

Key Words:
DWPF
Qualification

Retention:
Permanent

**DEMONSTRATION OF THE DWPF FLOWSHEET IN THE SRNL
SHIELDED CELLS WITH TANK 40 AND H CANYON NEPTUNIUM**

J. M. Pareizs
B. R. Pickenheim
C. J. Bannochie
M. E. Stone

April 2009

Savannah River National Laboratory
Savannah River Nuclear Solutions
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

Key Words:
DWPF
Qualification

Retention:
Permanent

**DEMONSTRATION OF THE DWPF FLOWSHEET IN THE SRNL
SHIELDED CELLS WITH TANK 40 AND H CANYON NEPTUNIUM**

J. M. Pareizs
B. R. Pickenheim
C. J. Bannochie
M. E. Stone

April 2009

Savannah River National Laboratory
Savannah River Nuclear Solutions
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

B. R. Pickenheim, Process Technology Programs Date

C. J. Bannochie, Process Technology Programs Date

M. E. Stone, Process Technology Programs Date

TECHNICAL REVIEWERS:

D. P. Lambert, Process Technology Programs Date

APPROVERS:

C. C. Herman, Manager, Process Technology Programs Date

S. L. Marra, Manager, E&CPT Research Programs Date

J. E. Occhipinti, Manager, Waste Solidification Engineering Date

TABLE OF CONTENTS

LIST OF FIGURES.....	III
LIST OF TABLES.....	IV
LIST OF ACRONYMS.....	V
1.0 EXECUTIVE SUMMARY.....	1
2.0 INTRODUCTION AND BACKGROUND.....	2
3.0 APPROACH.....	3
3.1 SRAT RECEIPT PREPARATION.....	3
3.2 SRAT AND SME CYCLES.....	4
3.3 RHEOLOGY MEASUREMENTS.....	6
4.0 RESULTS AND DISCUSSION.....	8
4.1 SRAT RECEIPT PREPARATION.....	8
4.1.1 Acid Calculation.....	10
4.2 SRAT CYCLE.....	12
4.2.1 Nitrite Destruction and Mercury Removal.....	13
4.3 SME CYCLE.....	15
4.4 SRAT AND SME ANTIFOAM ADDITIONS AND FOAMING.....	15
4.5 ANION DESTRUCTION AND CONVERSION.....	17
4.6 OFFGAS ANALYSIS.....	18
4.7 RHEOLOGY MEASUREMENTS.....	20
5.0 CONCLUSIONS.....	23
6.0 RECOMMENDATIONS.....	24
7.0 REFERENCES.....	25
8.0 ACKNOWLEDGEMENTS.....	27
APPENDIX A. EXCERPT FROM TANK FARM PLANNING SPREADSHEET	
SB456_010809B.XLS.....	28
APPENDIX B. DECANT AND ADDITION CALCULATIONS.....	29
APPENDIX C. RESULTS OF SRAT CYCLE PERIODIC SAMPLES.....	32

LIST OF FIGURES

Figure 1. Schematic of SRAT Equipment Set-Up.....	5
Figure 2. Photograph of SRAT/SME Apparatus in SRNL Shielded Cells.....	5
Figure 3. Formate, Nitrate, and pH as a function of SC-8 SRAT Cycle Boiling Time.....	13
Figure 4. Mercury Content of Total Solids as a Function of SC-8 SRAT Cycle Boiling Time.....	14
Figure 5. SC-8 SRAT Cycle Offgas Data (DWPF Scale).....	19
Figure 6. SC-8 SME Cycle Offgas Data (DWPF Scale).....	19
Figure 7. Graphical presentation of SME Product Yield Stress Results.....	21

LIST OF TABLES

Table 1. Summary of CPC Processing.....	4
Table 2. MV I and MV II Rotor Specifications and Flow Curve Program	7
Table 3. Characterization Results of the SRAT Receipt Sample	8
Table 4. Comparison of Selected Tank Farm Projections to SC-8 SRAT Receipt.....	9
Table 5. SC-6 and SC-8 Acid Calculation Inputs	10
Table 6. SC-6 and SC-8 Acid Calculation Results.....	11
Table 7. Characterization Results of the SC-8 SRAT Product	12
Table 8. Anions, Mercury, and pH of the SC-8 Periodic Samples	12
Table 9. Characterization Results of the SC-8 SME Product	15
Table 10. SC-8 SRAT Cycle Antifoam Additions.....	16
Table 11. SC-8 SME Cycle Antifoam Additions.....	16
Table 12. SC-8 Assumed and Measured Anion Destruction and Conversion with Comparison to SC-6.....	17
Table 13. Maximum Observed Hydrogen, Carbon Dioxide, and Nitrous Oxide Volume Percent and DWPf Scale Generation Rates during SC-8 CPC Processing.....	18
Table 14. Rheology Measurements of SC-8 SRAT Receipt, SRAT Product, and SME Product.....	20
Table 15. Rheology of SC-8 SME Product at Various Weight Percent Total Solids	20
Table 16. Comparison Between SC-6 and SC-8 SRAT Receipt, SRAT Product, and SME Product	22

LIST OF ACRONYMS

ACTL	<i>Aiken County Technologies Laboratory</i>
AD	<i>Analytical Development</i>
CPC	<i>Chemical Process Cell</i>
DWPF	<i>Defense Waste Processing Facility</i>
FAVC	<i>Formic Acid Vent Condenser</i>
GC	<i>Gas Chromatograph</i>
GC/MS	<i>Gas Chromatograph – Mass Spectrometer</i>
IC	<i>Ion Chromatography</i>
ICP-AES	<i>Inductively Coupled Plasma – Atomic Emission Spectroscopy</i>
IS	<i>Insoluble Solids</i>
LWO	<i>Liquid Waste Organization/Operations</i>
MWWT	<i>Mercury Water Wash Tank</i>
NIST	<i>National Institute of Standards and Testing</i>
QA	<i>Quality Assurance</i>
REDOX	<i>REDuction / OXidation potential</i>
RSD	<i>Relative Standard Deviation</i>
SB4	<i>Sludge Batch 4</i>
SB5	<i>Sludge Batch 5</i>
SME	<i>Slurry Mix Evaporator</i>
SMECT	<i>Slurry Mix Evaporator Condensate Tank</i>
SRAT	<i>Sludge Receipt and Adjustment Tank</i>
SRNL	<i>Savannah River National Laboratory</i>
SRS	<i>Savannah River Site</i>
SS	<i>Soluble Solids</i>
TIC	<i>Total Inorganic Carbon</i>
TOC	<i>Total Organic Carbon</i>
TS	<i>Total Solids</i>
TTQAP	<i>Task Technical and Quality Assurance Plan</i>
TTR	<i>Technical Task Request</i>
WAPS	<i>Waste Acceptance Product Specification</i>

1.0 EXECUTIVE SUMMARY

The Defense Waste Processing Facility (DWPF) is currently processing Sludge Batch 5 (SB5) from Tank 40. SB5 contains the contents of Tank 51 from November 2008, qualified by the Savannah River National Laboratory (SRNL) and the heel in Tank 40 remaining from Sludge Batch 4. Current Liquid Waste Operations (LWO) plans are to 1) decant supernatant from Tank 40 to remove excess liquid caused by a leaking slurry pump and 2) receive a Np stream from H Canyon. The Np stream contains significant nitrate requiring addition of nitrite to Tank 40 to maintain a high nitrite to nitrate ratio for corrosion control.

SRNL has been requested to qualify the proposed changes; determine the impact on DWPF processability in terms of hydrogen generation, rheology, etc.; evaluate antifoam addition strategy; and evaluate mercury stripping. Therefore, SRNL received a 3 L sample of Tank 40 following the transfer of Tank 51 to Tank 40 (Tank Farm Sample HTF-40-08-157) to be used in testing and to perform the required Waste Acceptance Product Specifications radionuclide analyses. Based on Tank Farm projections, SRNL decanted a portion of the sample, added sodium nitrite, and added a Np solution from H Canyon representative of the Np stream to be dispositioned to Tank 40 (neutralized to 0.6 M excess hydroxide). The resulting material was used in a DWPF Chemical Process Cell (CPC) demonstration – a Sludge Receipt and Adjustment Tank (SRAT) cycle and a Slurry Mix Evaporator (SME) cycle. Based on these simulations:

- The DWPF can process Tank 40 following the targeted decant and addition of sodium nitrite and a Np-bearing stream from H Canyon. The SRNL simulations showed that:
 - The DWPF hydrogen generation rate limits in the SRAT and SME cycles were not exceeded. The observed DWPF scale peak hydrogen generation rates were 0.24 lb/h in the SRAT cycle and 0.15 lb/h during the SME cycle.
 - Nitrite was destroyed to below DWPF limits within twelve hours of boiling in the SRAT cycle.
 - Mercury was removed to below DWPF limits within 28 hours of boiling in the SRAT cycle at a boilup rate of 2,500 lb/h.
 - The SRAT (and SME during canister decon dewatering) was prone to foaming as boiling progressed.
 - Although rheological properties of SRAT and SME products exceeded DWPF design bases, SRNL had no difficulties in mixing or heating these materials.
- Based on these simulations, SRNL recommends:
 - SRAT product solids concentration target of no greater than 20 wt% total solids
 - SRAT boiling time (dewater plus reflux) of 28 hours at 2,500 lb/hr steam (70,000 lb of steam total) to ensure Hg reduction
 - SME product concentration of 45 wt% total solids
 - The following antifoam addition strategy:
 1. 200 ppm prior to SRAT cycle heatup
 2. 100 ppm after addition of nitric acid is complete
 3. 500 ppm after addition of formic acid is complete
 4. 300 ppm every 6 hours of SRAT boiling
 5. 300 ppm every 6 hours during canister decon boiling and 100 ppm each 8 hours during the rest of the SME cycle

2.0 INTRODUCTION AND BACKGROUND

The Defense Waste Processing Facility (DWPF) is currently processing Sludge Batch 5 (SB5) from Tank 40. SB5 contains the contents of Tank 51 from November 2008, qualified by the Savannah River National Laboratory (SRNL)¹ and the heel in Tank 40 remaining from Sludge Batch 4. Current Liquid Waste Operations (LWO) plans are to 1) decant supernatant from Tank 40 to remove excess liquid caused by a leaking slurry pump and 2) receive a Np stream from H Canyon. It should be noted that the Np stream contains significant nitrate requiring addition of nitrite to Tank 40 to maintain a high nitrite to nitrate ratio for corrosion control.

SRNL has been requested to qualify the proposed changes; determine the impact on DWPF processability in terms of hydrogen generation, rheology, etc.; evaluate antifoam addition strategy; and evaluate mercury stripping. Therefore, SRNL received a 3 L sample of Tank 40 following the transfer of Tank 51 to Tank 40 (Tank Farm Sample HTF-40-08-157 to be used in testing and to perform the required Waste Acceptance Product Specifications radionuclide analyses). Based on Tank Farm projections, SRNL decanted a portion* of the sample, added sodium nitrite, and added a Np solution from H Canyon representative of the Np to be dispositioned to Tank 40 (neutralized to 0.6 M excess hydroxide). The resulting material was used in a DWPF Chemical Process Cell (CPC) demonstration – a Sludge Receipt and Adjustment Tank (SRAT) cycle and a Slurry Mix Evaporator (SME) cycle. Preliminary data from the demonstration has been reported previously.^{2,3} This report includes discussion of these results and additional results, including comparisons to Tank Farm projections and the SB5 demonstration.

This work was requested by a Technical Task Request (TTR)⁴ and was guided by a Task Technical and Quality Assurance Plan (TTQAP)⁵ and Analytical Study Plan (ASP)⁶.

* The remaining Tank 40 material will be used for Waste Acceptance Product Specification (WAPS) characterization.

3.0 APPROACH

3.1 SRAT RECEIPT PREPARATION

The SRAT receipt sample was prepared using a portion of the 3 L SB5 – Tank 40 WAPS sample received by SRNL in November 2008 (Tank Farm Sample ID HTF-40-08-157). Due to water in-leakage from the tank slurry pumps and a planned addition of Np from H Canyon, the Tank 40 sample was modified to match these changes. The as-received Tank 40 sample was characterized,⁷ and these results were used as the starting point for modification of the sample.

Per Tank Farm plans,

- A 100 kgal decant from Tank 40 will be performed because of water in-leakage from slurry pumps that has diluted SB5 such that caustic boiling is required in DWPF to maintain a reasonable solids level, prior to sodium nitrite and Np stream additions.
- Sodium nitrite will be added after the decant to maintain the required nitrite to nitrate ratio for corrosion control upon Np addition. Note that the Np stream will add significant amounts of nitrate to Tank 40.
- Approximately 11 kgal of a Np stream will be received into Tank 40 from the H Canyon Material Disposition Program.

An excerpt from Tank Farm Spreadsheet SB456_010809B, the basis for SRNL modifications to the Tank 40 sample, is included in Appendix A. The spreadsheet includes projected Tank 40 compositions before and after decant and additions; sodium nitrite addition quantity; and Np-bearing H Canyon stream quantity and bulk composition (major sodium, nitrite, nitrate, and hydroxide).

An excerpt from Tank Farm Spreadsheet SB456_010809B, the basis for SRNL modifications to the Tank 40 sample, is included in Appendix A. The spreadsheet includes projected Tank 40 compositions before and after decant and additions; sodium nitrite addition quantity; and Np stream quantity and bulk composition (major sodium, nitrite, nitrate, and hydroxide).

SRNL repeated the planned operations with the exception of simulation of pump bearing water in-leakage. Water in-leakage was not simulated to ensure SRNL had a sample that bounded Tank Farm projections with respect to weight percent total and insoluble solids and nitrite, major inputs to the DWPF acid demand.

To estimate the adjustments that would be required for the SRNL Tank 40 sample,

- Decant amount was calculated using a volumetric ratio to the Tank Farm decant.
- Sodium nitrite amount (as a 40wt% solution) was calculated using a volumetric ratio.
- The Np-bearing H Canyon stream volume was calculated using a volumetric ratio.
- The mass of Np added was calculated by multiplying the H Canyon discharge mass by the SRNL volume to Tank Farm volume ratio. An Np-bearing H Canyon sample from July 2008, which was representative of the planned Np transfer, was used as the source of Np. Reagent chemicals (sodium hydroxide, nitric acid) and water were added to the sample to match the required neutralization and nitrate content of the Np stream for disposal.

Since the Tank 40 WAPS sample had already been characterized, the resulting Np-adjusted material required minimal characterization. Weight % solids, density, anions, and titration for base equivalents were characterized, while mercury and manganese content, required for the DWPF acid calculation, were calculated from the analysis of the as-received sample⁷ by mass balance with the assumption that mercury and manganese are insoluble (i.e., the decant did not remove significant mercury and manganese).

SRNL's calculations are shown in Appendix B.

3.2 SRAT AND SME CYCLES

DWPF simulations (SRAT and SME cycles) using the SB5 – Tank 40 WAPS sample with Np were conducted following procedures in the SRNL L29 procedure manual.⁸ A summary of each cycle is presented in Table 1.

Table 1. Summary of CPC Processing

SRAT Cycle	SME Cycle
<ul style="list-style-type: none"> • Heating of SRAT Receipt to 93 °C • Addition of nitric and formic acids per acid calculation • Heating to boiling • Concentration (water removal) to a target wt% total solids • Reflux to obtain a total time at boiling of 44 hours 	<ul style="list-style-type: none"> • Addition and removal of water to simulate addition and removal of water from the decontamination of 5 DWPF canisters • Addition of frit and dilute formic acid in two batches to target 34% waste loading • Concentration (water removal) to target 45-50 wt% total solids.

The CPC processing, designated as SC-8, was 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 performed with the rig can be found in References 9 and 10. 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 cycles, 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 (GC) for characterization. The Slurry Mix Evaporator Condensate Tank (SMECT) is represented by a sampling bottle that is used to remove condensate through the MWWT. For the purposes of this paper, the condensers and wash tank are referred to as the offgas components. A sketch of the experimental setup is given in Figure 1, and a photograph of the equipment in the Shielded Cells is shown in Figure 2.

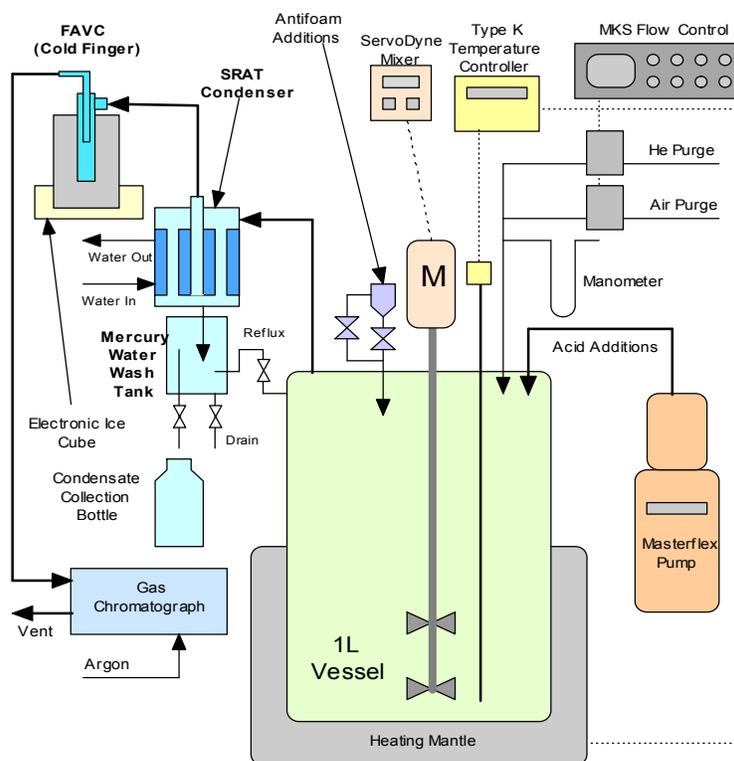


Figure 1. Schematic of SRAT Equipment Set-Up



Figure 2. Photograph of SRAT/SME Apparatus in SRNL Shielded Cells

Offgas hydrogen, oxygen, nitrogen, nitrous oxide, and carbon dioxide concentrations were measured during the experiments using in-line instrumentation (an Agilent M200 series micro GC). Helium was introduced at a concentration of 0.5% of the total air purge as an inert tracer gas so that total amounts of generated gas and peak generation rates could be calculated. During the runs, the kettle was visually monitored to observe reactions that occurred including foaming, air entrainment, rheology changes, loss of heat transfer capabilities, and offgas carryover. Observations were recorded in laboratory notebooks^{11,12} and are discussed in Sections 4.2 (SRAT cycle) and 4.3 (SME cycle).

