SRNL-STI-2013-00116
Revision 0

SLUDGE WASHING AND DEMONSTRATION OF THE DWPF FLOWSHEET IN THE SRNL SHIELDED CELLS FOR SLUDGE BATCH 8 QUALIFICATION

J. M. Pareizs
C. L. Crawford

April 2013

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

Prepared for the U.S. Department of Energy under
contract number DE-AC09-08SR22470.

DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2013-00116
Revision 0

Keywords: *DWPF, SLUDGE, QUALIFICATION, SLUDGE BATCH 8, TANK FARM*

Retention: *Permanent*

SLUDGE WASHING AND DEMONSTRATION OF THE DWPF FLOWSHEET IN THE SRNL SHIELDED CELLS FOR SLUDGE BATCH 8 QUALIFICATION

J. M. Pareizs
C. L. Crawford

April 2013

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

REVIEWS AND APPROVALS

AUTHORS:

J. M. Pareizs, Process Technology Programs Date

C. L. Crawford, Date

TECHNICAL REVIEW:

Document Review per E7, 2.60
D. C. Koopman, Process Technology Programs Date

Document Review per E7, 2.60
J. W. Amoroso, Process Technology Programs Date

APPROVAL:

D. R. Click, Manager Date
Environmental & Chemical Process Technology Research Programs

S. L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

E. J. Freed, Manager Date
SRR Engineering

ACKNOWLEDGEMENTS

The authors would like to recognize the invaluable support of the Savannah River National Laboratory (SRNL) Shielded Cells technicians and management for the in-cells work; SRNL-Analytical Development (AD) researchers and technicians for all other analyses; T. B. Edwards of the SRNL Statistical Consultation group for statistical analysis support; and the SRNL Glass Shop for providing glassware and other miscellaneous hardware. The authors would also like to acknowledge B. R. Pickenheim for assistance with setting up and assisting with running the processing experiments.

EXECUTIVE SUMMARY

The current Waste Solidification Engineering (WSE) practice is to prepare sludge batches in Tank 51 by transferring sludge from other tanks to Tank 51. Tank 51 sludge is washed and transferred to Tank 40, the current Defense Waste Processing Facility (DWPF) feed tank. Prior to transfer of Tank 51 to Tank 40, the Savannah River National Laboratory (SRNL) typically simulates the Tank Farm and DWPF processes using a Tank 51 sample (referred to as the qualification sample). WSE requested the SRNL to perform characterization on a Sludge Batch 8 (SB8) sample and demonstrate the DWPF flowsheet in the SRNL shielded cells for SB8 as the final qualification process required prior to SB8 transfer from Tank 51 to Tank 40.

A 3-L sample from Tank 51 (the SB8 qualification sample; Tank Farm sample HTF-51-12-80) was received by SRNL on September 20, 2012. The as-received sample was characterized prior to being washed. The washed material was further characterized and used as the material for the DWPF process simulation including a Sludge Receipt and Adjustment Tank (SRAT) cycle, a Slurry Mix Evaporator (SME) cycle, and glass fabrication and chemical durability measurements. Key observations, comments, and results relating to these activities were:

- SRNL did not explicitly mimic Tank Farm washing due to schedule constraints. Instead, SRNL washed to the target endpoint as quickly as possible. This methodology had no effect on wash endpoint target. However, evaluations of settling during washing were not possible. In reality, Tank Farm washed-Tank 51 was washed past the original target, so the SRNL qualification sludge bounded the acid requirement of the final composition in Tank 51 at transfer.
- During washing, there were no settling issues and no obvious rheological changes.
- All processing goals were accomplished in the DWPF SRAT and SME cycles:
  - Nitrite was adequately destroyed (<130 mg/kg slurry)
  - SRAT product mercury was 0.71 wt% of total solids, below the target of 0.8 wt%.
  - SRAT product was concentrated to 31.5 wt% total solids with no mixing or heat transfer issues (target was 30 wt%).
  - SME product was concentrated to 50.1 wt% total solids with no mixing or heat transfer issues (target was 50 wt%).
  - Hydrogen generation in both cycles was well below DWPF limits for the SRAT and SME.
  - Some foaming was observed during formic acid addition and after approximately 9 and 13 hours of boiling prompting 100 ppm antifoam additions.
  - Peak DWPF-scale SRAT cycle offgas nitrous oxide concentration and generation rate were 3.5 vol% and 72 lb/h, respectively
- A glass was fabricated with SME product (36 wt% waste loading with Frit 803). The glass was acceptable with reference to the Product Consistency Test and comparison to the Environmental Assessment Glass.
- Rheological properties of the washed sludge, SRAT product, and SME product were within DWPF design basis criteria even though the wt% total solids were higher than in previous batches.

As a result of this work, SRNL recommends the following:

- DWPF should accept the material in Tank 51 for blending with the SB7b Tank 40 heel to produce SB8 for feed to DWPF.
- Inductively coupled plasma-atomic emission spectroscopy is more bounding for determining the potential sulfur content in the melter feed than ion chromatography.

- The SB8 qualification run validated the suitability of the DWPF stoichiometric acid equation for the new waste. DWPF acid stoichiometry for SB8 will be derived from simulant studies used in concert with the results from SC-12 (qualification run of SB7b-Tank 40) and this SB8-Tank 51 qualification run.[a]
- Antifoam additions may need to be supplemented (e.g., an antifoam addition during formic acid addition) if SB8-Tank 40 acts like SB8-Tank 51 during processing.

---

[a] Koopman, D. C. Recommendations for SB8 Processing in DWPF-CPC; SRNL-L3100-2013-00008; Savannah River National Lab: Aiken, SC, 2013.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AA	atomic absorption
AD	SRNL Analytical Development
AR	aqua regia
ARG-1	Analytical Reference Glass-1
ARM	Analytical Reference Material
CPC	Chemical Process Cell
CVAA	cold vapor-atomic absorption
DI	deionized
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
FAVC	Formic Acid Vent Condenser
GC	micro gas chromatograph
IC	ion chromatography
ICP-AES	inductively coupled plasma atomic emission spectroscopy
ICP-MS	inductively coupled plasma mass spectroscopy
KMA	Koopman minimum acid equation
MAR	Measurement Acceptability Region
MWWT	Mercury Water Wash Tank
n	number of replicate measurements
NA	not applicable
NM	not measured
PCCS	Product Consistency Control System
PCT	Product Consistency Test
PF	peroxide fusion
R&D	research and development
REDOX	reduction-oxidation ($Fe^2/\Sigma Fe$ in this document)
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
St.Dev.	standard deviation
SVOA	semivolatile organic analysis
TIC	total inorganic carbon

TOC	total organic carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VOA	volatile organic analysis
WAPS	Waste Acceptance Product Specification
WL	waste loading
WSE	Waste Solidification Engineering

1.0 Introduction

The 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 Savannah River National Laboratory (SRNL) typically simulates the Tank Farm and DWPF processes with a Tank 51 sample (referred to as the qualification sample). WSE has requested that characterization and a radioactive demonstration of the next batch of sludge slurry – Sludge Batch 8 (SB8) – be completed in the Shielded Cells Facility of the SRNL via a Technical Task Request (TTR).[1]

This report documents:

- The characterization and washing of the Tank 51 SB8 qualification sample.
- The performance of a DWPF Chemical Process Cell (CPC) simulation using the washed SB8 sample. The simulation included a Sludge Receipt and Adjustment Tank (SRAT) cycle, where acid was added to the sludge to destroy nitrite and reduce mercury, and a Slurry Mix Evaporator (SME) cycle, where glass frit was added to the sludge in preparation for vitrification. The SME cycle also included replication of five canister decontamination additions and concentrations. Processing parameters were based on work with a non-radioactive simulant of washed SB8-Tank 51 slurry.
- Rheology measurements of the SRAT receipt, SRAT product, and 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.

This program was controlled by a Task Technical and Quality Assurance Plan (TTQAP)[2], and analyses were guided by an Analytical Study Plan[3]. This work is Technical Baseline Research and Development (R&D) for the DWPF.

2.0 Qualification Sample Characterization and Washing

The SB8 qualification sample, (a 3-L sample from Tank 51; Tank Farm sample HTF-51-12-80) was received by SRNL on September 20, 2012. The as-received sample was characterized and then washed. The washed material was further characterized and used in a DWPF sludge only flowsheet simulation (including glass fabrication and chemical durability measurements). This section describes the as-received sample characterization, washing, and the washed sample characterization.

2.1 As-Received Sample Characterization

A 500-mL subsample from the 3-L Tank 51 sample was used for characterization.

2.1.1 *Density and Weight Percent Solids*

Density measurements were conducted at ~20 ºC. Densities were measured using weight-calibrated balances and 8 mL (nominal) volume-calibrated plastic test tubes.[4] Supernatant was generated via filtration of slurry through a 0.45 µm filtration membrane.

Slurry and supernatant aliquots were used to determine total solids and dissolved solids, respectively. Each aliquot was ~3 g and was heated at a nominal temperature of ~115 ºC to remove the water.[4] Insoluble and soluble solids concentrations were calculated based on the total solids and dissolved solids measurements. Presented in Table 2-1 are the average analytical results for density and weight percent solids results, along with standard deviation and number of replicates.

Table 2-1. As-Received Densities and Weight Percent Solids

Property	Average (St.Dev., n)
Slurry Density (g/mL)	1.28 (0.01, 4)
Supernatant Density (g/mL)	1.23 (0.002, 4)
Wt % Total Solids (Slurry Basis)	34.6 (0.09, 4)
Wt % Dissolved Solids (Supernatant Basis)	26.8 (0.06, 4)
Wt % Soluble Solids (Slurry Basis)	23.9 (NA*)
Wt % Insoluble Solids (Slurry Basis)	10.7 (NA*)

St.Dev. = standard deviation of the replicate measurements; n = number of replicates.
* Wt % soluble and insoluble solids were calculated from the average wt % total and dissolved solids.

2.1.2 *Supernatant Characterization*

Supernatant (obtained by passing slurry through a 0.45 µm filtration membrane) was diluted with water in the SRNL Shielded cells by a factor of approximately 50 (to reduce dose) and submitted to SRNL Analytical Development (AD) for analysis. Sodium, aluminum, potassium, and sulfur were measured by inductively coupled plasma-atomic emissions spectroscopy (ICP-AES). Carbonate was obtained from total inorganic carbon analysis. Free hydroxide was determined by titration. The remaining anions were determined from ion chromatography (IC) analysis. The analyte concentrations are presented in Table 2-2. As can be seen, sulfate is ~90% of the sulfur result. It is not clear if this difference is a bias in the ICP-AES or IC analysis, or if there are non-sulfate species in the supernatant. Nevertheless, the sulfur value correlates well with the total sulfur measurement (from the total solids digestions; see below). Therefore, it is recommended that the sulfur result be used in planning and projections.

Table 2-2. As-Received Supernatant Composition

Analyte	Result, M, Average (St.Dev., n)
Sodium	5.18 (0.02, 4)
Aluminum	0.491 (0.002, 4)
Potassium	0.0233 (0.0003, 4)
Sulfur	0.0954 (0.0005, 4)
Nitrite	0.773 (0.01, 4)
Nitrate	1.16 (0.02, 4)
Sulfate	0.084 (0.002, 4)
Oxalate	0.0056 (0.0002, 4)
Chloride	<0.1 (NA)
Fluoride	<0.03 (NA)
Formate	<0.01 (NA)
Carbonate	0.257 (0.001, 4)
Free OH	1.68 (0.06, 4)

2.1.3 *Total Solids Analysis*

Elemental concentrations in the total solids are presented in Table 2-3. Elements detected at concentrations greater than 0.05 wt% of the total solids are reported.[b]

For the elemental analyses, sludge solids aliquots were digested by aqua regia (AR) and sodium peroxide fusion (PF) methods in quadruplicate. The total solids mass of each aliquot was ~0.25 g, and the volume of each final digest solution was 100 mL. ICP-AES measurements were performed on both the AR and PF digest solutions. Cold vapor atomic absorption (CVAA), and inductively coupled plasma mass spectroscopy (ICP-MS) measurements were performed only on the AR digest solutions. When there were no significant differences between ICP-AES measurements of AR and PF digest solutions, all results were used to quantify the elements. ICP-AES measurements of AR digest solutions were used to quantify Ca, K, Na, P, S, and Zr. ICP-AES measurements of PF digest solutions were used to quantify Si. CVAA measurements were used to quantify Hg. The concentration of Nd was calculated from ICP-MS measurements by the sum of masses 143 to 146, 148, and 150. Noble metals (Ag, Rh, Ru, and Pd) were calculated from ICP-MS analysis using the methodology given in Reference 5. Concurrent with each set of dissolutions in the Shielded Cells, samples of the Analytical Reference Glass (ARG-1) were also dissolved as checks of the digestions. A multi-element standard containing known concentrations of Al, Fe, Ni, Na, and S was also submitted with each set of samples sent to AD for ICP-AES analysis to confirm the accuracy of the measurements

---

[b] Note that the TTR[1] requires elements at 0.1 wt% of the total solids and noble metals to be reported.

