

**WASHING AND DEMONSTRATION OF THE
DWPf FLOWSHEET IN THE SRNL SHIELDED
CELLS USING POST ALUMINUM DISSOLUTION
TANK 51 SLUDGE SLURRY**

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April 2008

Process Science and Engineering
Savannah River National Laboratory
Aiken, SC 29808

Prepared for the U.S. Department of Energy Under Contract Number
DEAC09-96SR18500



SRNL
SAVANNAH RIVER NATIONAL LABORATORY

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Printed in the United States of America

**Prepared For
U.S. Department of Energy**

**Key Words: DWPF, Sludge, SB5,
Washing, Aluminum**

Retention: Permanent

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EXECUTIVE SUMMARY

The remaining contents of Tank 51 from Sludge Batch 4 will be blended with Purex sludge from Tank 7 to constitute Sludge Batch 5 (SB5). The Savannah River Site (SRS) Liquid Waste Organization (LWO) has completed caustic addition to Tank 51 to perform low temperature Al dissolution on the H-Modified (HM) sludge material to reduce the total mass of sludge solids and Al being fed to the Defense Waste Processing Facility (DWPF). The Savannah River National Lab (SRNL) has also completed aluminum dissolution tests using a 3-L sample of Tank 51 sludge slurry through funding by DOE EM-21.

This report documents assessment of downstream impacts of the aluminum dissolved sludge, which were investigated so technical issues could be identified before the start of SB5 processing. This assessment included washing the aluminum dissolved sludge to a Tank Farm projected sodium concentration and weight percent insoluble solids content and DWPF Chemical Process Cell (CPC) processing using the washed sludge.

Based on the limited testing, the impact of aluminum dissolution on sludge settling is not clear. Settling was not predictable for the 3-L sample. Compared to the post aluminum dissolution sample, settling after the first wash was slower, but settling after the second wash was faster. For example, post aluminum dissolution sludge took six days to settle to 60% of the original sludge slurry height, while Wash 1 took nearly eight days, and Wash 2 only took two days.

Aluminum dissolution did impact sludge rheology. A comparison between the as-received, post aluminum dissolution and washed samples indicate that the downstream materials were more viscous and the concentration of insoluble solids less than that of the starting material. This increase in viscosity may impact Tank 51 transfers to Tank 40.

The impact of aluminum dissolution on DWPF CPC processing cannot be determined because acid addition for the Sludge Receipt and Adjustment Tank (SRAT) cycle was under-calculated and thus under-added. Although the sludge was rheologically thick throughout the SRAT and Slurry Mix Evaporator (SME) cycles, this may have been due to the under addition of acid.

Aluminum dissolution did, however, impact analyses of the SRAT receipt material. Two methods for determining total base yielded significantly different results. The high hydroxide content and the relatively high soluble aluminum content of the washed post aluminum dissolution sludge likely contributed to this difference and the ultimate under addition of acid. It should be noted that the simulant used to provide input for the SRAT cycle was an inadequate representation of the waste in terms of acid demand, likely due to the differences in the form of aluminum and hydroxide in the simulant and actual waste.

Based on the results of this task, it is recommended that:

- Sludge settling and rheology during washing of the forthcoming Sludge Batch 5 qualification sample be monitored closely and communicated to the Tank Farm.
- SRNL receive a sample of Tank 51 after all chemical additions have been made and prior to the final Sludge Batch 5 decant for rheological assessment. Rheology versus wt% insoluble solids will be performed to determine the maximum amount of decant prior to the Tank 51 to Tank 40 transfer.
- As a result of the problem with measuring total base and subsequently under-calculating acid for the DWPF CPC processing of the post aluminum dissolution sludge,

- Studies to develop understanding of how the sludge titrates (i.e., why different titration methods yield different results) should be performed.
- Simulants that better match the properties of post aluminum dissolution sludge should be developed.
- Work on developing an acid calculation less dependant on the total base measurement should be continued.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	iii
LIST OF FIGURES	vi
LIST OF TABLES	vii
LIST OF ACRONYMS	viii
1.0 INTRODUCTION AND BACKGROUND	1
2.0 APPROACH	2
2.1 General Description of Analytical Methods	2
2.2 Washing of Post Aluminum Dissolution Tank 51 Sample and Preparation of the SC-4 SRAT Receipt Sample	2
2.3 Post Aluminum Dissolution Boiling Evaluation	5
2.4 Simulant SRAT Receipt Preparation	5
2.5 Chemical Process Cell (CPC) Processing (SRAT Cycle, SME Cycle)	6
2.6 Rheology	8
3.0 RESULTS AND DISCUSSION	10
3.1 Washing and SRAT Receipt Preparation	10
3.2 Sludge Settling	13
3.3 Results of Boiling the Wash 2/Decant 2a Slurry	14
3.4 SRAT Receipt Characterization and Acid Addition Calculations	14
3.5 CPC Processing Results	17
3.5.1 SRAT Cycle Processing Observations	17
3.5.2 SRAT Cycle Sample Results	17
3.5.3 SRAT Cycle Anion Destruction and Conversion	18
3.5.4 SRAT Cycle Offgas Analysis	19
3.5.5 SME Processing Observations	21
3.5.6 SME Cycle Sample Results	21
3.5.7 SME Cycle Anion Destruction	22
3.5.8 SME Cycle Offgas Data	22
3.6 Rheology	23
4.0 CONCLUSIONS	25
5.0 RECOMMENDATIONS	26
6.0 REFERENCES	27
7.0 ACKNOWLEDGEMENTS	29
APPENDIX A. SETTLING DATA FROM POST ALUMINUM DISSOLUTION WASHING	30
APPENDIX B. CALCULATION OF ALUMINUM AND SODIUM REMOVAL USING IRON RATIOS	31
APPENDIX C. RHEOLOGICAL CHARTS AND FLOW CURVES	32
APPENDIX D. HYDROGEN GENERATION FROM THE SIMULANT SRAT CYCLES SUPPORTING THE POST ALUMINUM DISSOLUTION CPC PROCESSING	35

LIST OF FIGURES

Figure 2-1. Apparatus for Sludge Boiling Evaluation 5

Figure 2-2. Schematic of SRAT Equipment Set-Up..... 7

Figure 3-1. Sludge Settling During Aluminum Dissolution and Washing 14

Figure 3-2. Hydrogen Generation During SC-3 and SC-4 SRAT Cycles..... 20

Figure 3-3. Carbon Dioxide Generation During SC-3 and SC-4 SRAT Cycles..... 20

Figure 3-4. Nitrous Oxide Generation During SC-3 and SC-4 SRAT Cycles..... 21

Figure 3-5. SME Cycle Hydrogen Generation Data 23

Figure C - 1 Tank 51, As-Received, May 2007, Flow Curve 32

Figure C - 2 Tank 51, SRNL Post Aluminum Dissolution, Flow Curve 32

Figure C - 3 Tank 51, SRNL Post Aluminum Dissolution, Wash 1, Flow Curve 32

Figure C - 4 Tank 51, SRNL Post Aluminum Dissolution, Wash 2a, Flow Curve 33

Figure C - 5 Tank 51, SRNL Post Aluminum Dissolution, Wash 2b SC-4 SRAT Rcpt, Flow Curve 33

Figure C - 6 SRNL SC-4 SRAT Product, Flow Curve 33

Figure C - 7 SRNL SC-4 SME Product, Flow Curve 34

Figure C - 8 SRNL SC-3 SRAT Product, Flow Curve 34

Figure C - 9 SRNL SC-3 SME Product, Flow Curve 34

LIST OF TABLES

Table 2-1. SRNL Washing Amounts 4

Table 2-2. Summary of CPC Processing 6

Table 2-3. MV I and MV II Rotor Specifications and Flow Curve Program 9

Table 3-1. Weight Percent Solids and Density During Tank 51 Post Aluminum Dissolution Washing 10

Table 3-2. Major Components of the Supernate During Washing of the Post Aluminum dissolution
Sample 10

Table 3-3. Percentages of Aluminum and Sodium Removed by Dissolution and Washing..... 11

Table 3-4. Calculated Weight Percent Soluble Aluminum and Sodium..... 11

Table 3-5. Comparison of Major Elements (>0.1%) in the Total Solids in the As-Received Tank 51
Sample and the Post Aluminum Dissolution/Washed (SRAT Receipt) Sample 12

Table 3-6. Comparison of Major Elements in the As-Received Tank 51 Sample and the Post
Aluminum Dissolution/Washed (SRAT Receipt) Sample on a Calcined Solids Basis 13

Table 3-7. Characterization Results and Acid Calculation Inputs of the Post Aluminum Dissolution
Tank 51 (SC-4 SRAT Receipt) Sample and the Corresponding Non Rad Simulant SRAT Receipt
(SB5-4 & -5) With Comparison to a Pre Aluminum Dissolution SRAT Receipt (SC-3) Sample 15

Table 3-8. Acid Calculation Inputs of the Washed Post Aluminum Dissolution Tank 51 Sample (SC-
4 SRAT Receipt) and the Corresponding Non Rad Simulant SRAT Receipt (SB5-4 & -5) With
Comparison to a Pre Aluminum Dissolution SRAT Receipt Sample (SC-3)..... 16

Table 3-9. SRAT Cycle Acid Requirements..... 17

Table 3-10. SRAT Product Characterization Results 18

Table 3-11. Comparison of Assumed and Measured Anion Destruction and Conversion in the SRAT
Cycles 18

Table 3-12. SME Product Weight Percent Solids and Densities 22

Table 3-13. Comparison of Assumed and Measured Anion Destruction and Conversion in the SME
Cycles 22

Table 3-14. Rheological Properties of As-Received, Al Dissolved, Washed and SRAT/SME Products... 24

LIST OF ACRONYMS

ACTL	Aiken County Technologies Laboratory
AD	Analytical Development
ARG	Analytical Reference Glass
ARM	Approved Reference Material
ASP	Analytical Study Plan
CPC	Chemical Process Cell
CS	Calcine Solids
DWPF	Defense Waste Processing Facility
FAVC	Formic Acid Vent Condenser
GC	Gas Chromatograph
HLW	High Level Waste
HM	H-Modified
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
IS	Insoluble Solids
LIMS	Laboratory Information Management System
LWO	Liquid Waste Organization
MAR	Measurement Acceptability Region
MWWT	Mercury Water Wash Tank
NIST	National Institute of Standards and Testing
PCCS	Product Consistency Control System
PMP	Polymethyl propylene
PSAL	Process Science Analytical Laboratory
PS&E	Process Science and Engineering Section
QA	Quality Assurance
REDOX	REDuction / OXidation potential
SB4	Sludge Batch 4
SB5	Sludge Batch 5
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
SS	Soluble Solids
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TS	Total Solids
TT&QAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAPS	Waste Acceptance Product Specification
WL	Waste Loading

1.0 INTRODUCTION AND BACKGROUND

The current contents of Tank 51 will be blended with Purex sludge from Tank 7 to constitute Sludge Batch 5 (SB5). The Savannah River Site (SRS) Liquid Waste Organization (LWO) has completed caustic addition to Tank 51 to perform low temperature Al dissolution on the H-Modified (HM) sludge material to reduce the total mass of sludge solids and Al being fed to the Defense Waste Processing Facility (DWPF). The Savannah River National Lab (SRNL) has also completed aluminum dissolution tests using a 3-L sample of Tank 51 sludge slurry (funded by DOE EM-21).¹ The aluminum dissolved sludge resulting from this testing was then used to determine potential downstream impacts so technical issues could be identified before the start of SB5 processing. The potential downstream impacts assessed include the Tank Farm sludge washing and concentration process and the DWPF Chemical Process Cell (CPC) and melter processing envelopes.

This report documents:

- The washing (addition of water to dilute the sludge supernate) and concentration (decanting of supernate) of the Post Aluminum Dissolution sample to adjust sodium content and weight percent insoluble solids to Tank Farm projections of Tank 51 after aluminum dissolution.
- The performance of a DWPF Chemical Process Cell (CPC) simulation using the washed Post Aluminum Dissolution sample. This includes a Sludge Receipt and Adjustment (SRAT) cycle where acid is added to the sludge to destroy nitrite and remove mercury, and a Slurry Mix Evaporator (SME) cycle where glass frit is added to the sludge in preparation for vitrification. Processing parameters for the processing were based on work with a non radioactive simulant, also presented in this report.
- A comparison of CPC processing between Tank 51 with and without aluminum dissolution.