Concentrated nitric acid (50-wt%) and formic acid (90-wt%) were used to acidify the sludge and perform neutralization and reduction reactions during processing. The amounts of acid to add for each run were determined using the existing DWPF acid addition equation in the 6/1/07 version of the SRNL acid calculation spreadsheet¹³. The split of the acid was determined using the REDOX equation currently being used in DWPF processing^{14,15}. To account for the reactions and anion destructions that occur during processing, assumptions about nitrite destruction, nitrite to nitrate conversion, and formate destruction were made. Acid stoichiometry, processing assumptions, and reflux time were based on CPC processing of simulants and current DWPF operations.

With typical Shielded Cells simulations, DWPF design basis parameters are used. However, for this simulation, current DWPF operating parameters were targeted to try to help decrease processing time in DWPF and to provide a better antifoam strategy. Specifically,

- DWPF is feeding formic acid at one gallon per minute (design basis is two gallons per minute), and formic acid addition is paused for thirty minutes between each quarter of formic acid addition to try to minimize offgas pressure surges
- DWPF boilup rate is currently 2,500-3,000 lb/h in DWPF compared to the design basis of 5,000 lb/h because of in-leakage in the vessel vent system.

During the SRAT cycle, samples for pH measurement and anion and mercury analyses were taken after twelve hours of boiling and every eight hours thereafter. The pH was requested because of the high pH SRAT and SME products currently being produced in DWPF, and the goal was to use the anion data to help understand the mechanism for the increased pH. The Hg data were requested to help determine the minimum required boiling time.

3.3 RHEOLOGY MEASUREMENTS

Rheological properties of radioactive samples are 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 cup holder. The shear stress is determined from the torque measurement and is independent of the rheological properties. Conditions that impact the measured torque are; slip (material does not properly adhere to the rotor or cup), phase separation (buildup of liquid layer on rotor), sedimentation (particles settling out of the shearing zone), homogeneous sample (void of air), lack of sample (gap not filled), excess sample (primarily impacts rheologically thin fluids), completely filling up the void below the bob (air buffer that is now filled with fluid) and Taylor vortices. The first five items yield lower stresses

and the last three add additional stresses. The shear rate is geometrically determined using the equations of change (continuity and motion) and is that for a Newtonian fluid. This approach 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 the data to the rheological model or corrected as recommended by Darby¹⁶. 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.

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 1, where τ is the measured stress (Pa), τ_o is the Bingham Plastic yield stress (Pa), μ_∞ is the plastic viscosity (Pa-sec), and $\dot{\gamma}$ is the measured shear rate (sec^{-1}). During all these measurements, the sample remained in the cup for the 2nd measurement, due to the sample availability.

Equation 1

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

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

Rotor Design	Dimensions and Flow Curve Program		
	Rotor Type	MV I	MV II
	Rotor radius - R_i (mm)	20.04	18.40
	Cup Radius - R_a (mm)	21.0	21.0
	Height of rotor - L (mm)	60	60
	Sample Volume (cm^3) minimum	40	55
	A factor (Pa/%torque)	3.22	3.76
	M factor ($\text{s}^{-1}/\% \text{RPM}$)	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	

4.0 RESULTS AND DISCUSSION

The primary focus of this report is presentation and discussion of the DWPF simulation using SB5 – Tank 40 adjusted to incorporate an H-Canyon Materials Disposition Np stream. Comparisons are made between this simulation and the SB5 qualification simulation. To distinguish between these two simulations, the following designations are used:

- SC-6: Shielded Cells DWPF CPC simulation using SB5 qualification sample (Tank 51)
- SC-8: Shielded Cells DWPF CPC demonstration using SB5 material (Tank 40) with decant and additions (primarily a Np stream from H Canyon) based on Tank Farm projections

4.1 SRAT RECEIPT PREPARATION

Presented in Table 3 are the characterization results of the SC-8 SRAT receipt (following decant and additions).

Table 3. Characterization Results of the SRAT Receipt Sample

Measurement	SC-8 (SB5 Run w/ Tank 40 & Np)	%RSD, n *
Slurry Density (g/mL slurry)	1.11	1.2, 4
Supernatant Density (g/mL supernatant)	1.05	0.7, 4
Total Solids (wt% of slurry)	16.0	0.4, 4
Dissolved Solids (wt% of supernate)	5.6	1.3, 4
Insoluble Solids (wt% of slurry)	11.0	NA
Soluble Solids (wt% of slurry)	5.0	NA
Calcined Solids (wt% of slurry)	12.6	0.9, 4
Nitrite (mg/kg slurry)	14,600	1.0, 4
Nitrate (mg/kg slurry)	7,300	0.9, 4
Total Inorganic Carbon (TIC) mg/kg slurry	828	6.2, 4
Total Base mol/L slurry to pH = 7	0.43	0.3, 2

*%RSD = % relative standard deviation; n = number of replicate analyses. Insoluble and soluble solids are calculated from the average measured total and dissolved solids, thus, the %RSD and number of replicates is not applicable.

Table 4 shows a comparison between Tank 40 projections and the SC-8 SRAT receipt material. The SC-8 supernatant nitrite and nitrate values were calculated using the data from Table 3, and assuming that the nitrite and nitrate are all soluble:

$$\text{Equation 2} \quad C_i = X_i \cdot \frac{D_{sup}}{(1 - W_{is}) \cdot MW_i \cdot 1000}$$

where

C_i = concentration of component i in mol/L supernatant

X_i = concentration of component i in mg/kg slurry

D_{sup} = density of the supernatant in kg/L (equivalent to g/mL)

W_{is} = weight fraction of insoluble solids ($1 - W_{is}$ = weight fraction supernatant)

MW_i = molecular weight of component i in g/mol

1000 = conversion factor for mg to g.

As can be seen in the table, the SRAT receipt sample results are comparable or exceed Tank Farm projections with the exception of nitrate. Because nitrate does not contribute directly to the SRAT cycle acid demand, SRNL proceeded with processing.

Table 4. Comparison of Selected Tank Farm Projections to SC-8 SRAT Receipt

	Tank Farm Projection *	SC-8 SRAT Receipt
Slurry Density (g/mL slurry)	1.12	1.11
Supernatant Density (g/mL supernatant)	1.04	1.05
Total Solids (wt% of slurry)	15.7	16.0
Insoluble Solids (wt% of slurry)	10.3	11.0
Nitrite (mol/L supernatant)	0.35	0.37
Nitrate (mol/L supernatant)	0.18	0.14

* From Tank Farm planning spreadsheet SB456_010809B.xls

4.1.1 Acid Calculation

Acid calculation inputs for the SC-8 SRAT and SME cycles are presented in Table 5. Inputs for the SC-6 cycles are also included. As can be seen in the table, SC-8 nitrite is 1.7 times more than SC-6, while SC-6 total base is 1.7 times greater than SC-8 and SC-6 total inorganic carbon (TIC) is 1.5 times greater than SC-8. These results show that the total base, primarily hydroxide, and TIC have been “diluted” by nitrite in the SC-8 sample.