Table 2-3. Elemental Composition of As-Received Total Solids

Element	Wt% of Total Solids, Average (St.Dev., n)	Digestion and Analytical Method
Ag	0.00519 (NA)	AR, ICP-MS*
Al	4.75 (0.09, 8)	AR/PF, ICP-AES
Ca	0.607 (0.004, 4)	AR, ICP-AES
Ce	0.130 (0.02, 8)	AR/PF, ICP-AES
Cr	0.0858 (0.003, 8)	AR/PF, ICP-AES
Fe	8.90 (0.1, 8)	AR/PF, ICP-AES
Hg	1.14 (0.03, 4)	AR, CVAA
K	0.191 (0.003, 4)	AR, ICP-AES
Mg	0.0831 (0.007, 8)	AR/PF, ICP-AES
Mn	3.32 (0.06, 8)	AR/PF, ICP-AES
Na	26.1 (0.1, 4)	AR, ICP-AES
Nd	0.0818 (NA)	AR, ICP-MS†
Ni	0.416 (0.004, 8)	AR/PF, ICP-AES
P	0.132 (0.008, 4)	AR, ICP-AES
Pd	0.00109 (NA)	AR, ICP-MS*
Rh	0.00497 (NA)	AR, ICP-MS*
Ru	0.0208 (NA)	AR, ICP-MS*
S	0.644 (0.008, 4)	AR, ICP-AES
Si	0.481 (0.007, 4)	PF, ICP-AES
Th	0.314 (0.02, 8)	AR/PF, ICP-AES
U	1.37 (0.07, 8)	AR/PF, ICP-AES
Zr	0.0580 (0.01, 4)	AR, ICP-AES

* Noble metals content is calculated per Reference 5. Note that since this is a calculation, a standard deviation is not applicable.

† Nd is calculated from the sum of masses 142 to 146, 148, and 150.

2.1.4 *Oxalate Analysis*

Total oxalate (in slurry) was determined from analyzing hydrochloric acid/nitric acid dissolved slurry from the as-received sample. Total oxalate (in slurry) was measured by IC in quadruplicate. The total oxalate measured was 3,200 mg/kg slurry, which represents total oxalate in the slurry, and does not give an indication of the amount of oxalate that could or will be removed during washing. To determine 'washable oxalate', the same analysis was carried out on slurry samples that were first diluted with water. The 'washable oxalate' measured was 3,300 mg/kg slurry. The difference in the total and washable oxalate was insignificant, indicating no significant unwashable oxalate (e.g., iron or calcium oxalate) in this sludge.

2.2 Washing

The SB8 sample was washed to represent Tank Farm projections as of October 30, 2012.[6] Tank Farm targets and SRNL results are presented in Section 2.3.6. Because of schedule constraints, SRNL did not mimic Tank Farm plans. Instead, washing was completed as quickly as possible. Wash amounts were limited by the available equipment, resulting in 4 washes; thus, an evaluation of sludge settling during the washing process was not possible. It should be noted that the number and scale of washes, for a sample without significant quantities of partially soluble compounds (e.g., sodium oxalate), does not affect insoluble species such as noble metals and SRAT cycle acid demand constituents (e.g., total base, nitrite). Ultimately, Tank 51 was washed to lower sodium molarity than the qualification sample. Therefore, the acid requirement of the washed qualification sample bounds that of the Tank 51 material being transferred into Tank 40 to make SB8.

Decant and washing amounts are presented in Table 2-4. Washing was performed in a 4 L glass bottle. Sludge was allowed to settle, and, in most cases, as much supernatant was removed as possible using Tygon tubing and a peristaltic pump. For each wash, the slurry was mixed after wash water addition with an overhead mixer for 30 minutes prior to allowing the sludge to settle. Wash 3 included 110 g of sodium nitrite. All other washes contained only water. Decant 4 was completed in two stages. Samples of Decant 4a were submitted to AD for analysis to assist in determining the final wash amount. The amount of Decant 5 was planned to obtain slurry with a weight percent insoluble solids near Tank Farm projections.

There were no issues with settling; sludge settled to 60-70% of total sample volume within 3-4 days after agitation cessation.

Table 2-4. Washing Amounts and Mass Balance

	Added (Removed), g	Running Mass, g	Date
Initial	3,439	3,439	9/26/12
Decant 1	(1,004)	2,435	10/17/13
Wash 1	1,093	3,528	10/18/13
Decant 2	(780)	2,749	10/23/13
Wash 2	927	3,675	10/23/13
Decant 3	(1,066)	2,609	10/25/13
Wash 3	1,157	3,766	10/25/13
Decant 4a	(115)	3,651	10/29/13
Decant 4b	(1,068)	2,582	11/1/13
Wash 4	693	3,276	11/1/13
Decant 5	(601)	2,674	11/5/13

2.3 Washed Sample Characterization

A portion of the washed sample, also referred to as the SRAT receipt (heel free basis), was used for characterization, but the bulk of the washed sample was used in the DWPF CPC demonstration. This section documents the characterization of the washed sample.

2.3.1 *Density and Weight Percent Solids*

The measured density and weight percent solids are summarized in Table 2-5. The methods for determining density and weight percent total and dissolved solids are described in Section 2.1.1. Weight percent calcined solids were determined by heating the dried slurry aliquots (from the total solids measurements) to ~1100 ºC.

Table 2-5. Washed (SRAT Receipt) Sample Densities and Weight Percent Solids

Property	Average (St.Dev., n)
Slurry Density (g/mL)	1.16 (0.008,4)
Supernatant Density (g/mL)	1.09 (0.008, 4)
Wt % Total Solids (Slurry Basis)	22.7 (0.05, 4)
Wt % Dissolved Solids (Supernatant Basis)	10.9 (0.1, 5)
Wt % Soluble Solids (Slurry Basis)	9.5 (NA*)
Wt % Insoluble Solids (Slurry Basis)	13.2 (NA*)
Wt% Calcined Solids (Slurry Basis)	17.7 (0.04, 4)

* Wt % soluble and insoluble solids were calculated from the average wt % total and dissolved solids.
See Reference 7 for all weight percent solids data and calculations.
Note: this sample does not contain a SRAT heel and is not directly comparable to a DWPF SRAT receipt sample

2.3.2 *Supernatant Characterization*

Table 2-6 lists results from supernatant analysis. As described in Section 2.1.2, supernatant was obtained by filtering slurry. Supernatant was diluted by a factor of approximately 30 (to reduce dose) prior to submission to AD for analyses. This washed material was diluted less than the as-received supernatant because washing removes ^{137}Cs, a major contributor to dose.

Table 2-6. Supernatant Constituents

Analyte	Result, M, Average (St.Dev., n)
Sodium	1.79 (0.01, 4)
Aluminum	0.138 (0.0009, 4)
Potassium	0.00623 (0.0002, 4)
Sulfur	0.0259 (0.0003, 4)
Nitrite	0.490 (0.01, 4)
Nitrate	0.322 (0.009, 4)
Sulfate	0.018 (0.0002, 4)
Oxalate	0.025 (0.0005, 4)
Chloride	<0.008 (NA, NA)
Fluoride	<0.011 (NA, NA)
Formate	<0.006 (NA, NA)
Carbonate	0.079 (0.001, 4)
Free OH	0.403 (0.01, 4)

2.3.3 *Total Solids Analysis*

Total solids elemental concentrations in, and the digestion and analytical methods used for, the washed sample are shown in Table 2-7. Digestion and analytical methods were identical to those for the as-received sample (see Section 2.1.3) with the exception of Se, As, and Zr. Se and As were specifically requested in the TTR[1] for the SRAT receipt sample and were measured by atomic absorption (AA). Zr cannot be quantified from the PF digestion since PF is typically performed in Zr crucibles and the AR method does not completely dissolve Zr. Therefore, Zr was measured using the DWPF's cold chem (CC) method which uses hydrofluoric/nitric acid for digestion.[c]

---

[c] The CC digestion method was used in addition to AR and PF digestion methods for the SRAT receipt to verify DWPF analytical methods[8]; SRNL does not typically utilize this digestion method.

Table 2-7. Elemental Composition of Washed (SRAT Receipt) Sample Total Solids

Element	Average, wt% of Total Solids (St.Dev., n)	Digestion and Analytical Method
Ag	0.0140 (NA, NA)	AR, ICP-MS*
Al	5.50 (0.05, 4)	AR/PF, ICP-AES
As	<0.0011 (NA, 4)	AR, AA
Ba	0.0696 (0.0009, 8)	AR/PF, ICP-AES
Be	<0.001 (NA, 4)	AR, ICP-AES
Ca	1.12 (0.008, 4)	AR, ICP-AES
Cd	0.00496 (0.00004, 4)	AR, ICP-AES
Ce	0.269 (0.01, 8)	AR/PF, ICP-AES
Co	0.00782 (0.0001, 4)	AR, ICP-AES
Cr	0.102 (0.01, 8)	PF/AR
Cu	0.0502 (0.0003, 4)	AR, ICP-AES
Fe	17.2 (0.2, 8)	AR/PF, ICP-AES
Gd	0.0840 (0.003, 8)	AR/PF, ICP-AES
Hg	1.96 (0.04, 4)	AR, CVAA
K	0.0893 (0.004, 4)	AR, ICP-AES
Mg	0.163 (0.004, 8)	AR/PF, ICP-AES
Mn	6.31 (0.2, 8)	AR/PF, ICP-AES
Na	16.9 (0.08, 4)	AR, ICP-AES
Nd	0.162 (NA, NA)	AR, ICP-MS†
Ni	0.810 (0.01, 8)	AR/PF, ICP-AES
P	0.239 (0.03, 8)	AR/PF, ICP-AES
Pb	0.0356 (0.0007, 4)	AR, ICP-AES
Pd	0.00288 (NA, NA)	AR, ICP-MS*
Rh	0.00901 (NA, NA)	AR, ICP-MS*
Ru	0.0398 (NA, NA)	AR, ICP-MS*
S	0.357 (0.008, 4)	AR, ICP-AES
Sb	<0.027 (NA, 4)	AR, ICP-AES
Se	<0.002 (NA, 4)	AR, AA
Si	0.907 (0.01, 4)	PF, ICP-AES
Th	0.614 (0.03, 8)	AR/PF, ICP-AES
Ti	0.0128 (0.002, 8)	AR/PF, ICP-AES
U	2.63 (0.08, 8)	AR/PF, ICP-AES
Zn	0.0232 (0.0008, 8)	AR/PF, ICP-AES
Zr	0.143 (0.002, 4)	CC, ICP-AES

[*] Noble metals content is calculated per Reference 5. Note that since this is a calculation, a standard deviation is not applicable.

[†] Nd is calculated from the sum of masses 142 to 146, 148, and 150.

2.3.4 *Slurry Analysis*

Samples of diluted slurry were submitted to AD for total inorganic carbon (TIC) and total organic carbon (TOC) analysis. Aliquots of slurry were diluted by approximately 25X to lower dose. The remaining diluted slurry samples were filtered and submitted to AD for ICP-AES (Na, Al, and S) and IC (remaining anions and ammonium). Solids must be removed from samples prior to IC and ICP-AES analysis. Total base was determined by titration with 0.1 N hydrochloric acid of slurry diluted by 20X with water. The measured analyte concentrations are summarized in Table 2-8. These results are necessary for the DWPF acid demand calculation (see Section 12).

Total oxalate in slurry was determined by digesting un-diluted slurry aliquots with nitric and hydrochloric acid (see Section 2.1.4). The result was 1,000 mg/kg of slurry as compared to 1,600 mg/kg of slurry as measured in the water-diluted sample (see Table 2-8). The difference in measured total oxalate is thought to be due to oxalate destruction during the digestion. This destruction would not be significant for large oxalate concentrations (such as the as-received sample), but would be significant with lower oxalate concentrations. Fortunately, low oxalate levels have minimal impact on acid demand and control of glass redox, so an accurate value for oxalate is not critical to processing.

Table 2-8. Analysis of Washed (SRAT Receipt) Sample Slurry

Analyte	**Average (St.Dev., n)**
Sodium (mg/kg)	32,200 (40, 4)
Sulfur (mg/kg)	699 (2, 4)
Formate (mg/kg)	<300 (NA, NA)
Nitrite (mg/kg)	17,700 (800, 4)
Nitrate (mg/kg)	13,600 (600, 4)
Sulfate (mg/kg)	1,270 (50, 4)
Oxalate (mg/kg)	1,600 (40, 4)
Chloride (mg/kg)	<300 (NA, NA)
Fluoride (mg/kg)	<300 (NA, NA)
Total Inorganic Carbon (mg/kg)	810 (2, 4)
Total Organic Carbon (mg/kg)	720 (20, 4)
Total Base (mol/L)	0.79 (0.03, 3)
pH	13.4 (NA, 1)

2.3.5 *Semivolatile and Volatile Organic Compound Analysis Discussion*

Aliquots of the washed Tank 51 sample were prepared and analyzed for semivolatile and volatile organics. The volatile organic analysis (VOA) and semivolotile organic analysis (SVOA) were performed separately since methylene chloride used in the SVOA interferes with the VOA. Due to the high activity of the sludge material, dilutions in the SRNL Shielded Cells were necessary prior to submission to AD. For VOA, slurry samples were diluted by ~25X with water. No volatile organics were detected (detection limit was approximately 7 mg/kg slurry).

Slurry extractions performed at basic and neutral pH with methylene chloride were used for SVOA; slurry aliquots were diluted with basic and neutral buffer solutions prior to the extractions. The two pH conditions represent in-tank conditions (basic) and DWPF processing conditions (neutral) and were used to extract phenolic (aromatic compounds with hydroxyl substitution) compounds that may be deprotonated, and therefore more soluble in water than the extractant, at the elevated pH (12-13) in tank waste. Dibutylphthalate, at a concentration of 100 mg/L, and diisoctyladipate, at a concentration of 20 mg/L, were found in the basic samples. These compounds are common plasticizers. The plasticizers are most likely from Tygon tubing used in sample transfers and decants during washing. Also, plastics are used extensively through processing (e.g., samples are stored in polyethylene bottles). The source of the plasticizers is likely not the tank waste sludge.