This work is controlled by a Task Technical and Quality Assurance Plan (TTQAP)², and analyses are guided by an Analytical Study Plan³. This work is Technical Baseline Research and Development (R&D) for the Department of Energy (DOE) Office of Cleanup Technologies (EM-21).

2.0 APPROACH

The general experimental methods for this task are presented in this section. First, a broad overview of the analytical techniques is given. Second, a description of the washing process is presented, along with actual washing amounts. Third, a boiling test to evaluate the impact of potentially high aluminum in a SRAT receipt sample is described. Fourth, preparation of the simulant SRAT sample is presented. Fifth, laboratory scale CPC processing is outlined. Finally, the methodology for rheological measurements is given.

2.1 General Description of Analytical Methods

Analyses for this task used guidance of an Analytical Study Plan (ASP)³. Sample request forms were used for samples to be analyzed, and analyses followed the guidelines and means of sample control stated in the ASP for the task. A unique laboratory identification management system (LIMS) number was assigned to each sample for tracking purposes. Analyses were performed using approved analytical and Quality Assurance (QA) procedures.

Procedures for analysis of the simulant material can be found in Reference 4. For the radioactive materials, procedures and work instructions for density, percent solids, and supernate and slurry dilutions are also given in Reference 4. Procedures for digestions and sample analyses are given in Reference 5.

Radioactive slurry total base was determined by a direct in-Cell titration of slurry and a titration by SRNL Analytical Development (SRNL-AD) using diluted slurry.

2.2 Washing of Post Aluminum Dissolution Tank 51 Sample and Preparation of the SC-4 SRAT Receipt Sample

Sludge slurry remaining from the aluminum dissolution process¹ was to be washed following Tank Farm planned washes: three washes/decants.⁶ Because the Tank 7 addition was not simulated in the SRNL washes, wash addition amounts were based on sodium concentration rather than a combination of sodium and other anions. However, measured sodium was lower than predicted following each of the SRNL washes, and only two were required in the SRNL Shielded Cells demonstration. Washing results are discussed in Section 3.1. The general outline of a wash cycle was:

- Add deionized water
- Mix for 30 minutes
- Allow solids to settle and supernate to clarify
- Decant the supernate once the target amount is obtained

Washing was performed in a 4-L wide mouth glass bottle. The bottle had a centimeter scale taped to the side. This scale enabled estimation of the slurry and supernate volumes. Actual sludge and supernate amounts were determined by mass, and volumes were calculated from mass and density measurements. Washing strategy was based on Tank Farm planned washes as given in Reference 6 (after a Tank 7 to 51 transfer and a decant). Because the Tank 7 addition was not simulated in the SRNL washes, wash addition amounts were based on sodium concentration rather than a combination of sodium and other anions. Decant amounts were targeted based on weight percent insoluble solids. Also, since the nitrite to nitrate ratio in the post aluminum dissolution sludge was approximately two, well above the Tank Farm corrosion requirement of 1.66, and since the sludge had large quantities of hydroxide from the caustic addition during aluminum dissolution, deionized water was used for washing rather than inhibited water.

Wash water target amounts were determined by calculating the supernate volume in the sludge to be washed and then using a rearranged version of the dilution equation $V_1 \cdot C_1 = V_2 \cdot C_2$ with $V_2 = V_1 + V_w$. Note that the accuracy of this equation is dependant on the applicability of the assumptions that volume is conserved and there is no precipitation or dissolving of solids during washing. This is the same methodology used in Tank Farm planning spreadsheets.

$$V_w = V_1 \cdot \left(\frac{C_1 - C_2}{C_2} \right) \quad 2-1$$

where,

- V_w = volume of wash water to be added
- V_1 = volume of supernate
- C_1 = sodium concentration in supernate
- C_2 = target sodium concentration

Decant amounts were targeted based on an insoluble solids balance, assuming that the insoluble solids mass remained constant during the washing process. Sludge solids level was periodically recorded during settling between wash water additions. These recordings are presented in Appendix A and discussed in Section 3.2. However, actual decant amounts during each wash were limited by the settled sludge level, and the ability to remove supernate without disturbing the sludge solids. It should be noted that the interface between the sludge solids and supernate was very clear. Following Washes 1 and 2, a peristaltic pump was used to remove supernate. But, following the decant after Wash 2 (designated as Decant 2a), insoluble solids content was unacceptably low. More supernate was removed (Decant 2b) using a large slurry pipette after an additional 14 days of settling. Use of the pipette allowed decanting closer to the sludge solids without interfering with the solids layer, compared to the relatively higher suction of the pump. It should be noted that sludge level remained unchanged during these additional days of settling. Table 2-1 details actual wash and decant amounts along with targets and analytical results needed for subsequent washes. As stated above, only two washes were performed at SRNL rather than the Tank Farm planned three due to the lower than predicted sodium concentration following the SRNL second wash.

Sludge level was periodically recorded during settling between wash water additions. These recordings are presented in Appendix A and discussed in Section 3.2.

The sludge slurry remaining after Decant 2b was characterized for use in the SC-4 SRAT and SME cycles and will be subsequently referred to as the SRAT receipt.

Table 2-1. SRNL Washing Amounts

	Post Al Diss Tk51	Wash 1 ^a	Decant 1	After Decant 1 ^b	Before Wash 2 ^b	Wash 2 ^a	Decant 2a	After Decant 2a ^b	Before Decant 2b ^b	Decant 2b	After Decant 2b
Sludge Slurry Mass (g)	1,706			2,013	1,881			1,595	1,468		1,064
Wash Water or Decant (g)		1,118	(808)			884	(1170)			(404)	
Wt% Insoluble Solids	6.44			6.52	6.52			8.87	8.87		12.0
Supernate Mass (g) [*]	1,596			1,882	1,758			1,454	1,338		936
Supernate Density (g/mL)	1.21			1.12	1.12			1.07	1.07		1.07
Supernate Volume (mL) [†]	1,319			1,680	1,570			1,358	1,250		875
Target/Predicted Na (M)			2.65	2.65			1.60	1.60			
Measured Na (M)	4.86		2.42	2.42	2.42		1.42	1.42	1.42	1.42	1.42

^a Wash volume targets were calculated using Equation 2-1. Given in this table are actual wash water amounts added to the sludge slurry.

^b After each decant, a sample of the sludge slurry was taken. Therefore, the after decant and before wash values are not equal.

^{*} $Supernate\ mass = Sludge\ Slurry\ mass \cdot \left(1 - \frac{wt\% \text{ insol}}{100}\right)$

[†] $Supernate\ vol = \frac{Supernate\ mass}{Supernate\ density}$

2.3 Post Aluminum Dissolution Boiling Evaluation

Because of pump water in-leakage in Tank 40, DWPF is removing water from the SRAT receipt material by boiling to increase total solids prior to the start of the SRAT cycle. To determine whether “boiling” of post-aluminum dissolution Tank 51 sludge produces unusual changes in sludge consistency due to the relatively high aluminum content in the supernate, a sludge sample was evaluated.

Approximately 75 mL of washed post-aluminum dissolution sludge* was combined with ~15 mL distilled water (used for rinsing purposes) in a glass boiling vessel (see Figure 2-1 for a photo of the apparatus). While stirring, the mixture was boiled for eight hours. During this period, a total of ~45 mL of condensate was collected. Considering the contribution of the rinse water (15 mL), the volume of condensate derived from the sludge slurry was ~30 mL. Visual observations regarding the consistency of the sludge slurry were made during the boiling period and after completion of the boiling period. Total solids content of the final concentrated sludge (after boiling and cooling) was determined through replicate measurements.



Figure 2-1. Apparatus for Sludge Boiling Evaluation

2.4 Simulant SRAT Receipt Preparation

A Tank 51 simulant was prepared by precipitating MnO_2 , combining the MnO_2 with a metal nitrate solution, coprecipitation of the metals as hydroxides, addition of sodium carbonate, washing the supernate to lower the nitrate concentration below the final target, decanting excess supernate and adding soluble chemicals to reach the desired target. The sludge simulant can match the chemical composition target but does not necessarily contain the same aluminum species as are present in the waste tank. The simulant's aluminum is likely all present as the gibbsite form, an easily dissolved form of aluminum, with little or no boehmite, as the simulant does not have the same time and temperature history as the actual waste. To simulate the dissolution of aluminum, the sludge simulant was contacted with 50 wt% sodium hydroxide to dissolve insoluble aluminum then was washed/decanted with DI water to lower the sodium

* Wash 2 following Decant 2a slurry, with a total solids content of 16.3 wt % and a density of 1.14 g/mL

concentration to 1.36 M. No attempt was made to achieve a dissolved aluminum target. The sludge was thought to be conservative in that all the Al was dissolved and more aluminum was removed from the simulant (80%) than actual waste (35%).

2.5 Chemical Process Cell (CPC) Processing (SRAT Cycle, SME Cycle)

The SRAT and SME cycles were conducted following procedures in the Process Science and Engineering Section procedure manual.⁴ A summary of each cycle is presented in Table 2-2 below.

Table 2-2. Summary of CPC Processing

SRAT Cycle	SME Cycle
<ul style="list-style-type: none"> • Acid Calculation • Heating of SRAT Receipt to 93 °C • Addition of nitric and formic acids per acid calculation • Heat to boiling • Concentration (water removal) to a target wt% total solids • Reflux for 24 hours 	<ul style="list-style-type: none"> • Addition and removal of water to simulate addition and removal of water from the decontamination of 5 glass canisters • Addition of frit and dilute formic acid • Concentration (water removal) to target 45-50 wt% total solids.

Simulant and real-waste processing runs were performed using a vessel designed to process one liter of sludge. For the in-Cell run, the SRAT rig was assembled and tested in the SRNL Shielded Cells Mockup area and placed into the Shielded Cells fully assembled. A detailed description of the SRAT rig and testing of the rigs can be found in References 7 and 8. The intent of the equipment is to functionally replicate the DWPF processing vessels. The glass kettle is used to replicate both the SRAT and the SME, and it is connected to the SRAT Condenser and the Mercury Water Wash Tank (MWWT). Because the DWPF Formic Acid Vent Condenser (FAVC) does not directly impact SRAT and SME chemistry, it is not included in SRNL Shielded Cells CPC processing. Instead, a simple “cold finger” condenser is used to cool offgas to approximately 20 °C below ambient to remove excess water before the gas reaches the gas chromatograph for characterization. The Slurry Mix Evaporator Condensate Tank (SMECT) is represented by a sampling bottle that is used to remove condensate through the MWWT. For the purposes of this paper, the condensers and wash tank are referred to as the offgas components. A sketch of the experimental setup is given as Figure 2-2.

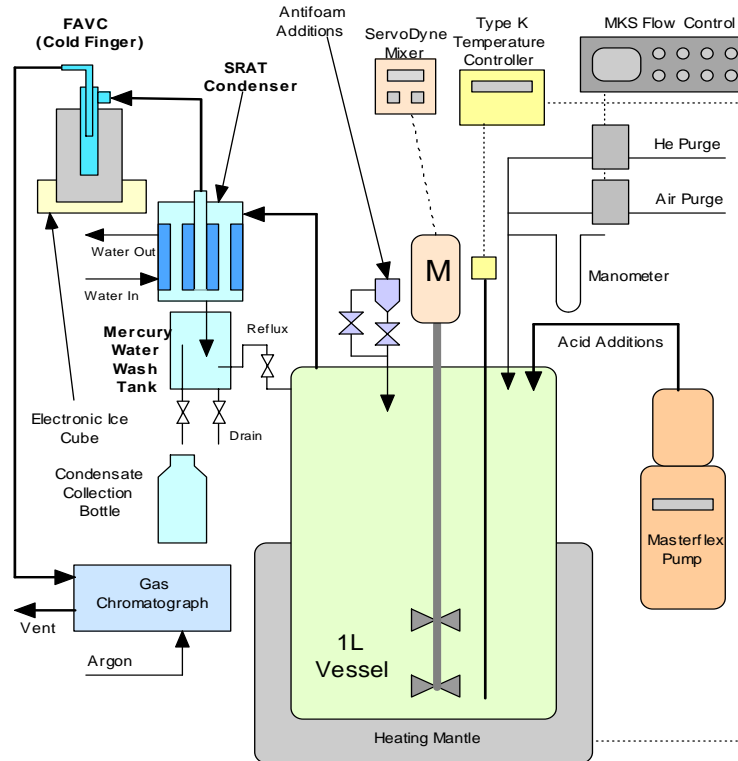


Figure 2-2. Schematic of SRAT Equipment Set-Up

SRAT and SME processing parameters are given in References 9 and 10. Offgas hydrogen, oxygen, nitrogen, nitrous oxide, and carbon dioxide concentrations were measured during the experiments using in-line instrumentation. Helium was introduced at a concentration of 0.5% of the total air purge as an inert tracer gas so that total amounts of generated gas and peak generation rates could be calculated. During the runs, the kettle was monitored to observe reactions that were occurring to include foaming, air entrainment, rheology changes, loss of heat transfer capabilities, and offgas carryover. Observations were recorded in laboratory notebooks^{9, 10} and are discussed in Section 3.0.

