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Antifoam Development for Eliminating Flammability Hazards and Decreasing Cycle Time in the Defense Waste Processing Facility

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S. C. Hunter

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) was requested to develop a new antifoam control method for the Defense Waste Processing Facility's (DWPF) Chemical Process Cell (CPC). SRNL completed testing of both chemical and nonchemical foam controls. The nonchemical foam controls were either ineffective (or worse, created more foam) or impractical (i.e., a water spray can control foam, but excessive water is needed). As a result, the focus of this study was on finding a superwetter or commercial antifoam for controlling foam.

Thirty potential antifoams were tested as part of this study. A series of tests were developed to help screen out ineffective alternatives including:

1. Spreading testing of superspreaders,
2. Foam column testing with physical simulants,
3. Boiling testing with physical and chemical simulants,
4. Days-only Sludge Receipt and Adjustment Tank (SRAT) process simulations with sludge (containing noble metals and mercury), Precipitate Reactor Feed Tank (PRFT), and Slurry Mix Evaporator Feed Tank (SEFT) simulants in the RC1 Reaction Calorimeter (purchased for antifoam testing), and
5. Around-the-clock SRAT and Slurry Mix Evaporator (SME) process simulations with sludge (containing noble metals and mercury), PRFT, and SEFT simulants in the RC1 Reaction Calorimeter.

Evonik Surfynol® MD20, a commercially available defoamer, was relatively effective in controlling foam, while remaining chemically stable in SRAT and SME processing across the pH range of 4 to 13. No degradation products were detected in the offgas, in the condensate or in the SRAT and SME products. In nitric-glycolic acid flowsheet testing, 250 mg/kg Evonik Surfynol® MD20 was needed for foam control compared to 1,625 mg/kg for Antifoam 747, DWPF's current antifoam. In nitric-formic acid flowsheet testing, 1,125 mg/kg of Evonik Surfynol® MD20 was needed to control foam throughout the SRAT and SME cycles.

The commercially available superspreader Momentive™ Y-17112 was even more effective than Evonik Surfynol® MD20 as both a defoamer and an antifoam. Not only was the foam destroyed upon addition but also was less persistent between additions. It was the most effective antifoam in testing using both the nitric-glycolic acid flowsheet and the nitric-formic acid flowsheet. In nitric-glycolic acid flowsheet testing, only 100 mg/kg Momentive™ Y-17112 was needed to control foam throughout the SRAT and SME cycles. In nitric-formic acid flowsheet testing, 300 mg/kg Momentive™ Y-17112 was needed to control foam throughout the SRAT and SME cycles. Momentive™ Y-17112 is also resistant to hydrolysis as demonstrated by its chemical stability in SRAT and SME processing across the pH range of 4 to 13 and lack of degradation products in offgas or condensate.

Both candidates were effective as potential replacements for Antifoam 747, with Y-17112 demonstrating superior foam control. During nitric-glycolic flowsheet testing 50% less antifoam was needed when using Momentive™ Y-17112 compared to MD20. During nitric-formic flowsheet testing 75% less antifoam was needed when using Momentive™ Y-17112 compared to MD20. Foam remediated with Momentive™ Y-17112 was less persistent throughout testing. In addition, no degradation products were detected in the offgas, in the condensate or in the SRAT and SME products. **Based on this testing, Momentive™ Y-17112 is clearly superior to Evonik Surfynol® MD20 and Antifoam 747. For both nitric-formic acid and nitric-glycolic acid flowsheet processing; it is recommended that Momentive™ Y-17112 replace Antifoam 747 in DWPF.**

An antifoam addition strategy is recommended for both the nitric-glycolic acid flowsheet and the nitric-formic acid flowsheet. Implementation of Momentive™ Y-17112 is expected to decrease SRAT and SME boiling times by up to 50%, eliminate the issues resulting from Antifoam 747 degradation products, and minimize foamovers.

To validate the effectiveness of Momentive™ Y-17112 and Evonik Surfynol® MD20 in a radioactive environment, SRNL irradiated sludge simulant containing fresh antifoam. Both defoamers remained effective at foam control during vigorous boiling after prolonged irradiation (53,100 krad over 30 days) and flammable degradation products were not generated.

Thermolytic Hydrogen Generation Rate (HGR) measurements in either a Tank 38 simulant or a high hydroxide simulant were performed with added Momentive™ Y-17112, Evonik Surfynol® MD20, or Antifoam 747 to ascertain potential impacts to flammability concerns downstream from their use in DWPF, including the High-Level Waste evaporators. From the applicable thermolytic HGR tests, Momentive™ Y-17112 had a lower HGR than was predicted by the Global TOC model and a lower HGR than Antifoam 747, the current DWPF antifoam. These results are consistent with the observation that Momentive™ Y-17112 does not contribute HGR to an extent greater than the Global TOC model and should therefore be approved for use in SRS waste streams. Additionally, no methane or other volatile degradation products were detected in the offgas. In comparison, Antifoam 747 required larger purge rates during testing due to the significant production of flammable antifoam degradation products in its offgas. Evonik Surfynol® MD20 was less stable at evaporator conditions compared to Momentive™ Y-17112; it had a significant HGR in comparison and both methane and methyl isobutyl ketone were observed in the offgas.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ADP	Antifoam Degradation Products
BDL	below detection limit
CPC	Chemical Process Cell
DI	deionized
DWPF	Defense Waste Processing Facility
ETF	Effluent Treatment Facility
FTIR	fourier transform infrared
GC	gas chromatograph
HGR	Hydrogen Generation Rate
HLW	High Level (radioactive) Waste
HMDSO	hexamethyldisiloxane
HTF	H-area Tank Farms
IC	ion chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
IIT	Illinois Institute of Technology (Illinois Tech)
IS	insoluble solids
LDRD	Lab Directed Research and Development
LEL	Lower Explosive Limit
M&TE	Measuring and Test Equipment
MCU	Modular Caustic Side Solvent Extraction Unit
MGR	Methane Generation Rate
MS	mass spectrometer
MS&E	Measurement Systems and Equipment
MWWT	Mercury Water Wash Tank
NA	not applicable
NIST	National Institute of Standards and Technology
NM	not measured
NMR	nuclear magnetic resonance
PISA	Potential Inadequacy in the Safety Analysis
PRFT	Precipitate Reactor Feed Tank
PSAL	Process Science Analytical Laboratory
PTFE	polytetrafluorethylene
RCT	Recycle Collection Tank
REDOX	Reduction/Oxidation

SEFT	Strip Effluent Feed Tank
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SS	soluble solids
SVOA	semi-volatile organic analysis
SWPF	Salt Waste Processing Facility
TCD	thermal conductivity detector
TIC	total inorganic carbon
TMS	trimethylsilanol
TOC	total organic carbon
TS	total solids
TTQAP	Task Technical and Quality Assurance Plan
TTR	Task Technical Request
VOA	volatile organic analysis

1.0 Introduction

Foam, due to the high gas generation rates of boiling and chemical reaction offgasing, requires control measures to prevent the foam from contaminating the condensate and to facilitate efficient plant operation. Antifoam was utilized to minimize foam production[1] during chemical processing in the DWPF and during High-Level Waste (HLW) evaporation at SRS[2] and Hanford[3]. However, the current antifoam used in the SRS DWPF increases flammability risk during chemical processing (generates three flammable degradation products) and while feeding the melter[4, 5](can decompose to CO/hydrogen). It is also the likely source of methyl functional groups for the organo-mercury present in the tank farm and excessive mercury in Saltstone[6]. Additionally, the planned startup of Salt Waste Processing Facility (SWPF), with much higher throughput, will challenge DWPF to process at higher gas generation rates.

DWPF employs Antifoam 747[7], a superspreader produced by Momentive Performance Materials, as an antifoaming agent during waste processing. During DWPF chemical processing, antifoam must be effective up to boiling (i.e., up to 103˚C) and between a pH of 3-13. Antifoam 747 is most effective at a pH range of 6-8[8] and degrades as pH deviates. In addition, SRNL identified three flammable antifoam degradation[9] products using mass spectrometer (MS) and fourier transform infrared (FTIR) offgas analyzers during simulations.[10]

A new antifoam or a new method to control foam is needed to minimize DWPF processing time and reduce the risk of contamination. In addition, testing should be completed to ensure that other antifoams used in HLW processing do not have similar flammability hazards or cause unintended impacts in downstream processing.

- Antifoam 747 is ineffective in controlling foam in the DWPF CPC.
    - Issue 1: Antifoam 747 hydrolyses quickly at pH <6.5 or >7.5 requiring periodic addition
    - Issue 2: Hydrolysis of antifoam produces 3 flammable species including an insoluble flammable gas and two soluble species
    - Issue 3: Antifoam is likely source of methyl in methyl mercury and dimethyl mercury
    - Issue 4: Any antifoam added will influence the melter offgas flammability as the H may produce H_2 and the C may produce CO. The less antifoam used, the better
- Goal: Foam control that is effective over pH range of 3-13 at boiling, with no degradation products in the condensate, no flammable decomposition products in the offgas, and minimal quantity needed

The major component of Antifoam 747 is shown in Figure 1-1 below. Two trimethylsilanol, $(CH_3)_3SiOH$, molecules can be hydrolyzed from each antifoam molecule (as the Si—O bond is fragile and easily cleaved where the ✖ is shown on Figure 1-1).

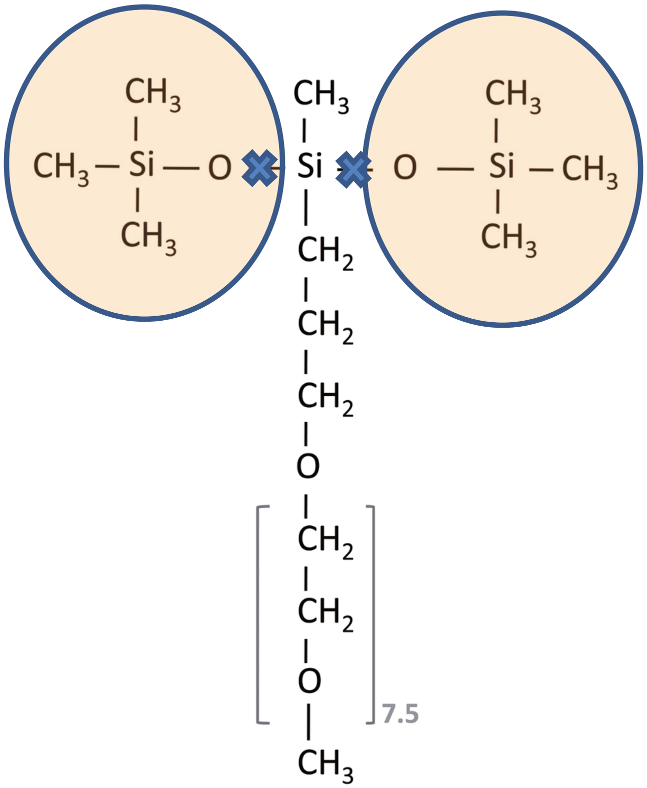
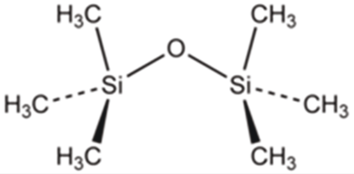
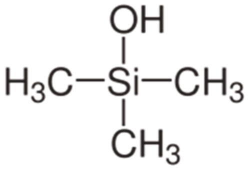
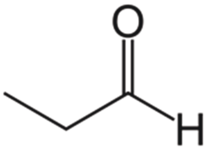


Figure 1-1. Antifoam 747 Degradation

The result is 2 molecules of trimethylsilanol and one molecule of the polyethoxy chain that is no longer effective as an antifoam. Two molecules of trimethylsilanol (soluble in water) can react through a condensation reaction to form hexamethyldisiloxane (insoluble in water). Both trimethylsilanol and hexamethyldisiloxane have significant vapor pressures and are potentially flammable. In addition, fragments from the ethoxy chain can form propanal (soluble in water), another flammability hazard. Elimination of these flammability hazards is one of the reasons for developing a new antifoam agent. The Antifoam 747 decomposition products' structures and properties are summarized in Table 1-1.

Table 1-1. Antifoam 747 Flammable Decomposition Products and Properties

Compound	Formula	Structure	Molar Mass, g/mol	Solubility	Lower Flammability Limit, vol %	Boiling Point
Hexamethyl disiloxane (HMDSO)	$C_6H_{18}OSi_2$		162.38	930.7 ppb	0.5-0.8	100 °C
Trimethyl silanol (TMS)	$C_3H_{10}OSi$		90.20	0.995 g/L	0.5-0.6	99 °C
Propanal	C_3H_6O		58.08	200 g/L	2.6	49 °C

1.1 Inadequacies of Antifoam 747

Antifoam 747 consists of two components; the primary component is a superspreader. Commercially, superspreaders are used to distribute pesticides to plant leaves from an airplane without wasting excessive pesticide which hits the leaf and drops to the ground without spreading across the whole leaf. The best superspreaders are known to easily hydrolyze if the pH isn't between 6 and 8.[11] SRNL determined that the degradation products of this hydrolysis for Antifoam 747 are three flammable gases, propanal, trimethylsilanol, and hexamethyldisiloxane.[9] Because the pH of the SRAT and SME slurries are rarely between pH 6 and 8, Antifoam 747 decomposes quickly and must be added often to control foam. And, in processing at pH 13 (during caustic boiling or PRFT addition), Antifoam 747 degrades so quickly, it is hard to add it fast enough to prevent a foamover. To minimize foamovers in DWPF, the boilup rate has been throttled to a maximum of 3,000 lb/h steam in the SRAT and 2,500 lb/h steam in the SME. This has resulted in doubling the time for boiling compared to a design basis boilup rate of 5,000 lb/h steam.

During 2011, DWPF was over-adding Antifoam 747 to control foam. This led to the discovery that the amount of Antifoam 747 added was not considered in the DWPF melter offgas flammability evaluation. A "Potential Inadequacy in the Safety Analyses" (PISA) was declared[12] and DWPF processing was halted for several months. The subsequent changes in processing limited the use Antifoam 747 and it is now included as part of the melter offgas flammability evaluation.

After the identification of the three flammable antifoam degradation products, a second PISA[13] was declared in 2015. The presence of antifoam degradation products (ADPs) was added to the CPC offgas flammability evaluation, which limits the allowable generation of other flammable gases (primarily hydrogen).

2.0 Experimental Procedure

The simulant makeup, equipment set-up, experimental parameters, offgas analysis, liquid sampling, and quality assurance are described in this section.

2.1 Identification of New Superspreaders for Foam Control

A meeting was held on October 14, 2017 with key antifoam experts to find a hydrolysis resistant superspreader which might have potential as an alternative to Antifoam 747[14]. Three samples were supplied to SRNL by Momentive, Y-17112, Y-17309 and Y-17581, along with Silwet L-77 and Y-17580, the ingredients in Antifoam 747. Each of these were tested to determine their effectiveness in controlling foam.

2.2 Identification of Nonchemical Solutions for Foam Control

A meeting was held on December 7, 2017[15,16] with key antifoam and mechanical experts from SRNL and Savannah River Remediation (SRR)-DWPF & Saltstone-Facility Engineering personnel to develop a short list of nonchemical solutions for foam control. Some alternatives that were considered included ultrasonics, a vapor space agitator and a liquid spray, and pressure oscillations. The testing of the nonchemical solutions was funded by SRNL Lab-Directed Research and Development (LDRD) funding.

2.3 Identification of New Antifoam Agents for Foam Control

The technical experts from the major antifoam manufacturers (Chemours, Dow, BASF, 3M, and Evonik) were contacted by Gita Golcar and a request for antifoam suggestions was solicited. Each of these manufactures provided SRNL with a sample of each of their recommended antifoams. 25 antifoams were identified, and these were tested to determine their effectiveness in controlling foam. A list is included in Table 2-1.

Table 2-1. List of Antifoams studied

Category A - Superwetters	**Type of Compound**
Siovation Antifoam 747	Superwetter Blend
Momentive™ Silwet L77	Superwetter
Momentive™ Y-17580	Superwetter
Momentive™ Y-17581	Superwetter
Momentive™ Y-17309	Superwetter
Momentive™ Y-17112	Superwetter
Chemours Capstone™ FS-3100	Fluorinated Superwetter
Chemours Capstone™ FS-50	Fluorinated Superwetter
Chemours Capstone™ FS-30	Fluorinated Superwetter
3M FC-4430	Fluorinated Superwetter
3M FC-4432	Fluorinated Superwetter
3M FC-4434	Fluorinated Superwetter
Evonik Dynol 607	Nonionic Superwetter
Category B - Traditional Antifoams	Type of Compound
BASF Foamaster® MO 2111 NC	Mineral Oil Defoamer
BASF Foamaster® MO 2140	Mineral Oil Defoamer
BASF Foamaster® MO 2172	Mineral Oil Defoamer
BASF Foamaster® MO 2185	Mineral Oil Defoamer
BASF FoamStar® ST 2412	Mineral Oil Defoamer
BASF FoamStar® ST 2420	Mineral Oil Defoamer
Dow XIAMETER® AFE-1010	Silicon Antifoam
Dow XIAMETER® ACP-1400	Silicon Antifoam
Dow XIAMETER® ACP-1430	Silicon Antifoam
Dow XIAMETER® AFE-1410	Silicon Antifoam
Dow XIAMETER® ACP-3183	Silicon Antifoam
Evonik Surfynol® AD01	Wetting surfactant
Evonik Surfynol® MD20	Oxirane/Diol defoamer
Evonik AEROSIL® R812	Silica Powder
Evonik AEROSIL® R812S	Silica Powder
Sodium Metasilicate	Silica Powder

2.4 Development of Simulants

A foamy chemical simulant could not be quickly identified for the initial screenings. As a result, physical simulants were developed first and used in initial foam column and boiling testing. The reduction of the particle size of SB6 chemical simulants led to the development of foamy chemical simulants as described below. In addition, a foamy PRFT simulant was made by reducing the particle size of the monosodium titanate particles. A simple SEFT simulant was prepared without organic entrainment by combining deionized (DI) water and nitric acid.

2.4.1 Development of Foamy Physical Simulants

Physical simulants at varying pH were developed with fine boehmite and iron oxide as sources of insoluble solid particles. The recipe for making these simulants in included in Table 2-2.

Table 2-2. Physical Simulant

Compound	Molecular Formula	Target wt %
Sodium Nitrate	$NaNO_3$	5.89
Sodium Nitrite	$NaNO_2$	4.78
Boehmite	$AlHO_2$	13.0
Iron (III) Oxide	Fe_2O_3	7.00

The pH was adjusted to 4, 7, or 13 through the addition of 50 wt % sodium hydroxide or 70 wt % nitric acid.

2.4.2 Development of Foamy Chemical Simulants

Two chemical simulants were developed for pH 4 and 13 using existing simulants. The particle size was reduced to make the simulant foamier. The measured composition of these two simulants is included in Table 2-3. The noble metal targets are included in Table 2-4.

Table 2-3. Chemical Simulants

Analysis	SB6-H Blend SRAT Simulant	**SB6 Version 1 Recipe A Sludge Simulant**
pH	4.79	13.1
total solids, wt %	5.56	15.31
insoluble solids, wt %	2.64	10.18
calcined solids, wt %	3.38	10.97
soluble solids, wt %	2.92	5.13
slurry density, g/mL	1.0389	1.1223
supernate density, g/mL	1.0196	1.0414
NO_2^-, mg/kg	118	9810
NO_3^-, mg/kg	14,650	9690
SO_4^{-2}, mg/kg	520	1430
$C_2O_4^{-2}$, mg/kg	127	850
Al, wt %	17.1	15.3
Ba, wt %	0.0155	0.135
Ca, wt %	0.744	1.20
Cr, wt %	0.0742	0.176
Fe, wt %	20.7	22.3
K, wt %	<0.568	0.263
Mg, wt %	0.580	0.849
Mn, wt %	5.47	6.39
Na, wt %	17.8	15.5
Ni, wt %	2.62	2.92
S, wt %	3.78	0.328
Si, wt %	0.221	1.35
Zn, wt %	0.0330	0.124
Zr, wt %	0.295	0.131

Table 2-4. Chemical Simulant Mercury and Noble Metal Concentration

Metal	Concentration, wt % total solids basis
Hg	2.48
Rh	0.0156
Ru	0.0762
Ag	0.0139
Pd	0.0037

2.4.3 Development of PRFT Simulant

A PRFT simulant containing monosodium titanate at pH 13 was developed using the recipe in Table 2-5. Foaminess was induced through high shear mixing to reduce particle size.