2.3.6 *Comparison of Tank Farm Target and the SRNL-Prepared Sample*

Table 2-9 summarizes specific molarities and percent solids measured in the washed sample prepared by SRNL and projected in Tank 51 by the Tank Farm (Tank Farm target wash endpoint as of October 30, 2012[6]). Measured nitrite, nitrate, and free OH measurements were within 10% of the target, while sodium was 11% higher than the target. To lower sodium, an additional wash would be needed which would in turn lower nitrite and total base, two significant inputs to calculations for CPC processing. Therefore, it was decided to proceed with the CPC simulation without further washing or adjustments of the sample. With respect to CPC processing acid demand, the SRNL prepared sample bounds both the Tank Farm projections as of 10/30/12 and the latest projections for SB8-Tank 51.

Table 2-9. Sludge Batch 8 Tank Farm Target and SRNL-Prepared Sample

	Tank Farm Target as of 10/30/13	SRNL Sample
Insoluble Solids (wt%)	13.9	13.2
Sodium (M)	1.61	1.79
Nitrite (M)	0.523	0.490
Nitrate (M)	0.293	0.322
Free OH (M)	0.423	0.403

3.0 Chemical Process Cell Simulation

The Chemical Process Cell simulations using the washed sample (SRNL-prepared) is presented in this section. An overview of processing and description of the equipment; acid calculation inputs and output; processing observations; SRAT and SME cycle analytical results; offgas data; anion conversion and ammonium results; and rheological measurements are presented.

3.1 CPC Simulation Overview and Equipment Description

DWPF simulations (SRAT and SME cycles) using the SRNL-prepared Tank 51 SB8 qualification sample (see Section 2.0) were conducted following procedures in the Environmental and Chemical Process Technology Research Programs Section procedure manual.[4] A summary of each cycle is given in Table 3-1.

Table 3-1. Planned SB8 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 30 wt % total solids • Reflux to obtain a total time at boiling of 21 hours at a DWPF boil-up rate of 5,000 lb steam/h	• Addition and removal of water to simulate addition and removal of water from the decontamination of 5 glass canisters • Addition of frit and dilute formic acid in two batches to target 36% waste loading • Concentration (water removal) to target 50 wt% total solids.

The SB8 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 off-gas to approximately 20 °C below the ambient temperature to remove excess water before the gas reached the micro gas chromatograph (GC) for 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 off-gas components. The SRAT rig was the same design used in the previous four qualification runs and was assembled and tested in the SRNL Shielded Cells Mockup area and placed into the Shielded Cells fully assembled. A schematic of the experimental setup is given as Figure 3-1.

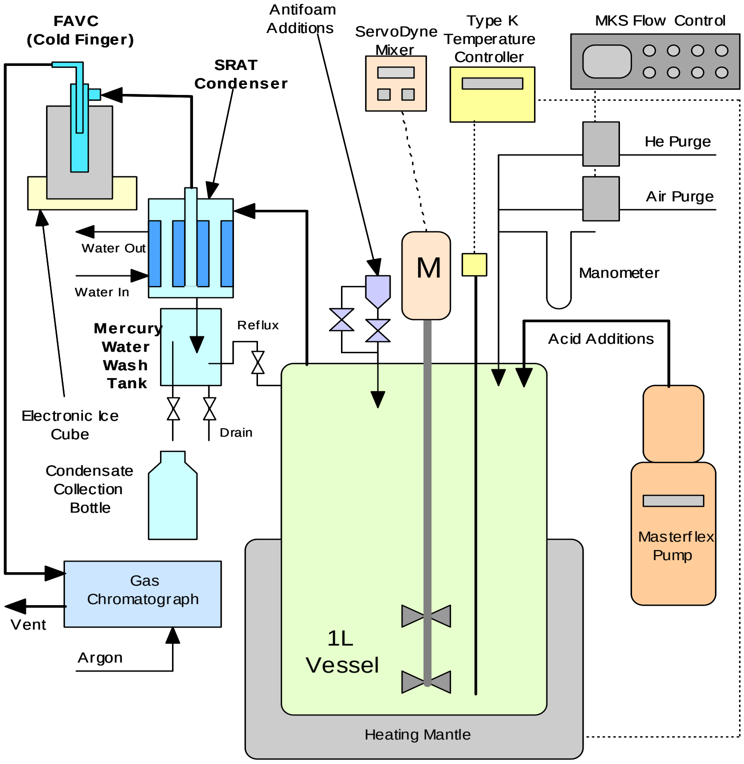


Figure 3-1. Schematic of SRAT Equipment Set-Up

Off-gas concentrations of hydrogen, oxygen, nitrogen, nitrous oxide (N_2O), 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% 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, loss of heat transfer capabilities, and off-gas carryover. Those observations are discussed in Section 3.3.

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.[9] 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 SB8-Tank 51 simulant (non-rad) CPC testing. Acid stoichiometry and reflux time were also based on CPC processing of SB8-Tank 51 simulant sludge slurry.

3.2 SRAT Receipt Acid Calculation

An acid addition calculation was made prior to SRAT cycle initiation. In this calculation, the amount of acid required to destroy nitrite, reduce mercuric oxide to elemental mercury for steam stripping, and neutralize the slurry is determined. SRNL uses the Koopman Minimum Acid equation (KMA)[10] to calculate a stoichiometric acid amount. The stoichiometric result is then increased by an empirical factor determined during the SB8-Tank 51 simulant CPC testing.[11] In the SB8-Tank 51 CPC simulant testing, 105%, 115%, and 140% acid stoichiometries (KMA basis) or 115%, 126%, and 154% (DWPF acid equation) were tested. With all three acid stoichiometries, the nitrite was destroyed, mercury was reduced and removed, and hydrogen was below DWPF limits. The middle (126% DWPF stoichiometry) was recommended and used for the SB8-Tank 51 qualification simulation.

The SRAT and SME product target wt % solids were 30% and 50%, respectively. These targets, which are higher than the typical 25% and 45%, are a result of the sample being significantly less washed than previous sludge batches (~1.79 M Na vs 1 M Na). Less washing results in higher soluble solids relative to total solids. Because rheological properties are highly dependent on insoluble solids, the SB8-Tank 51 SRAT and SME products could be concentrated to these higher total solidsr levels without increasing insoluble solids concentrations above historical levels. These high targets cannot be directly applied to the blend of Tank 51 and 40 (SB8-Tank 40) since Tank 40 has higher insoluble solids, relative to total solids, than SB8-Tank 51.[12,d]

The split of the total acid between nitric and formic was determined using the latest Reduction/Oxidation (REDOX) equation.[9] Inputs to the KMA acid equation, along with assumptions for anion destruction and conversion (based on SB8-Tank 51 simulant work) is presented in Table 3-2.

Acid calculation results are shown in Table 3-3. DWPF currently uses the Hsu acid equation for acid demand.[10] Therefore, the stoichiometric acid demand based on this equation is also presented in the table. The differences between the Hsu and KMA results are: a) Hsu has a factor of 0.75 for nitrite, while KMA has a factor of 1.0; b) Hsu has a factor of 1.2 for Mn, while KMA has a factor of 1.5; c) KMA includes Ca and Mg in the acid demand calculation; and d) KMA uses supernate TIC while Hsu uses slurry TIC.

---

[d] SB8-Tank 51: 13.2% insoluble solids/22.7% total solids=0.58
SB7b-Tank 40: 10.8% insoluble solids/15.6% total solids=0.69

Table 3-2. Acid Calculation Inputs

Input	SRAT Receipt Results	Units
SRAT Receipt Mass	1,222	g slurry
SRAT Receipt Weight % Total Solids	22.7[†]	wt %
SRAT Receipt Weight % Calcined Solids	17.7[†]	wt %
SRAT Receipt Weight % Insoluble Solids	13.2[†]	wt %
SRAT Receipt Density	1.16[†]	kg/L slurry
SRAT Receipt Supernatant Density	1.09[†]	kg/L supernatant
SRAT Receipt Nitrite	17,700[†]	mg/kg slurry
SRAT Receipt Nitrate	13,600[†]	mg/kg slurry
SRAT Receipt Oxalate	1,600[†]	mg/kg slurry
SRAT Receipt Slurry TIC (treated as carbonate)	810[†]	mg/kg slurry
Fresh Supernatant TIC (treated as carbonate)	950[†]	mg/L supernatant
SRAT Receipt Hydroxide (Base Equivalents) pH = 7	0.79[†]	Equiv Moles Base/L slurry
SRAT Receipt Manganese	8.09[*]	wt % of calcined solids(
SRAT Receipt Mercury	2.00[†]	wt % of total solids
SRAT Receipt Magnesium	0.275[*]	wt % of calcined solids(
SRAT Receipt Calcium	1.44[*]	wt % of calcined solids(
Conversion of Nitrite to Nitrate in SRAT Cycle	29	gmol NO_3^-/100 gmol NO_2^-
Destruction of Nitrite in SRAT and SME cycle	100	% of starting nitrite destroyed
Destruction of Formic acid charged in SRAT	30	% formate converted to CO_2 etc.
Destruction of Oxalate charged	2	% of total oxalate destroyed
Percent Acid in Excess Stoichiometric Ratio (Koop. Min Acid Eqn)	115	%
Percent Acid in Excess Stoichiometric Ratio (DWPF Min Acid Eqn)	133	%
SRAT Product Target Solids	30	Wt %
SME Product Target Solids	50	Wt %
REDOX Target	0.1	$Fe^{+2} / \Sigma Fe$

[†] These results were originally presented in Section 2.3 above.

[*] wt% of calcined solids = wt% of total solids (see Table 2-7) x wt% total solids/wt% calcined solids.

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

	Acid Calculation Results
Hsu Total Stoichiometric Acid required (mol) *	1.67
Koopman Minimum Stoichiometric Acid required (mol) *	1.93
Total Acid Added (mol)	2.22
Stoichiometric Acid Hsu Eqn (%)	133
Stoichiometric Acid Koopman Minimum Eqn. (%)	115
Fraction of Formic Acid for REDOX Target	0.94

* See Reference 10 for a description of the acid equations. Note that in the document, Equation 1 is the Hsu Total Stoichiometric Acid equation, and Equation 2 is the Koopman Minimum Stoichiometric Acid equation.

It should be noted that the Shielded Cells SRAT cycle demonstration is made without a SRAT heel from a prior batch. Quantities such as moles acid/L SRAT receipt slurry or moles acid/kg total solids derived from the Shielded Cells test results apply only to fresh sludge, not to fresh sludge combined with SRAT heel. Furthermore, these results do not extend in a simple manner to the coupled flowsheet (processing sludge plus ARP slurry and strip effluent solution), since the acid demand per liter or kg of solids for the ARP MST slurry is not the same as the demand for the fresh Tank 40 sludge slurry. However, the SB8-Tank 51 SRAT demonstration had comparable results in terms of hydrogen generation, nitrite destruction, and mercury removal (see results below) to the comparable simulant SRAT cycle, showing that the DWPF acid calculation will apply to SB8 without any unexpected biases or issues. This was true for SB7b qualification as well. Therefore, the simulant testing of the Tank 40 blend of SB7b and SB8-Tank 51 can be expected to set a suitably conservative window for the acid equation stoichiometric factors.

3.3 SRAT and SME Cycle Experiment Details and Observations

The SB8 SRAT cycle began by heating the washed sludge to 93 °C. Nitric acid and formic acid were then added (amounts determined from the acid calculation described above) at scaled rates equivalent to two gal/min in DWPF. Following acid addition, the vessel and contents were heated to boiling and water was removed targeting 30 wt% total solids for the SRAT product slurry. The Shielded Cells boiling rate was scaled to a DWPF rate of 5,000 lbs steam/h. Boiling continued under reflux until 21 hours had elapsed. This was the time predicted to be necessary to steam strip mercury to below the current DWPF SRAT product limit of 0.8 wt% Hg in the total solids. The boiling time was determined by assuming 750 g of steam/g of mercury to be stripped

For the SME cycle, water was added and removed five times to simulate five canister decon water additions and removals. Each addition was equivalent to 1,000 gallons at DWPF scale. Frit 803 was then added with water and formic acid to simulate two frit slurry additions in DWPF. The mass of frit was chosen to target a final glass waste form with a waste oxide loading of 36%. Concentration followed each frit slurry addition. The final concentration following the second frit slurry addition concentrated the SME product slurry to the target of 50 wt% total solids.

IIT-747 antifoam (Siovation Lot 101876-1111) addition strategy was: 200 ppm at start of SRAT, 100 ppm prior to formic acid addition, 500 ppm prior to boiling, and 100 ppm additions as necessary. During formic acid addition, an additional 100 ppm was added when foam was observed. Also, two 100 ppm additions were made during boiling, one at nine hours and one at 13 hours (total boiling time was 21 hours). This behavior was foamier than in the simulant tests. A planned 100 ppm antifoam addition was made at the start of the SME cycle. No additional antifoam additions were planned or needed during the SME cycle.