Concentrated nitric acid (50-wt%) and formic acid (90-wt%) were used to acidify the sludge and perform neutralization and reduction reactions during processing. The amounts of acid to add for each run were determined using the existing DWPF acid addition equation¹¹. The split of the acid was determined using the REDOX equation currently being used in DWPF processing¹². 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 for each run. The values used for each run are provided in Section 3.0.

SRAT processing included the dewater time in boiling plus an additional time of reflux to simulate DWPF processing conditions. SME processing included the addition and removal (by boiling) of water to simulate DWPF's addition and removal of water used for decontaminating canisters of glass. The frit addition was split into two equal portions. The frit was added with water and formic acid at DWPF prototypical conditions. Concentration was performed after each frit addition and then heat was removed to allow for the next frit addition. A final concentration was performed at the end of the run to meet the target total solids. The SRAT condenser was maintained at 25 °C during the run, while the cold finger condenser remained below 5 °C.

2.6 Rheology

Rheological properties 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 that holds the cup. The shear stress is determined from the torque measurement and is independent of the rheological properties. Conditions that impact the measured torque are; slip (material does not properly adhere to the rotor or cup), phase separation (buildup of liquid layer on rotor), sedimentation (particles settling out of the shearing zone), homogeneous sample (void of air), lack of sample (gap not filled), excess sample (primarily impacts rheologically thin fluids), completely filling up the void below the bob (air buffer that is now filled with fluid) and Taylor vortices. The first five items yield lower stresses and the last three add additional stresses. The shear rate is geometrically determined using the equations of change (continuity & motion) and is that for a Newtonian fluid. This assumption also assumes that the flow field is fully developed and the flow is laminar. The shear rate can be calculated for non-Newtonian fluid using the measured data and fitting this data to the rheological model or corrected as recommended by Darby¹³. 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 thinner fluid. Correcting the flow curves will not be performed in this task, resulting in a slightly more viscous fluid.

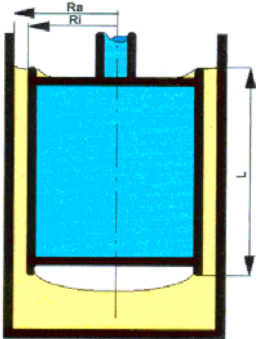
The bob typically used for measuring tank sludge or SRAT product is the MV I rotor. For SME product, the MV II rotor is used to perform the measurements, due to the larger frit particles that are present in the SME product. The MV II has a larger gap to accommodate the larger frit particles. The shape, dimensions, and geometric constants for the MV I and MV II rotors are provided in Table 2-3.

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

The flow curves for the sludge are fitted to the down curves using the Bingham Plastic rheological model, Equation 2-2, where τ is the measured stress (Pa), τ_o is the Bingham Plastic yield stress (Pa), μ_∞ is the plastic viscosity (Pa-sec), and $\dot{\gamma}$ is the measured shear rate (sec^{-1}). During all these measurements, typically the sample remained in the cup for the 2nd measurement, due to the sample availability. If thixotropic properties or unique flow behavior were obvious on the first sample, efforts were made to perform additional measurements by reloading the sample.

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

Table 2-3. 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 ($\text{s}^{-1}/\% \text{RPM}$)	11.7	4.51
	Shear rate range (s^{-1})	0 – 600	0 – 300
	Ramp up time (min)	5	5
	Hold time (min)	1	1
	Ramp down time (min)	5	5

3.0 RESULTS AND DISCUSSION

3.1 Washing and SRAT Receipt Preparation

Presented in Table 3-1 are the percent solids and density measurements of the Tank 51 Post Aluminum Dissolution sample throughout washing.

Table 3-1. Weight Percent Solids and Density During Tank 51 Post Aluminum Dissolution Washing

Physical Property	Post Al Diss.	Wash/Decant 1	Wash/Decant 2a *	Decant 2b *
Wt % Total Solids (Slurry Basis)	28.0	18.5	16.3	19.1
Wt % Insoluble solids (Slurry Basis)	6.44	6.52	8.87	12.0
Wt % Soluble Solids (Slurry Basis)	21.5	11.9	7.41	7.16
Slurry Density (g/mL)	1.27	1.19	1.14	1.20
Supernate Density (g/mL)	1.21	1.12	1.07	1.07

* For Wash 2, there were two decants (a and b). A second decant, using a pipette instead of a relatively high suction peristaltic pump, was necessary to increase total and insoluble solids content.

Given in Table 3-2 are the aluminum, sodium, nitrite, and nitrate content of supernates during washing. From this data it appears that soluble aluminum is being removed from the sludge along with the soluble species. To confirm that the decrease is caused by washing and not precipitation, the ratio of total aluminum to iron (essentially insoluble and inert in washing) in the sludge can be used. A decrease in this ratio indicates aluminum removal. Sodium removed during washing can also be calculated using this methodology. Table 3-3 shows results of this calculation. Calculations and the ratios are given in Appendix B.

Table 3-2. Major Components of the Supernate During Washing of the Post Aluminum dissolution Sample

	Post Al Dissolution	Wash 1 Supernate	Wash 2 Supernate ^b
Al (M)	0.355	0.170	0.095
Na (M) ^a	4.86	2.42	1.42
NO ₂ ⁻ (M)	0.415	0.187	0.107
NO ₃ ⁻ (M)	0.218	0.0871	0.0510

^a Sodium was also measured by ICP-AES: 5.26 M Post Diss., 2.55 M Wash 1, and 1.43 M Wash 2. During the washing process, AA was used since it was available sooner, and AA is generally a better method for determining Na.

^b It should be noted that there were two decants after Wash 2 – Decant 2a and Decant 2b, having the same composition.

Table 3-3. Percentages of Aluminum and Sodium Removed by Dissolution and Washing

% Al Removed by Dissolution (relative to Al in as-received Tank 51 sample)	21
% Al Removed by Washing (relative to Al in as-received Tank 51 sample)	14
Total % Al Removed (relative to Al in as-received Tank 51 sample)	35
% Na Removed by Washing (relative to post Al dissolution sample)	66
% Increase in Na (relative to Na in as-received Tank 51 sample)	14

The table above does show that aluminum was removed during washing. However, a comparison of predicted (by mass balances) to measured insoluble solids indicates some precipitation, most likely a sodium-aluminum compound. Therefore, the weight percents of Al and Na were calculated prior to and after washing using Equation 3-1. This equation converts the supernate (soluble) and total solids (total) concentrations of element *i* to a slurry basis.

$$Wt\%_{sol} = \frac{C_i \cdot MW_i \cdot (100 - Wt\%_{IS})}{\rho_{sup} \cdot W_i \cdot Wt\%_{TS}} \cdot 10 \quad [3-1]$$

where,

$Wt\%_{sol}$ = weight % of element *i* that is soluble (mass soluble/total mass x 100)

C_i = concentration of element *i* in the supernate (mol/L supernate)

MW_i = molecular weight of element *i*

ρ_{sup} = supernate density (g/mL)

W_i = weight percent of element *i* in the total solids.

$W\%_{IS}$ = weight fraction insoluble solids in the slurry ($1 - W_{IS}$ is the weight fraction supernate)

$W\%_{TS}$ = weight percent total solids

Percent soluble aluminum and sodium are presented in Table 3-4[†]. As can be seen, a significant amount of sodium precipitated during washing. Unfortunately, analysis of the sludge solids to determine the precipitated species (e.g., x-ray diffraction or scanning electron microscopy) is not practical due to the high dose rate of the solids. One implication of insoluble sodium is that a washing target based on soluble sodium may underestimate the sodium content in the next sludge batch.

Table 3-4. Calculated Weight Percent Soluble Aluminum and Sodium

	As-Received Tank 51	Post Al Dissolution	After Washing
Al (% soluble)	1	30	8
Na (% soluble)	92	87	62

A comparison of the elemental analysis of the total solids before and after aluminum dissolution and washing is presented in Table 3-5. As expected the primarily insoluble species (e.g., Fe, Mg) increase in

[†] Data used to calculate the percent soluble in Table 3-4 can found in Table 3-1, Table 3-2, Table 3-5, and Appendix B.

concentration as primarily soluble species such as nitrate and nitrite are removed by washing. The effect of washing on the partially soluble Al is not obvious on a total solids basis. At first glance, it might appear that Al was not significantly removed during Al dissolution/washing since its concentration in the total solids dropped only slightly. But, a comparison of Fe (predominantly insoluble) to Al ratios does show that Al was removed during dissolution and washing: Al/Fe = 2.15 in the as-received Tank 51 sample, 1.7 before washing, and 1.4 after washing – see discussion on aluminum removal above.

Table 3-5. Comparison of Major Elements (>0.1%) in the Total Solids in the As-Received Tank 51 Sample and the Post Aluminum Dissolution/Washed (SRAT Receipt) Sample

	As-Received Tank 51 ^a	After Wash 2/ Decant 2b
	Wt% of Total Solids	
Al	15.6	13.9
Ca	0.81	1.12
Fe	7.27	9.97
Hg	1.73	2.84
Mg	0.30	0.42
Mn	1.73	2.44
Na	14.5	22.6
Ni	0.65	0.86
Si	0.44	0.60
U	1.63	2.41

^a Data from Reference 1.

A better elemental basis for DWPF use, and ultimately glass fabrication, is weight percent of calcined solids (elementals based on solids heated to 1100 °C for two hours). This basis is essentially an oxide basis. The total solids measurement includes nitrates, nitrites, and other cations, while the calcined solids contain primarily cations and oxygen (oxides), the actual components of the waste that are vitrified. Weight percent of calcined solids basis is calculated as follows:

$$\text{wt\% of element } i \text{ in calcined solids} = \text{wt\% of element } i \text{ in total solids} \times \frac{\text{wt\% total solids}}{\text{wt\% calcine solids}}$$

Presented in Table 3-6 are the elemental compositions on a wt% calcined solids basis of the as-received Tank 51 sample and the post aluminum dissolution sample after washing (the SRAT receipt sample). The as-received Tank 51 sample is very similar to the Sludge Batch 4 qualification sample,¹⁴ and the washed sample composition should be similar to Sludge Batch 5 with less Purex sludge contribution. This comparison shows that the aluminum dissolution process will indeed lower the aluminum contribution from the waste to the DWPF glass, but sodium content may increase due to difficulties in washing to obtain the target endpoint.

Table 3-6. Comparison of Major Elements in the As-Received Tank 51 Sample and the Post Aluminum Dissolution/Washed (SRAT Receipt) Sample on a Calcined Solids Basis

	As Received Tank 51 ^a	After Wash 2/ Decant 2b ^b
Wt% of Calcined Solids		
Al	22.7	16.0
Ca	1.18	1.29
Fe	10.6	11.5
Mg	0.43	0.48
Mn	2.52	2.81
Na	21.1	26.0
Ni	0.94	0.99
Si	0.63	0.69
U	2.37	2.77

^a wt% total solids = 15.5, wt% calcined solids = 10.7

^b wt% total solids = 19.1, wt% calcined solids = 16.6

3.2 Sludge Settling

Sludge level was recorded during dissolution and washing. The results are presented graphically in Figure 3-1.[‡] Because starting sludge heights were different during dissolution and the two washes, sludge height is given in terms of height relative to the start of settling. As can be seen in the figure, there is no trend in settling behavior during washing; settling during the first wash was slower than during dissolution, but Wash 2 settling was faster. In all cases, sludge level dropped to 60% of the original height after approximately one week, and then nearly leveled off. Note that the settling behavior for Wash 2 was recorded only until the first Wash 2 decant (Decant 2a); sludge level remained essentially unchanged after the first decant.[§]

[‡] Settling data during aluminum dissolution was published previously in Reference 1.