Table 2-5. PRFT Simulant

Compound	Molecular Formula	Target wt %
DI Water	H_2O	94.56
Monosodium Titanate	$NaTi_2O_5H$	2.67
Sodium Carbonate	Na_2CO_3	0.43
Sodium Aluminate Hydrate	$Na_2O\cdot Al_2O_3\cdot 3H_2O$	0.41
Sodium Nitrite	$NaNO_2$	0.48
Sodium Nitrate	$NaNO_3$	0.52
Potassium Carbonate	K_2CO_3	0.03
Sodium Hydroxide	NaOH	0.89
Sodium Formate	NaHCOO	0.01

2.4.4 Development of SEFT Simulants

A simple SEFT simulant was prepared by combining DI water and nitric acid. The entrainment of solvent was not included in this recipe. The recipe for making this simulant is included in Table 2-6.

Table 2-6. SEFT Simulant Composition

Compound	Molecular Formula	Target wt %
DI Water	H_2O	98.68
70 wt % Nitric Acid	HNO_3	0.15

2.5 <u>Development of Tests for Evaluation of New Antifoam Agents for Foam Control</u>

Because we wanted to evaluate almost 30 antifoam candidates, a series of screenings was performed to limit the amount of testing needed. The following screenings were used as summarized in Table 2-7.

Table 2-7. Testing Completed in Development of New Antifoam

Property to Test	**Test method**	**Goal**
Initial Screening	Review of chemical composition, Safety Data Sheet	Screen and eliminate candidates
Chemical Stability pH 3-13 and Spreading	Automated Spread Testing	Determine spreading over time and pH range
Antifoaming and Defoaming	Teclis FoamScan	Determine critical antifoam concentration over pH range
Defoaming at boiling with physical and chemical simulants at pH extremes	Beaker testing	Determine critical antifoam concentration during acidic and caustic boiling
Demonstration of Antifoam strategy in SRAT operations with sludge containing noble metals and mercury	2-L Mettler Toledo RC1 short, days-only SRAT simulation	Demonstrate antifoam effectiveness in complete simulant
Demonstration of Antifoam strategy in SRAT/SME testing with sludge containing noble metals and mercury	2-L Mettler Toledo RC1 SRAT/SME simulation with sludge, PRFT and SEFT simulants	Demonstrate antifoam strategy, determine decomposition products in offgas and condensate

2.5.1 Screening 1: Hydrolysis Stability of Superspreaders

Antifoam experts at the Illinois Institute of Technology (IIT) identified the hydrolysis-resistant superwetters Momentive™ Y-17112, Momentive™ Y-17309, and Momentive™ Y-17581 as alternative antifoam agents. The chemical stability of these superwetters and Silwet L-77 (the main component of Siovation Antifoam 747) were investigated through a series of spread testing. The superwetters were diluted in buffer solutions (pH 1 – pH 13) at varying concentrations (100ppm – 5000ppm). Blue dye was added to the solutions to improve visibility and image capture. A 50 µL drop was placed on a backlit Petri dish. Utilizing a specialized camera and software, the coverage area was measured over a 60 second time interval as each droplet spread, as shown in Figure 2-1. The photo on the left (Momentive™ Y-17112) shows spreading, while the photo on the right (Antifoam 747) shows no spreading. These tests were repeated over a two-week period to monitor degradation of the defoamer over time.

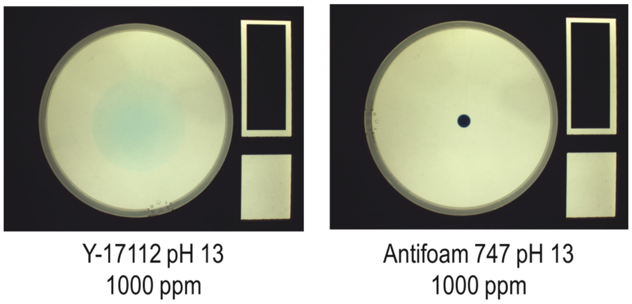
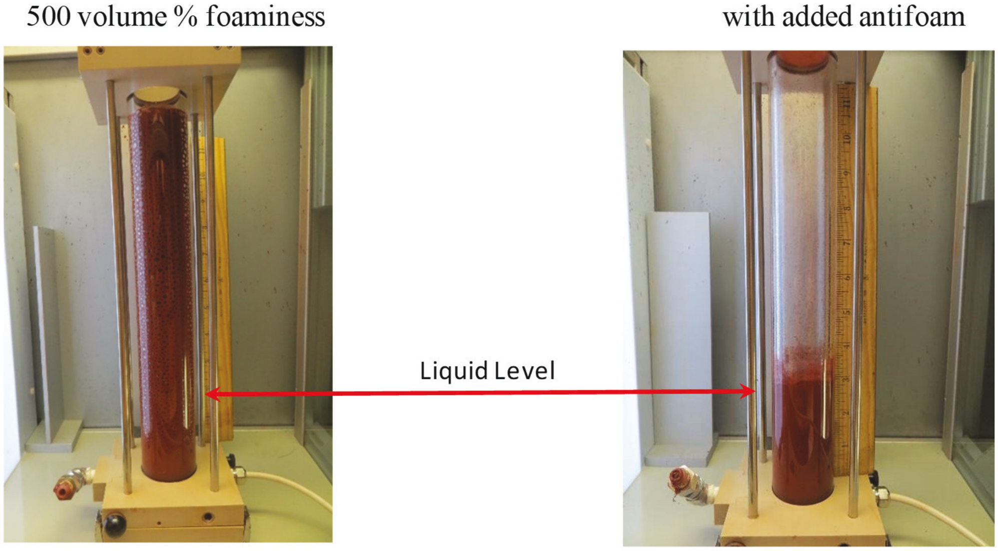


Figure 2-1. Photo of Momentive™ Y-17112 and Antifoam 747 Spreading Test

2.5.2 Screening 2: Simple Foam Testing

The Teclis FoamScan equipment was used for evaluating the effectiveness of antifoam ingredients or mixtures to prevent or destroy foam. The ability of the slurry to generate foam is measured by measuring the volume of foam produced when a known amount of air is injected. The stability or persistence of the foam can also be measured by the change in foam volume over time. The new antifoam agents were initially tested at minimum, neutral, and maximum pH to ensure that the components are effective in controlling foam. Later testing was completed only with minimum and maximum pH as no new information was learned from the neutral pH testing. In addition, the minimum concentration of antifoam needed for foam control was determined to support the development of a new method for deploying antifoam. A photo of the equipment is included in **Figure 2-2**.



Caustic Physical Simulant
No Defoamer

Caustic Physical Simulant
25 mg/kg Evonik Surfynol® MD20

Figure 2-2. Photo of Teclis FoamScan – Used for Determining Antifoam Effectiveness

2.5.3 Screening 3: Life Expectancy Testing of New Antifoam Agents

The effectiveness of each antifoam was determined by boiling sludge simulant and monitoring the foam level. Both physical and chemical simulants were developed as described in this report. Testing was completed in glass equipment without insulation so the foaming could be observed. Based on the concentrations needed for foam control in the simple foam testing, testing continued for one hour or until the foam was excessive. A photo of the equipment in use with Antifoam 747 is included in Figure 2-3.

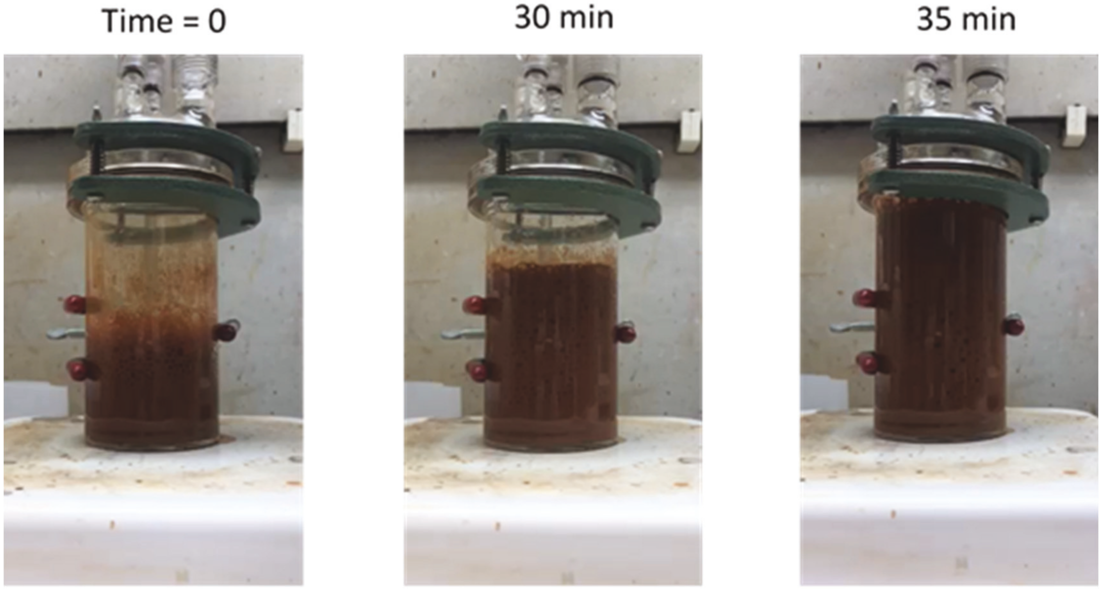


Figure 2-3. pH 4 Chemical Simulant with Antifoam 747 (25 ppm)
Initial foam collapse (duration ~20 min); Foaming resumes with greater than initial volume

2.5.4 Screening 4: SRAT and SME Testing of New Antifoam Agents

Based on the results of previous screenings, SRAT and SME cycles were completed utilizing the foamy sludge chemical simulant. This simulant contained mercury and noble metals for the first time during this antifoam testing. Both the nitric-glycolic acid flowsheet and the nitric-formic acid flowsheet at 100% acid stoichiometry were examined and processing included the introduction of Precipitate Reactor Feed Tank (PRFT) and SEFT simulants to represent anticipated feed volumes from SWPF. Additionally, complete SME cycles consisting of five dewater segments and two process frit slurry additions were performed. Operations were completed using design basis boilup rates, acid addition rates, and boiling time. The testing utilized the antifoam concentration and addition strategy developed in the previous screenings. Gas chromatograph (GC), MS, and/or FTIR analyzers were used to monitor the offgas throughout processing. Testing using both the nitric-glycolic and nitric-formic acid flowsheet was completed in case the new antifoam is utilized prior to DWPF switching to the nitric-glycolic acid flowsheet.

The testing was completed in the Mettler Toledo RC1mx, as this equipment was purchased for the antifoam investigations due to its use of a jacketed glass vessel. This allows visual observation of the foam and slurry so that antifoam could be added during processing prior to the onset of a foamover. Since the equipment had not been used at SRNL previously, extensive water testing, followed by days only SRAT segment testing, and later full around-the-clock SRAT and SME testing were completed to evaluate and screen out the remaining alternative antifoam candidates. A photo of the equipment is included in Figure 2-4. The acid calculation inputs for the sludge, PRFT and SEFT are summarized in Table 2-8, Table 2-9, and Table 2-10. The SRAT processing inputs are summarized in Table 2-11.

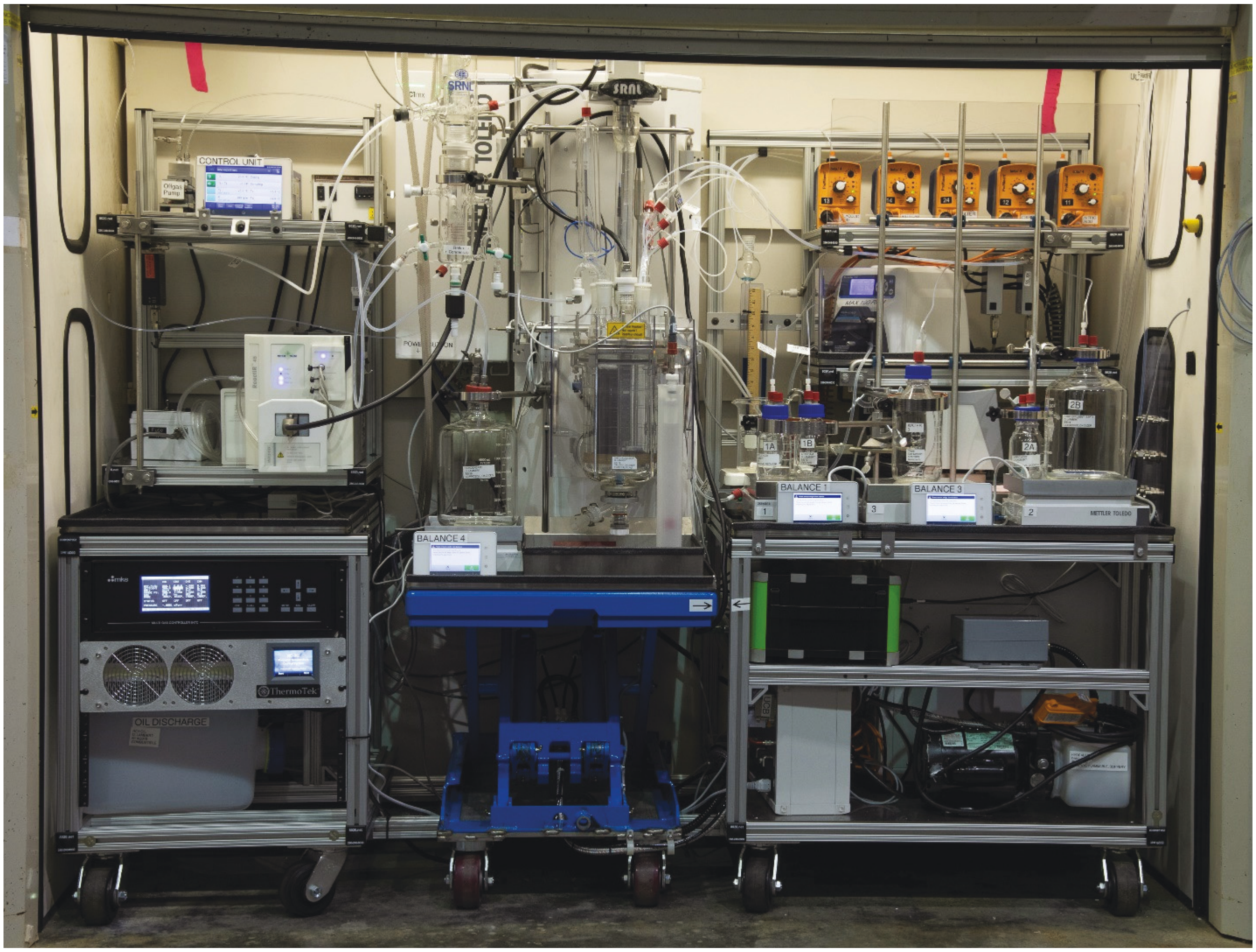


Figure 2-4. Photo of RC1mx used for SRAT/SME Testing

Table 2-8. Sludge Acid Calculation Inputs

Input	Value	Units
Fresh Sludge Mass without trim chemicals	1,650.0	g slurry
Fresh Sludge Weight % total solids	15.31	wt %
Fresh Sludge Weight % calcined solids	10.97	wt %
Fresh Sludge Weight % insoluble solids	10.18	wt %
Fresh Sludge density	1.122	kg / L slurry
Fresh Sludge Supernate density	1.041	kg / L supernate
Fresh Sludge Nitrite	9,813	mg/kg slurry
Fresh Sludge Nitrate	9,685	mg/kg slurry
Fresh Sludge Formate	0	mg/kg slurry
Fresh Sludge Sulfate (mg/kg)	1,432	mg/kg slurry
Fresh Sludge Chloride (mg/kg)	315	mg/kg slurry
Fresh Sludge Phosphate (mg/kg)	0	mg/kg slurry
Fresh Sludge Oxalate	849	mg/kg slurry
Fresh Sludge Slurry total inorganic carbon (TIC) treated as carbonate	1,384	mg/kg slurry
Fresh Supernate TIC (treated as carbonate)	1605	mg/L supernate
Fresh Sludge Hydroxide (Base Equivalents) pH = 7	0.319	mol/L slurry
Fresh Sludge Carbon Source	0.000	wt% dry basis
Fresh Sludge Manganese (% of Calcined Solids)	6.390	wt % calcined basis
Fresh Sludge Magnesium (% of Calcined Solids)	0.849	wt % calcined basis
Fresh Sludge Sodium (% of Calcined Solids)	15.546	wt % calcined basis
Fresh Sludge Potassium (% of Calcined Solids)	0.263	wt % calcined basis
Fresh Sludge Cesium (% of Calcined Solids)	0.000	wt % calcined basis
Fresh Sludge Calcium (% of Calcined Solids)	1.195	wt % calcined basis
Fresh Sludge Strontium (% of Calcined Solids)	0.000	wt % calcined basis
Fresh Sludge Nickel (% of Calcined Solids)	2.924	wt % calcined basis
Fresh Sludge Supernate manganese	0	mg/L supernate

Table 2-9. PRFT Acid Calculation Inputs

Input	Value	Units
PRFT Mass without trim chemicals	767.29	g slurry
PRFT volume being simulated	3000.00	Gallons
PRFT Weight % total solids	5.71	wt %
PRFT Weight % calcined solids	4.31	wt %
PRFT Weight % insoluble solids	2.37	wt %
PRFT Density	1.04	kg/L slurry
PRFT Supernate density	1.02	kg/L supernate
PRFT Nitrite	3538	mg/kg slurry
PRFT Nitrate	3575	mg/kg slurry
PRFT Oxalate	0	mg/kg slurry
PRFT Sulfate (mg/kg)	0	mg/kg slurry
PRFT Slurry TIC (treated as carbonate)	2572	mg/kg slurry
PRFT Supernate TIC (treated as carbonate)	2696	mg/L supernate
PRFT Hydroxide (Base Equivalents) pH = 7	0.41	Equiv Moles Base/L slurry

Table 2-10. SEFT Acid Calculation Inputs

Input	Value	Units
Modular Caustic Side Solvent Extraction Unit (MCU) Mass without trim chemicals (SRAT cycle)	3668.14	g
MCU Mass without trim chemicals (SME cycle)	0.00	g
MCU volume being simulated (SRAT cycle)	15000.00	gallons
MCU volume being simulated (SME) cycle)	0.00	gallons
MCU Weight % Total Solids	0.010	wt %
MCU Density	0.998	kg/L slurry
MCU Supernate density	0.998	kg/L supernatant
MCU Nitrate	1,000	mg/kg slurry
MCU Hydroxide (Base Equivalents) pH = 7	0	moles of base / L of slurry
MCU Sodium (% of Calcined Solids)	0	wt % calcined basis

