WSRC-STI-2007-00212
Revision 0

SLUDGE BATCH 4 FOLLOW-UP QUALIFICATION STUDIES TO EVALUATE HYDROGEN GENERATION

D. C. Koopman
J. M. Pareizs
D. P. Lambert
C. J. Bannochie

June 2007

Process Science & Engineering Section
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

DISCLAIMER

Printed in the United States of America

Prepared For
U.S. Department of Energy

WSRC-STI-2007-00212
Revision 0

Key Words: DWPF, Sludge, SB4,
Hydrogen

Retention: Permanent

SLUDGE BATCH 4 FOLLOW-UP QUALIFICATION STUDIES TO EVALUATE HYDROGEN GENERATION

D. C. Koopman
J. M. Pareizs
D. P. Lambert
C. J. Bannochie

June 2007

Process Science & Engineering Section
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

REVIEWS AND APPROVALS

AUTHOR(S):

D. C. Koopman, Process Science & Engineering Date

J. M. Pareizs, Process Science & Engineering Date

D. P. Lambert, Process Science & Engineering Date

C. J. Bannochie, Process Science & Engineering Date

TECHNICAL REVIEWERS:

M. E. Stone, Process Science & Engineering Date

E. B. Fox, Materials Science & Technology Date

APPROVERS

R. E. Edwards, Manager, Process Science & Engineering Section Date

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

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

EXECUTIVE SUMMARY

Follow-up testing was conducted to better understand the excessive hydrogen generation seen in the initial Sludge Batch 4 (SB4) qualification Sludge Receipt and Adjustment Tank/Slurry Mix Evaporator (SRAT/SME) simulation in the Savannah River National Laboratory (SRNL) Shielded Cells. This effort included both radioactive and simulant work. The initial SB4 qualification test produced 0.59 lbs/hr hydrogen in the SRAT, which was just below the DWPF SRAT limit of 0.65 lbs/hr, and the test produced over 0.5 lbs/hr hydrogen in the SME cycle on two separate occasions, which were over the DWPF SME limit of 0.223 lbs/hr.

A fresh sample of Tank Farm washed Tank 51 slurry was obtained to perform a duplicate test under the same conditions used in the initial SB4 qualification SRAT/SME simulation. Extensive analysis of the sludge as well as SRAT and SME products was performed, but the acid addition strategy (i.e., total moles of acid added per liter of slurry) for the SRAT cycle was not varied due to any small changes in measured quantities in the input to the stoichiometric acid calculation.

A new SB4 simulant was prepared in parallel with the radioactive work. This simulant was a very close match to the measured composition of the slurry used in the initial qualification test. A portion of this simulant was subjected to a heat-treatment intended to qualitatively simulate what happened to a portion of the radioactive material used in the SB4 qualification test. The main purpose of the simulant tests was to determine whether or not subjecting some of the SRAT feed to a heat-treatment would cause a significant difference in the observed hydrogen generation rates during SRAT/SME processing.

Three new SRAT/SME simulations were performed. One was performed in the SRNL Shielded Cells using the Tank Farm washed Tank 51 sample. The other two were performed with simulants at Aiken County Technology Laboratory (ACTL). These runs used new 1.4 L lab-scale Chemical Process Cell equipment equivalent to that used in the SB4 qualification test. The two simulant tests were both at 130% acid stoichiometry. This factor matched the one in the SB4 qualification run, but led to a slightly larger actual acid addition due to small differences in the inputs to the stoichiometric acid calculation. Simulant noble metal concentrations were selected to bound those measured in the qualification sample.

The new SRAT/SME demonstration with the radioactive Tank 51 sample failed to replicate the high hydrogen generation results of the initial SB4 qualification test. SRAT hydrogen peaked at 0.22 lbs/hr (34% of the limit) and SME cycle hydrogen peaked at 0.12 lbs/hr (54% of the limit). For the SRAT, the hydrogen generation rates were, however, greater than those seen in the simulant runs. The maximum hydrogen seen in the two simulant tests was 0.14 lb/hr in the SRAT. A small increase in hydrogen was seen in the SRAT cycle with partially heat-treated feed, but hydrogen in the SME cycle was similar. During the SME cycles, all three tests produced fairly similar hydrogen generation rates that were less than the original qualification run.

The direct follow-up testing with the new Tank 51 sample and SB4 simulants has failed to explain the excessive hydrogen generation rates seen in the initial Tank 51 testing. A strong probability exists that the results in the initial Tank 51 demonstration were an aberration. The initial test appears to be the aberration based on the fact that the new runs did not replicate the high hydrogen generation rates and were more typical of SRAT/SME processing behavior. In particular, nitrite was detected in the SME cycle after significant hydrogen generation, which had not been seen in any previous runs. The most feasible explanation for this behavior was poor mixing of the high yield stress sludge with a

localized zone of slurry that did not completely react during the SRAT cycle. The poor mixing can be attributed to laboratory scale mixing limitations and poor visibility in determining mixing effectiveness in the first run. Verification of mixing was more easily confirmed in subsequent runs through the use of better lighting and camera position and by the use of a digital mixer controller which enabled the agitator speed to be precisely controlled and monitored.

SRNL has defined an extensive hydrogen generation understanding program to more thoroughly understand the reactions that cause hydrogen generation. A program has also been defined to gain a better understanding of the acid addition equation used to predict the amount of acid to add for each SRAT batch and to refine the analytical methods to decrease the uncertainty in the equation.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

AA	Atomic Adsorption
ACTL	Aiken County Technology Laboratory
AD	Analytical Development
CPC	Chemical Processing Cell
CWAO	catalytic wet air oxidation
DWPF	Defense Waste Processing Facility
FAVC	Formic Acid Vent Condenser
GC	Gas Chromatography or Gas Chromatograph
IC	Ion Chromatography
ICP-AES	Inductively Couple Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Couple Plasma-Mass Spectrometry
LIMS	Laboratory identification management system
M	Molarity (mol/L)
Mol%	Mole percent applied to gas compositions, equivalent to volume percent
MWWT	Mercury Water Wash Tank
PS&E	Process Science and Engineering section
PSAL	Process Science Analytical Laboratory
QA	Quality Assurance
SB	Sludge Batch
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SpGr	Specific gravity
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TTR	Technical Task Request
WSRC	Washington Savannah River Company
wt%	Weight Percent
$wt\%_{DS}$	weight percent dissolved solids (soluble solids in a supernate or solution)
$wt\%_{IS}$	weight percent insoluble solids
$wt\%_{SS}$	weigh percent soluble solids (soluble solids on a slurry or sludge basis)
$wt\%_{TS}$	weight percent total solid

1.0 INTRODUCTION AND BACKGROUND

The Savannah River National Laboratory (SRNL) conducted a DWPF process simulation in the Shielded Cells as part of the Sludge Batch 4 (SB4) qualification process in August 2006.[1] The simulation included the DWPF Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) cycles. SRAT hydrogen generation rates were high, peaking at 0.59 lb/hr, but within the DWPF limit of 0.65 lbs/hr. SME hydrogen generation rates exceeded the DWPF limit of 0.223 lb/hr at two different points. Data on formate consumption tended to confirm significant conversion to hydrogen and carbon dioxide. Simulant testing conducted in June 2006 had indicated a high probability for a successful SB4 qualification run.[2] However, certain significant differences in processing parameters and the inputs to the DWPF stoichiometric acid calculation existed between the simulant and radioactive SRAT feeds. In addition, the qualification material represented a combination of several different materials that were prepared individually and combined including a small fraction that had been potentially subjected to high temperatures.

Most of the differences with regards to processing were identified and tested. See *Evaluation of Potential Causes of High Hydrogen in Shielded Cells SB4 Qualification*[3] and *Sludge Batch 4 Simulant Flowsheet Studies: Phase II Results*[4] for details. A brief summary of the items and the findings are provided:

1. Equipment Scale: Due to limited radioactive sample size, the Shielded Cells uses smaller scale equipment. A 1.4-L simulant DWPF process simulation[3] was performed to match the 4-L 150% SB4 flowsheet simulation in terms of the acid addition strategy.[4] No significant differences in hydrogen generation or in other off-gas profiles were seen.

2. Longer Processing Time: Equipment and processing issues with acid addition and boiling caused the Shielded Cells simulation to take longer than expected. A simulant run duplicating the processing timeline of the qualification run showed no impact on peak hydrogen generation in the SRAT cycle.[5]

3. Reflux Time and Form of Mercury: Mercury stripped slowly in the original qualification simulant tests[2] leading to a recommendation to extend reflux time in the SRAT from 12 to 24 hours. Very little mercury was found in the original Shielded Cells qualification SRAT product. It was hypothesized that the simulant mercury, added as HgO, might not behave the same as mercury precipitated in the sludge matrix. Simulant was prepared where the mercury was added as the nitrate salt and precipitated into the SRAT feed.[5] A small increase in hydrogen was observed during the SRAT cycle relative to the matching 150% flowsheet test with HgO, along with a reduced mercury concentration in the SRAT product. Based on this test, it was hypothesized that more efficient mercury reduction and stripping could have led to higher than expected hydrogen generation in the SB4 qualification run relative to the simulant runs. This hypothesis was supported by historical simulant data where increasing the initial mercury concentration correlated with reduced peak hydrogen generation rates.

Additional studies were also performed related to two of the inputs to the acid addition equation. These studies were intended to identify potential sources of bias between the simulant and radioactive sample measurements used as inputs to the DWPF acid addition equation. The two inputs and a high level summary of the potential bias is given below:

- <u>Impact of mercury form on titration</u>: The current DWPF stoichiometric acid calculation assumes that mercury is converted to a mercury salt during the titration of the slurry to determine the base equivalents titrated in reaching pH 7. One additional mole of acid is added per mole of measured mercury for the reduction to the element. Titrations with varying concentrations of HgO in SB4 simulants had no significant effect on the titration results. Thus, there is an identifiable acid demand due to mercury that is not being accounted for in the simulant stoichiometric acid calculation. Because of differences in the simulant and radioactive titrations, the potential exists for the radioactive method to have titrated the mercury in the Cells sample. If so, the stoichiometric demand of the Cells sample would be increased relative to an equivalent simulant sample. The appropriate correction would be to decrease the stoichiometric factor applied to radioactive SRAT feed relative to the value used in the simulant testing. Additional study of this issue is included in the scope of work for the FY07 DWPF stoichiometric acid calculation improvement task.

- Impact of total inorganic carbon (carbonate): The second study involved the role that carbonates play during the titration for the base equivalents input. Radioactive and simulant SRAT feeds contain a mixture of soluble and insoluble carbonates. Simulants were spiked with either sodium carbonate (soluble) or calcium carbonate (insoluble). Pairs of samples were prepared where the additional carbonate from sodium carbonate in one was equivalent to the additional carbonate from calcium carbonate in the other. The automatic titrator showed little response to additional insoluble calcium carbonate, however additional soluble sodium carbonate added about one mole of acid required per mole of carbonate to the pH 7 titration result. The carbonate titration results raised the concern that the distribution of carbonate between soluble and insoluble species was nearly as important as knowing the total carbonate in determining the stoichiometric acid requirement, since soluble carbonate would be “double counted”, once in the TIC input and once in the titration. Further study of the issue of soluble and insoluble carbonate is included in the FY07 task to improve the current DWPF stoichiometric acid equation.

Since no obvious explanation for the potential high hydrogen was gained, SRNL decided to perform additional radioactive and simulant testing to determine if the hydrogen generation rate could be repeated. The radioactive test was performed with a fresh sample of Tank 51 slurry. The original qualification test used a feed that was a composite of slurry that remained in the SRAT vessel following an accidental boil-over prior to starting acid addition, slurry recovered from sample returns, slurry from the original qualification sample that had been reserved for washing studies, and slurry from more recent Tank 51 dip samples. These materials of different origins were brought to an essentially equivalent wash endpoint and combined to make the feed for the SB4 qualification run. The unusual feed history was one of the justifications for repeating the test.

The second goal was to attempt to evaluate, at least qualitatively the impact that elevated temperatures experienced during the boil-over might have had on hydrogen generation. The original SB4 qualification simulant was rewashed and trimmed to better match the qualification SRAT receipt acid calculation inputs. Two tests were performed with the adjusted simulant such that a baseline would be available. The baseline test used a portion of this material and processed it through SRAT/SME cycles in equipment identical to that used in the Shielded Cells qualification test. The second test heat-treated a portion of the adjusted simulant to boiling temperatures. This material was blended with the baseline simulant and processed through a SRAT/SME cycle. Both tests would also provide a more effective comparison to the SB4 qualification test since they had more comparable acid addition stoichiometry inputs.