[§] As discussed in Section 2.2, Decant 2b was accomplished with a slurry pipette, enabling a decant very close to the sludge level.

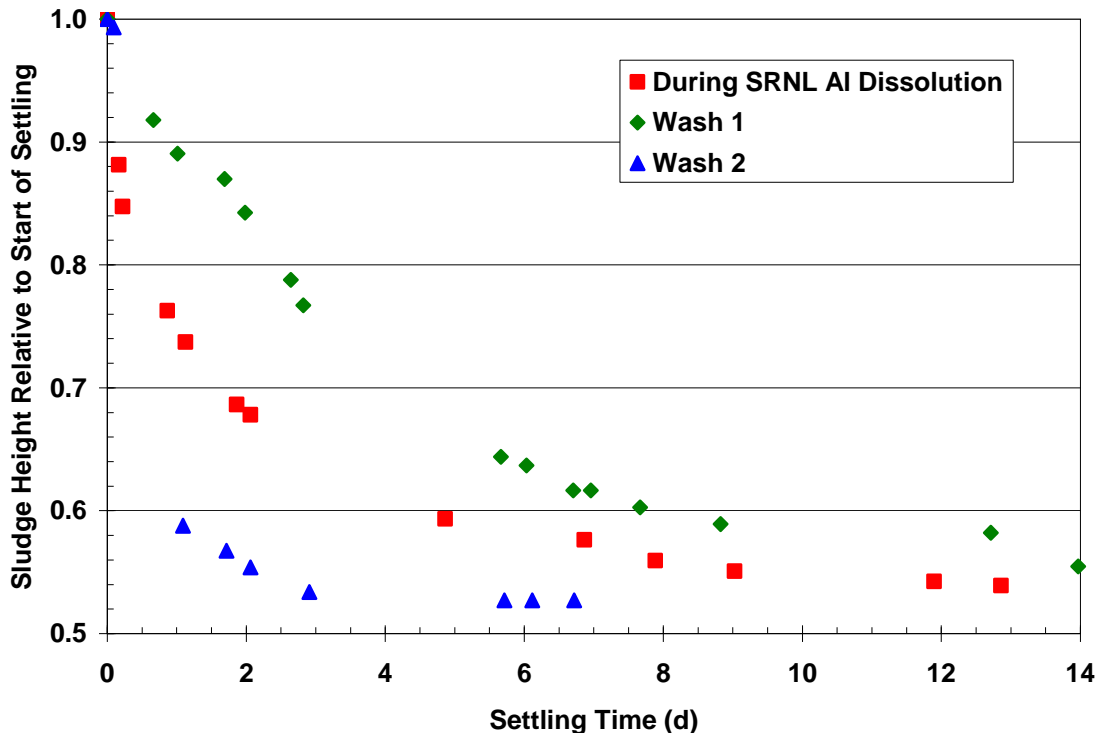


Figure 3-1. Sludge Settling During Aluminum Dissolution and Washing

3.3 Results of Boiling the Wash 2/Decant 2a Slurry

No unusual changes in sludge consistency were observed during or after the boiling of a sample of sludge after Wash 2/Decant 2a. Although the final concentrated sludge was very thick, it remained fluid, not gelatinous. The total solids content of the final sludge was 33.4%, which was about twice that of the initial material (16.3 wt %, prior to rinse water addition and boiling).

Based on the solids content and density of the initial material, approximately 40% of the slurry's original water was removed during this demonstration. These conditions bound what is targeted in normal DWPF operations. Therefore, boiling of post-dissolution Tank 51 sludge is not expected to produce unusual changes in sludge consistency.

3.4 SRAT Receipt Characterization and Acid Addition Calculations

The DWPF SRAT process relies upon use of the acid calculation to estimate the required acid necessary to complete reactions. This calculation uses measured analytical inputs. Errors in these measurements can result in too little acid being added resulting in incomplete reactions or too much acid being added resulting in excess formic acid causing high hydrogen generation rates. Therefore, the washed post aluminum dissolution Tank Farm Tank 51 sample was extensively characterized to determine the inputs. The results of the SC-4 SRAT receipt characterization are provided in Table 3-7, along with the SC-3 (washed Tank 51 sample without Al dissolution)¹⁵ and the simulant used to recommend the acid

stoichiometry for the SC-4 run. Table 3-8 gives the additional acid calculation inputs (e.g., formate destruction).

For the SC-4 total base measurement, two methods were used to measure total base: 1) a titration of slurry diluted by a factor of ~30 was performed by SRNL-AD (this method used an autotitrator and yielded a result of 1.5 mol base per liter of slurry), and 2) a direct titration of slurry was performed in the Shielded Cells by SRNL-PS&E (this titration was performed manually and yielded a result of 2.1 mol base per liter of slurry). This second method is the nominal method used in the Shielded Cells DWPF demonstrations.

Table 3-7. Characterization Results and Acid Calculation Inputs of the Post Aluminum Dissolution Tank 51 (SC-4 SRAT Receipt) Sample and the Corresponding Non Rad Simulant SRAT Receipt (SB5-4 & -5) With Comparison to a Pre Aluminum Dissolution SRAT Receipt (SC-3) Sample

Measurement	Units	SC-3 ^a	SB5-4/SB5-5	SC-4
Total Solids,	wt% of slurry	19.5	13.00	19.1
Insoluble Solids, wt% of slurry	wt% of slurry	12.5	5.98	12.0
Soluble Solids, wt% of slurry	wt% of slurry	7.0	7.02	7.16
Calcined Solids, wt% of slurry	wt% of slurry	14.3	10.02	16.6
Slurry Density, kg/L	kg/L slurry	1.14	1.11	1.20
Supernate Density, kg/L	kg/L supernate	1.06	NA	1.07
Na, wt% of total solids	wt% of total solids	11.8	NA	22.6
Hg, wt% of total solids	wt% of total solids	2.57	5.55	2.84
Mn, wt% of total solids	wt% of calcined solids	2.65	4.80	2.81
Nitrite, mg/kg slurry	mg/kg slurry	20,500	4,205	6,550
Nitrate, mg/kg slurry	mg/kg slurry	15,400	3,470	4,550
TIC, mg/kg slurry	mg/kg slurry	2,510	1,153	1,060
Total Base, mol/L slurry	mol/L slurry to pH = 7	0.316	1.269	1.50/2.1 ^c
pH		12.6	NA	>13

^a See Reference 15.

^b SB5-4 and SB5-5 designate the same SRAT receipt (sludge) material. SB5-4 and SB5-5 utilize different acid addition amounts (see Table 3-8 and Table 3-9) and therefore different SRAT product results (see Table 3-10).

^c Two values for total base are presented here. The first is a titration of diluted slurry. The second is a titration of undiluted slurry. See the preceding paragraph for details.

As can be seen from the above table, there are some striking differences in the SC-3 (pre aluminum dissolution) and SC-4 (post aluminum dissolution) SRAT receipt samples caused primarily by the addition of caustic for aluminum dissolution. For the acid calculation, the most significant change is the replacement of nitrite and nitrate by hydroxide. Another significant difference between pre and post aluminum dissolution sludge is the aluminum concentration in the SRAT receipt supernate - the current DWPF feed (Tank 40) contains 0.008 M Al¹⁶, while the SC-4 SRAT receipt sample was 0.35 M (Table 3-2). Both of these differences impact the SRAT receipt total base measurement, a major contributor to the acid demand calculation. It is not clear at this time how the additional hydroxide and the aluminum in the supernate impact the total base measurement. Based on the results of the SC-4 SRAT cycle (see Section 3.5), it appears that a titration of diluted slurry under calculates acid demand. Further studies of the titration methodology or an acid calculation less dependant on total base are needed.

Table 3-8. Acid Calculation Inputs of the Washed Post Aluminum Dissolution Tank 51 Sample (SC-4 SRAT Receipt) and the Corresponding Non Rad Simulant SRAT Receipt (SB5-4 & -5) With Comparison to a Pre Aluminum Dissolution SRAT Receipt Sample (SC-3)

Input/Assumption	Unit	SC-3 ^a	SB5-4	SB5-5	SC-4
Conversion of Nitrite to Nitrate in SRAT Cycle	gmol NO ₃ ⁻ /100 gmol NO ₂ ⁻	15	30	30	15
Destruction of Nitrite in SRAT and SME cycle	% of starting nitrite	100	100	100	100
Destruction of Formic acid charged in SRAT	%	25	33	33	25
Destruction of oxalate charged	%	NA	50	50	NA
Percent Acid in Excess Stoichiometric Ratio	%	130	115	130	115
SRAT Product Target Solids	%	20	15	15	20
Predicted or Target REDOX	Fe ⁺² / ΣFe	0.21 ^b	0.20	0.20	0.20
Number of basis antifoam additions added during SRAT cycle		8	8	8	11
Destruction of Formic acid in SME	%	0	NA	NA	0
Destruction of Nitrate in SME	%	0	NA	NA	0
Assumed SME density	kg / L	1.45	NA	NA	1.45
No. of basis antifoam additions added during SME cycle		3	NA	NA	3
Sludge Oxide Contribution in SME (Waste Loading)	%	30	NA	NA	30
Target SME Solids total Wt%	Wt%	45	NA	NA	45

^a See Reference 15.

^b A specific split between formic and nitric acid was used for this run. That is, this is a calculated (predicted) REDOX value. Note that typically a REDOX value is chosen, and the acid calculation uses this as input to determine the split between nitric and formic acids.

The primary results of the acid calculation (the acid requirements) are presented in Table 3-9. Note that for the SC-4 SRAT cycle, two stoichiometric acid amounts are given based on the two titration results (see discussion above). The actual amount of acid added for the SC-4 cycle was based on the lower total base result. Acid amounts using both titration results were calculated and prepared. At the conclusion of formic acid addition, the SRAT pH was measured and found to be less than 4. Based on this measurement, it was determined that no additional acid was required. However, post cycle analytical results (nitrite and mercury in the SRAT product) indicate that insufficient acid was added. These results are presented in Section 3.5.

Table 3-9. SRAT Cycle Acid Requirements

	SC-3 ^a	SB5-4	SB5-5	SC-4
Calculated Stoich. Acid, moles/L	1.30	1.53	1.53	1.99/2.59 ^b
Actual Acid Added, moles/L	1.46	1.98	2.23	2.29
Ratio of Formic Acid to Total Acid	0.99	0.85	0.84	0.83

^a See Reference 15.

^b The two values correspond to 1.5 mol total base/L and 2.1 mol total base/L, respectively. The actual amount of acid added was 115% of the lower acid amount.

3.5 CPC Processing Results

Results of the two simulant runs SB5-4 and SB5-5 and the Shielded Cells SC-4 run are presented here, along with the previously published SC-3 (Tank 51 pre aluminum dissolution)¹⁵ run for comparison. The simulant runs were performed to provide input (e.g., excess acid amount) for the SC-4 run. Comparing these simulant results to the SC-4 results show that the simulant was not a good representation of the actual waste. SC-3 results are given to show the impacts of aluminum dissolution on CPC processing. Note that the discussion below is primarily focused on the SC-4 post aluminum dissolution in-Cells run with the actual Tank 51 material.

3.5.1 SRAT Cycle Processing Observations

There were no significant processing problems during the SC-4 SRAT cycle other than foaming. There were no difficulties in mixing or heating the sludge slurry, but the sludge was prone to foaming. The following antifoam addition strategy was used:

- 200 ppm addition prior to starting the cycle
- 100 ppm addition between nitric and formic acid additions
- 500 ppm addition after acid addition, prior to boiling
- 100 ppm addition every 8 hours thereafter

The above strategy contains an additional 100 ppm addition (between nitric and formic acid additions) compared to recent antifoam addition strategies. It should be noted that the above strategy is equivalent to DWPF's current addition strategy. In the three previous runs containing Tank 51 – SB4, antifoam was needed shortly after formic acid was begun.^{14, 15} It was decided to add the antifoam before it was needed and to help ensure against a foam over in this run.

Even with the extra antifoam prior to formic acid addition, an additional 100 ppm of antifoam was needed during the final third of formic acid addition. Also, an extra 100 ppm of antifoam was added with the scheduled antifoam addition eight hours after formic acid addition.

