported in vol%. Hydrogen is adjusted to the DWPF scale and is reported in lb/hr. The adjustment is based on scaling of the initial laboratory SME slurry volume to 6,000 gallons of DWPF scale SME receipt.[11] See Table 3-24 for the volume based scale factor.

The measured peak H_2 concentration in the SME of 0.095 lb/hr on the DWPF scale (prior to application of analytical uncertainty) was below the DWPF limit of 0.223 lb/hr.[33] The peak production and release of CO_2 and N_2O during the SME was upon the initiation of boiling. Prior to the application of uncertainty, the measured peak concentrations of CO_2 and N_2O were 12.0 vol% and 0.42 vol%, respectively.

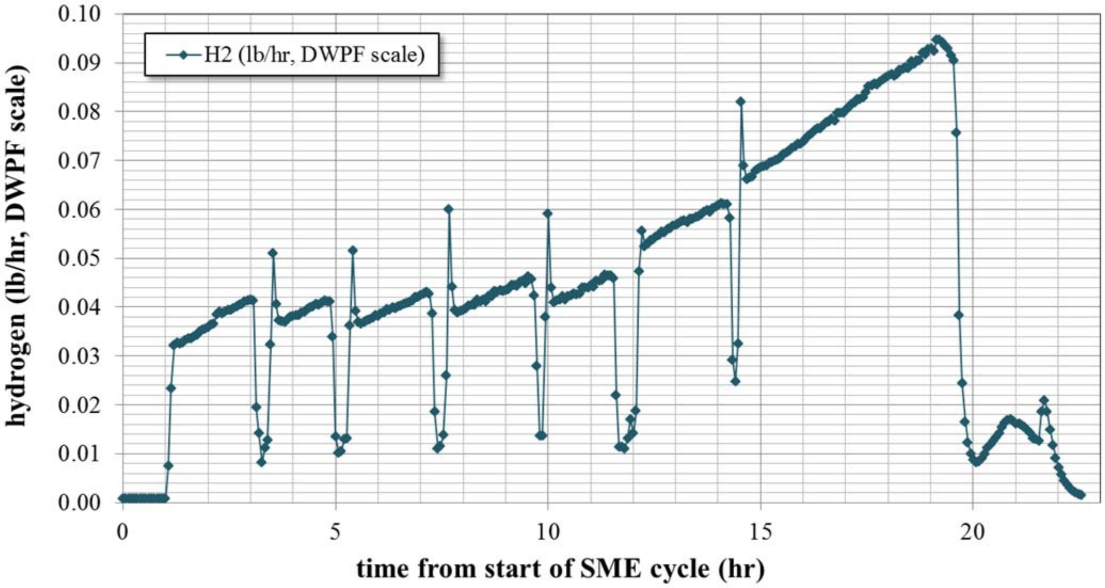

Figure 3-4. SC-17 SME Cycle Hydrogen Quantified by GC

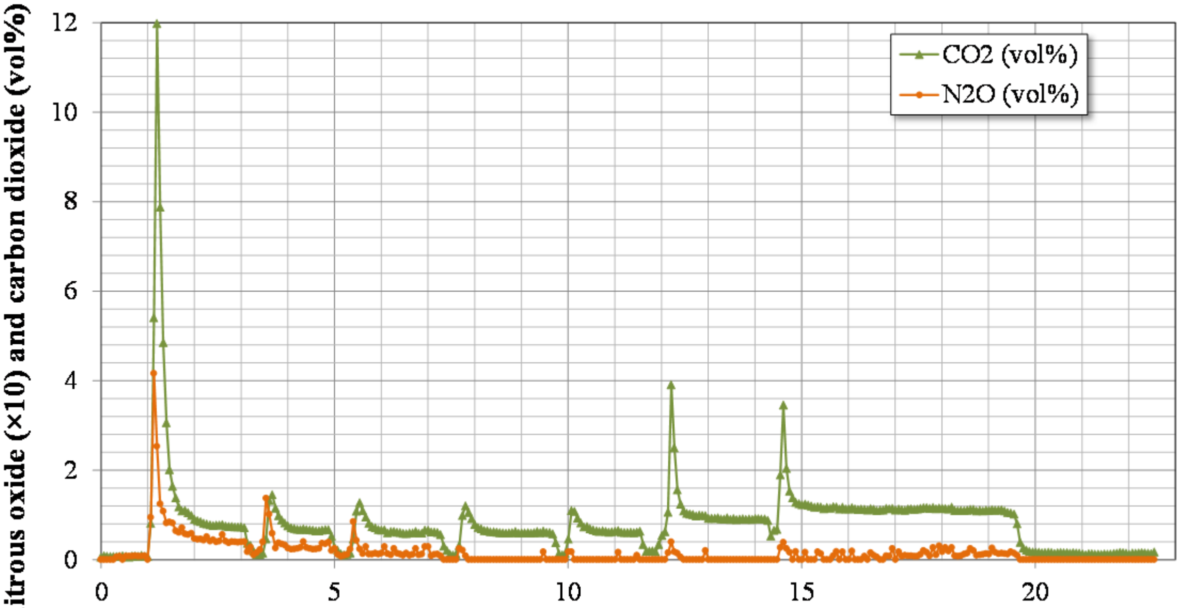

Figure 3-5. SC-17 SME Cycle Carbon Dioxide and Nitrous Oxide Quantified by GC

SRNL performed an uncertainty analysis in order to place an upper bound (with 95% confidence) on the reported maximum H_2 and N_2O generation rates and maximum H_2 and N_2O concentrations encountered during the SB9 demonstration. Several factors contribute to uncertainty in the H_2 and N_2O measurements and generation rates for the SB9 shielded cells qualification run. The factors considered in this analysis include the following:

- Uncertainty in the air purge flowrate
- Uncertainty in the helium (He) tracer flowrate

- Uncertainty in the H_2 and N_2O concentrations in the GC calibration gasses
- Uncertainty due to variance in GC measurements
- Bias due to drift in the calibration during the run

The MKS Instruments, Inc., flow meter / flow controllers used for the flowrates of the air purge and He tracer had tolerances of 2% of full scale and were tracked in the Measurement and Test Equipment (M&TE) program. The standards used to calibrate the GC for concentration of H_2, He, and other gasses have an analysis certification to 2% of the reported concentrations. The variance in the GC measurements is estimated from the data collected during the instrument calibration check. The bias due to the calibration drift is handled by processing the calibration of the GC in a manner to provide conservatively large H_2 and N_2O generation measurements. The pre- and post-run calibration checks are compared, and the sets of calibration data are used that would maximize the instrument-measured H_2 and N_2O concentrations and minimize the He tracer concentration.

