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DWPF FLOWSHEET STUDIES WITH SIMULANTS TO DETERMINE MCU SOLVENT BUILD-UP IN CONTINOUS RUNS

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May 25, 2006

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

SRNL
SAVANNAH RIVER NATIONAL LABORATORY

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EXECUTIVE SUMMARY

The Actinide Removal Process (ARP) facility and the Modular Caustic Side Solvent Extraction Unit (MCU) are scheduled to begin processing salt waste in fiscal year 2007. A portion of the streams generated in these salt processing facilities will be transferred to the Defense Waste Processing Facility (DWPF) to be incorporated in the glass matrix. Before the streams are introduced, a combination of impact analyses and research and development studies must be performed to quantify the impacts on DWPF processing. The Process Science & Engineering (PS&E) section of the Savannah River National Laboratory (SRNL) was requested via Technical Task Request (TTR) HLW/DWPF/TTR-2004-0031 to evaluate the impacts on DWPF processing.

Simulant Chemical Process Cell (CPC) flowsheet studies have been performed using previous composition and projected volume estimates for the ARP sludge/monosodium titanate (MST) stream.[,4] Initial MCU incorporation testing for the DWPF flowsheet indicated unacceptable levels of Isopar®L were collecting in the Sludge Receipt and Adjustment Tank (SRAT) condenser system and unanticipated quantities of modifier were carrying over into the SRAT condenser system. This work was performed as part of Sludge Batch 4 (SB4) flowsheet testing and was reported by Baich et al. Due to changes in the flammability control strategy for DWPF for salt processing, the incorporation strategy for ARP changed and additional ARP flowsheet tests were necessary to validate the new processing strategy. The last round of ARP testing included the incorporation of the MCU stream and identified potential processing issues with the MCU solvent.[,4] The identified issues included the potential carry-over and accumulation of the MCU solvent components in the CPC condensers and in the recycle stream to the Tank Farm. Solvent retention in the DWPF condensers contradicts the DWPF solvent control strategy. Therefore, DWPF requested SRNL to perform additional MCU flowsheet studies to better quantify the organic distribution in the CPC vessels.

The earlier rounds of testing used a Sludge Batch 4 (SB4) simulant since it was anticipated that both of these facilities would begin salt processing during SB4 processing. The same sludge simulant recipe was used in this round of MCU testing to minimize the number of changes between the three phases of testing so a better comparison could be made. The MCU stream simulant was fabricated to perform the testing. The MCU stream represented the "Maximum Volume" case from the material balances provided by Campbell. ARP addition was not performed during this set of runs since the ARP evaluation had been completed in earlier runs. The MCU stream was added at boiling during the normal reflux phase of the SRAT cycle. SRAT cycle completion corresponded to the end of MCU stream addition.

A total of ten 4-liter SRAT runs were performed to meet the objectives of the testing. The first series of five tests evaluated the organic portioning and mass balance for the addition of 50 mg/kg solvent. The second series of five tests evaluated the organic portioning and mass balance for the addition of 125 mg/kg solvent. A solvent concentration of 50 mg/kg is close to the nominal concentration anticipated in the effluent from the Salt Waste Processing Facility (SWPF). The organic solvent used in the testing was fabricated by the Chemical Science & Technology section. BOBCalixC6 was not added to this solvent due to the high cost and limited availability. All runs targeted 150% acid stoichiometry and 1% Hg in the sludge slurry dried solids.

The organic analyses and material balances suggest the following:

Isopar®L results
Almost all (> 99%) of the added Isopar®L exited via the offgas system. This occurs since at both 50 mg/kg and 125 mg/kg solvent, the Isopar®L concentration in the offgas is below the saturation pressure so no Isopar®L is condensed even at the Formic Acid Vent Condenser (FAVC) outlet temperature of 4 °C.

- Isopar®L collected in both the Mercury Water Wash Tank (MWWT) and the FAVC to a very small extent (i.e., <1% of the total Isopar®L in each case). Of this small quantity, appreciably more Isopar®L was found in the vessel rinses versus the actual condensate samples. The starting solvent concentration did not appear to have a direct impact on the amount condensed in the SRAT system. During testing it was noted that mercury and organic looking deposits accumulated in the horizontal leg between the SRAT condenser and the MWWT. It is possible that these accumulations were due to the small diameter tubing and minimal slope of the SRAT condenser drain line. However, it is also possible that this will be the accumulation point for these insoluble organic species in the DWPF.
- The recovery of Isopar®L was78.9% at 50 mg/kg solvent and 94.1% at 125 mg/kg solvent, based on mass balances. The higher recovery in experiments with 125 mg/kg was related to the higher addition rate and improvements (resulting from the earlier 50 mg/kg test) in testing protocol used only during experiments at 125 mg/kg.

Modifier results

- The carbon tubes were not analyzed for modifier, based on previous studies. The modifier was found in the MWWT, the SRAT condenser rinse, and in the Slurry Mix Evaporator Condensate Tank (SMECT) condensate. Based on the five runs at 125 mg/kg, roughly 55% of added modifier was found in the SRAT product, 29% of added modifier was found in the condensate and 14% of the modifier was found in the MWWT, both in liquid samples and deposits.
- The modifier is primarily removed via steam distillation. This means that longer boiling times will lead to lower concentrations of modifier in the SRAT product and a higher concentration of modifier in the SMECT condensate. In the DWPF, the SRAT product will be transferred to the Slurry Mix Evaporator (SME) and will undergo more than 40 hours of boiling in a typical SME cycle (compared to 10 hours in our SRAT cycle). This will lead to lower modifier concentrations in the melter feed than were measured in the SRAT testing. In previous MCU testing, SRAT product modifier concentration was 97 ppm versus 44 ppm in the SME product (without any decontamination frit boiloff) and the modifier concentration in the SME dewater was 22 ppm vs. 12 ppm in the SRAT condensate.
- The recovery of modifier was 73.1% at 50 mg/kg solvent and 93.8% at 125 mg/kg solvent, based on mass balances. As with the Isopar®L, the higher recovery was found in experiments with 125 mg/kg, which is once again related to the higher addition rate and improvements (resulting from the prior 50 mg/kg tests) in testing protocol.
- No modifier was detected in the FAVC condensate samples and very little modifier was found in the FAVC rinses (only after run SB4-47 was the concentration above the detectable quantity of 1 mg/kg).
- A significant fraction (10-14%) of the modifier was found in MWWT deposits. The deposits might be due to the small scale of the experiments as slugs of mercury and organic seemed to accumulate in the MWWT over several runs before draining. However, if the modifier continues to buildup in the MWWT, the deposits might eventually have to be removed as a third phase in the MWWT and may interfere with normal processing in the MWWT.

Based on the results of the testing, the following modifications are recommended in future MCU testing.

- The use of two hydrocarbons such as decane ($C_{10}H_{24}$) and tetradecane ($C_{14}H_{30}$) as a substitute for Isopar®L should be considered for lab-scale testing only. The tetradecane, the higher molecular weight Isopar®L component may lead to conservative deposition information.
- The addition of a SMECT and ammonia scrubber should be considered in any future testing. The ammonia scrubber's internals and packing are a likely collection point for solvent deposits.
- Testing at solvent concentrations leading to Isopar®L vapor concentrations above and below the Isopar®L vapor pressure at the FAVC outlet temperature is recommended to determine the impact of a second phase in MCU testing.

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LIST OF ACRONYMS

ACTL	Aiken County Technology Laboratory
AD	Analytical Development
ARP	Actinide Removal Process
ASP	Analytical Study Plan
CPC	Chemical Process Cell
CSSX	Caustic Side Solvent Extraction
DWPF	Defense Waste Processing Facility
DWPF-E	DWPF Engineering
FAVC	Formic Acid Vent Condenser
GC	Gas Chromatograph
GC/MS	Gas Chromatography/Mass Spectrometry
HPLC	High Pressure Liquid Chromatography
HLW	High Level Waste
IC	Ion Chromatograph
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
MCU	Modular Caustic Side Solvent Extraction Unit
MST	Monosodium Titanate
MWWT	Mercury Water Wash Tank
PSAL	Process Science Analytical Laboratory
PS&E	Process Science & Engineering
SB3	Sludge Batch 3
SB4	Sludge Batch 4
SEFT	Strip Effluent Feed Tank
SIM	Selective Ion Monitoring
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SVOC	Semi-Volatile Organic Compound
TOA	Tri-N-OctylAmine
TTR	Technical Task Request
WAC	Waste Acceptance Criteria

1.0 INTRODUCTION AND BACKGROUND

The Process Science & Engineering (PS&E) section of the Savannah River National Laboratory (SRNL) was requested by the Defense Waste Processing Facility (DWPF) via Technical Task Request (TTR) HLW/DWPF/TTR-2004-0031[1] to evaluate the impacts on DWPF processing for streams from the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Side Extraction (CSSX) Unit (MCU). These two facilities will treat the salt currently being stored in the High Level Waste (HLW) tanks and are currently planned to begin operations during fiscal year 2007. Initial flowsheet demonstrations with the two salt streams have previously been completed.[2,3,4] However, additional studies with added MCU were necessary to determine the partitioning of the MCU organics during processing.

In DWPF, the ARP sludge/monosodium titanate (MST) stream will be incorporated in the Sludge Receipt and Adjustment Tank (SRAT) during caustic boiling of the sludge and the MCU stream will be incorporated into the SRAT during post acid addition aqueous boiling.

Earlier MCU testing indicated minimal impact on SRAT processing due to the incorporation of the MCU stream.[3] However, the testing did identify potential issues with organic carryover to the SRAT condenser system. Therefore, additional testing was necessary with more prototypic solvent concentrations, a better organic addition system, and with improved methods for closing the organic mass balance.

A Task Technical & Quality Assurance Plan[5] was previously written outlining the activities and controls necessary to meet the objectives and requirements of the TTR. This set of testing was performed using the guidance and protocols outlined in the Task Technical Plan.

A total of ten SRAT runs were performed to meet the objectives of this phase of testing. The first five runs were completed at 50 mg/kg added MCU organic and the last five runs were completed at 125 mg/kg. The run ID and the particular parameters investigated were as follows:

SB4-36	~50 mg/kg MCU organic, 1st of 5 consecutive experiments
SB4-37	~50 mg/kg MCU organic, 2nd of 5 consecutive experiments
SB4-38	~50 mg/kg MCU organic, 3rd of 5 consecutive experiments
SB4-39	~50 mg/kg MCU organic, 4th of 5 consecutive experiments
SB4-40	~50 mg/kg MCU organic, 5th of 5 consecutive experiments
SB4-43	~125 mg/kg MCU organic, 1st of 5 consecutive experiments
SB4-44	~125 mg/kg MCU organic, 2nd of 5 consecutive experiments
SB4-45	~125 mg/kg MCU organic, 3rd of 5 consecutive experiments
SB4-46	~125 mg/kg MCU organic, 4th of 5 consecutive experiments
SB4-47	~125 mg/kg MCU organic, 5th of 5 consecutive experiments

2.0 APPROACH

This section describes the approach that was used to perform the MCU organic carry-over testing. It is divided into three subsections. Section 2.1 describes the simulant compositions and preparation methods. Section 2.2 describes the procedures and equipment utilized in the testing. Finally, Section 2.3 describes the analytical methods and procedures that were used in performance of the test.

2.1 Simulant Compositions and Preparation Methods

Since Sludge Batch 4 (SB4) simulant flowsheet studies have been and are being performed in parallel and the SB4 simulant was used in the earlier ARP and MCU runs, PS&E used the same blended sludge composition in this testing. The SB4 composition was based on projections provided by Lilliston and represented the scenario where SB4 is blended with SB3 after producing 1200 equivalent canisters.[6] This SB4 composition contained Tank 4, which is no longer a component of SB4, but allows for a more direct comparison to the other runs. The "Maximum" MCU case, where "Maximum" represents the highest dose/Cs loading case, from the Preliminary Material Balance Calculations performed by Campbell[7] served as the basis for the MCU composition and volume tested. For a 6000 gallon DWPF SRAT batch, the MCU target volume was 6400 gallons. The MCU aqueous stream was consistent with the stream used in the earlier MCU runs.[3]

Two new batches of sludge simulant were prepared to support these runs. Runs SB4-36 to SB4-40 used batch 020606 and runs SB4-43 to SB4-47 used batch 030606. The target sludge simulant elemental calcined composition is given in Table 2-1, while the supernate chemistry is provided in Table 2-2. The sludge was fabricated using the generic B and C sludges that were fabricated at the Clemson Environmental Technologies Laboratory. Trim chemicals were added to the two sludge simulants to obtain the target composition.

The MCU strip effluent stream consisted of water, $CsNO_3$, HNO_3, and the organic solvent. The target mass balance values and nitrate concentration for the aqueous fraction of the MCU strip effluent stream are given in Table 2-3. For the all runs, MCU solvent fabricated by the CS&T section for the Strip Effluent Feed Tank (SEFT) mixing testing was used[8]. The CS&T fabricated solvent did not contain BOBCalixC6 due to the limited quantity available and the cost of the material. This component was not anticipated to have an impact on SRAT processing based on earlier testing. The SEFT testing also identified a fluorescent dye to allow easier tracking of the solvent. This dye, Risk Reactor DFSB-K43, was used in this testing.

Table 2-1: Target Composition for SB4 Simulant

Element	Wt%	Ratio To Fe
Al	12.75	0.743
Ba	0.147	0.009
Ca	1.49	0.087
Ce	0.172	0.010
Cr	0.175	0.010
Cu	0.065	0.004
Fe	17.15	1
K	0.987	0.058
La	0.075	0.004
Mg	0.964	0.056
Mn	4.36	0.254
Na	16.20	0.945
Ni	3.22	0.188
Pb	0.158	0.009
Si	1.23	0.072
Th	0.031	0.002
Ti	0.012	0.001
U	7.65	0.446
Zn	0.099	0.006
Zr	0.208	0.012

*Based on projections from Lilliston[6]

Table 2-2: Target Supernate Chemistry and Solids Concentration

Parameter	Baseline Wash
Density (g/mL)	1.0542
Na (M)	1.1044
NO_2 (M)	0.4620
NO_3 (M)	0.2381
OH (M)	0.2668
Cl (M)	0.0010
SO_4 (M)	0.0220
F (M)	0.0041
CO_3 (M)	0.0496
AlO_2^{-2} (M)	0.0190
$C_2O_4^{-2}$ (M)	0.0074
PO_4^{-3} (M)	0.0013
Insoluble Solids (wt%)	15.67
Total Solids (wt%)	21.62

Table 2-3: MCU Aqueous Fraction Mass Balance Values for the Maximum Case

Species	Strip Effluent to DWPF	Additive Used
Water (lb/hr)	252.8	Water
$CsNO_3$ (lb/hr)	0.0988	$CsNO_3$
HNO_3 (lb/hr)	0.016	HNO_3
Total (lb/hr)	252.9	
NO_3 (M)	0.003	

Mercury will be contained in the sludge to be processed at DWPF. It must be reduced below 0.45 wt% to meet DWPF processing criteria. Previous runs, as well as SB4 sludge-only flowsheet runs to date, have used 1 wt% Hg based on a dried solids basis. This amount was also used in this set of runs for consistency. Noble metals at levels equivalent to previous testing were added to determine representative hydrogen generation from the inclusion of the ARP and MCU stream. Table 2-4 contains the target concentrations, which represent an upper limit based on the projected compositions for SB4.

Table 2-4: Target Levels of Noble Metals Used in Testing

Noble Metal	Wt% in Total Solids
Ag	0.00024
Pd	0.0120
Rh	0.0220
Ru	0.0810

Table 2-5: Solvent Used in Testing#

Component	wt % by Mass
Modifier Cs-7SBb	29.87%
Trioctylamine	0.12%
Isopar® L	69.70%
Dye	0.31%
Bob Calix*	0%

* Calix[4]arene-bis(t-octylbenzo-crown-6)
#WPT Solvent 081905 #2

2.2 Procedures and Equipment Used in Testing

The testing was performed at the Aiken County Technology Laboratory (ACTL) using a four-liter glass kettle to represent the SRAT and other glassware to functionally replicate the DWPF SRAT condenser system. The SRAT kettle is connected to the SRAT Condenser, the Mercury Water Wash Tank (MWWT), and the Formic Acid Vent Condenser (FAVC). A take-off line from the MWWT is used to drain condensate from the system, and it is collected in a bottle that represents the Slurry Mix Evaporator Condensate Tank (SMECT). For purposes of this report, the condensers and MWWT are referred to as the offgas components. The SRAT and FAVC condenser liquid temperatures were set at 25ºC and 4ºC respectively based on DWPF-E recommendation.

A one-liter glass vessel was used as the MCU aqueous feed tank. A MasterFlex pump with a Tygon feed line was connected to the bottom of the one-liter vessel to dispense the aqueous stream to the SRAT at a controlled rate. Due to the small quantities of solvent needed in testing and the desire to feed the solvent at a constant rate, a syringe pump was used to feed the MCU solvent. The solvent was fed using a syringe pump through a feed line tied in to the aqueous line. A sketch of the experimental setup is given as

Figure 2-1, while Figure 2-2 provides a picture of the equipment set-up.

