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SRNL
SAVANNAH RIVER NATIONAL LABORATORY

REVIEWS AND APPROVALS

AUTHORS:

Mark Baich   7/12/05

M.A. Baich, Immobilization Technology Section   Date

Connie C. Herman   7/12/05

C.C. Herman, Immobilization Technology Section   Date

Russell E. Eibling   7/13/05

R.E. Eibling, Immobilization Technology Section   Date

Mae F. Williams   7-13-05

M.F. Williams, Immobilization Technology Section   Date

Frank G. Smith   7-14-05

F. G. Smith, Immobilization Technology Section   Date

TECHNICAL REVIEWER:

MEStone   7/13/05

M.E. Stone, Immobilization Technology Section   Date

APPROVERS:

E.W. Holtzscheiter   7/18/05

E. W. Holtzscheiter, Manager, Immobilization Technology Section   Date

Sharon L. Marra   7/18/05

S. L. Marra, Manager, Glass Formulation & Process Development   Date

W. B. Van Pelt   7-21-05

W. B. Van-Pelt, Manager, Waste Solidification Engineering   Date

J. E. Occhipinti   7-21-05

J. E. Occhipinti, Manager, DWPF Process Engineering   Date

EXECUTIVE SUMMARY

Before a new stream can be added to the Defense Waste Processing Facility (DWPF), an impact analysis has to be performed and limited research and development studies may also be performed to quantify the impacts on DWPF processing. Two facilities for treating the salt currently being stored in the High Level Waste (HLW) tanks are currently planned to begin operations during the processing of Sludge Batch 4 (SB4). The Immobilization Technology Section (ITS) of the Savannah River National Laboratory (SRNL) was requested to evaluate the impacts on DWPF processing for streams from the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction Unit (MCU). Simulant Chemical Process Cell (CPC) flowsheet studies for the sludge/monosodium titanate (MST) from the ARP have previously been performed by Baich et. al. (2003). Therefore, CPC flowsheet studies were necessary to determine the impact of the cesium strip effluent stream from the MCU.

Waste Solidification Engineering issued Technical Task Request (TTR) HLW/DWPF/TTR-2004-0031 (Washburn, 2004) to SRNL to perform flowsheet studies to investigate the impacts of the projected MCU stream on DWPF processing. In particular, the TTR requests SRNL to validate the existing process flowsheet and establish a coupled operations flowsheet for use with SB4.

Concurrent with the MCU studies, ITS is also performing process evaluation studies in support of qualification of SB4. The sludge simulant fabricated for the SB4 testing was used in the MCU testing. ARP and MCU stream simulants were also fabricated to perform the testing. The ARP stream represented the sludge/MST stream from Appendix E of the material balance provided by Subosits (2004). The MCU stream represented the "Maximum Volume" case from the material balances provided by Campbell (2004). The processing plan for the MCU stream involves adding this stream during boiling after acid addition. The MCU strip effluent stream will contain a small amount of organic solvent. The organic solvent is a solution of 4 organic materials: 0.007 M calix[4]arene-bis(t-octyl benzo-crown-6), known as BOBCalixC6; 0.75 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, known as Cs-7SB modifier; and 0.003 M tri-n-octylamine (TOA) in the diluent Isopar®L. Isopar®L represents the majority of the organic material and has significant vapor pressure at the Sludge Receipt and Adjustment Tank (SRAT) processing conditions. Modifier has a small vapor pressure at SRAT processing temperatures.

Six 4 liter SRAT runs and one Slurry Mix Evaporator (SME) run were performed to determine the impact of the MCU stream on the process. The first test (SB4-5) was intended to determine if any of the MCU organic materials can be nitrated or otherwise reacted during SRAT processing. The next test consisted of a series of five runs to determine the potential build-up of MCU organics during multiple SRAT runs. In these runs, a heel from the previous run was left in the SRAT and no attempt was made to flush the system between runs. A SME cycle was run after the fifth SRAT cycle was completed to evaluate the potential impact on the SME. All runs used 150% acid stoichiometry and 1% Hg in the dried solids.

The organic concentration of the MCU stream and the MCU addition method utilized were as follows:
Single organic reactivity run: ~1,500 mg/L (~30x the MCU material balance provided by Campbell, (2004)) MCU organic solvent added to the SRAT prior to nitric acid addition; aqueous MCU stream added during boiling.
Series of five continuous runs: ~500 mg/L (~10x the MCU material balance) MCU organic included in MCU aqueous fraction with MCU stream fed at boiling conditions.

The tests performed as part of this testing were as follows:
SB4-5   Organic reactivity run
SB4-13   Fresh sludge batch, 1st in the series of continuous runs

SB4-14   Fresh sludge batch with heel from SB4-13, 2nd in the series
SB4-15   Fresh sludge batch with heel from SB4-14, 3rd in the series
SB4-16   Fresh sludge batch with heel from SB4-15, 4th in the series
SB4-17   Fresh sludge batch with heel from SB4-16, 5th in the series with a SME cycle

Findings of lab-scale experiments were as follows:
- No adverse reaction of Isopar®L (i.e., no nitration reactions) was observed in detailed Gas Chromatography/Mass Spectrometry (GC/MS) analysis of all products and process streams. Small amounts of nitrated Modifier were detected in the Mercury Water Wash Tank (MWWT) samples.
- A material balance on Modifier had a 69% closure for the continuous series runs. The missing Modifier may be present as nitrated species, but quantification would require standards which are not known to exist at this time.
- Small amounts (<100 ppm) of chloromethyl mercury were detected in the Formic Acid Vent Condenser (FAVC) condensate. Chloromethyl mercury was also detected in the SRAT off gas line where high acidity has been present.
- The addition of the MCU stream did not appear to impact nitrite destruction or mercury stripping based on a comparison with a run using SB4 only simulant (i.e., SB4-2 run documented by Baich et. al., 2005) at an equivalent acid addition amount per liter of slurry (i.e., 1.6 moles/liter). A larger acid stoichiometry was required for feed in this testing, but the moles/liter was the same as for sludge only.
- The SRAT pH profiles were all very similar to each other and to the SB4 only runs. As expected, the minimum SRAT pH was obtained at the end of acid addition and ranged from 4.6-4.7 for all runs. All runs had a SRAT product pH in the range of 6.7 to 7.4 when measured at the end of SRAT processing.
- The peak CO_2 concentration was seen during acid addition in the SRAT. As in previous investigations, peaks during acid addition were attributed to carbonate and nitrite destruction. The SB4-5 run had the greatest concentration likely due to the higher total solids for this run, but SB4-13 was also a higher concentration than all of the SB4 sludge only runs.
- Based on the simulants (sludge, ARP, and MCU) used and the ARP and MCU addition amounts tested, no foaming or processing issues such as air entrainment were identified. However, it should be noted that concentration of the ARP stream was not performed during SRAT processing. ARP was pre concentrated before addition to the SRAT. This may have an impact on the slurry behavior; however, MCU is not anticipated to directly impact the behavior. Previous ARP testing has shown some thickening of the sludge during concentrations but mixing behavior was still acceptable (Baich et. al. 2003). No additional antifoam was required as the result of the MCU addition during boiling. No problems with mixing or heating were encountered.

Potential impacts of MCU addition on DWPF SRAT/SME processing were as follows:
- All condensate samples contained moderate amounts of modifier (<20 ppm). Condensate in DWPF would be expected to contain these same levels of modifier. It was not determined whether the modifier was soluble or finely divided particles.
- BOB-Calix and TOA were detected in the SRAT samples by GC/MS, but the instrument used does not quantify the species. The High Pressure Liquid Chromatography (HPLC) instrument can quantify these species, but the low concentrations used were below the detection limits of the HPLC instrument.
- Runs SB4-13 to SB4-17 showed that organic build-up occurred in the MWWT and would be expected to also occur in the MWWT in the DWPF because of similar designs. Both a floating phase at the condensate surface and a dense phase above the mercury layer at the bottom of the MWWT were observed. The floating phase was presumed to be highly concentrated in Isopar®L,

but when the concentration of steam stripped modifier became higher, this phase dropped into the bulk of the MWWT.
- Isopar®L was found to collect in both the MWWT and the FAVC to a small extent. The majority of the Isopar®L was not captured by the condensers and was assumed to exit with the offgas vapor.
- Isopar®L, Modifier, and BOB-Calix were found in the MCU feed vessel at the end of the continuous run series at 3 times the target concentration. This indicated that the organic phase was building up in the vessel and may occur in DWPF as well. Thus, the initial organic concentration of the MCU stream may not reflect the concentration of organic that was fed to the SRAT at any instance in time.

A model of the DWPF process developed in Aspen Custom Modeler™ (ACM, Version 11.1) was used to estimate concentrations of Isopar®L and Modifier in the DWPF CPC that would be expected to occur under the operating conditions used in this experimental study. The comparison of model predictions to experimental data was intended to provide additional insight into behavior of the organic in the CPC process.

In general, the model shows that Isopar®L is almost entirely stripped out in the SRAT and exits in the process offgas which agrees with the experimental results. Also in agreement with the experimental data, the model predicts an accumulation of Isopar®L in the MWWT although the model predicted concentration is about one third of the experimentally measured value. As discussed in the report, the organic feed was not well mixed with the aqueous phase MCU feed to the SRAT. If large amounts of Isopar®L suddenly evaporated in the SRAT during the experiments it could saturate the condenser and accumulate to a greater extent in the MWWT. This is most likely the explanation for the higher concentration of Isopar®L measured in the MWWT at the end of the experiments.

Like Isopar®L, modifier is steam stripped out in the SRAT during feeding but the evaporated modifier largely condenses in the SRAT condenser and thereby enters the MWWT, Slurry Mix Evaporator Condensate Tank (SMECT), Recycle Collection Tank (RCT) and recycle stream. The higher concentration of modifier in the MWWT predicted by the model is the largest difference between model and experimental results. A significant amount of modifier was found in the SRAT condenser rinse following the experiments. Adding this material to the MWWT would almost double the experimentally measured concentration. In practice, mixing may be slow and fresh condensate may preferentially be decanted from the MWWT to the SMECT lowering the measured concentration. However, the modifier is denser than water and would be expected to accumulate in the MWWT.

Based on the results of the testing, the following path forward is recommended:
- Mixing studies should be performed with a representative DWPF MCU aqueous feed tank to determine the degree of organic accumulation and means for preventing the accumulation.
- For the next sludge only SRAT runs, condensate samples should be analyzed for the presence of chloromethyl mercury. The formation of di-methylmercury should also be investigated. The goal is to determine if the compounds are strictly a product of MCU processing or if they are occurring in the presence of antifoam (i.e., organic material) also.
- Additional runs should be performed to attempt to complete the system material balance for the Isopar®L and modifier. On-line measurements or a collection system will be installed on the exhaust to quantify the amount of organic material being emitted. Two possibilities are a cold trap to condense any volatile species and carbon tubes inserted in the vent line to capture the volatiles.
- Given changes in the safety strategy for the addition of the ARP stream, testing should be performed to determine the impact of adding the ARP stream during caustic boiling of the sludge. This testing should monitor changes in the pH and composition of the condensate and in the rheology of the slurry.
- An assessment of the impact of the MCU organics on melt redox and melter flammability should be performed.

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LIST OF ACRONYMS

ACTL	Aiken County Technology Laboratory
ADS	Analytical Development Section
ARP	Actinide Removal Process
ASP	Analytical Study Plan
CPC	Chemical Process Cell
CSSX	Caustic Side Solvent Extraction
DSS	Decontaminated Salt Solution
DSSHT	Decontaminated Salt Solution Hold Tank
DWPF	Defense Waste Processing Facility
FAVC	Formic Acid Vent Condenser
GC	Gas Chromatograph
GCMS	Gas Chromatography/Mass Spectrometry
HPLC	High Pressure Liquid Chromatography
HLW	High Level Waste
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ITS	Immobilization Technology Section
MCU	Modular Caustic Side Solvent Extraction Unit
MFT	Melter Feed Tank
MST	Monosodium Titanate
MWWT	Mercury Water Wash Tank
RCT	Recycle Collection Tank
SB3	Sludge Batch 3
SB4	Sludge Batch 4
SEFT	Strip Effluent Feed Tank
SEHT	Strip Effluent Hold Tank
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SPF	Saltstone Production Facility
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
TOA	Tri-N-OctylAmine
TTR	Technical Task Request
WAC	Waste Acceptance Criteria

1.0 INTRODUCTION AND BACKGROUND

Two facilities for treating the salt currently being stored in the High Level Waste (HLW) tanks are currently planned to begin operations during the processing of Sludge Batch 4 (SB4). The Immobilization Technology Section (ITS) 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 (Washburn, 2004) 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). In particular, the TTR requests SRNL to validate the existing process flowsheet and establish a coupled operations flowsheet for use with SB4. The flowsheet runs are required so an evaluation of potential chemical processing issues, quantification of the potential hydrogen generation rates, and estimation of the required acid stoichiometry can be made.

Previous testing (Baich et. al., 2003) was performed for incorporating ARP/MST in Sludge Batch 3 (SB3) and recommendations were made to DWPF on possible flowsheet options. However, since that time, some changes have occurred to the ARP facility processing strategy, and material balances have been revised (Subosits, 2004). Thus, testing with updated compositions was necessary. Since the MCU is a new design and project, no CPC flowsheet studies have been performed for this stream. This testing will validate the previously recommended ARP stream addition methods based on the new information and based on the need to also incorporate the MCU stream.

The basic principle of solvent extraction is to use a sparingly soluble diluent material that carries an extractant that will complex with the cesium ions in the caustic HLW solution. The decontaminated aqueous stream (raffinate) is then sent to Saltstone for disposal. The cesium contained in the organic phase (solvent) can then be stripped into an aqueous phase ready for transfer to the DWPF. The solvent is then recycled.

The CSSX process described by Van Pelt (2004), which is the basis for the MCU, removes cesium from alkaline salt solutions. This is accomplished by contacting an immiscible organic solvent with the waste, then separating the phases again using centrifugal contactors. The contactors are arranged in banks of multiple contactors. The process is broken down into four sections. The extraction section is a bank of 7 contactors where the cesium is extracted from the waste into the solvent. Once the waste exits the extraction bank, it has been decontaminated of cesium. The waste is then considered Decontaminated Salt Solution (DSS). The solvent flows to the scrub section next. This bank of 2 contactors neutralizes any alkaline carryover from the extraction section and returns any sodium or potassium to the aqueous waste feed stream. The aqueous phase for the scrub section is a dilute nitric acid, which is combined with the waste feed to the extraction section as it exits the scrub section. The solvent then flows to the strip section, which is another bank of 7 contactors. The strip section strips the solvent of the cesium and concentrates it in a very dilute nitric acid stream. The nitric acid stream exiting the strip section contains the cesium and is called strip effluent. Finally, with the cesium removed, the solvent flows to the wash section. The solvent is washed with caustic solution to prevent the buildup of unwanted organics in a bank of 2 contactors. Once the solvent exits the wash section, it is ready to be reused in the process.

Both the strip effluent and DSS are sent to decanters to remove any solvent carryover before being collected for transfer in the Strip Effluent Hold Tank (SEHT) and the DSS Hold Tank (DSSHT), respectively. The DSSHT is transferred to Tank 50, which is the feed tank to the Saltstone Production Facility (SPF) for solidification in grout. Streams destined for Tank 50 must meet the SPF Waste Acceptance Criteria (WAC). The strip effluent in the SEHT is sent to the Strip Effluent Feed Tank (SEFT) in the CPC of the DWPF for vitrification.

The MCU stream to DWPF is comprised primarily of aqueous cesium nitrate solution with a small amount of organic phase. The organic phase comes from incomplete phase separation in the MCU process. Figure 1-1 (Steele 2002) lists the MCU organic components that make up the extraction solvent. The solvent used in this investigation had a concentration of BOB-Calix of 0.007 molar, a concentration of modifier of 0.75 molar, and a concentration of TOA of 0.003 molar, in Isopar®L solvent. The modifier has 2 chiral carbons and is present as a racemic mixture of 4 isomers.

Figure 1-1: MCU Organics

In response to the DWPF TTR, a Task Technical & Quality Assurance Plan (Baich, 2004) was written outlining the activities and controls necessary to meet the objectives and requirements of the TTR. This task plan outlined the approach to be used to evaluate the impacts of the MCU stream, as well as the approach to

be used for the SB4 simulant flowsheet studies. The impact of the addition of MCU on DWPF processing is being studied as the primary focus of this investigation. This report addresses the initial studies to determine the impact of MCU addition on DWPF operations.

Since SB4 simulant flowsheet studies are being performed in parallel, SRNL used the same blended sludge composition to evaluate the impacts of MCU addition. This composition was based on projections provided by Lilliston (2005). The MCU case used for the assessment was the "Maximum" (where "Maximum" represents the highest dose/Cs loading case) from the Preliminary Material Balance Calculations performed by Campbell (2004). The volume of MCU addition was scaled based upon 6400 gallons added per 6000 gallon DWPF SRAT batch. ARP stream makeup was based upon Appendix E of X-CLC-S-00113 by Subosits (2004). The ARP case was selected by DWPF as the possible upper bound on the volume of ARP material to be processed.

Both mercury and noble metals have been shown to have a large impact on the CPC behavior. Neither of these component concentrations has been firmly defined for SB4. Projections of the mercury content for SB4 indicate that the concentration is fairly high compared to previous sludge batches. The SB4 sludge only runs have used 1 wt% Hg based on a dried solids basis (Baich et. al., 2005), and this level was also used in the MCU testing to provide a comparison. The noble metals level used in SB4 sludge only testing was also used in the MCU testing. The noble metals concentrations represent an upper limit based on the projected compositions.

The tests performed as part of this testing all used the SB4 Baseline Feed composition, 150% acid stoichiometry, and 1 wt% Hg. The run ID and the particular parameters investigated were as follows:

SB4-5   ~1500 mg/L MCU organic charge to the sludge containing ARP prior to heating, ~30x the material balance concentration (52 ppm) presented by Campbell (2004)[*]

SB4-13   ~500 mg/L MCU organic mixed in MCU aqueous stream and fed at boiling with sludge containing ARP, ~10x the material balance concentration and first in series of runs

SB4-14   ~500 mg/L MCU organic mixed in MCU aqueous stream and fed at boiling with sludge containing ARP and heel from first run, ~10x the material balance concentration and second in series of runs

SB4-15   ~500 mg/L MCU organic mixed in MCU aqueous stream and fed at boiling with sludge containing ARP and heel from second run, ~10x the material balance concentration and third in series of runs

SB4-16   ~500 mg/L MCU organic mixed in MCU aqueous stream and fed at boiling with sludge containing ARP and heel from third run, ~10x the material balance concentration and fourth in series of runs

SB4-17   ~500 mg/L MCU organic mixed in MCU aqueous stream and fed at boiling with sludge containing ARP and heel from fourth run, ~10x the material balance concentration and fifth in series of runs, included a SME cycle also.