Gas of known concentration (calibration gas) is run through the GC and multiple measurements are made. A response factor is determined as the relationship between the integrated chromatogram area with the concentration in the gas standard ($C^{std}/area^{std}$). The response factors are then used to determine concentration of gasses in the SRAT and SME offgas. Uncertainty can be applied to the H_2 and N_2O concentrations by the following equations (Equations 3-1 through 3-3). The concentrations of H_2, N_2O, and He ($C_{\mathrm{H_2}}$, $C_{\mathrm{N_2O}}$, and C_{He}, respectively) are in mole fraction (mol/mol). The flowrate of air and He purges at lab scale (F_{air} and F_{He}, respectively) and the SRNL purge rates ($F_{\mathrm{SRNL\text{-}purge}}$) are in standard cubic centimeters per minute (sccm). While the ratio ($F_{\mathrm{SRNL\text{-}purge}}$ / ($F_{\mathrm{air}} + F_{\mathrm{He}}$)) is by definition equal to 1 (the sum of the air and He flowrates are set to equal the SRNL purge rate), the equations allow one to account for the uncertainty in the air and He flow controllers. The GC response for H_2 is in terms of an area ($area_{H_2}$). Equation 3-1 is written in terms of H_2, but similar relationships are also formed for N_2O and He (Equation 3-2 and Equation 3-3, respectively). Although He is used as a tracer rather than being produced as an offgas, it is necessary to include it in the uncertainty analysis because it is used in the calculation of the H_2 and N_2O generation rates.

Equation 3-1
$$C_{\mathrm{H_2}} = area_{\mathrm{H_2}}\left(\frac{C^{std}_{\mathrm{H_2}}}{area^{std}_{\mathrm{H_2}}}\right)\left(\frac{F_{\mathrm{SRNL\text{-}purge}}}{F_{\mathrm{air}} + F_{\mathrm{He}}}\right)$$

Equation 3-2
$$C_{\mathrm{N_2O}} = area_{\mathrm{N_2O}}\left(\frac{C^{std}_{\mathrm{N_2O}}}{area^{std}_{\mathrm{N_2O}}}\right)\left(\frac{F_{\mathrm{SRNL\text{-}purge}}}{F_{\mathrm{air}} + F_{\mathrm{He}}}\right)$$

Equation 3-3
$$C_{\mathrm{He}} = area_{\mathrm{He}}\left(\frac{C^{std}_{\mathrm{He}}}{area^{std}_{\mathrm{He}}}\right)\left(\frac{F_{\mathrm{SRNL\text{-}purge}}}{F_{\mathrm{air}} + F_{\mathrm{He}}}\right)$$

The values calculated by Equation 3-4 and Equation 3-5 are the DWPF scale generation rates of H_2 and N_2O, respectively, in lb/hr scaled from the results of the shielded cells SB9 qualification run. The flowrate of air and He purges at lab scale (F_{air} and F_{He}, respectively) and the flowrate of purge at DWPF scale ($F_{\mathrm{DWPF\text{-}purge}}$) are all in sccm. The DWPF scale flowrates are based on 186 standard cubic feet per minute (scfm) purge in the SRAT and 72 scfm in the SME. MW values are the molecular weights of the gasses and A_{constant} is a combination of multiple unit conversions (including the ideal gas molar volume at 70 °F and 1 atmosphere). Per these equations, the He tracer concentration is used to correct the offgas data for the unknown total offgas flowrate.

Equation 3-4 $$H_{2(\text{DWPF-scale})}(\text{lb/hr}) = \frac{C_{H_2}}{C_{He}} * F_{He} * \frac{F_{\text{DWPF-purge}}}{F_{air} + F_{He}} * MW_{H_2} * A_{\text{constant}}$$

Equation 3-5 $$N_2O_{(\text{DWPF-scale})}(\text{lb/hr}) = \frac{C_{N_2O}}{C_{He}} * F_{He} * \frac{F_{\text{DWPF-purge}}}{F_{air} + F_{He}} * MW_{N_2O} * A_{\text{constant}}$$

Results were processed using the statistical package GUM Workbench[34] to propagate the uncertainty in the measurements to the calculated results. Table 3-28 and Table 3-29 contain the results of the uncertainty analysis for the DWPF scale maximum concentrations and generation rates, respectively. The expanded uncertainties are the half-widths of the two-sided 95% confidence intervals (CI) on the average analytical measurements adjusted to DWPF scale. The upper 95% bounds are the sum of the averages and the half-widths of the CI. Thus, these upper 95% bounds are the maximum values adjusted for the uncertainty based on the SB9 qualification demonstration.

For a gas, vol% is considered to be equivalent to 100% multiplied by (mol/mol).