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

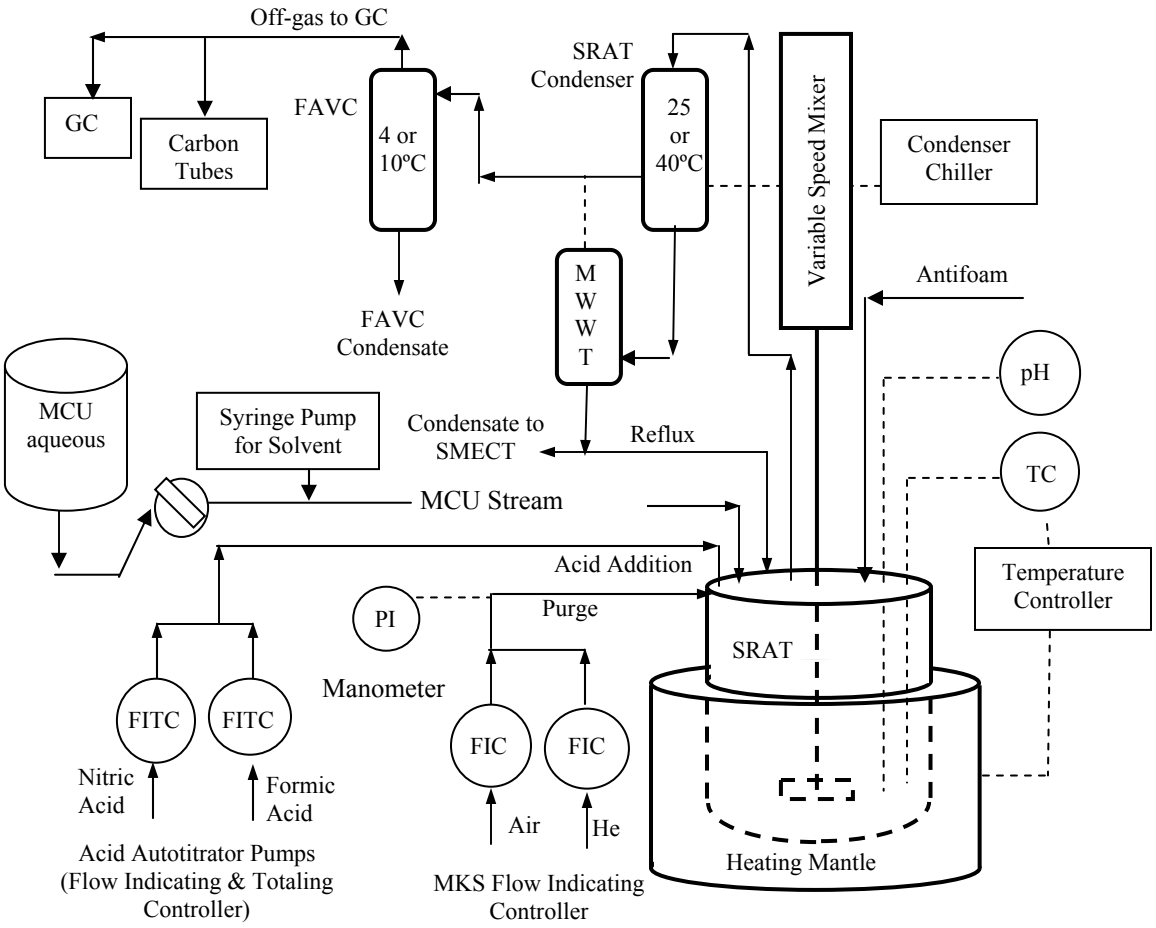


Figure 2-2: 4-L SRAT Vessel Set-up

*Note the photo shows ARP in the feed tank, not the clear MCU aqueous feed.

SRAT processing parameters are summarized in Table A - 1. Each SRAT test followed a run plan specifically written for that run.[9,10,11,12,13, 14,15,16,17,18] The runs were performed in accordance with Procedure ITS-0094 ("Laboratory Scale Chemical Process Cell Simulations") of Manual L29. Slurry pH and offgas were measured during the experiments using in-line instrumentation. For the gas analysis, helium was introduced at a concentration of 0.5% of the total air purge as an inert tracer gas so that total amounts of generated gas and peak generation rates could be calculated. During the runs, the kettle was monitored to observe reactions that were occurring during each run to include foaming, air entrainment, rheology changes, and offgas carryover. When the dyed solvent was used, the kettle and condensers were periodically checked with a black light to determine the location of the dyed solvent. The condensers were continuously monitored to determine if any organics were collecting. Observations were recorded in laboratory notebook WSRC-NB-2004-00030 and are discussed in Section 3.0.

The split of the acids was determined using the redox equation currently being used in DWPF processing[19] and no adjustments were made for the MCU organics. The redox target ($Fe^{2+}/\Sigma Fe$) was 0.2. To account for the reactions and anion destructions that occur during processing, assumptions about nitrite destruction, formate destruction, and nitrite to nitrate conversion were made based on the data seen in previous ARP and MCU testing[3]. The same values were used in all runs for consistency and are provided in Section 3.0. To minimize the lag time between runs and since all of the fresh sludge used in each set of five runs was the same, the composition of the sludge (fresh sludge plus heel remaining from previous run) was calculated for each run. The heel composition from run SB4-29 was used to estimate the sludge composition. This

minimized the number of samples to be analyzed and eliminated the 2-3 day delay in processing to analyze the SRAT receipt sample.

The sludge was heated to 93ºC with 200 ppm IIT 747 antifoam added at 40ºC. Concentrated nitric acid (50-wt%) was added first and then formic acid (90-wt%) was added to acidify the sludge and perform neutralization and reduction reactions during processing. After formic acid addition was completed, 500 ppm IIT 747 antifoam was added before going to boiling. The SRAT contents were concentrated by removing the equivalent volume of the acids, antifoam, and any flush water. After concentration, MCU addition was initiated. The goal was to add the MCU stream at the rate equivalent to the boiling rate. Therefore, continuous removal of the condensate was performed through the MWWT as the MCU was added. Once the entire MCU stream was added, heat to the kettle was removed. Once the SRAT temperature dropped below 80ºC, the SRAT product was pumped down to a heel of ~600 mL. Even during cooldown, the air flow through the carbon tubes continued to allow any organic vapors to be captured.

At the completion of all five runs in each set, the SRAT kettle and the condensers were triple rinsed with hexane to recover any remaining organic. Hexane was chosen in previous testing as it provided the best recovery. The rinses for each component were submitted as one sample.

A leak check was performed between runs and a post leak check was performed on the SRAT equipment to determine if any of the seals had degraded or connections had become loose during SRAT processing. A reduction in the recovery from the pre-run leak check would have indicated a potential loss of organic vapor or SRAT generated gases.

2.3 Analytical

Analyses for this task used guidance of Analytical Study Plan (ASP), SRNL-GPD-2005-00001[20]. Sample request forms were used for samples to be analyzed, and analyses followed the guidelines and means of sample control stated in the ASP for the task. A unique lab identification number was assigned to each sample for tracking purposes. Analyses were performed using approved analytical and Quality Assurance procedures.

Samples of the sludge simulant (batch 020606 and 030606), the SRAT products, the offgas condensate, and from the rinsing of the SRAT equipment were taken for analyses. The MCU aqueous simulant was not analyzed because of the simplicity of its make-up (see Table 2-3). Analyses were performed by the Process Science Analytical Laboratory (PSAL), the PS&E section, and Analytical Development (AD). The discussion of the analytical methods is subdivided into organic analyses and all other methods for analyses.

2.3.1 Organic Analyses Methods

Since completing the organic material balance was the primary objectives of this testing, a significant quantity of samples were submitted for organic analyses. AD analyzed the SRAT product, condensate samples, and the vessel rinses to quantify the concentrations of Isopar®L and modifier. PSAL analyzed the SRAT product, to quantify the concentrations of anions, cations, and solids along with measuring the density and pH.

Gas Chromatography/Mass Spectrometry (GC/MS) was used for semivolatile organic compound (SVOC) analysis. Isopar®L results were reported from this method. Analytical separations were carried out on a Hewlett Packard 6890 gas chromatograph, equipped with a 30 meter DB-XLB column, with 0.18 mm diameter and 0.18 micron film thickness. Quantification was performed using a Hewlett Packard 5973 mass selective detector. The mass spectrometer tuning was confirmed within 24 hours prior to each measurement using perfluorotributylamine. When necessary, samples were prepared by extracting each sample with a

known amount of hexane. If the sample was a vessel rinse that already contained hexane, this additional extraction was not necessary and only a spike was performed. Isopar®L quantitation was performed using a mixed isotopic dilution standard of nonane-d20, decane-d22, and dodecane-d26. The one sigma error associated with each value was ±20%.

High Pressure Liquid Chromatography (HPLC) was used for modifier measurements. Aqueous samples were prepared for analysis by liquid/liquid extraction. Table 2-6 presents the individual measurements, the average measurement and associated standard deviation, as well as the relative recovery numbers. The average recovery for a single extraction with hexane of the modifier from water was 98 %, and the average recovery for a single extraction with hexane of the extractant from water was 95%. For the modifier extracts, the HPLC method used a normal-phase cyano column with 96% hexane and 4% isopropanol as the mobile phase. Table 2-7 summarizes the conditions for the modifier analysis. The one sigma error associated with each value was ±10%.

Table 2-6: Recovery Studies for HPLC Measurements

Reported Value	Modifier
Measurement 1 (mg/L)	244
Measurement 2 (mg/L)	247
Measurement 3 (mg/L)	246
Measurement 4 (mg/L)	247
Measurement 5 (mg/L)	239
Average Measurement (mg/L)	245
Measurement Standard Deviation (mg/L)	3.0
%Relative Standard Deviation	1.4
Expected Value (mg/L)	250
% recovery	98

Table 2-7: HPLC Modifier Isocratic Elution Conditions

Method	Conditions
Solvent system	Hexane/Isopropanol
t_o to t_1 = 8.0 min	96%/4%
Normal Phase Cyano Column	Agilent Technologies Zorbax CN
Oven temperature	Ambient
Flow-rate	1 ml/min
UV	230 nm
injection volume	5 µL
Retention time for Extractant	6.3 min
Linear calibration curve	12 mg/L to 240 mg/L, r^2 = 0.999
Modifier	
R.S.D. (%) (n=7)	0.73

The offgas from the runs was collected on activated carbon passive sampling tubes to adsorb any organics given off during the process. All carbon tubes were prepared by PS&E personnel and then the prepared samples were analyzed by PS&E personnel. Each activated carbon passive sampling tube consists of two activated carbon beds. The “front” bed , closest to the sampling point, is surrounded by glass wool, and the “back” bed, approximately half as much activated carbon as the “front”, is between glass wool and a foam

filter. First, the tubes are "cracked" by breaking the end off the tube to allow extraction of the activated carbon. Cracking involves scoring the tubes using a tungsten carbide blade to facilitate a clean break. After breaking the tube, the carbon is extracted with a combined technique. Initially, the glass wool is removed with a metal hooking device and placed into the appropriate vial. Then most of the front carbon bed will flow freely from the tube and can be poured into the appropriately labeled vial. However, in some cases, the metal hook is required to free the carbon from the glass wool previously separating the two beds. The dividing glass wool is then pulled from the tube and placed into the same preparation vial. For desorption purposes, both sets of glass wool and the front carbon bed are all placed into the "front" vial. The remaining carbon bed and any foam filters at the back of the tube are then extracted in a similar manner and placed into the "back" vial.

After all the tubes are "cracked" and the carbon is extracted, each vial is desorbed. Desorption is necessary to remove all organics from the activated carbon into a solvent for analysis. Carbon disulfide was the solvent used for every sample analyzed in accordance with NIOSH method 1501. Eight milliliters of carbon disulfide were added to each "front" vial, and two milliliters were added to each "back" vial. The added solvent volume for each vial was based on prescribed addition amounts for the mass of activated carbon in each bed. After adding the carbon disulfide, each vial was slightly shaken and then allowed to sit for at least thirty minutes prior to analysis (again, according to NISOH method 1501).

To perform the analysis, an aliquot of each sample of approximately one milliliter is removed from the sample vial and placed into an appropriately labeled autosampler vial. The final portion of sample preparation consisted of determining the analytical sequence for the GC Mass Selective Detector. The analytical sequence is the sequence in which the samples are analyzed allowing for establishment of calibration curves to ensure analytical accuracy. The analytical sequence was as follows: standards (to establish the calibration curve), six samples, another set of standards, six samples, etc (see Table 2-8). This sequence is continued until all samples and a final set of standards are analyzed.

Table 2-8: Analytical Sequencing for Carbon Tube Analysis

1	Solvent Blank	7	Solvent Blank	13	Sample 6	19	2500ppm Standard*
2	1ppm Standard	8	Sample 1	14	Solvent Blank	20	Sample 7
3	10ppm Standard	9	Sample 2	15	1ppm Standard*	21	Sample 8
4	100ppm Standard*	10	Sample 3	16	10ppm Standard*	22	Sample 9
5	1000ppm Standard*	11	Sample 4	17	100ppm Standard*	23	Sample 10
6	2500ppm Standard*	12	Sample 5	18	1000ppm Standard*	24	etc.

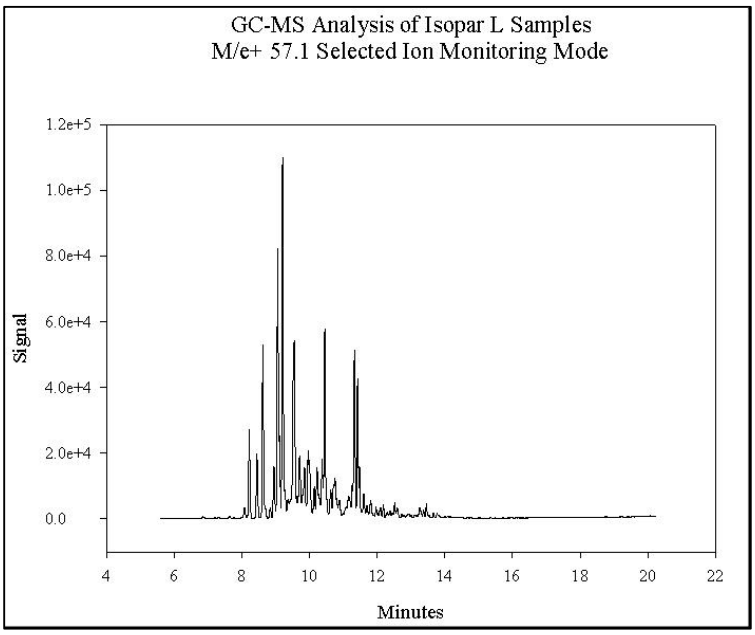
All analyses were performed using an Agilent 6890 series Gas Chromatograph and 5973n series Mass Selective Detector. The chromatography column was a 5% diphenyl/ 95% dimethylsiloxane stationary phase column. Injection volume was set to 1.0 microliters with an autosampler and autoinjector. The Mass Selective Detector utilized the Selective Ion Monitoring (SIM) mode for detection of Isopar®L. Table 2-9 lists the instrument parameters for the analysis of Isopar®L.

Table 2-9 Isopar®L GC-MS Method at ACTL

Gas Chromatograph	Agilent 6890
Mass Spectrometer	Agilent 5973n
Capillary Column	5% Phenyl, 95% Dimethyl Silicones (DB-5MS)
Column Length	30 meters
Column Inner Diameter	0.25 mm
Film Thickness	1.0 µm
Carrier Gas	He, constant flow
Carrier Flow Rate	1 mL/minute
Injection Method	Split 1:10
Injector Temperature	300 ºC
Initial Oven Temperature	100 ºC (hold for 4 minutes)
Temperature Ramp	8.0 degrees/minute to 230 ºC
GC Run Time	20.25 minutes
GC-MS Interface Temperature	280 ºC
Detector	Quadrupole Mass Spectrometer
Ionization	Electron Impact
GC-MS Mode	Selective Ion Monitoring
Ion Monitored	m/e 57
Autosampler Rinse Agent	Methanol

Isopar®L is comprised of a multitude of aliphatic branch-chained hydrocarbon compounds that all share the sample distillation fraction point. Therefore, analysis with Gas Chromatography must take into account the total sum of all peaks resulting from the Isopar®L. The results for these analyses were all reported as the summation of the integrated peak areas of each peak within a given retention period. Figure 2-1 shows a chromatogram of Isopar®L, with a retention period of 8 minutes to 14 minutes (nominally).

Figure 2-3: Chromatograph of Isopar®L



Analytical sequences typically consisted of approximately thirty to fifty samples and standards. The calibration curve for the five standards is calculated using a weighted linear regression using one over the square of the concentration as the weighting factor. This weighting factor keeps the fitted equation as close to the low concentration standard as to the high concentration standard. The typical r^2 for the calibration curve is 0.999 or greater. The concentration of Isopar®L in each set of six samples is calculated based on the set of standards that immediately follows the six samples to insure that changes in the instrument response factor are accounted for in the results.