Table 2-11. SRAT Processing Assumptions Acid Calculation Inputs

Input	Nitric-Glycolic Flowsheet	Nitric-Formic Flowsheet	Units
Conversion of Nitrite to Nitrate in SRAT Cycle	52.56	25.00	mol NO_3^-/100 mol NO_2^-
Destruction of Nitrite in SRAT and SME cycle	100.00	100.00	% of starting nitrite destroyed
Destruction of formate	not applicable (NA)	20.00	% formate converted to CO2 etc.
Glycolate conversion to formate	1.00	NA	% glycolate converted to formate.
Destruction of Glycolic acid charged in SRAT	18.82	NA	% glycolate converted to CO_2 etc.
Conversion of Glycolic acid to Oxalate	1.00	NA	% glycolate converted to C_2O_4
Percent Acid in Excess Stoichiometric Ratio	100.00	110	%
SRAT Product Target Solids	25.00	23.00	%
Nitric Acid Density, 20 °C	1.30180	1.30611	g/mL
Formic Acid Density, 20 °C	NA	1.0250	g/mL
Glycolic Acid Density, 20 °C	1.26260	NA	g/mL
Glycolic Acid Density, 50 °C	1.23850	NA	g/mL
Nitric Acid Molarity	10.244	10.244	Molar
Glycolic Acid Molarity	11.827	NA	Molar
Formic Acid Molarity	NA	23.570	Molar
DWPF Nitric Acid addition Rate	179.000	75.0	mol/min
DWPF Glycolic Acid addition Rate	179.000	NA	mol/min
DWPF Formic Acid addition Rate	NA	179.00	mol/min
Reduction/Oxidation (REDOX) Target	0.150	0.150	Fe^{+2} / ΣFe
Trimmed Sludge Target Ag metal content	0.0100	0.0100	total wt % dry basis after trim
Trimmed Sludge Target wt% Hg dry basis	2.5000	2.5000	total wt % dry basis after trim
Trimmed Sludge Target Pd metal content	0.0040	0.0040	total wt % dry basis after trim
Trimmed Sludge Target Rh metal content	0.0160	0.0160	total wt % dry basis after trim
Trimmed Sludge Target Ru metal content	0.0800	0.0800	total wt % dry basis after trim
Water to dilute fresh sludge and/or rinse trim chemicals	100.00	100.00	g
Water to rinse PRFT simulant into vessel	10.00	10.00	g
Sample Mass of Sludge after PRFT step (before SRAT cycle)	16.83	16.83	g
Sample Mass during/after SRAT	140.29	140.29	g
PRFT Addition Rate	7	7	gallons/min
SEFT Addition Rate	7	7	gallons/min
SRAT air purge	93.7	230	scfm
DWPF Standard Temperature	70	70	degrees F
DWPF Standard Temperature	294.26	294.26	Kelvin
DWPF Standard Pressure	1	1	atmosphere
SRAT boil up rate	5000	5000	lbs/h
SRAT Mercury Product Target Concentration	0.45	0.45	wt % total solids basis
SRAT Steam Stripping Factor	750	750	(g steam/g mercury)

The above inputs were used in an acid calculation for both the nitric-glycolic acid flowsheet and the nitric-formic acid flowsheet. Table 2-12 summarized addition amounts and flowrates for the experiments:

Table 2-12. Nitric-Glycolic and Nitric-Formic Flowsheet Acid Addition Targets and Flowrates

Output	Nitric-Glycolic Flowsheet	Nitric-Formic Flowsheet	Units
SRAT Air Purge	158.6	419	sccm
SRAT Helium Purge	0.797	1.957	sccm
Sludge Mass	1650	1650	g
Sludge Flush Water	100	100	g
Silver Nitrate	0.0410	0.0410	g
$Pd(NO_3)_2$ Solution (15.27% Pd)	0.0683	0.0682	g
$Rh(NO_3)_3$ Solution (4.933% Rh)	0.8456	0.8449	g
Ru(III) nitrosyl nitrate (1.5% Ru)	13.8966	0.0000	g
$RuCl_3$	0.0000	0.4274	g
HgO	7.0336	7.0273	g
PRFT Addition	767.29	767.29	g
PRFT Addition Time	5	5	hours
PRFT Dewater	735.1	735.1	g
PRFT Dewater Rate	2.45	2.45	g/min
PRFT line rinse	10	10	g
Nitric Acid	100.79	17.72	g
Nitric Acid Rate	1.48	0.64	g/min
Glycolic Acid	131.74	0.00	g
Glycolic Acid Rate	1.24	0.00	g/min
Formic Acid	0.00	106.74	g
Formic Acid Rate	0.00	0.59	g/min
SRAT Dewater	466.15	414.55	g
SRAT Dewater Rate	2.45	2.45	g/min
SEFT Addition	3668.14	3668.14	g
SEFT Addition Rate	2.45	2.45	g/min
SEFT Dewater	3668.14	3668.14	g
SEFT Dewater Rate	2.45	2.45	g/min
E Air Purge	104.9	103	sccm
SME Helium Purge	0.529	0.516	sccm
Number of Decon Canisters	5	5	
Water per Decon Canister	235.97	235.97	g
Dewater per Decon Canister	235.97	235.97	g
Decon Dewater Rate	1.87	1.87	g/min
Number of Frit Additions	2	2	
Frit Addition	156.0	155.1	g
Water per Frit Addition	156.0	155.1	g
Dewater per Frit Addition	156.0	155.1	g
Frit Dewater Rate	1.87	1.87	g/min
Final SME Dewater	210.45	190.3	g

2.6 Offgas Analysis

In testing in the RC1mx, the offgas was monitored by GC, MS, and/or FTIR. The specific monitors used in each short segment experiment are detailed in Table 2-13.

Table 2-13. Offgas Monitoring Used

Defoamer	Segment	GC	MS	FTIR
Momentive™	Short	X	X	
Momentive™ Y-17112	Full Nitric- Glycolic SRAT/SME	X	X	X
Momentive™ Y-17112	Full Nitric- Formic SRAT/SME	X		X
Evonik Surfynol® MD20	Short	X	X	X
Evonik Surfynol® MD20	Full Nitric- Glycolic SRAT/SME	X	X	X
Evonik Surfynol® MD20	Full Nitric-Formic SRAT/SME	X		X
3M FC-4430	Short	X	X	X
BASF FoamStar® ST 2412	Short	X	X	X
Dow XIAMETER® AFE-1010	Short	X	X	X

The offgas leaving the SRAT condenser was passed through a Nafion® dryer in counter-current flow with a dried air stream to reduce the moisture content of the gases to the analyzers. A sample pump pulled a side stream from the venting stream and transported it by the GC inlet, the MS inlet, and through the FTIR gas cell. The GC inlet, utilizing the internal pump, pulled a sample side-stream at approximately five-minute intervals from this offgas stream. The inlet to the MS, through differential pressure across a capillary, drew in a sample side-stream continuously, providing analysis across a 200 mass-to-charge (m/z) range approximately once a minute. The entirety of the remaining offgas stream flowed through the FTIR gas cell, being analyzed approximately every 16 seconds, and out to ventilation. Mass flow controllers were used to regulate the amount of gases pulled into the offgas stream from the overall venting stream (~80% of the total purge flow).

Raw chromatographic data were acquired by the GC from the post condenser offgas stream using separate computers interfaced to the data acquisition computer. Each experiment had a dedicated Agilent (or Inficon) 3000A dual column micro GC. Column-A can collect data related to He, H_2, O_2, N_2, NO, and CO, while column-B can collect data related to CO_2, N_2O, and water. Data for NO, CO, and water are only qualitative. The GCs were calibrated with a standard calibration gas containing He, H_2, O_2, N_2, CO_2 and N_2O. The calibration was verified prior to starting the SRAT cycle and after completing the SME cycle; room air was used to give a two-point calibration. The GC data were additionally post-processed, as necessary, to adjust for inaccuracies in the measured concentrations. The concentrations measured in air at the beginning and end of each experiment were used to perform linear interpolation corrections.

An Extrel CMS MAX300LG MS was used in survey mode to qualitatively monitor a 2-200 m/z range. Qualitative intensity measurements were tracked to look for the presence of volatile, water-insoluble antifoam degradation products in the offgas stream. Scanning across the entire range of m/z ratios takes approximately one minute per scan. The data, though qualitative, was utilized to pinpoint potential points in time where spikes in previously unaccounted for offgas species may have been present. For example, in experiments utilizing Antifoam 747, hexamethyldisiloxane may be monitored at m/z ratios of 147 and 73 while trimethylsilanol may be monitored at m/z ratio 75. These points in time could then be correlated to data observed in the FTIR to aid in identification of offgas species related to the observed m/z ratios.

The FTIR was specifically set up to quantify CO, CO_2, NO, NO_2, N_2O, and H_2O concentrations. Although the GC detects water, the FTIR gives a quantitative concentration for moisture in the chilled offgas leaving the Nafion® drier. The FTIR obtained data roughly every 15 seconds. Post-reprocessing of the FTIR spectra could be utilized to additionally qualitatively and/or quantitatively identify previously unidentified or unaccounted for offgas species.

A summary listing offgas species and analyzer used is seen in Table 2-14.

Table 2-14. Analyzer Used in Quantifying Offgas Species

Offgas Species	GC	MS	FTIR
H_2	X	X	
CO_2	X	X	X
NO		X	X
NO_2		X	X
N_2	X	X	
N_2O	X		X
O_2	X	X	
He	X	X	
Ar		X	
NH_3			X
HMDSO			X

2.7 Liquid Sampling

Samples were analyzed by semivolatile organic analysis (SVOA), volatile organic analysis (VOA), Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), ion chromatography (IC) Anions, IC Cations, TIC, total organic carbon (TOC), ICP-AES for mercury, Ultraviolet-Visible (UV-Vis) spectrophotometry, weight, and rheology. Condensate samples were taken from the Mercury Water Wash Tank (MWWT), and the SRAT/SME dewater material. Slurry samples were taken before, during, and after processing.

Selected cations were evaluated in the SRAT supernate and the SRAT condensates. The SRAT and SME product slurries were sampled once the vessel contents had cooled slightly, but still while mixing. SRAT and SME product samples were analyzed for cation and anion composition in addition to solids analyses and rheological characterization. The MWWT was drained after both the SRAT and SME cycles.

Although there was some variation in the sampling plan between experiments, the basic sampling plan can be seen in Table 2-15. The sampling plan is consistent with previous simulant flowsheet work and what has been specified in the Task Technical and Quality Assurance Plan (TTQAP).[10]

Table 2-15. Sampling Plan

Vessel	Sample Description	Analysis
SRAT	SRAT post PRFT Addition	ICP-AES, IC, SVOA, VOA
PRFT Dewater (SMECT)	PRFT dewater condensate	SVOA, VOA, IC, ICP-AES
SRAT Dewater (SMECT)	SRAT dewater	IC, ECP-AES, SVOA, VOA
SEFT Dewater (SMECT)	SEFT dewater	IC, ECP-AES, SVOA, VOA
SRAT	SRAT product	ICP-AES, IC, pH, density, TS, IS, SVOA, VOA, rheology
Post SRAT MWWT	MWWT dewater	TS, ICP-AES, SVOA, VOA
SME	SME product	TS, IS, SS, pH, density, ICP-AES, SVOA, VOA, rheology
SME Dewater (SMECT)	SME frit dewater condensate	IC, ECP-AES, SVOA, VOA

All analytical instruments used, except pH probes, were Measurement Systems and Equipment (MS&E). Balances and pipettes used are a part of the Measuring and Test Equipment (M&TE) program.

Total solids, soluble solids, and calcined solids were analyzed in the slurry. Total solids content was determined by weighing a 5 to 10 g aliquot of the slurry sample after it was dried in a platinum crucible at 110 °C in an oven for about 12 hours. The dried total solids are then calcined in an 1100 °C furnace for 1 hour to determine the mass of calcined solids. The soluble solids content was determined by weighing a dried 5 to 10 g sample of 0.45 μm filtered, centrifuged slurry. The filtered sample was dried in a platinum crucible at 110 °C in an oven for about 12 hours. Insoluble solids are calculated by taking the difference between total solids and soluble solids.

An Agilent 730 ES ICP-AES was used to analyze for metals in the supernate, slurry, and dewater using L29, ITS-0079. The ICP-AES is calibrated before each experiment and National Institute of Standards and Technology (NIST) certified standards are analyzed with each set of samples to verify the calibration. Dewater samples were diluted as needed prior to performing ICP-AES. Mercury was determined by ICP-AES after digesting the sludge with aqua regia and diluting. Slurry samples are eluted through a 0.45 μm filter and then diluted as needed before being analyzed to determine Ag, Al, B, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pd, Rh, Ru, S, Si, Sn, Ti, Zn, and Zr in the supernate. If solids were still visible, aqua regia was added to the filtrate prior to analysis. To determine metals in the slurry, the calcined solids were ground with a mill grinder, and then sieved to collect a powder that is less than 149 μm particle size. The powder was digested by peroxide fusion (L29 ITS-0040) to determine B and Li and by lithium metaborate (L29 ITS-0071) and lithium tetraborate (L29 ITS-0070) to determine all other metals.

A Dionex DX-500 and ICP-5000 IC were used to measure anions in the slurry and dewater via L29 ITS-0027. The IC is calibrated before each set of samples being analyzed and NIST certified standards are processed with each set to verify the calibration. Dewater was diluted as needed prior to IC. Two grams of 50 wt % NaOH is added to a 10 g aliquot of slurry if the sample was not immediately caustically quenched after being pulled. At points in the process when a significant amount of chemistry is occurring, two mL of 50 wt % NaOH is added to the sample to prevent the chemical reactions from continuing further. The aliquot is then diluted 100x, 500x, and 5000x and filtered with a 0.45μm filter prior to being analyzed for F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{-2}, $C_2H_3O_3^-$, $C_2O_4^{-2}$, and HCO_2^-.

A Dionex ICS-3000 Reagent-Free IC was used to analyze for ammonia via L16.1 ADS-2310. The sample was diluted with DI water to within the calibration curve range of 1-50 mg/L prior to being analyzed through the IC. Calibration is performed prior to performing analysis and a quality control sample is examined with each sample set.

TIC and TOC were analyzed separately. Sludge samples were analyzed using wet chemical oxidation (sodium persulfate addition) on an OI Analytical 1030W TOC Analyzer using procedure L16.1 ADS-1209 r2. Approximately 0.1 g of sample was weighed and mixed with 40 mL of water. The samples were analyzed in triplicate with one sample per set spiked with standards. TIC was determined by acidification with 20 wt % phosphoric acid followed by infrared detection.

The elemental Hg samples were dissolved at room temp with HNO_3 + HCl. The digested samples were diluted with water and analyzed with the ICP-AES for mercury.

2.8 Antifoam irradiation

To validate the effectiveness of Momentive™ Y-17112 and Evonik Surfynol® MD20 in a radioactive environment, SB6 Version 1 Recipe A sludge simulant (Table 2-3) containing fresh antifoam was irradiated utilizing a Co-60 gamma source. Subsequent boiling tests were performed. The goal of this testing was to determine whether the irradiation causes decomposition of the antifoam, which would make it less effective at foam control and produce new species in the offgas or slurry.

Two sets of irradiations were performed. The first set of irradiations simulated the dose received from being in the SRAT Receipt SB9 Alternate Reductant Blend Slurry (Table 2-16) for one week (typical dose of SB9 sludge-only processing). The second set of irradiations simulated the dose received from being in the Coupled Operations Curie Balance - Sludge and SWPF Feed (Table 2-17) for two weeks (worst case radiation dose to antifoam from high Cs-137 from high SWPF volume of SE, approximately 700 times the dose rate compared to the SB9 Alternative Reductant Blend Slurry irradiation).

Table 2-16. SB9 Alternate Reductant Blend Slurry

Isotope	Mass Concentration (wt. % solids)	Activity Concentration (Ci/gal slurry)	% RSD
Tc-99	1.58E-03	1.98E-04	2.6
U-233	6.65E-04	4.76E-05	2.3
U-234	7.71E-04	3.56E-05	0.4
U-235	3.18E-02	5.08E-07	0.8
U-236	1.84E-03	8.79E-07	1.5
U-238	3.29E+00	8.18E-06	1.0
Np-237	2.80E-03	1.46E-05	0.4
Pu-238	1.06E-03	1.36E-01	25
Pu-239	9.28E-03	4.27E-03	1.3
Pu-240	9.07E-04	1.53E-03	2.4
Pu-239/240	NA	6.81E-03	31
Pu-241	3.67E-05	2.82E-02	26
Am-241	5.58E-04	1.43E-02	22
Am-242	1.75E-07	1.27E-05	7.1
Am-243	8.04E-05	1.20E-04	19
Cm-242	4.26E-10	1.05E-05	7.2
Cm-244	8.23E-06	4.96E-03	11
Cm-245	< 1.1E-04	< 1.4E-04	NA

Table 2-17. Coupled Operations Curie Balance - Sludge and SWPF Feed

Isotope	SRAT Activity Concentration (Ci/gal)
Co-60	2.73E-01
Sr-90	7.38E+01
Y-90	7.58E+01
Ru-106	5.48E-02
Rh-106	5.48E-02
Sb-125	1.34E+00
Te-125m	3.27E-01
Cs-134	1.15E+00
Cs-137	2.50E+02
Ba-137m	2.37E+02
Pr-144m	1.89E-01
Pm-147	3.90E+01
Sm-151	3.93E-01
Eu-152	5.94E-03
Eu-154	9.98E-01
Eu-155	7.67E-01
Pu-238	2.37E+00
Pu-239	2.06E-02
Pu-240	1.38E-02
Pu-241	2.66E+00
Am-241	1.72E-02
Cm-244	1.71E-01

Approximations of radiation dose absorbed in the SB9 Alternate Reductant Blend Slurry and Coupled Operations Curie Balance - Sludge and SWPF Feed were determined based upon their nuclide distributions. The volumetric activity concentration and known radioactive decay energy per disintegration of each nuclide were used to calculate an energy deposition rate, or dose, to the sludge material. It is conservatively assumed that all radioactive decay energy from alphas, betas, and photons are deposited locally in the sludge and no energy escapes. This approximation is reasonable for very massive systems such as a waste tank. The resulting sludge dose rate estimates are given in Table 2-18 and Table 2-19.

Table 2-18. SB9 Alternate Reductant Blend Slurry – Dose Rate Estimate

SRAT Receipt SB9 Alternate Reductant Blend Slurry					
Nuclide	SRAT [Ci/gal]	W/Ci	W/L	W/kg	Rad/hr
Tc99	1.98E-04	5.01E-04	2.62E-08	2.38E-08	8.58E-03
U233	4.76E-05	2.86E-02	3.59E-07	3.27E-07	1.18E-01
U234	3.56E-05	2.83E-02	2.66E-07	2.42E-07	8.71E-02
U235	5.08E-07	2.71E-02	3.64E-09	3.31E-09	1.19E-03
U236	8.79E-07	2.66E-02	6.18E-09	5.62E-09	2.02E-03
U238	8.18E-06	2.49E-02	5.39E-08	4.90E-08	1.76E-02
Np237	1.46E-05	2.88E-02	1.11E-07	1.01E-07	3.63E-02
Pu-238	1.36E-01	3.26E-02	1.17E-03	1.06E-03	3.83E+02
Pu-239	4.27E-03	3.02E-02	3.41E-05	3.10E-05	1.12E+01
Pu-240	1.53E-03	3.06E-02	1.24E-05	1.12E-05	4.04E+00
Pu-241	2.82E-02	3.20E-05	2.38E-07	2.17E-07	7.80E-02
Am-241	1.43E-02	3.28E-02	1.24E-04	1.13E-04	4.06E+01
Am242m	1.27E-05	4.05E-04	1.36E-09	1.24E-09	4.45E-04
Am243	1.20E-04	3.15E-02	9.98E-07	9.08E-07	3.27E-01
Cm242	1.05E-05	3.57E-02	9.90E-08	9.00E-08	3.24E-02
Cm-244	4.96E-03	3.44E-02	4.50E-05	4.09E-05	1.47E+01
				Total:	**4.54E+02**

Table 2-19. Coupled Operations Curie Balance - Sludge and SWPF Feed - Dose Rate Estimate

Coupled Operations Curie Balance – Sludge and SWPF Feed					
Nuclide	SRAT [Ci/gal]	W/Ci	W/L	W/kg	Rad/hr
Co-60	2.73E-01	1.54E-02	1.11E-03	1.01E-03	3.64E+02
Sr-90	7.38E+01	1.16E-03	2.26E-02	2.06E-02	7.40E+03
Y-90	7.58E+01	5.54E-03	1.11E-01	1.01E-01	3.63E+04
Ru-106	5.48E-02	5.95E-04	8.62E-06	7.83E-06	2.82E+00
Rh-106	5.48E-02	1.89E-02	2.74E-04	2.49E-04	8.97E+01
Sb-125	1.34E+00	3.37E-03	1.19E-03	1.08E-03	3.90E+02
Te-125m	3.27E-01	8.69E-04	7.51E-05	6.82E-05	2.46E+01
Cs-134	1.15E+00	1.02E-02	3.10E-03	2.81E-03	1.01E+03
Cs-137	2.50E+02	1.01E-03	6.67E-02	6.06E-02	2.18E+04
Ba-137	2.37E+02	3.94E-03	2.47E-01	2.24E-01	8.07E+04
Pr-144m	1.89E-01	3.43E-04	1.71E-05	1.56E-05	5.60E+00
Pm-147	3.90E+01	3.67E-04	3.78E-03	3.44E-03	1.24E+03
Sm-151	3.93E-01	7.41E-04	7.69E-05	6.99E-05	2.52E+01
Eu-152	5.94E-03	7.65E-03	1.20E-05	1.09E-05	3.93E+00
Eu-154	9.98E-01	9.08E-03	2.39E-03	2.18E-03	7.84E+02
Eu-155	7.67E-01	7.59E-04	1.54E-04	1.40E-04	5.03E+01
Pu-238	2.37E+00	3.26E-02	2.04E-02	1.86E-02	6.68E+03
Pu-239	2.06E-02	3.02E-02	1.65E-04	1.50E-04	5.39E+01
Pu240	1.38E-02	3.06E-02	1.11E-04	1.01E-04	3.65E+01
Pu-241	2.66E+00	3.20E-05	2.25E-05	2.04E-05	7.36E+00
Am-241	1.72E-02	3.28E-02	1.49E-04	1.36E-04	4.88E+01
Cm-244	1.71E-01	3.44E-02	1.55E-03	1.41E-03	5.08E+02
				Total:	**1.58E+05**

Gamma irradiation was performed using a J.L Shepherd Model 484 Co-60 gamma irradiator. This model features a 10” x 10” x 40” irradiation chamber with two Co-60 radionuclide sources at one end to deposit a desired dose rate as a function of the target’s distance to the source (Figure 2-5). Dosimetry at various points in the irradiator was performed by the vendor at the time of installation with NIST traceable calibration. Additional dose rate modeling was performed at SRNL using Monte Carlo N-Particle version 6.1 (MCNP 6.1), an industry standard and highly benchmarked radiation transport code. Dose rate modeling accounts for geometric and self-shielding attenuation of the target itself. The volumetric average dose rate to the sludge given the experimental setup and vessel placement within the irradiator was determined to be 74.2 krad/hr.