Table 3-28. Maximum Concentrations of H_2 and N_2O Observed During the SC-17 SRAT Cycle

	Maximum Concentration, prior to applying uncertainty (vol%)	Expanded Uncertainty, half-width of 95% CI (vol%)	Maximum Concentration, upper 95% bound (vol%)
SRAT H_2	0.089	0.014	0.103
SRAT N_2O	3.39	0.25	3.64
SME H_2	0.404	0.099	0.503
SME N_2O	0.42	0.11	0.53

Table 3-29. Peak DWPF Scale Generation Rates of H_2 and N_2O Observed During the SC-17 SRAT Cycle)

	DWPF Scale Rate, prior to applying uncertainty (lb/hr)	Expanded Uncertainty , half-width of 95% CI (lb/hr)	DWPF Scale Rate, upper 95% bound (lb/hr)
SRAT H_2	0.0539	0.0086	0.0625
SRAT N_2O	51.6	3.9	55.5
SME H_2	0.095	0.023	0.118
SME N_2O	2.24	0.59	2.83

3.2.8 Condensate Analytical Results

Presented in Table 3-30 are antifoam degradation product and ammonium results from the SC-17 SRAT and SME cycles. Note that hexamethyldisiloxane (HMDSO) was not detected in any of the samples.

Table 3-30. SC-17 SRAT and SME Cycle Antifoam Degradation Products and Ammonium in Condensates

Sample Description	HMDSO (mg/L)	Trimethylsilanol (mg/L)	Propanal (mg/L)	Ammonium (mg/L)
Taken during SRAT processing				
Pre Formic Acid Addition	<0.25	<0.25	<0.25	NM
Post Formic Acid Addition	<0.25	3.5	36	NM
End of Concentration	<0.25	18	2.2	NM
End of Cycle	<0.25	14	28	NM
Taken from collected SRAT and SME condensates				
SRAT Dewater	<0.25	27	0.48	<10
SRAT MWWT	<0.25	16	0.97	18
SME Dewater 1	<0.25	7.5	1.5	36
SME Dewater 5	<0.25	7.4	2	25
Frit Dewater 1	<0.25	29	5.9	<10
Frit Dewater 2	<0.25	35	2.8	<10
Final SME Dewater	<0.25	15	2.4	<10

3.2.9 Retained Hydrogen

Figure 3-6 shows the release of hydrogen at the start of agitation for the SRAT cycle (prior to heating and acid addition). The sludge was mixed and added to the vessel one day before the SRAT cycle. On the day of the SRAT cycle, the purge was started (the rate was scaled to a 6,000 gal SRAT receipt - see Table 3-18). Agitation was initiated and hydrogen was detected by the GC in the first gas sample after initiation of agitation. In less than 25 minutes, hydrogen was no longer detected. Note that heating was initiated 60 minutes after agitation began, and no hydrogen was detected during heating or acid addition.

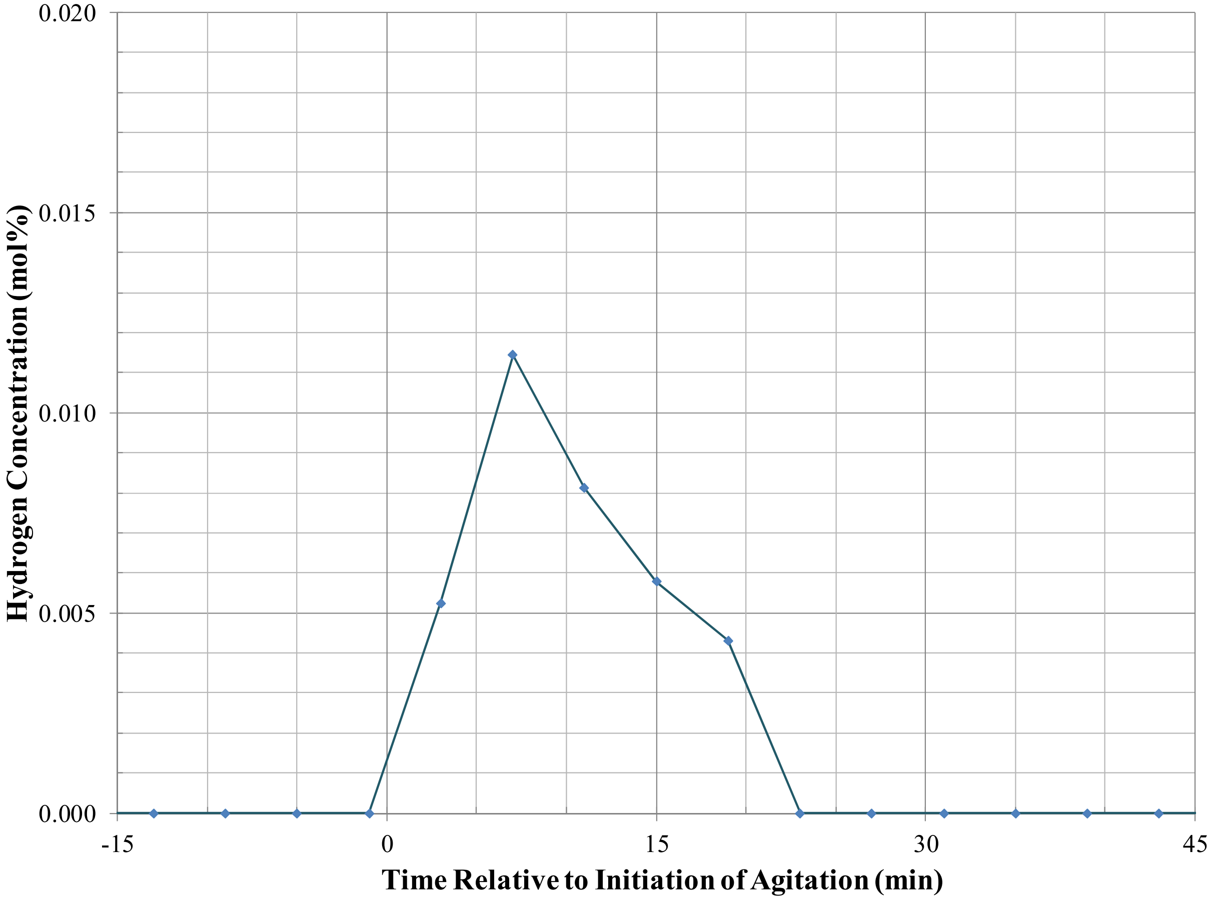

Figure 3-6. SC-17 SRAT Cycle Retained Hydrogen Released Before Initiation of Heating and Acid Addition