Details and results from analytical measurements performed on SRAT and SME product are presented in subsequent sections. The essential conclusions from those measurements, along with observations, were:

- Nitrite was adequately destroyed (<130 mg/kg slurry)
- SRAT product mercury was 0.71 wt% of total solids, below the target of 0.8 wt%.
- SRAT product was concentrated to 31.5 wt% total solids with no mixing or heat transfer issues.
- SME product was concentrated to 50.1 wt% total solids with no mixing or heat transfer issues.

- Hydrogen generation in both cycles was below DWPF limits.
- During the SRAT cycle, foam was observed during formic acid addition and after 9 and 13 hours of boiling.
- No foaming was observed during the SME cycle.

3.4 SRAT and SME Cycle Product Characterization Results

Samples were taken at the end of the SRAT and SME cycles for analytical measurements. Density, weight percent solids, slurry analyses, and Hg were determined for SRAT and SME cycle products. Elemental composition was also determined for the SRAT cycle product.

Presented in Table 3-4 are the measured SRAT and SME product densities and solids concentrations. Methodology identical to that described in Section 2.1 and 2.3 was used.

Table 3-4. SRAT and SME Product Densities and Weight Percent Solids

Property	SRAT Product Average (St.Dev., n)	SME Product Average (St.Dev., n)
Slurry Density (g/mL)	1.27 (NA, 1)	1.48 (0.01, 4)
Supernatant Density (g/mL)	1.13 (0.004, 4)	1.14 (0.002, 4)
Wt % Total Solids (Slurry Basis)	31.5 (0.05, 4)	50.1 (0.7, 4)
Wt % Dissolved Solids (Supernatant Basis)	18.8 (0.08, 4)	19.5 (0.4, 4)
Wt % Soluble Solids (Slurry Basis)	15.8 (NA, NA)*	12.1 (NA, NA)*
Wt % Insoluble Solids (Slurry Basis)	15.7 (NA, NA)*	38.0 (NA, NA)*
Wt% Calcined Solids (Slurry Basis)	21.3 (0.07, 4)	42.7 (0.8, 4)

* Wt % soluble and insoluble solids were calculated from the average wt % total and dissolved solids.

SRAT and SME product slurry anions and carbon were analyzed by IC, TIC, and TOC. Aliquots from both the SRAT and SME cycle product diluted with water (nominally 25X) were used for analysis. SRAT and SME product slurry pH was determined from undiluted samples of SRAT and SME product. Results from those measurements are summarized in Table 3-5. Based on simulant testing, it is not likely that oxalate was completely destroyed in the SRAT cycle. However, there is no additional sample available for reanalysis.

Table 3-5. SRAT and SME Product Slurry Anions, Carbon, and pH

Analyte	SRAT Product Average (St.Dev., n)	SME Product Average (St.Dev., n)
Formate (mg/kg)	66,700 (6,000, 4)	52,500 (700, 4)
Nitrite (mg/kg)	<130 (NA, NA)	<130 (NA, NA)
Nitrate (mg/kg)	37,900 (2,000, 4)	25,100 (500, 4)
Sulfate (mg/kg)	1,680 (30, 4)*	1,100 (40, 4)
Oxalate (mg/kg)	<130 (NA, 4)	<130 (NA, NA)
Chloride (mg/kg)	471 (60, 4)	636 (10, 4)
Fluoride (mg/kg)	<270 (NA, NA)	<260 (NA, NA)
TIC (mg/kg)	960 (60, 4)	918 (40, 4)
TOC (mg/kg)	18,800 (200, 4)	13,800 (100, 4)
pH	7.9	8.1

* Sulfate converted to sulfur yields 560 mg/kg, significantly less than the ICP-AES result of 692 mg/kg (see Table 3-6)

Aliquots from the SRAT product (diluted 25X) were analyzed by ICP-AES for elemental concentrations. Table 3-6 summarizes the measured concentrations for major elements in addition to Fe, U, and Th, which were below detection. (Sulfur concentration was specifically requested by the customer for comparison purposes to values obtained via IC analysis). These results represent soluble elements in the slurry *after* a 25X dilution with water and filtration. These results could be higher than a supernatant result for elements that may have dissolved from the insoluble solids in the water dilution. .

Table 3-6. SRAT Product Slurry Dilution Elementals

Result	Result, mg/kg slurry Average (St.Dev., n)
Ca	1,430 (20, 4)
Fe	<2 (NA, NA)
K	184 (4, 4)
Li	7.80 (0.07, 4)
Mg	190 (3, 4)
Mn	5,800 (60, 4)
Na	44,600 (400, 4)
S	692 (5, 4)
Si	415 (40, 4)
Sr	9.07 (0.1, 4)
Th	<9 (NA, NA)
U	<4 (NA, NA)

The elemental composition of the SRAT product solids is presented in Table 3-7. SME product elementals were not directly measured; instead, the SME product was vitrified and the resulting glass was characterized (see Section 4.0). Methodology for the SRAT product elementals was identical to that described in Sections 2.1.3 and 2.3.3. Se and As were not measured in the SRAT product since they were neither explicitly requested, nor were they detected in the SRAT receipt solids (see Table 2-7). One of the four AR digestion replicates was statistically determined to be an outlier using both Grubbs and Dixon tests and was not used in the averages.[13]

All iron replicate measurements were specifically requested in the TTR[1] and are presented in Table 3-8.

Table 3-7. SRAT Product Elemental Composition of Total Solids

Element	Result, wt% of total solids, Average (St.Dev., n)	Digestion and Analytical Method
Ag	0.00924 (NA, NA)	AR, ICP-MS*
Al	4.66 (0.3, 4)	PF, ICP-AES
Ba	0.0643 (0.003, 7)	PF/AR, ICP-AES
Be	<0.001 (NA, 3)	AR, ICP-AES
Ca	0.986 (0.02, 3)	AR, ICP-AES
Cd	0.00448. (0.00003, 3)	AR, ICP-AES
Ce	0.2502.(0.02, 7)	PF/AR, ICP-AES
Co	0.00749 (0.00008, 3)	AR, ICP-AES
Cr	0.0880 (0.006, 7)	PF/AR, ICP-AES
Cu	0.0446 (0.0006, 3)	AR, ICP-AES
Fe	15.5 (1, 7)	PF/AR, ICP-AES
Gd	0.0707 (0.004, 7)	PF/AR, ICP-AES
Hg	0.71 (0.01, 3)	AR, CVAA
K	0.0819 (0.001, 3)	AR, ICP-AES
Mg	0.143 (0.008, 7)	PF/AR, ICP-AES
Mn	5.73 (0.3, 7)	PF/AR, ICP-AES
Na	14.8 (0.2, 3)	AR, ICP-AES
Nd	0.141 (NA, NA) †	AR, ICP-MS
Ni	0.748 (0.05, 7)	PF/AR, ICP-AES
P	0.227 (0.02, 7)	PF/AR, ICP-AES
Pb	0.0321 (0.0006, 3)	AR, ICP-AES
Pd	0.00177 (NA, NA)	AR, ICP-MS*
Rh	0.00783 (NA, NA)	AR, ICP-MS*
Ru	0.0336 (NA, NA)	AR, ICP-MS*
S	0.324 (0.007, 3)	AR, ICP-AES
Sb	<0.0256 (NA, 3)	AR, ICP-AES
Si	0.925 (0.08, 4)	PF, ICP-AES
Th	0.533 (0.03, 7)	PF/AR, ICP-AES
Ti	0.0109 (0.001, 7)	PF/AR, ICP-AES
U	2.13 (0.1, 7)	PF/AR, ICP-AES
Zn	0.0216 (0.002, 7)	PF/AR, ICP-AES
Zr	0.101 (0.002, 4)	CC, ICP-AES

* Noble metals content is calculated per Reference 5. Note that since this is a calculation, a standard deviation is not applicable.

† Nd is calculated from the sum of masses 142 to 146, 148, and 150.

Table 3-8. Iron Replicates

Digestion Method	SRAT Receipt (wt% of total solids)	SRAT Product (wt% of total solids)
Alkali Fusion	17.4	15.6
	17.3	17.5
	17.4	15.6
	17.0	15.1
Aqua Regia	17.1	14.6
	17.2	15.1
	17.0	14.8
	17.1	*

* Results from the fourth aqua regia digestion are not reported (and were not used in reporting the elemental composition presented in Table 2-7); the fourth digestion result was significantly different from the other three replicates as determined from Grubbs and Dixon tests.[13].

3.5 Offgas Data

Presented in Table 3-9 and Table 3-10 are maximum SRAT and SME gas concentration and corresponding calculated gas generation data. Maximum hydrogen generation rates were below the DWPF limits (0.65 lb/h for the SRAT and 0.223 lb/h for the SME).

The SRAT cycle peak CO_2 generation rate was much less than in the matching simulant test (710 lb/h). This was likely due to the 1700 mg TIC/kg simulant compared to the 810 mg TIC/kg Shielded Cells, although the Shielded Cells value still seems somewhat low for such a high sodium molarity wash endpoint based on historical results. Conversely, the peak N_2O generation rate was more than double that in the simulant test. Volume percent data translate without correction to a DWPF furpge rate of 230 scfm, i.e., they are DWPF-scale coming off the GC.

Table 3-9. SRAT Cycle Maximum Gas Concentrations and Generation Rates

	Maximum Observed DWPF-Scale Concentration (vol%)	Maximum Observed DWPF-Scale Generation Rate (lb/h)
Hydrogen	0.034	0.028
Carbon Dioxide	20	440
Nitrous Oxide	3.5	72

See Reference 14 for all SRAT offgas data.

The formation of nitrous oxide in the SME cycle is typically a sign of nitrate destruction by formic acid. The total amount destroyed is a strong function of the SME boiling time.

Table 3-10. SME Cycle Peak Gas Concentrations and Generation Rates

	Maximum Observed Concentration (vol%)	Maximum Observed DWPF-Scale Generation Rate (lb/h)
Hydrogen	0.094	0.028
Carbon Dioxide	4.1	27
Nitrous Oxide	0.3	1.7

See Reference 14 for all SME offgas data.

Plots of hydrogen, carbon dioxide, and nitrous oxide generation during the SRAT cycle are shown in Figure 3-2. Carbon dioxide production occurred during acid addition and significantly decreased after the acid addition as expected from reactions known to occur with acid additions (e.g., destruction of carbonate). Hydrogen generation increased as nitrite was destroyed (as shown by the nitrous oxide generation decline).

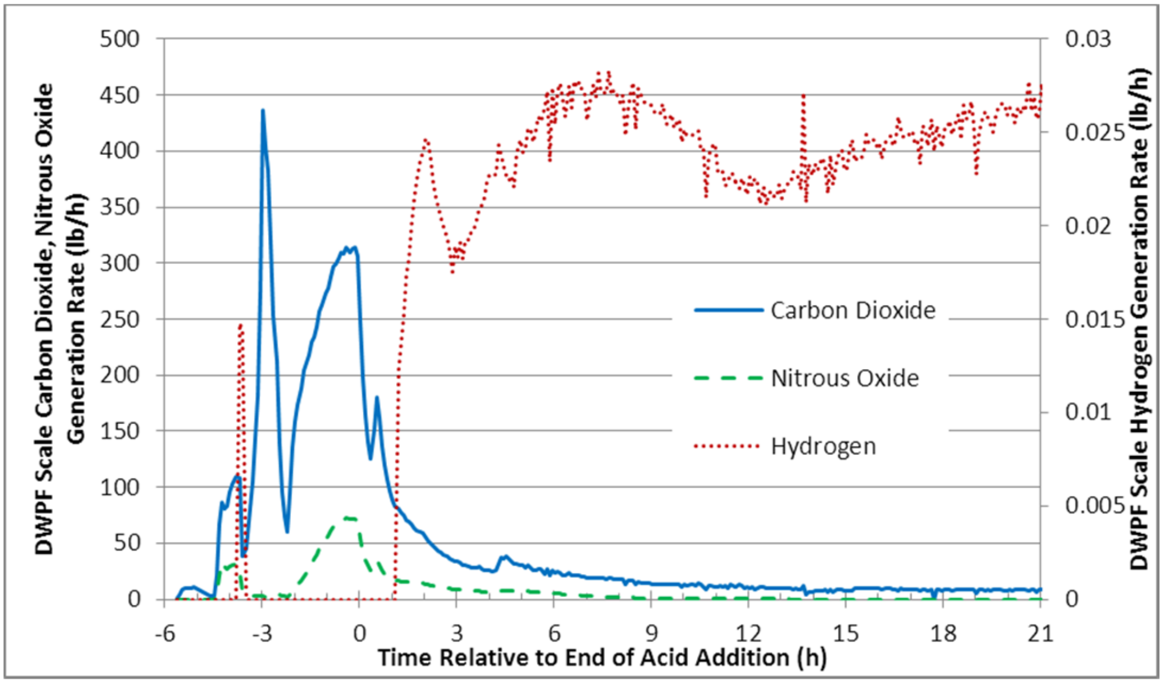


Figure 3-2. SRAT Cycle Offgas Generation

Nominal acid stoichiometry testing with SB8-Tank 51 simulant followed a similar profile for the hydrogen generation. There was an initial peak of about an hour duration, followed by a second peak, a long broad valley at mildly lower rates, and then a generally increasing trend during the last 8-9 hours of reflux.