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[*] The current assumed carryover is 237 ppm and was used for the DWPF safety basis.

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2.0 APPROACH

This section describes the approach that was used to perform the MCU impact testing. It is divided into three subsections. The first, Section 2.1, describes the sludge simulant, ARP, and MCU composition and the 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 to characterize the simulants, SRAT/SME products, and offgas condensates.

2.1   Sludge, ARP, and MCU Simulant Preparation

As stated above, the sludge simulant for the MCU runs was the same as the baseline sludge used in the SB4 sludge only testing. This projected composition was for the scenario where SB4 is blended with SB3 after producing 1200 equivalent canisters. The target elemental calcined composition is given in Table 2-1, while the supernate chemistry is provided in Table 2-2. The target noble metals for the sludge portion of the feed are given in Table 2-3. Noble metals contribution from the other streams was not included. Details of the sludge fabrication are provided in Baich et. al. (2005). Table A - 1 shows the typical recipe for the simulant. The recipe was followed for fabrication and the resulting sludge was analyzed before testing was initiated.

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 (2005)

Table 2-2: Target Supernate Chemistry

Parameter	Baseline Wash
SpG (kg/L)	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:   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

Simulants of the ARP and MCU streams were also fabricated for the testing. The nominal components for the Appendix E case of the ARP stream are given in Table 2-4. During ARP operation, this stream will be generated at 102.4 lbs/hr; therefore, ~2367 gallons of ARP will be fed per SRAT batch according to Subosits (2004). The ARP simulant was made from reagent grade chemicals, dried SB4 sludge solids, and vendor supplied sodium titanate slurry. Table A - 2 provides the recipe for the ARP simulant.

The ARP feed was made with 75% less water (i.e., concentrated 4-fold), but all of the elemental compounds. This eliminated the need for caustic boiling which would be performed prior to the start of the batch. Caustic boiling would not be expected to alter the ARP feed based on previous testing by Baich et. al. (2003).

The MCU strip effluent stream is primarily water, $CsNO_3$, HNO_3, and the organic solvent. The recipe used to fabricate the aqueous fraction of the MCU strip effluent stream is given in Table A - 3. As mentioned in Section 1.0, the MCU solvent consists of four different compounds. The components are present at a concentration of 0.007 molar BOB-Calix, 0.75 molar Modifier, 0.003 molar TOA, and a balance in Isopar L solvent. MCU solvent was obtained from the Waste Processing Technology Section[†].

[†] The solvent sample was from a mixture of 700 ml of solvent, Lot #PVB B000894-31W from P.V. Bonnesen at ORNL, and 800 ml of modifier/Isopar mixture (0.50 M modifier), Lot #B000894-6DM from P.V. Bonnessen at ORNL. Tom Peters performed the re-working of the mixture to obtain the latest blend ratios for the solvent.

Table 2-4: Nominal Appendix E ARP Components for DWPF Stream

Component	lb/hr
Water	97.58
KNO_3	0.0015
NaOH	0.38
$NaNO_3$	0.96
$NaNO_2$	0.02
$Sr(NO_3)_2$	1.30E-03
sludge	1.838
MST	0.705
NaHgOOH	9.75E-06
CH_3OH	1.83E-06
$(CH_3)2CHOH$	1.32E-06
$Na_2C_2O_4$	0.594
Water	97.58

*Information is from Subosits (2004).

2.2 Procedures and Equipment Used in Testing

The testing was performed at the Aiken County Technology Laboratory (ACTL) using four-liter kettles with various glassware fabricated to functionally replicate the DWPF processing vessels. The 4-liter glass kettle is used to replicate both the SRAT and the SME, and it is connected to the SRAT Condenser, the Mercury Water Wash Tank (MWWT), and the Formic Acid Vent Condenser (FAVC). A separate bottle is used to represent the Slurry Mix Evaporator Condensate Tank (SMECT) and a take-off line from the MWWT is used to drain condensate from the system. For the purposes of this report, the condensers and MWWT are referred to as the offgas components. A four-liter vessel was also used as a MCU feed tank. The same autotitrator pump was used for MCU addition as was used for acid addition. A separate pump head was dedicated to MCU as is done for nitric and formic acids to minimize potential for contamination. A magnetic stirrer was used for agitation of the MCU feed tank. The feed tank was sealed except for a tiny vent hole. A sketch of the experimental setup is given as Figure 2-1. The MCU was added through the same port that acids were added.

Immediately after the last SRAT in the five continuous runs, the SME cycle for SB4-17 was started. Frit 320 was used with a targeted waste loading of 35%. The frit was added in three equal portions with water and formic representative of the slurry used in DWPF (i.e., ~50 wt% solids slurry with 1.5 wt% formic acid). The SME was brought to boiling after each addition and the water and formic mass added with each addition was removed. After concentration, the SME was cooled to below boiling and the next addition was performed. After the final addition, additional water was removed to obtain the targeted total solids. The SME cycle was stopped by turning the heat off after the last concentration was performed.

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

SRAT processing parameters are summarized in Table A - 4, while the SME processing parameters are summarized in Table A - 5. Each SRAT and SME test followed the run plans written for each run (Baich 2005a, Baich 2005b, Baich 2005c, Baich 2005d, Baich 2005e, and Baich 2005f), and the memo numbers are given in Table A - 4 of Appendix A. 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. Helium was also introduced as a tracer gas so that the total amounts of generated gases 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, loss of heat transfer capabilities, and offgas carryover. Observations were recorded in laboratory notebooks WSRC-NB-2005-00003 and WSRC-NB-2005-00035 and are discussed in Section 3.0.

Concentrated nitric acid (50-wt%) and formic acid (90-wt%) were used to acidify the sludge and perform neutralization and reduction reactions during processing. The amounts of acid to add for each run were determined using the existing DWPF acid addition equation (Marek and Eibling, 1992). For the first run (SB4-5), the equation inputs for the sludge and the ARP simulant were calculated separately and then the total acid requirement was calculated. The sludge and ARP were mixed in the vessel before the start of the run. For the continuous series runs, ARP was mixed with the starting sludge and a sample of the combined material was used for inputs to the acid addition calculation. Therefore, the sludge/ARP feed was added to the vessel as one pre-mixed stream. No adjustments to the acid addition equation were performed for the addition of MCU stream. The split of the acid was determined using the redox equation currently being used

in DWPF processing (Jantzen et. al., 2003) 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 for each run. The values used for each run are provided in Section 3.0.

To prevent foaming during processing, 200 ppm IIT 747 antifoam was added during heat-up at 40°C and 500 ppm was added at the completion of acid addition. The addition strategy was conservative relative to the current DWPF addition strategy to increase sensitivity to foaming issues. SRAT processing included the dewater time in boiling plus the time required to add all of the MCU aqueous stream (typically 13 – 14 hours).

2.3   Analytical

Analyses for this task and all other phases of the flowsheet testing used guidance of Analytical Study Plan (ASP), SRNL-GPD-2005-00001 (Baich 2005g). 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 ITS, ITS - Mobile Lab, and/or Analytical Development Section (ADS) lab identification number was assigned to each sample for tracking purposes. Analyses were performed using approved analytical and Quality Assurance procedures.

Samples were taken of the sludge and ARP simulants, of the SRAT and SME products, and of the offgas condensate for analyses. The MCU aqueous simulant was not analyzed because of the simplicity of its make-up (see Table A-3). The samples were analyzed by the Mobile Lab, the ITS, and the ADS. The Mobile Lab performed analyses on the sludge and ARP slurries to determine the chemical composition, total and dissolved solids, density, and pH. The chemical composition was determined in duplicate by calcining the samples at 1100°C and then dissolving the product using Na_2O_2/NaOH fusion, lithium metaborate fusion, and aqua regia dissolution. The preparations were then analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) to measure the cations present. The filtered supernate was also measured using ICP-AES to determine the soluble cations present in the product samples. Samples for anion analyses were prepped using weighted dilutions and were analyzed using Ion Chromatography (IC). The total and dissolved solids were measured on two aliquots and the insoluble and soluble solids fractions were calculated from the results. Density, pH, and rheology measurements of the samples were also performed on the initial and product samples. ITS performed the titration on the starting sludge samples to provide the necessary input for the acid calculation. A manual titration was performed at ACTL using a 1M HNO_3 solution and 10:1 dilution of the sample. The calibration curve was performed to a pH of 5.5 and was performed in duplicate at a minimum. Finally, the ADS measured the total inorganic carbon of the sludge simulant using the ITS Acid Calculation method. The total inorganic carbon information was needed as an input in the acid calculation.

Hydrogen, oxygen, nitrogen, carbon dioxide, and nitrous oxide were monitored during the runs using a high-speed micro Gas Chromatograph (GC). Monitoring these species provides insight into the reactions occurring during processing and demonstrates whether a flammable mixture is formed. Helium was used as a GC internal standard and was also monitored during the runs. The GC is self-contained and is designed specifically for fast and accurate analysis. The GCs had five main components. The first is the carrier gas (argon for this testing) to transport the sample through the molecular sieve and poraplot Q columns. The second is the injector, which introduces a measured amount of sample into the inlet of the analytical columns where it is separated. 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 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 single calibration standard was used in each run to bound upper quantities of the expected gases. The concentrations of these calibration standards were specified based upon previous work. These concentrations are re-evaluated when new calibration gases are ordered. Calibration checks are performed before and after each run, and calibration is considered acceptable if within 5%. The calibration standards are balanced in nitrogen because helium is used as an internal standard and is also used to detect leakage during the actual runs.

Organic analysis performed by ADS for Isopar®L were carried out on an Agilent 6890 gas chromatograph, equipped with a 30 meter DB-XLB column, with 0.18 mm diameter and 0.25 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. Sample preparation involved extraction of each sample with a known amount of methylene chloride.

Samples from the SB4-5 run were also analyzed by ITS using gas chromatography-mass spectrometry (GCMS) using an Agilent 5973 GCMS to determine if the MCU components reacted or decomposed during the CPC processing. Aqueous samples were extracted three times with methylene chloride (CH_2Cl_2) and the extracts were combined. The pHs of the aqueous samples were not adjusted before extraction. The extracts were injected into the GCMS using the splitless injection mode and separated on a DB-5-MS capillary column (30 meter length, 0.25 mm ID, 0.25 micron film thickness). The GCMS oven was temperature programmed to vary from 35 to 300°C in order to elute all of the semivolatile compounds. The mass spectrometer scanned from mass/charge ratio of 50 to 600 to provide mass spectrums of the compounds separated by the column. The results of the GCMS sample analysis are qualitative and can be used for qualitative descriptions of the behavior of the organic compounds in the CPC. Quantitative results for the MCU compounds added to the CPC were provided by ADS.

High Pressure Liquid Chromatography (HPLC) analysis was used for Modifier and BOB-Calix determinations. Aqueous samples were prepared for analysis by liquid/liquid extraction. The average recovery for a single extraction with methylene chloride of the extractant (n=3) from water was 90% and the average recovery for a single extraction with methylene chloride of the modifier (n=3) from water was 97%. The extracts were analyzed for Modifier and extractant by HPLC. For the Modifier, the HPLC method used a normal-phase cyano column with 96% hexane and 4% isopropanol as the mobile phase. Table 2-5 summarizes the conditions for the Modifier analysis. The extractant HPLC analysis (Table 2-6) used a reversed-phase C18 column with the mobile phase acetonitrile.

Table 2-5: 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	Dychrom Chemcosorb 5 ODS-UH 4.6 x 150 mm, 5 mm pore size
Oven temperature	Ambient
Flow-rate	1 ml/min
UV	230 nm
injection volume	5 mL
Retention time for Extractant	6.3 min
Linear calibration curve Modifier	12 mg/L to 240 mg/L, r^2 = 0.999
R.S.D.(%) (n=7)	0.73

Table 2-6: HPLC BOB-Calix Isocratic Elution Conditions

Method	Conditions
Solvent system	Isopropanol
t_o to t_1 = 8.0 min	100%
Reversed-phase C18 Column	Dychrom Chemcosorb 5 ODS-UH 4.6 x 150 mm, 5 mm pore size
Oven temperature	45°C
Flow-rate	0.5 ml/min
UV	220 nm
injection volume	5 mL
Retention time for Extractant	5.0 min
Linear calibration curve Extractant	10 mg/L to 100 mg/L, r^2 = 0.999
R.S.D.(%) (n=7)	1.6

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3.0 RESULTS

The data from the testing and any observations will be discussed in this section. This section has been divided into six subsections. Section 3.1 discusses the analyses of the starting sludge and ARP material and the necessary inputs for the acid calculation. Section 3.2 discusses the general observations about processing and the pH profiles. Section 3.3 discusses the generated gas data and any data from in-process sampling. Section 3.4 discusses the organic profile and the fate of the organics. Section 3.5 discusses the organic carry over modeling results. Finally, Section 3.6 discusses the SRAT and SME product characterization.

3.1   Starting Sludge and ARP Compositions

Two different feeds were used during this investigation. For run SB4-5, SB4 simulant from SB4 simulant flowsheet testing was used. It was combined with the ARP simulant in the kettle before SRAT processing was initiated. The SB4 simulant was identified as Feed SB4-5 (020705), where the number in parenthesis identifies the date of fabrication. The continuous runs used a different batch of SB4 simulant, which was identified as Feed 031505. For this series of testing, the ARP was mixed with the SB4 simulant and analyzed before processing was initiated. Table 3-1 presents the analysis of the SB4 simulant (SB4-5 feed), the ARP stream simulant, and the SB4 simulant (Feed 031505) combined with the ARP stream. Adding the ARP to the simulant increased the sodium, titanium, nitrate, and oxalate concentrations and the base equivalents.

For the SB4-5 feed, some problems occurred with the sludge fabrication (see Baich et. al., 2005, for complete details). The feed had to be trimmed with additional $Al(OH)_3$ to obtain the target Al concentration. The composition in Table 3-1 represents the trimmed composition. The insoluble solids and soluble solids were not re-measured for the sludge since the numbers were not needed for the acid calculation. This analysis was not available before the acid calculation was performed for run SB4-5, so the acid calculation was performed using calculated numbers for the input parameters. Based on the post-trimmed analysis (i.e., the composition given in Table 3-1), the acid amount used in run SB4-5 represents an approximately 2% higher acid stoichiometry.

The inputs to the acid addition calculation are given in Table 3-2. As mentioned above, the inputs for run SB4-5 accounted for the individual inputs of the sludge and the ARP feed. The adjusted number is given in the SB4-5 column. For the continuous series runs, the only inputs changed were associated with the volume/mass of sludge since a heel was present in all of the runs after SB4-13.

Rheological data for these feeds are presented for completeness in Appendix B (see Figure B - 1 and Figure B - 2). Because the SRAT products were fairly thin rheologically, Taylor vortices were observed in their flow curves. The Taylor vortices data was not included in the analysis. The up curve was used to calculate the rheological data. While the feeds used are chemically similar to real waste, their rheology may not be reproduced well. The analysis technique is more suitable to thicker non-Newtonian fluids. Simulant development efforts are currently directed at producing feeds that are both chemically and physically similar to real waste. In general, no impact was seen on the rheological properties from the addition of the ARP material.

Table 3-1: Sludge Simulant, ARP, and Sludge with ARP Analyzed Compositions

Sample ID	Sludge Simulant SB4-5 (020705)	4X ARP Simulant	031505 Sludge Simulant with 4X ARP
Runs	SB4-5	All Runs	SB4-13 to SB4-17
Elemental (wt% in calcined solids)			
Al	14.5	6.87	13.3
Ba	0.178	0.102	0.159
Ca	2.23	1.25	2.06
Cr	0.131	0.071	0.156
Cu	0.066	0.035	0.064
Fe	22.5	8.50	22.9
K	0.818	0.096	1.03
Mg	0.886	0.485	0.862
Mn	5.96	3.82	5.70
Na	11.9	31.2	14.8
Ni	3.21	0.937	3.05
P	0.045	0.019	0.028
Pb	<0.010	0.030	<0.010
S	0.281	0.066	0.304
Si	1.47	0.769	1.31
Ti	0.024	9.61	0.540
Zn	0.104	0.049	0.121
Zr	0.344	0.187	0.244
Anions (mg/kg in slurry)			
NO_2	17100	1470	16750
NO_3	10100	32900	14200
SO_4	1325	159	1300
C_2O_4	<1000	11800	2185
Physical Properties			
Total Solids	23.5%	13.0%	19.8%
Insoluble Solids	16.9%*	6.39%	13.6%
Soluble Solids	5.73%*	6.56%	6.15%
Calcined Solids	16.6%	8.22%	13.8%
Density (g/ml)	1.19	1.11	1.17
pH	12.2	12.7	12.50
Other Measured Properties			
TIC (mg/kg)	2207	N/A	752
Base Equivalents at pH 7 (Eq/L)	0.325	0.360	0.410

*Measurements are from original SB4-5 feed analysis and were not re-measured after trimming, since they were not necessary for the acid calculation.
N/A – Not analyzed

Table 3-2: Pre-Run Measured Inputs and Assumptions for Acid Calculation

Input Parameter	SB4-5	SB4-13	SB4-14 through SB4-17
Nitrite (mg/kg)	16654	16750	16750
Nitrate (mg/kg)	14248	14200	14200
Oxalate (mg/kg)	1956	2185	2185
TIC (mg/kg)	1067#	752	752
Base Eqv. (M)	0.329	0.410	0.410
Mn (wt% in total solids)	3.96	3.98	3.98
Total Solids (wt%)	22.57	19.8	19.75
Density (g/ml)	1.18	1.17	1.17
Calcine Factor	0.7123	0.6987	0.6987
Hg (% in Total Solids)	0.945%	1%	1%
Nitrite to Nitrate Conversion %	21	21	21
Formate Destruction %	14	14	14
Feed Mass (g)	2795	2500	2000*
Acid Stoichiometry	150%	150%	150%
Redox Target	0.200	0.200	0.200
Ratio of Formic to Nitric	0.9168	0.9151	0.9151
Acid/Liter of Slurry	1.652	1.601	1.595

*A 500 ml heel of SRAT product was present in all of these runs and the mass is not included here.
#TIC input value was based on one measurement believed to be the correct result since it was near the target.