Figure 3-7 shows the release of retained hydrogen for the SME cycle. On the day of the SME cycle, the purge was started (the rate was scaled to a 6,000 gal SRAT product – see Table 3-24). Vessel agitation was initiated approximately three hours before heating began. Retained hydrogen was then released and detected until approximately 0.5 hours before initiating of heating. At approximately 1 hour after heating was initiated, boiling began and hydrogen concentration began increasing. This hydrogen is likely primarily catalytic.

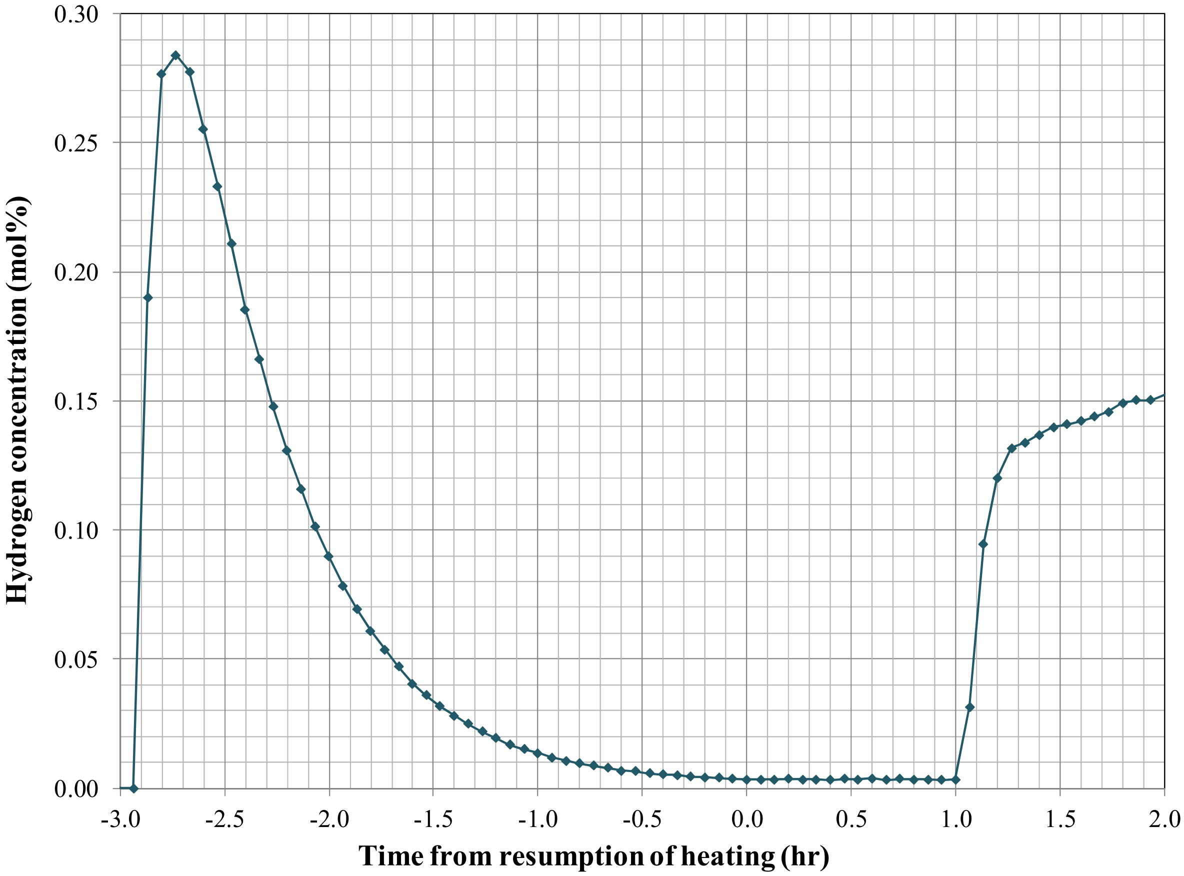

Figure 3-7. SC-17 SME Cycle Retained Hydrogen Released Prior to Initiation of Heating

3.2.10 Rheology

Presented in Table 3-31 are rheology measurement results of four SB9 related samples. DWPF design basis values are included for reference.[35] The first sample is the SB9 qualification sample (HTF-51-15-81) washed at SRNL.[24] The second sample is the SC-16 SRAT receipt sample, which is comparable to the material used in the SC-17 SB9 SRAT/SME cycles. The third and fourth samples are results from the SB9 run (SC-17) SRAT and SME products. Flow curves are presented in Appendix A. Both the SRAT and SME products results are outside of design basis values. Thus, DWPF may not be able to concentrate SRAT and SME products to the same levels as this qualification demonstration. This is further discussed in the SB9 processing recommendations.[36]

Table 3-31. Rheology of Sludge Batch 9 Related Samples

Sample Description	Consistency (cP)	Yield Stress (Pa)
Washed Sludge Slurry Design Basis	*4-12*	*2.5-10*
SB9 Qualification Sample (HTF-51-15-81 washed at SRNL)	6.9	4.6
SC-16 SRAT Receipt	7.2	4.2
SRAT Slurry Design Basis	*5-12*	*1.5-5*
SC-17 SRAT Product	12	7.7
Melter Feed Design Basis	*10-40*	*2.5-15*
SC-17 SME Product	93	43

3.3 Glass Fabrication, Analysis, and PCT

3.3.1 Compositional Analysis

Table 3-32 shows a comparison of the published[19] and measured composition of the ARG-1 glass. The preparation method along with the percent difference is also noted for each analyte. Oxides having concentrations greater than 0.25 wt% are within 10% of the published values, which demonstrates the effectiveness of the specified preparation method. While the sum of oxides[‡‡] is within the DWPF Product Composition Control System (PCCS) limit (95-105 wt%), the measured SiO_2 is approximately 2.6 wt% lower than the published value, which does account for a lower sum of oxides for the measured glass (97.74 wt%) versus the published value of 100.08 wt%.