The sample results for Isopar®L are adjusted for the desorption fluid volume of either eight milliliters or two milliliters of carbon disulfide. All results were reported in conjunction with the other thirty-five samples analyzed for a given process (three sets of six tubes per run, with front and back samples for each tube equals thirty-five). Finally, a sum total of all results for a given run are reported to determine the recovery of Isopar®L in the offgas.

2.3.2 Other Analytical Methods

The sludge simulant was analyzed by the PSAL, PS&E, and AD. The PSAL determined the chemical composition (both elemental and anions), total and dissolved solids, calcined solids, density, and pH. To determine the elemental composition of the sludge simulant, duplicate samples of the simulant were calcined at 1100°C and then dissolved using Na_2O_2/NaOH and lithium metaborate ($Li_2B_4O_7$/$LiNO_3$) fusions. The dissolved sludges were analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) to determine the concentration of each cation. For the anion analyses, sludge preparation involved weighted dilution of the two samples before introduction into the Ion Chromatograph (IC). The total and dissolved solids were measured by the PSAL on two aliquots, and the insoluble and soluble solids fractions were calculated from the results. Due to the rapid settling problems with the sludge simulant, confirmatory total solids analyses were performed by PS&E on each batch of sludge once it was added to the kettle. Rheology of this type of sludge simulant had been previously performed[21] and, therefore, was not repeated in this series of testing.

The PS&E performed an autotitration using a 0.1M HCl solution and 25:1 sample dilution to determine the base equivalents at pH 7 and 5.5 for the sludge simulant.

AD analyzed the sludge simulant to determine the total inorganic carbon (TIC) for input to the acid addition calculation. The Immobilization Technology Section (ITS) Acid Demand TIC method was performed on three samples, with one of the samples diluted 20:1 to try to match the nominal TIC operating region.

The SRAT products from all runs were analyzed by the PSAL and PS&E. A complete analysis (similar to what was done for the SRAT receipt sample) was performed on the SRAT products. This allowed for comparison to the sludge-only SRAT product and to the coupled feed SRAT product from earlier incorporation strategies.

Gases were monitored during the runs using a high-speed Agilent model 3000 micro GC to provide insight into the reactions occurring during processing and to determine whether a flammable mixture was formed. As mentioned above, helium was used as a purge gas tracer. Two calibration standards were used to calibrate the GCs before each run to attempt to bound the quantities of the expected gases. The concentrations of these calibration standards were 0.5 mol% helium, 0 and 1 mol% hydrogen, 0 and 21% oxygen, 55 and 66.5 mol% nitrogen, 2.5 mol% nitrous oxide, 0.5 mol% carbon monoxide, 20 mol% carbon dioxide, and 0 and 10 mol% nitric oxide. Calibration checks were performed before and after each run.

The GC is self-contained and is designed specifically for fast and accurate analysis. The GCs have 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, nitrogen, oxygen, nitric oxide and carbon monoxide) 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 60ºC, while the Channel B column is set at 70ºC. The fourth 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 system, Cerity. 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 minutes.

3.0 RESULTS

The data from the testing and any observations will be discussed in this section. This section has been divided into seven subsections. Section 3.1 discusses the analyses of the sludge simulant, and the necessary inputs for the acid calculation. Section 3.2 discusses the general observations about processing, the pH profiles, and the generated gas data. Section 3.3 discusses the material balance for the organics. Section 3.4 discusses the condensation of Isopar®L in DWPF condensers. Section 3.5 discusses the distribution of Isopar®L components found in FAVC deposits. Section 3.6 discusses the accumulation of Isopar®L and modifier in MWWT, SRAT condenser and FAVC. Finally, Section 3.7 discusses the SRAT product characterization.

3.1 Sludge Simulant

Two fifteen liter batch of sludge simulant were fabricated using the same recipe as used in earlier testing. The SB4 simulant was identified as SB4-020606 and SB4-030606, where the number indicates the date of fabrication. Table 3-1 presents the analysis of the two SB4 simulants.

The two simulants were similar in composition. When compared to the target composition given in Table 2-1, the aluminum concentration is slightly lower than the target ratio to iron in batch SB4-020606 and slightly higher in batch SB4-030606, while potassium and sodium are lower. The lower sodium and potassium were expected since the target assumes some amount of the insoluble forms of these materials and insoluble forms were not added to try to match the target. It was felt that matching the supernate chemistry was more important for the SRAT testing, and any additional sodium added to try to match the target may have impacted the supernate chemistry. Nickel (along with calcium and iron for the SB4-030606 batch) is slightly above the target composition, but is lower than the projection when the ratio to iron is considered. Although the elemental compositions are slightly different than the target, this should not impact the results of this testing since the data is being compared internally for the impact of MCU addition and all runs used the same simulant composition. When compared to the supernate and solids targets in Table 2-2, the anion targets were met. However, Batch SB4-020606 was low in total and insoluble solids and Batch SB4-030606 was low in total solids and slightly high in insoluble solids, but the total and insoluble solids were slightly higher than targeted. This would be conservative from a SRAT processing perspective since increased solids would increase the acid demand and the yield stress of the sludge.

Table 3-1: Sludge Simulant, wt %, calcined solids basis

Sludge Batch	SB4-020606	SB4-030606
Sample ID	06-SB4MCU-649	06-SB4MCU-781
Al	15.4	16.6
Ba	0.154	0.150
Ca	1.76	2.00
Cr	0.181	0.171
Cu	0.074	0.065
Fe	21.8	20.3
K	0.932	0.828
Mg	1.03	0.98
Mn	5.51	5.16
Na	12.7	12.2
Ni	3.77	3.42
P	0.037	0.033
Pb	0.011	<0.02
S	0.300	0.282
Si	1.39	1.32
Sn	0.058	0.031
Ti	0.020	0.018
Zn	0.128	0.119
Zr	0.287	0.335
NO_2	1.70E4	1.675E4
NO_3	1.065E4	9.865E3
SO_4	1.29E3	1.315E3
C_2O_4	716.5	775.0
Cl^-	323.5	354.5
Total Solids	20.83%	21.87%
Insoluble Solids	15.02%	16.21%
Soluble Solids	5.81%	5.66%
Calcined Solids	14.66%	15.34%
Density (g/ml)	1.168	1.166
pH	13.1	12.7
TIC (mg/kg)	770	770*

* Analysis from sludge batch SB4-020606 was used, not the measured result.

The actual sludge, noble metals, and Hg masses added to each SRAT run are given in Table A - 1. The inputs to the acid addition calculation are given in Table 3-2. Sludge batch SB4-020606 was used for runs SB4-36 to SB4-40 and sludge batch SB4-030606 was used for runs SB4-43 to SB4-47. Note that in all ten runs, the total and insoluble solids input was measured on each of the five aliquots and these solids numbers were used in the acid calculation, not the PSAL measured total and insoluble solids. If the PSAL solids numbers had been used in the acid calculation for run SB4-36, it would have led to the addition of 0.7% more acid and 3.4% more trim chemicals. If the PSAL solids numbers has been used in the acid calculation for run SB4-43, it would have led to the addition of 0.8% less acid and 4% less trim chemicals. Because of the variability of total and insoluble solids from multiple aliquots pulled from the same batch, the aliquot solids numbers were used for the acid calculation.

Table 3-2: SRAT Receipt Measured Inputs, Assumptions for Acid Calculation, and Target Acid Addition Amounts

Sludge Batch	SB4-020606	SB4-030606
Input Parameter	SB4-36	SB4-43
Nitrite (mg/kg)	17,000	16,750
Nitrate (mg/kg)	10,650	9,865
TIC (mg/kg)	770	770
Base Eqv. (M)	0.409	0.405
Mn (wt% in total solids)	3.874	3.613
Total Solids (wt%)	21.53	21.03
Density (g/ml)	1.1678	1.166
Calcine Factor	0.7037	0.7009
Hg (% in total Solids)	1.00	1.00
Nitrite to Nitrate Conversion, %	10.70	10.70
Formate Destruction, %	21.60	21.60
SRAT Receipt Mass, g	2684.7	2691.9
Acid Stoichiometry, %	150.00	150.00
Redox Target, $Fe^{+2}/\Sigma Fe$	0.20	0.20
Ratio of Formic to Total Moles	0.889	0.882
Target Nitric Acid (ml)	40.24	41.67
Nitric Acid Molarity (M)	10.573	10.573
Target Formic Acid (ml)	143.84	139.14
Formic Acid Molarity (M)	23.59	23.67
Acid/Liter of Slurry	1.630	1.588
Target Solids in Product (wt%)	24.57	24.01

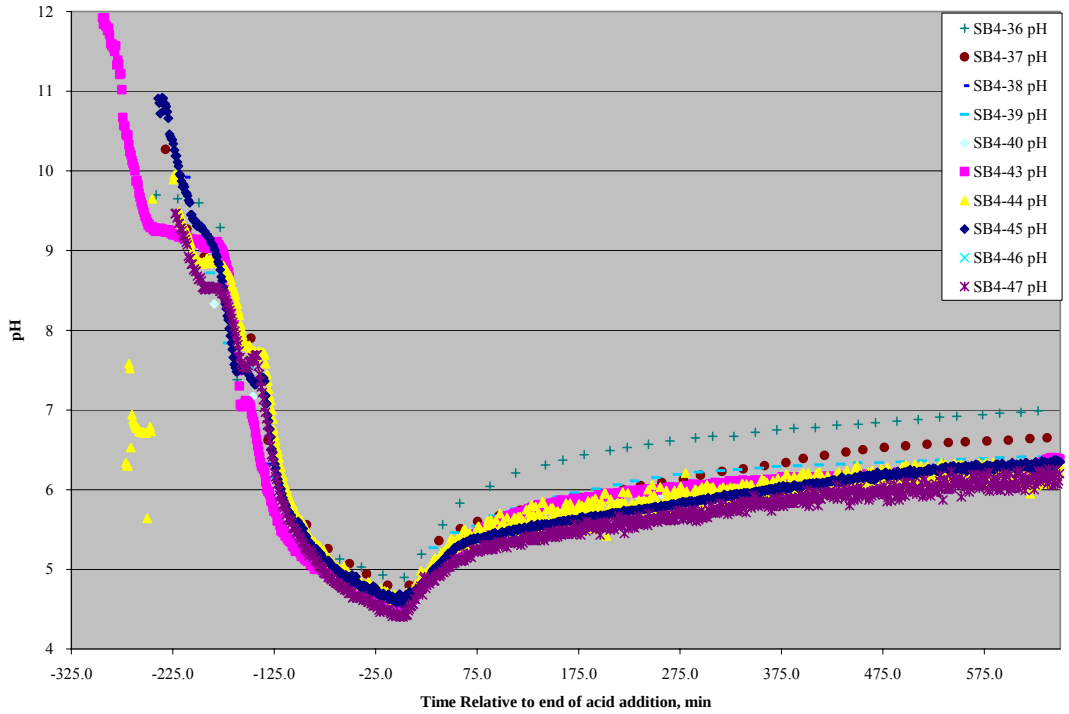
3.2 SRAT Processing Including Offgas Data

The runs were performed at the ACTL in a chemical hood and the parameters for the runs are given in Table A - 1. Each run was started by adding the sludge simulant to the kettle and the noble metals were added. Heating was initiated and 200 ppm antifoam was added with an equal mass of water. Nitric acid was added first and then formic acid. After the completion of acid addition, 500 ppm antifoam was added and the vessel was ramped to boiling. Once boiling was initiated, the SRAT contents were dewatered/concentrated to bring the sludge to the target solids concentration.

MCU addition was initiated after dewatering was completed. The target solvent level was 50 mg/kg for runs SB4-36 to SB4-40 and 125 mg/kg for runs SB4-43 to SB4-47. As mentioned above, the MCU aqueous was in one vessel and was added with a MasterFlex pump, while the solvent was added using a syringe pump. The feed rate of the MCU aqueous was set to match the boil-up rate, while the organic addition rate was calculated and set based on the estimated time to add the aqueous. Feeding the MCU took ~10 hours. Mixing and heating of the slurries during the SRAT cycles were not an issue. No problems with foaming or processing of the slurries were evident.

The pH was measured throughout the SRAT cycle. Figure 3-1 provides the pH plots for all the runs.

Figure 3-1: pH Plots for All Runs



When the pH plots from this set of MCU runs is compared to the previous MCU runs and to SB4 sludge only runs, the plots are very similar. The SB4-36 and SB4-43 (the first run in each set) pH data were higher than the other runs in each set of 5 runs. This is likely due to overestimating the acid requirement with a heel present. Also, the low pH data at the beginning or run SB4-44 is likely due to a problem with the pH probe that fixed itself during the acid addition. The pH probe was replaced after the run because of this anomaly. Therefore, it does not appear that the salt stream addition will have a significant impact on the pH during SRAT processing at least at the acid addition level tested.

As mentioned in Section 2.2, hydrogen, oxygen, nitrogen, carbon dioxide, nitric oxide, and nitrous oxide were measured throughout the runs using GCs. Figure A - 1 through Figure A - 10 of Attachment A contain plots of the GC data from the individual runs. Generally, carbon dioxide was the first detected gas followed by the generation of nitrous oxide and/or nitric oxide. As these gases were generated, oxygen was depleted slightly. After acid addition was completed, oxygen concentration began to increase and additional peaks of carbon dioxide, nitrous oxide, and nitric oxide were detected. This first peak occurred when the SRAT contents started to boil and the second peak occured approximately mid-way through dewatering/concentration. For the most part, little gas was generated three hours past the end of acid addition in all of the runs.

Figure 3-2 through Figure 3-4 contain plots of the carbon dioxide, nitrous oxide, and nitric oxide, respectively, from this set of runs. Only a portion of the SRAT cycle data is shown since the gases are not generated throughout the run.