3.2 SRAT/SME Processing

The SRAT runs were performed in a hood at the ACTL in the 4-liter vessel. The SRAT cycles were initiated after the trim chemicals and ARP, as appropriate, were added. In SB4-5, a single 1500 mg/L charge (4.5 mL solvent to 2750 ml of MCU aqueous) of MCU organic solvent was made before heat-up. In SB4-13 to SB4-17, 500 mg/L of MCU organic (nominally 1.67 ml added to 2667 ml of MCU aqueous) was added to the MCU aqueous fraction in the feed vessel. Nitric acid was added first and then formic acid. After the completion of acid addition, 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 and then the addition of MCU aqueous fraction was started. The feed rate of MCU aqueous was set to match the boil-up rate. The time required to feed and boil off the MCU was approximately 13-14 hours. No additional reflux period was performed.

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. No additional antifoam, other than the baseline addition, was required during MCU addition. No nitrite was detected in any of the SRAT product samples. Mercury reduction and steam stripping appeared to be comparable to other runs without MCU.

Only one SME cycle was performed at the end of the series of 5 runs. Frit 320 at 35% waste loading was targeted. No foaming or any other problems were observed during the SME operation.

The pH was measured throughout the runs. Figure 3-1 plots the measured pH during the SRAT cycles.

Figure 3-1: pH Plots for All Runs
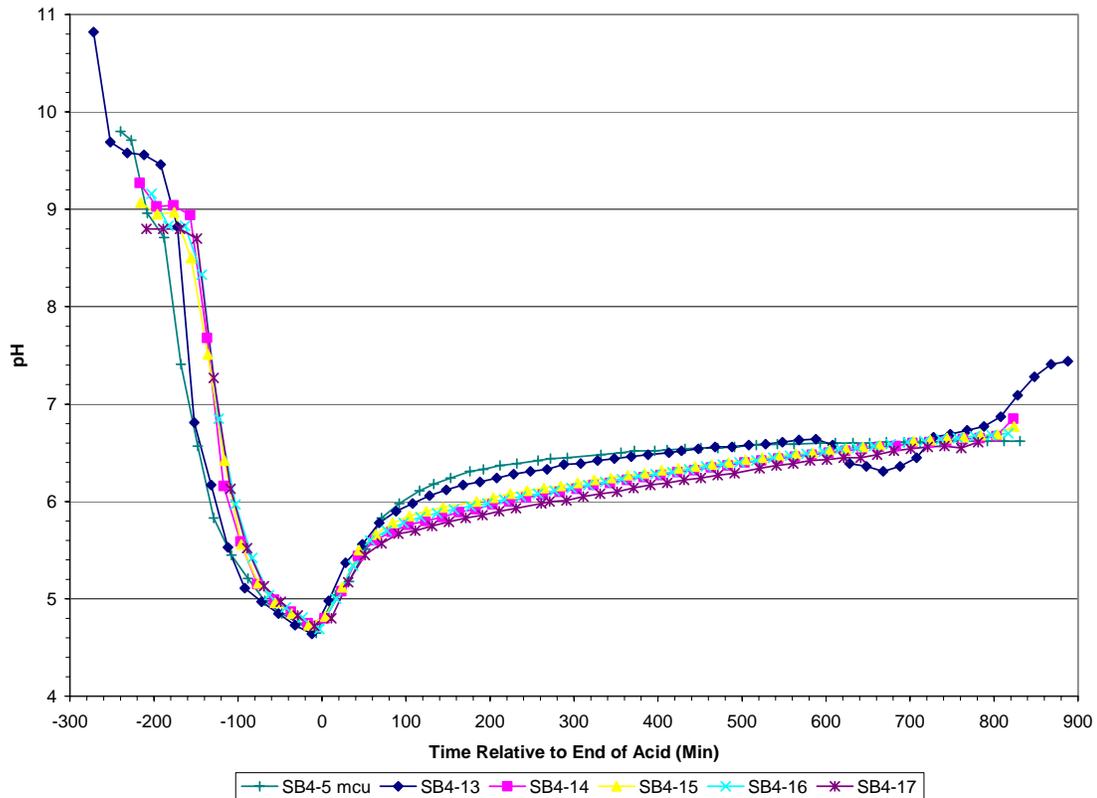
The profiles are very similar. The starting pH of the first run in the continuous processing series was higher than the others because of the absence of the heel. It was also similar to SB4-5 which used a different feed and all of the MCU organics were added prior to the start of the run.

When the pH plots from the MCU runs were compared to SB4 sludge only runs, similar behavior was seen through the end of dewater (~40 min). Figure 3-2 shows this comparison for run SB4-2 from the sludge only testing. For the sludge only runs, the pH continued to rise sharply for ~160 minutes after acid addition was completed and then rose at a much slower level for the rest of the run. In the MCU runs, the runs without heels (SB4-5 and SB4-13) tracked fairly well with the sludge only run through about 180 minutes after acid addition and then pH rose to higher levels for the MCU runs. In the run with the heel (SB4-17), the pH change after dewater rose at a constant rate through the end of the run.

During the SB4-17 SME cycle, the pH cycled between 6.0 and 6.5 with the higher pHs occurring near the end of the dewater/concentration periods. Final pH at the end of the SME was 6.3, which was lower than the final SRAT pH.

Figure 3-2: pH Plot of MCU Runs with SB4 Sludge Only Run
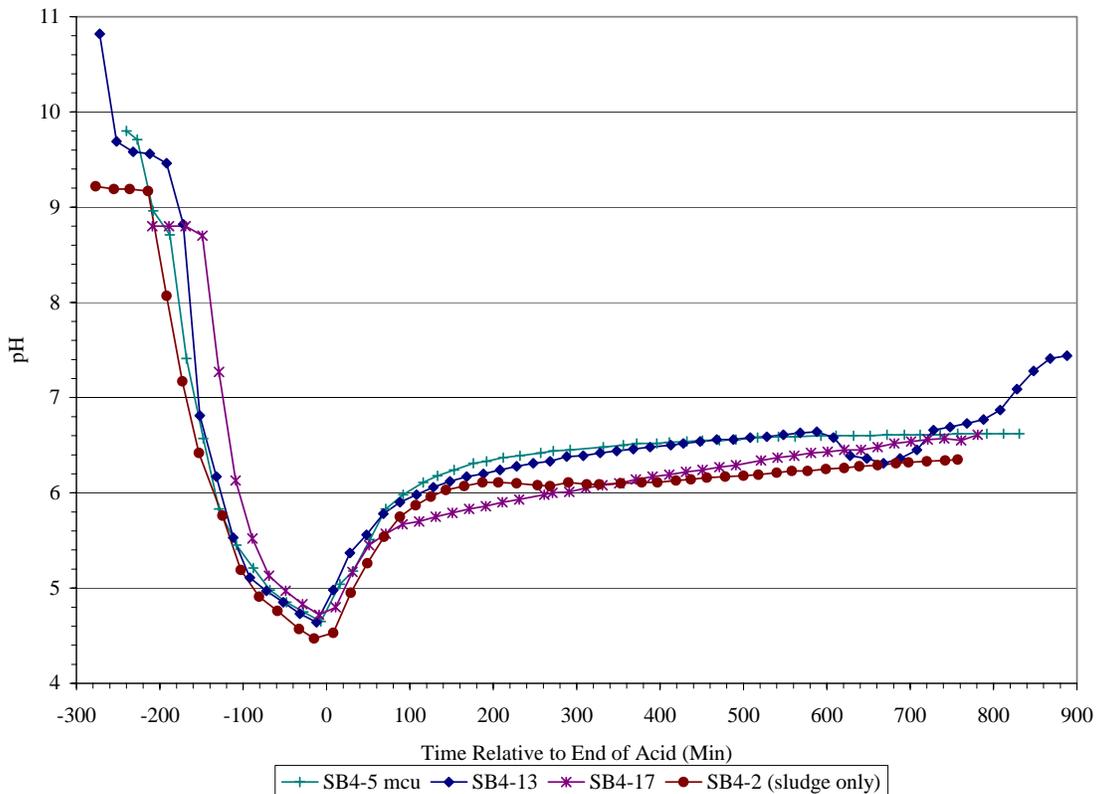
3.3 Generated Off Gas Data

As mentioned in Section 2.3, hydrogen, oxygen, nitrogen, carbon dioxide, nitric oxide, and nitrous oxide were measured throughout the runs using GCs. Figure A - 1 through Figure A - 6 of Appendix 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 increases and small amounts of hydrogen were generated in a few of the runs. For the most part, little gas was generated after five hours into reflux.

Figure 3-3 through Figure 3-5 contain plots of the carbon dioxide, nitrous oxide, and nitric oxide, respectively, from all of the MCU runs. Only a portion of the data is shown for each gas since the gases are not generated throughout the run. The timing and concentrations were fairly consistent from run to run, with reproducibility evident in the four runs containing the heel. Runs SB4-5 (organic reactivity run) and SB4-13 (no heel) showed slightly different behavior than the four heel runs.

Figure 3-3: Measured CO₂ Concentration
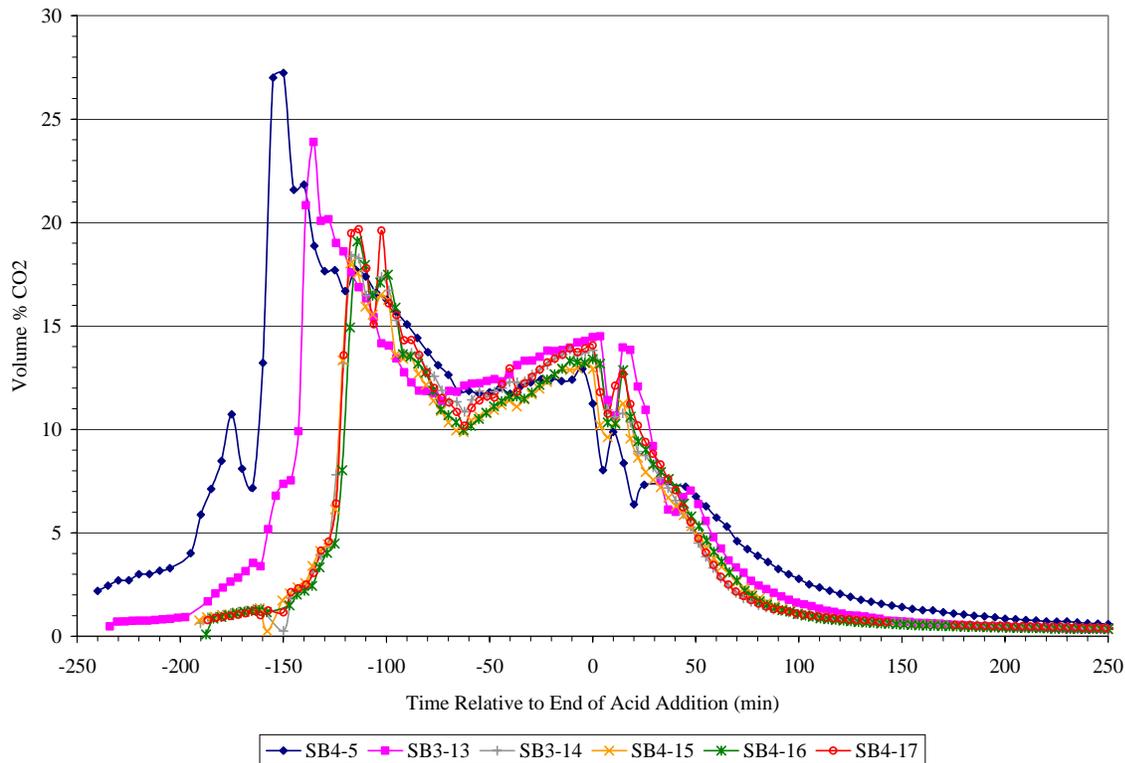
For carbon dioxide, both runs without a heel started generating carbon dioxide earlier and had a greater peak concentration than the four heel runs. Part of the difference in timing is related to the larger amounts of acid that had to be added in these runs and, therefore, acid addition took longer (i.e., more negative time relative to the end of acid addition). Nitrous oxide for run SB4-13 was consistent with the heel runs, but lower concentrations and a delay in generation were seen for run SB4-5. Run SB4-13 had the highest measured nitric oxide peak and the timing of the generation was consistent with the other runs. Run SB4-17 had the lowest peak nitric oxide concentrations. Compared to run SB4-2 that had an equivalent moles of acid per liter of slurry added and showed equivalent nitrite destruction from the sludge only testing (Baich et. al., 2005), carbon dioxide behavior and concentration was very similar to the heel runs. The nitrous oxide behavior, on the other hand, was more typical of the SB4-5 run. Very little nitric oxide was seen in the SB4-2 run, especially compared to this set of runs. No appreciable hydrogen was detected in any runs, which would be expected from the relatively slow nitrite destruction. Very small quantities of hydrogen were detected in sludge only runs at this equivalent acid addition level (Baich et. al, 2005). No hydrogen was detected in the single SME cycle run.

Table 3-3 presents the observed peak off gas concentrations for each run. The data for hydrogen has not been converted to DWPF scale generation rate because the values are at the detection limits of the GC and are well below the DWPF hydrogen limit of 0.65 lb/hr for the SRAT and 0.233 lb/hr for the SME.

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Figure 3-4: Measured N₂O Concentration
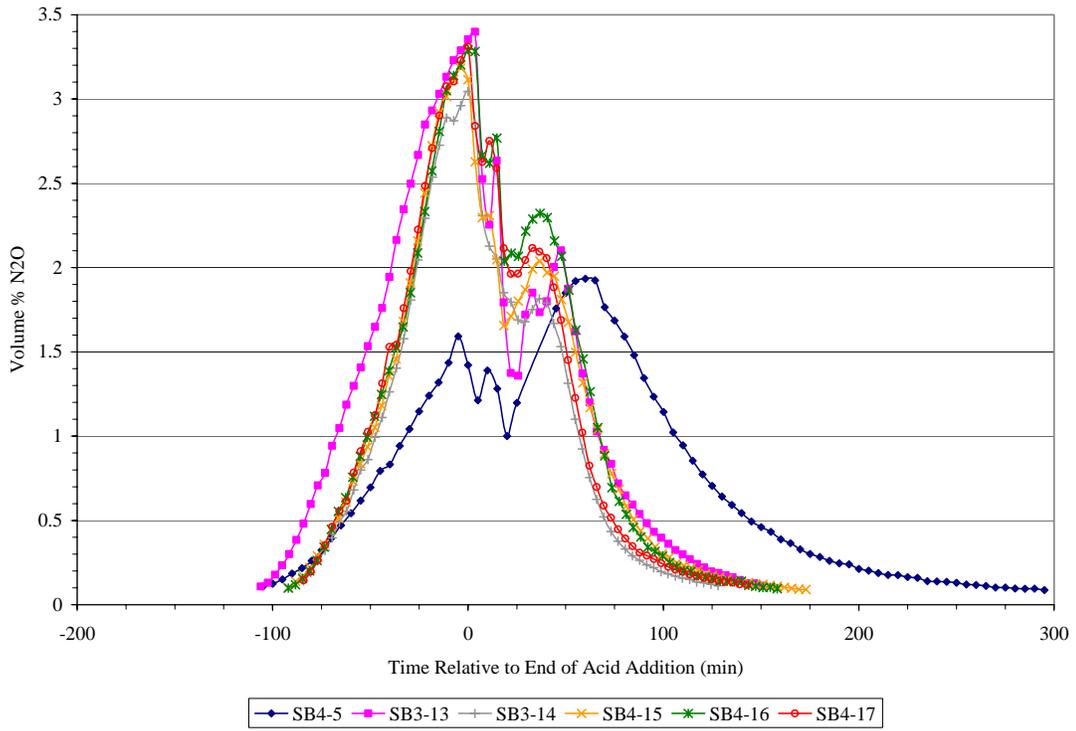
Figure 3-5: Measured NO Concentration
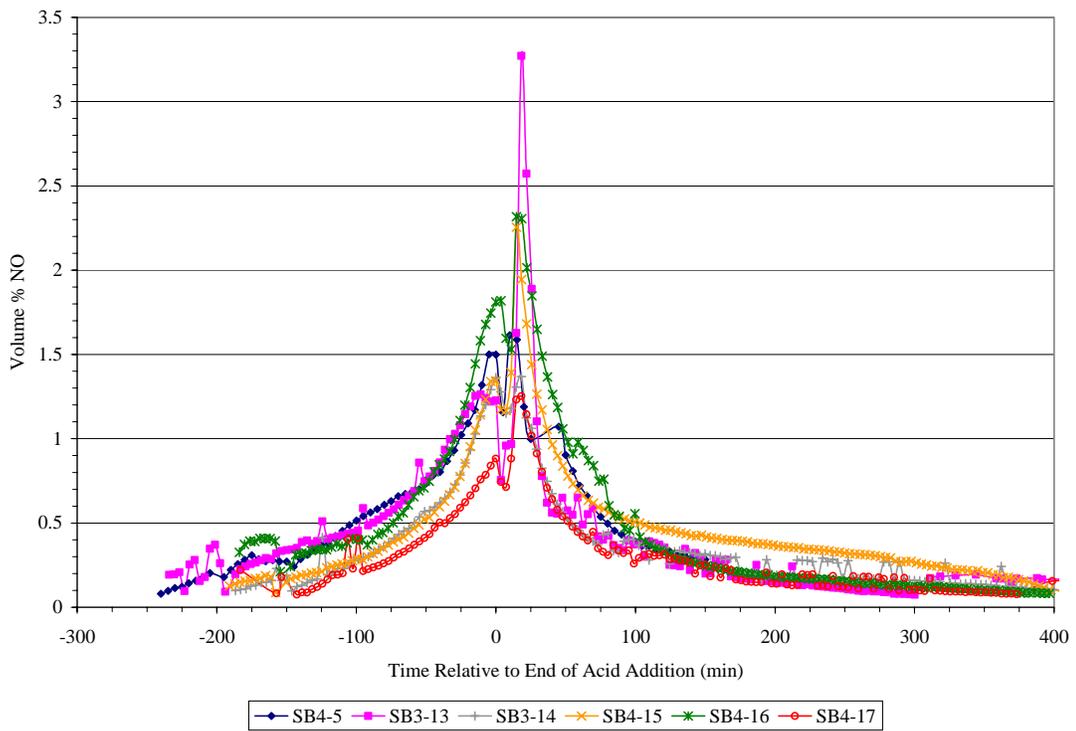
Table 3-3 presents the observed peak off gas concentrations for each run. Generally speaking, NO and N_2O concentrations were higher for the MCU runs than for the SB4 sludge only runs (see Baich et. al., 2005). This may be due to the presence of a heel in these runs or possibly different reactions being driven by the addition of MCU and reflux not being performed.