Table 3-33 provides a comparison of the measured multi-element standard solution results (measured with glass samples prepared by the indicated preparation method) to the reference values. All of the measured values are within 10% of the reference values, thereby confirming the accuracy of the ICP-AES measurements.

[‡‡] The totals shown in the table were calculated using more significant figures than shown and were rounded to two decimal places.

Table 3-32. Published and Measured Oxide Values for the ARG-1 Glass

Oxide	Published (wt%)[19]	Measured (wt%)	Difference (%)	Preparation Method
Al_2O_3	4.73 ± 0.022	4.72	-0.1	AR
B_2O_3	8.67 ± 0.040	8.69	0.3	AR
BaO	0.088 ± 0.001	0.09	-2.6	AR
CaO	1.43 ± 0.009	1.48	3.7	AR
Cr_2O_3	0.093 ± 0.001	0.09	-1.6	AR
CuO	0.004 ± 0.000	<0.005	15.2	AR
Fe_2O_3	14.0 ± 0.073	14.00	0.0	AF
K_2O	2.71 ± 0.016	2.81	3.6	AR
Li_2O	3.21 ± 0.015	3.31	3.3	AF
MgO	0.86 ± 0.005	0.86	0.3	AR
MnO_2	2.31 ± 0.012	2.33	0.7	AR
Na_2O	11.5 ± 0.023	11.55	0.5	AR
NiO	1.05 ± 0.006	1.02	-2.8	AR
P_2O_5	0.22 ± 0.011	0.24	10.4	AR
SiO_2	47.9 ± 0.157	45.35	-5.3	AF
SrO	0.0037 ± 0.000	0.003	-6.0	AR
TiO_2	1.15 ± 0.007	1.10	-4.5	AF
ZnO	0.02 ± 0.000	0.02	20.7	AR
ZrO_2	0.13 ± 0.005	0.05	-59.8	AR
Total	100.08	97.74	----	----

Table 3-33. Multi-Element Standard Solution Results (SM-744-063)

Element	Reference Value (mg/L)	Measured Value (mg/L)	Difference (%)	Glass Sample Preparation Method
Al	50	51.6	3.2	AR
Fe	50	49.4	-1.2	AF
Mn	20	20.5	2.5	AR
Ni	10	9.96	-0.4	AR
Na	150	151	0.7	AR
S	10	10.3	3.0	AR

Table 3-34 presents the measured elemental and oxide compositions of the SB9 SC-17 Qualification Glass, along with the preparation method and percent relative standard deviation (RSD) for each analyte. The measured value for each analyte is the average of four replicates. A majority of the components have percent RSD values that are less than 5%, which indicates minimal scatter amongst the four replicates. The sum of oxides is 100.72 wt%, which is within the DWPF PCCS limit (95-105 wt%).

Table 3-34. SB9 SC-17 Qualification Glass Composition

Element	Average Measured (wt%)	Oxide	Average Measured (wt%)	RSD (%)	Preparation/Analytical Method
Al	3.15	**Al_2O_3**	5.95	2.4	AR/ICP-ES
B	1.59	**B_2O_3**	5.10	2.6	AR/ICP-ES
Ba	0.03	**BaO**	0.04	2.5	AR/ICP-ES
Ca	0.47	**CaO**	0.66	2.7	AR/ICP-ES
Ce	0.01	**Ce_2O_3**	0.02	5.2	AR/ICP-ES
Cr	0.03	**Cr_2O_3**	0.05	2.2	AR/ICP-ES
Cs	0.001	**Cs_2O**	0.001	4.5	AF ICP-MS
Cu	0.04	**CuO**	0.05	3.8	AR/ICP-ES
Fe	7.23	**Fe_2O_3**	10.33	0.4	AF/ICP-ES
K	0.14	**K_2O**	0.17	14.3	AR/ICP-ES
La	0.02	**La_2O_3**	0.02	2.1	AR/ICP-ES
Li	1.93	**Li_2O**	4.14	0.5	AF/ICP-ES
Mg	0.11	**MgO**	0.18	2.8	AR/ICP-ES
Mn	2.63	**MnO**	3.39	2.6	AR/ICP-ES
Mo	0.004	**MoO_3**	0.01	9.1	AR/ICP-ES
Na	9.91	**Na_2O**	13.35	3.0	AR/ICP-ES
Nd	0.05	**Nd_2O_3**	0.06	----	AF ICP-MS
Ni	0.54	**NiO**	0.68	2.5	AR/ICP-ES
P	0.11	**P_2O_5**	0.26	2.3	AR/ICP-ES
Pb	0.02	**PbO**	0.02	4.9	AR/ICP-ES
S	0.09	**SO_4**	0.27	4.3	AR/ICP-ES-S
Si	25.05	**SiO_2**	53.59	1.3	AF/ICP-ES
Th	0.36	**ThO_2**	0.41	3.1	AR/ICP-ES
Ti	<0.12	**TiO_2**	<0.21	----	AF/ICP-ES
U	1.41	**U_3O_8**	1.66	2.9	AR/ICP-ES
Y	0.01	**Y_2O_3**	0.01	1.4	AF/ICP-MS
Zn	0.02	**ZnO**	0.02	3.7	AR/ICP-ES
Zr	0.05	**ZrO**	0.07	2.5	AR/ICP-ES
----	----	**Total**	100.72	----	----