Figure 3-2: Measured CO_2 Concentration

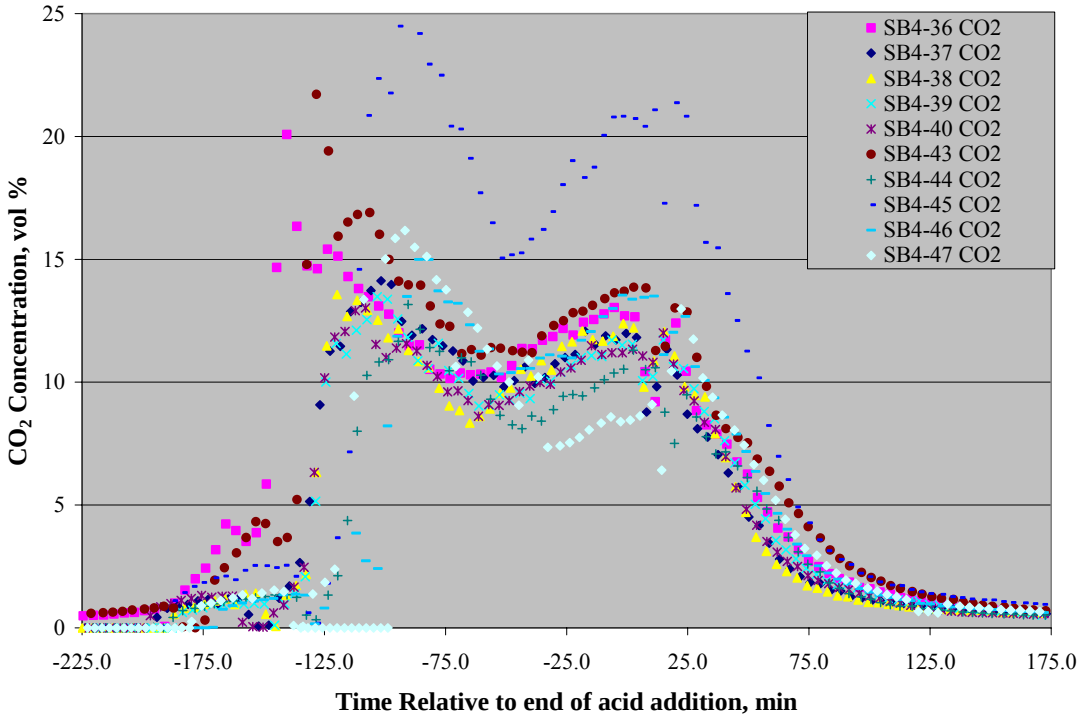


Figure 3-3: Measured N_2O Concentration

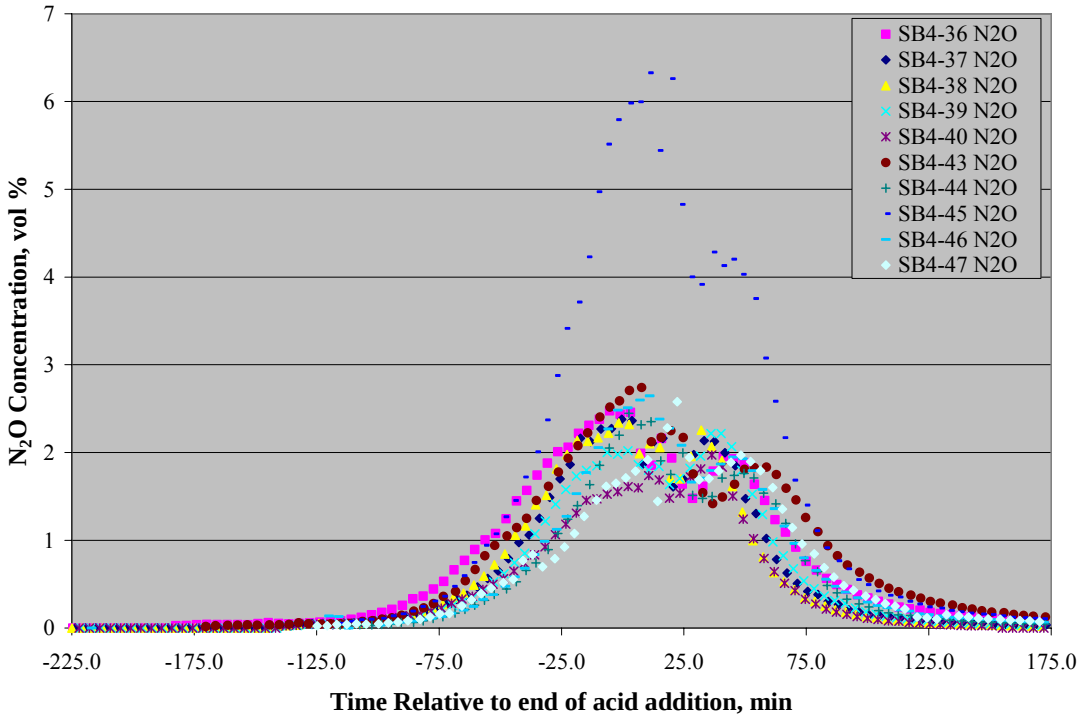
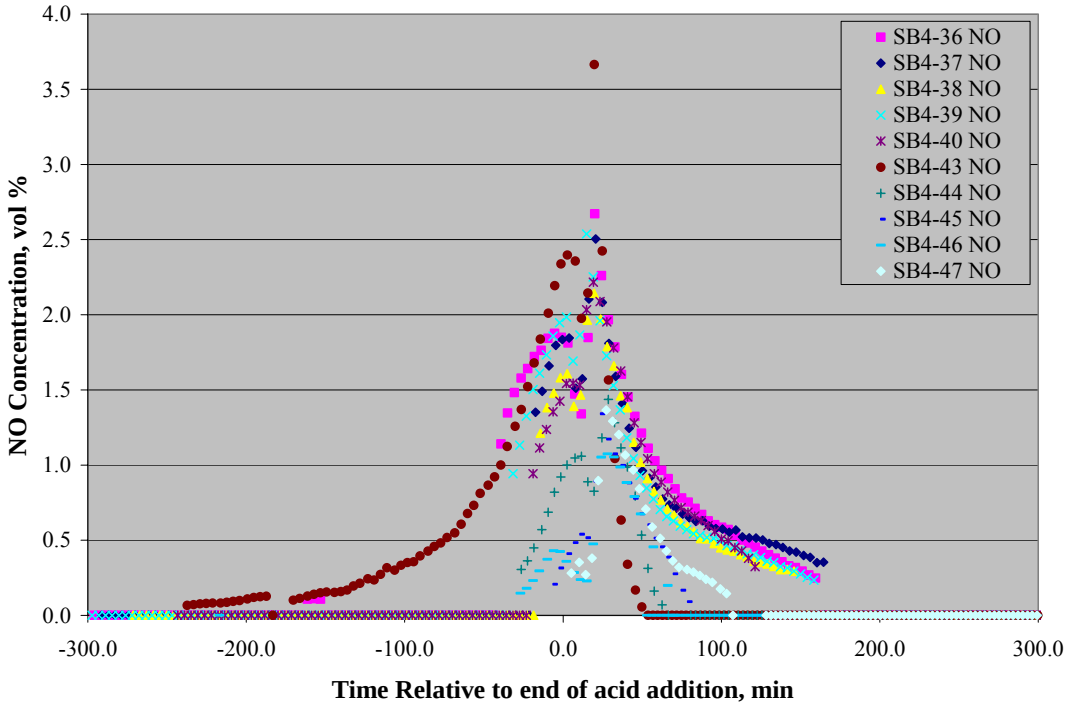


Figure 3-4: Measured NO Concentration



The timing and concentrations were fairly consistent from run to run. All of the runs had two peaks of nitric oxide that occurred at relatively the same time, which was just before the end of acid addition and as dewatering/concentration started. The timing and relative size of the peaks were consistent with previous ARP/MCU testing[3] and with SB4 sludge only testing of this simulant[21].

Table 3-3 presents the observed peak off gas concentrations for each run. Significant variation was seen in the peak concentration from run to run during this set of testing. In most cases, nitric oxide and nitrous oxide peak rates were higher for the MCU runs than for the SB4 sludge only runs. If other runs that were run at higher acid stoichiometries are considered from SB4 sludge only testing[21], then the peak generation rates are more consistent. Therefore, while the peak generation rates may be slightly different for processing with MCU, the rates still appear to be within the range of variation expected for the SRAT processing window for SB4.

Table 3-3: Peak Off Gas Generation Rates (Volume %)

RUN	Peak CO_2	Peak NO	Peak N_2O	Peak H_2
SB4-36	20.1	2.7	2.5	0.004
SB4-37	20.0	8.9	2.7	0.005
SB4-38	13.6	2.1	2.3	0.015
SB4-39	13.5	2.5	2.2	0.025
SB4-40	13.0	2.2	2.0	0.039
SB4-43	21.7	3.7	2.7	0.000
SB4-44	13.2	1.4	2.4	0.004
SB4-45	26.5	1.3	6.3	0.006
SB4-46	15.0	1.1	2.7	0.004
SB4-47	16.2	1.4	2.6	0.004

3.3 Organic Data

The results from the organic analyses were closely monitored and adjustments were made to the testing protocol as necessary to try to gain a better material balance closure. The testing protocol/equipment configuration included the following:

- Teflon lines were reduced or shortened to minimize the area available for solvent plating/coating;
- The solvent line and aqueous/solvent line were sloped downward toward addition port to minimize separation of lower density solvent.
- A triple rinse of each component was incorporated to ensure that all of the MCU organic was being removed;
- System fittings were tightened to obtain an outlet flow within 5% of the target to minimize the potential for solvent loss;
- MCU solvent containing a fluorescent dye was used to provide a visual tracer for the solvent; and
- Between run flushing of the equipment with an air purge to try to capture any vaporized Isopar®L.

The organic samples were divided into three primary groupings. The first set included samples of the SRAT product and condensates generated during processing. The second set included the solvent rinse solutions that were generated from rinsing the SRAT equipment to remove any organic that adhered to the equipment surfaces. The final grouping included the carbon tubes that were installed downstream of the FAVC to capture any gaseous organic species exiting the offgas system.

The first set of samples included the SRAT product, the condensate or SMECT samples collected during MCU addition, and the FAVC samples. This set also included the MWWT sample which was pulled only after the last of the five runs. This set of samples required extraction by AD to determine the concentration of MCU organics present. Data from SVOC analyses for Isopar®L are contained in Table 3-4, while the HPLC data for modifier are contained in Table 3-5.

The second set samples were prepared by rinsing the drained equipment with hexane to extract any residual solvent remaining. This set of solvent rinse samples did not require extractions by AD since they already contained hexane as the rinse solvent. The equipment rinses were identified as follows (with an explanation of the equipment included):

1) MWWT Rinse - MWWT.
2) FAVC Rinse - the FAVC and offgas line from the SRAT condenser, the carbon tube holder and the offgas line from the FAVC to the GC and carbon tubes
3) SRAT Condenser Rinse - SRAT condenser and off gas line from the SRAT kettle.
4) SRAT Vessel Rinse - SRAT vessel, lid, and attached glassware.

Analytical data from SVOC for Isopar®L are contained in Table 3-4, while the HPLC data for modifier are contained in Table 3-5.

To better estimate the actual solvent that was added to the system, the syringe pump and the feed line were also rinsed to determine the amount of solvent remaining in the syringe and in the feed line. The data from the syringe rinses is given in Table 3-6.

Table 3-4: Concentration of Isopar®L as Measured by SVOC, mg/kg

Solvent Concentration	50 mg/kg					125 mg/kg				
Sample	SB4-36	SB4-37	SB4-38	SB4-39	SB4-40	SB4-43	SB4-44	SB4-45	SB4-46	SB4-47
MWWT	N/A	N/A	N/A	N/A	0.11	N/A	N/A	N/A	N/A	<0.2
MWWT rinse	N/A	N/A	N/A	N/A	3.60	N/A	N/A	N/A	N/A	87.00
SRAT Dewater	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.2	<0.2	<0.2
SRAT product	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.2	<0.2	<0.1
	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2	<0.1	<0.2	<0.2	<0.1
	N/A	N/A	N/A	N/A	<0.1	<0.2	<0.2	<0.2	<0.2	<0.1
	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	<0.1
SMECT condensate*	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2
	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.2
	<0.2	<0.2	<0.1	<0.1	0.10	<0.1	<0.1	<0.1	<0.1	<0.1
FAVC	0.32	0.19	0.27	0.12	0.12	0.60	0.40	0.40	0.50	<0.2
SRAT condenser rinse	N/A	N/A	N/A	N/A	0.85	N/A	N/A	N/A	N/A	<1.0
FAVC rinse	N/A	N/A	N/A	N/A	0.27	N/A	N/A	N/A	N/A	1.60
SRAT vessel glassware rinse	N/A	N/A	N/A	N/A	0.58	N/A	N/A	N/A	N/A	<1.0
SRAT vessel rinse	N/A	N/A	N/A	N/A	0.70	N/A	N/A	N/A	N/A	<1.0

Notes: N/A – Sample not taken.
* The SMECT condensate is taken in three bottles and, thus, has three samples for analysis.
The one sigma error associated with each value was ±10%.

Table 3-5: Concentration of Modifier as Measured by HPLC, mg/kg

Solvent Concentration	50 mg/kg					125 mg/kg				
Sample	SB4-36	SB4-37	SB4-38	SB4-39	SB4-40	SB4-43	SB4-44	SB4-45	SB4-46	SB4-47
MWWT	N/A	N/A	N/A	N/A	73	N/A	N/A	N/A	N/A	86
MWWT rinse	N/A	N/A	N/A	N/A	454	N/A	N/A	N/A	N/A	2500
SRAT Dewater	<1	2.6	2.1	25.0	13	<1	8.4	5.3	15	16
SRAT product	5.9	5.3	7.2	5.0	4.2	19	20	16	20	15
	5.8	5.0	6.6	6.3	6.2	19	20	16	21	16
	N/A	N/A	N/A	N/A	6	19	20	16	21	23
	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	36
SMECT condensate*	<1	1.8	2.0	4.7	4.6	<1	3.6	7.7	7.9	8
	1.7	2.9	3.4	5.1	3.9	8.0	8.1	12	10	10
	4.8	5.3	5.3	6.7	4.7	14	14	15	15	11
FAVC	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SRAT condenser rinse	N/A	N/A	N/A	N/A	145	N/A	N/A	N/A	N/A	494
FAVC rinse	N/A	N/A	N/A	N/A	<1	N/A	N/A	N/A	N/A	12
SRAT vessel glassware rinse	N/A	N/A	N/A	N/A	1.5	N/A	N/A	N/A	N/A	3
SRAT vessel rinse	N/A	N/A	N/A	N/A	<1	N/A	N/A	N/A	N/A	22

Notes: N/A – Sample not taken.
* The SMECT condensate is taken in three bottles and, thus, has three samples for analysis.
The one sigma error associated with each value was ±10%.

Table 3-6: Syringe and Tubing Rinse Data for Isopar®L and Modifier, mg/kg

RUN ID	LOCATION	50 mg/kg	125 mg/kg
Isopar®L	Syringe	16,000	75,000
	Tubing	770	21,000
Modifier	Syringe	6,249	4,800
	Tubing	1,174	1,681

The carbon tubes, were prepared as indicated in section 2.3.1. Preparation included carbon disulfide extraction of the carbon tubes. A total of 18 carbon tubes were generated in each run, with 6 tubes being used at a time to collect the offgas. The tubes were changed roughly every 4 - 4 ½ hours during MCU addition. The 18 carbon tubes were analyzed as individual tubes. During the analysis of the carbon tubes from earlier runs, it was noticed that drift in the Isopar®L concentration was occurring over time. By interspersing standards throughout the run, the impact of the drift was minimized and more accurate Isopar®L numbers were obtained. Table 3-7 and Table 3-8 present the data from the analysis of the carbon tubes. Figure A - 11 through Figure A - 12 show the plots of the individual carbon tube measurements. Some variation was seen from tube to tube within a set and also from set to set. Typically higher concentrations of Isopar®L were found on the middle sets of carbon tubes (middle of SRAT cycle).

Table 3-7: Isopar®L Data from Carbon Tubes (50 mg/kg solvent), g

In Process Sample	SB4-36	SB4-37	SB4-38	SB4-39	SB4-40
Tubes 1 - 6	0.0001	0.0037	0.0169	0.0232	0.0137
Tubes 7 – 12	0.0336	0.0268	0.0315	0.0258	0.0209
Tubes 13 – 18	0.0240	0.0221	0.0208	0.0228	0.0285
Total	0.0577	0.0526	0.0692	0.0718	0.0631

Table 3-8: Isopar®L Data from Carbon Tubes (125 mg/kg solvent), g

In Process Sample	SB4-43	SB4-44	SB4-45	SB4-46	SB4-47
Tubes 1 - 6	0.0447	0.0447	0.0421	0.0608	0.0701
Tubes 7 – 12	0.0706	0.0770	0.0738	0.0744	0.0860
Tubes 13 – 18	0.0684	0.0563	0.0559	0.0533	0.0482
Total	0.1837	0.1780	0.1717	0.1885	0.2042

The information from tables Table 3-4 through Table 3-8, along with the associated masses/volumes of the sample, were used to determine the material balance around the system for Isopar®L and modifier for each run. Table 3-9 and Table 3-10 presents both the mass and relative percent of Isopar®L found in each sample or within each location in the SRAT system.

In the case of Isopar®L, very little was found in the SRAT system. More than 99% of the Isopar®L quantified exited though the offgas system and was collected on the carbon tubes. The modifier recovery was 78.9% in the 50 mg/kg runs and 94.1% in the 125 mg/kg runs. Recovery here is defined as the percent of fed solvent that is quantified through mass balances. In both sets of runs, more Isopar®L was found in the condensate and SRAT product than was found in the vessel rinses. Typically, the rinse solutions contained higher concentrations of Isopar®L than the actual condensate solutions. Most of the samples were less than the detection limit of the SVOA analysis, so the detection limit was used for quantification calculations (i.e. if the analysis was <1 mg/kg, 1 mg/kg was used).

Table 3-9: Isopar®L Material Balance SB4-36 to SB4-40 (50 mg/kg solvent)

	Vessel Rinses		**Solutions**		**Total**	
	Mass, g	% of Mass	Mass, g	% of Mass	Mass, g	% of Mass
SRAT Condensate		0.00%	0.00133	0.42%	0.00133	0.42%
SRAT Product	0.00004	0.01%	0.00107	0.34%	0.00111	0.35%
Vapor (Carbon tubes)		0.00%	0.31459	99.20%	0.31459	99.20%
FAVC		0.00%	0.00002	0.01%	0.00002	0.01%
MWWT	0.00006	0.02%	0.00001	0.00%	0.00007	0.02%
Condenser	0.00002	0.01%	0.00000	0.00%	0.00002	0.01%
Total Quantified	0.00012	0.04%	0.31702	99.96%	0.31714	100.00%
% recovered						78.9%
Calculated Solvent, mg/kg					**41**	

Table 3-10: Isopar®L Material Balance Runs SB4-43 to SB4-47 (125 mg/kg solvent)

	Vessel Rinses		Solutions		Total	
	Mass, g	% of Mass	Mass, g	% of Mass	Mass, g	% of Mass
SRAT Condensate			0.00124	0.13%	0.00124	0.13%
SRAT Product	0.00006	0.01%	0.00188	0.20%	0.00194	0.21%
Vapor (Carbon tubes)			0.92612	99.46%	0.92612	99.46%
FAVC	0.00004	0.00%	0.00004	0.00%	0.00008	0.01%
MWWT	0.00170	0.18%	0.00001	0.00%	0.00171	0.18%
Condenser	0.00002	0.00%			0.00002	0.00%
Total Quantified	**0.00182**	**0.20%**	**0.92929**	**99.80%**	**0.93111**	**100.00%**
% recovered						94.1%
Calculated Solvent, mg/kg					**120**	

Table 3-11and Table 3-12 provide similar data for the modifier.