3.5.2 SRAT Cycle Sample Results

A sample was pulled at the conclusion of the SRAT cycle. The total solids, anions, and mercury analysis were performed. These results are presented in Table 3-10, along with the results of the SC-3 SRAT cycle and the simulant SRAT cycles for comparison. As shown in the table, nitrite was not adequately

destroyed to less than 1,000 mg/kg, and mercury was not removed to below the DWPF requirement of 0.45% of the total solids.

It should also be noted that the simulant used for the SB5-4 and SB5-5 runs did not adequately represent the radioactive waste sample. With less acid added per liter of slurry (both runs), the goals of destroying nitrite and removing mercury were accomplished. This may be related to the soluble versus insoluble aluminum in the simulant and radioactive waste. In the simulant, all the aluminum was soluble, while only 8% of the aluminum was soluble in the SC-4 SRAT receipt sample. This difference was likely due to different forms of aluminum in the simulant compared to the aluminum in the radioactive material. Development of a more representative simulant may be necessary to develop an understanding of how aluminum affects SRAT receipt acid demand.

Table 3-10. SRAT Product Characterization Results

	SC-3 ^a	SB5-4	SB5-5	SC-4
Wt % Total Solids (slurry basis)	21.3	15.6	15.2	22.6
Wt % Insoluble Solids (slurry basis)	11.1	5.77	5.77	10.0
Wt % Soluble Solids (slurry basis)	10.2	6.50	9.43	12.6
Slurry Density (g/mL)	1.22	1.08	1.07	1.17
Supernate Density (g/mL)	1.09	NM	NM	1.10
Formate (mg/kg slurry)	33,400	47,900	50,700	51,900
Nitrite (mg/kg slurry)	<1,000	<100	<100	2,710
Nitrate (mg/kg slurry)	26,100	16,950	18,200	25,000
Mercury (wt % of total solids)	0.23	<0.01	<0.01	0.79

^a See Reference 15

3.5.3 SRAT Cycle Anion Destruction and Conversion

Inputs to the acid calculation include formate destruction and conversion of nitrite to nitrate. Presented in Table 3-11 is a comparison between these assumed values (based on simulant runs) and measured results. As can be seen in the table, formate destruction and nitrite destruction were lower than predicted for SC-4. Also, the high nitrite to nitrate conversion shows that most of the destroyed nitrite was converted to nitrate. These results show that the acid added for the SC-4 run was lower than needed for the SRAT cycle. This is confirmed in the offgas data given below.

Table 3-11. Comparison of Assumed and Measured Anion Destruction and Conversion in the SRAT Cycles

		SC-3	SB5-4	SB5-5	SC-4
Formate Destruction (%)	Assumed	25	33	33	25
	Measured	21	25	23.6	14.3
Nitrite Destruction (%)	Assumed	100	100	100	100
	Measured	100	>99.5	>99.5	51
Nitrite to Nitrate Conversion (% of destroyed nitrite)	Assumed	15	30	30	15
	Measured	37	22.8	33.2	94

3.5.4 SRAT Cycle Offgas Analysis

Offgas data for the SC-4 SRAT cycle, along with the SC-3 offgas data, are presented in the following figures. ** The offgas data, specifically the nitrous oxide data, suggest the under-addition of acid. The SC-3 nitrous oxide data is typical. As acid is added to sludge, carbon dioxide is generated as pH drops and carbonate is destroyed. Acid added to the sludge also destroys nitrite, producing NO_x (note that only nitrous oxide is measured in SRNL simulations). The majority of nitrite destruction is complete near the end of acid addition, resulting in a drop of measured nitrous oxide. Hydrogen generation from the noble metals-catalyzed decomposition of excess formic acid typically begins one to three hours after the nitrous oxide peak (i.e., after nitrite destruction¹⁷).

The SC-4 run does not show this typical behavior. There was no extreme peak for nitrous oxide generation, and it is detected throughout the cycle at a significant rate (~2.5 lb/hr, DWPF scale), showing that nitrite was present in the SRAT contents throughout the cycle. SRAT product analytical results confirm this (see Table 3-10). Also, the low hydrogen generation suggests that there was little excess acid for hydrogen generation.

It is interesting to note the effect of mixing and foaming on offgas. After acid addition was complete, the SRAT vessel was allowed to cool to approximately 80 °C and mixing was stopped to measure the pH. The spike in gas generation at approximately two hours corresponds to the resumption of mixing when gas retained in the sludge slurry was quickly released. Note that the mixing was stopped for approximately 30 minutes.

Large amounts of foam could be seen in the SRAT vessel during the second offgas spike (approximately 24.5 hours after acid addition, and 8 hours after the previous antifoam addition). It may be possible to use offgas data as an indication of foaming. However, this indication may not be soon enough in the DWPF to prevent a foam-over.

** SB5-4 and SB5-5 are presented in Appendix D. In both runs, hydrogen generation was well below DWPF limits, indicating the recommended acid addition strategy for SC-4 would not exceed DWPF limits.

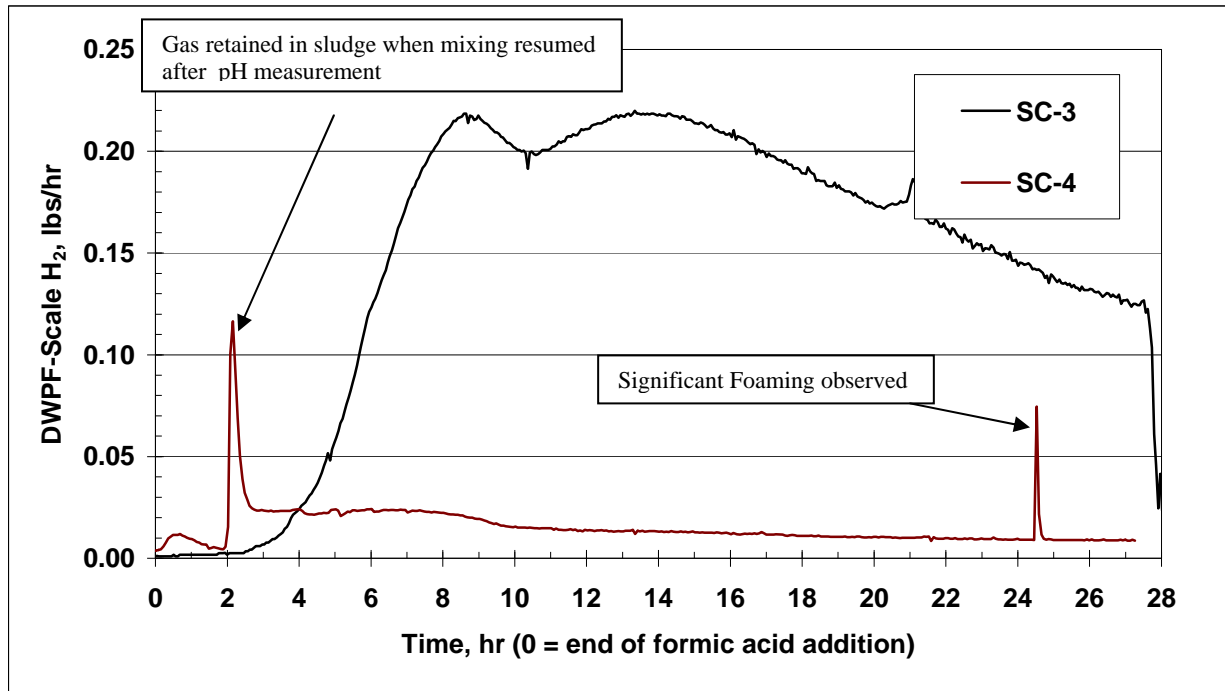


Figure 3-2. Hydrogen Generation During SC-3 and SC-4 SRAT Cycles

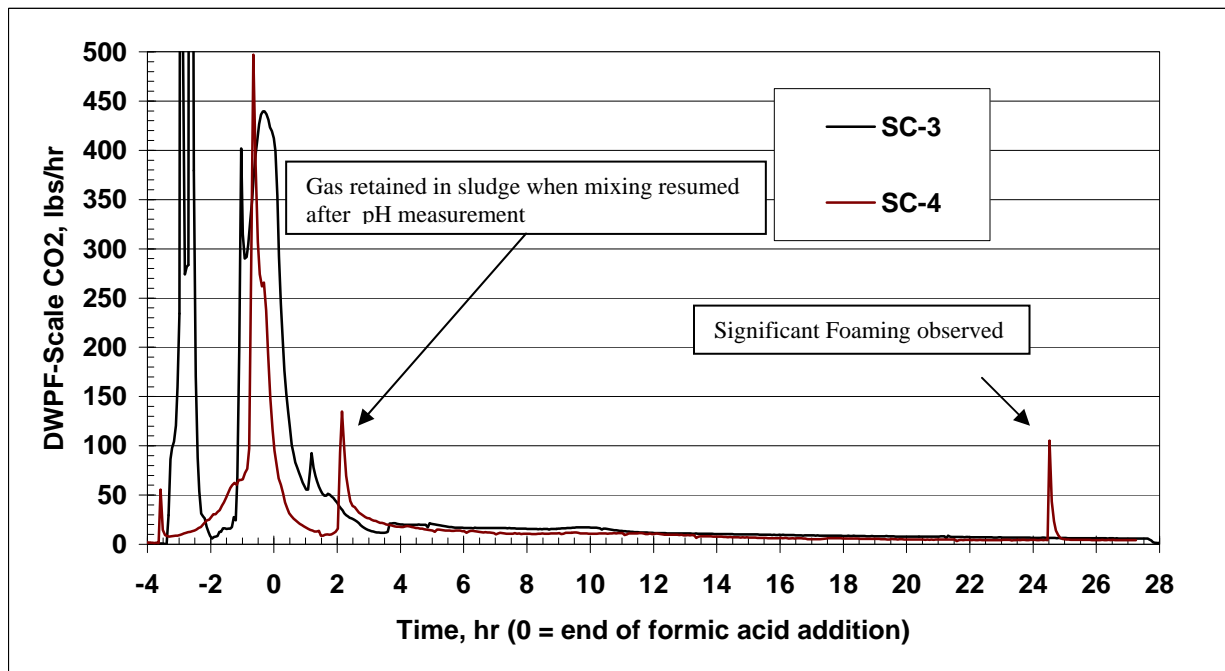


Figure 3-3. Carbon Dioxide Generation During SC-3 and SC-4 SRAT Cycles

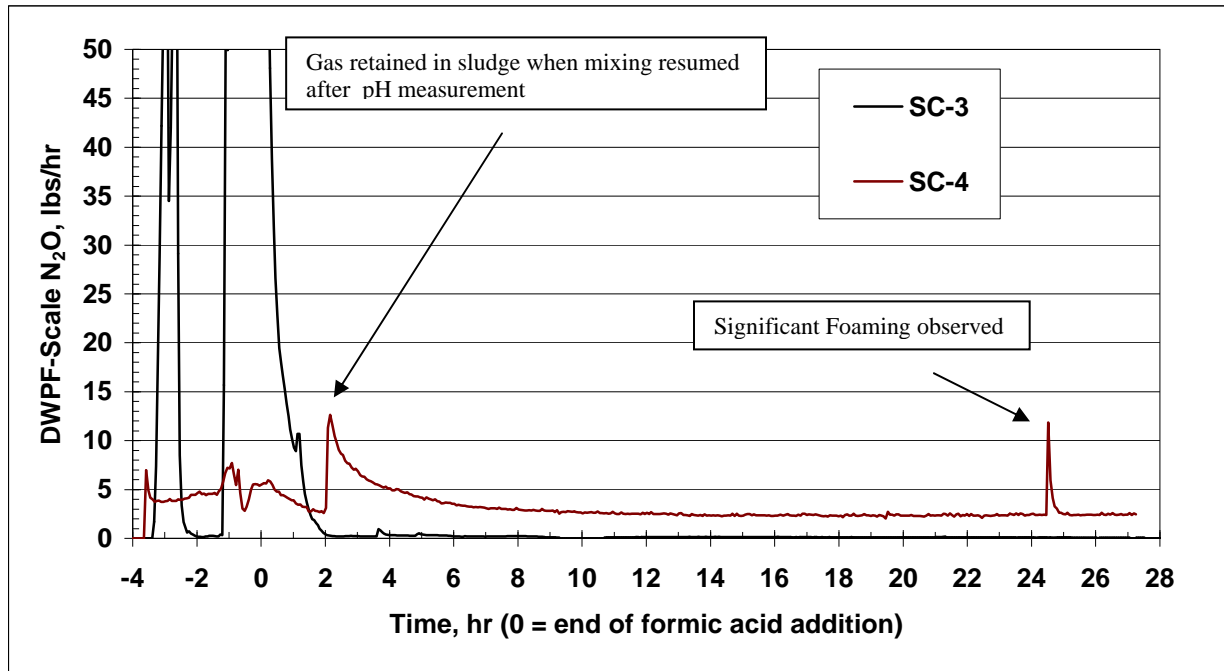


Figure 3-4. Nitrous Oxide Generation During SC-3 and SC-4 SRAT Cycles

3.5.5 SME Processing Observations

There were no processing issues with the SC-4 SME cycle; vessel contents mixed well, and there were no problems achieving target boil up rates. The SME contents however were prone to foaming. Antifoam was needed every 3 to 5 hours during the cycle.