Plots of hydrogen, carbon dioxide, and nitrous oxide generation during the SME cycle are shown in Figure 3-3. The off-gas data correlate with concentration changes associated with decon water additions and frit/water/formic acid additions. As the vessel was cooled prior to additions, gas generation rates decreased consistent with the temperature dependence of the gas-producing reactions. Correspondingly, as the vessel was heated back to boiling, gas generation rates spiked as retained or “trapped” gases were released. The carbon dioxide peak at approximately one hour is likely the result of carbon dioxide retained in the slurry between the time of adding the SRAT product to the vessel and the initiation of mixing and heating for the SME cycle (approximately 20 hours).

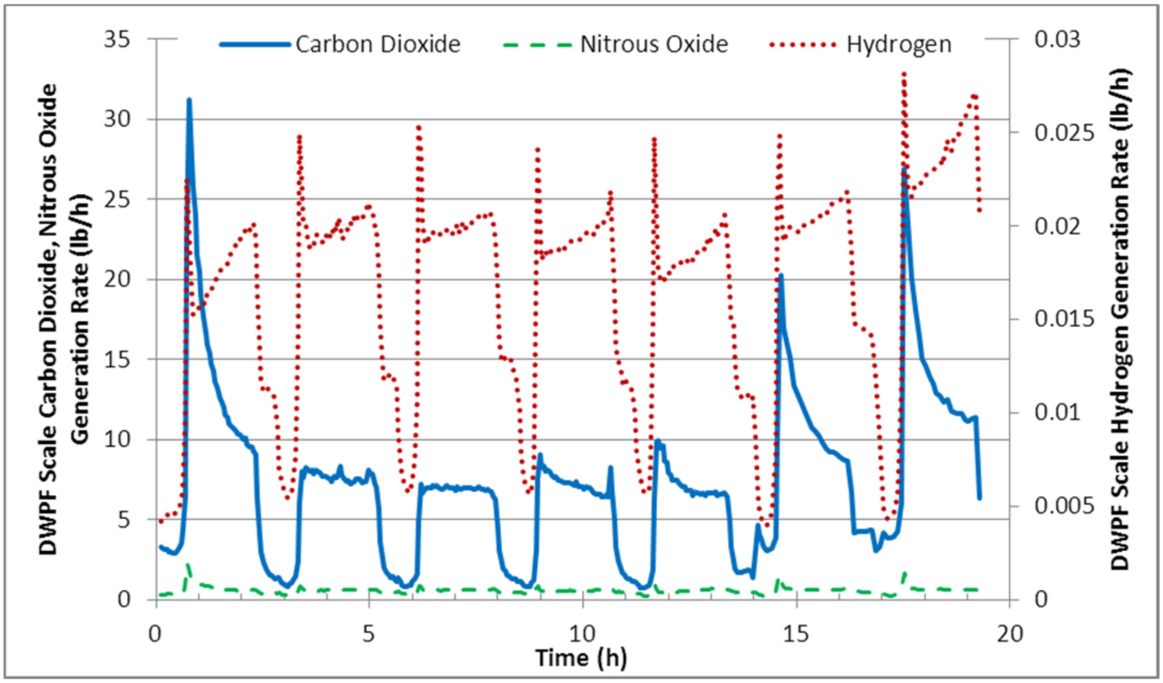


Figure 3-3. SME Cycle Offgas Generation

The hydrogen generation rate followed a fairly repetitive pattern during canister decon dewatering, but moved slowly toward higher rates once the frit-formic acid-water slurries were added, and the slurry was brought to higher wt% total solids. Similar increases in hydrogen generation rates were noted during SME dewatering following frit additions in the simulant tests. The corresponding increases in CO_2 generation rate were not observed in the simulant testing, or were much less pronounced (at about 5 lb/h versus the 10-15 seen here).

3.6 Anion Conversions and Ammonium

Table 3-11 lists the predicted (used in the acid calculation) and measured anion conversion and destruction percentages. Predicted anion conversions were based on AB8-Tank 51 simulant tests (see Appendix B). The measured nitrite to nitrate conversion was much greater than predicted. The difference between prediction and calculated conversion has been observed in previous sludge batches. It has been attributed to the smaller off-gas flux (boil up rate/SRAT surface area) in the Cells SRAT rig compared to simulant testing at 4L scale, and a corresponding increase in the impact of internal refluxing of absorbed NO_x in the condensate as additional nitrate. It is not expected that DWPF could exceed 33% nitrite to nitrate conversion at full scale based on the current knowledge of nitrite destruction reaction pathways. As alluded to in Section 3.4 above, it is not likely that all of the oxalate was destroyed in the SRAT cycle. It is recommended that DWPF base its anion conversion inputs on the recommendations from the simulant testing memorandum.[15]

Table 3-11. Comparison of Predicted and Measured Anion Destruction and Conversion

Input	Predicted, %	Measured, %
Conversion of Nitrite to Nitrate in SRAT Cycle	29	44
Destruction of Nitrite in SRAT and SME cycle	100	100
Destruction of Formic acid charged in SRAT	30	31
Destruction of Oxalate charged	2	100

Slurry dilutions (nominally 25X to reduce dose and condensates were submitted for ammonium analysis. Non-diluted samples of dewaters from the SME decon additions and removals were also submitted for ammonium analysis. The ammonium concentrations are presented in Table 3-12. The requirement to dilute the slurry samples prior to submission to AD to minimize dose resulted in the large difference in detection limits compared to the undiluted dewater samples. Simulant testing also showed a decrease in ammonium ion production compared to recent sludge batches

Table 3-12. SRAT and SME Ammonium Results

Sample	Ammonium Concentration
SRAT Receipt (mg/kg slurry)	<200
SRAT Product (mg/kg slurry)	<300
SME Product (mg/kg slurry)	<300
SRAT Dewater (mg/L)	<5
SME Cycle Dewaters During Decon Water Removal (mg/L)	16
SME Cycle Final Dewater – After Frit/Formic Acid Addition (mg/L)	<5

See References 7 and 14 for ammonium raw data and calculations.

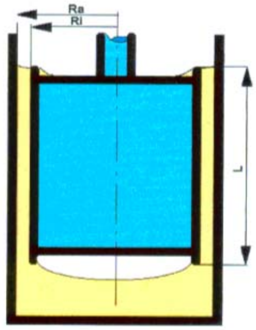
3.7 Rheology

Rheological properties of radioactive samples were determined using a Haake M5/RV30 rotoviscometer. The M5/RV30 is a Searle sensor system, where the bob rotates, and the cup is fixed. The torque and rotational speed of the bob are measured. Heating/cooling of the cup/sample/bob is through the holder for the cup. The shear stress is determined from the torque measurement and is independent of the rheological properties. Conditions that impact the measured torque are; slip (material does not properly adhere to the rotor or cup), phase separation (buildup of liquid layer on rotor), sedimentation (particles settling out of the shearing zone), homogeneous sample (void of air), lack of sample (gap not filled), excess sample (primarily impacts rheologically thin fluids), completely filling up the void below the bob (air buffer that is now filled with fluid) and Taylor vortices. The first five items yield lower stresses and the last three add additional stresses. The shear rate for a Newtonian fluid is geometrically determined using the equations of change (continuity and motion). This assumption also assumes that the flow field is fully developed and the flow is laminar. The shear rate can be calculated for non-Newtonian fluids using the measured data and fitting this data to the rheological model or corrected as recommended by Darby.[16] 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 3-13.

Table 3-13. 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 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 1 $$\tau = \tau_o + \mu_\infty \dot{\gamma}$$

Rheology measurements of the SRAT Receipt, SRAT product, and SME product are presented in Table 3-14. Flow curves are shown in Appendix A. Although the SRAT and SME product total solids (>30% and >50%, respectively) were relatively high, all results were within Design basis limits.[17]

Table 3-14. Slurry Rheology

		Yield Stress (Pa)	**Consistency (cP)**
SRAT Receipt	SB8	7.2	9.1
	Design Basis	*2.5-10*	*4-12*
SRAT Product	SB8	2.5	10.2
	Design Basis	*1.5-5*	*5-12*
SME Product	SB8	3.8	30
	Design Basis	*2.5-15*	*10-40*

4.0 Glass Fabrication, Analysis, and Durability Testing

Approximately 120 g of SB8 SME product was divided into four nearly equal portions, placed into high-purity alumina crucibles, and dried overnight at 110 °C. After thoroughly drying, the first portion was rapidly heated to 1150 °C in an open Pt/Au crucible in an electrically heated furnace. Upon reaching 1150 °C, the sample was held at temperature for approximately 30 minutes. The remaining portions were then added incrementally, allowing the crucible to rapidly return to temperature between each addition, resulting in a total time at the melting temperature of 1150 °C of 3.5 hours. The crucible was removed from the furnace while at temperature and bottom quenched (cooled) in a shallow pan of water, making sure no water contacted the glass during the process. The resulting glass appeared visually black and shiny, without the presence of a visible salt layer, crystals, or other inhomogeneities. This fabricated glass is referred to as the SB8 Qualification Glass and was used for the glass chemical and PCT analyses.

To support compositional analysis, a portion of the SB8 Qualification Glass had to be dissolved. In order to enhance dissolution, approximately 4 g of the glass was crushed and ground using a mechanical pulverizing mixer mill with agate media. The glass was sieved and only the portion that passed through a 200 mesh (<75 μm) brass sieve was used for the dissolutions. Nominally 0.25 g of the crushed and sieved glass was then dissolved by two different methods to ensure that all the elements of interest were dissolved and could be analyzed in at least one of the preparations. The two methods were a PF, and a mixed acid dissolution (MA) in sealed vessels at 115 °C using a combination of HF, HCl, and HNO_3 acids. Boric acid was added to this latter dissolution method to complex excess fluoride. The solutions of the dissolved glass were diluted to known volumes so that approximately 15 mL aliquots could be safely removed from the Shielded Cells without exposing personnel to excess radiation. The aliquots from both dissolution methods were then submitted to AD where they were analyzed by ICP-AES and ICP-MS. Concurrent with each set of dissolutions in the Shielded Cells, three samples of the ARG-1 were also dissolved to confirm complete dissolution of the SB8 Qualification glass. A multi-element standard containing known concentrations of Al, B, Fe, K, Li, Na, and Si was also submitted with each set of samples sent to AD to confirm the accuracy of the measurements.

The durability of the SB8 Qualification Glass was measured by following Test Method A of the ASTM 1285 standard nuclear waste glass leach test.[18] The ASTM 1285 Test Method A is a crushed glass (-100 to +200 mesh or 75 to 149 μm) leach test at 90 °C for seven days using deionized DI water in sealed stainless steel vessels. This test is commonly referred to as the PCT. The purpose of the PCT was to confirm that the SB8 Qualification Glass had a durability that met the criterion specified by the Waste Acceptance Product Specification (WAPS) for repository acceptance.[19] WAPS 1.3 specifies that the mean concentrations of B, Li, and Na in the leachate, after normalizing for the concentrations in the glass, shall each be less than those of the Environmental Assessment (EA) glass. These normalized concentrations represent the concentration of leached glass in PCT solutions assuming all elements in the glass are soluble.

DWPF complies with this criterion by demonstrating that the mean PCT results are at least two standard deviations below the mean PCT results of the EA glass.

The test was performed in quadruplicate for the SB8 Qualification Glass. Duplicate blanks and triplicate samples of the standard glass [Approved Reference Material (ARM)] and triplicate samples of the EA glass were also tested with the SB8 Qualification glass samples. In the PCT, 10 mL of DI water are used for each gram of glass. Nominally 1.5 g of glass and 15 mL of DI water were used in stainless steel vessels that were sealed tightly and weighed in order to ensure enough leachate was generated for analysis. After 7 days at 90 °C, the stainless steel vessels were removed from the oven, allowed to cool, weighed to determine water loss, and then opened. Due to the radioactivity of the glass, the initial portion of the test was performed remotely in a Shielded Cell using manipulators. The leachates from each vessel were then decanted into clean scintillation vials. The radioactivity levels of the leachates were low enough to be transported to a radiochemical hood where they could be handled directly. The pH of each leachate was measured and then filtered through a 0.45 μm filter and acidified to 1 volume percent HNO_3. The leachates were then diluted and submitted to AD, where the concentrations of B, Na, Li, and Si, were determined using ICP-AES. Average analyzed leachate concentrations for the SB8 Qualification glass were divided by the analyzed SB8 Qualification glass elemental composition to calculate the normalized release for B, Li, Na and Si. Normalized releases for the EA and ARM glasses were calculated from the average analyzed leachate concentrations using reference values for the elemental compositions in the respective glasses.

Table 4-1 shows the full measured composition of the SB8 Qualification Glass. Elements specifically requested in the TTR[1] (e.g., elements greater than 0.1 wt% in the sludge), along with elements necessary for Product Composition Control System (PCCS) calculations (e.g., Cu and Nd) and elements detected by ICP-AES and ICP-MS, are reported. Essentially, all of the B, Li and Si and a portion of the Na are from the glass frit added to the SRAT product in order to prepare the glass. The frit used was Frit 803, which has a nominal composition of 78 wt % SiO_2, 8 wt % B_2O_3, 6 wt % Li_2O and 8 wt % Na_2O. This frit was recommended for use during the SME cycle based on a Measurement Acceptability Region (MAR) assessment completed on the analyzed SRAT Receipt material.[20] Depending upon the element, the results in Table 4-1 represent an average of up to eight measurements resulting from the glass dissolution methods and analysis techniques mentioned in the experimental procedure. The dissolution method(s), analytical technique(s) used to determine the average composition are noted in Table 4-1 next to each element.