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

RUN	Peak CO_2	Peak NO	Peak N_2O	Peak H_2
SB4-5	27.23	1.614	1.933	0.0050
SB4-13	23.89	3.271	3.399	Not Detected
SB4-14	18.26	1.368	3.044	Not Detected
SB4-15	18.02	2.255	3.184	0.0062
SB4-16	19.09	2.317	3.292	0.0071
SB4-17 SRAT	19.67	1.252	3.311	Not Detected
SB4-17 SME	2.854	0.316	Not Detected	Not Detected

3.4 Organic Data

Run SB4-5 employed a single charge of 4.5 ml of MCU organic solvent prior to SRAT heat-up. Figure C - 1 presents a picture of the MWWT as the SRAT approached the start of acid addition (temperature of 93ºC). This picture shows that a good portion of the Isopar®L was distilled from the SRAT before acid addition started. It was estimated that approximately 70% of the 4.5 ml charge was distilled based on the dimensions of the MWWT. Later in the process simulation, the organic phase in this leg worked its way to the bulk of the MWWT and formed a floating layer for the remainder of the run. Analysis of the MWWT contents at the end of the cycle indicated the MWWT contained 26,000 mg/L Isopar®L and 3300 mg/L modifier or about 60% of the Isopar®L and 35% of the modifier charge. Four samples of condensate collected during SRAT dewater and MCU aqueous addition had modifier concentrations of 26, 51, 34, and 32 mg/L. No BOB-Calix was detected in any of the condensate or rinse samples. The SRAT product had a modifier concentration of 134 mg/L and a BOB Calix concentration of 10 mg/L. Rinsing the entire system demonstrated less than a milligram of Isopar®L remained in the glassware after products were removed. Rinse samples of the MWWT and SRAT condenser contained approximately 14.5% of the Modifier charged.

The results of the ITS GCMS examination for evidence of organic reactions are shown in Table 3-4. Each of the individual categories of compounds is discussed separately.

Table 3-4: GCMS Examination of SB4-5 Experiment

Sample	Isopar® L Detected	Trioctylamine Detected	Cs7SB Detected	"Nitrated Cs7SB" Detected	Methylmercury Compounds Detected	747 Antifoam Detected
Initial Dewater	no	no	yes	yes	yes	yes
Condensate #2	no	no	yes	no	no*	yes
Condensate #3	no	no	yes	no	no*	yes
MWWT Contents	yes	yes	yes	yes	no	yes
FAVC Condensate	yes	no	yes	yes	yes	yes
FAVC/Offgas Line Rinse	yes	yes	yes	yes	yes	yes
MWWT Rinse	yes	yes	yes	yes	no	yes
SRAT Condenser/ Offgas Line Rinse	yes	no	yes	yes	yes	yes
SRAT Vessel Rinse	yes	no	yes	no	no	yes

* Mercuric Iodide detected.

Analysis of the semivolatiles showed no evidence of nitration or decomposition for the Isopar®L hydrocarbons. The lack of reaction for the isoparraffinic compounds present in Isopar®L was expected since the nitration of such compounds requires very aggressive nitration conditions, which are not present in the SRAT system. The absence of Isopar®L from the aqueous SRAT condensates was due to the very low solubility of these compounds in water and the underflow-overflow design of the small scale and DWPF MWWT. The aqueous phase exited the MWWT through an underflow weir, which prevented a floating phase (such as Isopar®L or antifoam) from exiting the tank. Isopar®L entering the MWWT would concentrate on the surface of the aqueous phase until it was either lost to the ventilation system or sufficient organic phase accumulated to reach the under flow weir. The MWWT sample had globules of a second phase floating in the aqueous phase and the analysis showed the presence of substantial amounts of Isopar®L in this material. The surfaces of all of the equipment also showed the presence of the isoparraffinic hydrocarbon. The only aqueous sample that showed any evidence of the hydrocarbon was the condensate from the FAVC which had only a trace of the least volatile hydrocarbon present in the Isopar®L.

Trioctylamine (TOA) was barely detectable in three of the samples: the MWWT contents, the MWWT vessel rinse, and the FAVC and offgas line rinse. The solvent extraction method used was not optimized to obtain high extraction efficiencies for a basic compound such as trioctylamine. Additional work would be necessary if TOA chemistry needs to be examined, but levels of TOA are extremely low. The TOA is expected to remain in the SRAT product due to its low volatility.

The solvent Modifier Cs7SB (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol) was detected in every sample analyzed by GCMS. Cs7SB was also the prime candidate for a nitration reaction due to the phenoxy portion of the molecule. The most probable locations for nitration are the positions marked with an asterisk in Figure 3-6 below.

Figure 3-6: Modifier Probable Locations for Nitration *
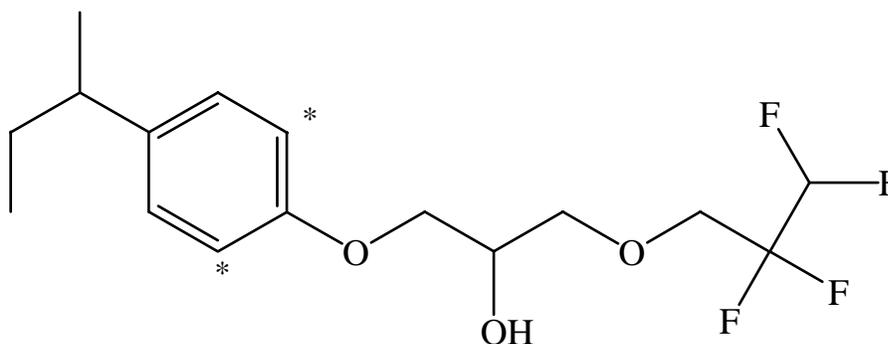
Some minor trace compounds were detected which could be decomposition or reaction products of the Cs7SB. The decomposition product detected was the butylphenol end of the molecule and was observed at a lower temperature zone as expected for a decomposition product. The column labeled "Nitrated Cs7SB" was a trace peak whose primary ion could be explained as a nitrated version of a fragment observed in the unreacted Cs7SB peak. This suggests that some nitration at a very low level may have occurred. The identification at this point is very tenuous and would require considerably more work and the synthesis of a standard to refine (or confirm) the identification. Note that this compound was present in the portions of the vessel and run that would be effective at nitration.

The IIT 747 antifoam used in the SRAT was detected in all of the samples. The compounds detected ranged from the simplest siloxane to some of the modified siloxanes that are present in the antifoam. The simple siloxanes and the cyclic siloxanes are typical decomposition products expected from the 747 antifoam.

The BobCalix was not observed in any of the extracts or rinses presumably due to its extremely low volatility.

The methylmercury column indicates when methylmercury chloride or methylmercury bromide were observed in the extracts. Since dimethylmercury was not detected, these mercury species were initially attributed to mercury reaction with the methylene chloride solvent used in the GCMS study. Further investigation discussed below, strongly suggest that the presence of methylmercury chloride in the process samples is real and not an artifact of the analysis method. The presence of methylmercury bromide suggests the solvent reaction since the only source of bromine was the trace levels of bromine present in the solvent (as bromochloromethane). Also detected in two of the condensates were trace levels of mercuric iodide (marked in the table as no*). The source of the iodine may also be the solvent since the solvent does show a trace of iodochloromethane or impurities in the MCU organic since iodine compounds are known to be used in the synthesis of the MCU organics.

Table 3-5 presents the ADS analysis (Semi Volatile Organic Analysis (SVOA) and HPLC) of the process samples from the continuous series runs. BOB-Calix was not detected in any of the process samples from this series. One sample from the vessel rinses did show BOB-Calix. This sample was of the feed vessel rinse presented in Table 3-6. Chloromethyl mercury was found in all of the FAVC samples where the acidity is extremely high. Since this compound was not found in all samples containing mercury, the reaction to

form chloromethyl mercury appears to be process related and not from injection port reactions. Sample results reported above also indicate chloromethyl mercury compounds in samples that would be expected to be high in acidity. Calculations indicated that the concentration of BOB-Calix in the SRAT products would be below the detection limit and would not be detected. Isopar®L was detected in a couple of samples. The general increasing trend in Modifier concentration and Isopar®L for the first 3 runs was consistent, but the trend did not continue for the next 2 runs. The reason for the break in the trend is unknown, but it is thought that the degree of mixing in the MCU feed vessel resulted in less organic being feed in the 4th run.

Table 3-5: Process Samples for Series of Five Runs

In Process Sample	Modifier (mg/L)	Calix (mg/L)	Isopar®L (mg/L)	Chloromethyl mercury (mg/L)
SB4-13 Dewater	<10	<10	<0.5	<0.5
SB4-13 Condensate 1	<5	<10	<0.3	<0.3
SB4-13 Condensate 2	3	<10	<0.3	<0.3
SB4-13 Condensate 3	7	<10	<0.3	<0.3
SB4-13 FAVC	<20	<35	<1	27
SB4-13 Rheol. sample	15	<10	NA	NA
SB4-13 SRAT product	38	<2.5	1.4	<0.1
SB4-14 Dewater	11	<10	<0.1	<0.1
SB4-14 Condensate 1	2	<5	<1	<1
SB4-14 Condensate 2	11	<5	<1	<1
SB4-14 Condensate 3	5	<5	<1	<1
SB4-14 FAVC	<10	<20	<1	70
SB4-14 SRAT product	80	<2.5	2.8	<0.1
SB4-15 Dewater	5	<10	<0.1	<0.1
SB4-15 Condensate 1	<2	<5	<1	<1
SB4-15 Condensate 2	4	<5	<1	<1
SB4-15 Condensate 3	10	<10	<0.3	<0.3
SB4-15 FAVC	<20	<35	<1	64
SB4-15 SRAT product	158	<2.5	5.6	<0.1
SB4-16 Dewater	10	<10	4.3	33
SB4-16 Condensate 1	6	<5	<1	<1
SB4-16 Condensate 2	22	<10	<0.3	<0.3
SB4-16 Condensate 3	10	<10	<0.3	<0.3
SB4-16 FAVC	<20	<25	16	99
SB4-16 SRAT product	58	<2.5	<0.1	<0.1
SB4-17 Dewater	8	<2.5	<0.1	<0.1
SB4-17 Condensate 1	2	<10	<0.3	<0.3
SB4-17 Condensate 2	12	<10	<0.3	<0.3
SB4-17 Condensate 3	12	<10	<0.3	<0.3
SB4-17 SRAT FAVC	<20	<35	<1	96
SB4-17 SRAT Product	97	<2.5	<0.1	<0.1
SB4-17 SME Product	44	<2.5	<0.1	<0.1
SB4-17 SME FAVC	<300	<300	<15	<15
SB4-17 SME Dewater	22	<10	<0.3	<0.3

NA – Not Analyzed

Following the completion of the SME cycle after the fifth run (SB4-17), the equipment was taken apart and samples collected. All of the equipment was rinsed with methylene chloride to recover any adhering organic materials. The following samples were taken:

1) MWWT Bulk Sample; everything that would drain from the MWWT.
2) FAVC Rinse; methylene chloride rinse of FAVC and offgas line from SRAT condenser.
3) MWWT Rinse; methylene chloride rinse of MWWT.
4) SRAT Condenser Rinse; methylene chloride rinse of SRAT condenser and off gas line.
5) Feed Tank Rinse; methylene chloride rinse of MCU feed tank and pump including remaining aqueous heel.
6) SRAT Rinse; methylene chloride rinse of SRAT vessel and attached glassware.

Table 3-6 presents the analysis of the vessel rinse samples collected.

Table 3-6: Vessel Rinse Samples

In Process Sample	Modifier (mg/L)	Calix (mg/L)	Isopar L (mg/L)	Aqueous Volume (ml)	Organic Volume (ml)
MWWT Bulk Sample	5,464	<25	360	60	As Needed
FAVC Rinse	<25	<50	<2	6	As Needed
MWWT Rinse	7,035	<25	400	1.2	As Needed
SRAT Condenser Rinse	25,300	<250	<10	6.2	As Needed
Feed Tank Rinse	492	18	870	560	As Needed
SRAT Rinse	35	<25	<1	0	62

The analyses presented in Table 3-6 have been corrected based upon the aqueous volume of the sample. The SRAT rinse had no aqueous portion, and the analysis was based on the volume of methylene chloride used to rinse down the vessel.

The analysis of the Feed Tank rinse, which included the remaining aqueous MCU that wasn't fed to the SRAT, demonstrated an accumulation of organics in the vessel. MCU organic solvent (~ 30% modifier) was added at 500 mg/L, but the final modifier concentration was 492 mg/L. This sample also contained 870 mg/L of Isopar®L solvent and 18 mg/L of BOB-Calix. The sum of the organic analysis is approximately 3X above what was charged. This indicates the build up of organic in the feed vessel. Visual observation verified that the organic solvent forms a separate phase floating on top of the aqueous fraction. Agitation in the feed tank was vigorous with a vortex that extended 2/3rds of the way down to the bottom of the vessel, but could not prevent a build up of organic phase. The pump suction was set just below the 500 ml heel depth.

Using the mass of each of the samples and the measured modifier concentration, a material balance was performed. The balance indicates that 5.4% of the modifier made its way to the condensate (not including the MWWT), 28.9% was transferred with the SRAT products, 22.5% remained in the process vessels and off gas system, and 12.5% remained in the feed vessel and transfer pump. The amount of modifier remaining in the feed vessel is approximately 2.5 times what should be left in the feed vessel heel if the organic was uniformly fed to the SRAT. The remaining 30.7 % of the modifier is presumed destroyed by side reactions.

3.5 Organic Carry Over Modeling Results

A model of the DWPF process developed in Aspen Custom Modeler™ (ACM, Version 11.1) was used to estimate concentrations of Isopar®L and modifier in the DWPF CPC that would be expected to occur under the operating conditions used in this experimental study. The model predictions were used to obtain additional insight into CPC processing impacts. The model performs material and energy balance

calculations for the CPC and Melt Cell and provides a dynamic simulation of DWPF batch process operations. The model is described by Smith (2005). For the present calculations, the process model was extended to include modifier as well as Isopar®L as an organic component in DWPF feed coming from the SEFT. The model assumes ideal vapor-liquid equilibrium calculations for separate aqueous and organic phases in the DWPF vessels. Vapor pressures for Isopar®L were obtained from a plot supplied by the manufacturer and vapor pressures for the modifier were obtained from Steel (2002).

The model was run simulating DWPF process operations but using parameters that matched the lab-scale experimental conditions. In particular, both SRAT and SME condensers were operated at 40ºC, the FAVC was operated at 10ºC, and the SRAT and SME purge air flows were set to 230 scfm and 74 scfm, respectively. To simulate coupled operations with the MCU, the model added 6400 gallons of SEFT solution to the SRAT during boiling with no increase in SRAT volume during the addition. One difference from the experimental setup is that the model includes ammonia scrubbers in the SRAT, SME, and Melter Feed Tank (MFT) off-gas streams. The scrubbers work by circulating water from the SMECT through the scrubber and back to the SMECT. The model treats the scrubbers as condensers operating at the SMECT temperature. That is, the off-gas in the scrubbers is cooled to the SMECT temperature (17ºC) and vapors are allowed to condense. Since the scrubbers operate at a higher temperature than the FAVC and since condensate from the scrubbers and FAVC all go into the SMECT, it is not expected that including the ammonia scrubbers in the model will lead to a significant difference between the model and experimental results. The MWWT in the model is treated as a constant well-mixed liquid volume that collects condensate from the SRAT Condenser during coupled MCU operation and overflows into the SMECT. Gas flow through the MWWT is not modeled. To simulate experimental conditions, the model was modified to eliminate decon frit addition to the SME.

As described above, it was difficult to achieve a uniform feed of aqueous and organic material from the MCU feed tank to the SRAT. However, for modeling purposes, it has been assumed that the organic concentration in the MCU feed was constant. The feed composition was estimated based on the following assumptions:

- The organic concentration in the 13.9 liters of MCU feed was made up to the target composition.
- The increased organic concentrations in the 560 ml MCU tank heel represent material that accumulated over the five SRAT batches. The difference between the target feed and the heel is the amount of organic material that was fed to the SRAT and this material was distributed uniformly during feeding over the five SEFT batches.
- Table 3-7 shows the estimated average feed composition (Actual Feed) determined from these assumptions. This is the SRAT feed composition used in the model calculations.

Table 3-8 presents a summary of model results. Gas concentrations in the DWPF offgas stream in Table 3-8 are ppm by volume; all other concentrations are ppm by mass. The offgas and DWPF recycle stream concentrations are averaged over all five SRAT batches, the other concentrations in the process vessels are instantaneous values at the end of the simulation. Instantaneous concentrations in the SMECT and RCT can be somewhat misleading since the volume of liquid and concentrations in these tanks will change abruptly as condensate from different sources collects and the tanks are drained and filled. The model does not include evaporation of organics by the air purge flow through the vessels but the purge flow does dilute the offgas and influences condensation and the offgas concentration.

Table 3-7: Estimation of Average MCU Feed Composition.

Component	Target Feed (mg/L)	Heel (mg/L)	Actual Feed (mg/L)	Percent Fed
BOBCalixC6	5.0	18	4.5	89.2
Modifier	158.8	492	144.8	91.2
TOA	0.7		0.6	
Isopar®L	368.5	870	347.4	94.3
Total	533.0	1380	497.3	93.3

Table 3-8: Model Predicted Organic Concentrations after Five SRAT/SME Batches Compared to Experimental Results

Vessel/Stream	Isopar®L		Modifier	
	Model	Experiment	Model	Experiment
SRAT	«1 ppm	<0.1 ppm	93 ppm	97 ppm
SME	«1 ppm	<0.1 ppm	42 ppm	44 ppm
MFT	«1 ppm		35 ppm	
MWWT	110 ppm	360 ppm	2.3 wt%	0.5 wt%
SMECT	1 ppm		62 ppm	
RCT	0.1 ppm		6 ppm	
DWPF Recycle	1.2 ppm		16 ppm	
Offgas	10 ppm		0.1 ppm	

In general, the model shows that Isopar®L is almost entirely stripped out in the SRAT and exits in the process offgas which agrees with the experimental results. Also in agreement with the experimental data, the model predicts an accumulation of Isopar®L in the MWWT although the model predicted concentration is about one third of the experimentally measured value. As discussed above, the organic feed was not well mixed with the aqueous phase in the SRAT feed. If large amounts of Isopar®L suddenly evaporated due to a slug being fed to the SRAT during the experiments, it could saturate in the condenser and accumulate to a greater extent in the MWWT. A possible explanation for the higher concentration of Isopar®L measured in the MWWT at the end of the experiments is that the model assumes a uniform feed versus feeding slugs of organic with the aqueous as likely occurred in the experiment. Feeding a slug of organic causes more Isopar®L to be vaporized than can be carried by the SRAT air purge and the excess condenses in the SRAT condenser.