1.1 Description and Labeling of the Process Simulations

The initial qualification simulant SRAT/SME cycle tests were identified as SB4-57 to SB4-60. The parameters of the runs are provided in Table 1-1. The runs were used to prepare a recommended processing scheme for the original Shielded Cells SB4 qualification test, SC-0[*].[6] The SC-0 test was followed by several simulant runs using SB4 flowsheet simulants instead of qualification simulants,[3,5] and by two radioactive tests using two different SB3/SB4 blends, SC-1 and SC-2.

The two follow-up tests with modified qualification simulant was identified as SB4-70 and SB4-71. SB4-71 included some of the modified simulant that had been heat-treated. Parameters for these tests are given in Table 1-1. The repeated Shielded Cells SRAT/SME test with Tank Farm prepared SB4 (Tank 51) sludge was identified as SC-3. Parameters for this run are also contained in Table 1-1.

Based strictly on these parameters, SB4-57 from the initial simulant runs, compares most favorably to the recent simulant (SB4-70 and SB4-71) and radioactive run (SC-3).

Table 1-1. SB4 CPC Simulation Test Overview

Run Label	**Composition**	**Nominal Acid Stoichiometry**	**Reflux Time hr**	**Target Product Solids Loading**	
				SRAT, wt%	SME, wt%
SB4-57	5/06	130%	12	24	50
SB4-58	5/06	160%	12	24	50
SB4-59	5/06	125%	12	21	45
SB4-60	5/06	150%	12	21	45
SC-0	Qualification SRAT Receipt	130%	24	20	50[*]
SB4-70	2/07	130%	24	20	45
SB4-71	Heat-treated 2/07	130%	24	20	46
SC-3	Tank 51 Tank Farm Prepared	112%[†]	24	25	45

[†] For the SC-3 SRAT cycle, the same acid amount as the SC-0 cycle was used (1.46 mol/L) rather than calculating acid amount based on stoichiometry. Based on analysis of the SC-3 SRAT receipt slurry, the acid stoichiometry was 112%. The cause of this difference is a much higher TIC result for the SC-3 SRAT receipt sample.

The mercury and noble metal concentrations are known to be related to the hydrogen generation reactions in the SRAT and SME cycles.[7] The noble metals for the simulants were set to 110% of the values calculated from measurements on the unwashed Tank 51 radioactive slurry sample. The calculation assumed that 100% of the noble metals were insoluble.

Table 1-2 shows the nominal levels of noble metals and mercury. The simulant levels were calculated from the trim chemical masses added to a known mass of characterized slurry. The gravimetric calculation is considered more accurate than current chemical analytical methods. Values given are wt% in the total solids of the fully trimmed slurry and in mg noble metal per kg of slurry (both as of the start of the SRAT cycle).

---

[*] In Reference 1, this qualification test was simply referred to as TK 51. However, with the repeat of this cycle and the initiation of a numbering scheme for Shielded Cells simulations, this test was relabeled as SC-0 in this report.

Table 1-2. Concentrations of Noble Metals and Mercury Used in Testing

	SB4-57	SC-0	SB4-70, SB4 -71	SC-3
	wt% of Total Solids			
Ag	0.0036	0.0031	0.0032	0.0036 *
Hg	2.58	2.45	2.74	2.57
Pd	0.0010	0.00088	0.0010	0.0010 *
Rh	0.0124	0.011	0.0125	0.0124 *
Ru	0.0529	0.047	0.0511	0.0529 *

* The SC-3 noble metals content, on a total solids basis, is expected to be similar to the SC-0 noble metals content; these are not measured results.

2.0 EXPERIMENTAL METHODS

2.1 Radioactive Sample Analytical Details

Analyses for this task used guidance of an Analytical Study Plan (ASP).[8] 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 tasks. 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. A summary of the analytical methods follows.

Densities of slurry and supernate samples were accomplished in the following manner. Sealed pipette tips were calibrated by weighing the pipette tips empty, filling them with water and weighing again. The temperature of the water was noted and used to obtain the density of the water from reference sources. The volume of each pipette tip was obtained by dividing the measured weight of the water by the density. Each pipette tip was labeled for traceability. The calibrated pipettes were then used in the Shielded Cells with radioactive supernate and sludge slurry samples. For both the slurry and supernate, three replicate measurements were done. In each measurement, an empty pipette tip was weighed, filled with slurry or supernate and then re-weighed. The measured sample weight was then divided by the calibrated volume of the pipette tip to obtain the density.

Weight percent solids of slurry and supernate, along with a standard (a solution of a known concentration of NaCl), were determined using Analytical Development (AD) procedure 2284 in the following manner. Clean and dry polymethylpentene (PMP) beakers were labeled with identifying numbers and weighed. Approximately 3 mL of supernate, slurry or standard solution (15 wt% NaCl) was added to separate pre-weighed beakers. The samples were dried in the oven at 115 °C for at least 4 hours, removed, and allowed to cool for 10-15 minutes and re-weighed. The drying and weighing cycles continued until consecutive weights for each vessel did not vary by more than 0.01 g. The weight percent total solids ($wt\%_{TS}$) is calculated using equation [1] and is designated as the total solids in the slurry, and the weight percent solids in the supernate ($wt\%_{DS}$) is designated as dissolved solids and calculated using equation [2]. The insoluble solids and soluble solids were calculated using equations [3] and [4]:

$$wt\%_{TS} = \frac{Mass\ of\ dried\ slurry}{Mass\ of\ slurry\ prior\ to\ drying} \cdot 100 \qquad [1]$$

$$wt\%_{DS} = \frac{Mass\ of\ dried\ supernate}{Mass\ of\ supernate\ prior\ to\ drying} \cdot 100 \qquad [2]$$

$$wt\%_{IS} = \frac{wt\%_{TS} - wt\%_{DS}}{100 - wt\%_{DS}} \cdot 100 \qquad [3]$$

$$wt\%_{SS} = wt\%_{TS} - wt\%_{IS} \qquad [4]$$

where,

$wt\%_{TS}$ = weight percent solids in slurry (weight percent total solids)
$wt\%_{DS}$ = weight percent solids in supernate (weight percent dissolved solids)
$wt\%_{IS}$ = weight percent insoluble solids in slurry
$wt\%_{SS}$ = weigh percent soluble solids in the slurry

Anion content and total inorganic carbon were determined from weighted dilutions. Weighted dilutions were prepared per the work instruction ITS-WI-016.[9] In summary, slurry is diluted with deionized water and agitated (by shaking). A portion is filtered and submitted to AD. SRAT receipt, SRAT product and SME product were submitted for anion analysis. Only the SRAT receipt was submitted for TIC.

Total base of SRAT receipt samples was determined in triplicate by an inflection end point acid titration. The sludge is titrated to below pH 7, while the total base is obtained from the resulting plot of acid versus pH at pH 7.

SRAT receipt and SRAT product samples were digested by aqua regia (AD procedure 2226). Approximately 1.3 g of sludge slurry containing ~0.25 g of solids (depending on the wt% solids in the sample) was added to a Teflon^{TM} pressure vessel followed by 9 mL of concentrated HCl and 3 mL of HNO_3. The resulting solutions were heated to 115 °C for 2 hrs, cooled, and diluted to 250 mL. The SRAT receipt digestions were submitted to AD for analysis of manganese by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), sodium by Atomic Adsorption (AA), and mercury by cold vapor. The SRAT product digestions were submitted for mercury only. A soil standard containing a known amount of mercury was digested in concert with the samples and submitted for mercury for quality control.

2.2 Simulant Sample Analytical Details

Simulant analyses followed the standard laboratory guidelines and means of sample control. A unique sample number and identifier were generated for each sample by the research team. These numbers were logged into a sample tracking system in FileMaker Pro. In addition, a second unique lab identification number was assigned to each sample for tracking purposes by either the Process Science Analytical Laboratory (PSAL) or by AD. Samples analyzed at ACTL received only a single number. Sample analyses were performed using approved analytical and QA procedures.

The sludge simulant was extensively analyzed as part of the simulant development and SB4 simulant flowsheet programs; therefore, those results were used to support this testing. See *Preparation of Sludge Batch 4 Qualification Simulants for DWPF Process Simulations* (WSRC-STI-2006-00242) for a complete description.[10] Samples were also taken of the SRAT and SME products. These samples were used to evaluate process chemistry. The PSAL performed analyses on product samples to determine the chemical composition, total and dissolved solids, calcined solids, and pH. The slurry chemical composition was determined in duplicate by calcining the samples at 1100 °C and then dissolving the product using Na_2O_2/NaOH fusion and a lithium metaborate fusion. The preparations were then analyzed using ICP-AES to measure the cations present.

Sludge slurry samples for anion analyses were prepared using weighted dilutions and were analyzed by IC. The total and dissolved solids were each measured on two aliquots and the insoluble and soluble solids fractions were calculated from the results for the SRAT and SME product samples using the methodology of equations [1]-[4]. Finally, pH data were taken on the simulant condensates using glass probes. Probes were calibrated with pH 4 and 10 buffer solutions and checked in pH 7 buffer solution prior to the measurements.

2.3 Procedures and Equipment Used in SRAT/SME Simulations

The radioactive testing was performed in the SRNL Shielded Cells using the 1.4-L SRAT equipment. The simulant testing was performed at ACTL using equivalent equipment. The SRAT rigs at ACTL were assembled following the guidelines of SRNL-PSE-2006-00074.[11] Assembly and testing of the Shielded Cells SRAT rigs are documented in SRNL-PSE-2006-00293.[12] The intent of the rig is to functionally replicate the primary DWPF processing vessels. The glass kettle is used to replicate both the SRAT and the SME. It is connected to the SRAT Condenser (doubles as SME condenser), the Mercury Water Wash

Tank (MWWT), and either a Formic Acid Vent Condenser (FAVC) or cold finger. The Slurry Mix Evaporator Condensate Tank (SMECT) is represented by a series of sample bottles that are used to remove condensate through the MWWT. The DWPF ammonia scrubbers are not simulated, since their operation does not impact the chemistry in the SRAT and SME. For the purposes of this report, the condensers and MWWT are referred to as the off-gas components. A sketch/picture of the experimental setup is given in Figure 2-1.

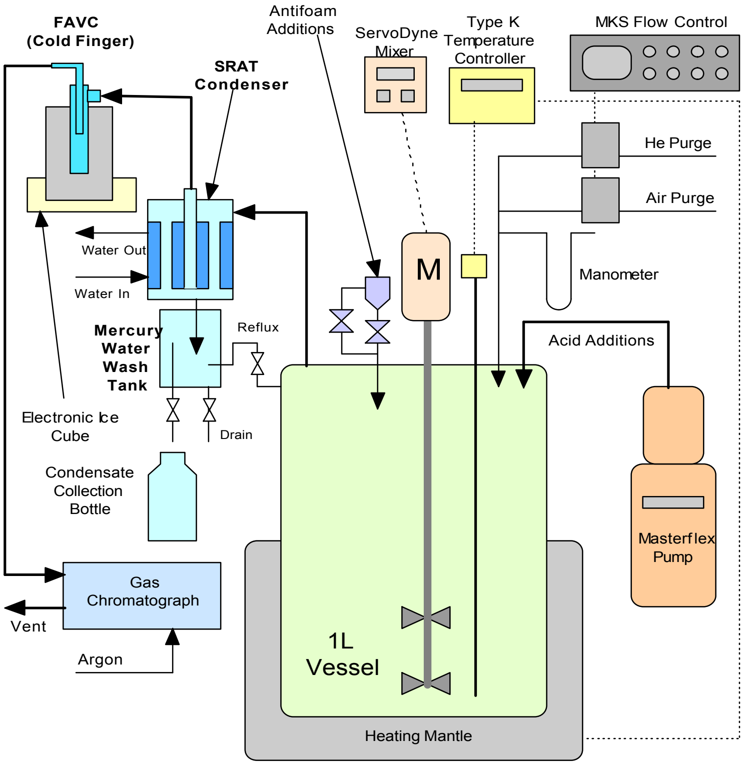

Figure 2-1. Schematic of SRAT Equipment Set-Up

Simulant equipment leak tests were performed on the equipment as set up in the lab hood before and after a process simulation, while the Cells equipment was leak tested in mock-up and then the assembled apparatus was placed into the Cells by overhead crane.