Figure 2-5. Photo of Irradiation Setup

Glass vessels were filled with approximately 150 mL SB6 Version 1 Recipe A sludge simulant.An antifoam concentration of 500 ppm was targeted. Two lots of Momentive™ Y-17112 were tested: Momentive™ Y-17112-14DSV and Momentive™ Y-17112-19FSV. Irradiation was also performed on a "Blank" that did not contain antifoam, acting as a control. The vessels were sealed and placed as close to the Co-60 source as possible. Two vessels were placed in the irradiator at a time. The vessels were continuously purged with gas (0.5% krypton and 20% oxygen in nitrogen) at a flow rate of 0.5 sccm (standard cubic centimeter per minute). Standard condition is defined as 0°C and 1 atm. The offgas was collected in Tedlar bags and later evaluated by VOA. The sludge was irradiated for the required timeframe as indicated in Table 2-20 and Table 2-21.

Table 2-20. SB9 Sludge-Only Dose – Irradiations

Antifoam	SB6 V1RA Simulant (g)	Antifoam Concentration (ppm)	Time Irradiated (min)	Simulated Dose Rate (rad/hr)	Simulated Dose One Week (krad)
Blank	168.3	0	62	454	76.3
MD-20	168.2	505	62	454	76.3
Y17112-14DSV	168.4	505	62	454	76.3
Y17112-19FSV	168.4	505	62	454	76.3

Table 2-21. Maximum Coupled Dose - Irradiations

Antifoam	SB6 V1RA Simulant (g)	Antifoam Concentration (ppm)	Time Irradiated (days)	Simulated Dose Rate (rad/hr)	Simulated Dose Two Weeks (krad)
Blank	168.3	0	30	1.58E+05	53,100
MD-20	168.3	505	30	1.58E+05	53,100
Y17112-14DSV	168.3	505	30	1.58E+05	53,100
Y17112-19FSV	168.4	505	30	1.58E+05	53,100

Post irradiation boiling tests were performed to determine whether the defoamers remained effective at controlling foam. The sludge was heated and agitated on a hot plate until vigorous boiling was achieved. The liquid and foam height were closely monitored for approximately one hour. Post irradiation sludge samples were analyzed for VOA and SVOA compounds.

2.9 Hydrogen Generation Rate Testing

HGR measurements were undertaken to ascertain the impacts of the antifoams on flammability concerns downstream of DWPF. The testing was governed by a run plan and the specifics of the testing can be found therein.[17] Testing was undertaken using a previously described apparatus that consists of a 1.2 L polytetrafluorethylene (PTFE) vessel and lid.[18] Fitted to the center of the lid was a Parr® high-torque magnetic drive connected to a PTFE agitator impeller and shaft that was used to mix the simulant inside the vessel. The speed of the agitator was 200 rpm. Surrounding the magnetic drive were eight ports with stainless-steel fittings used for the following: temperature control within the vessel by two Incoloy® 800 heating rods, monitoring liquid temperature within the vessel with an Inconel® 600 thermocouple, providing purge gas to continuously sweep the vapor space of the vessel, connecting the headspace of the vessel to a glass condenser, providing a route for reflux from the condenser back to the reaction vessel, and for adding the antifoams. Upstream from the reaction vessel, two M&TE MKS® mass flow controllers were used to supply CO_2-free compressed air or N_2 cylinder gas containing 0.5 vol % Kr and 20 vol % O_2. Downstream from the reaction vessel, a glass condenser was employed to remove condensable gases from the gas before proceeding to analysis. After passing through the condenser, the gas was sampled and quantified for hydrogen content by an Inficon Micro 3000 GC-TCD (thermal conductivity detector). An in-line, gas-phase FTIR was also employed as needed to monitor for potential volatile antifoam degradation products.

Simulants were prepared by dissolving predetermined amounts of sodium salts and aluminum trinitrate in DI water (targeted simulant concentrations can be found in the run plan and actual concentrations can be found in Table 3-12).[17] Reagent grade sodium nitrate, sodium nitrite, sodium carbonate, and a 50 wt % sodium hydroxide solution were purchased from Fisher Chemical and used as received. In the case where the targeted hydroxide concentration precludes the use of 50 wt % sodium hydroxide solution, solid sodium hydroxide was used as the hydroxide feedstock. Reagent grade aluminum trinitrate nonahydrate was purchased from Sigma-Aldrich and used as received. Reagent grade sodium sulfate was purchased from Alfa Aesar and used as received. The reagents were added directly to the reaction vessel before sealing. The order of addition to the vessel was as follows: sodium hydroxide and half of the DI water prior to the aluminum source, then the remaining species and remaining DI water.

After the addition of all chemicals, the vessel was sealed and checked for leaks by mass balance of air flow through the process headspace. Once leak-free conditions had been confirmed, stirring was initiated and a purge flow of dried air was applied to the process to sweep residual CO_2 from the vessel. The system controls were then set to apply heat via two electric heating rods such that the difference between the process (fluid) temperature and that of the heating rod interior could not exceed 30 °C. In experimental tests, the process fluid was brought to the desired temperature, at which point either the antifoam additive was added or not (blank tests). The purge gas was then switched to the typically lower purge rate process gas stream (0.5 vol % Kr and 20 vol % O_2 in N_2). This point was designated as the start of the experiment.

The experiment continued while monitoring for hydrogen concentration via GC. To ensure hydrogen and methane concentration stayed below their flammability limits, the purge rate was (manually) increased using both the air purge and the Kr tracer-containing gas stream as needed. The experiment duration was planned such that at a minimum, the vessel headspace could undergo approximately three vapor space volume turn-overs (achieving 99.7% of pseudo steady-state, assuming continuously-stirred reactor dynamics; note that this time is volume- and purge rate-dependent). Once this time was reached and hydrogen measurements by GC stabilized or began to decrease, heating rod power was turned off and the experiment stopped. The higher purge rate air was then reapplied to the vessel to sweep out residual hydrogen. The simulant mixture was then removed from the vessel and subsampled as needed for product analyses. Density of the simulant was checked by weighing a known volume of the simulant using an M&TE autopipette and an M&TE balance.

An Inficon Micro 3000 GC was used to analyze offgas content for all experiments. The GC was equipped with two analysis channels: one using a Molsieve 5A column for H_2, O_2, N_2, CH_4, and Kr analysis, and a second using a PoraPLOT Q column for N_2O and CO_2 analysis. Each column employed a thermal conductivity detector which measured against the background of pure argon (also used as a carrier gas). The GC calibration was verified before each experiment using a calibration gas with a composition of 50 ppm_v H_2, 100 ppm_v CH_4, 0.5 vol % Kr, 1 vol % N_2O, 1 vol % CO_2, and 20 vol % O_2 in N_2.

In addition, FTIR was used as needed to monitor for volatile degradation products. The FTIR was plumbed into the line after the GC.

When presented, HGR is reported in units of standard cubic feet per hour per gallon of simulant mixture ($ft^3\ hr^{-1}\ gal^{-1}$). The purge rates employed during this testing were supplied at standard conditions of 21.11 °C and 1 atm. The HGRs presented herein have been corrected to a standard temperature and pressure of 25 °C and 1 atm.

2.10 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

A functional classification of Production Support is selected in the Task Technical Request (TTR).[19] Thus, the technical review was performed as a design check by document review.

3.0 Results and Discussion

3.1 Non-Chemical Foam Control Methods

Several non-chemical foam control strategies were proposed, discussed, and evaluated by a multi-disciplinary team, including DWPF process control engineers.[15,16] The strategies that were ranked most likely to be effective for foam control were identified for further evaluation, including: the use of liquid spray/mist, agitators in the headspace, and ultrasonic energy. These alternative methods were tested in laboratory scale experiments using physical and chemical simulants. The simulant was heated to boiling (~102°C) and agitated, simulating DWPF processing. Foam generation was carefully monitored while the potential mechanical methods for foam control were tested. A photo without foam control is shown in Figure 3-1 A) and a photo using agitation to control foam is shown in Figure 3-1 B).

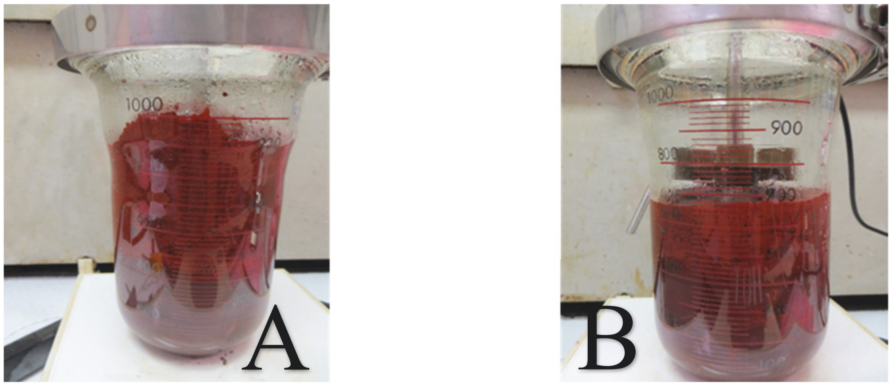


Figure 3-1. A: No Foam Control (left) and B: Headspace Agitators (right)

During the initial test, where no method for foam control was implemented, the liquid level increased from 500 to 980 mL during boil up. The liquid level nearly doubled, resulting in foam generation of 96 vol %. Ultra-sonication did not reduce foam production. Agitation through ultrasonic energy thickened the foam, stabilizing it further. Spraying the generating foam with fine water particles (at a rate of 380 mL/h) reduced the foam level to +8 vol %, but once the water mist was discontinued the foam level again increased to 96 vol %. The results from the testing of the non-chemical methods for foam control are summarized in Table 3-1.

Table 3-1. Results of Non-chemical Foam Control Methods

Non-chemical Method	Liquid Level Prior to Boiling (mL)	Liquid Level During Boiling (mL)	Foam Level (vol %)
No Foam Control	500	980	96
Water Spray/Mist (~380 mL/h)	500	540	8[1]
Headspace Agitators	450	750	67
Ultrasonic Energy (750 Watts)	500	980	96[2]

[1] During spraying/misting; Foam level increased to 96 vol % once spay/mist was stopped

[2] Ultra-sonication led to a thicker more stable foam

While spraying appeared promising, the quantity of water required to control foaming during HLW processing in DWPF would likely be unviable. The use of agitators in the headspace reduced the rate of foam generation and a maximum foam level of 67 vol % was achieved. Space in DWPF processing tanks, however, is limited due to the presence of existing equipment and instrumentation, making the installation and use of additional agitators in the headspace impractical. These results suggest that the implementation of effective non-chemical foam control strategies in DWPF is not feasible. Therefore, an alternative chemical defoamer is necessary to mitigate foam generation during HLW treatment at DWPF.

3.2 Spreading testing

Each superwetter's initial spread rate (cm^2/s) across a pH range of 1 to 13 and change in spread rate (cm^2/s) over time were utilized to determine the chemical stability. Silwet L-77 and Momentive™ Y-17112 outperformed Y-17309 and Y-17581, achieving greater spread rates and sustaining chemical stability. Silwet L-77 attained the highest spread rates of 2.7 cm^2/s and 2.0 cm^2/s at pH 8.5 and 9 respectively. In extreme acidic and alkaline conditions, however, Silwet L-77 solutions failed to spread at all. Momentive™ Y-17112 achieved consistent spread rates between 1.0 cm^2/s and 1.5 cm^2/s across the entire pH range, even at lower concentrations. These results are illustrated in Figure 3-2. Y-17581 did not blend with the buffer solutions and spreading was not achieved. As a result, Y-17581 was eliminated as a candidate from further testing.

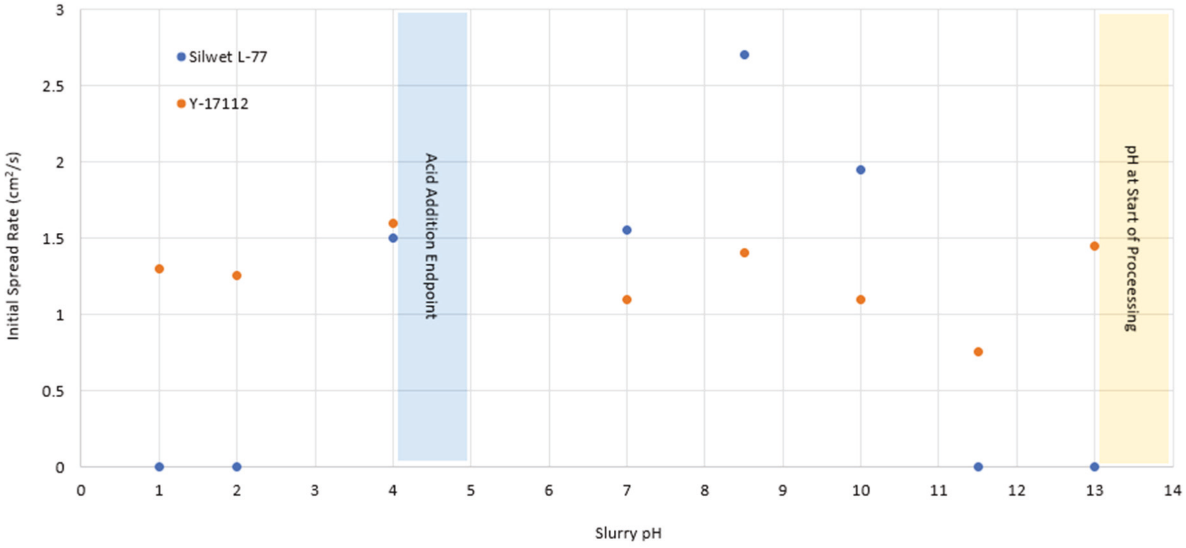
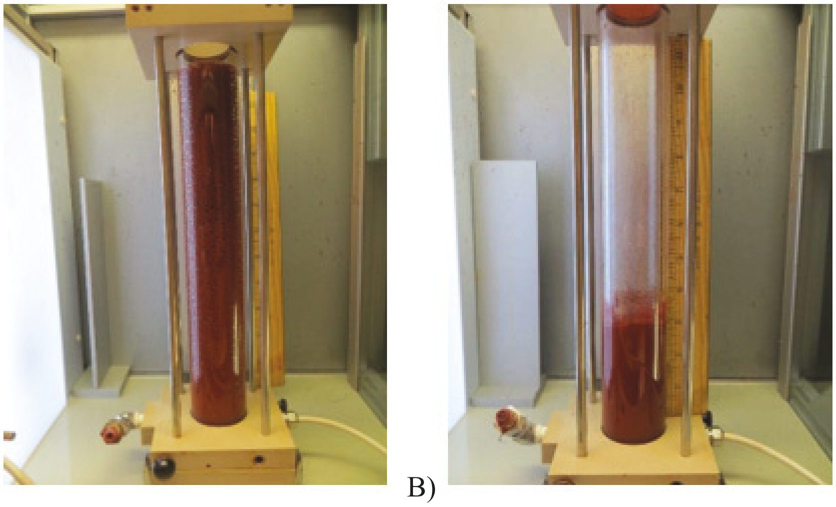


Figure 3-2. Initial Spread Rate vs pH of Silwet L-77 and Momentive™ Y-17112

3.3 Foam column testing

A Teclis FoamScan foam analyzer was used to estimate the required concentration of each defoaming agent necessary to control foaming of an acidic and caustic physical simulant. The foam column was filled with approximately 60 mL acidic (pH 4) or caustic (pH 13) physical simulant and continuously purged at a flowrate of 1.5-2.5 sL/min. Defoamer was added in concentrations ranging from 5 ppm to 500 ppm and the reduction in foam height was noted. The photos below show the height of the foam column without (Figure 3-3 A) and with (Figure 3-3 B) antifoam. The defoamers were ranked effective, moderately effective, or ineffective in Table 3-2. The defoamers deemed effective were further tested with chemical simulants at boiling.



A) B)

Figure 3-3. A: No Defoamer (left) and B: With 25 ppm Evonik Surfynol® MD20 (right)

3.4 Boiling Testing with physical and chemical simulants

Siovation Antifoam 747 and the most effective alternative defoamers were tested at a typical DWPF processing temperature of 102°C – 103°C in 150 mL acidic (pH 4) and caustic (pH 13) physical simulants. The simulant was heated to boiling in a glass vessel on a hotplate. A reflux condenser was used to return the generated condensate back into the reaction vessel, ensuring the solids concentration stayed constant. Diluted antifoam was added in 5 mL aliquots and the time required for foam reformation was observed. The duration of foam control is presented in Table 3-2.

Table 3-2. Test Results with Physical Simulants at Boiling

Defoamer	Physical Simulant (foam control duration) FoamScan	
	pH 4	pH 13
Siovation Antifoam 747	30 - 60 min	30 - 60 min
Evonik Surfynol® MD20	> 60 min	> 60 min
Momentive™ Y-17112	> 60 min	> 60 min
BASF FoamStar® ST 2412	> 60 min	> 60 min
3M FC-4430	> 60 min	> 60 min
Dow XIAMETER® AFE-1010	> 60 min	> 60 min
Momentive™ Y-17309	> 60 min	30 - 60 min
3M FC-4432	> 60 min	30 - 60 min
3M FC-4434	30 - 60 min	> 60 min
BASF Foamaster® MO 2111 NC	> 60 min	30 - 60 min
Dow XIAMETER® ACP-1430	30 - 60 min	30 - 60 min
BASF Foamaster® MO 2172	30 - 60 min	30 - 60 min
BASF Foamaster® MO 2185	30 - 60 min	30 - 60 min
BASF FoamStar® ST 2420	30 - 60 min	30 - 60 min
Evonik Dynol® 607	30 - 60 min	30 - 60 min
Dow XIAMETER® AEF-1410	< 30 min	> 60 min
Evonik Surfynol® AD01	30 - 60 min	< 30 min
Momentive™ Y-17581	< 30 min	< 30 min
Chemours Capstone™ FS-3100	< 30 min	< 30 min
Chemours Capstone™ FS-50	< 30 min	< 30 min
Chemours Capstone™ FS-30	< 30 min	< 30 min
BASF Foamaster® MO 2140	< 30 min	< 30 min
Dow XIAMETER® ACP-3183	< 30 min	< 30 min
Dow XIAMETER® ACP-1400	< 30 min	< 30 min

🟩 Effective 🟨 Moderately Effective 🟥 Ineffective

Siovation Antifoam 747 and the eight remaining most effective alternative defoamers were tested at a typical DWPF processing temperature of 102°C – 103°C in 150 mL acidic (pH 4) and caustic (pH 13) chemical simulants in identical tested as described above. The duration of foam control and concentrations required to control foaming are presented in Table 3-3. Note that three additional antifoams and defoamers were screened out during the chemical simulant testing.