Like Isopar®L, modifier is steam stripped out in the SRAT during feeding but the evaporated modifier largely condenses in the SRAT condenser and thereby enters the MWWT, SMECT, RCT, and recycle stream. The higher concentration of modifier in the MWWT predicted by the model is the largest difference between model and experimental results. A significant amount of modifier was found in the SRAT condenser rinse following the experiments. Adding this material to the MWWT would increase the experimentally measured concentration since the model does not account for accumulation in the offgas line from the SRAT and condenser. The model also assumes that condensate entering the MWWT is immediately completely mixed with the vessel contents. In practice, mixing may be slow and fresh condensate may preferentially be decanted from the MWWT to the SMECT lowering the measured concentration. However, the modifier is denser than water and would be expected to accumulate in the

MWWT. Density differences are not accounted for in the model. It is difficult to accurately model the behavior of the organic phase in the small MWWT volume.

There is no recycle from the MWWT to the SRAT in the simulation so modifier in the SRAT at the end of the run is residual material that did not evaporate. Modifier remaining in the SRAT is transferred into the SME where some material is again removed by steam stripping when the SME is boiled to reduce the volume during frit addition. Modifier left in the SME is transferred into the MFT where it would eventually reach the melter. Considering the significant differences between the model and the experimental conditions, particularly the modeling assumptions of ideal behavior and a uniform organic concentration in the SEFT feed, the very close agreement between model predictions and experimentally measured modifier concentrations in the SRAT and SME must be considered somewhat fortuitous. Nevertheless, the calculation shows that the model is capable of predicting the experimental results with reasonable accuracy.

3.6 SRAT and SME Product Characterization

The SRAT product from each run and the SME product from the last run were characterized for the anion concentration, cation concentration, solids content, density, pH, and rheology. The product anion concentrations for each run are given in Table 3-9. All runs met the DWPF <1000 mg/kg nitrite limit.

Table 3-9: SRAT/SME Product Concentration (mg/kg)

Run ID	Nitrite	Nitrate	Formate
SB4-5 SRAT	789	25800	54500
SB4-13 SRAT	<100	24350	45650
SB4-14 SRAT	232	23150	44050
SB4-15 SRAT	221	23600	45300
SB4-16 SRAT	123	24100	46050
SB4-17 SRAT	111	24950	47500
SB4-17 SME	<100	23850	49400

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

To determine the impact of the MCU process on nitrite to nitrate conversion and formate destruction, which ultimately control the relative amounts of formic and nitric acid to be added, estimates on SRAT receipt and product masses had to be made. For the SB4-5 run, masses of the receipt and product were measured and were known values, so calculating the conversions and destructions was straight forward. In the continuous series run, only the initial SRAT receipt mass of run SB4-13 and the final SME product mass from SB4-17 were measured. Instead of dismantling the equipment and weighing the SRAT heel after each run, the SRAT sampler was kept at a constant height so that a 500 ml heel would remain. Using the densities of the SRAT products from each run, the amount of heel remaining could be estimated. This could be compared against the starting mass and the amount of SRAT product removed after each run (which was weighed) to assess the accuracy of the estimates. This appeared to provide a reasonable estimate for the masses throughout the runs. The estimates are provided in Table 3-10 for the SRAT cycles.

Table 3-10: SRAT Estimated Nitrite to Nitrate Conversions and Formate Destructions

Run ID	Nitrite to Nitrate Conversion (%)	Formate Destruction (%)
SB4-5	4.98	24.29
SB4-13	12.02	19.91
SB4-14	3.30	20.05
SB4-15	6.16	17.96
SB4-16	9.09	16.70
SB4-17	10.46	16.04

None of the estimated values in Table 3-10 were close to the pre-run assumptions for nitrite to nitrate conversion (i.e., 21%). The last run in the series, SB4-17, was close to the projection for formate destruction (i.e., 14%) used in the acid calculations for all of the runs (see Table 3-2). For the continuous runs, the estimated values changed from run to run with larger variation seen in the nitrite to nitrate conversion values. Some of the variation is attributed to the assumptions that were made on the masses since measured values were not available. However, the trend appeared to be that formate destruction decreased as the runs continued to be processed. The highest nitrite to nitrate conversion for the continuous runs was seen for the run without the heel and then conversion dropped dramatically and then began to increase as processing continued. For the SME from run SB4-17, additional formate was destroyed during processing and the overall formate destruction (from start of SRAT to the end of SME) was estimated to be 18.37%. Nitrate was also destroyed during the SME process, with a system nitrate destruction estimated to be 16.30%. The destruction seen in the SME was higher than what was seen in SB3 testing (Herman et. al., 2003).

As mentioned in Section 2.3, the SRAT products were calcined at 1100°C in order to prepare them for cation analyses. The elements detected in the calcined solids are given as Table 3-11.

When the SRAT product compositions are compared with the simulant compositions given in Table 3-1, most of the oxides are very similar. The SME product from SB4-17 had a calculated waste loading of 37.3% based on the DWPF lithium waste loading method. This method uses the normalized Li_2O concentration from the SME calcined oxides relative to the Li_2O in Frit 320 (7.99% for this lot). This projection was slightly higher than the target of 35 wt%. Run SB4-5 was higher in Al, Ca, and Mg and was lower in K, Na, and Ti compared to the other runs. This could be attributed to the higher solids seen in this run and may indicate that some segregation of the sludge may have occurred as was experienced in the SB4 sludge only runs (see Baich et. al., 2005). Overall, the compositions represented a reasonable estimation of the SB4 simulant and major ARP components.

Table 3-11: SRAT/SME Product Results (Calcined Solids Wt%)

Element	SB4-5	SB4-13	SB4-14	SB4-15	SB4-16	SB4-17 SRAT	SB4-17 SME
Al	15.0	12.0	13.4	13.1	13.4	12.2	4.73
B	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100	0.864
Ba	0.169	0.159	0.152	0.157	0.155	0.158	0.079
Ca	2.61	1.99	1.81	1.85	2.10	1.87	0.833
Cr	0.163	0.142	0.141	0.143	0.141	0.145	0.056
Cu	0.072	0.064	0.064	0.065	0.065	0.064	0.027
Fe	21.2	21.7	21.7	21.4	21.6	21.3	7.14
K	0.742	1.07	1.04	1.03	1.04	1.05	0.471
Li	<0.100	<0.100	<0.100	<0.100	<0.100	<0.100	2.31
Mg	0.862	0.833	0.789	0.815	0.823	0.900	0.372
Mn	6.08	5.25	5.23	5.21	5.10	5.53	1.82
Na	11.8	16.2	15.3	15.3	15.5	15.7	11.1
Ni	3.00	2.96	3.00	2.90	2.85	3.02	0.977
Pb	0.032	<0.010	<0.010	<0.010	<0.010	<0.010	0.023
S	0.251	0.311	0.289	0.297	0.306	0.305	0.098
Si	1.44	1.30	1.31	1.26	1.26	1.30	23.2
Ti	0.400	0.525	0.518	0.532	0.511	0.535	0.234
Zn	0.120	0.110	0.111	0.112	0.104	0.108	0.055
Zr	0.316	0.258	0.272	0.299	0.305	0.289	0.144

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 and SME products, 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 3-12.

Table 3-12: Physical Property Data on SRAT/SME Products

RUN ID	Total Solids (wt%)	Insoluble Solids (wt%)	Soluble Solids (wt%)	Calcined Solids (wt%)	Slurry Density (g/ml)	pH
SB4-5	31.6	20.1	11.5	21.4	1.20	7.70
SB4-13	22.1	12.0	10.1	13.8	1.17	7.61
SB4-14	22.8	12.9	9.91	14.5	1.19	7.66
SB4-15	22.9	12.6	10.4	14.7	1.15	7.49
SB4-16	22.7	12.4	10.3	14.5	1.15	7.38
SB4-17 SRAT	23.2	12.6	10.6	14.7	1.18	7.13
SB4-17 SME	51.7	40.7	11.0	42.9	1.27	7.30

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.

A higher total solids was targeted for the first run since the ARP and sludge were added separately. The data supports this higher target from the first run compared to the series of 5 runs. In the SB4-5 run, all of the water associated with the ARP stream was removed to try to maintain a relatively high solids during SRAT

processing. For the other runs, the initial feed contained both the ARP and sludge that were pre-blended and the acid calculation used the analysis of this feed. This blend assumes that concentration has occurred and a nominal starting total solids is obtained. Therefore, when the amount of dewater necessary was calculated, only the mass associated with the acids, antifoam, and trim water was removed. In addition, SB4-5 feed had problems during the sludge only runs with rapids solids settling and the feed may have been high in solids when added to the vessel. This is somewhat supported by the slightly higher (~2%) than targeted product total solids, whereas the other runs were close to their target.

The SRAT products were also filtered to remove the supernate, so the soluble components could be determined. The ICP-AES data for all of the samples are given in Table A - 6. 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 assumed to be 1.06 g/ml for all of the samples. Table 3-13 presents the relative solubility data for the SRAT products.

Table 3-13: Relative Solubility of Elements in the SRAT Product Supernates

Test	Ba	Ca	Cu	K	Mg	Mn
SB4-5	0.289%	65.6%	0.044%	131%	73.3%	37.4%
SB4-13	0.340%	79.1%	0.072%	134%	98.5%	72.7%
SB4-14	0.335%	81.1%	0.079%	125%	89.7%	65.0%
SB4-15	0.288%	84.2%	0.081%	132%	88.5%	64.6%
SB4-16	0.306%	81.9%	0.072%	133%	88.8%	68.3%
SB4-17	0.304%	87.5%	0.078%	137%	84.9%	66.0%
Test	**Na**	**Ni**	**Pd**	**Rh**	**S**	**Si**
SB4-5	102%	0.003%	0.208%	0.412%	48.6%	0.259%
SB4-13	113%	0.014%	ND	0.367%	76.0%	0.842%
SB4-14	108%	0.029%	ND	0.283%	77.9%	0.982%
SB4-15	110%	0.026%	ND	0.280%	70.5%	1.69%
SB4-16	105%	0.022%	ND	0.247%	69.8%	1.55%
SB4-17	107%	0.029%	NA	NA	77.6%	1.17%

ND – Not detected, NA – Not analyzed

In general, the SB4-5 reactivity run had lower relative solubilities than all of the SRAT products from the continuous runs. Pd and Rh were an exception, but due to the very small concentrations present and the uncertainty associated with the analytical technique, the difference was probably not statistically significant. As expected, K and Na were completely soluble in the SRAT products. The >100% numbers for both elements reflect some of the uncertainty in the analytical data, especially for K. Analysis for K is typically a difficult element to measure on ICP-AES and the combined uncertainty in the product analyses and the supernate analyses is reflected in the >100% values. Although not measured in this run, Ca and Mg are typically insoluble in the sludge simulant. As was the case with the SB4 sludge only runs (Baich et. al., 2005), both Ca and Mg became very soluble during SRAT processing likely due to the creation of formate species. The relative amounts were comparable to most of the sludge only SB4 runs, with slightly higher solubilities seen in the lower acid runs performed as part of the sludge only testing. The metals Ba, Cu, and Ni showed minimal solubility in the SRAT products, which was also consistent with SB4 sludge only simulant testing. 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 is typically insoluble in the simulant (see Baich et. al. (2005) for SB4 sludge only simulant results) and was significantly reduced during this testing. Run SB4-5 was close to the reduction target, while the other runs were comparable to SB4 sludge only testing at higher acid stoichiometries. Sulfur was added in the form of sodium sulfate, so is typically very soluble in the simulant. Based on the calculated relative solubilities, ~30% S became insoluble during processing during the

continuous runs with only ~51% becoming insoluble in the SB4-5 run. The SB4-5 run was more consistent with the SB4 sludge only runs. Finally, limited noble metals data from the SRAT products were reported. ICP-AES is not the preferred method for analyzing the noble metals due to higher detection limits than ICP – Mass Spectroscopy, but general trends were investigated for the runs. Pd was only detected in the SB4-5 run, whereas Ru was not detected in any of the runs. Rh showed very limited solubility that appeared to decrease in the continuous runs but not by a significant amount. Although not shown in this table, Al, Fe, Pb, Ti, Zn, and Zr were almost completely insoluble in most of the samples. This was consistent with the SB4 sludge only runs also.

Mercury analysis was performed on the SRAT and SME product samples. All of the samples showed significant reduction of mercury during SRAT processing. Therefore, the addition of the MCU stream did not appear to impact mercury reduction.

Rheological analysis of the SRAT products and the SME product were performed at a minimum in duplicate. Appendix B presents the flow curves and the averaged Bingham Plastic yield stress and plastic viscosity using the Bingham Plastic rheological model. All of the products were visually and rheologically thin, and only minor differences were observed for product and feed slurries. The character of these feeds, cause the formation of Taylor vertices in the rheometer. The Taylor vortices data was not included in the analysis. The analysis technique used is more suitable to thicker non-Newtonian fluids.

The average yield stress for the feed material ranged from 0.15 to 0.18 Pa. The plastic viscosities of the feeds ranged from 2.44 to 2.64 cP. The measured viscosities and yield stresses were lower than those seen for SB4 sludge only runs (Baich et. al., 2005). The SME product was thicker than the SRAT product with a measured yield stress of 2.95 Pa and greater viscosity of 25 cP. These values would be on the lower end of the DWPF limits. For the simulant runs, this may have increased the potential for solids settling. The rheology of actual SB4 material is not known at this point, but should be monitored during radioactive characterization to determine if this will be a problem. In addition, future SB4 simulant development will also try to more closely mimic actual waste properties.

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4.0 CONCLUSIONS

Key findings from the runs with MCU and ARP include the following:

1. The MCU vessel configuration used for lab-scale testing resulted in organic phase separation. The likelihood of this occurring in DWPF needs to be investigated since the DWPF safety basis for MCU operations assumes a constant feed composition.

2. MCU organic in the lab-scale feed vessel was observed collecting in the inverted feed pump leg when transfers were not taking place. This may occur also for DWPF operation causing slugs of organic to be fed to the SRAT. This also needs to be evaluated given the pump design for DWPF.

3. More organic may be transferred at the end of the MCU feeding cycle than the beginning due to the proximity of the pump suction and the liquid surface. Maintaining continuous suspension for DWPF will be key factor in maintaining a uniform feed composition.

4. Modifier was steam distilled from the SRAT and collected in offgas piping and the MWWT. Modifier would be expected to work its way to the FAVC in time, but none was detected here.

5. The MWWT was found to collect both a floating organic phase and a dense organic phase that sunk to the mercury level. This phase is made up of Isopar$^®$L solvent and modifier.

6. BOB-Calix was not detected in any of the process samples from the continuous series runs. It was only detected in the feed vessel rinse. Analysis of SRAT products that showed significant modifier did not show BOB-Calix. It is proposed that the BOB-Calix did not steam strip, was below detection limits, or was reacted to form other compounds.

7. Isopar$^®$L was detected in the FAVC and MWWT condensate samples. The detected concentration appears to increase as processing continues batch after batch, but only a small fraction of the Isopar$^®$L was recovered. Most was likely lost in the off gas.

8. The MCU stream did not appear to impact nitrite destruction, hydrogen generation, mercury reduction, or foaming. Slight differences in rheology, nitrite to nitrate conversion, offgas concentrations, Mn reduction, formate destruction, and the pH profiles were observed; however, the differences at this point do not appear to have a significant impact on processing.

9. The formation of chloromethyl mercury in highly acidic environments was verified.

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5.0 RECOMMENDATIONS/PATH FORWARD

Implementation of MCU processing in DWPF would be expected to lead to organic buildup in the MWWT, RCT, and the process piping. This was supported by this testing and modeling efforts. Continued means of reducing the organic carryover to DWPF should be investigated.

Mixing studies should be performed to determine the degree of organic accumulation in the feed tank (SEFT), and means should be evaluated for preventing the accumulation.

In future testing with SB4 sludge only, condensate samples should be analyzed for the presence of methyl mercury phases. The presence of these compounds is thought to be possibly formed from antifoam and mercury and would be present without MCU organics.

Mercury pumped to the mercury purification cell would also be expected to contain some amount of organic. Most likely the organic would be a mix of Isopar®L and modifier. Investigation of an organic removal column in the mercury purification cell should be investigated.

Given changes in the safety strategy for the addition of ARP stream, perform testing to determine the impact of adding the ARP stream during caustic boiling of the sludge. The testing will focus on pH and condensate composition changes, as well as possible rheology impacts.