Select gases were monitored during the SRAT/SME process simulations using either a high-speed Agilent model 200 or model 3000 Micro Gas Chromatograph (GC) to provide insight into the reactions occurring during processing and to monitor the potential formation of a flammable gas mixture. Helium was used as a purge gas tracer. A calibration standard was used to calibrate the GC before each run. The concentration of this calibration standard was 0.497 vol% helium, 0.998 vol% hydrogen, 20.96 vol% oxygen, 55.045 vol% nitrogen, 2.50 vol% nitrous oxide, and 20.0 vol% carbon dioxide. Calibration checks were made after the SME cycle.

The Agilent Micro GC is self-contained and is designed specifically for fast and accurate analysis. The GC has five main components. The first is the carrier gas (argon for this testing) to transport the sample through the MolSieve 5A PLOT (Channel A) and PLOT Q (Channel B) columns. The second is the injector, which introduces a measured amount of sample into the inlet of the analytical columns where it is separated. Injection time is 50 milliseconds for the Channel A gases (helium, hydrogen, oxygen, and nitrogen) and 100 milliseconds for the Channel B gases (carbon dioxide and nitrous oxide). The third component is the column, which is capillary tubing coated or packed with a chemical substance known as the stationary phase that preferentially attracts the sample components. As a result, components separate as they pass through the column based on their solubility. Since solubility is affected by temperature, column temperature is controlled during the run. The Channel A column is set at 80 ºC and 30 psig, while the Channel B column is set at 70 ºC and 24 psig. The fourth GC component is a micro-machine thermo conductivity detector. The solid state detector monitors the carrier and senses a change in its composition when a component in the sample elutes from the column. The fifth component is the data software system, Cerity for the Model 3000 and EZChrome for the Model 200H. Its main purpose is to generate both qualitative and quantitative data. It provides a visual recording of the detector output and an area count of the detector response. The detector response is used to identify the sample composition and measure the amount of each component by comparing the area counts of the sample to the analysis of known calibration standards. A sample was taken every 4.5 minutes.

Process data also included gas flowrates and slurry temperature. Air and helium flowrates were controlled by MKS flow controllers. The calibration of these instruments is on a regular schedule. Slurry temperature was measured by a thermocouple connected to a temperature controller readout. Thermocouples were calibrated prior to use.

The simulant runs were performed using Revision 3 of Procedure ITS-0094 (“Laboratory Scale Chemical Process Cell Simulations”) of Manual L29.[13] The radioactive simulations were performed using Procedure ITS-0085 (“Laboratory Scale Chemical Process Cell Simulations in the Shielded Cells”).[14] Additional instructions including parameters unique to the individual demonstration were provided in the form of Research and Development (R&D) directions. The observations for runs SB4-70 and 71 were recorded in laboratory notebook WSRC-NB-2006-00183.

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 SRAT testing at 130% stoichiometry required nearly 99% formic acid and 1% nitric acid. This formic acid/nitric acid ratio was used for all of the simulations.

To prevent foaming during processing, 200 ppm of IIT 747 antifoam was added during heat-up prior to acid addition, and an additional 500 ppm was added at the completion of acid addition. In the rad runs, 100 ppm of antifoam was added between nitric and formic acid addition and every 8 hours of boiling. A further 100 ppm addition was made at the start of each SME cycle. Actual antifoam additions were made as if diluted to 10 wt% in de-ionized water, followed by an equal mass of pure de-ionized water to rinse all of the antifoam into the slurry. Additional antifoam was added to the slurry in 100 ppm increments as necessary to mitigate foaming.

After the completion of dewatering to meet the target total solids, SRAT processing involved 24 hours of refluxed boiling to simulate DWPF processing conditions. Once again, 24 hours replicated the previous qualification run with radioactive material.

After removing the necessary SRAT product samples, SME processing was initiated. SME processing included the scaled addition of five 1000 gallons of water from canister decontamination. The SME cycle frit addition was split into two equal portions. The frit was added with water and formic acid at DWPF prototypical conditions. The nominal waste loading was 30% sludge oxides in glass for all testing. Concentration of the SME slurry 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 SME cycle to attempt to meet the target total solids content of 45 wt%.

3.0 FEED PREPARATION AND CHARACTERIZATION

3.1 Characterization of Washed Tank 51 Sample

The DWPF SRAT process relies upon use of the acid calculation to estimate the required acid necessary to complete reactions. This calculation relies upon 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 hydrogen being generated. Therefore, the Tank Farm Tank 51 sample was extensively characterized to verify the inputs. The results of the SC-3 SRAT receipt characterization are provided in Table 3-1 along with the SC-0 results for comparison. In comparing the SRNL prepared SC-O and Tank Farm prepared SC-3, nitrate and TIC are not comparable. This may indicate a difference between small scale and large scale washing. However, the difference may only be due to analytical errors. A measured TIC value that was lower than the actual TIC value would potentially lead to acceptance of a stoichiometric factor that was too high when a correct TIC value was input to the stoichiometric acid equation.

Table 3-1. Characterization Results of the Tank 51 Qualification Sample (SC-0 SRAT Receipt) and Tank 51Tank Farm Prepared (SC-3 SRAT Receipt) Sample

Measurement	SC-0 SRAT Receipt (Tk51 Qualification Sample)	SC-3 SRAT Receipt (Tk 51 Tank Farm Prepared)
Total Solids, wt% of slurry	20.6	19.5
Insoluble Solids, wt% of slurry	12.9	12.5
Soluble Solids, wt% of slurry	7.7	7.0
Calcined Solids, wt% of slurry	14.7	14.3
Slurry Density, kg/L	1.11	1.14
Supernate Density, kg/L	1.07	1.06
Na, wt% of total solids	11.6	11.8
Hg, wt% of total solids	2.45	2.57
Mn, wt% of total solids	1.88	1.94
Nitrite, mg/kg slurry	21,000	20,500
Nitrate, mg/kg slurry	19,800	15,400
TIC, mg/kg slurry	1,522	2,510
Total Base, mol/L slurry	0.336	0.316
pH	12.6	12.6

3.2 Preparation of Modified SB4 Qualification Simulants

The original SB4 qualification simulant was adjusted to more closely approximate the Shielded Cells qualification sample SRAT receipt results. Particular attention was paid to the acid calculation inputs. Adjustment involved about a five-fold dilution of the supernate, supernate decanting, and subsequent addition of new soluble species. A significant increase in sodium carbonate and reduction in sodium hydroxide were needed to increase TIC while simultaneously reducing the titratable base equivalents.

Following the adjustment in simulant supernate composition, about 500 g of the modified simulant was taken to boiling with no mixing. This heat-treatment was done to qualitatively simulate what happened to about 200 g of the 863 g of radioactive feed for the SC-0 qualification SRAT cycle. More complete details of simulant heat-treatment are given in Appendix 1.

Simulant heat-treatment did not result in the material boiling-over as it did in the original SB4 qualification sludge. Slurry viscosity and/or yield stress appeared to be inadequate to prevent the simulant slurry from transitioning into free convection mixing prior to initiating localized boiling at the bottom of the vessel. Thermocouples were placed at three depths in the slurry during the heat-treatment. The bottom-most slurry reached temperatures ≥85 °C while the middle slurry was still at 20-25 °C prior to free convection mixing. Temperatures at the bottom of the vessel reached 107 °C or higher, which was 5-6 °C above the normal SRAT slurry boiling temperature.

As discussed in Section 1.0, a feed blend was made by combining the preheated simulant with some of the baseline modified simulant. The blend contained about 40% of the heat-treated material, while the SC-0 qualification test contained about 21% material recovered after inadvertent heat-treatment. The higher fraction of heat-treated simulant material was chosen to magnify any apparent effects on hydrogen generation due to the heat-treatment.

3.3 Acid Calculation Inputs and Acid Demand Comparison

The key acid calculation input parameters for the initial and recent qualification and radioactive runs are summarized in Table 3-2. One of the original simulant runs, SB4-57, is included in the table since it was the most comparable. With exception of the repeat radioactive qualification run (SC-3), all tests were nominally at 130% of the calculated stoichiometric acid requirement. SC-3, once again, targeted an equivalent acid addition amount instead of the stoichiometry.

Table 3-2. Inputs to Acid Equation and Relative Stoichiometric Demand

Run ID	**SB4-57**	**SC-0**	**SB4-70**	**SB4-71**	**SC-3**
Base Equivalents, M	0.446	0.336	0.366	0.371	0.316
TIC, mg/kg	971	1,522	1,749	1,770	2,510
Nitrite, mg/kg	19,850	21,000	21,300	21,250	20,500
Wt. % Total Solids	18.14	20.62	18.94	19.62	19.5
Wt% Insoluble Solids	11.70	12.9	11.51	11.97	12.5
Slurry Density, kg/L	1.140	1.11	1.146	1.149	1.14
Wt% Mn in Total Solids	2.03	1.90	1.83	2.05	1.94
Wt% Hg in Total Solids	2.58	2.45	2.74	2.74	2.57
Calculated Stoich. Acid, moles/L	1.10	1.12	1.21	1.24	1.30
Actual Acid Added, moles/L	1.43	1.46	1.58	1.61	1.46
Ratio of Formic Acid to Total Acid	1.00	0.99	0.99	0.99	0.99

Both of the new modified SB4 simulants appeared to provide upper bounds to the inputs of the two Shielded Cells run inputs.

The base equivalent molarity was determined on a sample of the simulant without the mercury and noble metal trim chemicals. It was determined before testing that the mercury contribution was not being detected with the ACTL automatic titrator in the expected manner. Samples of SB4 qualification simulant and SB4 flowsheet simulant were each doped to two nonzero levels of mercury with HgO. These four doped samples were run on the autotitrator. The results were compared to the results for the two simulants without mercury. Essentially no increase in base equivalents was seen due to the HgO.[15]

4.0 RESULTS OF SRAT/SME SIMULATIONS

4.1 Hydrogen Generation

The primary reason for performing the follow-up simulant tests and second Shielded Cells test was to determine if the hydrogen generation rate was repeatable to increase understanding of the hydrogen generation seen in the original SB4 Shielded Cells SRAT and SME cycles. The hydrogen results are discussed in this section. Volume percent data from the simulation GC's were converted to equivalent DWPF flowrates in lbs/hour using the helium concentration and known helium flowrate.

Figure 4-1 presents the data from the recent and original testing. Hydrogen generation was lower for the repeated run with the actual sludge material (SC-3). It was, however, still greater than hydrogen generated in simulant testing. In the two new simulant runs, SB4-70 and SB4-71, the pattern of hydrogen generation with time was very similar. Slightly more hydrogen was generated with the preheated simulant, SB4-71. Both simulant runs, however, produced more hydrogen than the original SB4 qualification simulant test, SB4-57, at nominally the same stoichiometric factor. This result indicates a significant relationship between the acid calculation inputs and the hydrogen generation rate.