Table 5. SC-6 and SC-8 Acid Calculation Inputs

Measurement/Assumption	Units	SC-6 (SB5 Qual Run)	SC-8 (SB5 Run w/ Tank 40 & Np)
Total Solids	wt% of slurry	17.1	16.0
Insoluble Solids	wt% of slurry	11.2	11.0
Soluble Solids	wt% of slurry	5.9	5.0
Calcined Solids	wt% of slurry	14.0	12.6
Slurry Density	g/mL slurry	1.14	1.11
Supernatant Density	g/mL supernatant	1.06	1.05
Hg	wt% of total solids	2.22	1.75
Mn	wt% of total solids	4.48	3.37
Nitrite	mg/kg slurry	8,660	14,600
Nitrate	mg/kg slurry	6,220	7,300
Total Inorganic Carbon (TIC)	mg/kg slurry	1,280	828
Total Base	mol/L slurry to pH = 7	0.739	0.43
Conversion of Nitrite to Nitrate in SRAT Cycle	gmol NO ₃ ⁻ /100 gmol NO ₂ ⁻	0	15
Destruction of Nitrite in SRAT and SME cycle	% of starting nitrite	100	100
Destruction of Formic acid charged in SRAT	% of total formate	25	40
Percent Acid in Excess of Stoichiometric Ratio	%	130	145
SRAT Product Target Total Solids	wt% of SRAT Product	25	20
Predicted or Target REDOX	Fe ⁺² / ΣFe	0.20	0.12
Destruction of Formic acid in SME	% of SRAT Product formate	10	10
Destruction of Nitrate in SME	% of SRAT Product nitrate	10	10
Sludge Oxide Contribution in SME (Waste Loading)	% sludge oxides	34	34
SME Product Target Total Solids	wt% of SME Product	45	45

Acid calculation outputs for runs SC-6 and SC-8 are presented in Table 6. In comparing the stoichiometric acid requirements, the SC-6 SRAT cycle required 32% more acid. This amount is consistent with the acid calculation inputs, specifically the lower total base and carbonate (as measured by TIC) in the SC-8 SRAT receipt. Although nitrite is substantially higher in SC-8, its acid demand (0.75 mol acid/mol nitrite) is more than offset by the decrease in total base and TIC (1 mol acid/mol total base and 2 mol acid/mol carbonate calculated from TIC).

Table 6. SC-6 and SC-8 Acid Calculation Results

Parameter	SC-6 (SB5 Qual Run)	SC-8 (SB5 Run w/ Tank 40 & Np)
Calculated Stoichiometric Acid (100% stoichiometry), moles/L – Hsu equation	1.32	0.99
Actual Acid to Add (130% stoichiometry for SC-6, 145% for SC-8), moles/L	1.72	1.44
Ratio of Formic Acid to Total Acid	0.85	0.88
<i>Stoichiometric acid amount by input (mol/L slurry)</i>		
Mercury	0.02	0.02
Manganese	0.16	0.13
Nitrite	0.16	0.26
Total Inorganic Carbon (TIC)	0.24	0.15
Total Base	0.74	0.43

4.2 SRAT CYCLE

During the SRAT cycle, there were no issues or problems with mixing, concentration (water removal), or maintaining the target boilup rate. Note that SRAT and SME foaming along with antifoam additions is discussed in Section 4.4.

Throughout the SRAT cycle (twelve hours after boiling began and every eight hours thereafter) samples were pulled. The final SRAT product (after 44 hours of boiling) was measured for density, total solids, anions, and pH. Results, averages of four measurements with the exception of pH, and the calculated values of insoluble and soluble solids are presented in Table 7. The remaining samples were characterized for anions and mercury (in duplicate) and pH to try to understand the cause for the rising pH and to determine the minimum boiling time to remove Hg. The average of these duplicate measurements is presented in Table 8, along with the SRAT product results (44-hour sample). Overall, there was good agreement between the duplicate results with the exception of the Hg analysis of the 20-hour sample. Relative standard deviations are not given in Table 8 because of space considerations. They are instead presented in Appendix C.

Table 7. Characterization Results of the SC-8 SRAT Product

Analysis	SRAT Product	%RSD, n *
Slurry Density (g/mL)	1.13	0.1, 4
Supernatant Density (g/mL)	1.06	0.7, 4
Weight % Total Solids (slurry basis)	19.3	0.6, 4
Weight % Dissolved Solids (supernatant basis)	9.7	0.6, 4
Weight % Insoluble Solids (slurry basis)	10.6	NA
Weight % Soluble Solids (slurry basis)	8.7	NA
Weight % Calcined Solids (slurry basis)	14.3	0.5, 4
Nitrite (mg/kg slurry)	<740	NA
Nitrate (mg/kg slurry)	29,800	2.3, 4
Formate (mg/kg slurry)	37,200	3.3, 4
TIC (mg/kg slurry)	<191	NA
pH	8.74	NA, 1

* %RSD = % relative standard deviation; n = number of replicate analyses. Insoluble and soluble solids are calculated from the average measured total and dissolved solids, thus, the %RSD and number of replicates is not applicable.

Table 8. Anions, Mercury, and pH of the SC-8 Periodic Samples

	Time at Boiling (h)				
	12	20	28	36	44
Formate (mg/kg)	44,600	42,900	40,000	39,100	37,200
Nitrite (mg/kg)	<730	<750	<819	<800	<740
Nitrate (mg/kg)	30,800	31,200	30,800	31,700	29,800
Mercury (wt% of total solids)	0.96	0.60	0.21	0.12	0.10
pH	7.89	8.08	8.32	8.56	8.74

4.2.1 Nitrite Destruction and Mercury Removal

The results for formate, nitrate, pH, and mercury from Table 8 are presented graphically in Figure 3 and Figure 4. Because nitrite is below detection limits and below the SRAT product limit of 1,000 mg/kg for all samples, it is not plotted.

Figure 3 shows clearly that minimal variation in nitrate concentration existed after twelve hours of boiling. That is, nitrate is not destroyed during the long boiling time. Formate, however, shows a decrease of nearly 17% between twelve hours and the completion of the SRAT cycle. This formate destruction corresponds to the increase in pH throughout boiling.

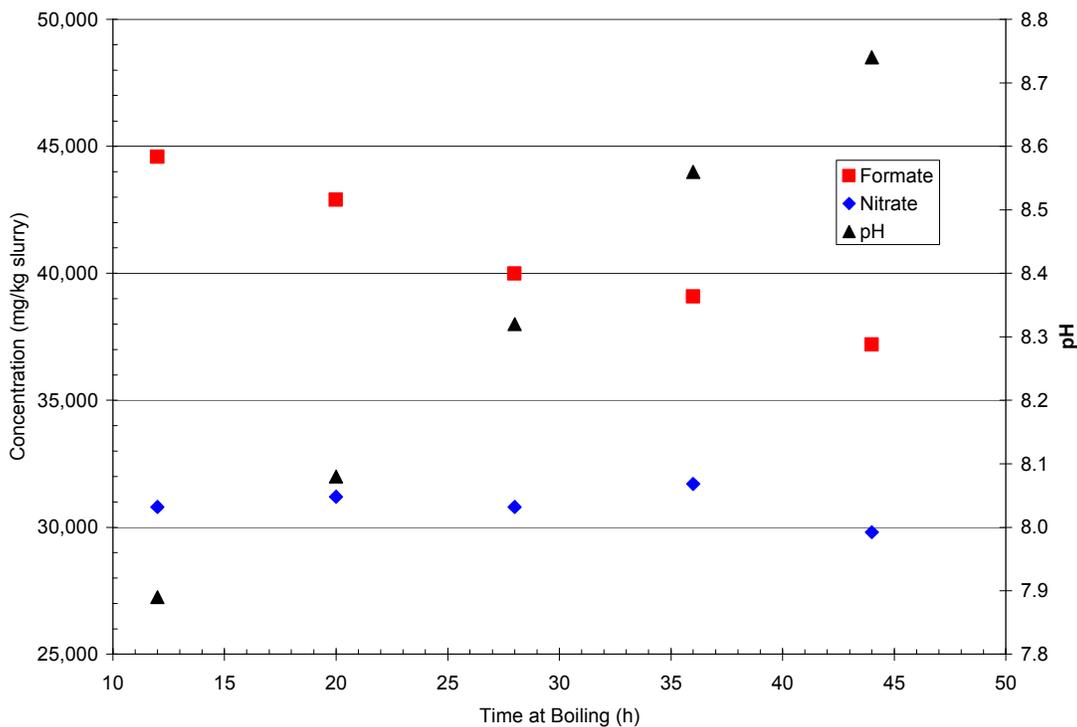


Figure 3. Formate, Nitrate, and pH as a function of SC-8 SRAT Cycle Boiling Time

Mercury concentration in the total solids as a function of time at boiling can be approximated by an exponential decay. MS Excel’s Trendline feature was used to draw the exponential curve (solid line) in Figure 4. The correlation coefficient (R^2) of this curve fit is 0.96. Based on the measured mercury in the total solids, mercury concentration falls below the DWPF limit within 28 hours of boiling. If one uses the Trendline, it appears the mercury limit is reached within 22 hours of boiling.