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7.0 ACKNOWLEDGMENTS

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**APPENDIX A. FEED MAKE-UP, SRAT/SME RUN PARAMETERS, AND GC
DATA**

Table A - 1: SB4 Simulant Batching Recipe (g)

Material to be Added/Step	Baseline Wash Scenario
Combine	grams
B Simulant	19754.27
C Simulant	5154.54
While stirring, add	
Water	8272.57
NaOH	250.68
$Ni(NO_3)_2 \cdot 6H_2O$	911.34
Wait 15 minutes, then add	
$Al(OH)_3$	1968.91
$BaSO_4$	1.587
Cr_2O_3	19.719
CuO	1.759
KOH	99.97
$Mg(OH)_2$	169.53
$PbSO_4$	8.027
SiO_2	89.247
ZnO	7.219
Water	2757.5
While stirring, add	
Na_2CO_3	166.69
Na_2SO_4	39.57
$NaNO_2$	971.57
$NaNO_3$	92.71
NaOH	255.04
Water	2757.5
TOTAL	**43750.0**

Table A - 2: 4X ARP Feed Make-Up

	NaTi2O5H		Target	Net		4x concentrate	added	Wt%
	Slurry		Batch			ARP	Grams	4X Conc.
	491.28		Makeup	491.282	NaTi2O5H	491.282		
Total solids, wt%	13.14		grams		Slurry			
Insoluble solids, wt%	11.21	Titanate						
Soluble solids, wt%	1.93	NaOH						
NaOH, gmol/l	0.5							
			143.580	143.580	Sludge	143.580		7.178986
Titanate	55.073	0.000	55.073	0.000	MST	0.000		2.753637
			1.562	1.562	NaNO2	1.562		0.078117
			74.993	74.993	NaNO3	74.993		3.749634
NaOH	9.48		29.685	20.203	NaOH	20.203		1.010143
			46.402	46.402	NaC2O4	46.402		2.320086
water	426.73		7648.706	7221.978	water	1221.978		17.0906
			8000.000			2000.000		

Table A - 3: MCU Aqueous Fraction Make-Up (Maximum Case)

Species	Strip Effluent to DWPF, lb/hr	Scale Factor	Lab Scale, g	Acid Molarity (M)	Acid (ml)	Mass to Add (g)	Additive
Water	252.8	0.1395	15989.9			15989.90	Water
$CsNO_3$	0.0988	0.1395	6.250			6.25	$CsNO_3$
HNO_3	0.016	0.1395	1.012	10.53	1.53	2.00	HNO_3
Organic	0.01314	0.1395	0.8312				
Total	252.92794	0.1395	16000			16000	
NO_3 (M)	0.003						

Table A - 4: SRAT Run Parameters

Parameter	SB4-5	SB4-13	SB4-14	SB4-15	SB4-16	SB4-17
Initial Sludge Mass (g)	2527	2500	2000#	2000#	2000#	2000#
4X ARP Feed (g)	268.9	*	*	*	*	*
MCU Aqueous Addition (ml)	2750	2667	2667	2667	2667	2667
MCU Solvent Addition (ml)	4.5	2.0	1.67	1.67	1.67	1.67
MCU Aqueous Addition Time (hr)	12.53	14.25	13.4	13.37	13.38	13.33
Hg Target (wt% in total solids)	1.0	1.0	1.0	1.0	1.0	1.0
HgO Added (g)	6.5262	5.4058	4.3243	4.3243	4.3239	4.3242
AgNO$_3$ Added (g)	0.0023	0.0019	0.0017	0.0017	0.0014	0.0017
Pd(NO$_3$)$_2$*H$_2$O Added (g) – 15.27% Solution	0.4750	0.3940	0.3147	0.3147	0.3149	0.3150
Rh(NO$_3$)$_3$*2H$_2$O Added (g) – 4.93% Solution	2.6969	2.2336	1.7873	1.7873	1.7868	1.7872
RuCl$_3$ Added (d)	1.1727	0.9718	0.7772	0.7772	0.7772	0.7769
Rinse Water for Trim Chemicals (g)	39.9998	40.0001	40.000	40.000	40.0001	40.000
DWPF SRAT Scale Factor (6,000 gallon basis)	9421	10425	10426	10426	10426	10426
Nitric Acid Amount Added (ml)	30.943	28.121	22.496	22.50	22.50	22.50
Nitric Acid Addition Rate (ml/min)	0.793	0.717	0.717	0.717	0.717	0.717
Nitric Acid Moles	0.3257	0.2961	0.2368	0.2369	0.2369	0.2369
Formic Acid Amount Added (ml)	152.044	134.659	107.728	107.73	107.73	107.73
Formic Acid Addition Rate (ml/min)	0.802	0.721	0.721	0.721	0.721	0.721
Formic Acid Moles	3.589	3.178	2.542	2.542	2.542	2.542
Total SRAT Dewater Amount (g)	539.9	283.8	239.2	243.4	267.7	235.1
SRAT Target Boil-up Rate (g/min)	4.01	3.63	3.63	3.63	3.63	3.63
MCU Aqueous Addition Rate (g/min)	4.01	3.63	3.58	3.58	3.58	3.58
SRAT Air Purge on System (sccm)	688	622	622	622	622	622
SRAT Helium Purge on System (sccm)	3.4	3.1	3.1	3.1	3.1	3.1
Initial Sludge pH with Trim Chemicals	11.51	12.13	10.93	10.75	10.85	10.43
pH at End of Acid Addition	4.64	4.63	4.68	4.66	4.68	4.67
pH at End of SRAT (at boiling)	6.67	7.44	6.89	6.77	7.28	6.66
Antifoam Addition (g)	20.02	17.85	17.85	17.85	17.85	17.85
Total Condensate Removed (g)	2750.1	2653.0	2680.8	2715.3	2668.3	2749.1
FAVC Mass Collected (g)	7.5	6.97	14.75	10.33	9.85	11.429
Run Plan Document Number	SRT-GPD-2005-00055	SRT-GPD-2005-00106	SRT-GPD-2005-00107	SRT-GPD-2005-00108	SRT-GPD-2005-00109	SRT-GPD-2005-00110

500 ml heel left from previous batch

* 4X ARP Feed Incorporated into SRAT Feed Material 10,922.7 gm Sludge feed (031505-5) with 1077.2 gm 4X ARP

Table A - 5: SME Processing Parameters

Parameter	SB4-17
Total Frit Added (g)	574.8
Total Formic Added (g)	8.61
Total Water Added (g)	566.1
Total Dewater during SME (g)	1133.47
DWPF SME Scale Factor (6,000 gallon basis)	11614
Dewater Time #1 (hr)	1
Dewater Time #2 (hr)	0.83
Dewater Time #3 (hr)	0.92
Final Dewater Time (hr)	2.87
SME Target Boil-up Rate (g/min)	3.25
SME Air Purge on System (sccm)	179.5
SME Helium Purge on System (sccm)	0.90
pH at End of SME (at boiling)	6.32
Antifoam Addition (g)	2.55
FAVC Mass Collected (g)	1.08
Run Plan Document Number	SRT-GPD-2005-00110

Table A - 6: ICP-AES Supernate Data from SRAT Products (mg/L)

Run	Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na
SB4-5	0.112	1.39	4865	<0.010	0.090	<0.010	2755	1795	6460	34350
SB4-13	0.111	0.897	2615	<0.100	0.077	<0.040	2375	1365	6350	30500
SB4-14	0.110	0.899	2685	<0.100	0.089	<0.040	2320	1255	5970	30150
SB4-15	0.110	0.805	2775	<0.100	0.094	<0.040	2405	1285	5995	29850
SB4-16	0.111	0.827	2830	<0.100	0.083	<0.040	2430	1290	6120	28700
SB4-17	0.052	0.855	2905	<0.100	0.089	<0.040	2550	1360	6500	29750
Run	Ni	P	Pb	Pd	Rh	Ru	S	Si	Zn	Zr
SB4-5	0.280	0.794	0.291	0.105	0.380	<0.010	347	10.6	0.095	<0.010
SB4-13	0.690	<0.500	<0.500	<0.100	0.215	<0.010	393	18.2	<0.010	<0.010
SB4-14	1.53	<0.500	<0.500	<0.100	0.173	<0.010	405	22.3	0.024	<0.010
SB4-15	1.37	<0.500	<0.500	<0.100	0.171	<0.010	373	38.0	0.025	0.024
SB4-16	1.08	<0.500	<0.500	<0.100	0.149	<0.010	365	34.2	<0.010	0.016
SB4-17	1.54	0.704	<0.500	NA	NA	NA	422	27.1	0.088	0.015

Figure A - 1: SB4-5 GC Data
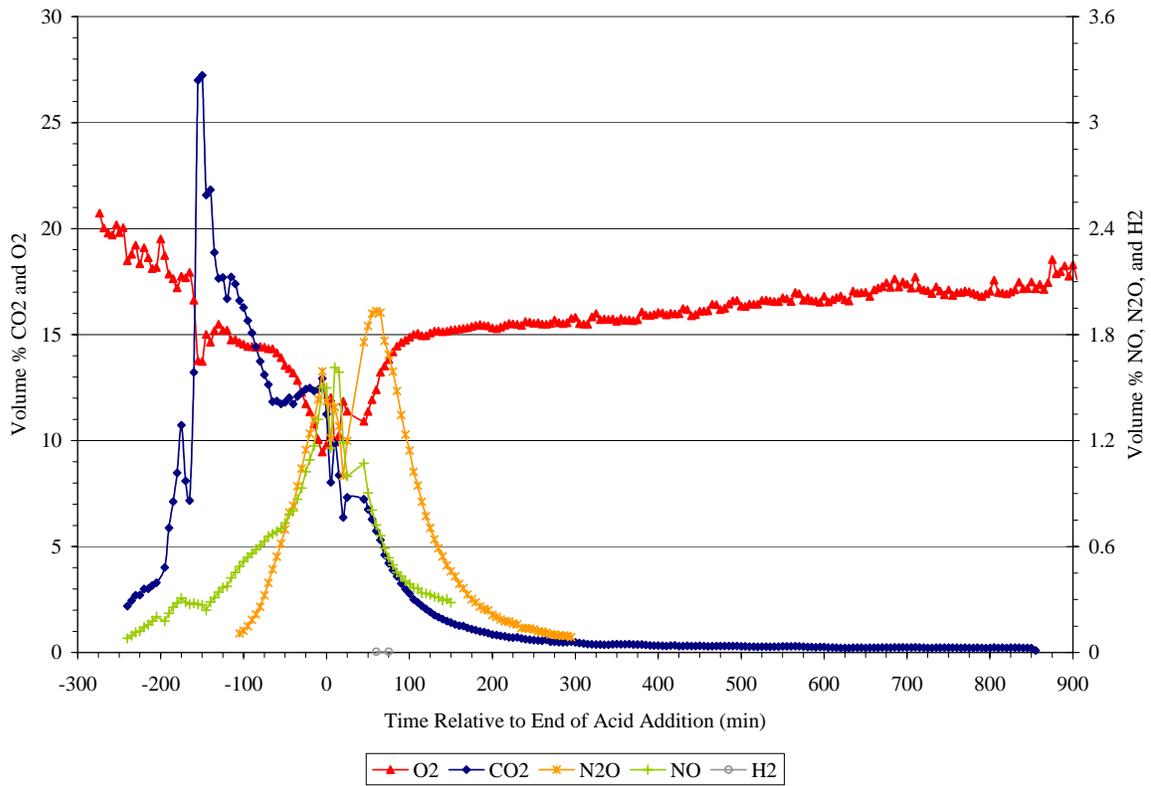
Figure A - 2: SB4-13 GC Data
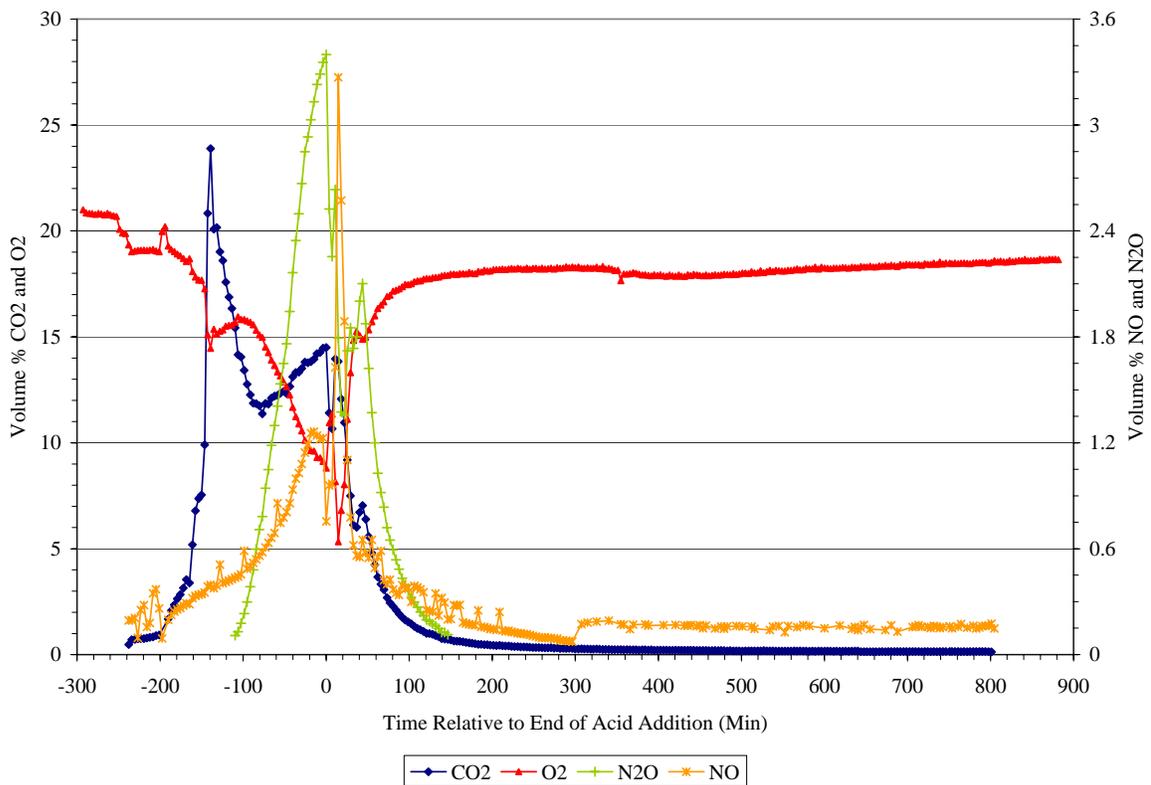
Figure A - 3: SB4-14 GC Data
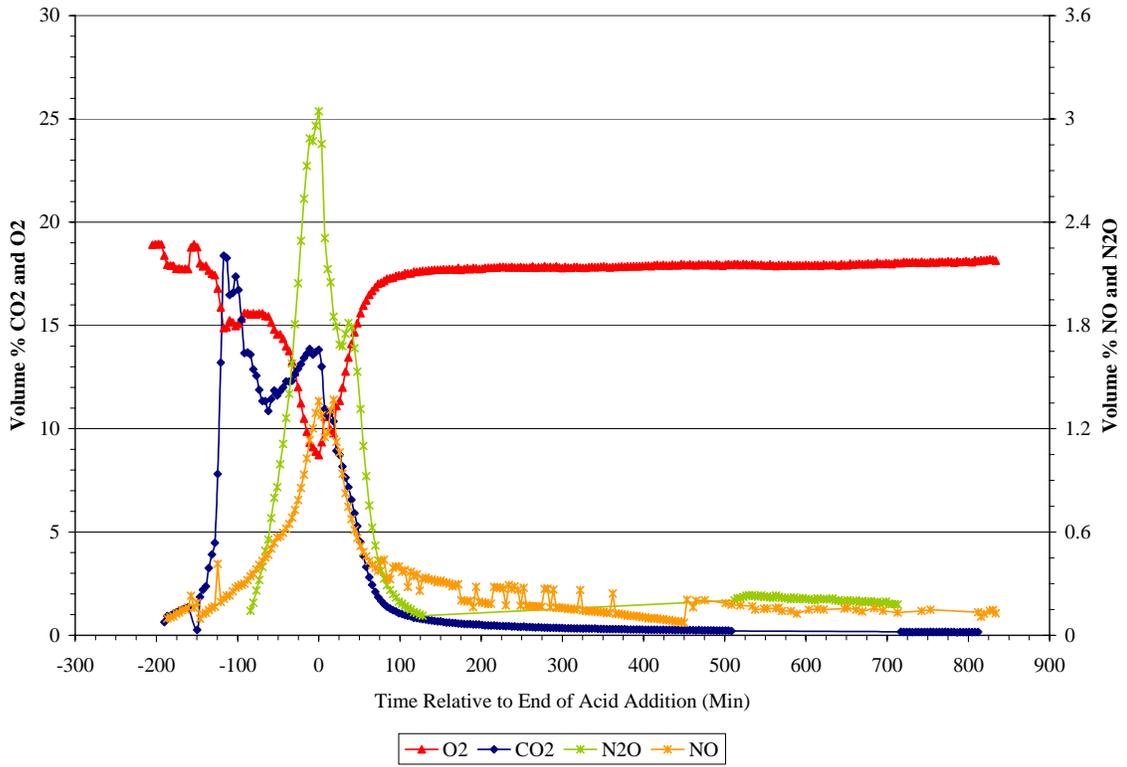
Figure A - 4: SB4-15 GC Data
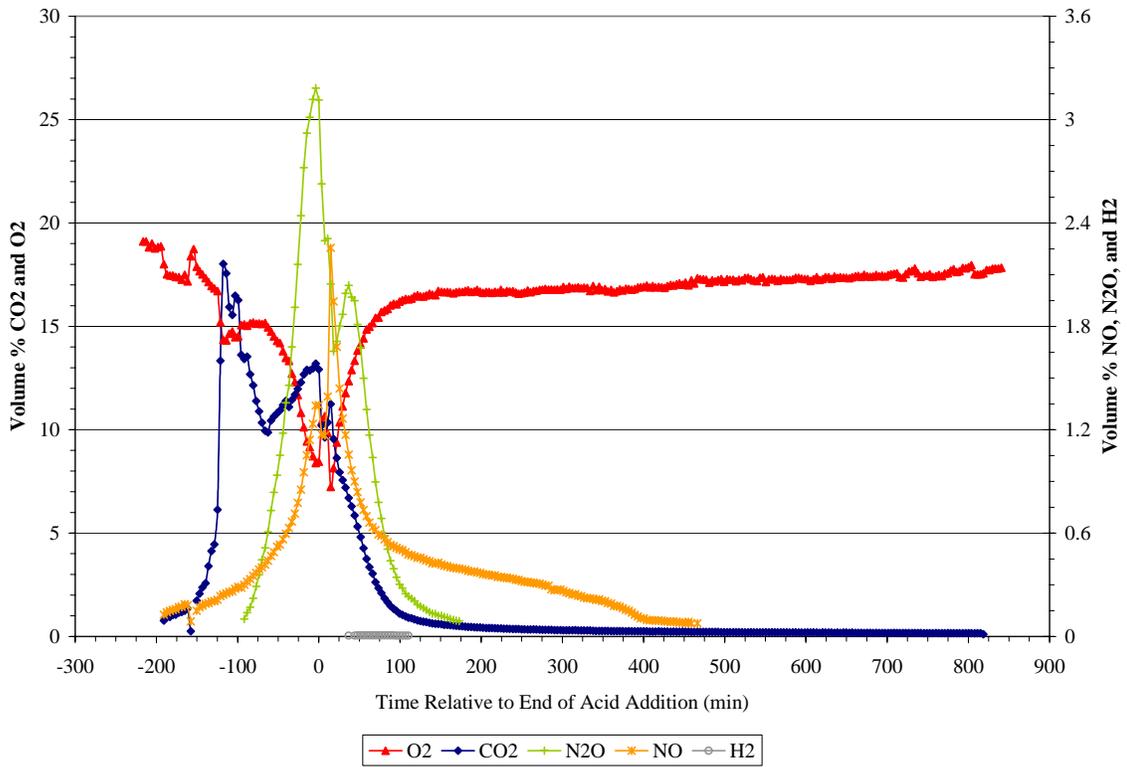
Figure A - 5: SB4-16 GC Data
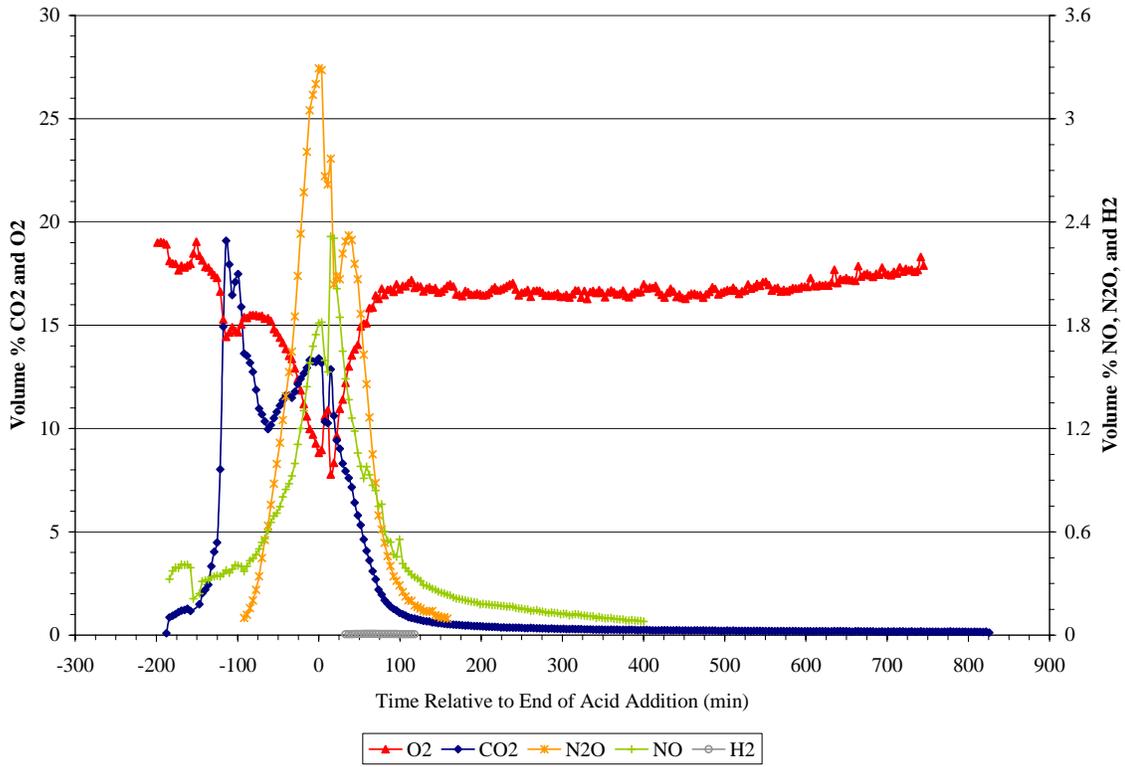
Figure A - 6: SB4-17 GC Data
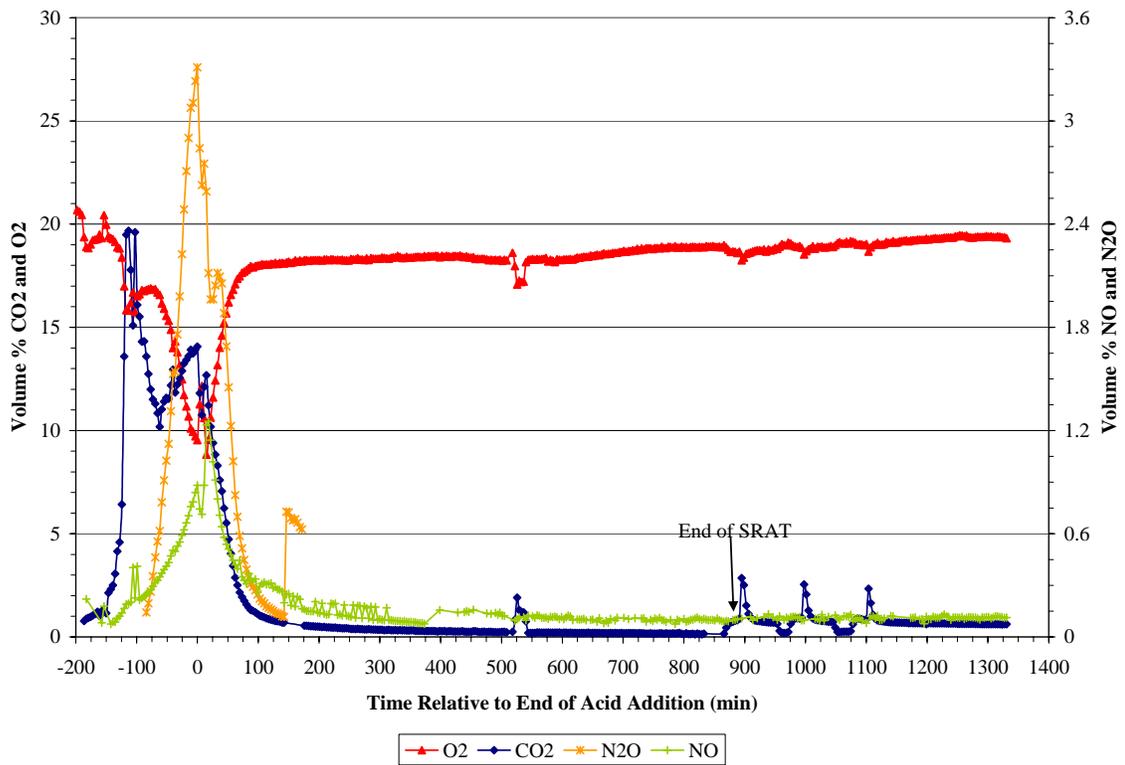
APPENDIX B.   RHEOLOGY DATA