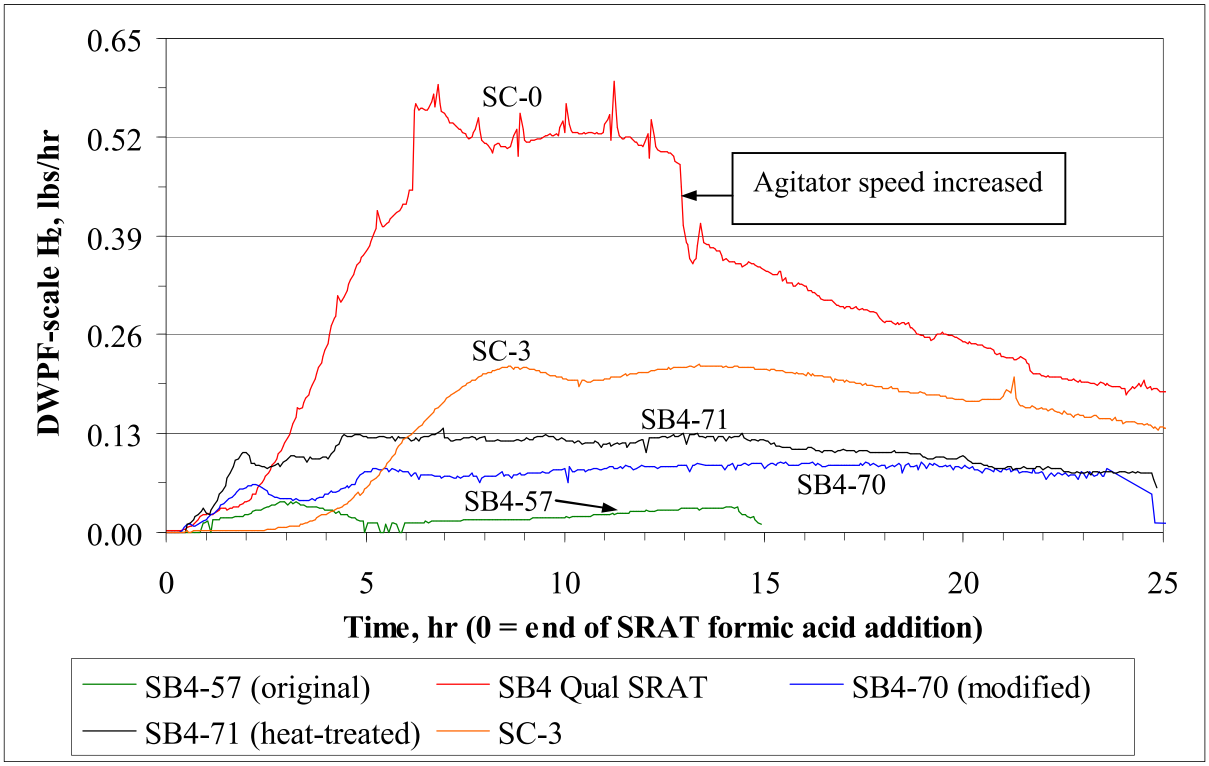

Figure 4-1. SRAT Hydrogen Generation

For the original qualification run, SC-0 SRAT product was cooled to ambient temperatures and remained there until analytical data was available to show that nitrite was destroyed and mercury was removed. For the repeat run, SC-3, the SME was immediately started after pulling SRAT products and it was assumed the necessary chemical reactions were completed since the goal was to understand hydrogen behavior. For the simulant runs, both new demonstrations produced a very thick SME product during final dewatering. The final simulant SME slurries were almost of peanut butter consistency (target 45-46 wt. % total solids), while radioactive slurries were still fluid. The thick consistency was also seen in the earlier simulant testing as well. It appears to be a property of this particular sludge simulant preparation method rather than a property of SB4 slurries in general. Some droplets of mercury were observed in the bottom of the SB4-71 vessel when the SME product was removed. The high slurry viscosity may have interfered with mercury stripping.

SME cycle hydrogen results are shown in Figure 4-2 at DWPF-scale. As with the SRAT cycle, the difference in hydrogen generation rates between the two new simulant runs was negligible indicating that the heat-treatment of the SB4-71 feed had no significant impact on SME cycle hydrogen generation. In addition, the simulant (SB4-70 and 71) and radioactive material (SC-3) exhibited similar hydrogen generation rate behavior with the exception of the spikes. SME cycle hydrogen generation was essentially constant at about half the DWPF limit through the five canister dewatering periods and the first frit addition dewatering period in all three new simulations.

As final dewatering occurred in the simulant SME cycles, however, both simulants began to produce increased quantities of hydrogen that were well in excess of the DWPF SME limit, 0.223 lbs/hr. The rates were attributed to local hot spots due to very poor mixing caused by the thick SME material. Based on the fluid nature of the SME material removed from SC-0 vessel, it is not believed that this was the cause of high hydrogen seen in the SB4 qualification run, SC-0, which was stopped before the second frit addition and final dewatering steps. A test of the impact of degraded mixing intensity was conducted in SB4-71 during the second decon canister dewatering period (before the slurry thickened to a semi-solid). Mixing speed was reduced from 600 rpm to 250 rpm. This change had no discernable impact on hydrogen generation. The slurry was already well-mixed at the time the speed was reduced, so minimal new settling would have been expected to occur. The only expected impact was a reduction in heat and mass transfer efficiency.

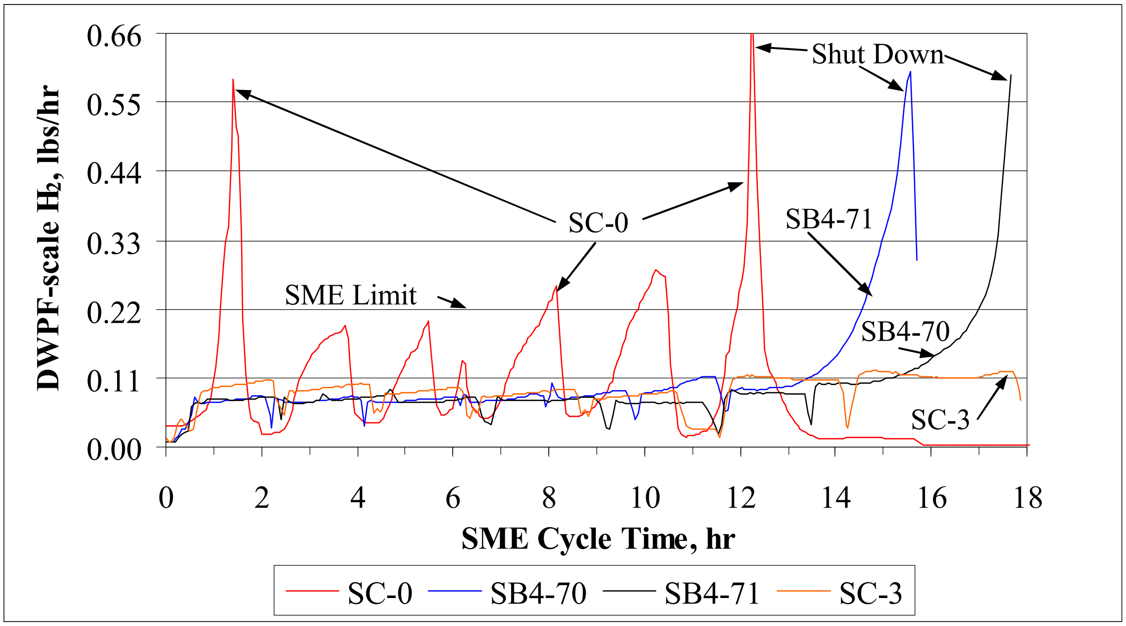

Figure 4-2. SME Hydrogen Generation in SB4 Qualification Tests

SB4-70, SB4-71, and SC-3 approached 50% of the DWPF SME limit for hydrogen generation prior to the final SME dewatering period when hydrogen production accelerated as mixing deteriorated in the simulant tests. This sustained rate near 0.1 lbs hydrogen/hr represents significant hydrogen generation for SB4 runs at 130% stoichiometry, especially in the context of data from SB4-57 from the qualification study[2] and the SB4 flowsheet runs[4]. The results indicate that recommendations for a stoichiometric factor are not guaranteed to produce a bounded result with respect to hydrogen generation if the inputs to the acid calculation vary between systems. The new SME cycle data represents more hydrogen than any of the prior SB4 simulant tests at 130% stoichiometry (drawn from SB4-1 through SB4-69 with a variety of stoichiometric acid requirements). Once the region of significant hydrogen generation has been located, small differences in the acid addition have been observed to produce varying effects including large changes in the maximum SRAT and SME hydrogen generation rates as well as changes to the point in processing time where the peak(s) occur. The region of significant hydrogen generation should be avoided during qualification testing based on past testing.

4.2 Carbon Dioxide Generation

Carbon dioxide data were obtained along with the hydrogen off-gas data. SRAT data for the set of repeated runs during acid addition, dewatering, and the start of reflux are given in Figure 4-3. Due to heating and acid addition problems, the SC-0 data is not included. SC-3 acid addition was interrupted by foaming, and formic acid addition was discontinued from about -2.5 hours to -1.2 hours relative to the end of acid addition. The volume percent axis was constrained so that the portions of the three runs that were similar could be clearly seen, but this choice meant that the two peaks went off-scale.

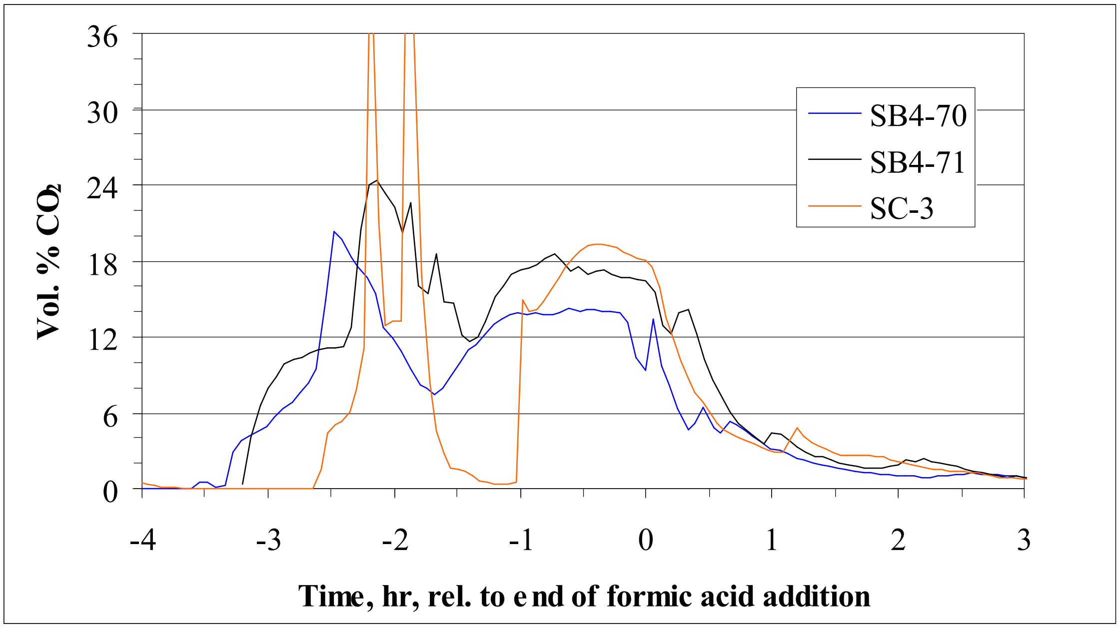

Figure 4-3. Comparison of Early SRAT Carbon Dioxide Evolution

Concentrations of CO_2 as high as 51.6% were seen in SC-3, but they were not sustained for consecutive readings. The carbon dioxide concentration spiked twice during formic acid addition with the timing corresponding to the appearance of foam. Release of gas trapped in the foam is probably responsible for the spikes in CO_2 concentration. Similar behavior was seen in the N_2O data.

The last hour of formic acid addition, dewatering, and the beginning of reflux showed very little difference between the radioactive and two simulant runs. This near equivalence is one piece of evidence that the simulant and radioactive tests were fairly similar chemically to this point.

Strong similarities between the two simulant runs were expected based on past simulant work, however SB4-71 data were consistently higher than SB4-70 data over most of the period of large carbon dioxide concentrations in the SRAT cycle. This difference seems to indicate a larger loss of mass to the off-gas system as CO_2. Calculated formate losses, however, are nearly identical for the two runs based on IC data from the SRAT product, and starting TIC concentrations are also nearly identical. No other species of consequence are assumed to produce CO_2. One possible explanation is that a difference in the air purge flow rate diluted the SB4-70 results more. Helium ran about 5% lower in SB4-70 than SB4-71, although the target air purges were the same. The offset in CO_2 production that can be explained by different air purge flow as indicated by helium concentration can only account for about one-third of the difference between the parts of the two simulant curves over 10 vol% CO_2.

The SC-3 run was very similar to SB4-71 during reflux. Figure 4-4 shows carbon dioxide during SRAT cycle refluxing for the two simulant runs and SC-3. Carbon dioxide generation remained larger in SB4-71 than in SB4-70 throughout the SRAT, i.e. ranked in the same direction as hydrogen generated during this period.