Table 3-3. Test Results with Chemical Simulants at Boiling

Antifoam Candidates	1 hr Boiling Testing Chemical Simulant		1 hr Boiling Testing Chemical Simulant	
	pH 4	pH 13	pH 4	pH 13
Momentive™ Y-17112[a]	25 ppm	25 ppm	>60 min	>60 min
Evonik Surfynol® MD20[b]	25 ppm	25 ppm	>60 min	>60 min
3M FC-4430[c]	75 ppm	75 ppm	>60 min	>60 min
BASF FoamStar® ST 2412	300 ppm	300 ppm	>60 min	>60 min
Dow XIAMETER® AFE-1010	200 ppm	300 ppm	>60 min	~30 min
Momentive™ Y-17309	25 ppm	25 ppm	~25 min	>60 min
Momentive™ Silwet L77	25 ppm	25 ppm	~30 min	NA
Siovation Antifoam 747	25 ppm	25 ppm	NA	~15 min
Sodium Metasilicate[d]	1000 ppm	1000 ppm	NA	NA

Foam Control Duration	<30 min	30-60 min	>60 min

Notes in table

[a] No Si-O Bond
[b] Si free
[c] Fluorinated
[d] Sodium metasilicate addition increased pH

3.5 Short SRAT segment testing with chemical simulant containing noble metals and mercury in RC1mx

The Mettler Toledo RC1mx was used in the "Short segment" SRAT and SME testing as both a test of the new five remaining antifoams and as a proficiency test of the new equipment, utilizing a Mettler Toledo RC1mx Reaction Calorimeter. Prior to this testing, the equipment, procedures, software, and laboratory personnel completed extensive water testing to ensure the equipment was ready for testing. The new equipment allowed for improved quality control: automated reagent additions, precise temperature control, repeatability, and data collection compared to the equipment used historically for SRAT and SME processing. One additional advantage this new equipment adds is that the reactor is jacketed, and a silicon heat transfer fluid is used to heat and cool the reactor. This allows much better visual observation of the foam compared to insulated reaction kettles, a significant improvement for antifoam testing. A photo of the RC1 equipment setup on the custom cart in the walk-in hood is shown in Figure 2-4.

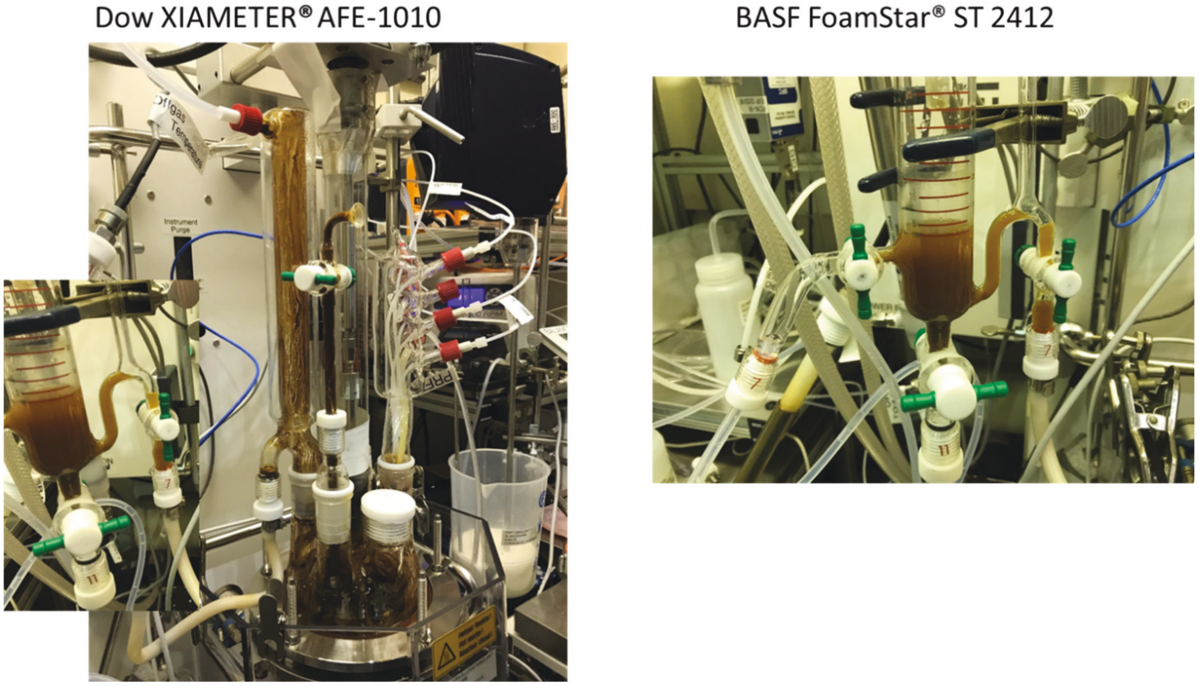
Conditions for testing included: SB6A sludge (foamiest sludge identified), addition of mercury and noble metals (Ag, Pd, Rh, and Ru), and a foamy PRFT simulant. This was the first testing where noble metals and mercury were added to the SB6 sludge slurry. In a few of the tests, a full SRAT and SME cycle was completed simulating HLW processing in DWPF. These full SRAT/SME cycles consisted of PRFT addition, nitric and glycolic acid addition, SRAT dewater, strip effluent addition, canister decontamination water addition, and process frit addition.

Based on experience with boiling of sludge and SRAT product, it was obvious that the segment of the SRAT cycle where PRFT was added (pH ~13 for both sludge and PRFT) was the most challenging for the antifoams, especially Antifoam 747. So, testing of each of the antifoams was conducted during the approximately five-hour PRFT addition and continued until the addition was complete or a large foamover stopped the testing.

The five best antifoam alternatives and Antifoam 747 were used in days only testing of segments of the SRAT and SME cycles (nitric-glycolic acid flowsheet only). The goal of this testing was to determine the effectiveness of the antifoam alternatives and to determine the amount and frequency of antifoam needed to control foam.

Three of the alternatives, Momentive™ Y-17112, Evonik Surfynol® MD20 and 3M FC-4430 were all effective in controlling foam with minimal antifoam additions. A total of 2-4 antifoam additions (50-100 ppm antifoam) were added during the five-hour PRFT addition to control foam. The Surfynol® MD20 was effective in controlling foam, but approximately twice as much foam was present than in the Momentive™ Y-17112 testing.

Large foamovers occurred using Dow Xiameter® AFE-1010 and BASF Foamstar® ST2412. The foamovers filled the offgas tubing, the condenser, and the MWWT (as shown in Figure 3-4). Sufficient defoamer couldn't be added fast enough to prevent these foamovers so both alternatives were eliminated from additional testing.


Dow XIAMETER® AFE-1010

BASF FoamStar® ST 2412

Figure 3-4. Foamovers During Short SRAT Segment Testing in RC1mx

Antifoam 747 required over 60 antifoam additions (each antifoam addition was 25 mg/kg sludge) during the five-hour PRFT addition, versus 2-4 needed for the three best alternatives. The foam was very high and was controlled by adding a new addition every four minutes throughout the five hours of testing. Antifoam 747 would have been eliminated based on the large antifoam addition and the high generation rate of hexamethyldisiloxane, which is both volatile and flammable. An increase in the air purge was needed to prevent exceeding 25% of the Lower Explosive Limit (the only antifoam that needed an increased air purge for flammability control). The only reason Antifoam 747 had not been screened out in earlier testing is that it is the current DWPF antifoam. No full SRAT/SME cycle was completed with Antifoam 747 due to its poor performance during the short segment testing.

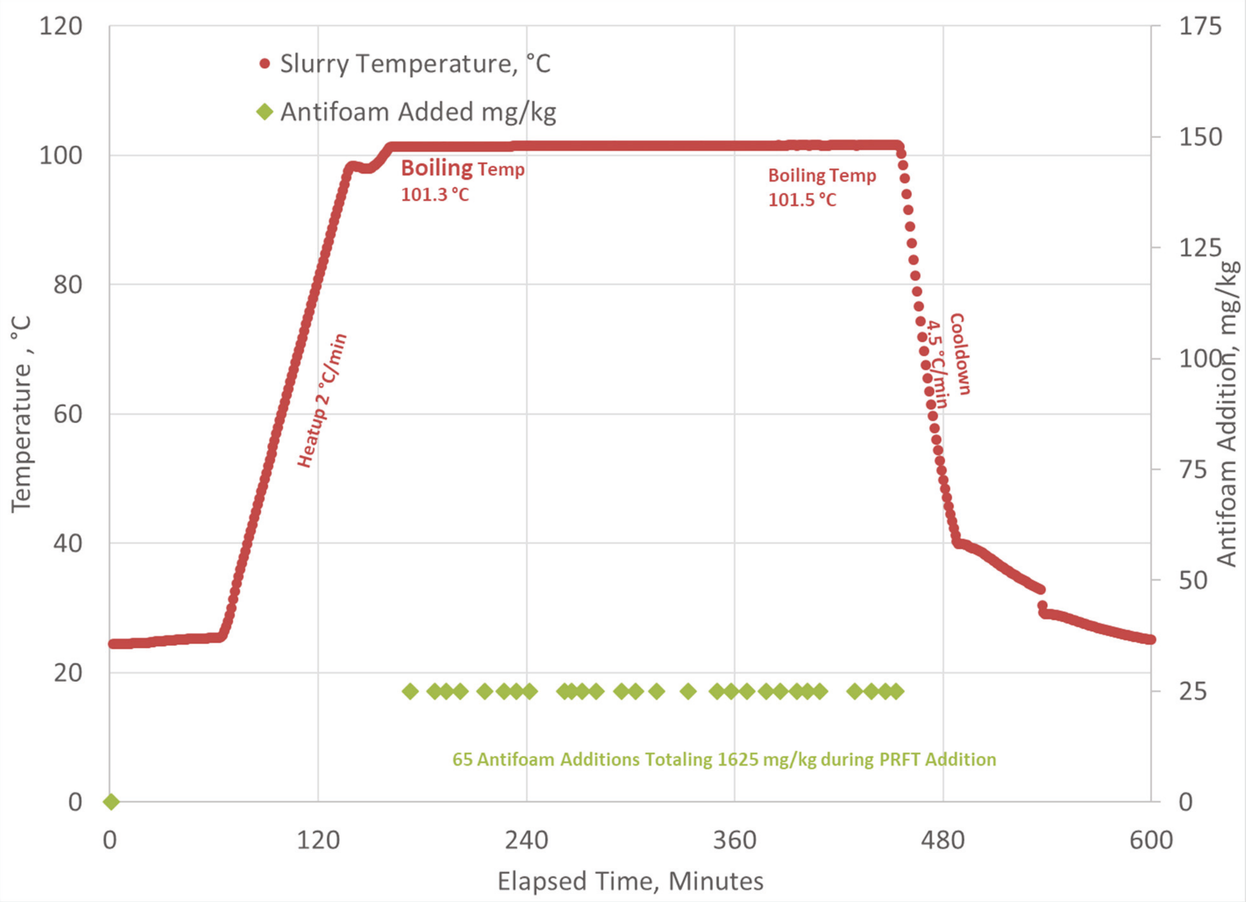


Figure 3-5. Antifoam 747 PRFT Addition Segment Showing Antifoam Additions

The test results of Antifoam 747 and the five best alternative antifoams are summarized in Table 3-4.

Table 3-4. Test Results – Antifoam 747 and Five Best Alternatives During PRFT Addition

Defoamer	Concentration	Foam Control Duration
Siovation Antifoam 747	3000 ppm	5 hours
Momentive™ Y-17112	50 ppm	5 hours
Evonik Surfynol® MD20	100 ppm	5 hours
3M FC-4430	50 ppm	5 hours
BASF FoamStar® ST 2412	~ 300 ppm	41 min
Dow XIAMETER® AFE-1010	~ 250 ppm	42 min

3.6 Full SRAT/SME testing with chemical simulant containing noble metals and mercury in RC1mx

Testing was performed to compare Momentive™ Y-17112, and Evonik Surfynol® MD20 during identical SRAT and SME simulations in the RC1mx. Note that no comparable around-the-clock testing was performed with the Siovation Antifoam 747 because the antifoam performed so poorly in the short segment testing. Although 3M FC-4430 was as effective in the days only testing, it was eliminated as a candidate as a result of discussions with DSE engineers. There were two reasons it was screened out, due to that fact that fluorine is an ingredient and DWPF would like to keep fluorine out of the melter system and due to the reproductive toxicity along with potential damage to liver and nervous system.

The testing was designed to be as aggressive as practical to maximize the foam generation. This included using the foamiest sludge and PRFT slurries available, using SWPF volumes for PRFT and SEFT to maximize processing time, and to use the DWPF scaled design basis PRFT addition rate, acid addition rate, dewater rate, SEFT addition rate, and boilup rate. The noble metals were high in case one of them catalyzed the antifoam decomposition. For the nitric-glycolic acid flowsheet experiments, the SRAT purge was reduced to approximately 1/3 of the typical SRAT purge for the nitric-formic acid flowsheet to lower the dilution of the offgas and maximize the chance of detecting any decomposition gases using the GC, MS and FTIR offgas probes.

An improved antifoam for the DWPF CPC would have the following characteristics:

- Effective as both an antifoam and defoamer (prevents foam and kills foam when added)
- Chemically stable – introduces no decomposition products to the condensate or offgas
- No contribution to flammability in offgas or melter
- Effective at a low concentration
- Persistent so it would only need to be added infrequently
- Does not adversely influence recovery of mercury and does not produce organo-mercury compounds

One processing note during the experiments is that the foam volume in the Momentive™ Y-17112 experiments was about half the volume as was noted in the Evonik Surfynol® MD20 experiments. A better antifoam will lead to less persistent foam and likely lead to fewer foamovers.

The discussion of these experiments is organized into the following sections to evaluate the effectiveness of the two best antifoam candidates and compare their performance to Antifoam 747.

3.6.1 Overall testing basis and antifoam results

Five full SRAT/SME cycles were completed in testing of the antifoam alternatives to compare this performance to the DWPF baseline antifoam, Antifoam 747. The experiments were completed around the clock, taking almost three days to complete. Key information is included in tables and figures in section 3.6 with additional detailed information contained in the appendices.

A timeline for the tests is summarized in Figure 3-6.

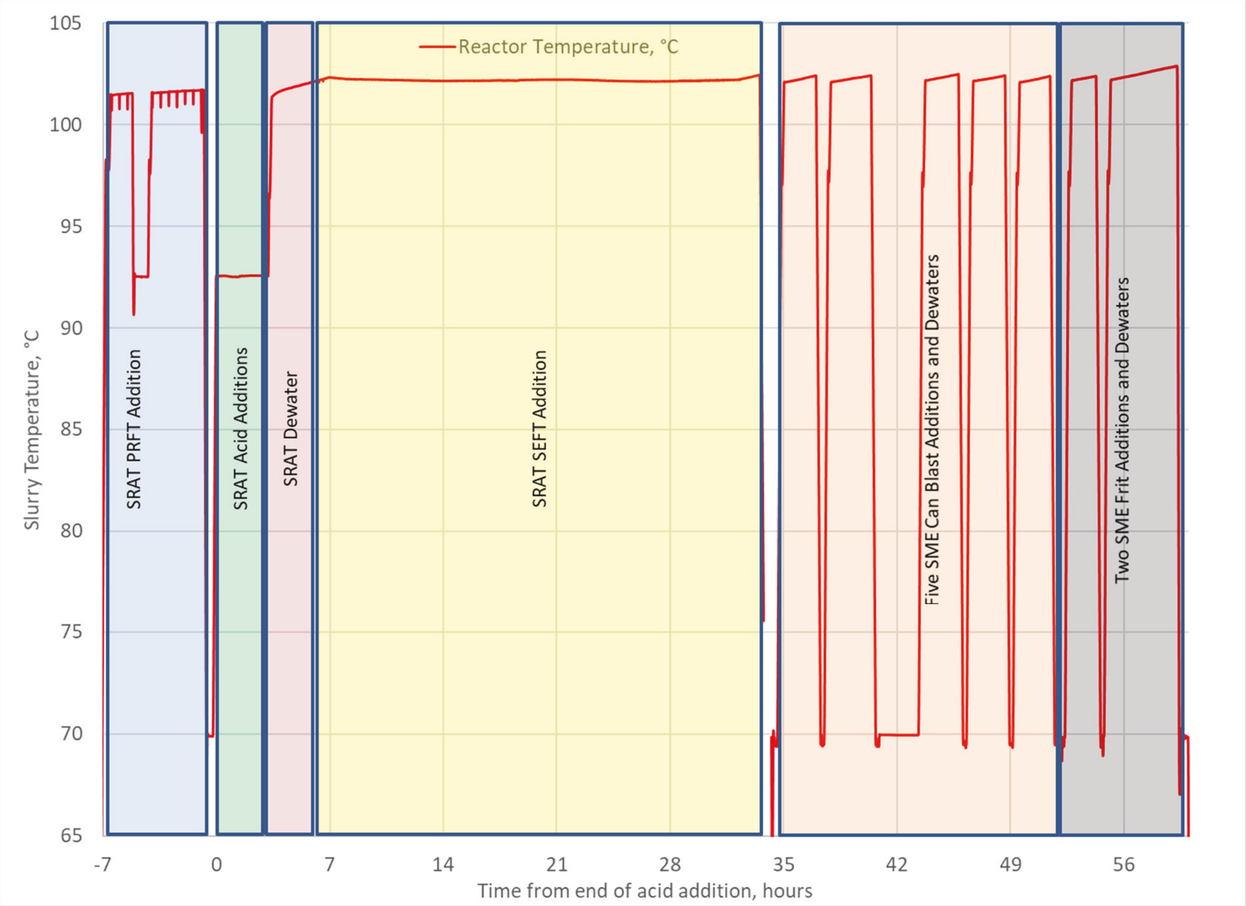


Figure 3-6. Timeline and Temperature Profile for SRAT and SME Cycles

The mass of major components added and dewater removed is summarized in Table 3-5. This information demonstrates that the testing was completed essentially as planned. The switch from the nitric-glycolic acid flowsheet to the nitric-formic acid flowsheet changes the acid mix and the dewater slightly. The PRFT addition in both flowsheets is the same so the variability of foaminess and foam control from test to test can be estimated by the variability in comparing either antifoam results. For example, for Momentive™ Y-17112, four 25 mg/kg antifoam additions were completed in the nitric-glycolic acid flowsheet experiment and twelve 25 mg/kg antifoam additions were completed in the nitric-formic acid flowsheet experiment. For Evonik Surfynol® MD20, ten 25 mg/kg antifoam additions were completed in the nitric-glycolic acid flowsheet simulation and forty-five 25 mg/kg antifoam additions were completed in the nitric-formic acid flowsheet simulation.

Table 3-5. Components added to RC1mx full SRAT/SME testing

Reducing Acid	**Glycolic**	**Glycolic**	**Formic**	**Formic**
Antifoam	Momentive™ Y-17112	Evonik Surfynol® MD20	Momentive™ Y-17112	Evonik Surfynol® MD20
Date	9-16-19	10-8-2019	12-2-19	12-8-19
# 25 mg/kg antifoam additions	4	10	12	45
1:20 Antifoam mass, g	3.52	8.80	10.56	39.6
SB6A sludge, g	1769.7	1772.4	1837.1	1694.3
PRFT, g	768.3	767.22	767.21	765.5
PRFT Dewater	735.77	740.56	737.26	738.73
Nitric Acid, g	100.93	100.79	17.9	17.69
Reducing Acid, g	131.80	131.77	106.6	106.8
SRAT Dewater, g	466.6	465.18	419.43	451.3
SEFT, g	3667.7	3668.14	3668.4	3668.4
Decon water, g	1181.2	1180.7	1179.2	1423.6
Frit, g	312	312	310.2	310.2
Frit Water, g	312.8	312	310.5	310.5
SME dewater, g	487.1	543.9	503.1	504.9

Siovation Antifoam 747, Momentive™ Y-17112, and Evonik Surfynol® MD20 were tested in full SRAT/SME simulations. 1625 mg/kg Siovation Antifoam 747 was necessary to control foam during the first experiment, where trimethylsilanol and hexamethyldisiloxane was detected. The purge was increased to prevent flammability. However, only 100 mg/kg Momentive™ Y-17112 and 200 mg/kg Evonik Surfynol® MD20 were able to control foam as summarized in Table 3-6.