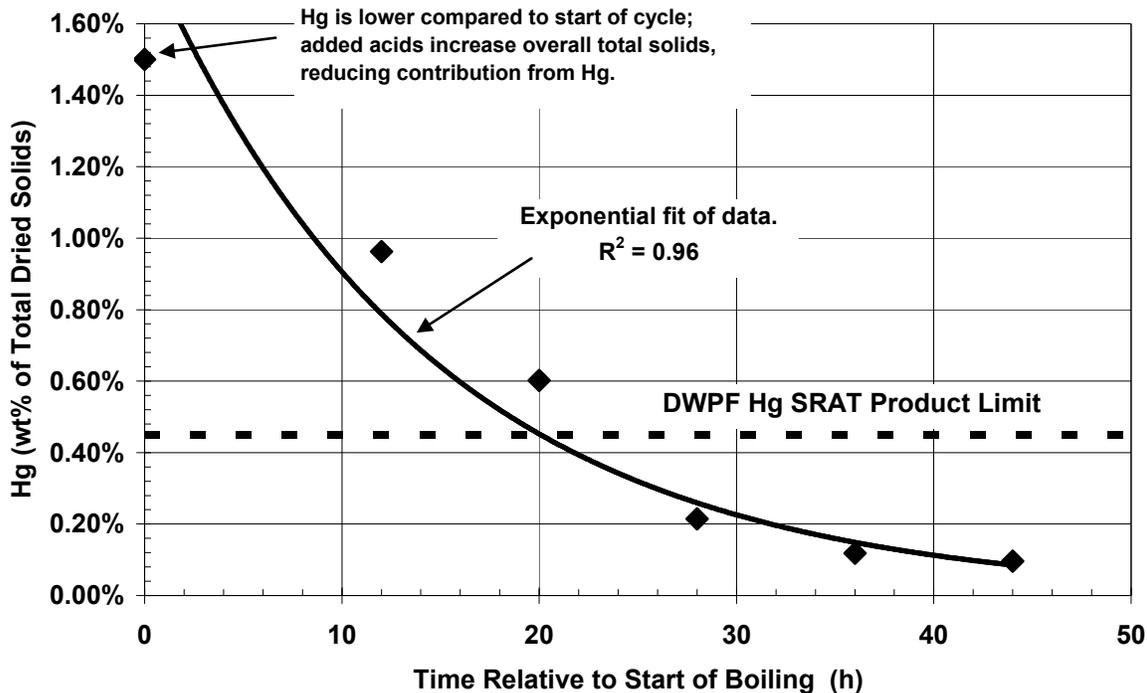


Figure 4. Mercury Content of Total Solids as a Function of SC-8 SRAT Cycle Boiling Time

4.3 SME CYCLE

Like the SRAT cycle, during the SME cycle, there were no issues or problems with mixing, concentration (water removal), or maintaining the target boilup rate. At the conclusion of the SME cycle, a sample for analysis was taken. Weight percent solids, density, anions, TIC, Total Organic Carbon (TOC), and pH were measured. Results are presented in Table 9. Note that SRAT and SME foaming along with antifoam additions is discussed in Section 4.4.

Table 9. Characterization Results of the SC-8 SME Product

Analysis	SME Product	%RSD, n*
Slurry Density (g/mL)	1.44	0.6, 4
Supernatant Density (g/mL)	1.10	0.2, 4
Weight % Total Solids (slurry basis)	48.5	0.8, 4
Weight % Dissolved Solids (supernatant basis)	14.4	0.2, 4
Weight % Insoluble Solids (slurry basis)	39.9	NA
Weight % Soluble Solids (slurry basis)	8.6	NA
Weight % Calcined Solids (slurry basis)	42.7	1.8,
Nitrite (mg/kg slurry)	<770	NA
Nitrate (mg/kg slurry)	29,800	3.9, 4
Formate (mg/kg slurry)	38,500	3.7, 4
TIC (mg/kg slurry)	<192	NA
TOC (mg/kg slurry)	12,100	2.0, 4
pH	8.44	NA, 1

* %RSD = % relative standard deviation; n = number of replicate analyses. Insoluble and soluble solids are calculated from the average measured total and dissolved solids, thus, the %RSD and number of replicates is not applicable.

4.4 SRAT AND SME ANTIFOAM ADDITIONS AND FOAMING

One of the goals of the run was to determine a refined antifoam strategy due to the problems seen with the SB5 qualification run. The following antifoam addition strategy was planned for the SRAT and SME cycles, which represented the minimum antifoam addition strategy and was used for the last several sludge batches in DWPF:

- 200 ppm addition prior to heating
- 500 ppm addition prior to boiling (after formic acid addition)
- 100 ppm every eight hours during boiling
- 100 ppm every eight hours during the SME cycle

Prior to beginning the processing, the decision was made to add antifoam whenever foam was seen in the upper window of the SRAT/SME apparatus (see Figure 2). Also, if the frequency of additions became greater than every four hours, additions of greater than 100 ppm would be used.

Antifoam additions for the SRAT and SME cycles are summarized in Table 10 and Table 11, respectively. During the early stages of SRAT boiling, antifoam was needed every six to eight hours. Excessive foaming became problematic after 27 hours of boiling, necessitating antifoam additions every one to three hours. This behavior continued into the decon water removal phase of the SME cycle. This result is not surprising, since decon water removal in the SME is in essence boiling/concentration of SRAT material. Following frit/formic acid addition (i.e., during frit water removal and final dewatering), no antifoam was needed.

Table 10. SC-8 SRAT Cycle Antifoam Additions

Antifoam Amount (mg/kg of SRAT Receipt)	Comment
200	Added during first quarter of formic acid addition. Note that this antifoam should have been added prior to startup; it was not added at that time due to antifoam addition funnel problems.
500	Added just prior to boiling.
100	Added after 6 hours of boiling.
100	Added after 12 hours of boiling.
100	Added after 20 hours of boiling.
120	Added after 27 hours of boiling.
100	Added after 28 hours of boiling.
160	Added after 33 hours of boiling.
190	Added after 34 hours of boiling.
180	Added after 36 hours of boiling.
200	Added shortly after previous addition. Previous addition was not effective.
190	Added after 38 hours of boiling.
220	Added after 40 hours of boiling.
470	Added after 42 hours of boiling.
2830	Total Antifoam Added in SRAT cycle

Table 11. SC-8 SME Cycle Antifoam Additions

Antifoam Amount (mg/kg of SME Receipt)	Comment
280	Added 2 hours after start of SME cycle (during decon water removal).
150	Added 5 hours after start of SME cycle (during decon water removal).
150	Added 8 hours after start of SME cycle (during decon water removal).
0	No antifoam was required during boiling to remove the frit water or during the final SME cycle dewatering.
580	Total Antifoam Added in SME cycle

Based on these observations, SRNL recommends the following antifoam strategy:

1. 200 ppm prior to SRAT cycle heatup
2. 100 ppm after addition of nitric acid is complete
3. 500 ppm after addition of formic acid is complete
4. 300 ppm every 6 hours of SRAT boiling
5. 300 ppm every 6 hours during canister decon boiling and 100 ppm each 8 hours during the rest of the SME cycle

4.5 ANION DESTRUCTION AND CONVERSION

The calculated anion destruction and conversion results for the SC-8 SRAT and SME cycles, with comparisons to the acid calculation input assumptions and the SC-6 simulations are given in Table 12 below. With the exception of nitrite to nitrate conversion, the SC-8 results are comparable to the acid calculation inputs.

Table 12. SC-8 Assumed and Measured Anion Destruction and Conversion with Comparison to SC-6

	Assumption (SC-8 Acid Calculation Input)	SC-6 (SB5 Qual Run)	SC-8 (SB5 Run w/ Tank 40 & Np)
SRAT Cycle Nitrite Destruction (%)	100	>92	>95
SRAT Cycle Formate Destruction (%)	40	18	36
SRAT Cycle Nitrite to Nitrate Conversion (%)	15	100 ‡	52
SME Cycle Formate Destruction (%)	10	32	8
SME Cycle Nitrate Destruction (%)	10	26	3

‡ This conversion is not reasonable based on the fact that nitrous oxide was measured in significant quantities in the offgas. That is, some nitrite was converted to NO_x gas. This result is likely due to a combination of analytical errors in the SRAT receipt and product anion analyses and the overall SRAT cycle mass balance.

4.6 OFFGAS ANALYSIS

Peak offgas volume percents and DWPF-scale generation rates are given in Table 13. The offgas data are presented graphically in Figure 5 (SRAT cycle) and Figure 6 (SME cycle). The figures show a typical SRAT/SME cycle pattern: large amounts of carbon dioxide during acid addition, a hydrogen peak several hours after nitrous oxide generation drops, and drops in gas generation rate as the vessel is breached for pulling samples (SRAT cycle) and adding water and frit (SME cycle). In both cycles, peak hydrogen generation was well below DWPF limits.