Table 4-1. Glass Composition

Element	Wt% of Glass	Oxide	Wt% of Glass	Digestion and Analytical Method
Ag	0.0262	Ag_2O	0.028	PF ICP-MS
Al	2.59	Al_2O_3	4.89	PF, ICP-AES
B	1.5	B_2O_3	4.87	PF, ICP-AES
Ba	0.031	BaO	0.035	MA/PF, ICP-AES
Ca	0.527	CaO	0.737	MA, ICP-AES
Cd	0.00244	CdO	0.003	MA, ICP-AES
Ce	0.112	Ce_2O_3	0.131	MA/PF, ICP-AES
Cr	0.0508	Cr_2O_3	0.075	MA/PF, ICP-AES
Cu	0.111	CuO	0.139	MA/PF, ICP-AES
Fe	8.01	Fe_2O_3	11.5	MA/PF, ICP-AES
Gd	0.0401	Gd_2O_3	0.045	MA/PF, ICP-AES
La	0.0276	La_2O_3	0.033	MA/PF, ICP-AES
Li	1.74	Li_2O	3.75	MA/PF, ICP-AES
Mg	0.0805	MgO	0.133	MA/PF, ICP-AES
Mn	3.05	MnO	3.94	MA/PF, ICP-AES
Na	8.35	Na_2O	11.26	MA, ICP-AES
Nd	0.0859	Nd_2O_3	0.100	PF ICP-MS
Ni	0.384	NiO	0.488	MA/PF, ICP-AES
P	0.121	P_2O_5	0.277	MA, ICP-AES
Pb	0.0141	PbO	0.015	MA, ICP-AES
Pd	0.000682	PdO	0.001	PF ICP-MS
Rh	0.00276	Rh_2O_3	0.003	PF ICP-MS
Ru	0.00379	RuO_2	0.005	PF ICP-MS
S	0.103	SO_4	0.309	MA, ICP-AES
Si	24.6	SiO_2	52.7	PF, ICP-AES
Sr	0.014	SrO	0.017	MA/PF, ICP-AES
Th	0.269	ThO_2	0.307	MA/PF, ICP-AES
Ti	0.0135	TiO_2	0.023	MA/PF, ICP-AES
U	1.09	U_3O_8	1.28	MA/PF, ICP-AES
Y	0.00670	Y_2O_3	0.009	PF ICP-MS
Zn	0.0281	ZnO	0.035	MA/PF, ICP-AES
Zr	0.0624	ZrO_2	0.084	MA, ICP-AES
		Sum of Oxides	97.2	

The PCT results for the reference glasses and the blanks indicated that the test was completed under control. More specifically, the blanks and leachates from the ARM and EA references all had elemental and normalized releases within the reference values.[21, 22] The vessels exhibited measurable but negligible water losses (within the bounds allowed by the ASTM procedure) during the course of the test. See Table 4-2 for the normalized releases and leachate pH values.

The average normalized releases for the SB8 Qualification Glass based on B were 15x lower than the EA benchmark glass and average normalized releases for Na, Li and Si were 6-8x lower than the EA benchmark glass. Thus the PCT on the SB8 Qualification Glass clearly shows that the WAPS 1.3 criterion of mean PCT normalized releases lower than two standard deviations below the mean normalized releases of the EA glass is met.

Table 4-2. PCT Results for ARM, EA and the SB8 Qualification Glass

Glass ID	NL (B) g/L	NL (Na) g/L	NL (Li) g/L	NL (Si) g/L	NL (U) g/L	pH
ARM[a]	0.48	0.52	0.58	0.29	NA	10.46
Est. Std. Dev. (1-Sigma)[b]	0.01	0.02	0.02	0.01	NA	0.07
EA[a]	17.09	13.79	9.70	4.10	NA	11.71
Est. Std. Dev. (1-Sigma)[b]	0.43	0.34	0.27	0.11	NA	0.16
SB8-QUAL[c]	1.14	1.92	1.21	0.71	0.45	11.23
Est. Std. Dev. (1-Sigma)[b]	0.02	0.02	0.01	0.01	0.01	0.06

[a]Average of 3 PCT replicates
[b]Est. Std. Dev. – Estimated Standard Uncertainty
[c]Average of 4 PCT replicates

The measured SB8 Qualification Glass composition reported in Table 4-1 was used to predict specific properties of the glass based on the PCCS models. The PCCS model property predictions are listed in Table 4-3. The predicted properties from this composition were compared to SME acceptability criteria to evaluate whether this glass compared to the DWPF processing and product quality constraints.[23] Based on the measured composition, all of the predicted properties met the PCCS MAR criteria.

Table 4-3. PCCS Results for SB8 Qualification Glass

PCCS Model	Predicted Value
B ΔG_p Value	-8.63
NL[B (g/L)]	0.46
T_L Prediction (ºC)	884
Viscosity Prediction (P)	87.5
Nepheline Constraint Value	0.77
Al_2O_3 (wt %)	4.89
All PCCS MAR Criteria Met	yes

With respect to model applicability, Figure 4-1 provides plots of the predictions from DWPF models[22] for B, Li, and Na that relate the logarithm of the normalized PCT (for each element of interest) to a linear function of a free energy of hydration term (ΔGp, kcal/100g glass) derived from the measured composition for the SB8 Qualification glass as reported in Table 4-1. Prediction limits at a 95% confidence level for an individual PCT result are also plotted along with the linear fit. The EA and ARM results are also indicated on this plot.

As previously mentioned, the SB8 Qualification glass is acceptable with respect to the normalized release values for B, Na, Li, and Si as compared to the EA glass. With respect to model applicability, the models appear to be applicable to boron (i.e., within the 95% confidence bands) with the lithium release being just outside the upper 95% confidence band. However, the sodium response is not predictable by the current models. Although this is somewhat concerning, one must recognize that the SB8 Qualification glass is based on Tank 51 – not the Tank 40 blend which will constitute SB8. To demonstrate that the PCCS models are applicable to the SB8 compositional region which will be processed through DWPF, a variability study[24] was performed which was based on the Tank 40 blend composition (with uncertainties applied), Frit 803, and both sludge-only and coupled operations covering a waste loading interval of interest (32 – 40% WL). As a result, 22 glasses were designed, fabricated, and characterized (more specifically, durability as defined by the PCT for both quenched and centerline canister cooled thermal heat treatments). The results of that study indicated that the PCT responses for all the study glasses, regardless of thermal history and compositional perspective, were acceptable with respect to durability when compared to the EA reference glass.[25] In addition, all of the study glasses, with the exception of one extreme vertex glass, were predictable by the current durability models. The one extreme vertex glass which was not predictable fell outside of the lower 95% confidence band, which demonstrated a conservatism of the models. It was also noted that the normalized boron PCT values measured for the extreme vertex glass were much lower than that of the EA glass and therefore lack of predictability should not be of any practical concern.

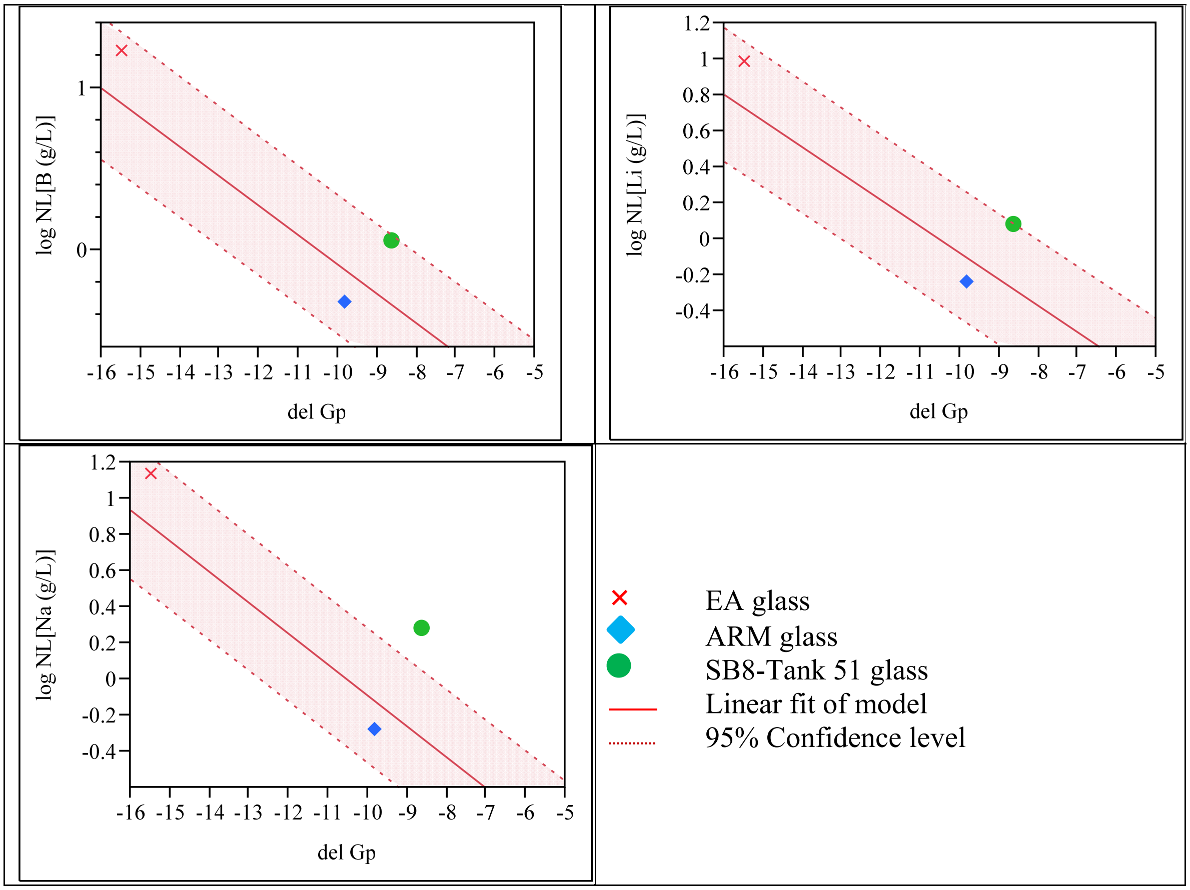


Figure 4-1. Plots of Delta G and Normalized Release

5.0 Conclusions

Tank 51 can be processed in DWPF. Assuming that a previously qualified waste (Tank 40 SB7b heel) mixed with the current qualified waste (Tank 51) is acceptable; Tank 51 can be transferred to Tank 40 to constitute the next sludge batch (SB8). SB8-Tank 51 simulant testing provided appropriate guidance for successful execution of the SB8 qualification sample CPC simulation. A stoichiometric factor of 133% by the DWPF-Hsu equation gave adequate nitrite destruction and acceptable levels of SRAT and SME hydrogen generation. The less washed nature of the Tank 51 material required a significant increase in the wt% total solids of the SRAT and SME products to achieve design basis level rheological properties. An intermediate level of increased solids concentration (between SB7b and the SB8 qualification testing) will presumably be needed to obtain reasonable rheological properties in DWPF with the SB8-Tank 40 feed. Some additional antifoam was added during formic acid addition and SRAT boiling to ensure successful completion of the SRAT cycle. DWPF may experience some increased foaming tendencies with SB8 if this behavior carries over into the SB8-Tank 40 blend. Ammonium ion formation was fairly minor at the acid stoichiometry of the Shielded Cells test. This does not mean that ammonium ion formation will be minor in DWPF with the Tank 40 blend, since the ammonium formation reactions tend to be sensitive to noble metals and slurry pH, and perhaps to other factors such as mercury and boiling time, which will not exactly mimic the processing seen in the SB8 qualification run.

6.0 Recommendations

- DWPF should accept the material in Tank 51 for blending with the SB7b Tank 40 heel to produce SB8 for feed to DWPF.
- Inductively coupled plasma-atomic emission spectroscopy is more bounding for determining the potential sulfur content in the melter feed than ion chromatography.
- DWPF acid stoichiometry for SB8 should be derived from simulant studies for SB7b, SB8-Tank 40, and SB8-Tank 51 used in concert with the results from SC-12 (qualification run of SB7b-Tank 40) and this SB8-Tank 51 qualification run.
- Antifoam additions may need to be supplemented if SB8-Tank 40 acts like SB8-Tank 51 during processing.

7.0 References

1. Samadi-Dezfouli, A. *Technical Task Request: Sludge Batch (SB) 8 Qualification Studies*; HLW-DWPF-TTR-2012-0009, Rev. 1; Savannah River Site: Aiken, SC, 2012.

2. Pareizs, J. M.; Click, D. R. *Task Technical and Quality Assurance Plan for Sludge Batch 8 Qualification in the Shielded Cells*; SRNL-RP-2012-00253; Savannah River National Laboratory: Aiken, SC, 2012.

3. Pareizs, J. M.; Click, D. R. *Analytical Study Plan for Sludge Batch 8 Qualification in the Shielded Cells*; SRNL-RP-2012-00561; Savannah River National Lab: Aiken, SC, 2012.

4. *E&CPT Research Programs Section Procedure Manual*; Manual L29; Savannah River National Lab: Aiken, SC, 2010.

5. Bibler, N. E. *Measuring and Predicting Fission Product Noble Metals in Savannah River Site High Level Waste Sludges*; WSRC-TR-2005-00098; Savannah River Site: Aiken, SC, 2005.