Table 3-6. Test Results – Full SRAT/SME Simulations

Defoamer	**Siovation Antifoam 747**	**Momentive™ Y-17112**	**Evonik Surfynol® MD20**
Commercial Ingredient	No	Yes	Yes
Solubility in Water	*Insoluble*	*Insoluble*	*Insoluble*
Nitric-glycolic acid flowsheet			
Degradation Products in Offgas	Trimethylsilanol Hexamethyldisiloxane	*None above 50 ppb*	*None above 50 ppb*
Quantity of Defoamer Required (mg/kg)	*1625*	*100*	*250*
Approximate DWPF Volume per Batch	~16 gal	~1 gal	~2.5 gal
Nitric-formic acid flowsheet			
Degradation Products in Offgas	Not Tested*	*None above 50 ppb*	*None above 50 ppb*
Quantity of Defoamer Required (mg/kg)		*300*	*1125*
Approximate DWPF Volume per Batch		~3 gal	~11 gal

*Note that no testing was completed with Antifoam 747 in the nitric-formic acid flowsheet as part of this study since the Antifoam 747 performance was so poor in testing with the nitric-glycolic acid flowsheet.

3.6.2 Offgas analysis with MS/FTIR during full SRAT/SME testing

The offgas was analyzed using a GC, MS and FTIR for most of the testing. The offgas data was carefully evaluated to identify any impurities in the antifoam or degradation products that might influence DWPF processing. The offgas has been condensed (condenser liquid temperature of 10 °C) and dried using a Nafion® air dryer prior to offgas analysis. As a result, only gases that are insoluble in the condensate are detected (the condensate analyses will be discussed in Section 3.6.4). It takes approximately 1 minute for the sample to reach the analyzers, so offgas species such as NO may have time to oxidize before being analyzed.

During the Antifoam 747 days-only experiment, excessive antifoam was required to control foam. During the five-hour PRFT addition, thirty-five antifoam additions were needed to control foam (875 mg/kg). The offgas generated during the Antifoam 747 days-only experiment was analyzed using the FTIR because it was expected that there would be significant hexamethyldisiloxane generation. During the testing, the hexamethyldisiloxane was monitored and the purge had to be increased to prevent exceeding 25% of the Lower Explosive Limit (LEL). The data from the experiment is summarized in Figure 3-7. The inset in the graph shows an almost perfect match for the pure hexamethyldisiloxane spectra (orange spectra).

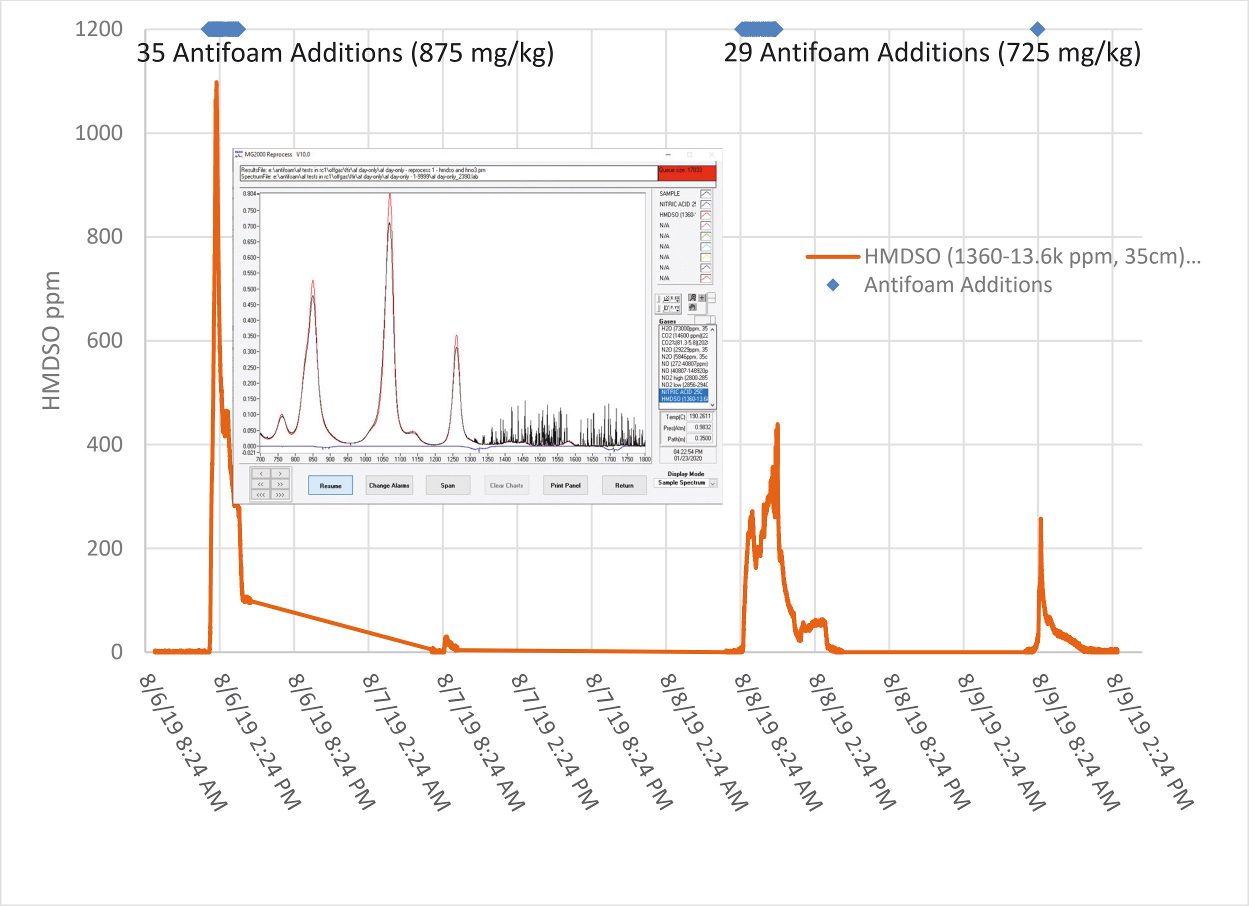


Figure 3-7. Nitric-Formic Acid Antifoam 747 Hexamethyldisiloxane Concentration, ppm

The most important result was that the offgas analysis showed no antifoam decomposition products were detected using the offgas instruments in the experiments with Momentive™ Y-17112 and Evonik Surfynol® MD20. In reviewing FTIR data, a very careful analysis is used to identify all quantifiable species. Once the major species are identified, they are subtracted from the spectra and the resulting spectra shows any peaks that haven't been identified. A careful search was made to identify these unknown peaks. A spectra after the subtraction of water, carbon dioxide, carbon monoxide, nitric oxide, nitrous oxide, and nitrogen dioxide (Figure 3-8) shows no components that can be identified (residual water and CO_2 are present as the subtractions are not perfect). The blue overlay showing the spectra for hexamethyldisiloxane demonstrated that no hexamethyldisiloxane was generated. In testing using the MS, a search was made for new peaks at m/z ratios that could represent antifoam degradation products or their fragments. Again, no unaccounted-for species were identified, with a detection limit of about 1 mg/L.

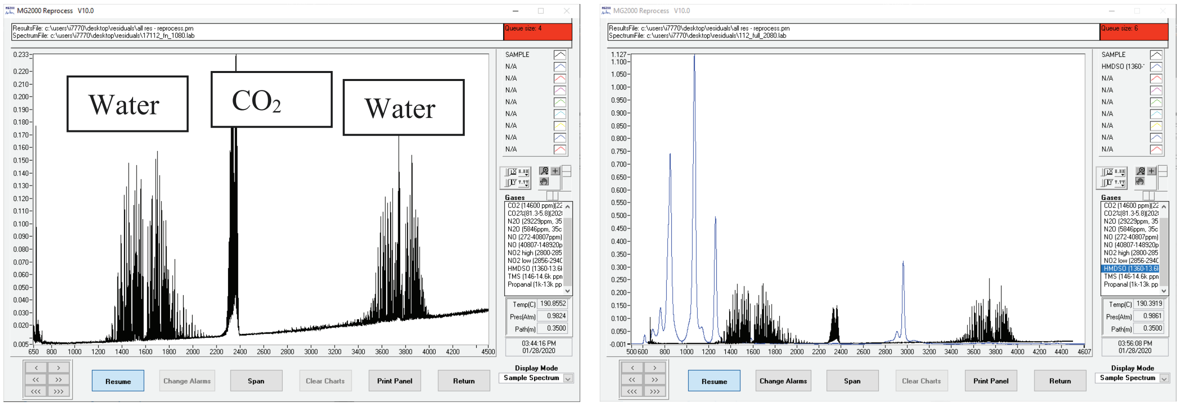


Figure 3-8. Example FTIR Spectra Before and After Subtracting Identified Gases

In most of the tests, the only identified gases were CO_2, N_2, H_2, N_2O, NO, NO_2 and He. Two graphs from each test are included in Appendix C.

3.6.3 Liquid sample analysis of samples pulled during full SRAT/SME testing

Slurry samples pulled before and during the experiments were analyzed using VOA and SVOA to look for antifoam decomposition products in the sludge (pre PRFT), slurry post PRFT and SEFT, along with the SRAT and SME products. The only SVOA organic analytes detected (above 1 mg/L detection limit) were 1,3-dichloro-3-methyl-butane and 2,3-dimethyl-2-butanol. These organic species were detected only in the Pre and Post PRFT samples, meaning they are unrelated to the Momentive™ Y-17112 antifoam as none was added prior to the Pre PRFT sample. No VOA analytes were detected (<1 mg/L). The VOA and SVOA results are summarized in Table 3-7.

Table 3-7. Momentive™ Y-17112 Nitric-glycolic acid Slurry and MWWT VOA and SVOA Results

Antifoam	Y-17112 Glycolic		MD20 Glycolic		Y-17112 Formic		MD20 Formic	
Analyte	VOA, mg/L	SVOA, mg/L	VOA, mg/L	SVOA, mg/L	VOA, mg/L	SVOA, mg/L	VOA, mg/L	SVOA, mg/L
Pre PRFT	<0.12	<1	<0.25	<1	<0.2	<1	<1	<1
Post PRFT	<0.12	<1*	<0.25	<1^	<0.2	<1	<0.2	<1
SRAT Product	<0.12	<1*	<0.25	<1^	<0.2	<1	<0.2	<1
SME Product	<0.12	<1	<0.25	<1	<0.2	<1	<0.2	<1
MWWT	<0.12	<1	<0.25	<1	<0.2	<1	<0.2	<1

^ Trace levels of several alkane compounds were observed but too low for quantification

* SVOA identified Cyclooctasiloxane, hexadecamethyl-Cyclononasiloxane, octadecamethyl-Cyclodecasiloxane, eicosamethyl-Tetracosamethyl-cyclododecasiloxane, the best match for the Y-17112 silane (not siloxane). These compounds were not identified in the Y-17112 nitric-glycolic SME product or in the Pre PRFT, Post PRFT, SRAT product or SME product for the Y-17112 nitric-formic experiment.

3.6.4 Condensate sample results

Condensate samples were pulled throughout testing and were analyzed by SRNL/Analytical Development (AD) and Process Science Analytical Laboratory (PSAL) to identify antifoam degradation products. Note that the antifoams are not volatile and will not contribute to the overall flammability of the vapor space. The antifoams will not be present in the condensate unless there has been a foamover. The samples looked very clear – no visual signs of a foamover. The results are summarized in Table 3-8.

Table 3-8. Condensate Results, specific gravity, g/mL, VOA, SVOA, and an ions, mg/L

Antifoam Flowsheet	Analyte	PRFT Dewater	SRAT Dewater	SEFT Dewater	SME Dewater
Y-17112 Nitric-Glycolic	Density, g/mL 20°C	1.002	1.008	0.9984	0.9982
	Nitrate, mg/L	631	17,300	246	39.1
	Glycolate, mg/L	<1	33.7	4.4	4.4
	Formate, mg/L	<10	170	<10	<10
	VOA, mg/L	<0.2	NR	<0.2	<0.2
	SVOA, mg/L	<1	NR	<1	<1
Y-17112 Nitric-Formic	Density, g/mL 20°C	0.9982	1.0116	1.008	1.009
	Nitrate, mg/L	3.31	20,500	208	12.4
	Nitrite, mg/L	<10	21.7	<10	<10
	Formate, mg/L	<10	111	11.3	<10
	VOA, mg/L	<0.2	<0.2	<0.2	<0.2
	SVOA, mg/L	<1	<1	<1	<1
MD20 Nitric-Glycolic	Density, g/mL 20°C	0.9982	1.0073	0.9985	0.9983
	Nitrate, mg/L	<10	12,600	331	33.9
	Glycolate, mg/L	<10	30.3	<10	<10
	Formate, mg/L	<10	49.1	<10	<10
	VOA, mg/L	NA	NA	NA	NA
	SVOA, mg/L	<1	<1	<1	<1
MD20 Nitric-Formic	Density, g/mL 20°C	0.9982	1.0115	0.9983	0.9983
	Nitrate, mg/L	8.98	21,000	124	12.1
	Nitrite, mg/L	<10	21.7	<10	10.3
	Formate, mg/L	<10	178.5	<10	<10
	VOA, mg/L	<0.2	<0.2	<0.2	<0.2
	SVOA, mg/L	<1	<1	<1	<1

* all other anions were below detection limit of 10 mg/L except Br <50 mg/L

For the Momentive™ Y-17112 nitric-glycolic acid test, a careful analysis of the dewater samples was performed. The samples were analyzed for mercury and by ICP-AES and IC to look for metals and anions. Results are shown in Table 3-9. The major anion present was nitrate. An attempt was made to get the lowest detection limit possible for glycolate so the glycolate was detectable in several of the samples (4.4 mg/L). Note that this concentration is much lower than has been used in glycolate destruction testing and in past testing would have been reported as lower than the detection limit. In addition, formate was detectable in the SRAT dewater condensate. The metals that were present above detection limit includes Hg, Ca, Cr, Fe, Mg, Mn, Na, Ni, Si, and Zn. The concentration of metals other than Hg were much lower than would be expected in the case of a foamover.

Table 3-9. Momentive™ Y-17112 Nitric-glycolic acid AD Dewater Hg, ICP-AES and IC Results, mg/L

Analyte	PRFT Dewater		SRAT Dewater		SEFT Dewater		SME Dewater	
Hg		33.6		NA		13.9		0.459
Fluoride	<	10	<	10	<	10	<	10
Formate	<	10		170	<	10	<	10
Chloride	<	10	<	10	<	10	<	10
Nitrite	<	10	<	10	<	10	<	10
Nitrate		631		17300		246		39.1
Phosphate	<	10	<	10	<	10	<	10
Sulfate	<	10	<	10	<	10	<	10
Oxalate	<	10	<	10	<	10	<	10
Bromide	<	50	<	50	<	50	<	50
Glycolate	<	1		NA		4.4		4.4
Ag	<	0.07	<	0.066	<	0.066	<	0.066
Al	<	0.13	<	0.129	<	0.129	<	0.129
B	<	0.12	<	0.12	<	0.12	<	0.12
Ba	<	0.01	<	0.005	<	0.005	<	0.005
Be	<	0.01	<	0.006	<	0.006	<	0.006
Ca		0.257		0.0868		0.19		0.0664
Cd	<	0.01	<	0.007	<	0.007	<	0.007
Ce	<	0.32	<	0.323	<	0.323	<	0.323
Co	<	0.07	<	0.068	<	0.068	<	0.068
Cr	<	0.02	<	0.022		1.26	<	0.022
Cu	<	0.05	<	0.05	<	0.05	<	0.05
Fe		0.0474		0.0646		2.17		0.0583
K	<	0.68	<	0.68	<	0.68	<	0.68
La	<	0.02	<	0.018	<	0.018	<	0.018
Li	<	0.02	<	0.017	<	0.017	<	0.017
Mg		0.0073		0.0155		0.0156		0.0047
Mn		0.0414		0.149		0.345		0.0988
Mo	<	0.17	<	0.173	<	0.173	<	0.173
Na		1.11		1.28	<	0.235	<	0.235
Ni	<	0.05	<	0.05		1.58	<	0.05
P	<	0.62	<	0.617	<	0.617	<	0.617
Pb	<	0.16	<	0.159	<	0.159	<	0.159
S	<	8.48	<	8.48	<	8.48	<	8.48
Sb	<	0.53	<	0.531	<	0.531	<	0.531
Si		2.19		2.2		0.519		0.365
Sn	<	0.22	<	0.215	<	0.215	<	0.215
Sr	<	0.04	<	0.043	<	0.043	<	0.043
Ti	<	0.01	<	0.014	<	0.014	<	0.014
V	<	0.02	<	0.015	<	0.015	<	0.015
Zn		0.0206		0.0108		0.0192	<	0.009
Zr	<	0.02	<	0.017	<	0.017	<	0.017

For the other three experiments, the condensate samples were analyzed by PSAL. Each of the dewater samples was analyzed in ICP-AES scan mode and only mercury was above detection limits. The samples were analyzed a second time to better quantify the B, Li, Na, Si, and Hg. The results are reported in Table 3-10. The mercury present in the SRAT-Dewater samples is likely the result of a small amount of dissolution of the mercury in the MWWT. The dewater sample results demonstrate that no detectable foamover occurred in the RC1 testing.

Table 3-10. PSAL Dewater Hg, ICP-AES Results, mg/L

Sample	Na, Ppm	Si, Ppm	Hg, Ppm
Post-PRFT Condensate – Glycolic – MD20 – S-10742	<1	1.83	<1
Post-SRAT-Dewater– Glycolic – MD20 – S-10743	<1	1.52	1070
Post-SEFT-Dewater– Glycolic – MD20 – S-10744	<1	1.40	39.2
Post-SME-Dewater– Glycolic – MD20 – S-10745	<1	1.16	1.30
Post-PRFT Condensate – Formic – MD20 – S-10746	<1	1.37	1.40
Post-SRAT-Dewater– Formic – MD20 – S-10747	1.28	1.15	1140
Post-SEFT-Dewater– Formic – MD20 – S-10748	<1	1.27	1.75
Post-SME-Dewater– Formic – MD20 – S-10749	<1	2.12	2.50
Post-PRFT Condensate – Formic – Y17112 – S-10750	<1	2.29	1.47
Post-SRAT-Dewater– Formic – Y17112 – S-10751	1.60	4.55	1430
Post-SEFT-Dewater– Formic – Y17112 – S-10752	<1	1.81	13.7
Post-SME-Dewater– Formic – Y17112 – S-10753	<1	1.90	1.20

Although separate dewater samples were pulled during each segment of the SRAT and SME cycles, the combined condensate that will be collected in the Slurry Mix Evaporator Condensate Tank (SMECT) can be calculated. The predicted concentration of metals and anions in the SMECT can be calculated using the individual dewater sample mass and concentration.

$$\text{SMECT, mg/L} = (X_{PRFT} * m_{PRFT} + X_{SRAT} * m_{SRAT} + X_{SEFT} * m_{SEFT} + X_{SME} * m_{SME})/(m_{PRFT} + m_{SRAT}\ m_{SEFT} + m_{SME})$$

where m is the mass of each dewater sample in g and X is the concentration in mg/L.

The predicted SMECT concentration of various analytes is summarized in Table 3-11 for the Y-17112 Nitric-Glycolic Acid experiment. This testing predicts the CPC condensate will have a nitrate concentration of 1,400 mg/L (pH 1.6, 0.02 M), a formate concentration of 21 mg/L, a glycolate concentration of 5.5-6.1 mg/L, and a mercury concentration of 100 mg/L.

The SRAT dewater glycolate concentration was about 10 times higher than in the SEFT and SME dewater samples. The sample was reanalyzed using a nuclear magnetic resonance (NMR) spectroscopy[20] at 29 mg/L. This higher glycolate concentration in this sample may be due to the higher offgas generation during this segment of the experiment, a 1 mL foamover, or the result of glycolic acid entrainment due to above surface addition. The dewater sample looked very clear (not brown as a foamover condensate would) and has very low Al and Fe concentration.