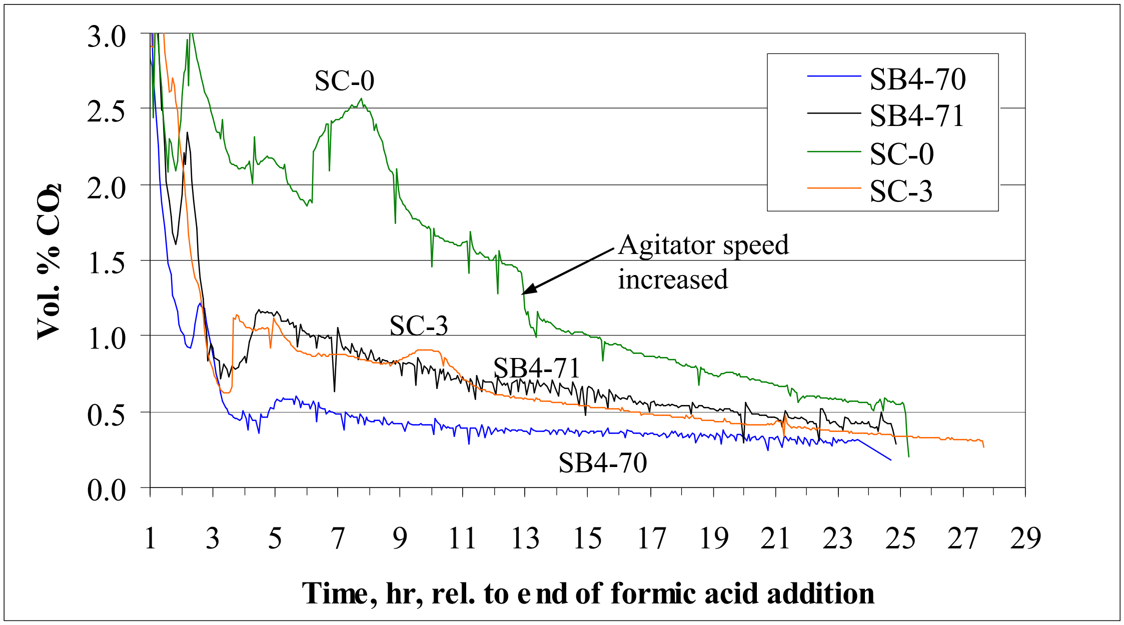

Figure 4-4. Comparison of CO_2 Data During SRAT Boiling

Carbon dioxide generation rates exceeded hydrogen generation rates by a factor of about four in both simulant runs. The factor was only two to three for SC-3, because hydrogen generation was somewhat higher. These results indicate that more reactions than just catalyzed formate destruction, $HCOOH \rightarrow CO_2 + H_2$ were occurring during this part of the SRAT cycle, and that there was a difference in the radioactive processing compared to the simulant processing.

Carbon dioxide data from the SME cycle are shown in Figure 4-5. The inclusion of data from SC-0 highlights how different the SME cycle of this simulation was compared to the other three. The first peak in CO_2 concentration for SC-0 at one hour went to 30.2 vol%. To scale the CO_2 axis to show this value would eliminate all detail from the profiles for the three new runs. The second major hydrogen event in SC-0 occurred 12 hours into the SME cycle. The CO_2 production with this event was greater than in the three simulant runs, but not nearly to the same extent as for the first peak.

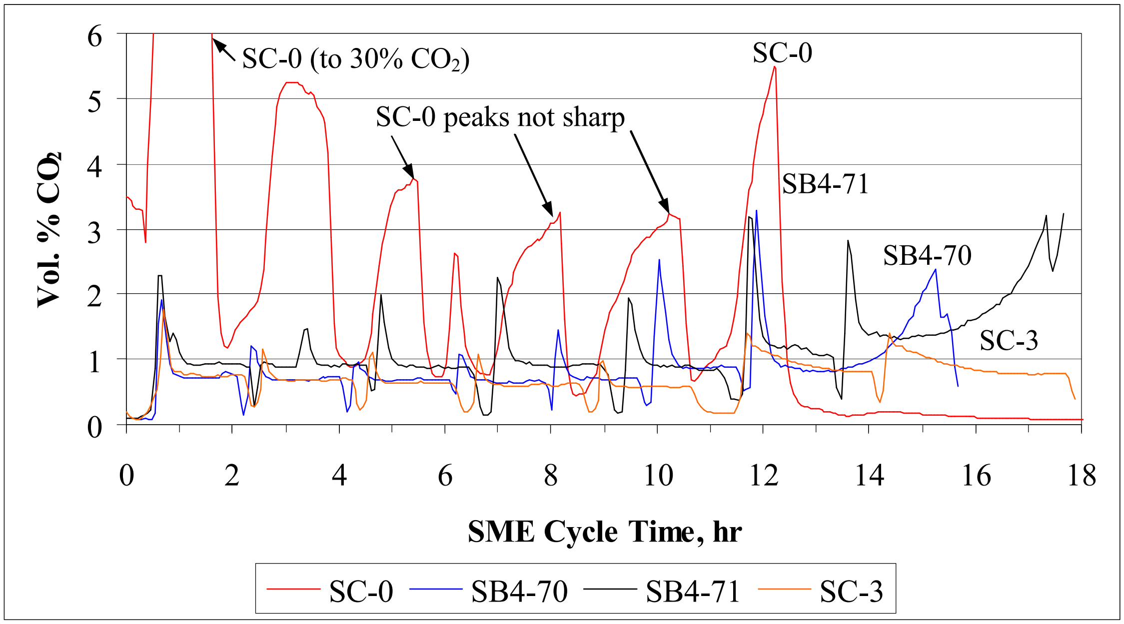

Figure 4-5. SME Cycle Carbon Dioxide Concentrations

The CO_2 peaks for SC-0 were less sharp than for SC-3 as the vessel returned to boiling after a canister decon water or frit slurry addition. Typically, SC-0 peaked after concentration as opposed to at the start of boiling as typically seen and as seen with the repeat cycles. The abruptness of quenching the CO_2 formation when cold water was added may help to confirm that there were no issues with the air purge in SC-0 being lower than reported (and consequently the vol% hydrogen converting to a biased high mass flowrate).

Additional unusual behavior in SC-0 during the first decon canister dewatering period was indicated by the measured oxygen concentration, Figure 4-6.

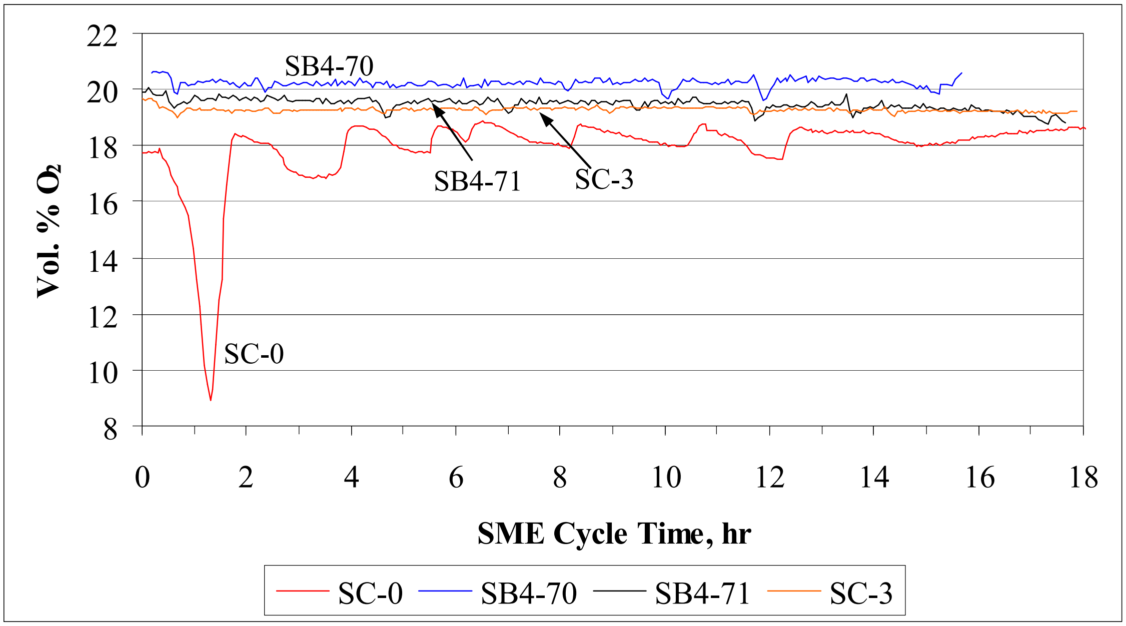

Figure 4-6. SME Cycle Oxygen Concentration

Figure 4-6 provides oxygen as another test comparison. Production of hydrogen and carbon dioxide in SC-3, SB4-70, and SB4-71 had very little impact on the oxygen concentration, but there was a noticeable impact in SC-0. Some, but not all, of the impact was simply due to dilution by other gases. A significant decrease in oxygen occurred with the first decon canister dewatering but no corresponding decrease followed the first frit addition (the two periods where hydrogen generation exceeded the DWPF SME limits in SC-0). If oxygen was not participating in chemical reactions, and assuming nitrogen also was not participating in reactions, then the ratio of oxygen to nitrogen should remain constant. To evaluate the extent that oxygen might be participating in reactions, the ratio of nitrogen to oxygen was calculated from the volume percent GC data for SC-0, SC-3, SB4-70, and SB4-71. The four sets of ratio data are shown in Figure 4-7.

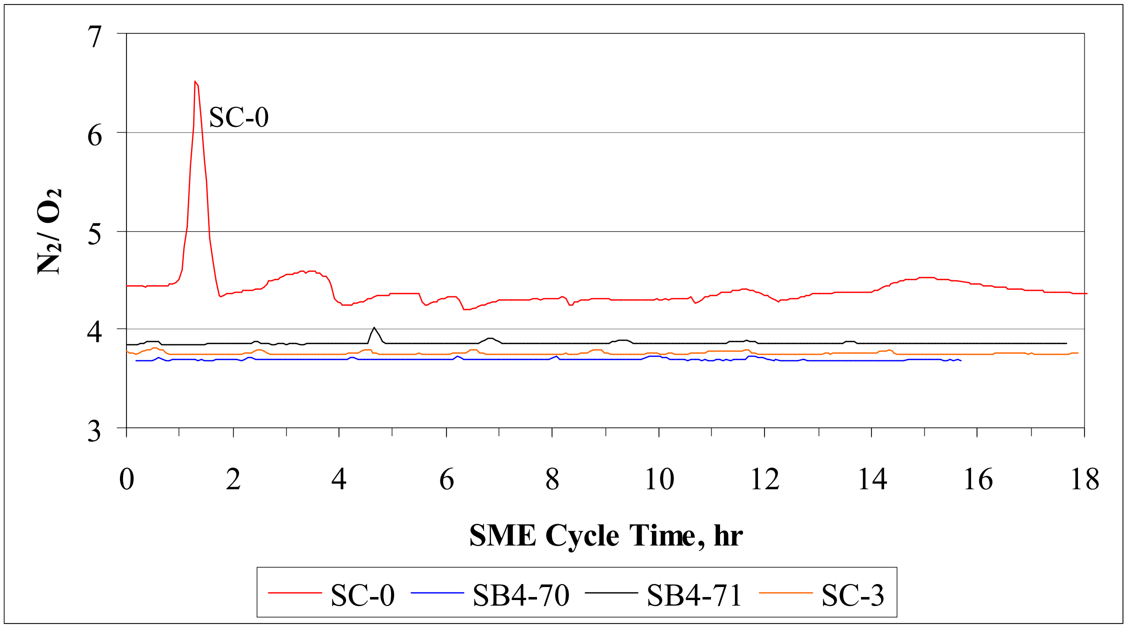

Figure 4-7. SME Cycle Ratio of Nitrogen to Oxygen

The ratio of nitrogen to oxygen remained nearly constant during the three SME cycles for SC-3, SB4-70, and SB4-71. The ratio was visibly more variable in general during SC-0 and particularly so during the first decon canister dewatering period at an hour into the SME cycle. This time is when hydrogen first exceeded the DWPF SME basis limit. The implication is that something unusual happened chemically during the large hydrogen spike at the start of the SC-0 SME cycle that was not typical of behavior seen in other SB4 radioactive and simulant tests and was not reproduced during the SC-3 test.

4.3 Nitrous Oxide Generation

Nitrous oxide, N_2O, was seen in the SRAT cycle during nitrite destruction. Data from SC-3 are compared to SB4-70 and SB4-71 in Figure 4-8. Results for both simulant runs were more similar than the corresponding hydrogen and carbon dioxide data. The data from SC-3 were similar, although subject to the same disruptions seen at 2.4-3.1 hours before the end of acid addition that were seen in the CO_2 data due to interrupted acid addition because of foaming.