6. Gillam, J. M. *SB8_103012_47Kgal NO2_1.6M endpoint.xlsm, Worksheet SB8: Tank Farm Washing Spreadsheet*, Savannah River Remediation: Aiken, SC, 2012.

7. Pareizs, J. M. *SB8 SRAT Receipt Sample Characterization*; L3293-00022-07; Savannah River National Lab: Aiken, SC, 2013.

8. Click, D. R.; Edwards, T. B.; Wiedenman, B. J.; Brown, L. W. *Verification of the Defense Waste Processing Facility's (DWPF) Process Digestion Methods for the Sludge Batch 8 Qualification Sample*; SRNL-STI-2013-00096; savannah River National Lab: Aiken, SC, 2013.

9. Jantzen, C. M.; Stone, M. E. *Role of Manganese Reduction/Oxidation (REDOX) on Foaming and Melt Rate in High Level Waste (HLW) Melters (U)*; WSRC-STI-2006-00066; Savannah River National Laboratory: Aiken, SC, 2007.

10. Koopman, D. C. *Preliminary Evaluations of Two Proposed Stoichiometric Acid Equations*; SRNL-L3100-2009-00146; Savannah River National Laboratory: Aiken, SC, 2009.

11. Koopman, D. C. *DWPF Simulant CPC Studies for SB8*; SRNL-STI-2013-00106; Savannah River National Lab: Aiken, SC, 2013.

12. Bannochie, C. J. *Tank 40 Final SB7b Chemical Characterization Results*; SRNL-STI-2012-00097, Rev. 1; Savannah River National Lab: Aiken, SC, 2012.

13. *Standard Practice for Dealing With Outlying Observations*; American Society for Testing and Materials (ASTM): West Conshohocken, PA, 2008.

14. Pareizs, J. M. *SB8 Qual SRAT/SME Run*; L3293-00022-08; Savannah River National Lab: Aiken, SC, 2013.

15. Koopman, D. C. *Recommendations for SB8 Processing in DWPF-CPC*; SRNL-L3100-2013-00008; Savannah River National Lab: Aiken, SC, 2013.

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

17. *Basic Data Report: Defense Waste Processing Facility Sludge Plant; Savannah River Plant 200-S Area*; DPSP-80-1033, Rev. 10; Savannah River Site: Aiken, SC.

18. *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses and Multiphase Glass Ceramics: the Product Consistency Test (PCT)*; American Society for Testing and Materials (ASTM): West Conshohocken, PA, 2002.

19. *Waste Acceptance Product Specification for Vitrified High-Level-Waste Forms*; DOE/EM-0093, Rev. 2; Office of Environmental Management USDOE: 1996.

20. Peeler, D. K.; Edwards, T. B. *Frit and Waste Loading Recommendation for SB8 Qualification*; SRNL-L3100-2012-00204; Savannah River National Laboratory: Aiken, SC, 2012.

21. Jantzen, C. M.; Bibler, N. E.; Beam, D. C.; Crawford, C. L.; Pickett, M. A. *Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material*; WSRC-TR-92-346; Savannah River Site: Aiken, SC, 1994.

22. Jantzen, C. M.; Pickett, M. A.; Brown, K. G.; Edwards, T. B.; Beam, D. C. *Process/Product Models for the Defense Waste Processing Facility (DWPF): Part I. Predicting Glass Durability From Composition Using a Thermodynamic Hydration Energy Reaction Model (THERMO)*; WSRC-TR-93-0672; Savannah River Technology Center: Aiken, SC, 1993.

23. Brown, K. G.; Postles, R. L.; Edwards, T. B. *SME Acceptability Determination for DWPF Process Control*; WSRC-TR-95-00364, Revision 5; savannah River National Lab: Aiken, SC, 2006.

24. Edwards, T. B.; Peeler, D. K. *Analytical Plans Supporting the Sludge Batch 8 Glass Variability Study Being Conducted by EnergySolutions and CUA's Vitreous State Laboratory*; SRNL-STI-2012-00725, Rev. 0; Savannah River National Lab: Aiken, SC, 2012.

25. Kot, W. K.; Pegg, I. L.; Peeler, D. K.; Edwards, T. B. *Sludge Batch 8 Variability Study with Frit 803, WK Kot, IL Pegg, DK Peeler, and TB Edwards, VSL-13R2580-1, March 2013*; VSL-13R2580-1; Vitreous State Laboratory: Washington, DC, 2013.

Appendix A. Flow Curves

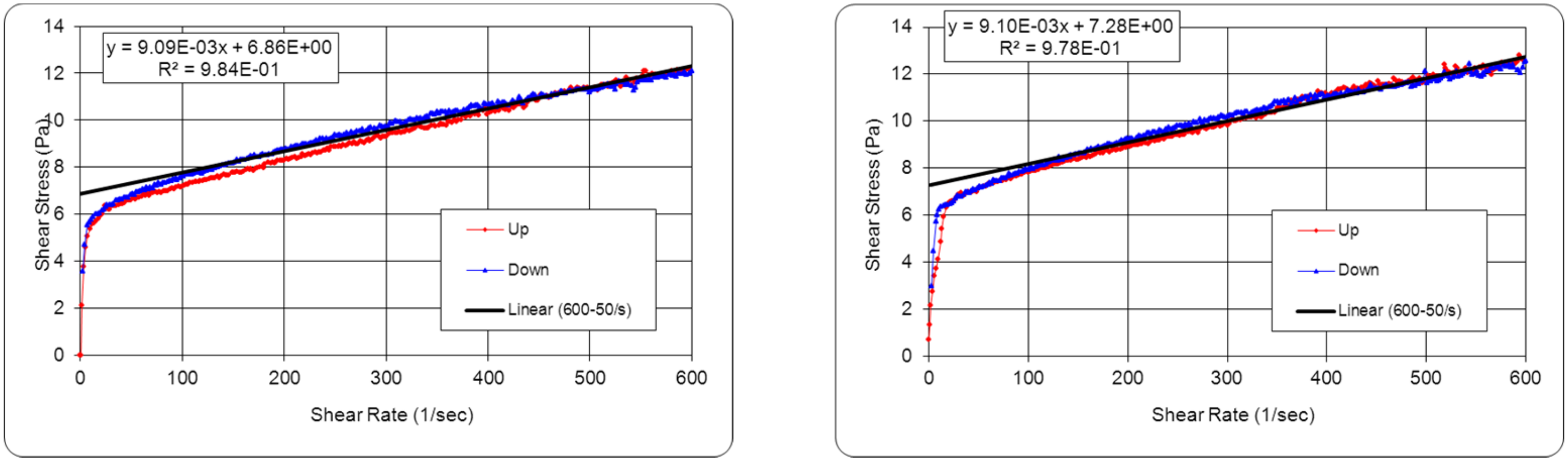


Figure A-1. SRAT Receipt

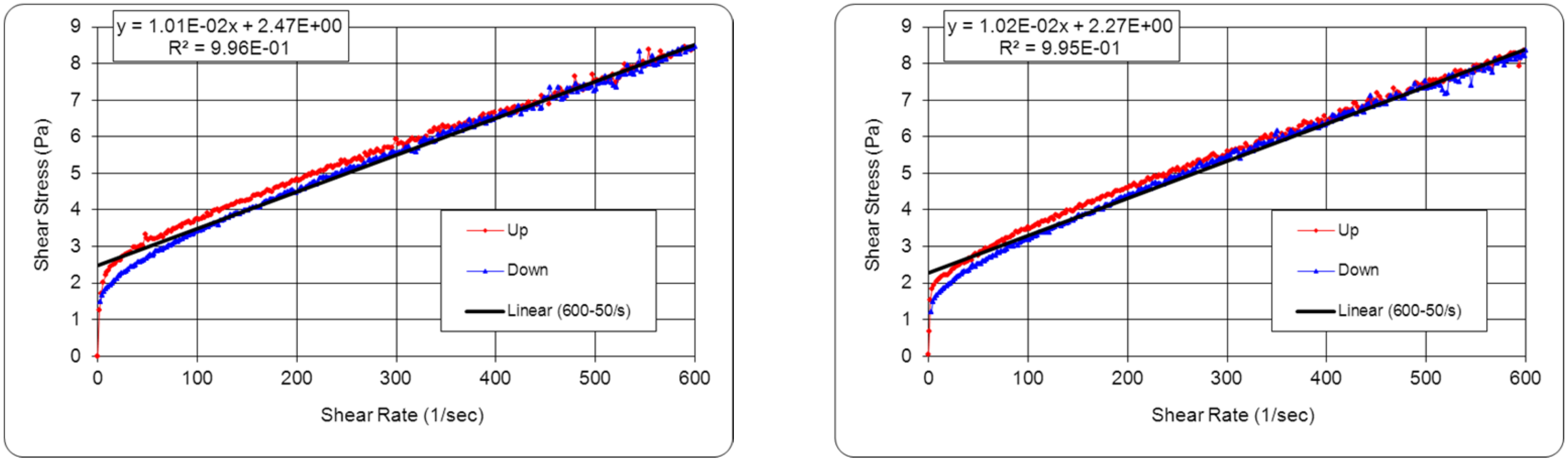


Figure A-2. SRAT Product

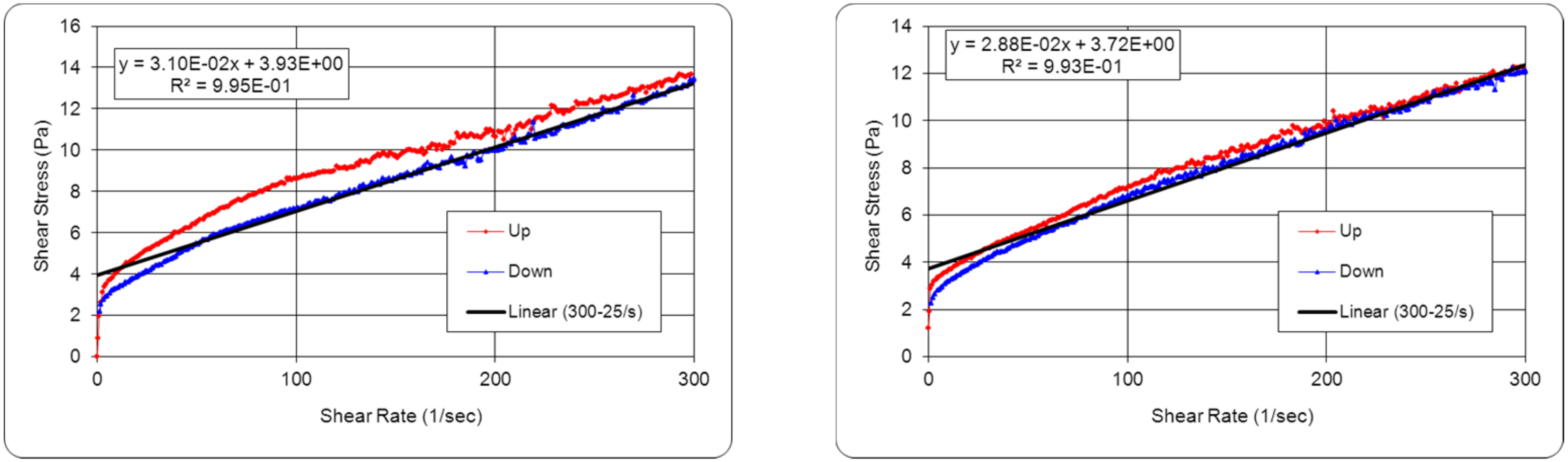
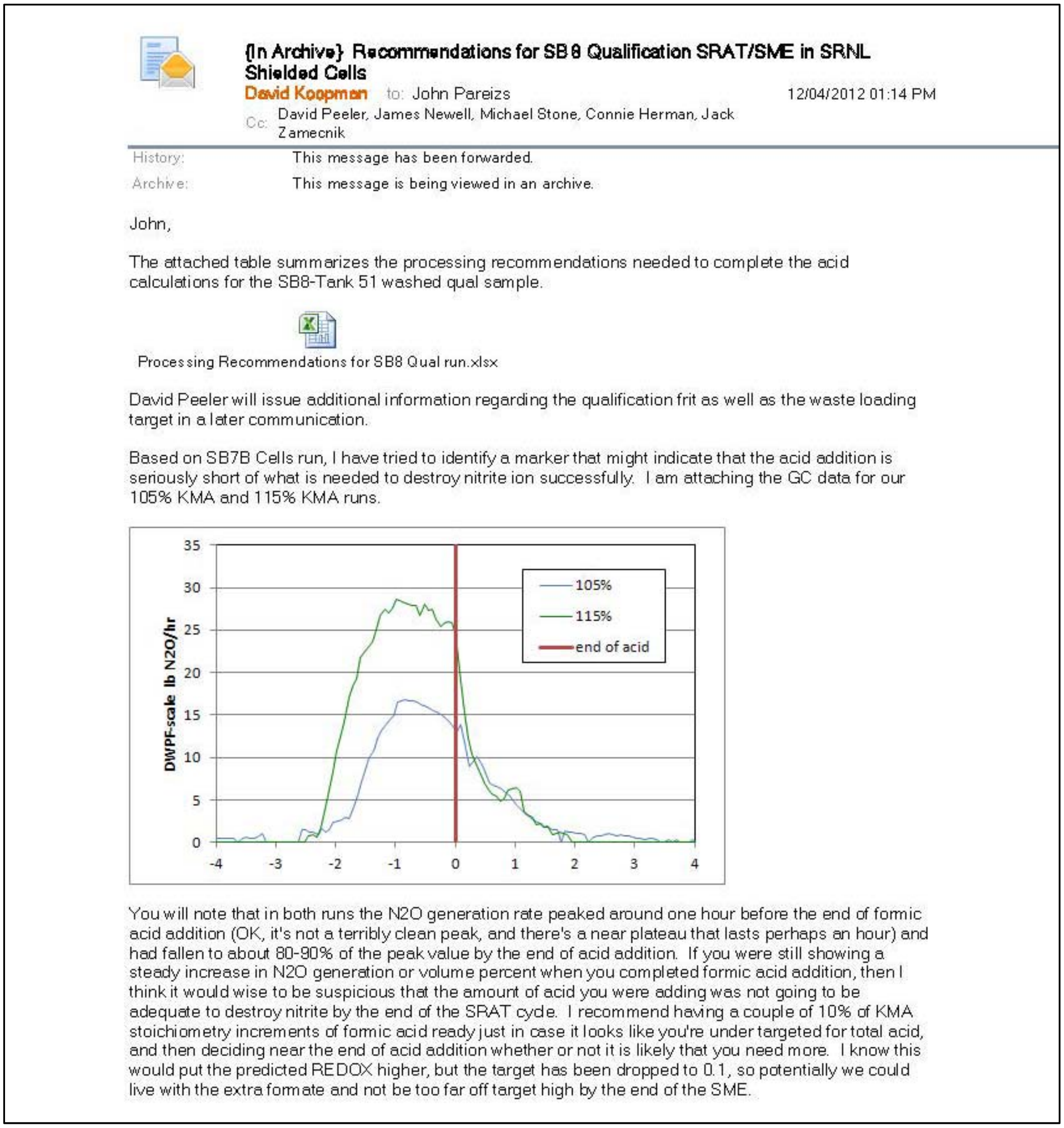