Figure B - 1: Rheology of SB4-5 Feed (Sludge Only)

Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
SB4 Feed For Runs SB4-5 to SB4-8 R1	2.81	0.50	0.9962	Z41	Samples Run 3-22-05	
SB4 Feed For Runs SB4-5 to SB4-8 R2	2.78	0.50	0.9957	Z41	Samples Run 3-22-05	
					Results are fitted to the up curve, which are slightly more viscous than the down curve. Down	
Average	2.79	0.50			curve fitted parameter are provided in the individual work sheets. Data fitted between 40 to 530	
Stdev	0.02	0.00			sec^{-1}. Upper limit capped to due Taylor vortices.	
%Stdev	0.9%	0.2%				

Figure B - 2: Rheology of Feed for MCU Continuous Run with ARP

Feed for SB4-13 to SB4-17 with ARP Added_R1

Feed for SB4-13 to SB4-17 with ARP Added_R1

Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
Feed for SB4-13 to SB4-17 with Added ARP_R1	2.47	0.36	0.9875	Z41	Samples Run 4-11-05	
Feed for SB4-13 to SB4-17 with Added ARP_R2	2.52	0.35	0.9903	Z41	Samples Run 4-11-05	
					Results fitted to up curve. Data fitted between 0 to 475 sec^{-1}. Taylor vortices impacting results above 475 sec^{-1}. Down curve has slightly less of a yield stress and essentially the same plastic viscosity.	
Average	2.50	0.35				
Stdev	0.04	0.01				
%Stdev	1.5%	2.8%				

Figure B - 3: Rheology of SB4-13 SRAT Product

SB4-13 SRAT Product_R1

SB4-13 SRAT Product_R2
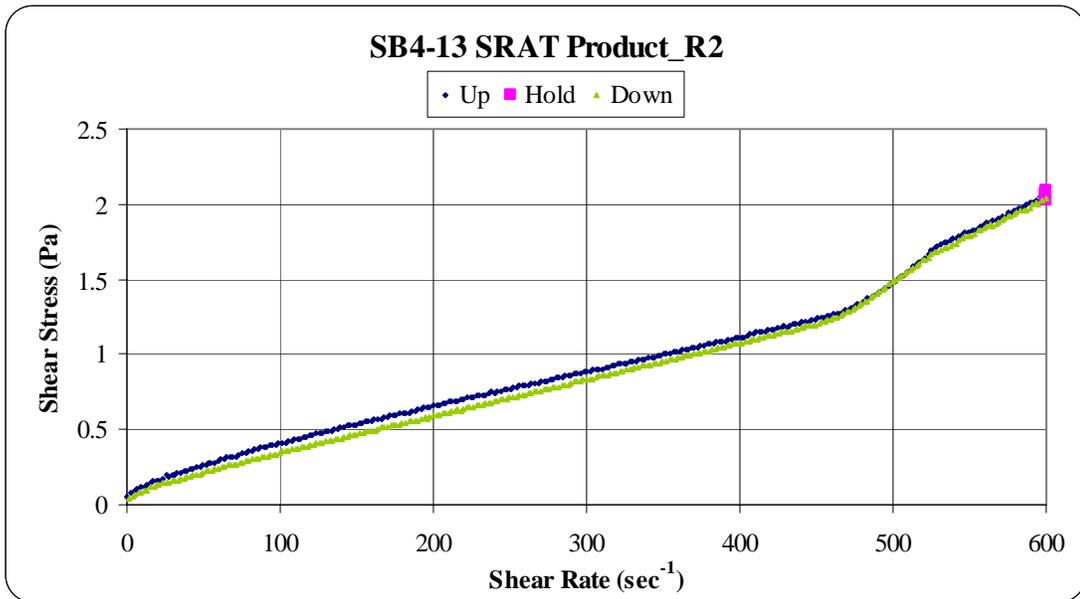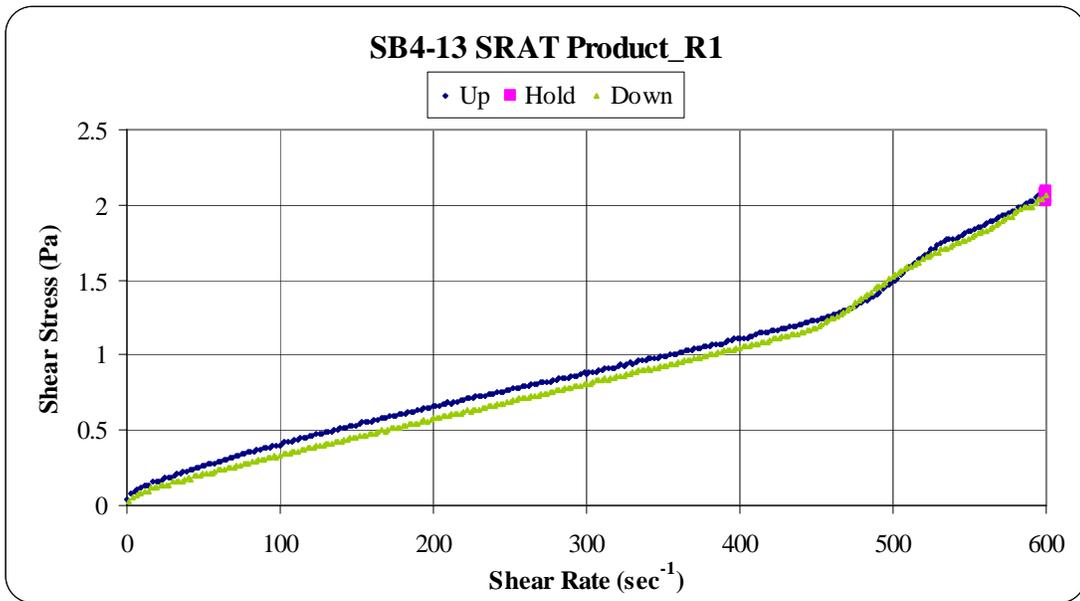
Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
SB4-13 SRAT Product_R1	2.43	0.15	0.9966	Z41	Samples Run 4-13-05	
SB4-13 SRAT Product_R2	2.44	0.15	0.9970	Z41	Samples Run 4-13-05	
					Results fitted to up curve. Data fitted between 0 to 475 sec^{-1}. Taylor vortices impacting results above 475 sec^{-1}. Down curve has slightly less of a yield stress and essentially the same plastic viscosity.	
Average	2.43	0.15				
Stdev	0.01	0.00				
%Stdev	0.3%	0.5%				

Figure B - 4: Rheology of SB4-14 SRAT Product

SB4-14 SRAT Product_R1

SB4-14 SRAT Product_R2
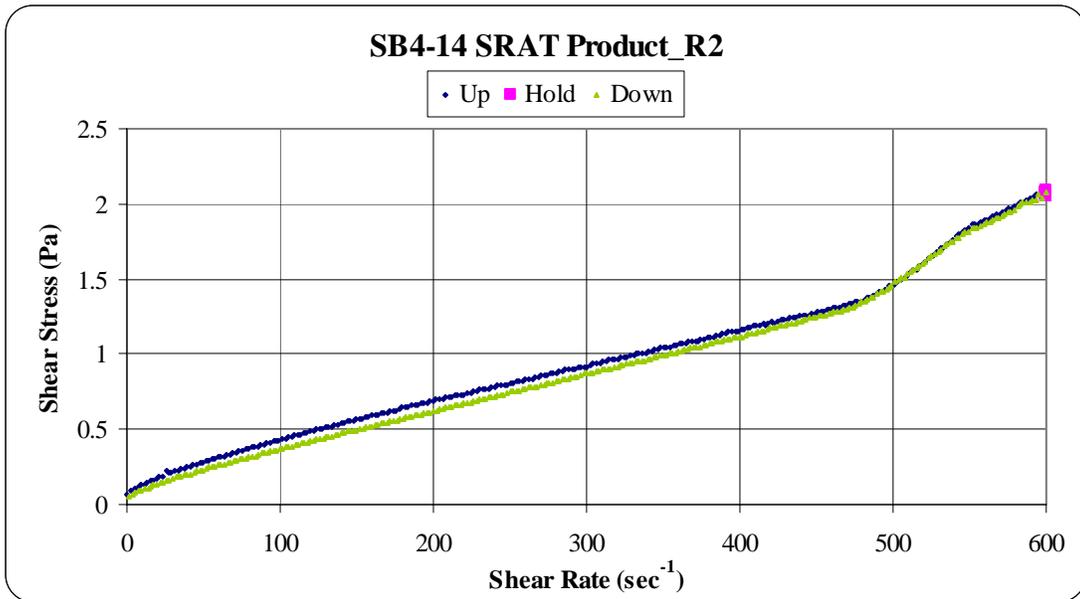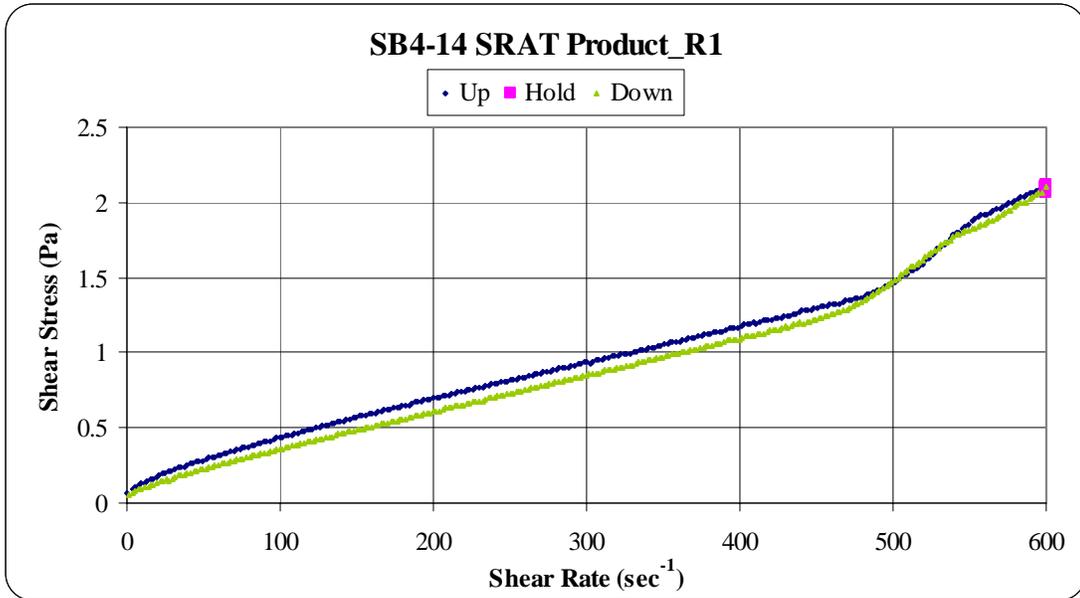
Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
SB4-14 SRAT Product_R1	2.54	0.17	0.9966	Z41	Samples Run 4-13-05	
SB4-14 SRAT Product_R2	2.50	0.17	0.9965	Z41	Samples Run 4-13-05	
					Results fitted to up curve. Data fitted between 0 to 475 sec^{-1}. Taylor vortices impacting results above 475 sec^{-1}. Down curve has slightly less of a yield stress and essentially the same plastic viscosity.	
Average	2.52	0.17				
Stdev	0.03	0.00				
%Stdev	1.0%	0.2%				

Figure B - 5: Rheology of SB4-15 SRAT Product
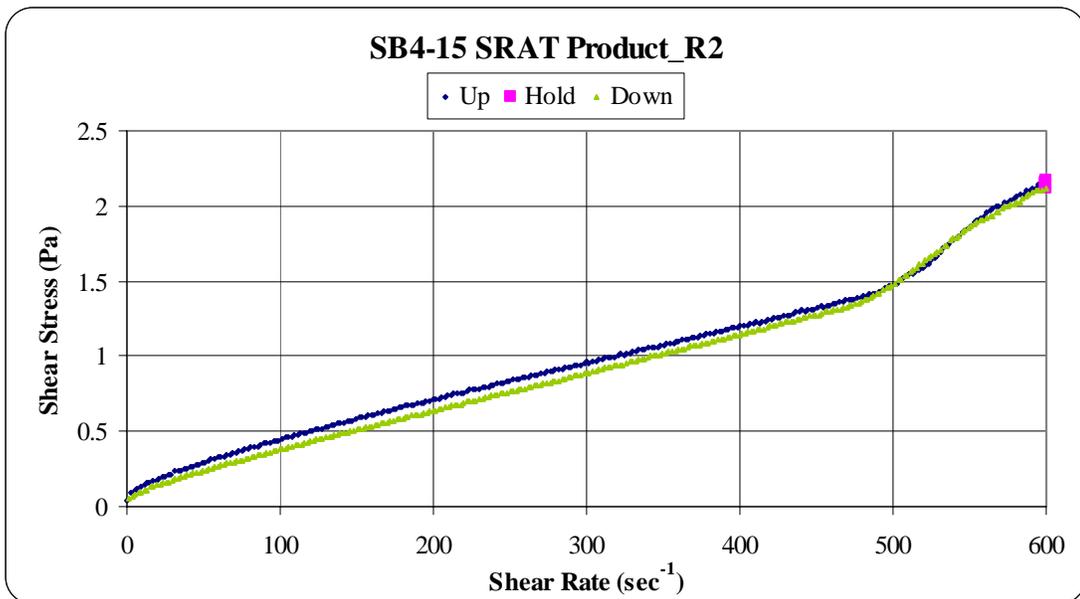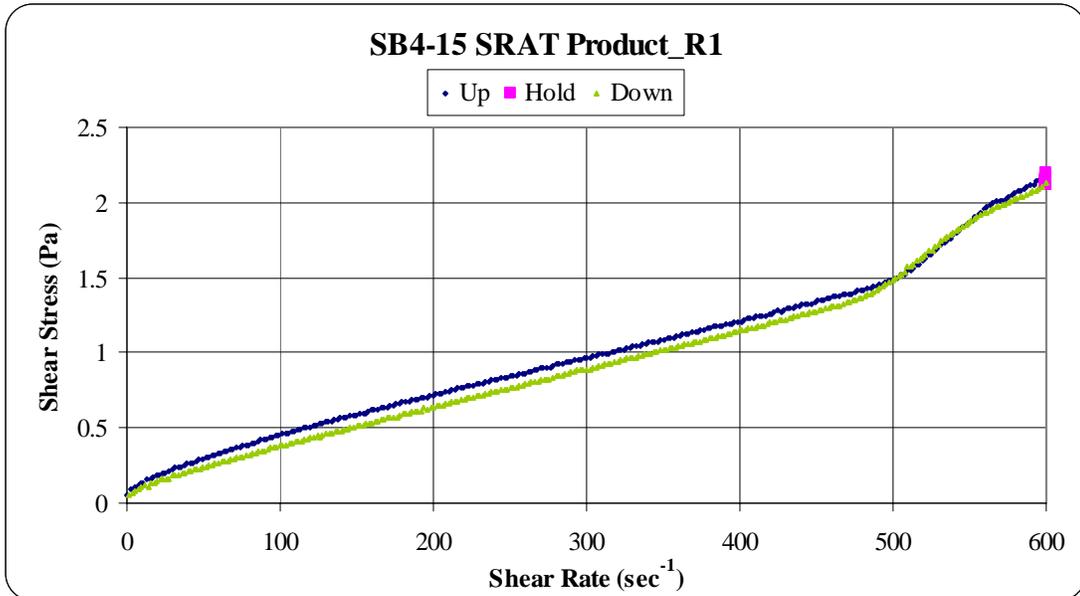
Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
SB4-15 SRAT Product_R1	2.62	0.18	0.9965	Z41	Samples Run 4-14-05	
SB4-15 SRAT Product_R2	2.58	0.17	0.9963	Z41	Samples Run 4-14-05	
					Results fitted to up curve. Data fitted between 0 to 475 sec^{-1}. Taylor vortices impacting results above 475 sec^{-1}. Down curve has slightly less of a yield stress and essentially the same plastic viscosity.	
Average	2.60	0.18				
Stdev	0.02	0.00				
%Stdev	0.9%	0.4%				