Table 13. Maximum Observed Hydrogen, Carbon Dioxide, and Nitrous Oxide Volume Percent and DWPF Scale Generation Rates during SC-8 CPC Processing

Gas	SRAT Cycle		SME Cycle	
	Maximum Observed Volume%	Maximum Gas Generation Rate (DWPF lb/h)	Maximum Observed Volume%	Maximum Gas Generation Rate (DWPF lb/h)
Hydrogen	0.29	0.24	0.51	0.15
Carbon Dioxide	12.2	235	3.80	23.9
Nitrous Oxide	2.65	49.8	0.33	1.91

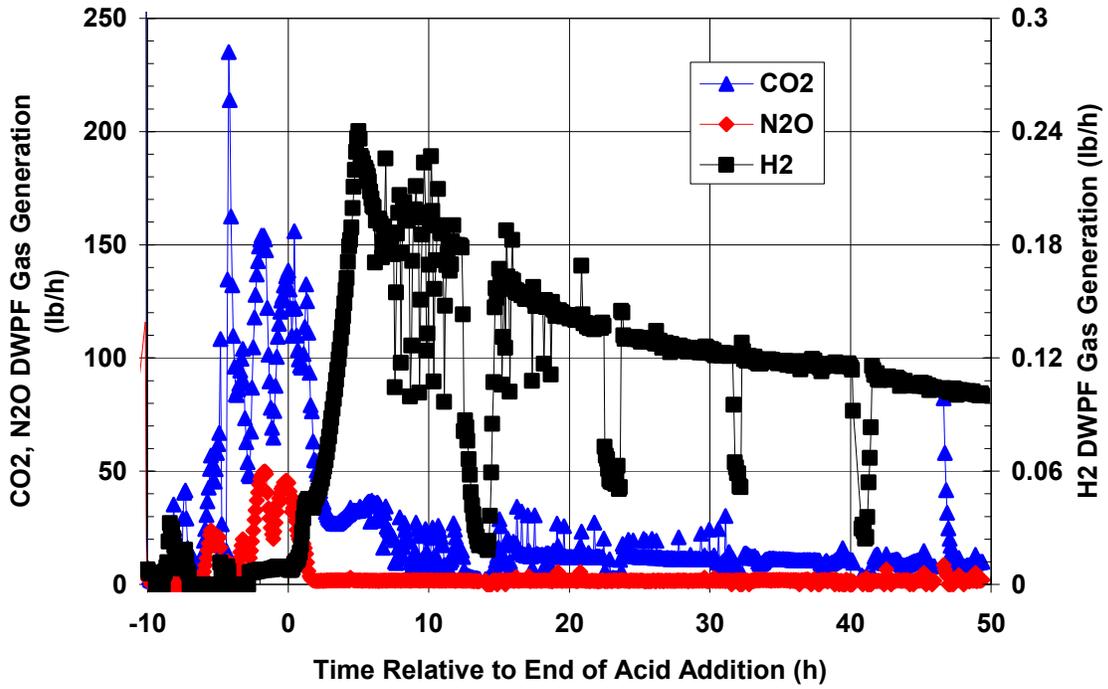


Figure 5. SC-8 SRAT Cycle Offgas Data (DWPf Scale)

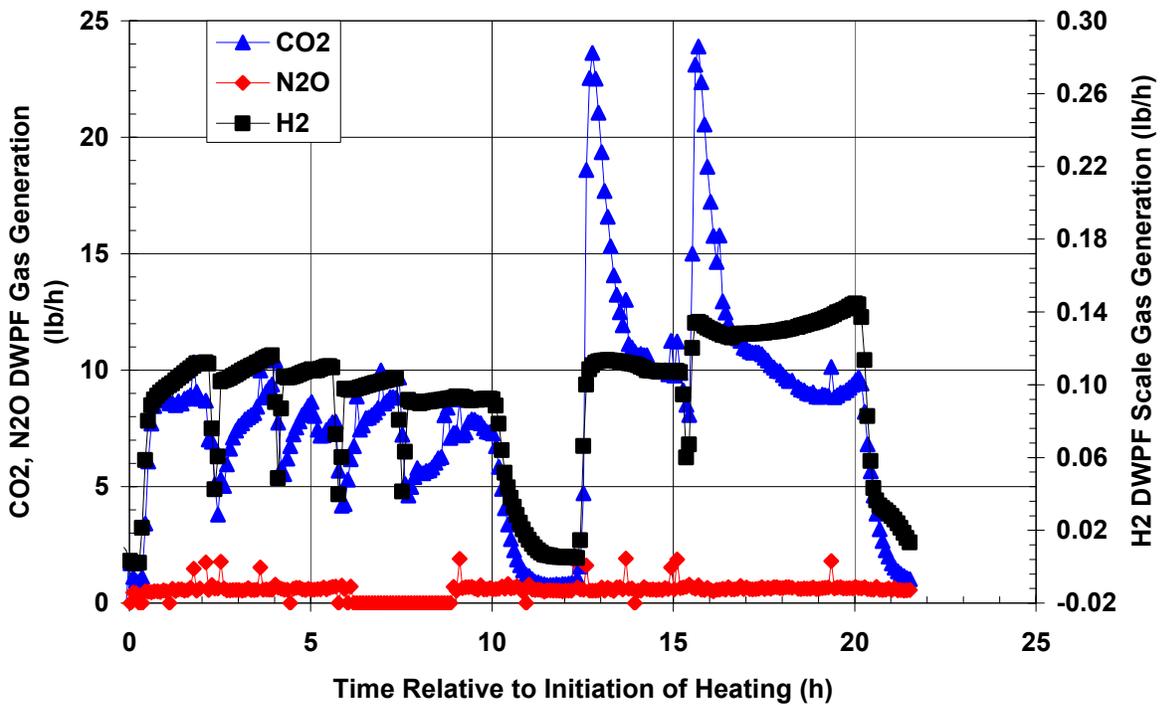


Figure 6. SC-8 SME Cycle Offgas Data (DWPf Scale)

4.7 RHEOLOGY MEASUREMENTS

Given in Table 14 are the results of rheology measurements (yield stress and consistency) for the SC-8 slurry samples (SRAT receipt, SRAT product, and SME product).

Table 14. Rheology Measurements of SC-8 SRAT Receipt, SRAT Product, and SME Product

Sample	Insoluble Solids (wt%)	Yield Stress (Pa)	Consistency (cP)	DWPF Design Basis Yield Stress (Pa) [†]	DWPF Design Basis Consistency (cP) [†]
SC-8 SRAT Receipt)	11.0	5.2	6.9	2.5 – 10	4 – 12
SC-8 SRAT Product (19.3 wt% total solids)	10.6	6.4	14	1.5 – 5.0	5 – 12
SC-8 SME Product (48.5 wt% total solids) [‡]	39.9 [‡]	38	9.6	2.5 – 15	10 – 40

[†] Design bases can be found in Reference 17.

[‡] The SME product material used for rheology was taken from the contents of the SRAT/SME vessel several weeks after the run. It is likely the wt% solids are higher than the SME analytical sample, analyzed immediately after the cycle. An attempt was made to measure the wt% solids of this material, but the results were lower than a sample diluted with water, implying a sub-sampling problem.

Because of the high yield stress of the SC-8 SME product, SME product samples at various weight percent solids were prepared and rheological properties were measured to provide data for a recommended SME product total solids target. These results are presented in Table 15 and Figure 7. As can be seen in the results, yield stress is a strong function of solids content; yield stress increases dramatically as wt% total solids increase beyond 43%

Table 15. Rheology of SC-8 SME Product at Various Weight Percent Total Solids

Wt% Total Solids	Yield Stress (Pa)	Consistency (cP)
40.0	8.8	5.8
42.9	9.9	5.7
47.5	21	9.0
48.5 [‡]	38	9.7

[‡] The SME product material used for rheology was taken from the contents of the SRAT/SME vessel several weeks after the run. It is likely the wt% solids are higher than the SME analytical sample, analyzed immediately after the cycle. An attempt was made to measure the wt% solids of this material, but the results were lower than a sample diluted with water, implying a sub-sampling problem.

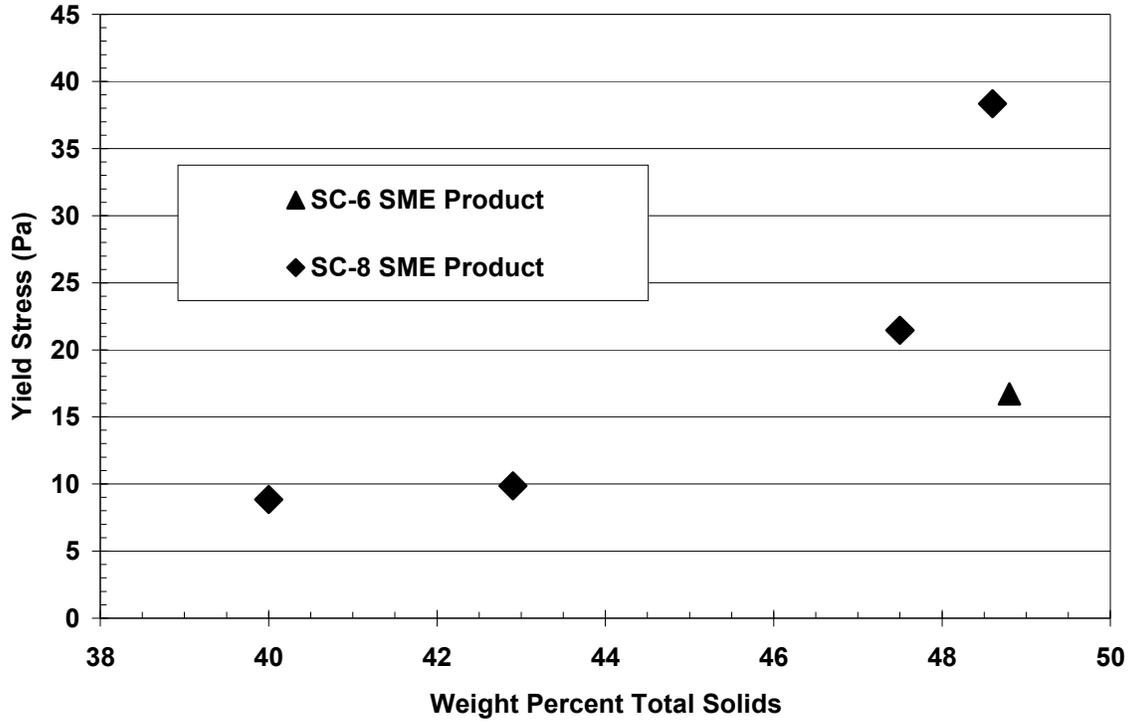


Figure 7. Graphical presentation of SME Product Yield Stress Results

Table 16 shows a comparison between SC-6 and SC-8 material. These results and comparisons show that:

- The SC-8 SRAT product yield stress and consistency exceed DWPF design bases, but the results are fairly close to the measured values for the SB5 SRAT cycle (SC-6).
- Yield stress of the SC-8 SME product is significantly higher than the corresponding SC-6 material even with comparable wt% total and insoluble solids (see also graphical comparison in Figure 7). However, the yield stress can be significantly lowered by decreasing SME product solids content.

These differences in rheological properties between SC-6 and SC-8 are likely a result of the differences in acid added in the respective SRAT cycles (1.72 mol/L for SC-6 and 1.44 mol/L for SC-8).

Table 16. Comparison Between SC-6 and SC-8 SRAT Receipt, SRAT Product, and SME Product

		Weight % Total Solids	Weight % Insoluble Solids	Yield Stress (Pa)	Consistency (cP)
SRAT Receipt	SC-6	17.1	11.2	6.8	8.6
	SC-8	16.0	11.0	5.2	6.9
SRAT Product	SC-6	20 [*]	11.3 [*]	6.4	6.1
	SC-8	19.3	10.6	6.4	14
SME Product	SC-6	48.8	40.3	16.7	13.8
	SC-8	48.5 [†]	39.9 [†]	38	9.6

^{*} This is an estimate. Dewater from the SC-6 SRAT cycle was added back to a portion of an SC-6 SRAT product sample to produce a sample at 20% total solids. The total solids were not measured.

[†] The SME product material used for rheology was taken from the contents of the SRAT/SME vessel several weeks after the run. It is likely the wt% solids are higher than the SME analytical sample, analyzed immediately after the cycle. An attempt was made to measure the wt% solids of this material, but the results were lower than a sample diluted with water, implying a sub-sampling problem.

5.0 CONCLUSIONS

The DWPF can process Tank 40 following a decant and addition of sodium nitrite and a Np-bearing stream from H Canyon. The SRNL simulations showed that:

- The DWPF hydrogen generation limits in the SRAT and SME cycles were not exceeded.
- Less acid was needed for the SC-8 SRAT cycle (Tank 40 with Np) compared to the qualification SRAT cycle (SC-6) due to “dilution” of total base because of the addition of nitrite and nitrate. Note that in the acid calculation, 1 mol of acid is required for each mol of total base (predominantly hydroxide), while 0.75 mol of acid is required per mol of nitrite.
- Nitrite was destroyed to below DWPF limits within twelve hours of boiling in the SRAT cycle.
- Mercury was removed to below DWPF limits within 28 hours of boiling in the SRAT cycle at a boilup rate of 2,500 lb/h.
- During the long boiling period, formate concentration decreased as pH increased.
- The SRAT (and SME during canister decon dewatering) was prone to foaming as boiling progressed; however, the antifoam was effective at suppressing the foam layer when added.
- Although rheological properties of SRAT and SME products exceeded DWPF design bases, SRNL had no difficulties in mixing or heating these materials. Rheological properties of the SC-8 SRAT product was comparable to the SB5 qualification SRAT product, but the yield stress of the SC-8 SME product greatly exceeded the SC-6 SME product.

6.0 RECOMMENDATIONS

Based on these simulations, SRNL recommends:

- SRAT product solids concentration target of no greater than 20 wt% total solids
- SRAT boiling time (dewater plus reflux) of 28 hours at 2,5000 lb/hr steam (70,000 lb of steam total) to ensure Hg reduction
- SME product concentration to no greater than 45 wt% total solids
- The following antifoam addition strategy:
 - 200 ppm prior to SRAT cycle heatup
 - 100 ppm after addition of nitric acid is complete
 - 500 ppm after addition of formic acid is complete
 - 300 ppm every 6 hours of SRAT boiling
 - 300 ppm every 6 hours during canister decon boiling and 100 ppm each 8 hours during the rest of the SME cycle

7.0 REFERENCES

1. Pareizs, J. M.; Bannochie, C. J.; Click, D. R.; Lambert, D. P.; Stone, M. E.; Pickenheim, B. R.; Billings, A. L.; Bibler, N. E. *Sludge Washing and Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells for Sludge Batch 5 Qualification*; WSRC-STI-2008-00111; Savannah River National Laboratory: Aiken, SC, 2008.
2. Pareizs, J. M.; Pickenheim, B. R.; Bannochie, C. J. *Data from the SC-8 DWPF CPC Simulation (Sludge Batch 5 With H Canyon Neptunium)*; SRNL-L3100-2009-00051; Savannah River National Laboratory: Aiken, SC, 2009.
3. Pareizs, J. M.; Pickenheim, B. R.; Bannochie, C. J. *Mercury Results from the SC-8 SRAT Cycle (DWPF CPC Simulation Using Sludge Batch 5 With H Canyon Neptunium)*; SRNL-L3100-2009-00055; Savannah River National Laboratory: Aiken, SC, 2009.
4. Fellingner, T. L. *Sludge Batch 5 SRNL Shielded Cells Testing: Technical Task Request*; HLW-DWPF-TTR-2008-0010, Rev. 2; Savannah River Site: Aiken, SC, 2008.
5. Bannochie, C. J.; Pareizs, J. M. *Qualification of DWPF Sludge Batch 5 (Macrobatches 6) in the SRNL Shielded Cells: Task Technical & Quality Assurance Plan*; WSRC-RP-2008-00137, Rev. 2; Savannah River National Laboratory: Aiken, SC, 2008.
6. Bannochie, C. J. *Qualification of DWPF Sludge Batch 5 in the SRNL Shielded Cells: Analytical Study Plan*; WSRCRP-2008-00138, Rev. 2; Savannah River National Laboratory: Aiken, SC, 2008.
7. Bannochie, C. J.; Click, D. R. *Tank 40 Final SB5 Chemical Characterization Results Prior to Np Addition*; SRNL-STI-2009-00060; Savannah River National Laboratory: Aiken, SC, 2009.
8. *Process Science and Engineering Section Procedure Manual*; Manual L29; Savannah River National Lab: Aiken, SC, 2007.
9. Stone, M. E. *Lab-Scale CPC Equipment Set-up*; SRNL-PSE-2006-00074; Savannah River National Laboratory: Aiken, SC, 2006.
10. Pickenheim, B. R. *SRAT Assembly for SB5 Shielded Cells Testing: SC-7*; SRNL-L3100-2008-00042; Savannah River National Laboratory: Aiken, SC, 2008.
11. *Sludge Batch 5 IV*; SRNS-NB-2008-00004; Savannah River National Laboratory: Aiken, SC, 2008.
12. *Sludge Batch 5 V*; SRNS-NB-2009-00007; Savannah River National Laboratory: Aiken, SC, 2009.
13. 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.

14. 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*; WSRC-TR-2003-00126; Savannah River National Laboratory: Aiken, SC, 2003.
15. Jantzen, C. M.; Newell, J. D. *Defense Waste Processing Facility (DWPF) Sludge Batch 5 (SB5) Redox Validation*; SRNL-PSE-2008-00184; Savannah River National Laboratory: Aiken, SC, 2008.
16. Darby, R., *Chemical Engineering Fluid Mechanics, 2nd edition*. Marcel Dekker: 2001.
17. *Technical Data Summary For the Defense Waste Processing Facility, Part 10*; DPSTD-80-38-2; Savannah River Site: Aiken, SC, 1982.

8.0 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; SRNL-AD researchers and technicians for chemical analyses; and the SRNL Glass Shop for providing glassware and other miscellaneous hardware.