Figure A-3. SME Product

Appendix B. Shielded Cells Run Processing Inputs Based on Simulant Testing



{In Archive} Recommendations for SB 8 Qualification SRAT/SME in SRNL Shielded Cells

David Koopman to: John Pareizs 12/04/2012 01:14 PM

Cc: David Peeler, James Newell, Michael Stone, Connie Herman, Jack Zamecnik

History: This message has been forwarded.

Archive: This message is being viewed in an archive.

John,

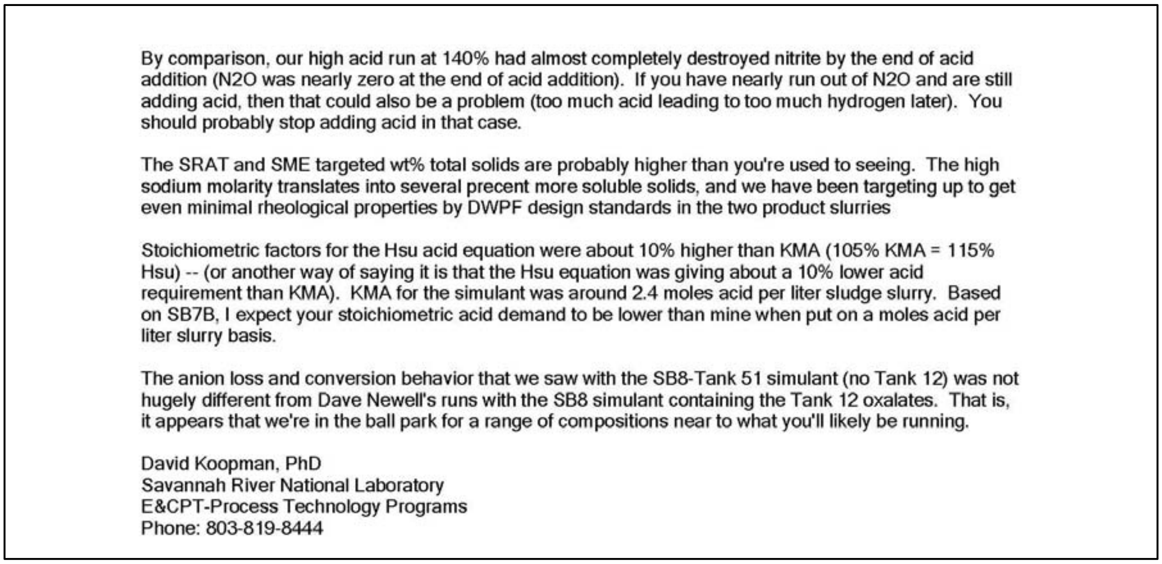
The attached table summarizes the processing recommendations needed to complete the acid calculations for the SB8-Tank 51 washed qual sample.

Processing Recommendations for SB8 Qual run.xlsx

David Peeler will issue additional information regarding the qualification frit as well as the waste loading target in a later communication.

Based on SB7B Cells run, I have tried to identify a marker that might indicate that the acid addition is seriously short of what is needed to destroy nitrite ion successfully. I am attaching the GC data for our 105% KMA and 115% KMA runs.

You will note that in both runs the N2O generation rate peaked around one hour before the end of formic acid addition (OK, it's not a terribly clean peak, and there's a near plateau that lasts perhaps an hour) and had fallen to about 80-90% of the peak value by the end of acid addition. If you were still showing a steady increase in N2O generation or volume percent when you completed formic acid addition, then I think it would wise to be suspicious that the amount of acid you were adding was not going to be adequate to destroy nitrite by the end of the SRAT cycle. I recommend having a couple of 10% of KMA stoichiometry increments of formic acid ready just in case it looks like you're under targeted for total acid, and then deciding near the end of acid addition whether or not it is likely that you need more. I know this would put the predicted REDOX higher, but the target has been dropped to 0.1, so potentially we could live with the extra formate and not be too far off target high by the end of the SME.



By comparison, our high acid run at 140% had almost completely destroyed nitrite by the end of acid addition (N2O was nearly zero at the end of acid addition). If you have nearly run out of N2O and are still adding acid, then that could also be a problem (too much acid leading to too much hydrogen later). You should probably stop adding acid in that case.

The SRAT and SME targeted wt% total solids are probably higher than you're used to seeing. The high sodium molarity translates into several precent more soluble solids, and we have been targeting up to get even minimal rheological properties by DWPF design standards in the two product slurries

Stoichiometric factors for the Hsu acid equation were about 10% higher than KMA (105% KMA = 115% Hsu) -- (or another way of saying it is that the Hsu equation was giving about a 10% lower acid requirement than KMA). KMA for the simulant was around 2.4 moles acid per liter sludge slurry. Based on SB7B, I expect your stoichiometric acid demand to be lower than mine when put on a moles acid per liter slurry basis.

The anion loss and conversion behavior that we saw with the SB8-Tank 51 simulant (no Tank 12) was not hugely different from Dave Newell's runs with the SB8 simulant containing the Tank 12 oxalates. That is, it appears that we're in the ball park for a range of compositions near to what you'll likely be running.

David Koopman, PhD
Savannah River National Laboratory
E&CPT-Process Technology Programs
Phone: 803-819-8444

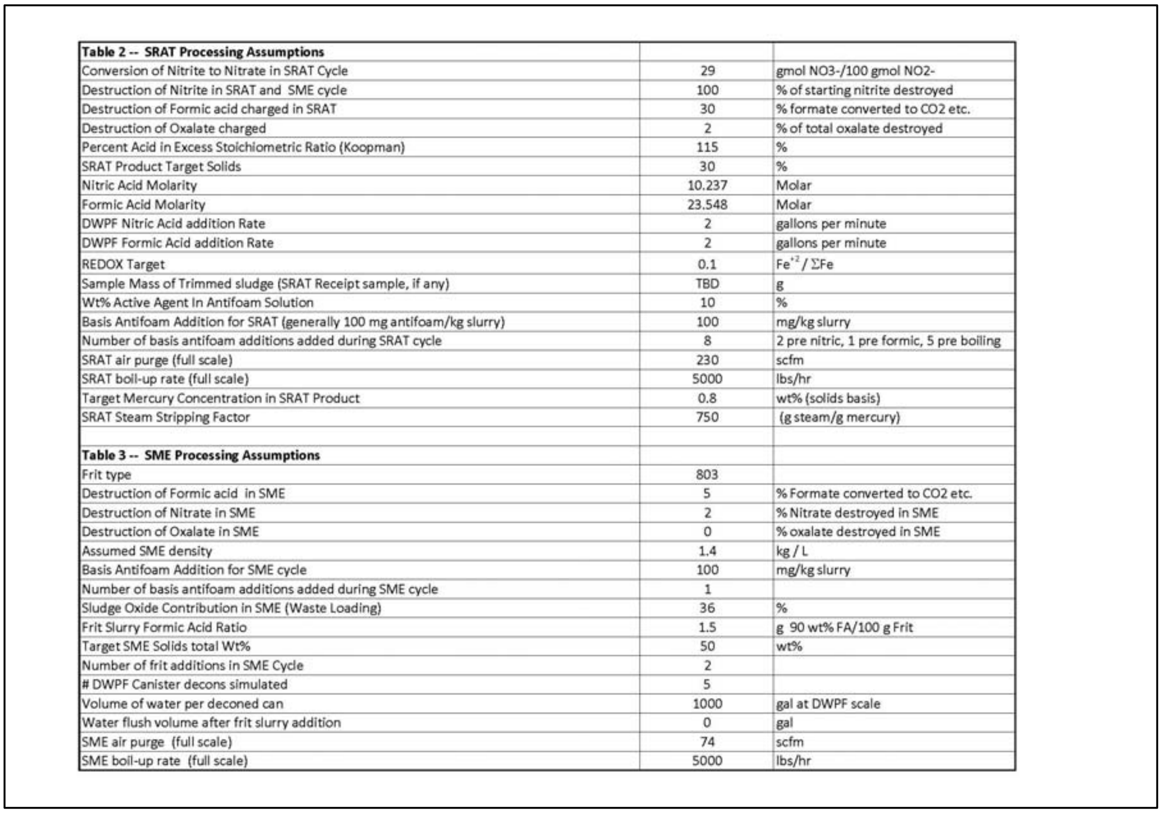


Table 2 -- SRAT Processing Assumptions		
Conversion of Nitrite to Nitrate in SRAT Cycle	29	gmol NO3-/100 gmol NO2-
Destruction of Nitrite in SRAT and SME cycle	100	% of starting nitrite destroyed
Destruction of Formic acid charged in SRAT	30	% formate converted to CO2 etc.
Destruction of Oxalate charged	2	% of total oxalate destroyed
Percent Acid in Excess Stoichiometric Ratio (Koopman)	115	%
SRAT Product Target Solids	30	%
Nitric Acid Molarity	10.237	Molar
Formic Acid Molarity	23.548	Molar
DWPF Nitric Acid addition Rate	2	gallons per minute
DWPF Formic Acid addition Rate	2	gallons per minute
REDOX Target	0.1	$Fe^{+2} / \Sigma Fe$
Sample Mass of Trimmed sludge (SRAT Receipt sample, if any)	TBD	g
Wt% Active Agent In Antifoam Solution	10	%
Basis Antifoam Addition for SRAT (generally 100 mg antifoam/kg slurry)	100	mg/kg slurry
Number of basis antifoam additions added during SRAT cycle	8	2 pre nitric, 1 pre formic, 5 pre boiling
SRAT air purge (full scale)	230	scfm
SRAT boil-up rate (full scale)	5000	lbs/hr
Target Mercury Concentration in SRAT Product	0.8	wt% (solids basis)
SRAT Steam Stripping Factor	750	(g steam/g mercury)
Table 3 -- SME Processing Assumptions		
Frit type	803	
Destruction of Formic acid in SME	5	% Formate converted to CO2 etc.
Destruction of Nitrate in SME	2	% Nitrate destroyed in SME
Destruction of Oxalate in SME	0	% oxalate destroyed in SME
Assumed SME density	1.4	kg / L
Basis Antifoam Addition for SME cycle	100	mg/kg slurry
Number of basis antifoam additions added during SME cycle	1	
Sludge Oxide Contribution in SME (Waste Loading)	36	%
Frit Slurry Formic Acid Ratio	1.5	g 90 wt% FA/100 g Frit
Target SME Solids total Wt%	50	wt%
Number of frit additions in SME Cycle	2	
# DWPF Canister decons simulated	5	
Volume of water per deconed can	1000	gal at DWPF scale
Water flush volume after frit slurry addition	0	gal
SME air purge (full scale)	74	scfm
SME boil-up rate (full scale)	5000	lbs/hr

Distribution:

D. R. Click, 999-W
A. P. Fellinger, 773-41A
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)

C. J. Bannochie, 773-42A
H. P. Boyd, 704-27S
J. M. Bricker, 704-27S
T. L. Fellinger, 704-26S
J. M. Gillam, 766-H
B. A. Hamm, 766-H
E. W. Holtzscheiter, 704-15S
J. F. Iaukea, 704-30S
M. T. Keefer, 766-H
D. D. Larsen, 766-H
E. J. Freed, 704-56H
D. K. Peeler, 999-W
J. W. Ray, 704-S
A. Samadi-Dezfouli, 704-27S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
A. V. Staub, 704-27S
A. R. Shafer, 704-27S
M. E. Stone, 999-W

P. R. Jackson, DOE-SR, 703-46A
K. H. Subramanian, 766-H

M. A. Broome, 704-29S
R. N. Hinds, 704-S
J. P. Vaughan, 773-41A

C. E. Duffey, 704-61H
A. W. Wiggins, 704-60H

.