Table 3-11. Y-17112 Nitric-Glycolic Acid Predicted SMECT Condensate Composition

Analyte	PRFT Dewater	SRAT Dewater	SEFT Dewater	SME Dewater	SMECT Predicted
Condensate Mass, g	735.1	466.6	3,667.7	1,824.7	6,694.1
spg, g/mL	1.002	1.008	0.996	0.9905	0.996
Nitrate, mg/L	631	17300	246	39.1	1,421
IC Glycolate, mg/L	<1	33.7	4.4	4.4	6.07
NMR Glycolate, mg/L	not measured (NM)	29	NM	NM	NM
IC Formate, mg/L	<10	170	<10	<10	21.2
VOA, mg/L	<0.2		<0.2	<0.2	<0.2
SVOA, mg/L	<1		<1	<1	<1
Hg, mg/L	33.6		13.9	0.459	13.8

6.5 g of mercury was added to each of the experiments as mercuric oxide. The mercury recovery in the MWWT was about 3 g for each experiment. In addition, approximately 0.5 g of mercury was dissolved in the four condensate samples. Other mercury was coating glassware in the condenser, offgas tubing, SRAT and SME product slurry but was not quantified.

3.6.5 Downstream Impacts Discussion

One of the most important questions regarding Momentive™ Y-17112 is what influence it will have on downstream processing facilities, particularly the condensate storage and processing in H-area Tank Farms (HTF). If Momentive™ Y-17112 can control foam in the CPC as well as was done in these experiments, the condensate collected in the SMECT will be primarily water, nitric acid, elemental mercury, and mercuric nitrate. There will also be ~6 mg/L glycolate and ~20 mg/L formate. Unless a foamover occurs with either antifoam, no antifoam is expected in the condensate based on this testing. The Momentive™ Y-17112 is a large molecule (~600 atomic mass units) with low vapor pressure (213 Pa at 20 °C,[21] approximately 1/10th the vapor pressure of water, which is 2,330 Pa at 20 °C). It is very similar in size to the main ingredient in Antifoam 747 (also ~600 atomic mass units, vapor pressure of <133 Pa[22]). Both ingredients have identical long ethoxy polymer chains and thus are expected to have similar vapor pressures. Based on this vapor pressure comparison, the flammability impact of Momentive™ Y-17112 in downstream processing facilities will be approximately equal to the impact of the same concentration of Antifoam 747. If Momentive™ Y-17112 reduces foamover events as expected, the flammability impact of Momentive™ Y-17112 in downstream facilities will be less than that of Antifoam 747.

A planned permanganate destruction process[23] is designed to destroy ≥68 mg/L glycolate in the Recycle Collection Tank (RCT) with a Permanganate to Glycolate molar ratio of ~5.7. The molar ratio of ~5.7 may be too low for the 6 mg/L glycolate concentration in these experiments. At these very low glycolate concentrations, the P/G ratio can be increased to counteract the very low starting glycolate concentration. In addition, the glycolate detection limit in the RCT is 5 mg/L so the decomposition cannot be verified using sample analysis.

The SMECT will be combined with other recycle streams in DWPF and then sodium hydroxide and sodium nitrite will be added in the RCT to ensure they comply with corrosion program in the HTF. In the case of a foamover, the glycolate and nitrate concentration will be much higher than predicted in the table above, possibly as high as 10,000 mg/L in the case of a 2,000-gallon carryover (largest foamover in DWPF's 800 plus batches). Any glycolate concentration would require using the permanganate oxidation process to destroy the resulting glycolate. If a large foamover occurred, the Momentive™ Y-17112 concentration would be ~100 mg/L. Assuming a large foamover occurs every 60 batches with no thermolytic destruction, the Tank 22 antifoam concentration would be 0.67 mg/L and the Tank 38 antifoam concentration would be 10 mg/L assuming a 15x concentration ratio. An estimate of the resulting hydrogen generation rate (HGR) for the antifoam carbon can be calculated using the Global TOC Thermolytic HGR equation below.[18] If both Tank 22 and Tank 38 are at 100 °C, the calculated HGR for Tank 22 is 4.02E-11 and the HGR for Tank 38 is 7.42E-09 $ft^3/h/gal$ using the equation below:

$$HGR_{AF} = 2.45E6 * ([OH]^{0.925}) * ([TOC]_{AF}) * e^{(-8.29E4/8.314/(273.15+T))}$$

Where,

HGR_{AF} is the hydrogen production rate from the thermolysis of the antifoam (AF) in $ft^3\ h^{-1}\ gal^{-1}$,
[OH] is the free hydroxide concentration in mol L^{-1},
$[TOC]_{AF}$ is the TOC concentration of AF in mol L^{-1} (where Y-17112 is 55.6% carbon), and
T is the slurry temperature in °C.

Testing was undertaken to evaluate the thermolytic hydrogen and methane generation rate (MGR) of Momentive™ Y-17112 and the other antifoam replacement candidate Evonik Surfynol® MD20. These were compared to the current DWPF Antifoam 747 in two different HTF simulants: a Tank 38 simulant at 100 °C that was previously used in HGR tests with common organics found in the tank farm, and a high hydroxide simulant at 140 °C that was chosen to mimic evaporator conditions.[18, 24] The conditions for each test are given in Table 3-12. An antifoam concentration of 100 mg/L was used in each test; this concentration is 10 times the maximum expected concentration, shown in the above paragraph, of Momentive™ Y-17112 in the 242-16H (2H) Evaporator system, but was chosen due to an expected measurable HGR above the detection limit of the instrument predicted using the Global TOC Thermolytic HGR Expression.

Table 3-12. HGR Test Conditions for New Antifoams

	Tank 38 Simulant				High Hydroxide Simulant			
Temp.	**100 °C**			**60 °C**	**140 °C**			**100 °C**
Antifoam	**Y-17112**	**MD20**	**747**	**Y-17112**	**Y-17112**	**MD20**	**747**	**Y-17112**
$[TOC]_{AF}$ (M)	4.71E-03	5.50E-03	4.35E-03	4.69E-03	5.49E-03	6.88E-03	5.37E-03	5.81E-03
[OH] (M)	2.80E+00	2.82E+00	2.83E+00	2.85E+00	1.92E+01	2.03E+01	1.98E+01	1.95E+01
$[NO_2]$ (M)	2.50E+00	2.52E+00	2.53E+00	2.54E+00	1.85E+00	1.96E+00	1.91E+00	1.89E+00
$[NO_3]$ (M)	1.22E+00	1.22E+00	1.23E+00	1.23E+00	1.57E+00	1.66E+00	1.61E+00	1.59E+00
[Al] (M)	8.28E-02	8.28E-02	8.28E-02	8.31E-02	3.76E-01	3.98E-01	3.87E-01	3.82E-01
$[CO_3]$ (M)	7.37E-01	7.41E-01	7.44E-01	7.47E-01	-	-	-	-
$[SO_4]$ (M)	7.06E-02	7.13E-02	7.13E-02	7.13E-02	-	-	-	-

The results of the HGR testing are given in Table 3-13. The model predicted HGR is based on the Global TOC model shown above at the conditions tested. It should be noted that the Global TOC model was derived by assessing the difference in apparent reactivity of "fresh organics" and those found in the Tank Farm. In comparison to "fresh" organic material, one can expect that the most reactive organic species have degraded in the Tank Farm after years of exposure to caustic environments and radiation fields. FTIR was used during most tests to monitor for any volatile degradation products in the offgas. The observed HGR is the measurement with added antifoam and the antifoam-free HGR is the "blank" run without antifoam. The actual HGR/MGR of the antifoam is considered the difference between the "blank" antifoam- free HGR/MGR measurement and the measurement with added antifoam. When the observed HGR from the antifoam experiment was less than the blank, it is considered a below detection limit (BDL) measurement (i.e. the HGR as a result of the antifoam cannot be ascertained). For the antifoam comparison tests, independent blank HGR measurements were obtained. For the two additional tests with Momentive™ Y-17112, a blank measurement was obtained just prior to the addition of the antifoam.

Table 3-13. Results of Antifoam HGR Testing

Antifoam	Simulant	Temp (°C)	Antifoam-Free HGR (ft^3 h^{-1} gal^{-1})	Observed HGR (ft^3 h^{-1} gal^{-1})	Model Predicted HGR (ft^3 h^{-1} gal^{-1})	MGR (ft^3 h^{-1} gal^{-1})	Volatile Species in Offgas
Y-17112	Tank 38	100	4.18E-07	2.89E-07	7.43E-08	-	-
MD20	Tank 38	100		3.49E-07	8.73E-08	-	-
747	Tank 38	100		5.19E-07	6.93E-08	-	TMS, HMDSO
Y-17112	High Hydroxide	140	1.24E-06	1.18E-06	6.82E-06	-	-
MD20	High Hydroxide	140		1.91E-05	9.02E-06	8.51E-07	methyl isobutyl ketone
747	High Hydroxide	140		9.92E-06	6.86E-06	2.00E-05	TMS, HMDSO
Y-17112	Tank 38	60	1.04E-07	4.78E-08	3.04E-09	-	-
Y-17112	High Hydroxide	100	3.77E-07	4.72E-07	5.52E-07	-	N/A*

*Offgas was not monitored by FTIR during this experiment.

In both the Tank 38 simulant test at 100 °C and the high hydroxide test at 140 °C, the HGR for Momentive™ Y-17112 could not be differentiated from the antifoam-free experiment. The HGR for Momentive™ Y-17112 for both tests would be expected to be lower than what is shown in Table 3-13 due to the contribution from other trace organics in the solution. Interestingly, the high hydroxide measurement falls well below the model-predicted HGR, perhaps signaling that Momentive™ Y-17112 is not very reactive towards the production of hydrogen. In the additional high hydroxide simulant test at 100 °C, a measurable HGR for Momentive™ Y-17112 was obtained that was below the model prediction. In the Tank 38 simulant HGR test at 60 °C, the HGR for Momentive™ Y-17112 was BDL. For all tests with Y-17112, no methane or other volatile degradation products were observed in the offgas.

Like Momentive™ Y-17112, the HGR for Evonik Surfynol® MD20 in the Tank 38 simulant test at 100 °C could not be differentiated from the antifoam-free experiment; additionally, no volatile degradation products were detected in the offgas of this test. A measurable HGR was obtained for Evonik Surfynol® MD20 from the test with the high hydroxide simulant at 140 °C that was larger than predicted from the Global TOC model. Methane and methyl isobutyl ketone were also observed in the offgas of the high hydroxide test, which suggests the breakdown of the antifoam at these extreme conditions. Methyl isobutyl ketone is most likely a degradation product of 2,4,7,9-tetramethyl-5-decyne-4,7-diol, the diol component of the oxirane/diol defoamer. We do not have a quantitative FTIR spectra for the ketone, so we can only qualitatively confirm its presence.

The Antifoam 747 HGR tests required higher purge rates than all other tests due to flammability concerns from the large amount of trimethylsilanol (TMS) and hexamethyldisiloxane (HMDSO) observed in both tests. The HGRs obtained for Antifoam 747 were slightly higher than predicted. Additionally, methane was produced at twice the rate of hydrogen in the high hydroxide test. Methane has been detected in previous HGR tests with TMS and the methane seen here is perhaps produced from a TMS degradation product in the simulant.

In all tests with Momentive™ Y-17112, the HGR was either BDL or below the predicted HGR from the Global TOC model. Momentive™ Y-17112 appears a less reactive species towards the thermolytic production of hydrogen than Evonik Surfynol® MD20 and Antifoam 747. Furthermore, no methane or other volatile degradation products were detected in the offgas of HGR tests with Momentive™ Y-17112, which suggests a greater chemical stability in Tank Farm conditions compared to both Evonik Surfynol® MD20 and Antifoam 747.

3.6.6 Antifoam irradiation results

The offgas collected in the Tedlar bags was evaluated by VOA by Analytical Development. 100 mL of gas was collected via an airtight syringe and injected into the GCMS for separation and MS analysis. The sludge was also examined by VOA and SVOA post irradiation. If the antifoams were to degrade, one would expect to detect methane, methanol, ethane, ethylene, ethyleneoxide, and dimethylsiloxane. No volatile organic compounds or semi volatile organic compounds were identified above the method detection limits. The method detection limit for VOA was 0.2 mg/L or 0.25 mg/L. The method detection limit for SVOA was 1 mg/L. During post irradiation boiling tests, foam was only generated in the "Blank" (Figure 3-9). The SB6 Version 1 Recipe A sludge simulant containing Momentive™ Y-17112-14DSV, Momentive™ Y-17112-19FSV, and Evonik Surfynol® MD20 did not foam post irradiation. The results are reported in Table 3-14 for the SB9 sludge-only dose irradiations and in Table 3-15 and Table 3-16 for the maximum coupled irradiations.

Table 3-14. SB9 Sludge-only Dose – Slurry Results

Antifoam	VOA Offgas (mg/L)	VOA Post Irradiation Sludge (mg/L)	SVOA Post Irradiation Sludge (mg/L)	Foam Generation Post Irradiation Boiling
Blank	< 0.25*	< 0.25*	< 1*	Yes
MD-20	< 0.25*	< 0.25*	< 1*	No
Y-17112-14DSV	< 0.25*	< 0.25*	< 1*	No
Y-17112-19FSV	< 0.25*	< 0.25*	< 1*	No

*Below Method Detection Limit

Table 3-15. Maximum Coupled Dose – Offgas Results

Antifoam	VOA Week 1 (mg/L)	VOA Week 2 (mg/L)	VOA Week 3 (mg/L)	VOA Week 4 (mg/L)
Blank	NA†	< 0.2*	< 0.2*	< 0.2*
MD-20	< 0.2*	< 0.2*	< 0.2*	< 0.2*
Y17112-14DSV	NA†	< 0.2*	< 0.2*	< 0.2*
Y17112-19FSV	< 0.2*	< 0.2*	< 0.2*	< 0.2*

† Offgas Quantity Collected Insufficient for Analysis
*Below Method Detection Limit

Table 3-16. Maximum Coupled Dose – Slurry Results

Antifoam	VOA Post Irradiation Sludge (mg/L)	SVOA Post Irradiation Sludge (mg/L)	Foam Generation Post Irradiation Boiling
Blank	< 0.2*	< 1*	Yes
MD-20	< 0.2*	< 1*	No
Y17112-14DSV	< 0.2*	< 1*	No
Y17112-19FSV	< 0.2*	< 1*	No

*Below Method Detection Limit

Figure 3-9. Maximum Coupled Dose Post Irradiation Boiling Tests – Blank (left); Y-17112-14DSV (right)

These results indicate that Momentive™ Y-17112 and Evonik Surfynol® MD20 did not significantly degrade and remained effective at foam control after being exposed to a simulated dose equivalent to 53,100 krad in a caustic environment (high dose for antifoam degradation) for a prolonged period of time (30 days). Furthermore, exposing Momentive™ Y-17112 and Evonik Surfynol® MD20 to these conditions did not lead to the formation of flammable degradation products.

3.6.7 Influence of Antifoam on Melter Offgas Flammability

The hydrogen and carbon monoxide contribution to melter offgas flammability from Antifoam 747 was predicted by Choi and Edwards.[25] Any Momentive™ Y-17112 added in the CPC will predominantly be fed to the melter as it is chemically stable during CPC processing. Both Antifoam 747 and Momentive™ Y-17112 are large molecules (MW approximately 600 g/mol) containing C, Si, O, and H. They are both about 50 wt % carbon and 10 wt % hydrogen. In the melter, most of the hydrogen is oxidized to H_2O but some will produce H_2 and most of the carbon will produce CO_2, but some will produce CO. So, the impact of either of these antifoams on melter offgas flammability will be primarily due to the amount added during processing. Since significantly less Momentive™ Y-17112 will be added compared to species that will degrade in the melter such as nitrate (80x higher), glycolate (60x higher), and Antifoam 747 (4x higher), the influence of Momentive™ Y-17112 on melter offgas flammability will be lower than, and thus bounded by the analysis of Choi and Edwards.[25] Although less Momentive™ Y-17112 is expected to be added during CPC processing, the control for melter offgas flammability remains the TOC in the melter feed.

3.6.8 Antifoam Strategy for nitric-formic acid flowsheet

The first use of Momentive™ Y-17112 will likely be during nitric-formic acid flowsheet processing in DWPF. If the first use of Momentive™ Y-17112 happens prior to SWPF startup, sludge-only processing of Sludge Batch 9 sludge is the likely processing scenario. If the first use of Momentive™ Y-17112 is after SWPF startup, processing in DWPF will include extended boiling at pH 13 during PRFT addition and will include extended boiling time during SEFT addition. Both SRNL and DWPF Engineering agree that the Momentive™ Y-17112 can be used in DWPF without performing any radioactive waste testing in the SRNL Shielded Cells.

The antifoam can be added either undiluted through the antifoam addition funnel as is the current practice or as low as a 5 wt % antifoam solution in water as has been the practice throughout most of DWPF's processing. The SRNL testing was completed without simulating heels, so DWPF may want to calculate the antifoam additions based on the mass of slurry in the SRAT at the start. In future batches, it is likely that antifoam additions could be based on the new sludge added, as the heel probably will have plenty of antifoam, based on its longevity in SRNL testing.

It should be noted that the boiling flux in the DWPF SRAT and SME is approximately twelve times higher than the RC1 testing. In our experiments there was as much as 1-2 inches of foam present so this would scale to up to 1-2 feet of foam in DWPF. The times that are most critical for foaming are during PRFT addition, acid addition, and SRAT dewater when the SRAT volume is highest. This coincides with the time when gas generation is highest, during the initiation of boiling during dewater and for the next several hours. Special note of the foam height and freeboard in the SRAT is recommended. Stopping acid addition, stopping boiling, or adding additional antifoam is recommended if the foam height is excessive.

It should also be noted that the antifoam requirement during nitric-formic acid flowsheet experiments was significantly higher than for comparable nitric-glycolic acid flowsheet testing. This was especially true during SRAT dewater, when the concentration of Momentive™ Y-17112 needed to be at its maximum. Although in our testing antifoam was added whenever needed, the data from our experiments was used to propose larger, less frequent additions to simplify processing in DWPF.

The recommended antifoam strategy for the nitric-formic acid flowsheet is:

1. Add 50 mg Momentive™ Y-17112/kg of slurry prior to caustic boiling or PRFT addition. Foaming isn't expected until boiling is initiated so add it in the later part of heatup. Add an additional 50 mg Momentive™ Y-17112/kg as needed during PRFT addition.
2. Add 50 mg Momentive™ Y-17112/kg of slurry prior to formic addition. Foaming isn't expected until midway through formic acid addition, when carbon dioxide and NO_x generation ramp up. Add an additional 50 mg Momentive™ Y-17112/kg as needed during acid addition.
3. Add 200 mg Momentive™ Y-17112/kg of slurry prior to boiling. Foaming isn't expected until boiling is initiated. Add an additional 50 mg Momentive™ Y-17112/kg as needed during SRAT dewater.
4. Add 25 mg Momentive™ Y-17112/kg of slurry every 12 hours during boiling (both SEFT addition and reflux).
5. Add 25 mg Momentive™ Y-17112/kg of slurry prior to the first SME canister blast addition. Foaming isn't expected until boiling is initiated so add it in the later part of heatup. Add an additional 25 mg Momentive™ Y-17112/kg every 12 hours of boiling or as needed during canister blast evaporation.
6. Add 25 mg Momentive™ Y-17112/kg of slurry prior to the first SME process frit addition (don't factor mass of frit in calculating the volume of antifoam to be added). Foaming isn't expected until boiling is initiated so add it in the later part of heatup. Add an additional 25 mg Momentive™ Y-17112/kg every 12 hours or as needed during process frit evaporation.

The expected antifoam addition is approximately 550 mg/kg or about 3.7 gallons.

3.6.9 Antifoam Strategy for nitric-glycolic acid flowsheet

If the first use of Momentive™ Y-17112 is after SWPF startup and DWPF has transitioned to the nitric-glycolic acid flowsheet, DWPF processing will include extended boiling at pH 13 during PRFT addition and will include extended boiling time during SEFT addition.