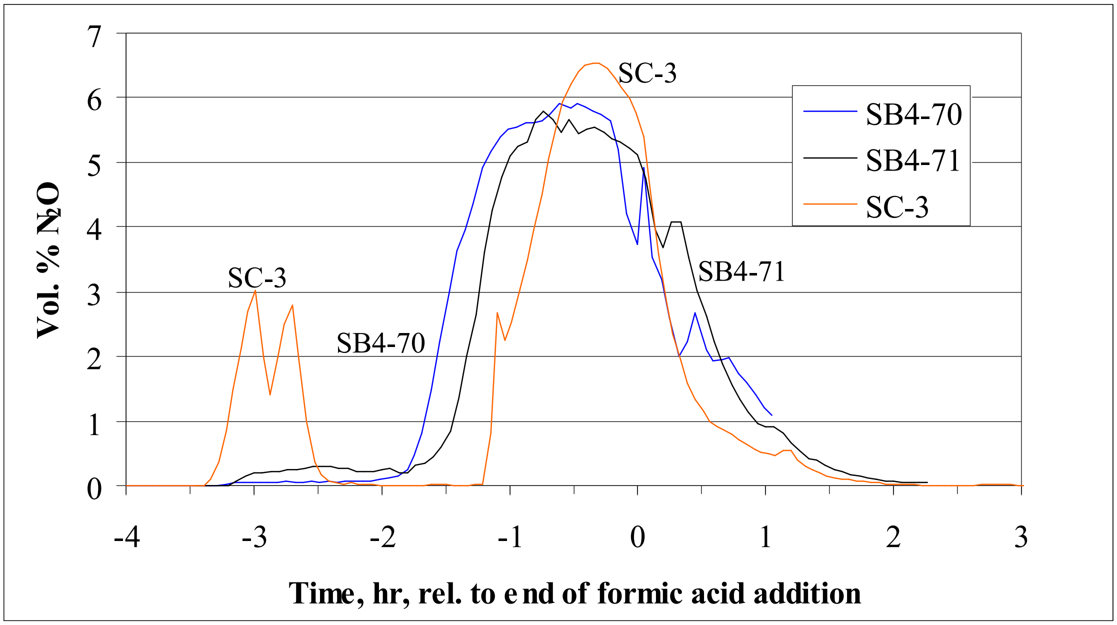

Figure 4-8. SRAT Cycle Nitrous Oxide Comparison

As discussed for CO_2, data from the SC-0 SRAT cycle are not shown because the acid addition period did not follow prototypical timing as closely as SC-3. The SC-0 main peak in N_2O occurred 3-4 hours before the end of acid addition. Both SB4-70 and SB4-71 had normal prototypical acid additions at the equivalent of two gallons per minute of acid. The period from one hour before the end of acid addition until two hours after the end of acid addition had nearly identical N_2O concentrations in all three new runs. CO_2 behavior was also nearly identical in this period. These results suggest that much of the chemistry going on in SC-3 and the two simulant runs was nearly identical.

Nitrous oxide was detected in the SC-0 and SC-3 SME cycles, but not in the simulant SME cycles. Data are given in Figure 4-9.

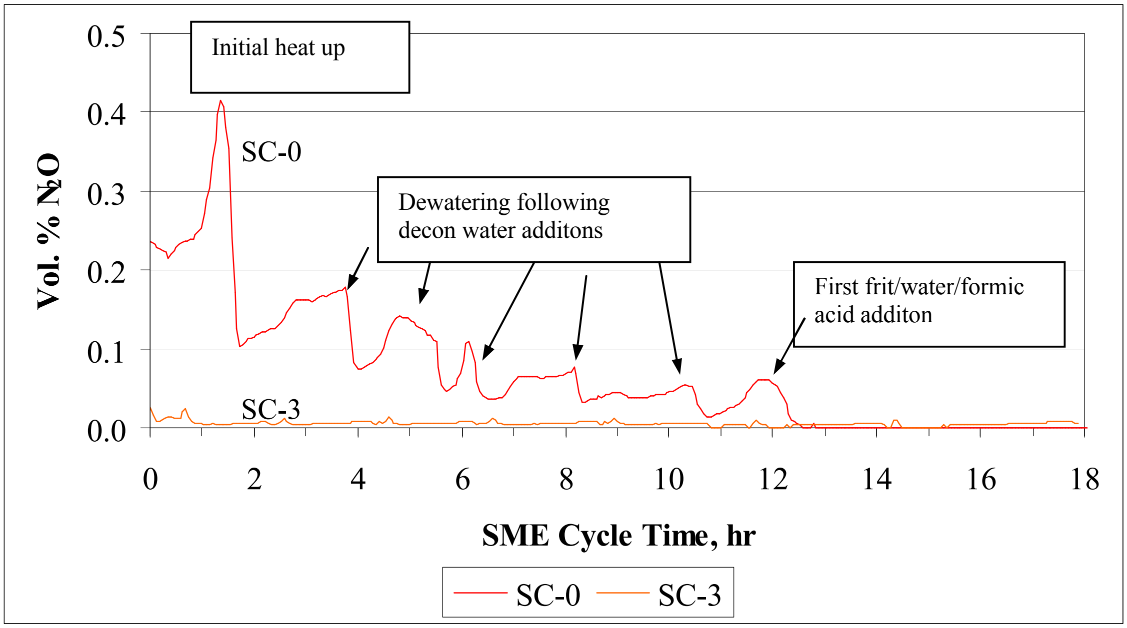

Figure 4-9. SME Cycle Nitrous Oxide Concentration

The two Shielded Cells runs had very different profiles of nitrous oxide during the SME cycle. This is not surprising based on the nitrite detected in the SC-0 SME material (see Table 4-1 – nitrite was measured to be 3,000 ppm). The SC-3 results are comparable to the SB4-70 and SB4-71 results. Nitrous oxide was detected at around 0.005%, near the detection limit of the Shielded Cells GC (Agilent model M200 using EZChrome software). Although no nitrous oxide was detected in the SB4-70 and SB4-71 runs, it should be noted that the detection limit is approximately 0.03% on the GCs used for these simulations (Agilent Model 3000 with Cerity QA-QC software).

The same argument cannot be made for SC-0. The N_2O peaks were not trivial on the GC. Nitrite ion was also found in the SME product of SC-0. This result was unexpected given the sustained hydrogen generation that had occurred during this run. Past data where sustained hydrogen was made always correlated with negligible nitrite ion. It may be that nitrite ion was at a low pseudo-steady state concentration balanced between formation and destruction reactions. Significant nitrite formation has not been indicated in past process simulations, however the condensation of NO_2 into water produces both HNO_3 and HNO_2 in equal amounts by:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq) \qquad [5]$$

This reaction is believed to happen within the SRAT (and SME) between NO, formed from destroyed nitrite or nitrate, which has reacted with oxygen in the air purge to form NO_2, and then absorbed onto liquid condensate droplets on the vessel wall. This reaction is also known to occur in the SRAT and SME condensers where a more abundant supply of condensate is available. The presence of nitrate ions in the condensates has been confirmed analytically.

Another possible explanation exists with regards to mixing effectiveness. If a region of unmixed sludge slurry existed within the SC-0 SRAT vessel, and if acid were diffusing into this region at a slow rate, then nitrite destruction could continue to occur during processing in the SRAT and SME cycles in one region while hydrogen generation was occurring in the primary mixed slurry. The presence of a stagnant region within the vessel could explain many of the phenomena observed during SC-0. For example, such an unmixed region could account for the residual nitrite ion seen in the bulk SME product sample (see Section 4.4). The quantity of acid available for hydrogen (and carbon dioxide) generation in both the SRAT and the SME would also be higher if some of the normal acid consumers were trapped in a stagnant region.

4.4 SRAT and SME Product Analyses

Sample results for the SRAT and SME product samples are given in Table 4-1. Both simulant SME products were diluted to about 84% SME product – 16% deionized water. This dilution was necessary to obtain representative samples for analyses, because the two SME products were semi-solids rather than readily mixable slurries. Following dilution, it was possible to mix the SME slurries and obtain samples from a well-mixed system. Measured SME results were converted back to an original slurry basis. It was assumed in the simulant SME product calculations that there was no dilution dissolution. If there was, then the results for soluble and insoluble SME cycle solids are in error, but the total solids result should still be accurate.

Table 4-1. Sample Result Summary for SRAT and SME Products

Measured or calculated result	SC-0	SB4-70	SB4-71	SC-3
SRAT wt% total solids	19.9	21.05	20.66	21.3
SRAT wt% insoluble solids	10.1	10.52	10.55	11.1
SRAT wt% soluble solids	9.8	10.53	10.11	10.2
SRAT formate, mg/kg	27,300	42,400	40,800	33,400
SRAT nitrate, mg/kg	27,100	28,750	30,250	26,100
SRAT mercury, wt% of total solids	0.09	NM	NM	0.23
SRAT product sample mass, g	190	120.8	130.9	302.36 *
SME wt% total solids	33.8 †	46.8	45.2	49.6
SME wt% insoluble solids	24.3 †	35.3	33.4	40.8
SME wt% soluble solids	9.5 †	11.5	10.1	9.2
SME formate, mg/kg	22,300 †	47,460	42,870	36,000
SME nitrate, mg/kg	19,400 †	31,600	32,420	30,400
SME nitrite, mg/kg	3,020	<100	<100	<200
SME sulfate, mg/kg	1,940 †	1,760	1,990	2,390
SME product mass, g	775.08 †	646.1	654.5	610.86

* The large sample was pulled to provide material for an SRNL-AD analytical development task.

† The SC-0 cycle was discontinued after the first frit addition due to high hydrogen. The wt% solids results are calculated from a mass balance, and the anion results and SME product mass are measured.

Simulant sample results were fairly similar. However, some minor dewatering issues occurred in SB4-70. The MWWT was not drained after the SRAT cycle in SB4-70. This omission was noted during canister dewatering and was corrected in the second canister dewater cycle by increasing the amount to include the contents in the MWWT. It appears, however, that about 20 grams of extra condensate was removed relative to SB4-71. This appears to explain why SB4-70 with a smaller SRAT product sample removed from it relative to SB4-71 ended up with less SME product mass (both runs started with identical masses). It also tends to confirm that the two runs were very similar in an overall mass balance sense and that no significant difference existed due to the heat-treatment of a portion of the SB4-71 feed.

In comparing SC-0 and SC-3, the sample results correspond to the offgas data. SC-0 had lower formate and nitrate concentrations than SC-3, corresponding to higher hydrogen and carbon dioxide in both the SRAT and SME cycles. The lower formate content in SC-3 compared to the simulant runs correlates to the higher hydrogen.

In both SC-0 and SC-3, mercury was stripped to below the DWPF limit of 0.45 wt% of total solids. The difference between the two runs may not be significant due to the difficulty in obtaining a representative sample for mercury analysis. Mercury was not measured in the simulant SRAT products because of this. Elemental mercury could be observed on various parts of the SRAT apparatus, and it was concluded that a representative sample could not be obtained.

Anion concentrations and solids data were used with material balance results from the tests to calculate formate loss in the SRAT and SME cycles, nitrite to nitrate conversion in the SRAT cycle, and nitrate loss in the SME cycle. These results are presented in Table 4-2 along with corresponding data from the original qualification simulant test at 130% acid, SB4-57.

Table 4-2. Anion Reaction Results

Run	SRAT Formate Loss	SRAT Nitrite to Nitrate Conversion	SME Formate Loss	SME Nitrate loss
SB4-57	25%	15%	8%	11%
SC-0	46%	37%	27% *	26% *
SB4-70	34%	31%	8%	3%
SB4-71	35%	37%	12%	4%
SC-3	21%	37%	26%	4%

* Note that the SME cycle for SC-0 was stopped after the first of two frit/flush water/formic acid addition due to high hydrogen generation so loss is calculated through that point.

The formate and nitrate loss percentages are based on the relative difference between the content of the SRAT or SME cycle product relative to the total available from the feed plus other additions during the cycle. (These calculations do not account for nitrate and formate removed in the condensates, so they are not equivalent to formate or nitrate destruction by chemical reactions during processing.) Nitrite to nitrate conversion is calculated from the increase in nitrate mass in the SRAT product relative to the feed nitrate plus SRAT nitric acid addition.