Table 3-11: Modifier Material Balance Runs SB4-36 to SB4-40 (50 mg/kg solvent)

	Vessel Rinses		Solutions		Total	
	Mass, g	% of Mass	Mass, g	% of Mass	Mass, g	% of Mass
SRAT Condensate	0.00000	0.00%	0.04804	38.16%	0.04804	38.16%
SRAT Product	0.00008	0.06%	0.06089	48.37%	0.06097	48.43%
Vapor (Carbon tubes)	0.00000	0.00%	0.00000	0.00%	0.00000	0.00%
FAVC	0.00000	0.00%	0.00008	0.07%	0.00008	0.07%
MWWT	0.00819	6.51%	0.00506	4.02%	0.01325	10.52%
Condenser	0.00355	2.82%	0.00000	0.00%	0.00355	2.82%
Total Quantified	0.01183	9.39%	0.11407	90.61%	0.12590	100.00%
% recovered						73.1%
Calculated Solvent, mg/kg					**38**	

Table 3-12: Modifier Material Balance Runs SB4-43 to SB4-47 (125 mg/kg solvent)

	Vessel Rinses		Solutions		Total	
	Mass, g	% of Mass	Mass, g	% of Mass	Mass, g	% of Mass
SRAT Condensate			0.11398	28.66%	0.11398	28.66%
SRAT Product	0.00115	0.29%	0.21957	55.22%	0.22073	55.51%
Vapor (Carbon tubes)						
FAVC	0.00032	0.08%	0.00032	0.08%	0.00064	0.16%
MWWT	0.04875	12.26%	0.00566	1.42%	0.05441	13.68%
Condenser	0.00790	1.99%			0.00790	1.99%
Total Quantified	**0.05813**	**14.62%**	**0.33953**	**85.38%**	**0.39766**	**100.00%**
% recovered						93.8%
Calculated Solvent, mg/kg					**119**	

The modifier recovery was 73.1% in the 50 mg/kg runs and 93.8% in the 125 mg/kg runs. Therefore, the indicated partitioning should be a fairly good indicator of where the modifier will collect in the SRAT system. The data indicate that roughly half of the modifier will remain in the SRAT product. Very little is expected to collect in the FAVC or be emitted from the offgas.

Note that these runs did not include a SME cycle. As a result, DWPF will have a lower concentration of modifier in the melter feed and a higher concentration of modifier in the condensate since more modifier will be steam distilled during SME boiling. A typical DWPF SME cycle will have >40 hours of boiling time compared to the 10 hours of boiling time in these runs. In previous MCU testing with SME processing (no canister decontamination water boil off), the SRAT product was 97 ppm compared to the SME product of 44 ppm. Also, the dewater for the SME was 22 ppm vs. 12 ppm in the SRAT condensate.

3.4 Condensation of Isopar®L in DWPF Condensers

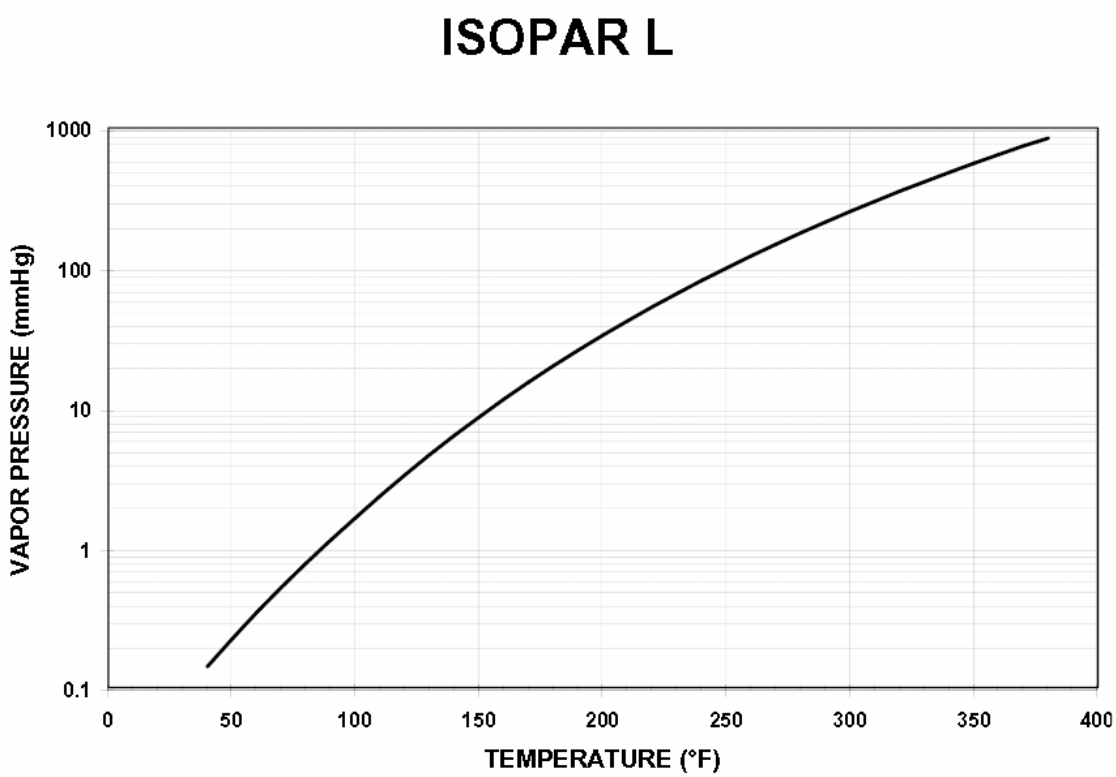
The experiments at both 50 mg/kg solvent and 125 mg/kg both demonstrated that >99% of the Isopar®L exited through the offgas system. This demonstrates that the virtually no Isopar®L is being condensed in the condensers. There could be several reasons, (1) the Isopar®L concentration in the offgas is less than saturation at the condenser liquid temperature, (2) the condensers are inefficient or (3) the offgas is much higher in temperature than the cooling water, or a supersaturated stream (fog) is exiting the condenser. It turns out that the first explanation, (the average Isopar®L concentration is below the saturation value) is valid so no Isopar®L is condensing. Note there could be times that the Isopar®L is above saturation entering the FAVC, for example, just after a slug of solvent is added to the SRAT. After adding a slug, the Isopar®L could exceed saturation and a small fraction of the Isopar®L would condense.

At the FAVC temperature of 4.4 °C, Isopar®L has a vapor pressure of 0.14 mm Hg[22] (1.84E-4 mol Isopar®L/mol of gas). The data is extracted from Figure 3-5. At a solvent concentration of 300 mg/kg, the vapor concentration in the offgas would be 1.84E-4 mol Isopar®L/mol of gas). At solvent concentrations above 300 mg/kg, a second phase of Isopar®L would begin to accumulate in the FAVC condensate (SMECT). Note that this analysis assumes a 10 hour addition time for the MCU aqueous and that the solvent is delivered at the same rate throughout the feed period. If the solvent is actually fed as slugs (we saw this in our testing), there will be times where the Isopar®L will be higher than this average and Isopar®L may accumulate in the FAVC.

Note that the data in Figure 3-5 was fit to the Antoine Equation, an equation often used for predicting vapor pressure. The curve fit had an adjusted r^2 of 0.9999 over a temperature range of 4.4-148.9 °C.

$Log_{10}P^*=7.6525-2024.250/(T+236.762)$, where P = vapor pressure of Isopar®L and T= Temperature, °C

Figure 3-5: Isopar®L Vapor Pressure



Temperature (°F)	Vapor Pressure (mmHg)
40	0.14
50	0.22
60	0.34
68	0.478
77	0.69
100	1.63
150	8.60
200	32.95
250	99.82
300	253.01

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3.5 Distribution of Isopar®L components found in FAVC deposits

Isopar®L is a mixture of straight chained and branch chained hydrocarbons. The composition of Isopar®L that will be used in the MCU solvent is not constant but varies based on the feedstock and degree of hydrocarbon cracking. As a result, some batches are likely to be higher in some components than other batches. In addition, the Isopar®L components entrained in the feed sent to DWPF may not always be the

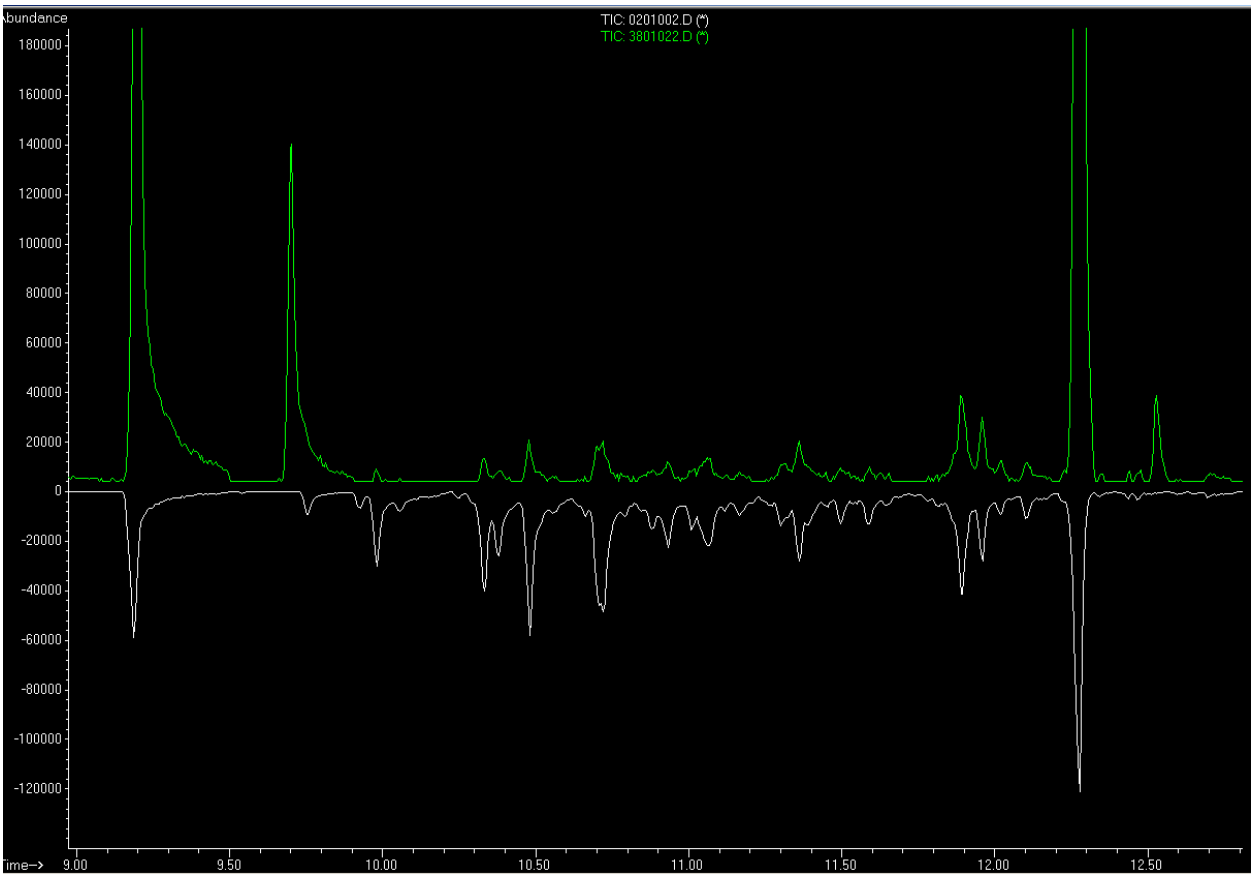
same. The shorter hydrocarbons have a higher vapor pressure and are more likely to evaporate during processing so the entrained solvent may be enriched in the higher boiling fraction of the Isopar®L.

AD analyzed the solvent and compared it to the FAVC Isopar®L deposits. In both samples, 10 hydrocarbons peaks were identified ($C_{10}H_{22}$ to $C_{15}H_{32}$). The 10 peak intensities were compared to determine if the Isopar®L deposits were identical in composition to the original solvent. The original solvent peak intensity was compared to the FAVC deposit peak intensity to determine whether the FAVC deposit had become enriched or depleted in one or more of the Isopar®L components. For example, the ratio of t the $C_{10}H_{22}$ peak for the solvent divided by the peak for the FAVC rinse was 0.062. The ratio of t the $C_{15}H_{32}$ peak for the solvent divided by the peak for the FAVC rinse was 0.553. The conclusion is that the higher molecular weight fraction Isopar®L components are enriched in the FAVC deposits. Although very little of the solvent was deposited in the FAVC (<0.005%), the Isopar®L that was found was enriched in the higher molecular weight and more highly branched hydrocarbon components in the Isopar®L. The data is summarized in Table 3-13 and Figure 3-6.

Table 3-13: Isopar®L Components Ratio of Pure Solvent to FAVC Deposits

Component	Branch Points	Ratio Pure Solvent: FAVC Rinse
$C_{10}H_{22}$	1	0.062
$C_{11}H_{24}$	1	0.070
$C_{12}H_{26}$	1	0.076
$C_{12}H_{26}$	2	0.080
$C_{14}H_{30}$	1	0.240
$C_{14}H_{30}$	4	0.156
$C_{10}H_{22}$	2	0.174
$C_{14}H_{30}$	1	0.415
$C_{12}H_{26}$	4	0.496
$C_{15}H_{32}$	3	0.553

Figure 3-6: Isopar®L Chromatograms from AD GC/MS (Solvent Green, FAVC Rinse White)



3.6 Accumulation of Isopar®L and Modifier in MWWT, SRAT condenser and FAVC

The largest accumulation of Isopar®L was found in the MWWT. Isopar®L found in the MWWT after draining was a small fraction of the quantified isopar, 0.02% in the 50 mg/kg run and 0.18% in the 125 mg/kg run. During testing it was noted that mercury and organic looking deposits accumulated in the horizontal leg between the SRAT condenser and the MWWT. It appeared that material accumulated for several batches before the mass became high enough to move as a slug to the MWWT. It is possible that these accumulations were due to the small diameter tubing and minimal slope of the SRAT condenser drain line. However, it is also possible that this will be the accumulation point for these insoluble organic species in the DWPF. This may lead to a third phase (organic, aqueous and mercury), which may have to eventually be removed.

In comparing the 50 mg/kg run to the 125 mg/kg run, the modifier mass in the MWWT rinse was 6 times higher in the 125 mg/kg run than 50 mg/kg (see Table 3-14). This is higher than the 2.5 times expected. In contrast, the SRAT Condenser modifier mass was 2.2 times higher in 125 mg/kg run than 50 mg/kg, which was closer to expectations. The mass of modifier in the MWWT solution was the same in both sets of runs. No modifier was detected in the FAVC, so the FAVC is unlikely to be an accumulation point for the modifier.

Table 3-14: Modifier in MWWT

	Vessel Rinses		Solutions		Total	
Sample	Mass, g	% of Mass	Mass, g	% of Mass	Mass, g	% of Mass
MWWT, 50 mg/kg	0.0082	6.52%	0.00504	4.01%	0.01323	10.53%
MWWT, 125 mg/kg	0.0486	12.23%	0.00566	1.42%	0.05426	13.66%

3.7 SRAT Product Characterization

A SRAT product sample from each run was submitted for non-organic analysis. The product anion concentrations are given in Table 3-15.

Table 3-15: SRAT Product Anion Concentration (mg/kg)

SRAT Product Anion Concentration (mg/kg)

RUN ID	NITRITE	NITRATE	FORMATE	CHLORIDE
SB4-36	<100	24,944	46,258	494
SB4-37	<100	23,278	46,294	477
SB4-38	<100	24,166	48,221	487
SB4-39	<100	23,944	47,216	473
SB4-40	<100	24,481	49,092	516
SB4-43	264	25,300	43,950	492
SB4-44	<100	27,400	43,350	514
SB4-45	<100	28,300	43,000	500
SB4-46	<100	26,500	44,400	492
SB4-47	<100	25,100	44,900	495
Average	<126	25,341	45,668	494

Note: Analyses performed on weighted dilution of samples.
Results represent an average of two measurements.

The data indicate that the DWPF goal of nitrite destruction to <1000 mg/kg was met in all runs. \Before the testing was initiated and in order to calculate the acid addition amounts, assumptions on the nitrite destruction, nitrite to nitrate conversion, and formate destruction had to be made. The values assumed in the calculations (see Table 3-2) were based on the calculated values from previous MCU/ARP testing. After the testing was completed, the anion concentrations in Table 3-15, along with the mass balance for the runs, were used to calculate the destruction and conversion values all runs. The calculated numbers are given in Table 3-16. Based on the data in Table 3-16, it appears that formate destruction may be slightly impacted by the MCU incorporation.

Table 3-16: SRAT Nitrite to Nitrate Conversions and Formate Destructions

Run ID	Nitrite Destruction	Nitrite to Nitrate Conversion	Formate Destruction	Predicted Redox
SB4-36	100%	24.1%	15.2%	0.184
SB4-37	100%	13.5%	16.9%	0.187
SB4-38	100%	21.5%	13.5%	0.188
SB4-39	100%	18.7%	16.1%	0.184
SB4-40	100%	22.3%	12.4%	0.186
Average SB4-36 to 40	100%	20.0%	14.8%	0.186
SB4-43	98.4%	25.8%	18.5%	0.162
SB4-44	100%	20.9%	17.6%	0.181
SB4-45	100%	23.0%	18.0%	0.167
SB4-46	100%	27.7%	18.2%	0.152
SB4-47	100%	22.2%	17.9%	0.157
Average SB4-36 to 40	99.7%	23.9%	18.0%	0.164
Average all runs	99.8%	22.0%	16.4%	0.175
Pre-Run Assumption*	100%	10.7%	21.6%	0.200
SB4 Sludge Only	95.2%	10.4%	24.3%	NA

*Based on SB4-29 run from previous ARP/MCU testing.