3.3.2 PCT

Based on the measured masses of the PCT vessels before and after the 7-day test, there was negligible water loss, which was within the bounds allowed by the ASTM procedure. The measured elemental concentrations in the blanks were reported as less than detectable and thus confirmed to be insignificant (less than 10% of the concentration of the respective element in the sample leachates). The leachate concentrations of B, Li, Na, and Si for the ARM reference glass were within the Thermodynamic Hydration Energy Model (THERMO) control chart limits[22], which demonstrates that the test was completed under control. Table 3-35 provides a comparison of the measured multi-element standard solution results to the reference values. The nominal range of acceptability for comparing the ICP-AES results to the reference values is typically ± 10%. The measured value for Na is slightly greater than 10% of the reference value. However, as explained below, the deviation will not impact the conclusions of this study.

Table 3-35. Multi-Element Standard Solution Results (SM-744-013)

Element	Reference Value (mg/L)	Measured Value (mg/L)	Difference (%)
Al	4	4.25	6.3
B	20	20	0
Fe	4	4.31	7.7
K	10	10	0
Li	10	10.2	2.0
Na	81	89.4	10.4
Si	50	53.7	7.4

Results from the PCT are shown in Table 3-36 including standard deviations and percent RSD values. Values of pH are also shown for comparison. Normalized concentrations (NC_i in units of $g_{\text{wasteform}}/L_{\text{leachant}}$ for element "*i*") of the SB9 SC-17 Qualification Glass were calculated based on the measured composition (Table 3-34) using the average of the common logarithms of the leachate concentrations. The density of the SB9 SC-17 Qualification Glass was not measured. However, the measured densities of the SB9 variability study glasses[37] were in the range of 2.67-2.74 g/cm^3 and are comparable to the assumed glass waste form density of 2.7 g/cm^3, which was used as the basis for the NC_i calculation as discussed in all previous versions of ASTM C1285.[38-41] Thus, no adjustment for the density of glasses was necessary in normalizing the PCT results from this study.

The average normalized concentrations of B, Li, and Na for the SB9 SC-17 Qualification Glass are more than an order of magnitude lower than the corresponding values for the EA glass, which satisfies the acceptability criterion stated in Section 1.3 of the WAPS.[§§,23] If the measured Na values in the leachate are adjusted to account for the apparent approximately 10.4% high bias observed for the multi-element standard solution (Table 3-35), then all of the measured Na leachate values would be decreased by approximately 10%, which would subsequently reduce the values of NC_{Na} for the SB9 SC-17 Qualification Glass shown in Table 3-36. Thus, the average NC_{Na} for the SB9 SC-17 Qualification Glass would still be more than an order of magnitude lower than the corresponding value for EA glass.

Although not specifically listed in the WAPS, the NC_{Si} values for the SB9 SC-17 Qualification Glass and EA glass are also shown for comparison. The NC_U value shown for the SB9 SC-17 Qualification Glass is

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[§§] The normalized releases of B, Li, and Na must be at least two standard deviations below the reported releases for these elements in the EA glass.

less than the NC_B value (see Table 3-36), indicating that that the release of radioactive uranium is bounded by the boron release.

Table 3-36. PCT Results for ARM, EA and the SB9 SC-17 Qualification Glass

Glass ID	**NC_B (g/L) Std. Dev. (g/L) RSD (%)**	**NC_{Li} (g/L) Std. Dev. (g/L) RSD (%)**	**NC_{Na} (g/L) Std. Dev. (g/L) RSD (%)**	**NC_{Si} (g/L) Std. Dev. (g/L) RSD (%)**	**NC_U (g/L) Std. Dev. (g/L) RSD (%)**	**pH**
ARM[a]	0.50 0.01 2.4	0.61 0.02 2.7	0.59 0.01 1.2	0.31 0.01 2.2	----	10.1
EA[b]	16.69 1.2 7	9.56 0.7 7	13.35 0.9 7	3.9 0.4 10	----	11.9
SB9-Qual[c]	0.72 0.01 1.7	0.82 0.01 1.0	0.99 0.02 1.7	0.57 0 0.7	0.42 0.02 5.6	10.7

[a] Normalized concentrations are the average of 3 replicates.
[b] Published values[23]
[c] Normalized concentrations are the average of 4 replicates.