Figure B - 6: Rheology of SB4-16 SRAT Product

SB4-16 SRAT Product_R1

• Up ■ Hold ▴ Down

SB4-16 SRAT Product_R2

• Up ■ Hold ▴ Down
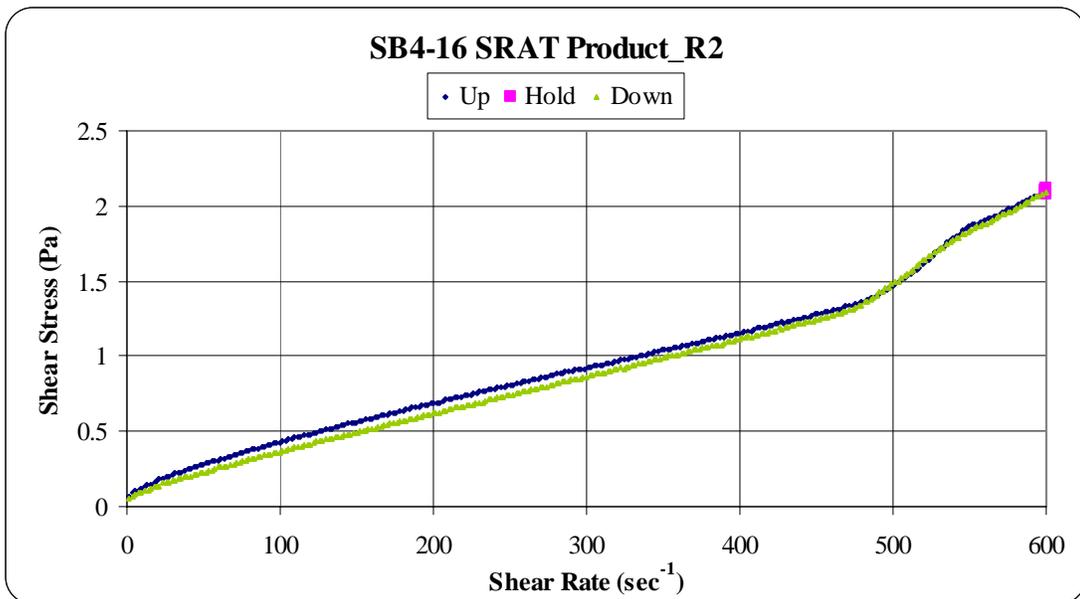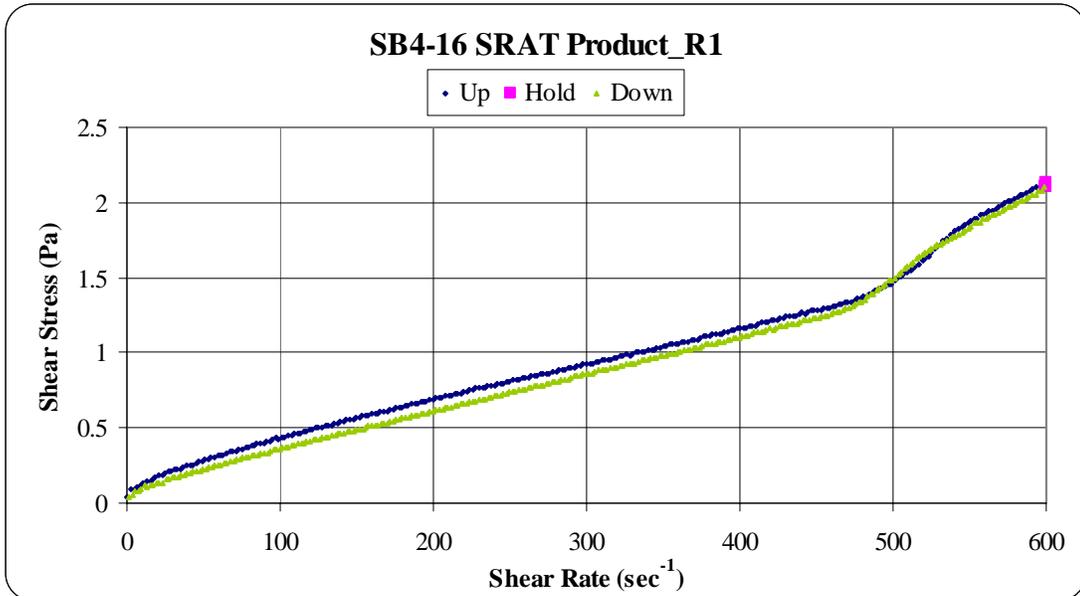
Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
SB4-16 SRAT Product_R1	2.51	0.17	0.9961	Z41	Samples Run 4-15-05	
SB4-16 SRAT Product_R2	2.50	0.17	0.9964	Z41	Samples Run 4-15-05	
Average	2.51	0.17	Results fitted to up curve. Data fitted between 0 to 475 sec^{-1}. Taylor vortices impacting results above 475 sec^{-1}. Down curve has slightly less of a yield stress and essentially the same plastic viscosity.			
Stdev	0.01	0.00				
%Stdev	0.2%	0.5%				

Figure B - 7: Rheology of SB4-17 SRAT Product

SB4-17 SRAT Product_R1

SB4-17 SRAT Product_R2
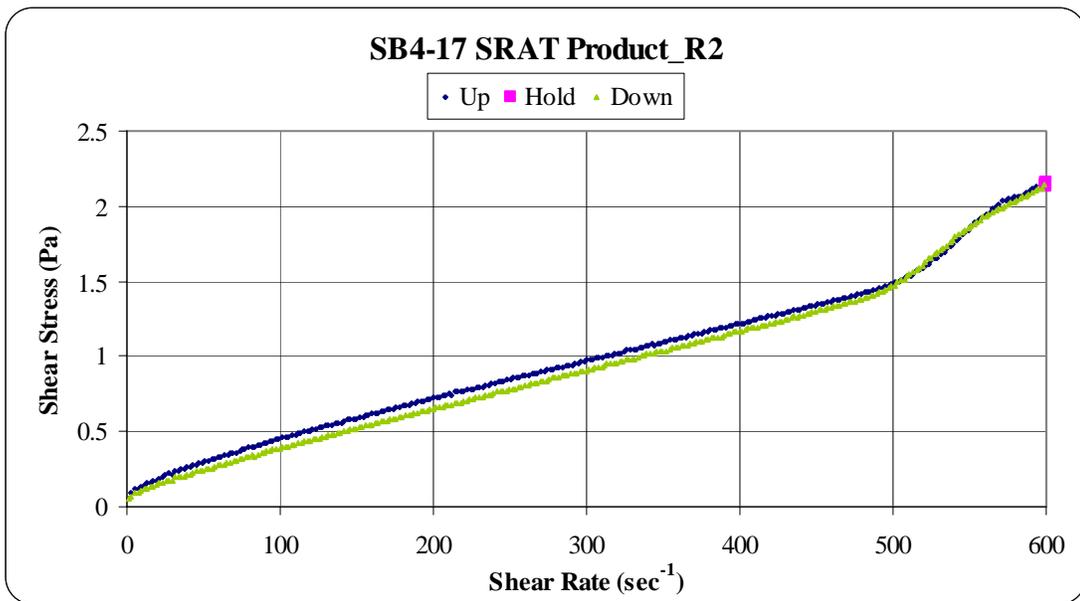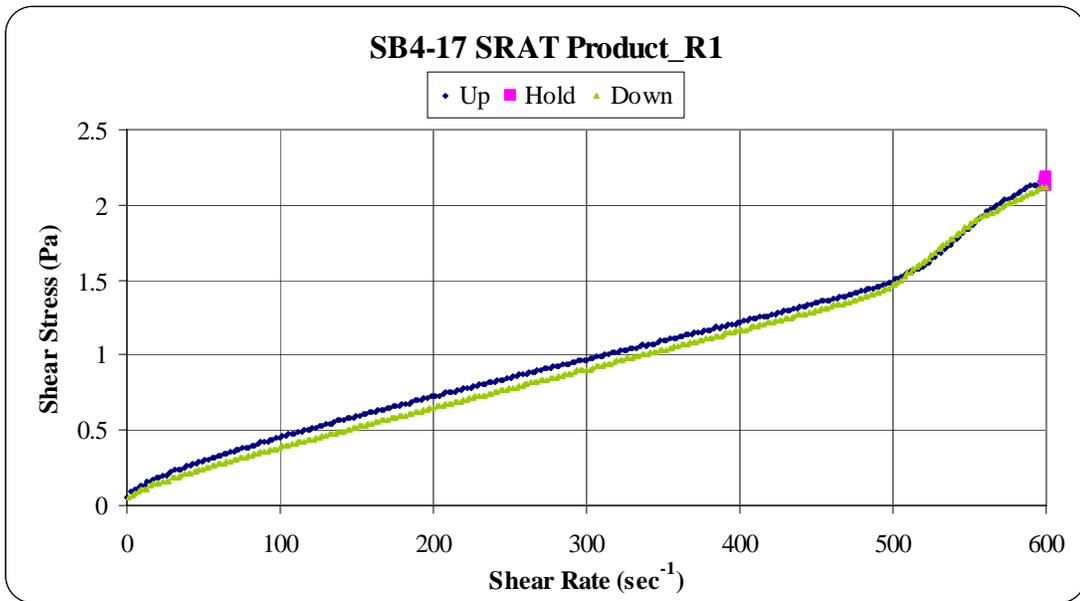
Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
SB4-17 SRAT Product_R1	2.64	0.18	0.9964	Z41	Samples Run 4-20-05	
SB4-17 SRAT Product_R2	2.64	0.17	0.9967	Z41	Samples Run 4-20-05	
					Results fitted to up curve. Data fitted between 0 to 475 sec^{-1}. Taylor vortices impacting results above 475 sec^{-1}. Down curve has slightly less of a yield stress and essentially the same plastic viscosity.	
Average	2.64	0.18				
Stdev	0.00	0.00				
%Stdev	0.0%	0.6%				

Figure B - 8: Rheology of SB4-17 SME Product
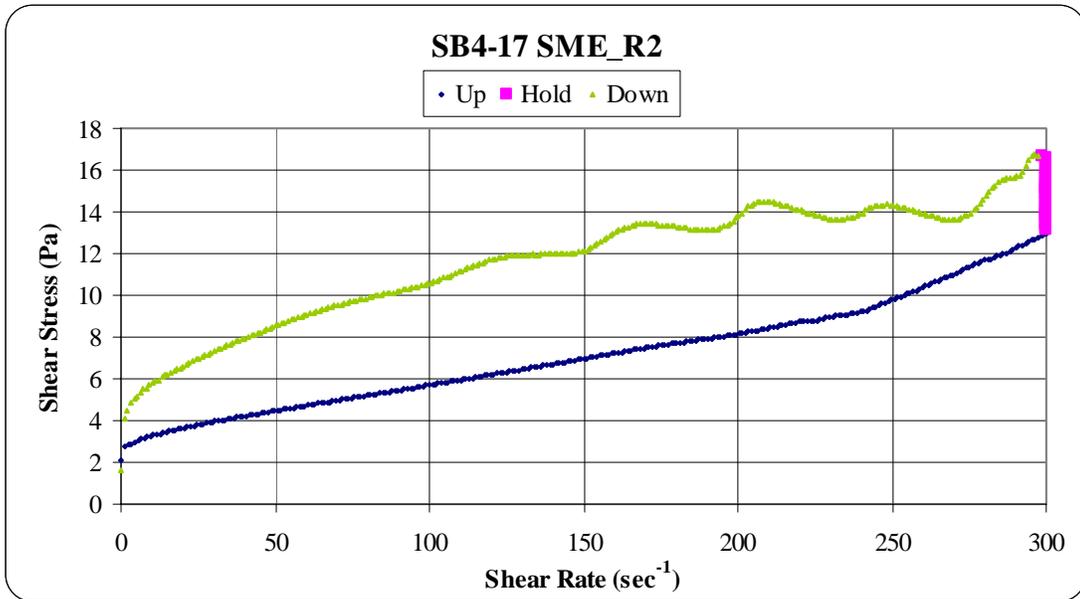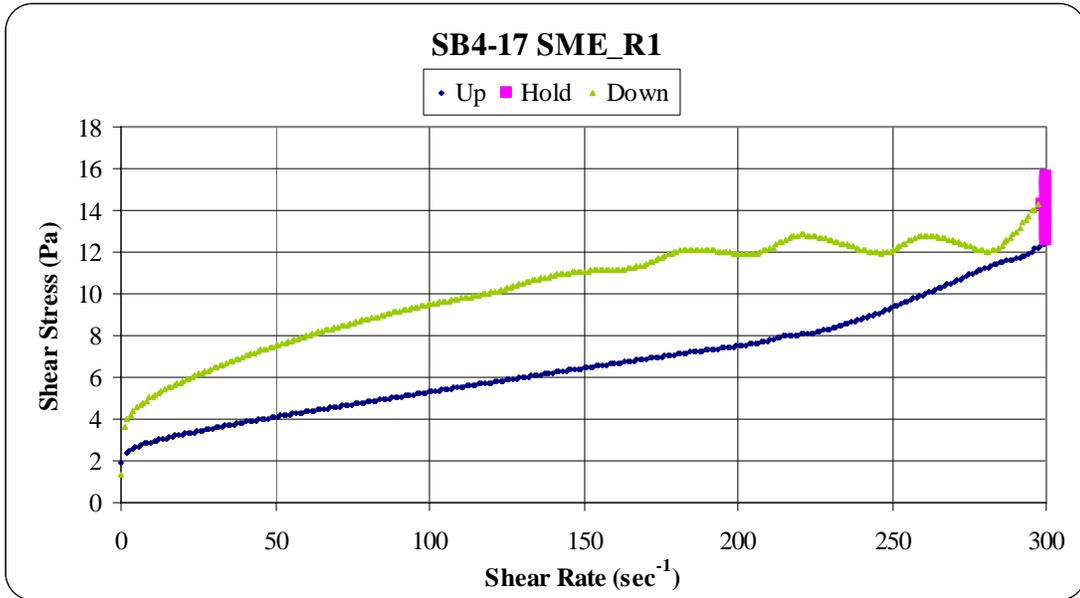
Sample	Plastic Viscosity (cP)	Yield Stress (Pa)	R^2	Rotor	Comments	
SB4-17 SME Product_R1	24.19	2.81	0.99	Z38	Samples Run 4-20-05	
SB4-17 SME Product_R2	25.71	3.10	1.00	Z38	Samples Run 4-20-05	
Average	24.95	2.96	Results fitted to up curve. Data fitted between 0 to 200sec^{-1}. Down curve can not be analyzed, impacted by frit solids.			
Stdev	1.07	0.21				
%Stdev	4.3%	7.0%				

APPENDIX C.   MCU Pictures

Figure C - 1: Organic Phase Distilled to MWWT in SB4-5

Figure C - 2: Organic Phase Floating in MWWT

Figure C - 3: Picture of Organic Phase in Line to MWWT

Figure C - 4: Picture of Organic Phase above Mercury in MWWT

Distribution:

M. A. Baich, 999-W
C. J. Bannochie, 773-42A
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, 773-A
S. L. Crump, 773-A
R. E. Eibling, 999-W
H. H. Elder, 766-H
P. E. Filpus-Luyckx, 773-A
S. D. Fink, 773-A
J. C. George, 999-W
J. M. Gillam, 766-H
J. R. Harbour, 773-42A
E. K. Hansen, 999-W
C. C. Herman, 773-42A
R. M. Hoeppel, 704-27S
E. W. Holtzscheiter, 773-A
J. F. Iaukea, 704-30S
C. M. Jantzen, 773-A
D. C. Koopman, 773-42A
S. L. Marra, 999-W
M. S. Miller, 704-S
M. A. Norato, 704-27S
J. E. Occhipinti, 704-S
J. M. Pareizs, 773-A
D. K. Peeler, 999-W
S. G. Phillips, 704-27S
J. W. Ray, 704-S
M. Rios-Armstrong, 766-H
H. B. Shah, 766-H
J. A. Smith, 704-99S
T. K. Snyder, 999-W
A. V. Staub, 704-27S
M. E. Stone, 999-W
W. B. Van-Pelt, 704-S
J. P. Vaughan, 773-A
F. A. Washburn, 704-28S
T. L. White, 773-A
G. G. Wicks, 773-A
M. F. Williams, 999-1W