3.5.6 SME Cycle Sample Results

Samples were collected at the conclusion of the SME cycle and analyzed for total solids, anions, and total organic carbon. Total solids are higher than the target of 45%. This is likely due to small losses of water from leaks and losses from carbonate destruction and other reactions not accounted for in the mass balance used to calculate dewater amount. Even with this higher total solids, there were no issues with mixing or heating. Results are given in Table 3-12, along with the SC-3 Cycle. Note that a SME cycle was not completed with the simulant.

Table 3-12. SME Product Weight Percent Solids and Densities

Physical Property	SC-3	SC-4
Wt % Total Solids (slurry basis)	49.6	48.3
Wt % Insoluble Solids (slurry basis)	40.8	37.6
Wt % Soluble Solids (slurry basis)	9.2	10.8
Slurry Density (g/mL)	1.44	1.46
Supernate Density (g/mL)	1.12	1.13
Formate (mg/kg slurry)	36,000	46,600
Nitrite (mg/kg slurry)	<1,000	1,360
Nitrate (mg/kg slurry)	30,400	22,400
Total Organic Carbon (mg/kg slurry)	NA	15,300

3.5.7 SME Cycle Anion Destruction

Inputs to the acid calculation for the SME cycle include formate and nitrate destruction. Presented in Table 3-13 is a comparison between these assumptions and measured results for SC-3 and SC-4. These results provide further evidence that acid addition in the SRAT cycle was inadequate: there was no measurable formate or nitrate destruction in the SME cycle.

Table 3-13. Comparison of Assumed and Measured Anion Destruction and Conversion in the SME Cycles

		SC-3	SC-4
Formate Destruction (%)	Assumed	0	0
	Measured	26	0
Nitrate Destruction (%)	Assumed	0	0
	Measured	4	0
Nitrite Destruction (%)	Measured	NA	40

3.5.8 SME Cycle Offgas Data

SME cycle hydrogen generation data for the SC-4 run (with the SC-3 SME cycle) is presented in Figure 3-5. The low hydrogen generation again shows that acid was under-added in the SC-4 CPC processing.

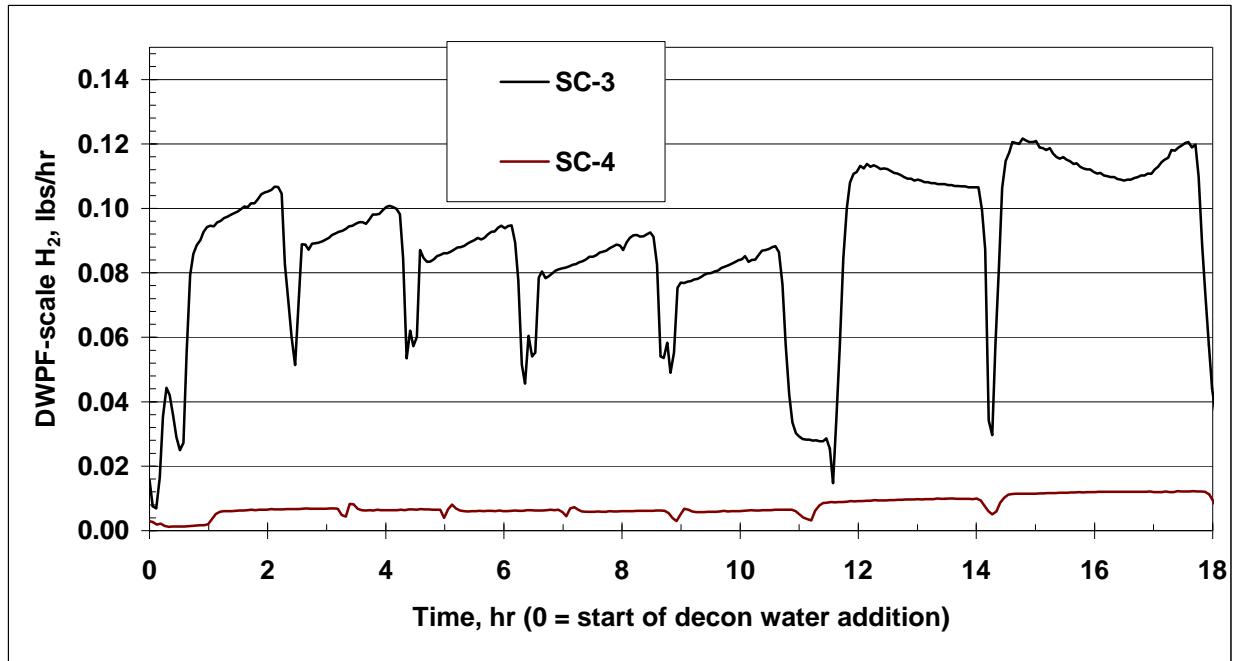


Figure 3-5. SME Cycle Hydrogen Generation Data

3.6 Rheology

The rheological properties are summarized in Table 3-14, with flow curves given in Appendix C. A comparison between the As-received, post aluminum dissolution and washed samples indicate that the aluminum dissolution process impacts the rheological properties of the Tank 51 sludge. In all these cases, the downstream materials were more viscous and the concentration of insoluble solids less than that of the starting material. The ability to pump the washed material, at a given solids concentration, from Tank 51 to Tank 40 must be considered¹⁸ when concentrating the contents in Tank 51. The SC-4 SRAT and SME products exceed (i.e., do not meet) the design basis rheological properties,¹⁹ but due to the probable under addition of acid, these rheological results must be used with caution. These results are compared to the SC-3 SRAT and SME products results, which are also provided in Table 3-14. The SC-4 material is rheologically thicker than the SC-3 material.

Table 3-14. Rheological Properties of As-Received, Al Dissolved, Washed and SRAT/SME Products

Sample	Yield Stress (Pa)	Plastic Viscosity (cP)	Wt% Total Solids	Wt% Insoluble Solids	Slurry Density (g/ml)
Tank 51, As-Rcvd	5.83	7.64	15.50	9.39	1.08
Post Al Dissolution	9.24	19.32	27.98	6.44	1.27
Wash 1	4.70	8.97	18.46	6.52	1.19
Wash 2/Decant 2a	7.21	9.83	16.27	8.87	1.14
Wash 2/Decant 2b, SC-4 SRAT Rcpt	19.92	18.22	19.12	11.96	1.20
SC-4-SRAT Product	13.35	16.47	22.63	10.02	1.17
SC-4-SME Product	21.59	29.15	48.35	37.59	1.46
SC-3-SRAT Product	7.21	10.16	21.30	11.10	1.22
SC-3-SME Product	10.88	19.80	49.60	40.80	1.44
DWPF Design Basis ¹⁹					
SRAT/SME – Minimum	2.5	10	-	-	1.20
SRAT/SME – Maximum	15.0	40	-	-	1.43

4.0 CONCLUSIONS

The purpose of this task was to determine potential downstream impacts of aluminum dissolution so technical issues could be identified before the start of SB5 processing using an SRNL prepared post aluminum dissolution sludge sample. The potential downstream impacts assessed include the Tank Farm sludge washing and concentration process and the DWPF Chemical Process Cell.

The impact of aluminum dissolution on sludge settling is not clear. Settling during prototypical sludge washing and concentration steps did not follow a trend. Compared to the post aluminum dissolution sample, settling after the first wash was slower, but settling after the second wash was faster.

Aluminum dissolution did impact sludge rheology. A comparison between the As-received, post aluminum dissolution and washed samples indicate that the downstream materials were more viscous and the concentration of insoluble solids less than that of the starting material. This increase in viscosity may impact Tank 51 transfers to Tank 40. It also has the potential to impact processing in DWPF if the SRAT process does not reduce the slurry yield stress as seen with other DWPF sludge batches.

DWPF CPC processing was not successfully completed on the aluminum dissolved sludge due to the acid addition for the SRAT cycle being under-calculated and, thus, under-added. Although the sludge was rheologically thick throughout the SRAT and SME cycles, this may have been due to the under-addition of acid. It should be noted that one of the purposes of acid addition during CPC processing is to adjust rheological properties (i.e., reduce yield stress).

Aluminum dissolution did impact analyses of the SRAT receipt material. Two methods for determining total base yielded significantly different results. The high hydroxide content and the relatively high soluble aluminum content of the washed post aluminum dissolution sludge likely contributed to this difference and the ultimate under addition of acid. It should be noted that the simulant used to provide input for the SC-4 SRAT cycle was an inadequate representation of the waste in terms of acid demand due to the inability to replicate the form of aluminum in the sludge and supernate.

5.0 RECOMMENDATIONS

Sludge settling and rheology during washing of the forthcoming Sludge Batch 5 qualification sample should be monitored closely and communicated to the Tank Farm.

It is recommended that SRNL receive a sample of Tank 51 after all chemical additions are complete and prior to the final Sludge Batch 5 decant for rheological assessment. Rheology versus wt% insoluble solids will be performed to determine the maximum amount of decant prior to the Tank 51 to Tank 40 transfer.

As a result of the problem with measuring total base and subsequently under-calculating acid for the DWPF CPC processing of the post aluminum dissolution sludge, the following is recommended:

- Perform studies to develop understanding of how the sludge titrates (i.e., why different titration methods yield different results).
- Develop simulants that better match the properties of post aluminum dissolution sludge.
- Continue work on developing an acid calculation less dependant on the total base measurement.

6.0 REFERENCES

1. Hay, M. S.; Pareizs, J. M.; Bannochie, C. J.; Stone, M. E.; Click, D. R.; McCabe, D. J. *Characterization and Aluminum Dissolution Demonstration With A 3 Liter Tank 51H Sample*; WSRC-STI-2007-00697, Rev. 0; Savannah River National Laboratory: Aiken, SC, 2008.
2. Bannochie, C. J.; Hay, M. H.; Pareizs, J. M.; Peeler, D. K. *Technology Demonstration of Sludge Mass Reduction via Aluminum Dissolution: Task Technical and Quality Assurance Plan*; TTQAP WSRC-RP-2007-00512, Rev. 0; Savannah River National Lab: 2007.
3. Bannochie, C. J.; Hay, M. S. *Analytical Study Plan: Demonstration of Dissolution of Tank 51 Sludge*; Analytical Study Plan WSRCRP-2007-00396, Rev. 2; Savannah River National Lab: Aiken, SC, 2007.
4. *Process Science and Engineering Section Procedure Manual*; Manual L29; Savannah River National Lab: Aiken, SC, 2007.
5. *Analytical Development Procedures Manual*; Manual L16; Savannah River National Laboratory: Aiken, SC.
6. Pike, J. A.; Gillam, J. M. *Flowsheet for Aluminum Removal From Sludge Batch 5*; LWO-PIT-2007-00042, Rev. 2; Aiken, 2007.
7. Stone, M. E. *Lab-Scale CPC Equipment Set-up*; Interoffice Memorandum SRNL-PSE-2006-00074; 2006.
8. Stone, M. E. *SRAT Assembly for SB4 Shielded Cells Testing: SC-4*; Inter-office memorandum SRNL-PSE-2007-00277; Savannah River National Lab: Aiken, SC 29808, 2007.
9. *SB5 Aluminum Dissolution II*; Notebook WSRC-NB-2007-00144; Savannah River National Laboratory: Aiken, SC, 2007.
10. *SB5 Aluminum Dissolution III*; Notebook WSRC-NB-2007-00191; Savannah River National Laboratory: Aiken, SC, 2008.
11. Lambert, D. P. *Acid Calculation Spreadsheet for DWPF Simulations, Revision 1*; Inter-Office Memorandum SRNL-PSE-2006-00173; Savannah River National Laboratory: Aiken, SC, 2006.
12. Jantzen, C. M.; Zamecnik, J. R.; Koopman, D. C.; Herman, C. C.; Pickett, J. B. *Electron Equivalents Model for Controlling Reduction-Oxidation (REDOX) Equilibrium during High Level Waste (HLW) Vitrification*; Technical Report WSRC-TR-2003-00126; Savannah River National Laboratory: Aiken, SC, 2003.
13. Darby, R., *Chemical Engineering Fluid Mechanics, 2nd edition*. Marcel Dekker: 2001.
14. Pareizs, J. M.; Bannochie, C. J.; Barnes, M. J.; Bibler, N. E.; Click, D. R.; Hansen, E. K.; Lambert, D. P.; Stone, M. E. *Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells in Support of Sludge Batch 4 Qualification*; Technical Report WSRC-STI-2007-00053; Savannah River National Laboratory: Aiken, SC, 2007.