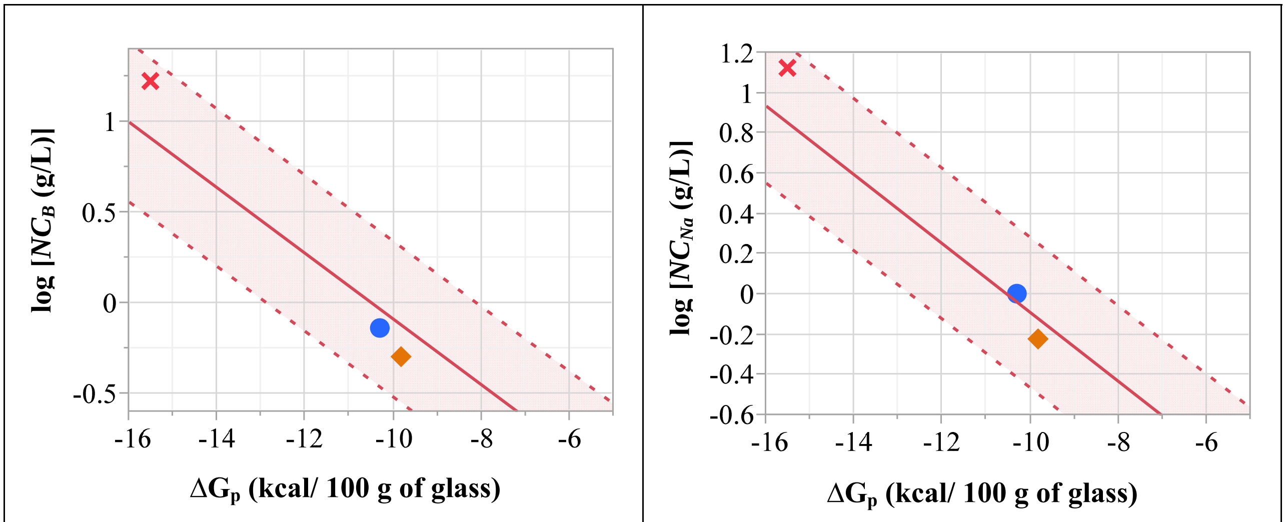
3.3.3 PCCS Model Predictions

The measured SB9 SC-17 Qualification Glass composition reported in Table 3-34 was used to predict specific properties of the glass using the DWPF PCCS model. The results are shown in Table 3-37. All of the predicted properties were compared to SME acceptability criteria[42] to evaluate whether this glass met the DWPF processing and product quality constraints. Based on the measured composition, all of the predicted properties met the PCCS MAR criteria. In addition, Figure 3-8 demonstrates that the measured PCT releases of the SB9 SC-17 Qualification Glass are predictable by the PCCS models for durability. Prediction limits at a 95% confidence for an individual PCT result (- - - -) are plotted along with the linear fit (——).

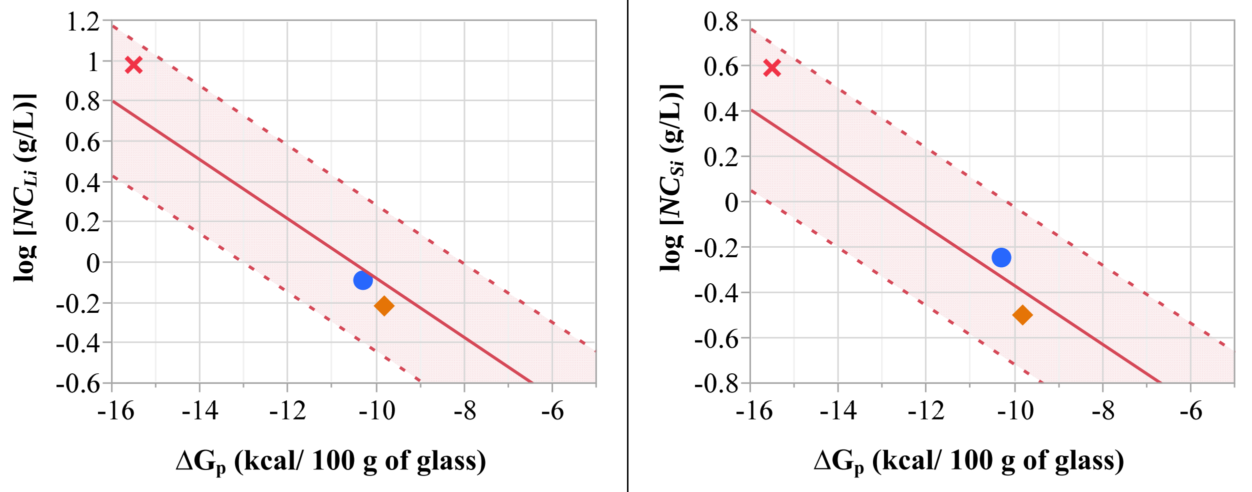
Table 3-37. PCCS Model Prediction Results for the SB9 SC-17 Qualification Glass

PCCS Model	**Predicted Value**
Free Energy of Hydration (ΔG_p)Value (kcal/100 g glass)	-10.31
Boron Normalized Concentration (NC_B)	0.93 g/L
Lithium Normalized Concentration (NC_{Li})	0.93 g/L
Sodium Normalized Concentration (NC_{Na})	0.91 g/L
Liquids Temperature	846 °C
Viscosity	69 Poise
Al_2O_3 Concentration	5.95 wt%
Sum of Oxides*	100.45 wt%
Nepheline Discriminator Ratio	0.74
All PCCS MAR Criteria Met	yes

*PCCS does not include SO_4^{2-} in the sum of oxides



Fit of log [NC_B (g/L)] by ΔG_p **Fit of log [NC_{Na} (g/L)] by ΔG_p**



Fit of log [NC_{Li} (g/L)] by ΔG_p **Fit of log [NC_{Si} (g/L)] by ΔG_p**

✕	EA (published)[23]
♦	ARM
●	SB9 SC-17 Qualification Glass (measured)

Figure 3-8. Normalized Concentration as a Function of ΔG_p Predictions for B, Li, Na, and Si

4.0 Conclusions

SRNL has qualified SB9 with the nitric acid/formic acid flowsheet. SRNL has demonstrated that SB9 can be processed using an acid addition strategy that has been shown to destroy nitrite without exceeding the DWPF H_2 generation rates in the SRAT and SME. The PCT responses from the SB9 SC-17 Qualification Glass (fabricated from the SC-17 SME cycle product) are acceptable relative to the chemical durability of the EA benchmark glass and predictable by current PCCS models for durability. All other PCCS MAR criteria were met based on the measured glass composition.