Due to the changes in destruction numbers realized and some variation in the actual acid addition and dewatering numbers in the runs, the acid stoichiometry and redox values changed slightly versus the targets given in Table 3-2. The acid stoichiometry for all runs was within 0.1%.

As mentioned in Section 2.3.2, the SRAT products were calcined at 1100°C in order to prepare the samples for cation analyses. The elements detected in the calcined solids are given in Table 3-17. When the SRAT product composition is compared with the simulant compositions given in Table 3-1, very slight variation is seen. However, the variation is not unreasonable given the sampling methods and analytical uncertainty.

Table 3-17: SRAT Product Elemental Data - Calcined Solids Wt%

Run	SB4-36	SB4-37	SB4-38	SB4-39	SB4-40	SB4-43	SB4-44	SB4-45	SB4-46	SB4-47
Al	14.8	15.1	12.9	14.9	14.8	14.8	14.9	14.5	14.5	12.9
Ba	0.161	0.162	0.161	0.160	0.155	0.152	0.154	0.155	0.154	0.160
Ca	1.67	1.60	1.98	1.63	1.67	1.76	1.85	1.83	1.70	1.73
Cr	0.186	0.180	0.193	0.185	0.183	0.175	0.176	0.176	0.176	0.185
Cu	0.076	0.065	0.076	0.072	0.074	0.072	0.069	0.070	0.074	0.073
Fe	20.9	21.4	21.0	20.0	20.6	21.1	19.9	19.9	20.7	21.5
K	0.782	0.785	0.895	0.871	0.876	0.837	0.932	0.965	0.835	0.863
Mg	1.05	1.03	1.07	1.01	1.00	1.07	0.99	0.99	1.02	1.07
Mn	5.22	5.22	5.15	4.50	4.86	5.33	5.01	4.93	5.11	5.37
Na	13.0	13.8	14.7	13.0	13.0	13.2	12.6	13.4	13.4	13.8
Ni	3.67	3.78	3.73	3.21	3.44	3.64	3.41	3.39	3.56	3.71
P	0.0320	0.0295	0.0310	0.0255	0.0280	0.0330	0.0305	0.0320	0.0310	0.0320
Pb	<0.020	<0.020	0.051	0.055	0.054	<0.020	<0.020	<0.020	<0.020	<0.020
S	0.319	0.325	0.333	0.314	0.318	0.324	0.313	0.324	0.329	0.347
Si	1.40	1.37	1.36	1.33	1.35	1.40	1.34	1.32	1.36	1.36
Ti	0.019	0.017	0.018	0.016	0.016	0.020	0.017	0.018	0.017	0.018
Zn	0.133	0.134	0.142	0.130	0.129	0.129	0.127	0.132	0.131	0.140
Zr	0.264	0.266	0.220	0.252	0.262	0.268	0.279	0.280	0.263	0.274

Note: Two aliquots were removed from the product sample then calcined and analyzed.
Results represent an average of the two measurements.

The total and dissolved solids were measured on the SRAT products from all runs, and the insoluble and soluble solids were then calculated. As mentioned above, the calcined solids were also measured. To complete the physical property analyses, the slurry density and pH were measured. The results are given in Table 3-18. Note that both the PSAL measured total solids and calcined solids are significantly lower than predicted (for example, Run 4-36 predicted total solids is 24.49 wt % versus the measured 22.70 wt %). The predicted solids measurement comes from the PS&E Acid Calculation Spreadsheet. Lower than predicted solids were likely caused by a combination of factors including solids adhering to SRAT vessel, inadequate sampling and the fact that not all reactions are accurately predicted in the acid calculation spreadsheet. Also, sludge total wt % predictions were ~0.7 wt % less as measured by sludge batch SB4-020606 than the individual aliquot measurements used for the acid calculation.

Table 3-18: Physical Property Data for SRAT Products

Run ID	Total Solids (wt%)	Insoluble Solids (wt%)	Soluble Solids (wt%)	Calcined Solids (wt%)	Slurry Density (g/ml)	pH
SB4-36	23.1%	13.8%	9.3%	14.7%	1.17	7.29
SB4-37	22.7%	13.0%	9.7%	14.4%	1.18	7.51
SB4-38	21.8%	11.9%	9.9%	14.0%	1.16	7.21
SB4-39	22.7%	13.1%	9.6%	14.7%	1.15	7.18
SB4-40	23.8%	13.5%	10.3%	15.3%	1.19	7.19
SB4-43	22.7%	13.3%	9.4%	14.7%	1.16	7.34
SB4-44	22.9%	13.4%	9.5%	14.6%	1.16	7.13
SB4-45	22.6%	13.0%	9.6%	14.4%	1.16	7.12
SB4-46	22.7%	13.3%	9.4%	14.5%	1.15	7.05
SB4-47	21.7%	12.2%	9.5%	13.9%	1.15	7.07
Average	22.7%	13.0%	9.6%	14.5%	1.16	7.21

Note: Measured on two aliquots from the same sample. Data reported is an average. Total and dissolved solids were actually measured and insoluble and soluble solids were calculated.

The SRAT products from Runs SB4-43 to SB4-47 were filtered to remove the supernate, so the soluble components could be determined. Relative solubility of the elements was determined by considering the amount of supernate present in the samples and the total amount of the particular element in the SRAT product. The supernate density was determined to be 1.11 g/mL. Table 3-19 presents the supernate data.

Table 3-19: SB4-43 to SB4-47 SRAT Product Supernate % Solubility Data*

Element / Run	SB4-43	SB4-44	SB4-45	SB4-46	SB4-47
Ca	89.5%	85.3%	85.3%	89.8%	92.7%
Cu	0.1%	0.1%	0.1%	0.1%	0.1%
K	139.1%	123.4%	118.5%	135.3%	138.0%
Mg	87.6%	91.4%	92.9%	92.0%	88.3%
Mn	60.5%	71.5%	78.5%	71.7%	71.4%
Na	103.6%	111.4%	103.6%	109.7%	104.9%
Ni	0.0%	0.1%	0.1%	0.2%	0.2%
P	1.9%	1.9%	1.8%	1.9%	1.8%
S	39.5%	38.6%	36.4%	35.6%	34.5%
Si	0.6%	0.9%	1.0%	1.0%	1.1%

*Al, B, Ba, Cd, Cr, Fe, Li, Nd, Pb, Ti, Tl, Zn, Zr below detection limits

The SB4-43 to SB4-47 SRAT product supernate was analyzed by ICP-ES to determine the relative solubility of the above species. In general, the soluble species were consistent with other SRAT runs and with the anticipated SRAT chemistry. As expected, K and Na were completely soluble, while both Ca and Mg became very soluble during SRAT processing likely due to the creation of formate species. The metals Al, B, Ba, Cd, Cr, Fe, Li, Nd, Pb, Ti, Tl, Zn, Zr all had solubility in filtrate below the detection limit, consistent with previous SB4 sludge only simulant testing[21]. One of the objectives of SRAT processing is to reduce the Mn^{+4} to Mn^{+2} during SRAT processing with a goal of 40% reduction. Mn reduction was more than targeted

and higher than the sludge only run at an equivalent acid level but less than previous ARP/MCU testing[21]. The S solubility was consistent with previous SB4 sludge only testing more so than with previous MCU/ARP testing. Although not shown, aluminum and iron were almost completely insoluble, which is consistent with predicted SRAT chemistry.

4.0 CONCLUSIONS

A total of ten 4-liter SRAT runs were performed to meet the objectives of the testing. The first series of five tests evaluated the organic portioning and mass balance for the addition of 50 mg/kg solvent. The second series of five tests evaluated the organic portioning and mass balance for the addition of 125 mg/kg solvent. A solvent concentration of 50 mg/kg is close to the nominal concentration anticipated in the effluent from the Salt Waste Processing Facility (SWPF).

No significant findings were noted related to typical SRAT processing parameters (nitrite destruction, hydrogen generation, mercury reduction, offgas concentration, nitrite to nitrate conversion, Mn reduction, pH profiles, or foaming, etc.) due to the MCU addition, based on these lab-scale experiments. As was mentioned in earlier reports, slight differences in rheology along with nitrite and formate destruction were observed; however, the differences at this point do not appear to have a significant impact on processing. One significant change is that no refluxing will be needed post acid addition, unless it is needed for mercury stripping. This may lead to improved steam distillation of the mercury.

Almost all (> 99%) of Isopar®L added exited via the offgas system. This is because at both 50 mg/kg and 125 mg/kg solvent, the average Isopar®L concentration in the offgas is below the saturation vapor pressure so no Isopar®L condensed at the FAVC outlet temperature of 4 °C. However, if a slug of solvent is fed to the SRAT, the Isopar®L concentration in the offgas could exceed the saturation vapor pressure of Isopar®L. During this time, some Isopar®L components would condense. Isopar®L was found to collect in both the MWWT and the FAVC to a very small extent (i.e., <1% of the total Isopar®L in each case). Of this small quantify, appreciably more Isopar®L was found in the vessel rinses versus the actual condensate samples implying that the material was coating surfaces as opposed to becoming soluble in the condensate. The starting solvent concentration did not appear to have a direct impact on the amount condensed in the SRAT system.

The modifier was steam distilled from the SRAT (approximately half of the modifier was in the SRAT product). The rest (approximately half) collected in the SRAT condenser, the SMECT, and the MWWT. Very little modifier was found in the FAVC with only one run indicating ~0.1% in the FAVC rinses. A significant fraction (14%) of the modifier was found in MWWT deposits. The deposits might be due to the small scale of the experiments as slugs of mercury and organic seemed to accumulate in the transfer line to the MWWT over several runs before draining. However, if the modifier continues to buildup in the MWWT, the deposits might eventually have to be removed as a third phase in the MWWT may interfere with normal processing in the MWWT.

The recovery of Isopar®L and modifier was >70% at 50 mg/kg solvent and >90% at 125 mg/kg solvent, based on mass balances. The higher recovery in experiments at 125 mg/kg were due to the higher addition rate (further from detection limits) and improvements in testing protocol used only during experiments at 125 mg/kg.

5.0 RECOMMENDATIONS/PATH FORWARD

This MCU testing quantified the small quantities of the MCU organics that would be expected to buildup in the SRAT condenser and process vessel vent system. The use of three sets of carbon tubes gives three estimates for the average of Isopar®L offgas concentration. However, no estimate for the minimum or maximum concentration of Isopar®L in the offgas system was made. This could be quantified by using an online gas chromatograph with an organic column throughout the SRAT processing. In addition, future testing should:

- Consider the use of two hydrocarbons such as decane ($C_{10}H_{24}$) and tetradecane ($C_{14}H_{30}$) as a substitute for Isopar®L. The tetradecane, the higher molecular weight Isopar®L component, may lead to conservative deposition information.
- The addition of a SMECT and ammonia scrubber should be considered in future testing. The ammonia scrubber's internals and packing are a likely collection point for solvent deposits.
- Testing at solvent concentrations leading to Isopar®L vapor concentrations above and below the Isopar®L vapor pressure at the FAVC outlet temperature is recommended to determine the impact of a second phase in the FAVC MCU testing.

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ATTACHMENT A. SRAT RUN PARAMETERS, GC, AND CARBON TUBE DATA

Table A - 1: SRAT Run Parameters SB4-36 to SB4-40, g, unless otherwise noted

Parameter	SB4-36	SB4-37	SB4-38	SB4-39	SB4-40	Sum
Sludge Simulant	2,684.7	2,012.0	2,012.1	2,012.0	2,012.2	10,733.0
$AgNO_3$	0.0024	0.0014	0.0016	0.0016	0.0015	0.0085
HgO	6.3272	4.6915	4.6913	4.6913	4.6914	25.0927
$Pd(NO_3)_2*H_2O$	0.4602	0.3416	0.3414	0.3414	0.3416	1.8262
$Rh(NO_3)_3*2H_2O$	2.6152	1.9384	1.9390	1.9388	1.9390	10.3704
$RuCl_3$	1.1376	0.8429	0.8431	0.8431	0.8432	4.5099
Water to dilute/rinse trim chemicals	40.00	40.00	40.00	40.00	40.00	200.00
Total Slurry	2,735.2	2,059.8	2,059.9	2,059.8	2,060.0	10,974.8
Sample Trimmed Sludge	0.00	20.85	20.05	19.80	20.63	81.33
Slurry Mass after sample	2,735.2	2,039.0	2,039.9	2,040.0	2,039.4	10,893.5
SRAT Antifoam	38.30	38.98	38.98	38.98	38.98	194.22
Nitric Acid	52.90	38.30	38.40	38.30	38.30	206.20
Formic Acid	172.60	139.20	138.90	138.00	138.80	727.50
Added Aqueous	2,231.0	2,231.0	2,231.0	2,231.0	2,231.0	11,155.0
Added Organic	0.1347	0.1038	0.1429	0.0948	0.1008	0.5770
Calculated Organic Concentration, mg/kg*	60.38	46.53	64.05	42.49	45.18	51.73
Total In	**5,230.2**	**4,486.6**	**4,487.3**	**4,486.4**	**4,486.6**	**23,177.1**
Total Dewater	145.53	129.06	128.76	129.70	130.30	663.35
SRAT Product PSAL Sample	90.20	219.04	99.61	81.05	97.16	587.06
SRAT Product AD Samples	1,627.7	1,904.3	1,921.7	1,913.0	2,754.8	10,123.5
Total SRAT Product Samples	1,719.9	2,123.3	2,021.3	1,994.1	2,137.3	9,995.9
Removed Aqueous	2,231.4	2,225.9	2,229.0	2,231.5	2,349.8	11,267.6
FAVC Mass Loss	6.2	7.4	5.9	13.8	15.4	48.7
Total Out	**4,103.2**	**4,478.3**	**4,385.0**	**4,369.1**	**5,332.1**	**22,667.7**
Expected Mass Loss (CO_2, NO_x, etc.)	59.28	46.15	46.14	46.18	46.20	243.93
Net Balance	**-1127.0**	**-8.3**	**-102.3**	**-117.3**	**845.5**	**-509.4**
Estimated SRAT Heel after sampling	733.7	733.7	733.7	733.7	0.00	2,934.8
Time Line and Flowrates	**SB4-36**	**SB4-37**	**SB4-38**	**SB4-39**	**SB4-40**	**Average**
Nitric Acid Feed Time, min	54	38	37	39	40	
Formic Acid Feed Time, min	188	148	148	148	146	
Dewater Time, min	38	27	24	30	30	
Total Boiling Time, min	646	642	617	643	635	
Nitric Acid Feed Rate, mL/min	0.768	0.778	0.778	0.778	0.733	
Formic Acid Feed Rate, mL/min	0.780	0.790	0.790	0.790	0.788	
Air Purge, sL/min	0.670	0.677	0.677	0.677	0.677	
Helium Purge, sccm	3.400	3.390	3.390	3.390	3.390	
Inlet Flow, sL	653.198	608.949	591.259	604.186	606.908	
Calculated Offgas Outlet Flow, sL	692.113	674.110	639.330	672.928	853.385	
Formate Destruction (%)	15.24	16.92	13.45	16.12	12.43	14.83
% nitrite conversion remaining in product	24.09	13.48	21.54	18.71	22.29	20.02
Predicted Redox (post run)	0.184	0.187	0.188	0.184	0.186	0.186

* solvent concentration is calculated by dividing the solvent mass by the total aqueous and organic mass and multiplying by 1E6

Table A - 2: SRAT Run Parameters SB4-43 to SB4-47, g (unless note otherwise)