15. Koopman, D. C.; Pareizs, J. M.; Lambert, D. P.; Bannochie, C. J. *Sludge Batch 4 Follow-up Qualification Studies to Evaluate Hydrogen Generation*; Technical Report WSRC-STI-2007-00212; Savannah River National Laboratory: Aiken, SC, 2007.
16. Bannochie, C. J. *Tank 40 Final SB4 Chemical Characterization Results*; Technical Report WSRC-STI-2007-00674; Savannah River National Laboratory: Aiken, SC, 2008.
17. King, R. B.; Bhattacharyya, N. K., Catalytic reactions of formate 4. A nitrite-promoted rhodium (III) catalyst for hydrogen generation from formic acid in aqueous solution. *inorganica Chimica Acta* **1995**, 237, 65-69.
18. Hansen, E. K. *Tank 51 Sludge Batch 4 Transfer to Tank 40*; Technical Report WSRC-STI-2006-00218, Rev. 0; 2006.
19. *Technical Data Summary For the DWPF, Part 3, Item 300 and Part 10, Item 230*; DPSTD-80-38-2; Savannah River Site: Aiken, SC, 1980.

7.0 ACKNOWLEDGEMENTS

The authors would like to recognize the invaluable support of the SRNL Shielded Cells technicians and management for the in-cells work; the ACTL technicians for assistance in equipment setup, reagent preparation, and consultation during the SRAT and SME cycles; S. H. Reboul for overseeing the apparatus fabrication and testing for the boiling evaluation; and the SRNL Glass Shop for providing glassware and other miscellaneous hardware.

APPENDIX A. SETTLING DATA FROM POST ALUMINUM DISSOLUTION WASHING

NOTE:

$$\text{Overall Volume(mL)} = \text{Sludge Level} \times 176 - 129$$

Wash 1						
Sludge Slurry Level		14.6	Sludge Slurry Volume (mL)	2440.6	mL	
Date/Time	Settling Time (d)	Sludge Level	Sludge Volume (mL)	Supernate vol (mL)	Sup vol change (mL/d)	Rel sludge ht
10/16/2007 14:45	0.0	14.6	2,441	0		1.00
10/17/2007 6:40	0.7	13.4	2,229	211	318	0.92
10/17/2007 15:00	1.0	13.0	2,159	282	203	0.89
10/18/2007 7:15	1.7	12.7	2,106	334	78	0.87
10/18/2007 14:20	2.0	12.3	2,036	405	239	0.84
10/19/2007 6:10	2.6	11.5	1,895	546	213	0.79
10/19/2007 10:25	2.8	11.2	1,842	598	298	0.77
10/22/2007 6:40	5.7	9.4	1,525	915	111	0.64
10/22/2007 15:30	6.0	9.3	1,508	933	48	0.64
10/23/2007 7:35	6.7	9.0	1,455	986	79	0.62
10/23/2007 13:40	7.0	9.0	1,455	986	0	0.62
10/24/2007 6:40	7.7	8.8	1,420	1,021	50	0.60
10/25/2007 10:35	8.8	8.6	1,385	1,056	30	0.59
10/29/2007 7:48	12.7	8.5	1,367	1,074	5	0.58
10/30/2007 14:00	14.0	8.1	1,297	1,144	56	0.55
10/31/2007 7:55	14.7	8.0	1,279	1,162	24	0.55

Wash 2						
Sludge Slurry Level		14.8	Sludge Slurry Volume	2475.8	mL	
Date/Time	Settling Time (d)	Sludge Level	Sludge Volume (mL)	Supernate vol (mL)	Sup vol change (mL/d)	Rel sludge ht
11/6/2007 13:30	0.0	14.8	2,476	0		1
11/6/2007 15:45	0.1	14.7	2,458	18	188	0.99
11/7/2007 15:40	1.1	8.7	1,402	1,074	1060	0.59
11/8/2007 6:40	1.7	8.4	1,349	1,126	84	0.57
11/8/2007 15:00	2.1	8.2	1,314	1,162	101	0.55
11/9/2007 11:15	2.9	7.9	1,261	1,214	63	0.53
11/12/2007 6:35	5.7	7.8	1,244	1,232	19	0.53
11/12/2007 16:15	6.1	7.8	1,244	1,232	0	0.53
11/13/2007 6:40	6.7	7.8	1,244	1,232	0	0.53

APPENDIX B. CALCULATION OF ALUMINUM AND SODIUM REMOVAL USING IRON RATIOS

Calculation inputs and results

	A	B	C	D
1				
2		As-Received	After Al Diss	After Wash
3	Al % of total solids	15.6	8.92	13.9
4	Fe % of total solids	7.27	5.26	9.97
5	Na % of total solids	14.5	35.4	22.6
6				
7	Al/Fe	2.15	1.70	1.39
8	Na/Fe	1.99	6.73	2.27
9	%Al removed by diss			21%
10	% Al removed by washing			14%
11	Total % Al removed			35%
12				
13	%Na removed in washing			66%
14	Overall % Na increase			14%

Inputs and formulas

	A	B	C	D
1				
2		As-Received Tank 51	After Al Diss	After Washing
3	Al % of total solids	15.6	8.92	13.9
4	Fe % of total solids	7.27	5.26	9.97
5	Na % of total solids	14.5	35.4	22.6
6				
7	Al/Fe	=B3/B4	=C3/C4	=D3/D4
8	Na/Fe	=B5/B4	=C5/C4	=D5/D4
9	%Al removed by diss			=(B7-C7)/B7
10	% Al removed by washing			=((C7-D7))/B7
11	Total % Al removed			=SUM(D9:D10)
12				
13	%Na removed in washing			=(C8-D8)/C8
14	Overall % Na increase			=(D8-B8)/B8

APPENDIX C. RHEOLOGICAL CHARTS AND FLOW CURVES

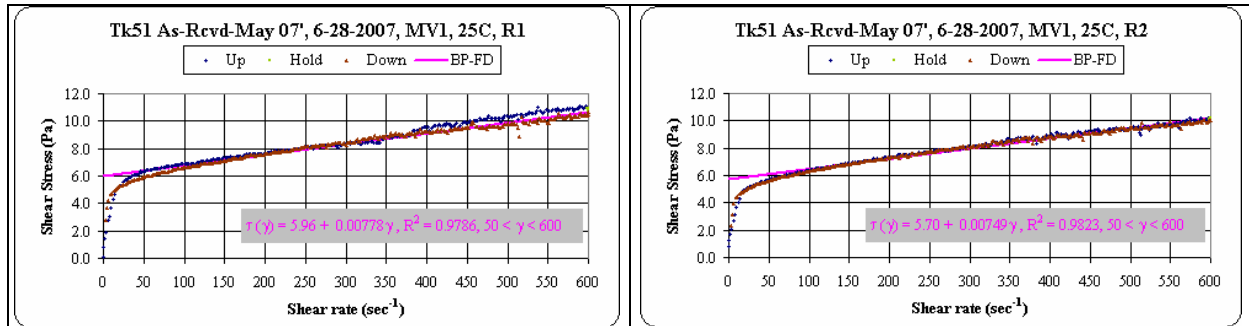


Figure C - 1 Tank 51, As-Received, May 2007, Flow Curve

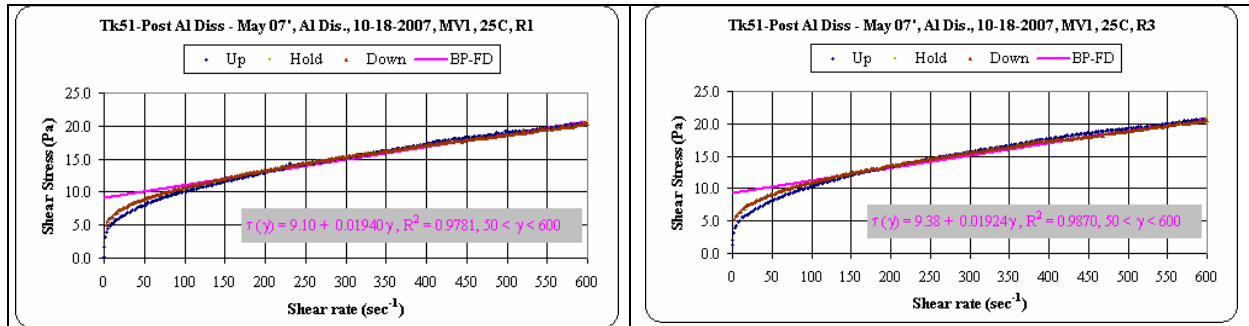


Figure C - 2 Tank 51, SRNL Post Aluminum Dissolution, Flow Curve

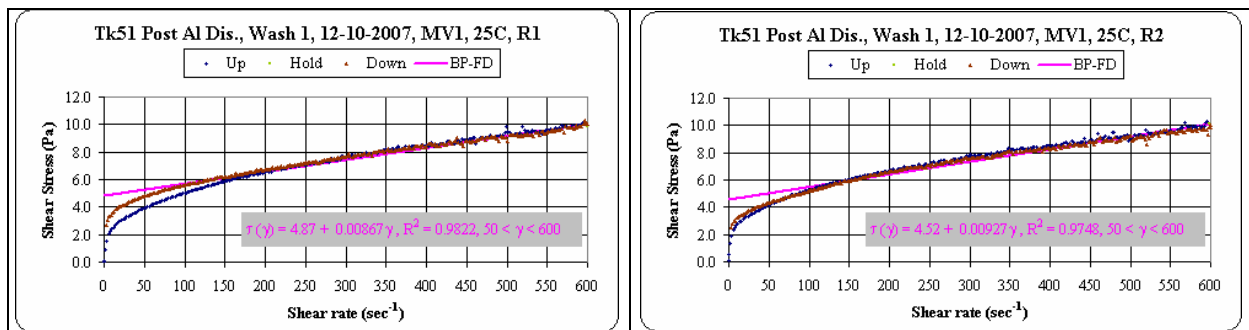


Figure C - 3 Tank 51, SRNL Post Aluminum Dissolution, Wash 1, Flow Curve

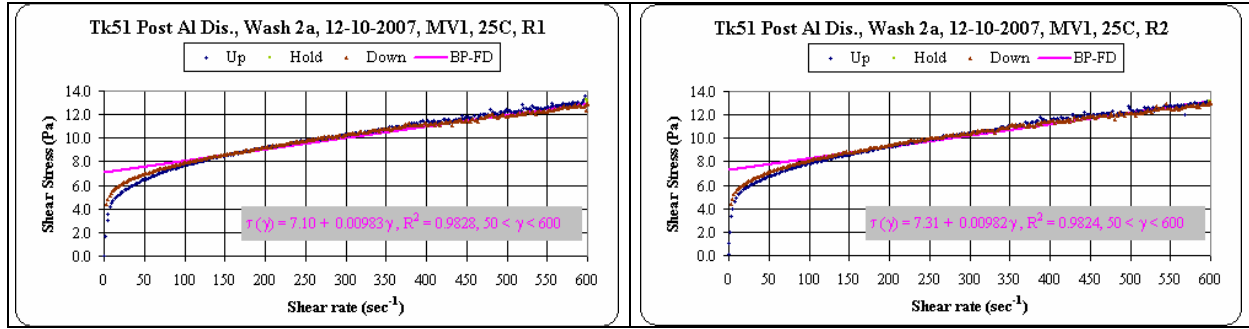


Figure C - 4 Tank 51, SRNL Post Aluminum Dissolution, Wash 2a, Flow Curve

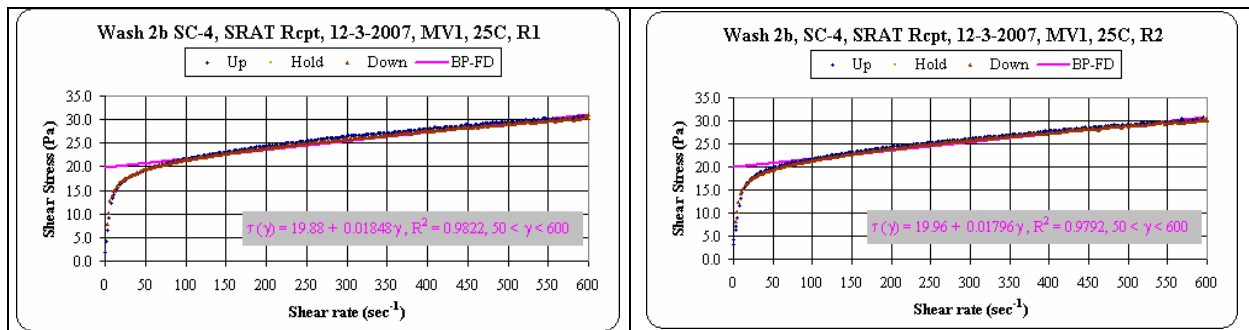


Figure C - 5 Tank 51, SRNL Post Aluminum Dissolution, Wash 2b SC-4 SRAT Rept, Flow Curve