Note: Specific recommendations for processing SB9 are published in a separate document and include results from SB9 simulant studies.[36, 43]

5.0 References

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Appendix A. Rheology Flow Curves

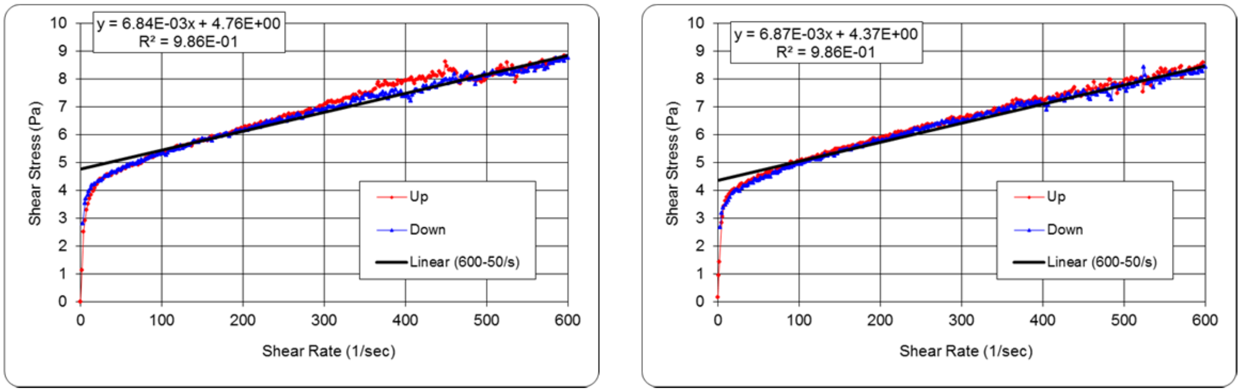

Figure A-1. SB9 Qualification Sample (HTF-51-15-81 washed at SRNL)

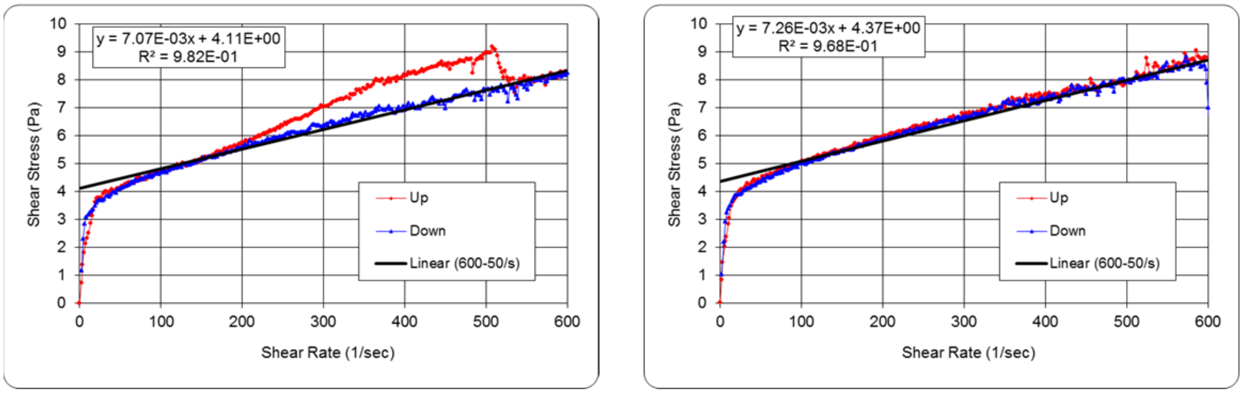

Figure A-2. SC-16 SRAT Receipt

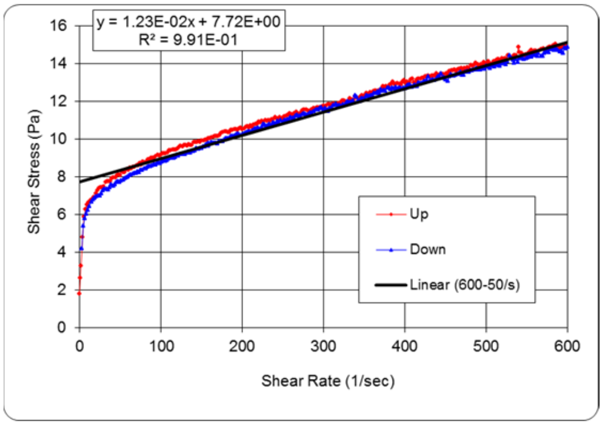

Figure A-3. SC-17 SRAT Product

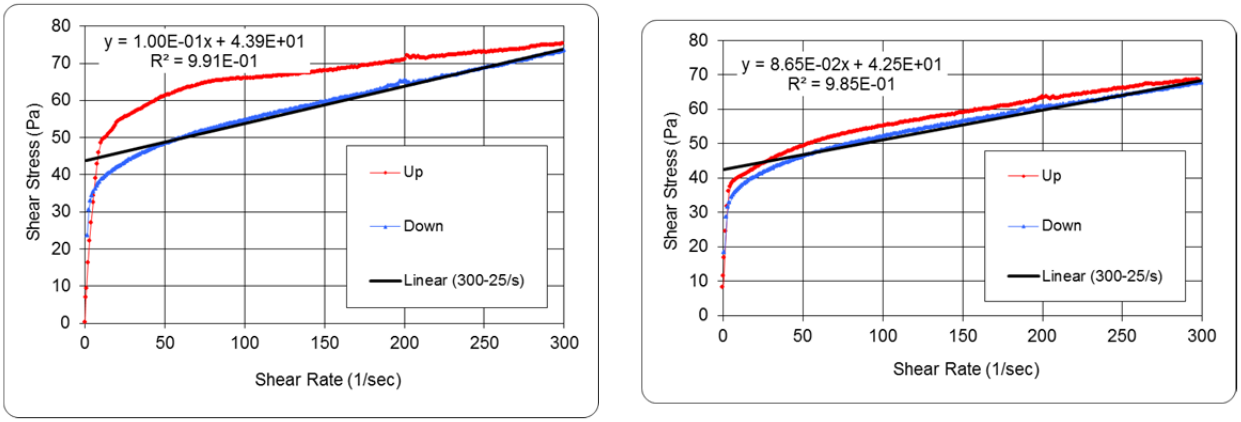

Figure A-4. SC-17 SME Product

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