Parameter	SB4-43	SB4-44	SB4-45	SB4-46	SB4-47	Sum
Sludge Simulant	2,691.50	2,012.00	2,012.00	2,012.00	2,012.00	10,739.50
AgNO3	0.0022	0.0016	0.0014	0.0017	0.0017	0.0086
HgO	6.1969	4.6188	4.5838	4.5486	4.5463	24.4944
$Pd(NO_3)_2*H_2O$	0.4512	0.3362	0.3334	0.3313	0.3311	1.7832
$Rh(NO_3)_3*2H_2O$	2.5611	1.9092	1.8945	1.8797	1.879	10.1235
RuCl3	1.1136	0.8299	0.8236	0.8176	0.817	4.4017
Water to dilute/rinse trim chemicals	40	40	40	40	40	200
Slurry Mass after sample	2,741.83	2,059.70	2,059.64	2,059.58	2,059.58	10,980.31
Slurry Mass after sample	2,741.80	2,059.70	2,059.60	2,059.60	2,059.60	10,980.30
SRAT Antifoam	38.38	38.98	38.98	38.98	38.98	194.3
Nitric Acid	54.5	54.5	54.9	39.1	39.1	242.1
Formic Acid	166.9	126.6	127.5	130.2	132.8	684
Added Aqueous	2,231.00	2,231.00	2,231.00	2,231.00	2,231.00	11,155.00
Added Organic	0.2895	0.2868	0.2795	0.2848	0.2795	1.4201
Calculated Organic Concentration, mg/kg*	129.7	128.5	125.2	127.6	125.2	127.3
Total In	**5,232.9**	**4,511.1**	**4,512.3**	**4,499.1**	**4,501.7**	**23,257.1**
Total Dewater	146.6	135.05	135.13	128.01	128.1	672.89
SRAT Product PSAL Sample	84.35	89.7	82.25	89.95	87.03	433.31
SRAT Product AD Samples	1,880.40	1,883.10	1,879.20	1,962.70	2,872.50	10,477.90
Total SRAT Product Samples	1,964.80	1,972.80	1,961.50	2,052.70	2,959.50	10,911.20
Removed Aqueous	2,232.90	2,230.50	2,232.70	2,230.80	2,232.60	11,159.50
FAVC Mass Loss	8.75	13.95	11.81	10.67	27.56	72.74
Total Out	**4,353.1**	**4,352.3**	**4,341.1**	**4,422.2**	**5,347.8**	**22,816.3**
Net Balance	**-879.8**	**-158.8**	**-171.2**	**-77.0**	**846.0**	**-440.8**
Estimated SRAT Heel after sampling	733.7	733.7	733.7	733.7		
Time Line and Flowrates	**SB4-43**	**SB4-44**	**SB4-45**	**SB4-46**	**SB4-47**	**Average**
Nitric Acid Feed Time, min	56	55	55	133	39	
Formic Acid Feed Time, min	180	135	135	23	142	
Dewater Time, min	35	35	26	0.78	29	
Total Boiling Time, min	699	647	649	651	643	
Nitric Acid Feed Rate, mL/min	0.771	0.779	0.779	0.788	0.768	
Formic Acid Feed Rate, mL/min	0.78	0.788	0.788	0.831	0.778	
Air Purge, sL/min	0.671	0.678	0.678	0.678	0.678	
Helium Purge, sccm	3.358	3.391	3.391	3.391	3.391	
Inlet Flow, sL	654.32	609.758	592.032	604.964	607.688	
Calculated Offgas Outlet Flow, sL	692.113	674.11	639.33	672.928	853.385	
Formate Destruction (%)	18.47	17.62	17.99	18.22	17.85	18.03
% nitrite conversion remaining in product	25.81	20.88	22.99	27.75	22.19	23.92
Predicted Redox (post run)	0.162	0.181	0.167	0.152	0.157	0.164

* solvent concentration is calculated by dividing the solvent mass by the total aqueous and organic mass and multiplying by 1E6