**APPENDIX A. EXCERPT FROM TANK FARM PLANNING
SPREADSHEET SB456_010809B.XLS**

Date				5/11/2009					05/11/09
Tank 51 and 40	Steam Outage 4/25-5/10/08	Tank 40 Settled	Decant from Tank 40	Tank 40 after Decant	40 wt% NaNO2	Extra Water with NaNO2 for wt% NaNO2 of:	Tank 40 (SB5) before Np Add	Np Waste stream	Tank 40 after Np Add
Initial tank Level (in)		142.66		114.10			117.5		120.6
liquid volume (gal)		485882	100246	385636	10043.4	1893.9	397573	11000	408573
sludge volume (gal)		14855	0	14855			14855	0	14855
settled sludge level (in)		88.10							
kg insol. solids		184230		184230			184230	0	184230
wt% insol solids		8.88		10.94			10.58		10.27
decant level		112.10							
NO2/NO3, or kg TS/day from 40H							5.55		1.950
additional nitrite solution									
additional volume									
SpG		1.027	1.027	1.0275	1.32	1	1.0347	1.25	1.0405
Na		0.618	0.618	0.618	7.65	0	0.7929	5.082	0.9084
NO2		0.167	0.167	0.167	7.65	0	0.3553	0.0000	0.3457
NO3		0.066	0.066	0.066	0	0	0.0641	4.270	0.1773
OH		0.269	0.269	0.269	0	0	0.2606	0.6	0.2698
Cl		0.002	0.002	0.002	0	0	0.0020	0.0035	0.0021
SO4		0.005	0.005	0.005	0	0	0.0051	0.1015	0.0077
F		0.001	0.001	0.001	0	0	0.0013	0.0035	0.0013
CO3		0.042	0.042	0.042	0	0	0.0412	0.0007	0.0401
AlO2		0.031	0.031	0.031	0	0	0.0300	0.0007	0.0293
C2O4-2		0.002	0.002	0.002	0	0	0.0015	0	0.0014
PO4-3		0.000	0.000	0.000	0	0	0.0003	0	0.0003
K		0.001	0.001	0.001	0	0	0.0012	0	0.0011
Soluble Na2C2O4, M				1.111		slurry spg=	1.115		1.119
Insol Na2C2O4, kg									
NOeff (M)				0.1442			0.2332		0.3382
Mass TS, kg		259734	15578	244156	20072	0	264228	16731	280959
wt% TS		12.525		14.50			15.17		15.67

APPENDIX B. DECANT AND ADDITION CALCULATIONS

DECANT AMOUNT

Inputs				Outputs			
	A	B	C		A	B	C
1	From SB456_010809B Sp			1	From SB456_010809B Spreadsheet		
2				2			
3	Tk 40 prior to decant	142.66	in	3	Tk 40 prior to decant	142.66	in
4	Tk40 vol	=B3*3510	gal	4	Tk40 vol	500,737	gal
5	Tk 40 decant	100246	gal decant	5	Tk 40 decant	100,246	gal decant
6				6			
7	SRNL Slurry mass	2108.72	g	7	SRNL Slurry mass	2,109	g
8	Slurry density	1.09	g/mL	8	Slurry density	1.09	g/mL
9	sup density	1.04	g/mL	9	sup density	1.04	g/mL
10	slurry vol	=B7/B8	mL	10	slurry vol	1,935	mL
11	wt% IS	0.095		11	wt% IS	9.50%	
12	Wt% TS	0.134		12	Wt% TS	13.40%	
13	wt% DS	0.0429		13	wt% DS	4.29%	
14				14			
15	Decant volume	=B10*B5/B4	mL	15	Decant volume	387	mL
16	Decant Mass	=B15*B9	g	16	Decant Mass	403	g
17	solids removed in decant	=B16*B13	g	17	solids removed in decant	17.3	g
18	Post Decant Slurry mass	=B7-B16	g	18	Post Decant Slurry mass	1,706	g
19	Post decant solids mass	=B7*B12-B17	g	19	Post decant solids mass	265	g
20	new wt% TS	=B19/B18	(calculated)	20	new wt% TS	15.6%	(calculated)
21	new wt% IS	=B11*B7/B18	(calculated)	21	new wt% IS	11.7%	(calculated)

ADDITIONS

Input

	SRNL		Tank Farm			
Slurry Mass	=Decant calc!D24	g				
Slurry Density	=Decant calc!B25	g/mL				
Slurry Ht			114	in		
Slurry Volume	=B4/B5	mL	=D6*3510	gal		
wt% IS	=Decant calc!H22		0.109			
Mass IS	=B4*B8	g				
Wt% TS	=Decant calc!H21		0.152			
Mass TS	=B10*B4	g				
NaNO ₂ (40wt% solution)	=D13/D7*B7	mL	10043	gal		
Water	=D14/D7*B7	mL	1894	gal		
Total H Canyon discharge	=D16/D7*B7	mL	11000	gal		
NO ₃	4.27	M				
OH	0.6	M				
Total NO ₃	=B16*B17	mmol				
Total OH	=B18*B16	mmol				
Np Mass	=D21*1000/(D7*3785)*B7	g	21	kg		
In(fr 9.6 smple Np Vol	=B21/0.0014	mL				
NO ₃	7.35	M				
NO ₃	=B23*B24	mmol				
Needed Additions						
NO ₃	=B19-B25	mmol				
OH	=B20+(B25+B28)	mmol				
			density		mass	
19 M NaOH	=B29/19	mL	1.52	g/mL	=B31*D31	g
Con Nitric acid	=B28/15.9	mL	1.42	g/mL	=B32*D32	g
Water	=B16-B23-B31-B32	mL	1	g/mL	=B33*D33	g

Output

	SRNL		Tank Farm		
Slurry Mass	1454	g			
Slurry Density	1.10	g/mL			
Slurry Ht			114 in		
Slurry Volume	1322	mL	400,140 gal		
wt% IS	11.8%		10.9%		
Mass IS	171	g			
Wt% TS	15.6%		15.20%		
Mass TS	227	g			
NaNO ₂ (40wt% solution)	33	mL	10,043 gal		
Water	6	mL	1,894 gal		
Total H Canyon discharge	36	mL	11,000 gal		
NO ₃	4.27	M			
OH	0.6	M			
Total NO ₃	155	mmol			
Total OH	22	mmol			
Np Mass	1.8E-02	g	21 kg		
In(fr 9.6 smple Np Vol	13.1	mL			
NO ₃	7.35	M			
NO ₃	96	mmol			
Needed Additions					
NO ₃	59	mmol			
OH	177	mmol			
			density		mass
19 M NaOH	9.3	mL	1.52	g/m	14.16 g
Con Nitric acid	3.7	mL	1.42	g/m	5.26 g
Water	10.2	mL	1	g/m	10.23 g

APPENDIX C. RESULTS OF SRAT CYCLE PERIODIC SAMPLES

	Time at	Hg wt%			
AD LIMS	boiling (h)	of TS	Average	stdev	% RSD
300256865	12	0.92%	0.96%	0.06%	6.24%
300256866	12	1.01%			
300256867	20	0.49%	0.60%	0.16%	26.34%
300256868	20	0.71%			
300256869	28	0.21%	0.21%	0.01%	6.22%
300256870	28	0.22%			
300256871	36	0.12%	0.12%	0.00%	1.84%
300256872	36	0.12%			
300256873	44	0.09%	0.10%	0.01%	5.41%
300256874	44	0.10%			

		Formate	Nitrate
		mg/kg slurry	mg/kg slurry
12 Hr Boil	Sample A	46034	31558
	Sample B	43199	30064
	Average	4.46E+04	3.08E+04
	Std Dev	2004	1056
	%RSD	4.5	3.4
20 Hr Boil	Sample A	45479	31590
	Sample B	40397	30795
	Average	4.29E+04	3.12E+04
	Std Dev	3593	563
	%RSD	8.4	1.8
28 Hr Boil	Sample A	38006	29283
	Sample B	41896	32315
	Average	4.00E+04	3.08E+04
	Std Dev	2750	2143
	%RSD	6.9	7.0
36 Hr Boil	Sample A	37669	31487
	Sample B	40549	31928
	Average	3.91E+04	3.17E+04
	Std Dev	2037	312
	%RSD	5.2	1.0

Distribution:

S. L. Marra, 773-A
A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
C. W. Gardner, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
F. M. Pennebaker, 773-42A
A. M. Murray, 773-A
J. E. Occhipinti, 704-S
D. C. Sherburne, 704-S
R. T. McNew, 704-27S
J. F. Iaukea, 704-30S
J. W. Ray, 704-S
H. B. Shah, 766-H
J. M. Gillam, 766-H
B. A. Hamm, 766-H
D. D. Larsen, 766-H
C. J. Bannochie, 773-42A
D. J. McCabe, 773-42A
D. K. Peeler, 999-W
N. E. Bibler, 773-A
A. I. Fernandez, 999-W
D. C. Koopman, 999-W
D. P. Lambert, 999-W
B. R. Pickenheim, 999-W
S. H. Reboul, 773-42a
M. E. Stone, 999-W
J. M. Bricker, 704-27S
T. L. Fellingner, 704-26S
E. W. Holtzscheiter, 704-15S
J. P. Vaughan, 773-41A
M. A. Broome, 704-29S
A. J. Cross, 704-71S
H. J. Kunis, 704-S