SRAT formate loss appeared to track hydrogen generation with the exception of SC-3. As hydrogen generation increased, the SRAT formate loss increased as well. Small formate losses are common in the SME cycles with active noble metals. However, formate loss in the two radioactive runs was significantly higher than the simulant SME cycles. While this would be anticipated with significant hydrogen in SC-0, it should not be equivalent to SC-3 given the hydrogen was similar to the simulant runs. The four tests in the 1.4 L equipment (SC-0, SC-3, SB4-70, and SB4-71) all had large and similar nitrite to nitrate conversions. These high conversions are not being seen in most of the 4 L equipment tests and the reason for the difference is not clear.

SME nitrate losses are low in all the simulations except SC-0. In addition to the high nitrate loss, nitrite was detected at 3,020 mg/kg slurry. SME nitrate losses do not have an associated chemical reaction at this time, and it is believed these calculated losses are a product of combined material balance and analytical errors rather than a measure of true nitrate ion loss. The high nitrate loss, the apparent creation of nitrite, the production of significant nitrous oxide, and the relatively high hydrogen production imply that SC-0 processing was abnormal.

5.0 HYPOTHESES FOR EXPLAINING OBSERVED BEHAVIOR

The repeat of the SB4 qualification Shielded Cells SRAT/SME run, SC-3, did not reproduce the hydrogen generation results seen in the original qualification run, SC-0. Simulant runs with modified and heat-treated simulant did not bound the radioactive runs. In addition, several hypotheses have been advanced to explain the potential differences. These include:

- The original qualification feed was collected from various available materials left over from the preparations for the first aborted qualification attempt plus some additional fresh dip sample slurry. Some foreign material may have been introduced that altered the processing characteristics of the feed to SC-0. However, this testing showed heat treatment should not have significantly contributed to hydrogen.

- The original SB4 qualification run used a feed that was washed in the Shielded Cells, while the repeat, SC-3, used feed that was washed in the Tank Farm. Tank Farm washing introduced changes to the rheology, and, by inference, the particle size distribution of the feed to SC-3. These physical changes may have impacted hydrogen generation.

- SC-0 was stopped for two weeks following the SRAT cycle, while SC-3 was run more like a simulant test with only a brief delay between the SRAT and SME cycles to adjust the air purge, add antifoam, etc. before continuing. The impact of a long delay between SRAT and SME cycles is not known. Slow reactions between the supernate and insoluble solids can proceed to a greater extent when more time is provided.

- Inadequate mixing in SC-0 could have led to a region in the vessel where there was essentially no mixing. Within this region the feed nitrite ion would only slowly be destroyed by diffusion limited reactions. Outside this region, the slurry would be treated with what was essentially a large quantity of excess acid, i.e. all of the acid needed to process the unmixed material would be unconsumed. This excess acid would be able to produce unexpectedly high hydrogen generation rates. The presence of unmixed slurry could possibly explain the large release of CO_2 and N_2O at the beginning of the SME cycle as the slurry was diluted with decon water and the settled solids began to erode. It should be noted that this hypothesis was rejected during initial reviews due to the belief that the settled solids could not be resuspended. However, recent testing with simulants has shown that a settled solids region can be eroded quickly if mixing is increased. The off-gas data at the start of the SME cycle resembles that during nitrite destruction in the SRAT except for the hydrogen generation, i.e. there were oxides of nitrogen, oxygen depletion, and CO_2 generation. The significant nitrite ion concentration at the end of the SME cycle can also be explained by the presence of an unmixed region of starting slurry.

- The oxygen lost about one hour into the SC-0 SME cycle was consumed in reactions with organic species such as formic acid, antifoam, etc. to produce the large spike in CO_2 that occurred at the same time. The noble metals that catalyze hydrogen generation are also suitable for catalytic wet air oxidation (CWAO). CWAO is a general class of reactions between oxygen and organic chemicals analogous to thermal oxidation that form CO_2 and water as the principal products. SC-0 sat for two weeks following the SRAT cycle, while SC-3 did not have a delay between the SRAT and SME cycles. Radiation and/or time may have activated a species in the SRAT product of SC-0 that was particularly active catalytically.

The original and modified simulant acid calculation data in Table 3-2 bound the Shielded Cells sample acid calculation input data below and above respectively. Nevertheless, none of the three simulant runs were able to bound the hydrogen generation rates seen in either of the two SB4 radioactive SRAT cycles or SME cycles. The scopes of several FY07 programs at the Savannah River National Laboratory (SRNL) include finding possible explanations for these differences. Specifically:

- Testing with spiked samples indicates that the new automatic titrator at ACTL is fairly insensitive to the red (large particle size) HgO being used as a trim chemical in SB4 simulant tests. The Hsu stoichiometric acid algorithm used by DWPF[16] assumes HgO is titrated (two moles acid per mole mercuric oxide) during the measurement of base equivalents at pH 7. In that case, only one additional mole of acid is required to reduce the mercury to the elemental form. The absence of HgO in the measured simulant base equivalents causes the simulant stoichiometric factor to be biased high, i.e. the simulant runs were not really at 130% stoichiometry but at about 124%. Adding 5-6% more acid to offset the bias would probably push the simulant SME hydrogen generation rate past the DWPF limit. Tests are planned to determine whether or not the Shielded Cells titration method is sensitive to the HgO present in real waste.[17] If it is, then the simulant tests are not really comparable to the radioactive tests in terms of acid stoichiometry. This work is part of the task to look at improvements to the DWPF acid calculation.

- Spiked sample testing has also indicated that the automatic titrator at ACTL is fairly insensitive to insoluble carbonate but very sensitive to soluble carbonate. Current SRAT receipt sample analyses do not attempt to differentiate between the two. If the relative distribution of soluble to insoluble carbonate in the simulant does not match that in the qualification sample, then there is another potential source of bias up or down in the stoichiometric percentage. A second potential bias exists if the manual Cells titration method has a different sensitivity to insoluble carbonate than the ACTL titrator. Both methods likely detect soluble carbonates since no dissolution step is required; however the use of 1M acid in the Cells method might create locally lower pH regions that could convert more insoluble carbonate to carbon dioxide than the dilute simulant titration with 0.1 M acid. Follow-up testing is part of the task to look at improvements to the DWPF acid calculation.

- The SB4-70 and SB4-71 simulant data show that the SB4 qualification system lies in a region sensitive to excessive hydrogen generation. When this is the case, the cumulative effect of small errors in the inputs to the acid calculation could put the actual calculated acid addition into the region where hydrogen generation exceeds the DWPF limits. This effect could occur whenever the random analytical errors tend to be additive rather than cancel out. A repeat analysis of a new SB4 sample indicated significant differences in the key inputs to the stoichiometric acid equation compared to the qualification sample.

6.0 CONCLUSIONS

Excessive hydrogen generation was observed in the initial SB4 qualification demonstration of the DWPF SRAT/SME cycles in the SRNL Shielded Cells, SC-0. Direct follow-up testing with SB4 samples and simulants has so far failed to explain the hydrogen generation rates seen in SC-0. A strong probability exists that the results in SC-0 were an aberration caused by unusual and/or unidentified external factors. Specifically,

- A repeated test with Tank 51 slurry in the Shielded Cells (SC-3), using an identical acid addition in moles acid per liter slurry, produced lower levels of hydrogen in both the SRAT and SME cycles. The SME limit was not exceeded in SC-3 and hydrogen was approximately half of the rate in the SRAT.

- Other data from SC-3, such as CO_2, O_2, and N_2O off-gas data along with anion concentrations in the SRAT and SME product, did not reproduce the results from SC-0. Off-gas phenomena seen in the first SC-0 SME cycle hydrogen peak, such as significant oxygen consumption and carbon dioxide generation, were not observed in SC-3 or the simulant runs at any point during hydrogen generation.

- Tests with simulants modified to better match the actual composition of the feed in the original qualification run, SC-0, did not reach the hydrogen generation levels of either of the radioactive tests, SC-0 or SC-3. These simulant tests did, however, have many processing similarities with SC-3 but not with SC-0. The similarities with SC-3 suggest this Shielded Cells run had the more typical behavior.

- Simulant testing of the impact of heat-treatment on a portion of the feed to the SRAT cycle indicated only a minor enhancement to SRAT cycle hydrogen and no impact on SME hydrogen generation. Most chemical reactions tracked by slurry analytical results and off-gas data were not significantly impacted by the heat-treatment.

- Potential reasons have been identified that may explain why the simulant results did not bound the radioactive results. These candidates are under study during FY07 tasks requested by DWPF and relate to simulant preparation and analytical techniques.

- Simulant testing produced a very viscous SME product during final dewatering with a yield stress outside of current DWPF rheology limits. Poor mixing of thick slurries can allow localized heating which causes increased hydrogen generation rates or increased hydrogen retention in the slurry. Laboratory scale equipment upgrades between SC-0 and SC-3 allowed for much better control and viewing of agitation in the SRAT vessel to mitigate this problem.

7.0 RECOMMENDATIONS/PATH FORWARD

Based on the comparison of these recent simulant and radioactive processing studies, it is recommended that:

- An improved or alternative acid calculation be developed that is less dependant on difficult-to-measure items such as total base, total inorganic carbon, and mercury.

- The differences between radioactive and simulated sludges and their impact on CPC testing be more fully investigated, specifically the form of mercury and the form of inorganic carbon (soluble vs. insoluble).

- An improved method for determining total inorganic carbon be developed, especially if this remains an input to the acid calculation.

- Improved instrumentation for monitoring mixing intensity be maintained in the Shielded Cells.

8.0 REFERENCES

[1] Pareizs, J. M., C. J. Bannochie, M. J. Barnes, N. E. Bibler, D. R. Click, E. K. Hansen, D. P. Lambert, and M. E. Stone, *Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells in Support of Sludge Batch 4 Qualification.* WSRC-STI-2007-00053, Savannah River Site, Aiken, SC 29808 (2007).

[2] Koopman, D. C., D. P. Lambert, D. R. Best, and M. J. Barnes, *DWPF CPC Simulant Testing in Support of Sludge Batch 4 Qualification*, WSRC-STI-2006-00062, Savannah River Site, Aiken, SC 29808 (2006).

[3] Pareizs, J. M., *Evaluation of Potential Causes of High Hydrogen in Shielded Cells SB4 Qualification*, SRNL-PSE-2006-00344, Savannah River Site, Aiken, SC 29808 (2006).

[4] Stone, M. E. and D. R. Best, *Sludge Batch 4 Simulant Flowsheet Studies: Phase II Results*, WSRC-STI-2006-00109, Savannah River Site, Aiken, SC 29808 (2006).

[5] Stone, M. E. and D. C. Koopman, *Results from SB4 Simulant Runs in Response to SB4 Qualification Test: SB4-67 and SB4-68*, SRNL-PSE-2007-00072, Savannah River Site, Aiken, SC 29808 (2007).

[6] Koopman, D. C., *Recommendations for SB4 Processing in the Shielded Cells*, SRNL-PSE-2006-00122, Savannah River Site, Aiken, SC 29808 (2006).

[7] Koopman, D. C. *Review of Catalytic Hydrogen Generation in the Defense Waste Processing Facility (DWPF) Chemical Processing Cell*, Technical Report WSRC-TR-2002-00034, Savannah River Site, Aiken, SC 209808 (2004).

[8] Bannochie, C. J., *Qualification of DWPF Sludge Batch 4 (Macrobatch 5) in the SRNL Shielded Cells: Analytical Study Plan*, WSRC-RP-2006-00458, Savannah River Site, Aiken, SC 29808 (2006).

[9] Pareizs, J. M. Preparation of Weighted Dilution Samples in the Shielded Cells, Manual L29, Work Instruction ITS-WI-0016, Savannah River Site, Aiken, SC 29808 (2007).

[10] Koopman, D. C., D. P. Lambert, and M. J. Barnes, *Preparation of Sludge Batch 4 Qualification Simulants for DWPF Process Simulations*, WSRC-STI-2006-00242, Savannah River Site, Aiken, SC 29808 (2006).

[11] Stone, M. E., *Lab-Scale CPC Equipment Set-up*. Interoffice Memorandum SRNL-PSE-2006-00074, Savannah River Site, Aiken, SC 29808 (2006).