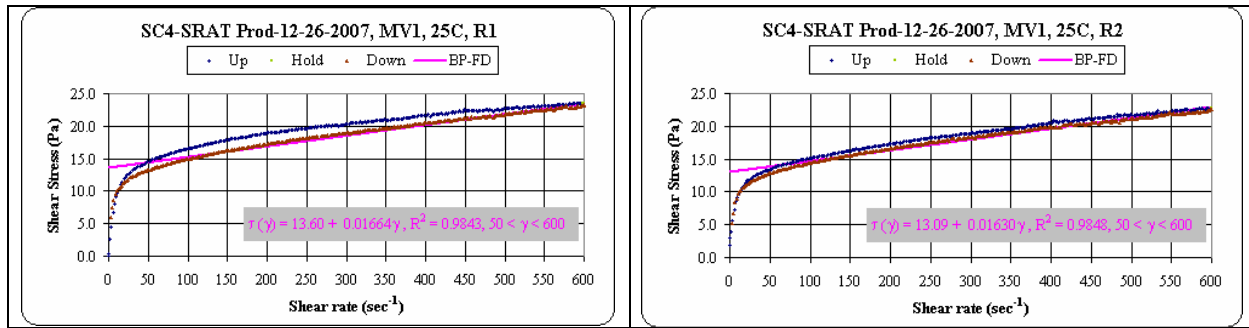


Figure C - 6 SRNL SC-4 SRAT Product, Flow Curve

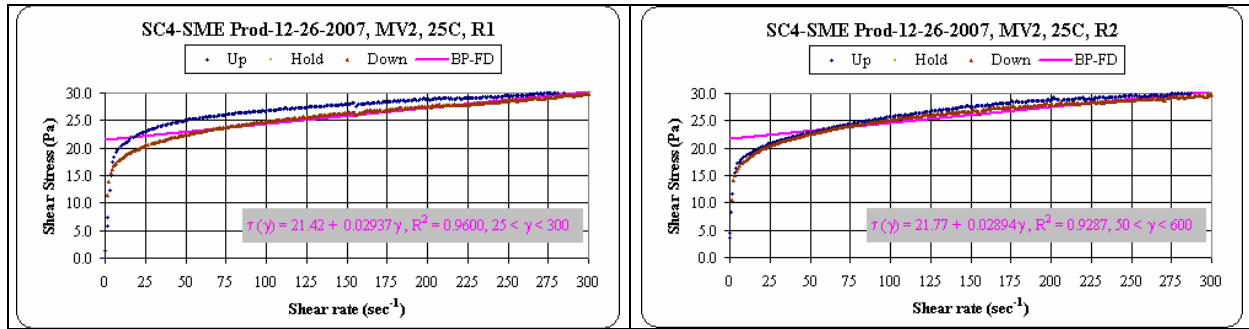


Figure C - 7 SRNL SC-4 SME Product, Flow Curve

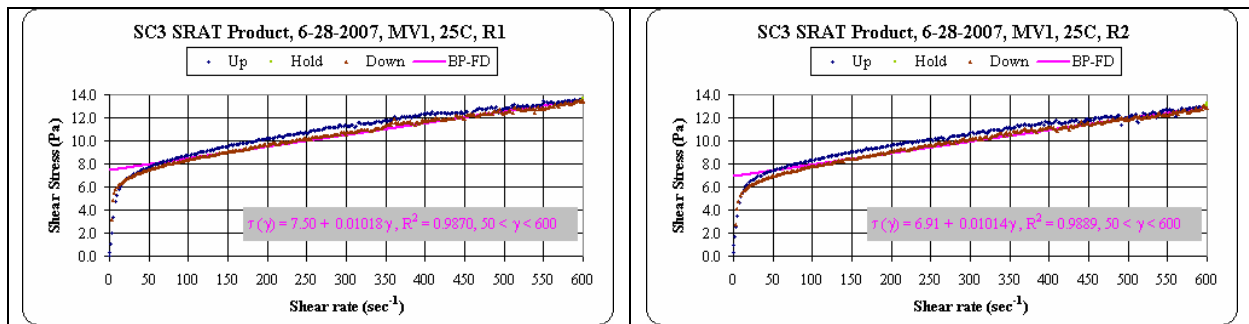
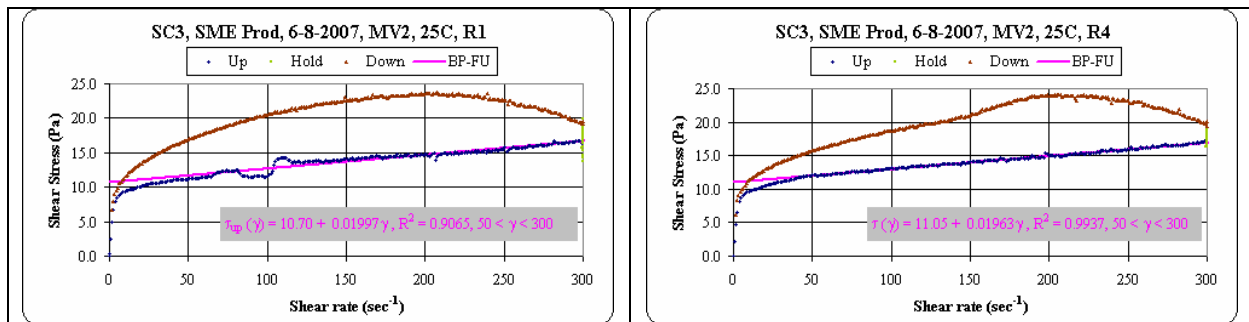


Figure C - 8 SRNL SC-3 SRAT Product, Flow Curve

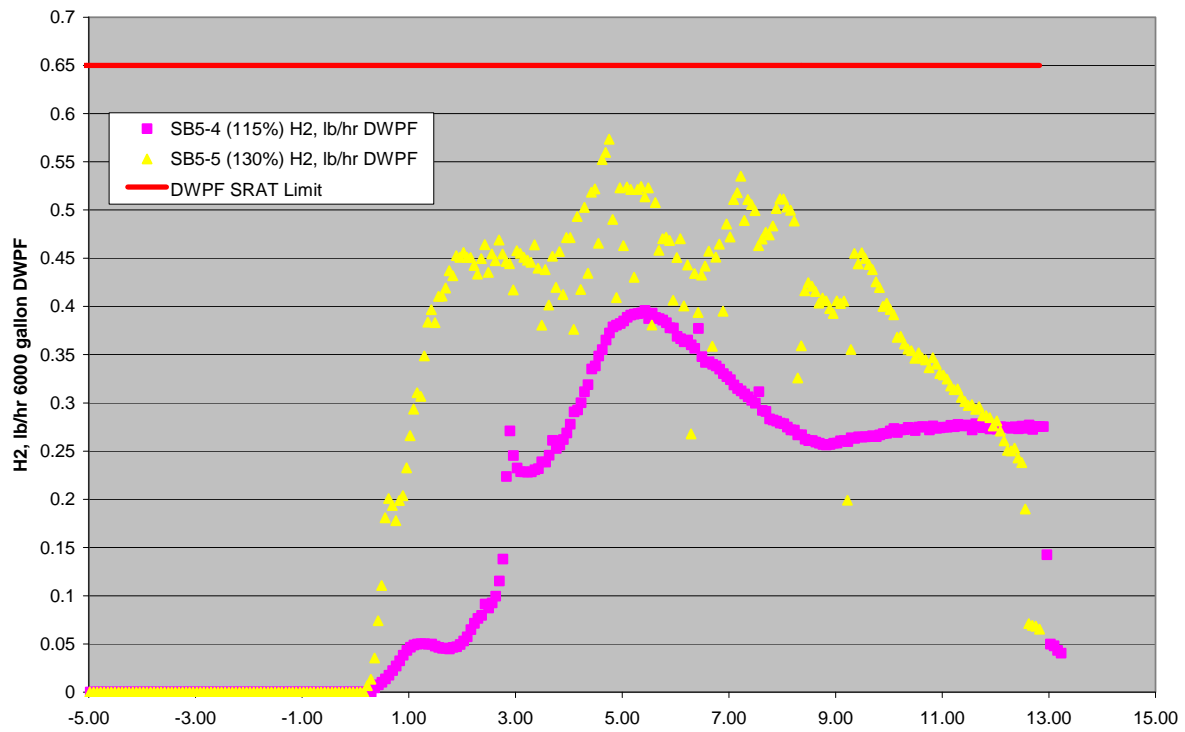


The upflow curves were fitted in this case. It is postulated that the rheology of the overall fluid is not adequate in keeping the Frit particles from migrating to the wall of the cup under centrifugal force, hence decreasing the gap between the bob and cup.

Figure C - 9 SRNL SC-3 SME Product, Flow Curve

APPENDIX D. HYDROGEN GENERATION FROM THE SIMULANT SRAT CYCLES SUPPORTING THE POST ALUMINUM DISSOLUTION CPC PROCESSING

SB5-4 (115%) and SB5-5 (130%) Hydrogen Generation, lb/hr DWPF 6000 gal DWPF Scale



x axis is time relative to end of acid addition.

Distribution:

J.E. Marra, 773-A
J.C. Griffin, 773-A
A.B. Barnes, 999-W
D.A. Crowley, 999-W
B.J. Giddings, 786-1A
C.C. Herman, 773-42A
C.J. Bannochie, 773-42A
M.J. Barnes, 773-A
N.E. Bibler, 773-A
J.M. Bricker, 704-27S
L.M. Chandler, 773-A
L.H. Connelly, 704-28S
B.A. Davis, 704-27S
R.E. Eibling, 999-W
H.H. Elder, 704-30S
T.B. Edwards, 999-W
T.L. Fellingner, 704-28S
S.D. Fink, 773-A
K.M. Fox, 999-W
J.M. Gillam, 766-H
B.A. Hamm, 766-H
J.R. Harbour, 773-42A
M.S. Hay, 773-42A
J.F. Iaukea, 704-30S
D.C. Koopman, 999-W
D.P. Lambert, 999-W
R.N. Mahannah, 704-28S
R.T. McNew, 704-27S
D.J. McCabe, 773-42A
J.E. Occhipinti, 704-S
J.M. Pareizs, 773-A
D.K. Peeler, 999-W
F.M. Pennebaker, 773-A
B.R. Pickenheim, 999-W
J.A. Pike, 703-H
T.M. Punch, 766-H
J.W. Ray, 704-S
S.H. Reboul, 773-42A
H.B. Shah, 766-H
M.E. Smith, 999-W
M.E. Stone, 999-W
J. Stuberfield, 766-H
P.C. Suggs, 704-S
W.D. Wilmarth, 773-42A