Figure A - 1: SB4-36 GC Data

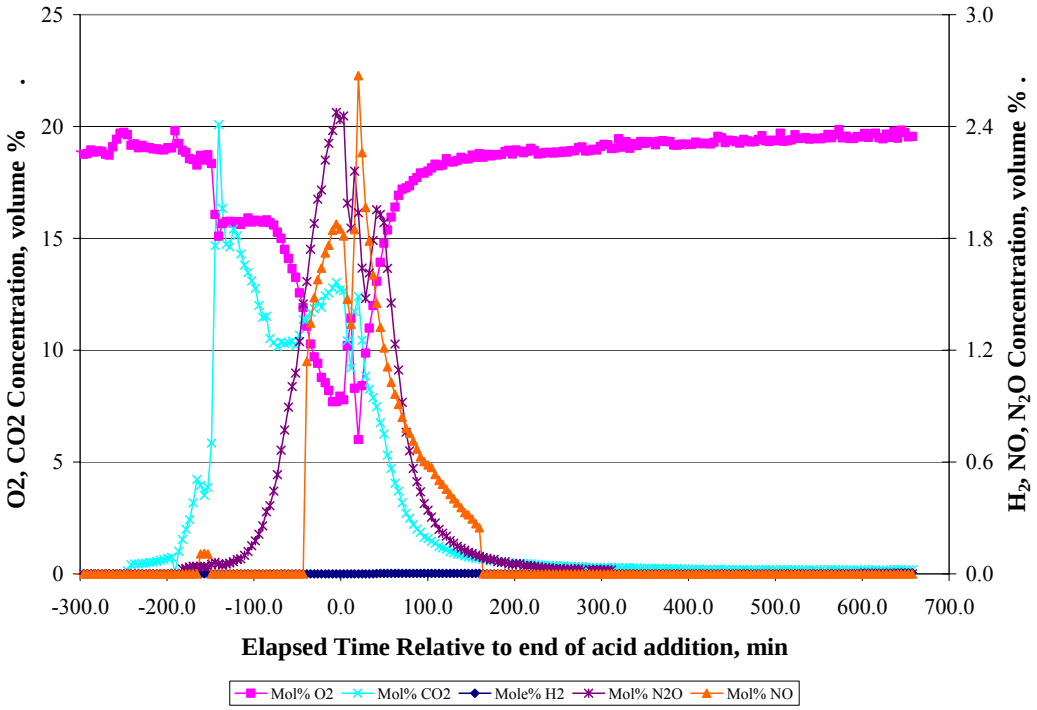


Figure A - 2: SB4-37 GC Data

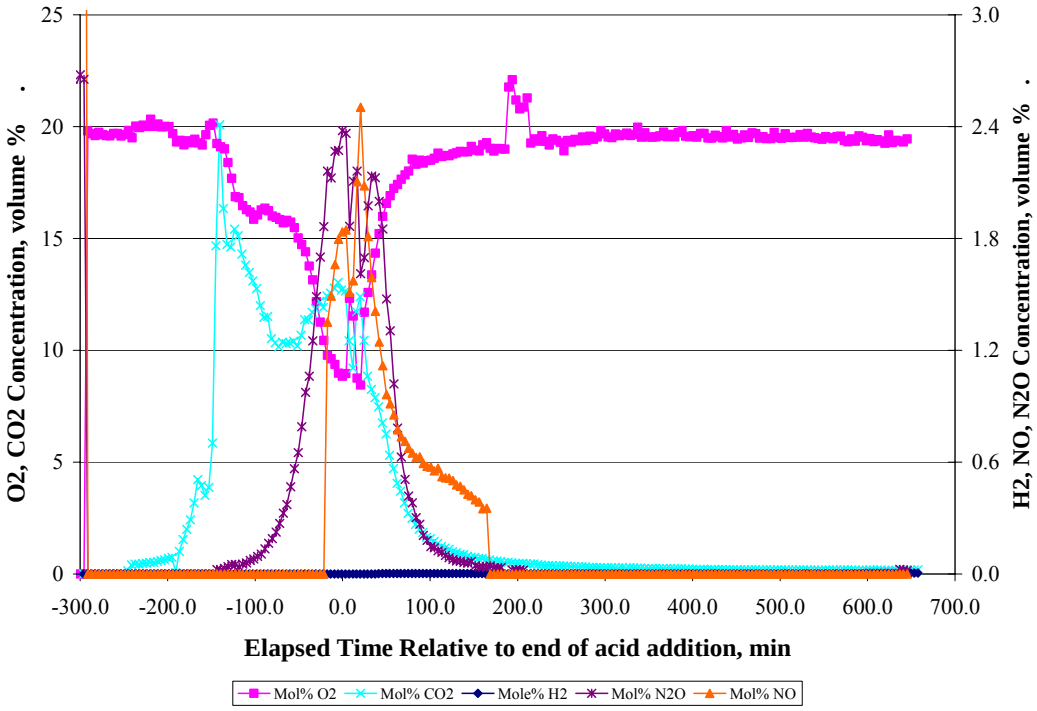


Figure A - 3: SB4-38 GC Data

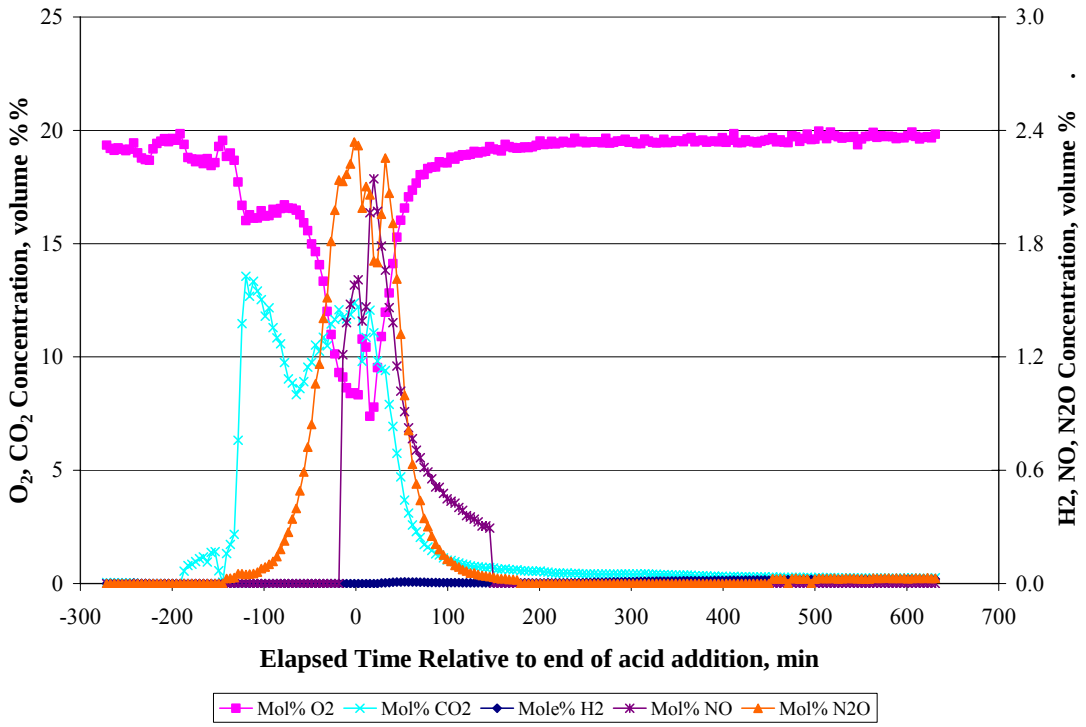


Figure A - 4: SB4-39 GC Data

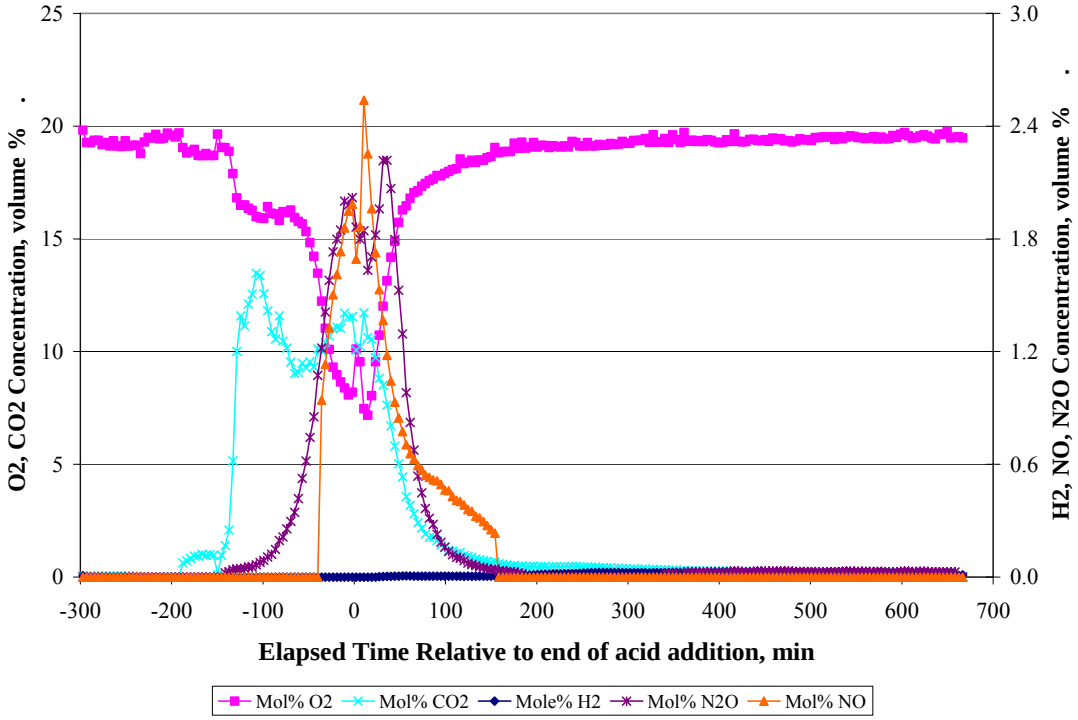


Figure A - 5: SB4-40 GC Data

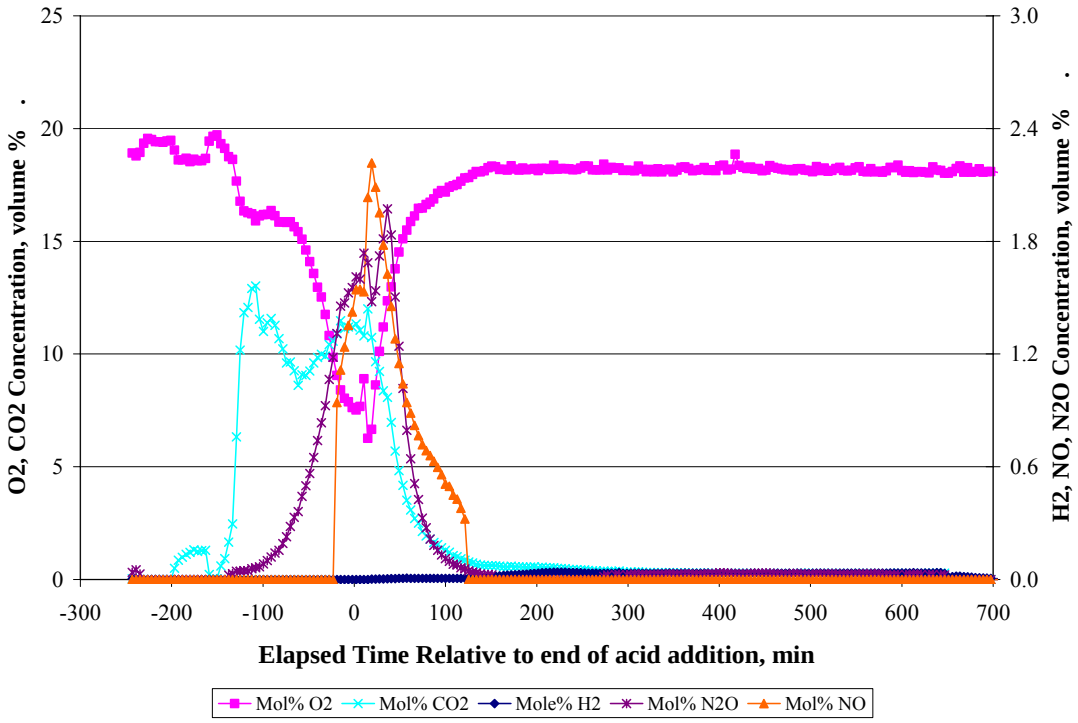


Figure A - 6: SB4-43 GC Data

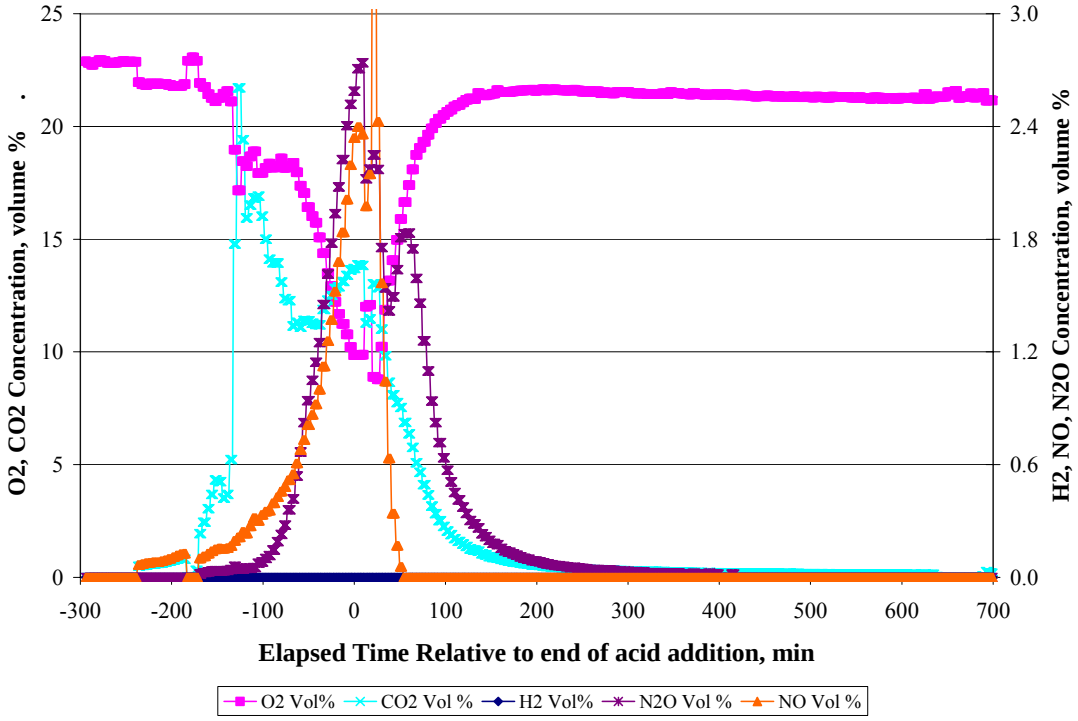


Figure A - 7: SB4-44 GC Data

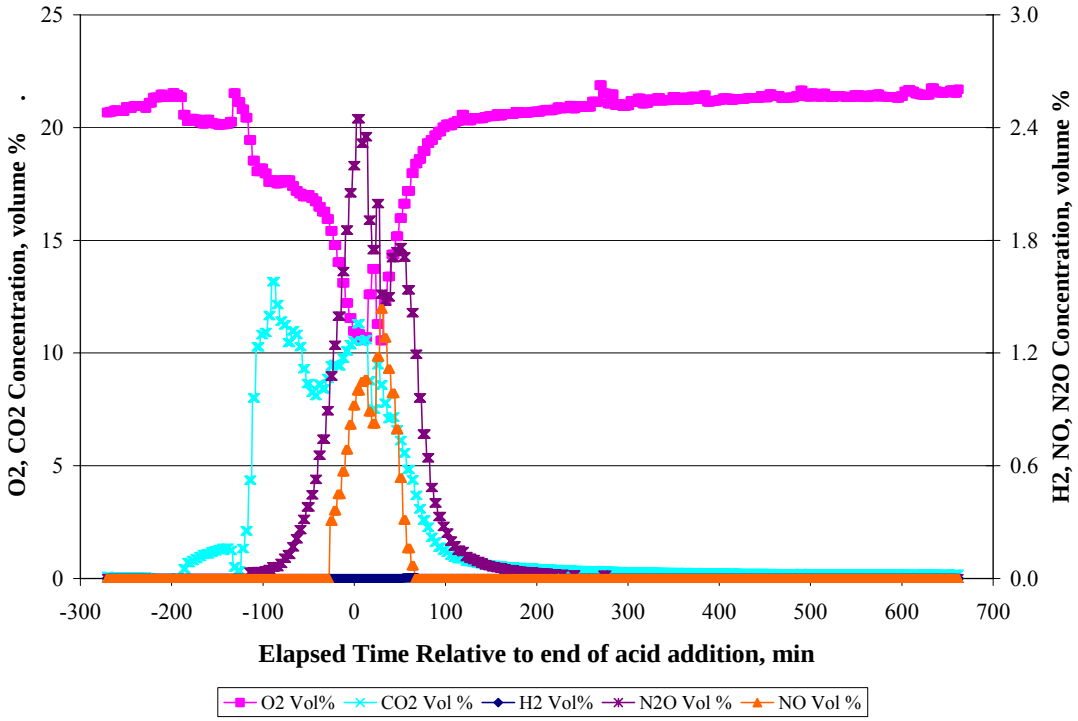


Figure A - 8: SB4-45 GC Data

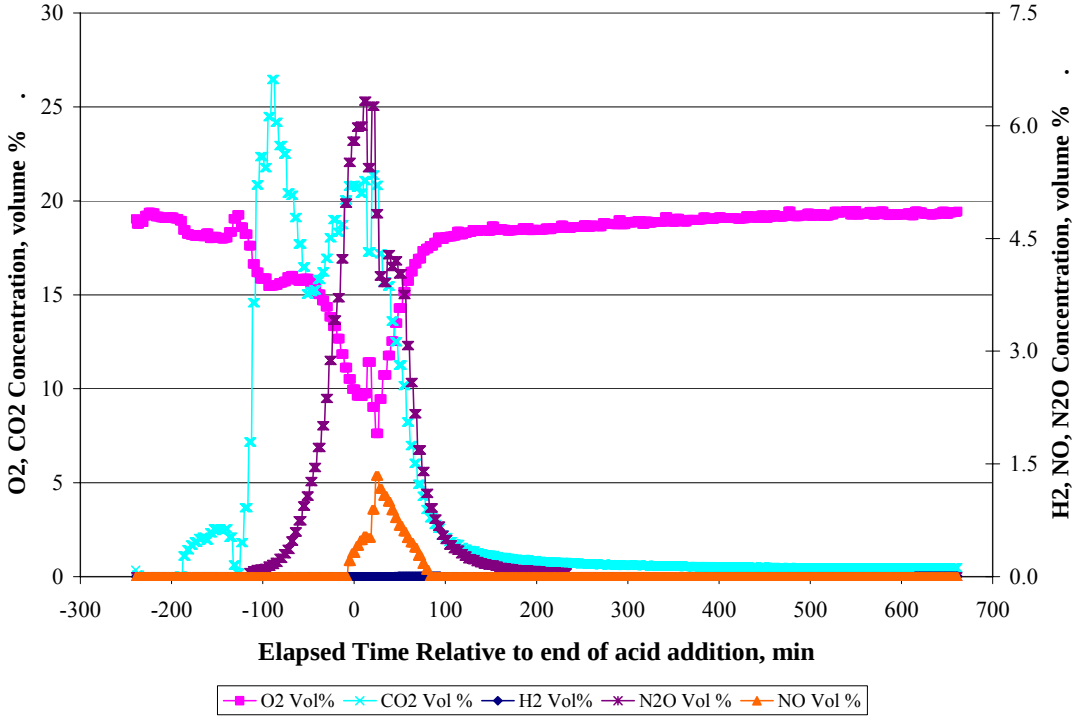


Figure A - 9: SB4-46 GC Data

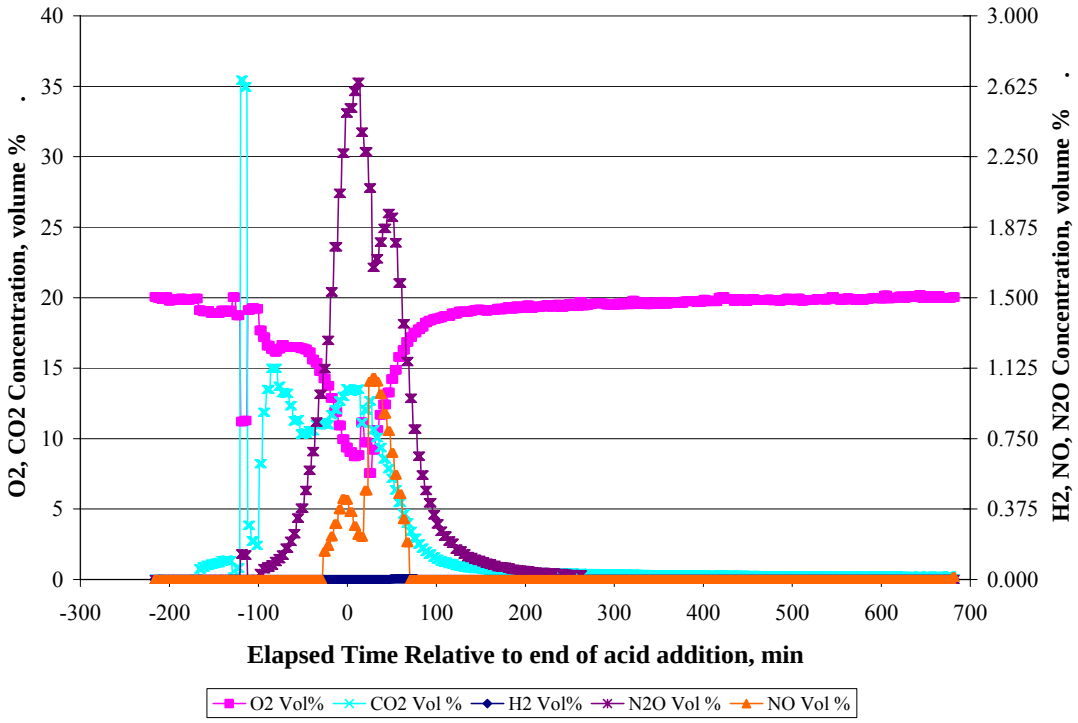


Figure A - 10: SB4-47 GC Data

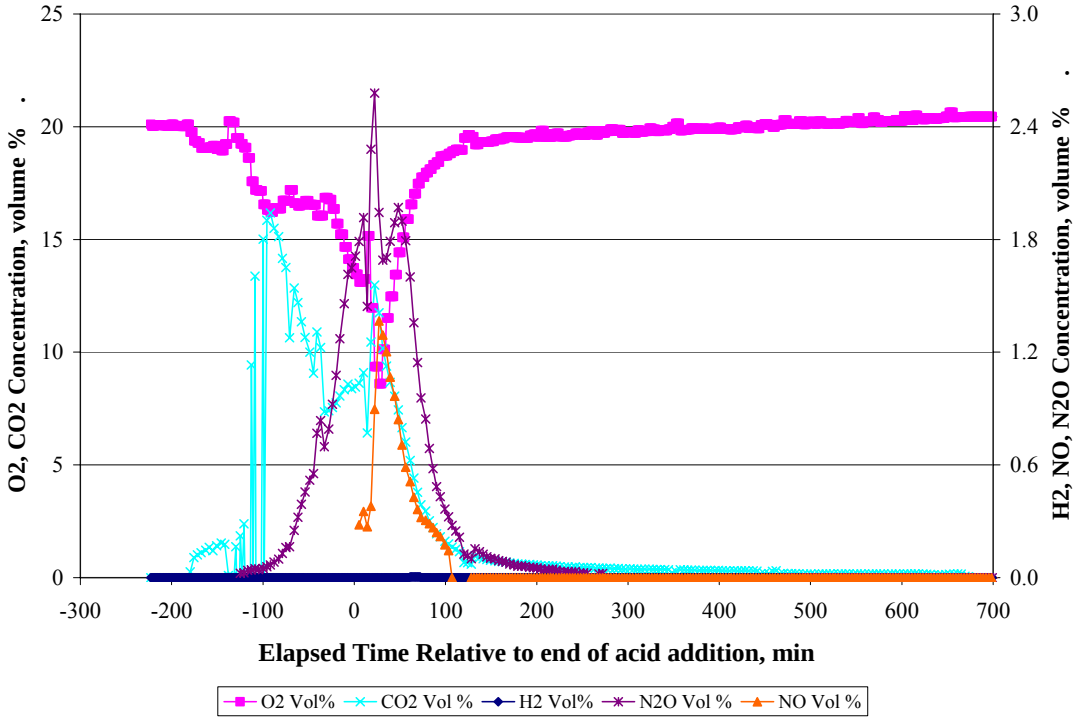


Figure A - 11: Isopar®L Tube Data from Runs SB4-36 to SB4-40

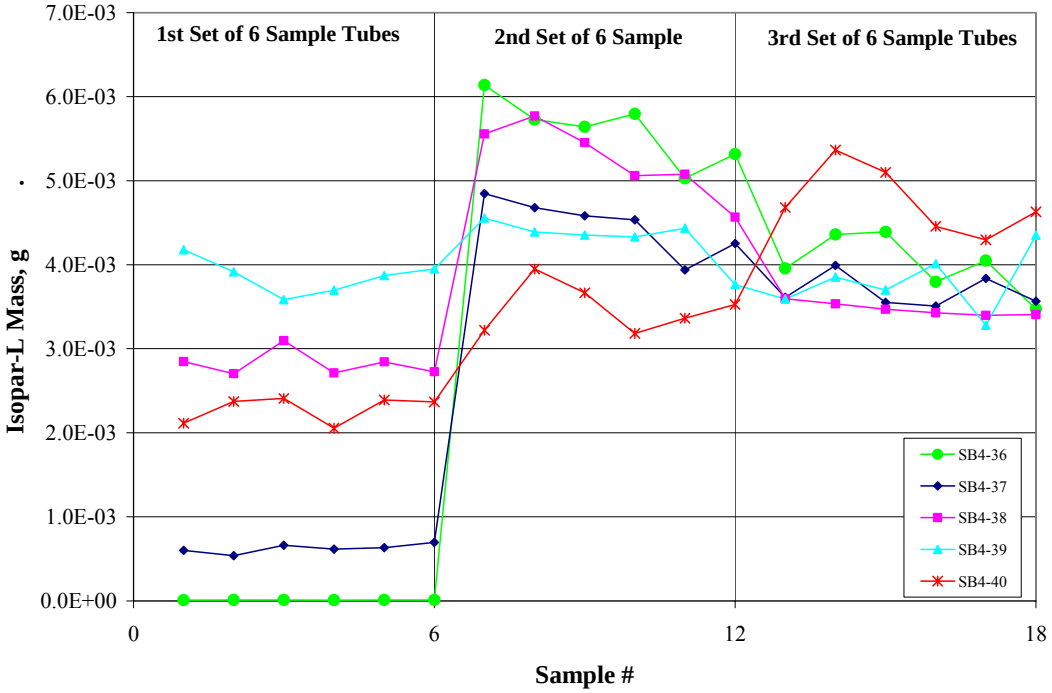
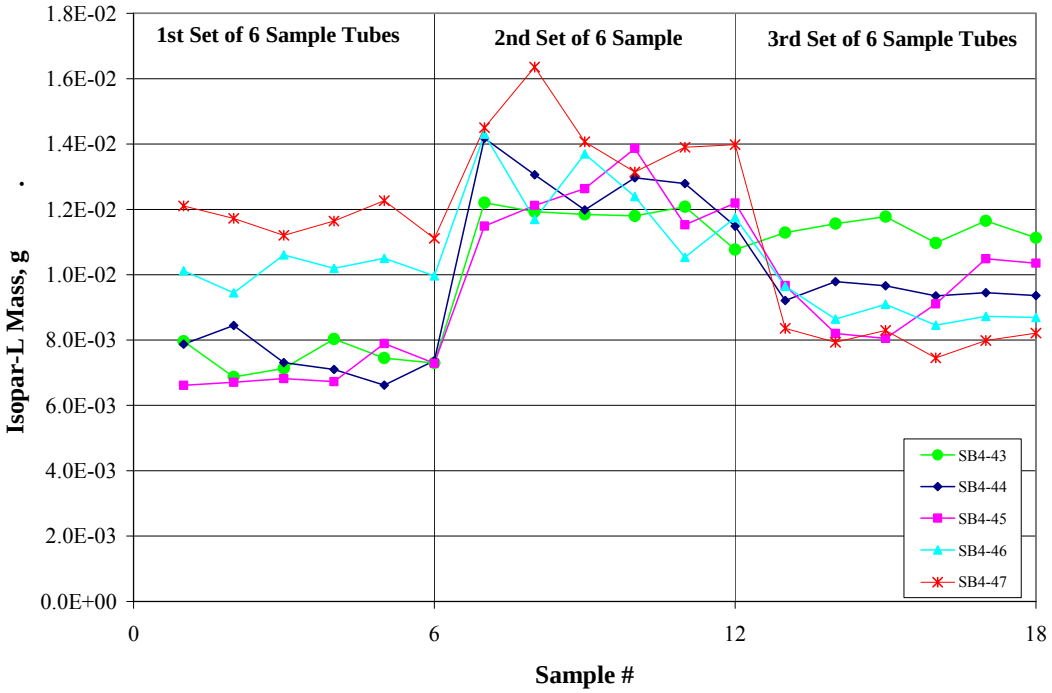


Figure A - 12: Isopar®L Tube Data from Runs SB4-43 to SB4-47



Distribution:

C. J. Bannochie, 773-42A
M. J. Barnes, 999-W
D. R. Best, 786-1A
N. E. Bibler, 773-A
E. A. Brass, 730-1B
T. B. Calloway, 999-W
L. M. Chandler, 773-A
D. A. Crowley, 999-W
S. L. Crump, 773-A
B. A. Davis, 704-27S
R. E. Edwards, 773-A
J. C. Griffin, 773-A
R. E. Eibling, 999-W
T. L. Fellinger, 704-27S
P. E. Filpus-Luyckx, 773-A
S. D. Fink, 773-A
J. M. Gillam, 766-H
J. R. Harbour, 773-42A
E. K. Hansen, 999-W
C. C. Herman, 773-42A
J. F. Iaukea, 704-30S
W. L. Isom, 766-H
C. M. Jantzen, 773-A
D. C. Koopman, 999-W
S. L. Marra, 773-A
M. S. Miller, 704-S
J. E. Occhipinti, 704-S
J. M. Pareizs, 773-A
P. M. Patel, 704-27S
J. W. Ray, 704-S
M. A. Rios-Armstrong, 766-H
H. B. Shah, 766-H
A. V. Staub, 704-27S
M. E. Stone, 999-W
W. B. Van-Pelt, 704-S
J. P. Vaughan, 773-41A
T. L. White, 773-A
G. G. Wicks, 773-A
M. F. Williams, 999-1W