[12] Stone, M. E., *SRAT Assembly for SB4 Shielded Cells Testing: March 2007,* Interoffice Memorandum SRNL-PSE-2007-00049, Savannah River Site, Aiken, SC 29808 (2007).

[13] Stone, M. E., *Laboratory Scale Chemical Process Cell Simulations*, Technical Reference Procedure ITS-0094 in Manual L29, Rev. 3, July 11, 2006.

[14] Barnes, M. J.., *Laboratory Scale Chemical Process Cell Simulations in the Shielded Cells*, Technical Reference Procedure ITS-0085 in Manual L29, Rev. 4, December 11, 2006.

[15] Koopman, D. C., *Impact of HgO on Base Equivalents Titration Results*, Interoffice Memorandum SRNL-PSE-2007-00002, Savannah River Site, Aiken, SC (2007).

[16] Hsu, C. W. *Nitric Acid Requirement for Treating Sludge*, Report WSRC-RP-92-1056, Savannah River Site, Aiken, SC 29808 (1992).

[17] Pickenheim, B. R. *Improvement of SRAT Acid Equation*, Task Technical and Quality Assurance Plan WSRC-RP-2007-00348, Savannah River Site, Aiken, SC 29808 (2007).

9.0 ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of SRNL Analytical Development, particularly K. E. Zeigler. The authors would also like to recognize the invaluable support of the SRNL Shielded Cells technicians and management for the in-Cells work, and M. E. Stone and the ACTL technicians for their assistance in equipment setup, reagent preparation, and consultation for the radioactive simulations. The authors appreciate the assistance of M. E. Stone, M. F. Williams, J. W. DuVall, V. J. Williams, I. A. Reamer, R. J. Workman, T. O. Burckhalter, D. M. Marsh, and D. P. Healy in conducting the supporting simulant tests. The authors thank D. R. Best, W. A. Thomas, and P. A. Toole for performing some of the simulant analytical work. Finally, the authors thank the SRNL Machine Shop for their excellent quality and fast response to the needs for SRAT rigs.

APPENDIX A. Simulation of Cells Boil-Over Event

Simulation of Shielded Cells Boil-over Event with Simulant

A 500 g charge of modified SB4 qualification simulant was added to the apparatus shown in Figure A - 1. This simulant was taken to boiling shortly after it was transferred to the equipment, i.e. before the slurry solids had time to settle. This treatment led to convective turnover of the vessel contents, as indicated by the three thermocouples at different depths when the lowest (hottest) thermocouple read 61°C. The slurry proceeded to boiling, and the treatment was terminated. The slurry was allowed to settle over night, and the heat-treatment test was repeated. This treatment also led to turnover of the vessel contents, as indicated by the three thermocouples at different depths when the lowest (hottest) thermocouple read 85°C. The two treatments were considered sufficient to induce any qualitative change to the sludge matrix that might result from an event similar to the Shielded Cells event. There is no way to prove conclusively that this was the case, since the simulant sludge matrix could not be expected to be identical to the radioactive sludge matrix (different composition, different history, etc.).

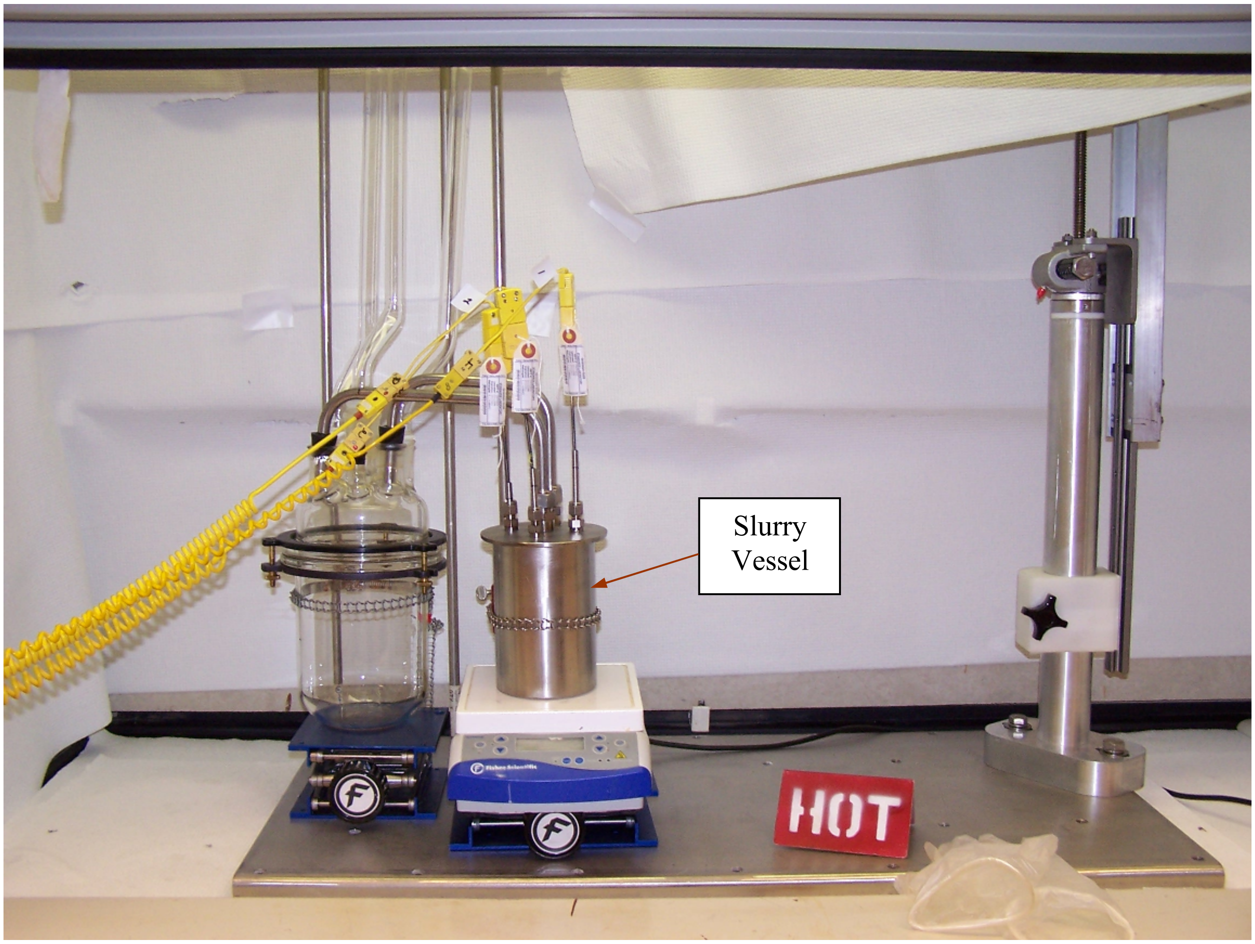

Figure A - 1. Photograph of Vessel and Receiver Used to Heat-treat the Simulant

The steel vessel had an outside diameter of about four inches and a height of six inches. The hot plate was temperature controlled at 350°C, although the time it took to reach steady-state was similar to the time it took to bring the slurry to boiling inside the vessel. Three thermocouples were mounted at three different depths. The lowest was 1/8th inch off the bottom, the middle thermocouple was 7/8th inch off the bottom, and the highest was 1-7/8th inch off the bottom. The slurry was about three inches deep.

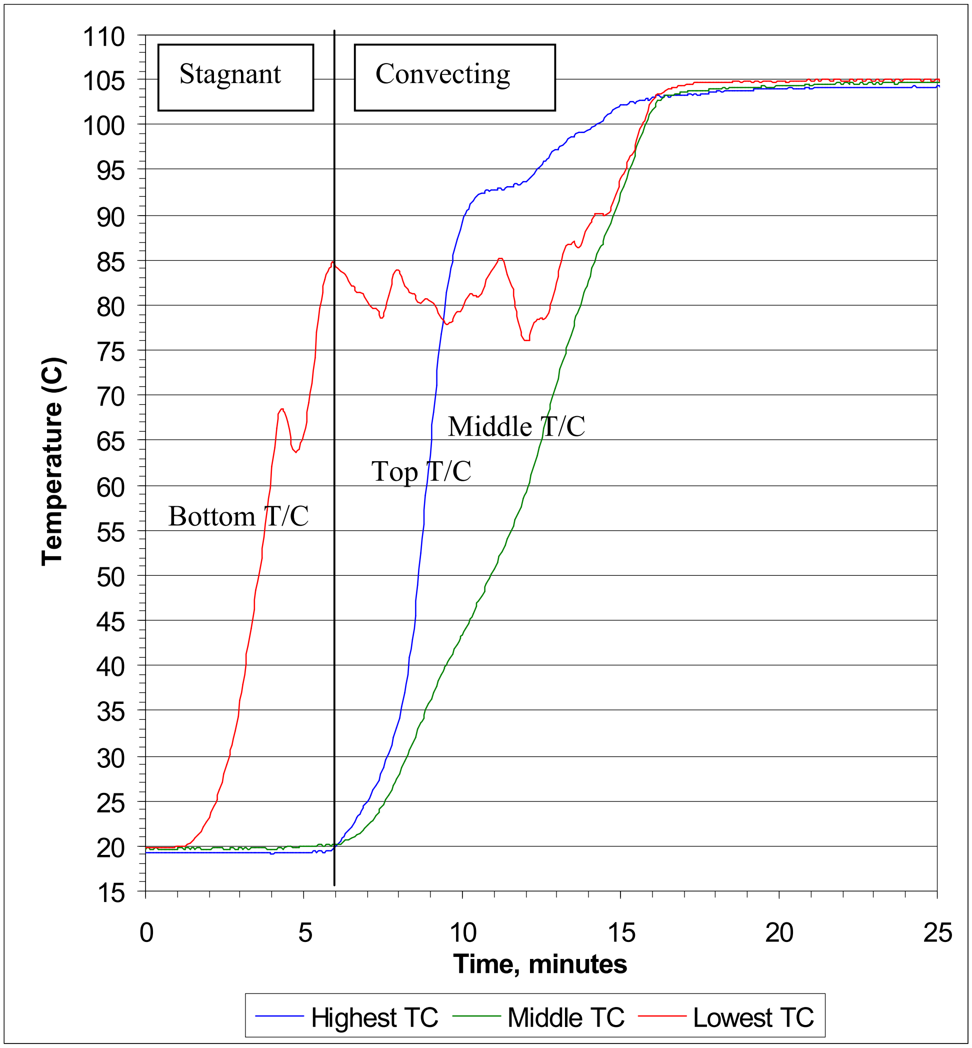

Figure A - 2. Thermocouple Data Following Overnight Settling

Three thermocouples are not sufficient to characterize all of the temperature gradients within the vessel once the slurry is no longer stagnant. Fluid can begin to circulate locally in one area while slurry in another region is still relatively stagnant. The thermocouples are able to indicate when vertical fluid motion begins to eliminate temperature differences between the hot slurry at the bottom and the bulk slurry, and this was their purpose. The maximum temperature observed on the second heat treatment was 105°C, but temperatures of 107°C were observed during the initial treatment at the bottom thermocouple when the slurry was still relatively well-mixed.

Distribution:

J.E. Marra, 773-A
R.E. Edwards, 773-A
A.B. Barnes, 999-W
D.B. Burns, 786-1A
D.A. Crowley, 999-W
C.C. Herman, 999-W
C.J. Bannochie, 773-42A
N.E. Bibler, 773-A
W.E. Daniel, 999-W
R.E. Eibling, 999-W
C.M. Jantzen, 773-A
D.C. Koopman, 999-W
D.P. Lambert, 999-W
J.M. Pareizs, 773-A
D.K. Peeler, 999-W
B.R. Pickenheim, 999-W
S.H. Reboul,766-H
M.E. Smith, 999-W
M.E. Stone, 999-W
S.D. Burke, 704-S
J.E. Occhipinti, 704-S
R.T. McNew, 704-27S
J.F. Iaukea, 704-30S
J.W. Ray, 704-S
B.A. Davis, 704-27S
T.L. Fellinger, 704-26S
A.V. Staub, 704-27S
C.G. Lampley, 766-H
H.B. Shah, 766-H
J.M. Gillam, 766-H
H.H. Elder, 704-30S
K.E. Zeigler, 773-41A
D.R. Click, 773-A
M.J. Plodinec, 773-A