The antifoam can be added either undiluted through the antifoam addition funnel as is the current practice or as a 5 wt % antifoam solution in water as has been the practice throughout most of DWPF's processing. The SRNL testing was completed without simulating heels, so DWPF may want to calculate the antifoam additions based on the mass of slurry in the SRAT at the first batch using Momentive™ Y-17112. In future batches, it is likely that antifoam additions could be based on the new sludge added, as the heel probably will have plenty of antifoam, based on its longevity in SRNL testing.

It should be noted that the boiling flux in the DWPF SRAT and SME is 12x higher than the RC1 testing. In our experiments there was often 1-2 inches of foam present so this would scale to 1-2 feet of foam in DWPF. The times that are most critical for foaming are during PRFT addition, acid addition, and SRAT dewater when the SRAT volume is highest. This coincides with the time when gas generation is highest, during the initiation of boiling during dewater and for the next several hours. Special note of the foam height and freeboard in the SRAT is recommended. Stopping acid addition, stopping boiling, or adding additional antifoam is recommended if the foam height is excessive.

It should also be noted that the antifoam requirement during nitric-glycolic acid flowsheet experiments was significantly lower than for comparable nitric-formic acid flowsheet testing. Although in our testing, antifoam was added whenever needed, the data from our experiments was used to propose larger, less frequent additions to simplify processing in DWPF.

The recommended antifoam strategy for the nitric-glycolic flowsheet is:

1. Add 50 mg Momentive™ Y-17112/kg of slurry prior to caustic boiling or PRFT addition. Foaming isn't expected until boiling is initiated so add it in the later part of heatup. Add an additional 25 mg Momentive™ Y-17112/kg as needed during PRFT addition.
2. Add 25 mg Momentive™ Y-17112/kg of slurry prior to glycolic acid addition. Foaming isn't expected until midway through glycolic acid addition, when carbon dioxide and NO_x generation ramp up. Add an additional 25 mg Momentive™ Y-17112/kg as needed during acid addition.
3. Add 50 mg Momentive™ Y-17112/kg of slurry prior to boiling. Foaming isn't expected until boiling is initiated. Add an additional 25 mg Momentive™ Y-17112/kg as needed during boiling.
4. Add 25 mg Momentive™ Y-17112/kg of slurry every 12 hours during boiling (both SEFT addition and reflux).
5. Add 25 mg Momentive™ Y-17112/kg of slurry prior to the first SME canister blast addition. Foaming isn't expected until boiling is initiated so add it in the later part of heatup. Add an additional 25 mg Momentive™ Y-17112/kg every 12 hours or as needed during canister blast evaporation.
6. Add 25 mg Momentive™ Y-17112/kg of slurry prior to the first SME process frit addition (don't factor mass of frit in antifoam calculation). Foaming isn't expected until boiling is initiated so add it in the later part of heatup. Add an additional 25 mg Momentive™ Y-17112/kg every 12 hours or as needed during process frit evaporation.

The expected antifoam addition is approximately 300 mg/kg or about 2 gallons. Note that in SRNL testing, the diluted antifoam was still effective as an antifoam after six weeks of storage. During typical DWPF processing, diluted antifoam is effective for six weeks, during a long outage, the antifoam solution should be drained.

3.7 Other Antifoam considerations

The SRR Design Authority requested an assessment of criteria developed by Terri Fellinger of SRR during development of a new antifoam for DWPF. The full list is included in Table 3-18. The yellow highlighted items have not been explicitly studied and an explanation for their not being significant is included in this section.

3.7.1 Any corrosion concerns? Any biological concerns? Is it a source for bacterial-fungal growth?

There are no corrosion concerns with the Momentive Y-17112™. Momentive states: Y-17112 and similar silicone surfactants are non-reactive and do not attack construction materials, such as stainless steel. No corrosion is expected in Hastelloy C276 or 316L. Momentive also stated that bacteria do not grow on pure silicones, such as Momentive Y-17112™., and therefore they do not add any preservative to them. No bacterial or fungal growth is anticipated from adding the Momentive Y-17112™.

3.7.2 Does the glycolate destruction process in the RCT remove these organic products?

The use of sodium permanganate to destroy the Momentive Y-17112™ will not be effective. However, if the Momentive Y-17112™ works as well during radioactive processing as it does during the laboratory testing, there should be no antifoam in the condensate. In addition, the fact that much less is needed and that it is very chemically stable with no degradation products detected means that Momentive Y-17112™ will not need to be destroyed.

3.7.3 REDOX equation revision needed?

The REDOX equation includes a term for Antifoam 747.[26] The antifoam term is not important even if the Antifoam 747 exceeds 3,000 mg/kg in a CPC batch (prediction of a REDOX increase of 0.0015). From a REDOX standpoint, the weight percent of carbon and hydrogen are similar (51.3% C in Antifoam 747, 55.6% C in Momentive Y-17112™, 9.7% H in Antifoam 747, 10.2% H in Momentive Y-17112™ so the impact of Momentive Y-17112™ on REDOX should be similar. But since one-tenth as much Momentive Y-17112™ will be added as was used in this calculation, the impact on REDOX is insignificant. So, the development of an effectiveness factor is not needed. Use of the REDOX equation without an antifoam term is recommended.

3.7.4 Perform Shielded Cells full SRAT/SME cycles under prolonged boiling conditions representing facility conditions (Coupled?). Determine how much is needed to control antifoam. Note off gas production under processing conditions.

A joint decision was made by SRNL and SRR to delay the first use of Momentive Y-17112™ until the Sludge Batch 10 Shielded Cells SRAT and SME cycles schedule for the middle to late FY21. The SRAT and SME processing in the shielded cells has a much lower boiling flux (essentially one inch of foam in a small-scale experiment will lead to about one foot of foam in the DWPF SRAT and SME). In addition, it very difficult to see the foam during processing so antifoam is often over added to eliminate a foamover. In addition, the offgas equipment during these tests would likely not detect the decomposition products, if any. Momentive™ Y-17112 may be used in the DWPF facility prior to this test. The risk of deploying Momentive™ Y-17112 prior to the Shielded Cells SRAT and SME cycles is that some component in actual waste not present in simulants decreases the antifoam's effectiveness.

3.7.5 Any criticality issues by solubilizing fissile material?

No testing of Y-17112 has been completed with the objective to determine whether it impacts the solubilities of fissile actinide metals or neutron poisons. One Shielded Cells experiment with the nitric-glycolic acid flowsheet has been completed (SC-18) using antifoam 747.[27] In addition, testing of the SME product from SC-18 was completed to determine the solubility of fissile actinides (U-233, U-235, Pu-239 and Pu-241) and potential neutron poisons (Gd, Mn, Fe).[28] As the pH drops due to acid addition, the solubility of the fissile actinides and poisons increase. U is more soluble than Pu, so Mn and Gd are effective poisons for U since it is less soluble than U. But Mn and Gd are not as effective at poisoning Pu because they are more soluble. Fe is less soluble than Pu so is a more effective poison for Pu. Figure 3-10 shows the solubility of the U, Pu, Gd, Fe and Mn from this study. The pH 7 data are from the SC-18 SME product before additional acid addition.

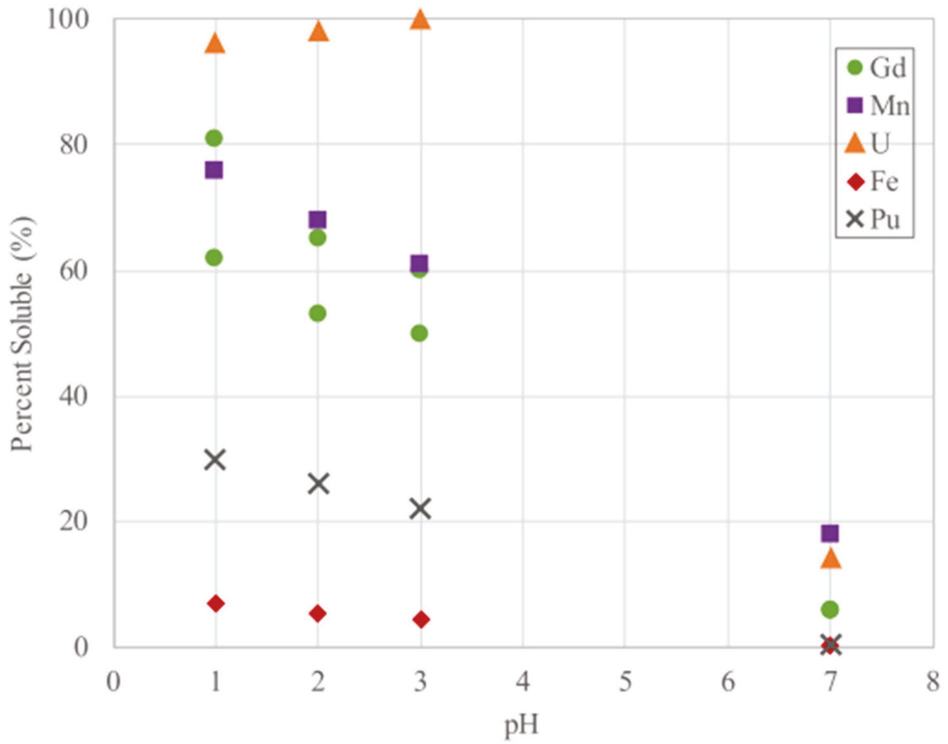


Figure 3-10. Partitioning of fissile and neutron poison components between solid and liquid phases for Nitric-Glycolic Acid flowsheet testing of radioactive SC-18 SME product and additional pH Adjustment

More than 100 Nitric-Glycolic Acid experiments have been completed with simulants. In these experiments, the solubility of the Fe and Mn has been tracked, although Gd has not been added in these documented simulant experiments. Two identical simulant experiments have been completed with the Nitric-Glycolic Acid flowsheet, one with Momentive Y-17112™ and one with Evonik Surfynol MD20. In these two experiments, the Fe, Mn, and Na solubilities in the SRAT and SME products were calculated and are summarized in Table 3-17. Note that Momentive Y-17112™ is a superspreader and Evonik Surfynol MD20 is not. In this testing, the Fe and Mn solubilities in the Momentive Y-17112™ experiment are not higher than for the Evonik Surfynol MD20 (except for Mn, which is slightly higher in the SME cycle). This demonstrates that the Momentive Y-17112™ is not significantly increasing the solubility of these metals. It is expected that Momentive Y-17112™ also does not significantly increase the solubility of the fissile actinides and neutron poisons, as they vary in solubility primarily due to the pH change. The sodium solubility is added to the table to demonstrate that both the slurry and supernate concentrations are accurate as the calculated solubility is just above the expected 100%.

Table 3-17. Solubility of Fe, Mn, Ni and Na in Nitric-Glycolic Flowsheet SRAT and SME products

Antifoam	**MD20**	**Y-17112**	**MD20**	**Y-17112**
Cycle	SRAT	SRAT	SME	SME
Fe Solubility, %	0.19	0.11	0.12	0.10
Mn Solubility, %	82.1	73.5	71.7	73.8
Na Solubility, %	101	101	65	69
pH	5.82	5.98	5.99	6.07

The concentration of glycolic and nitric acid (30,000 and 20,000 ppm respectively) in the SRAT and the SME products for the Nitric-Glycolic Acid flowsheet is important because their addition decreases and stabilizes the pH. The low pH together with a complexing acid can greatly increase the solubilities of the fissile actinides and neutron poisons. The use of Momentive Y-17112™ should not lead to an increase in the solubility of the fissile actinides or the neutron poisons, such as Gd, Mn, and Fe.

Table 3-18. Antifoam Assessment Criteria

Screening – Antifoam

- Shelf life
- Chemical formula of each (are we adding a new chemicals) antifoam or increasing the amount of a chemical contained in the antifoam?
- What impurities are in the antifoam.
- Chemical incompatibilities.
- Physical Properties (density viscosity, surface tension, etc.).
- Robustness under thermal (up to 1100 °C) and simple chemical (caustic, nitric/formic/glycolic acids) conditions (under thermal conditions what off gases are produced),
- Robustness (by itself, in caustic, and in acidic conditions) under radiation fields. Liquid and off gas measurements.
- Any interaction with existing antifoam that would be present in the vessels to give an unexpected response.
- Any corrosion concerns?
- Any biological concerns? Is it a source for bacterial-fungal growth?
- Check that TOC is adequate tool for detecting antifoam.

Testing for Top Antifoam(s):

- Full SRAT/SME cycles (coupled/uncoupled) under design basis and prolonged boiling conditions representing facility conditions. Determine how much is needed to control antifoam. Note off gas production under processing conditions and final solubility of elements in the SRAT/SME products.
- What by-products are introduced into the SRAT/SME Condensate streams back to the Tank Farm (organics, Methyl/Ethyl Hg compounds, etc.),
- If new organic is introduced to recycle stream, what is the impact to Evaporator, Effluent Treatment Facility (ETF)/Saltstone (Processing/Performance Assessment) and Tank Farm flammability?
- Does the glycolate destruction process in the RCT remove these organic products?
- Determine what by-products (liquid/off gas) are produced when SRAT/SME products containing the new antifoam are exposed to gamma source.
- REDOX equation revision needed?

Final Testing

- Perform Shielded Cells full SRAT/SME cycles under prolonged boiling conditions representing facility conditions (Coupled?). Determine how much is needed to control antifoam. Note off gas production under processing conditions.
- What by-products are introduced into the SRAT-SME Condensate streams back to the Tank Farm (organics, Methyl/Ethyl Hg compounds, etc.),

Any criticality issues by solubilizing fissile material?

4.0 Conclusions

Foaming of HLW slurries is an issue at the DWPF CPC which is currently mitigated with a chemical antifoam agent, Antifoam 747, and by limiting steam flow (boilup rate) and formic acid feedrate. Antifoam 747 is an effective antifoam and defoamer at pHs near 7 but hydrolyzes readily as the pH deviates from 7. This decomposition produces three flammable species, namely trimethylsilanol, hexamethyldisiloxane, and propanal. This decomposition requires the frequent addition of Antifoam 747 to control foam. A better foam control method is needed to eliminate the generation of flammable gases due to Antifoam 747 decomposition and to increase the SRAT and SME steam flow to allow efficient processing in the SRAT and handle the increase in processing volumes of PRFT and SEFT after SWPF startup.

SRR requested the identification of alternate foam controls for the SRAT and SME. The efficiency of alternative antifoams and the effectiveness of non-chemical methods for foam control were examined to improve HLW treatment at DWPF and to eliminate the flammability hazards associated with the Antifoam 747 currently in use. Non-chemical foam control methods were deemed unviable for chemical processing at DWPF, as the spray/mist technique requires too much water and space limitations make installation and implementation of headspace agitators unfeasible. The use of ultrasonic energy thickened foam and further stabilized it. Two suitable alternative defoaming agents, Momentive™ Y-17112 and Evonik Surfynol® MD20, were identified.

Evonik Surfynol® MD20, a commercially available defoamer, was relatively effective in controlling foam, while remaining chemically stable in SRAT and SME processing across the pH range of 4 to 13. No degradation products were detected in the offgas, in the condensate or in the SRAT and SME products. In nitric-glycolic acid flowsheet testing, 250 mg/kg Evonik Surfynol® MD20 was needed for foam control compared to 1,625 mg/kg for Antifoam 747, DWPF's current antifoam. In nitric-formic acid flowsheet testing, 1,125 mg/kg of Evonik Surfynol® MD20 was needed to control foam throughout the SRAT and SME cycles.

Based on this testing with foamy physical and chemical simulants, Momentive™ Y-17112 is recommended as a replacement antifoam for DWPF. The commercially available superspreader Momentive™ Y-17112 was even more effective than Evonik Surfynol® MD20 as both a defoamer and an antifoam. Not only was the foam destroyed upon addition but also was less persistent between additions. It was the most effective antifoam in testing using both the nitric-glycolic acid flowsheet and the nitric-formic acid flowsheet. In nitric-glycolic acid flowsheet testing, only 100 mg/kg Momentive™ Y-17112 was needed to control foam throughout the SRAT and SME cycles. In nitric-formic acid flowsheet testing, 300 mg/kg Momentive™ Y-17112 was needed to control foam throughout the SRAT and SME cycles. Momentive™ Y-17112 is also resistant to hydrolysis as demonstrated by its chemical stability in SRAT and SME processing across the pH range of 4 to 13 and lack of degradation products in offgas or condensate.

Both candidates were effective as potential replacements for Antifoam 747, with Y-17112 demonstrating superior foam control. During nitric-glycolic flowsheet testing 50% less antifoam was needed when using Y-17112 compared to MD20. During nitric-formic flowsheet testing 75% less antifoam was needed when using Y-17112 compared to MD20. Foam remediated with Y-17112 was less persistent throughout testing. In addition, no degradation products were detected in the offgas, in the condensate or in the SRAT and SME products. A second antifoam, Evonik Surfynol® MD20 was also effective in controlling foam, although more Surfynol® MD20 was needed than Momentive™ Y-17112. It too was chemically stable in SRAT and SME processing across the pH range of 4 to 13. Also, no degradation products were detected in the offgas, in the condensate or in the SRAT and SME products. In nitric-glycolic acid flowsheet testing, 200 mg/kg Surfynol® MD20 was needed to control foam throughout the SRAT and SME cycles versus 1,600 mg/kg in testing using Antifoam 747, DWPF's current antifoam.

Momentive™ Y-17112 and Evonik Surfynol® MD20 did not degrade and remained effective at foam control after being exposed to a simulated dose equivalent to 53,100 krad in a caustic environment for a prolonged period of time (30 days). Furthermore, exposing Momentive™ Y-17112 and Evonik Surfynol® MD20 to these conditions did not lead to the formation of flammable degradation products.

From applicable thermolytic HGR tests, Momentive™ Y-17112 had a lower HGR than was predicted by the Global TOC model and a lower HGR than Antifoam 747, the current DWPF antifoam. These results are consistent with the observation that Momentive™ Y-17112 does not contribute HGR to an extent greater than the Global TOC model and should therefore be approved for use in SRS waste streams. Additionally, no methane or other volatile degradation products were detected in its offgas. At evaporator conditions, Evonik Surfynol® MD20 was less stable than Momentive™ Y-17112; it had a significant HGR in comparison and both methane and methyl isobutyl ketone were observed in the offgas. Tests with the current DWPF antifoam, Antifoam 747, required larger purge rates due to flammability concerns from the antifoam degradation products detected in the offgas.

5.0 Recommendations

Based on this testing, Momentive™ Y-17112 is clearly superior to Evonik Surfynol® MD20 and Antifoam 747, for both the nitric-glycolic and nitric-formic acid flowsheet processing; it is recommended that Momentive™ Y-17112 replace Antifoam 747 in DWPF. It was superior to Antifoam 747, and the other 27 antifoam alternatives tested, especially for nitric-formic acid flowsheet processing. An antifoam addition strategy is recommended for both the nitric-glycolic acid flowsheet and the nitric-formic acid flowsheet. Implementation of Momentive™ Y-17112 is expected to decrease SRAT and SME boiling time by almost 50%, eliminating the issues resulting from Antifoam 747 degradation products and minimize foamovers.

The ability to visually observe the SRAT during gas generating processing would be very helpful to determination the best antifoam strategy in DWPF. Having a fully functional sight glass with viewing in the control room would be an effective tool in ensuring antifoam is added when needed.

6.0 References

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Appendix A. Acid Calculation

The acid calculation spreadsheet was used for calculating the mass of all additions, and the condensate removals in each experiment. A separate acid calculation was completed for both the nitric-formic acid flowsheet tests (Table A-1) and the nitric-glycolic acid flowsheet tests (Table A-2).

Table A-1 Acid Calculation for Nitric-Glycolic Acid Flowsheet Experiments

SRNL SRAT Acid, Trim Chemical, Dewater and Redox Calc Revised:	1/12/2017	
Run Description:	SRAT/SME run with Nitric/Glycolic Flowsheet Testing	
Total nitrite	0.404	mol
Total Mn minus soluble Mn	0.207	mol
Total carbonate	0.349	mol
Total hydroxide	0.757	mol
Total mercury	0.032	mol
Total oxalate	0.016	mol
Trim Chemicals Calculations		
Fresh Sludge Calcine Factor (1100 °C), g oxide/g dry solids (calculated)	0.7165	g/g
Fresh Sludge Calcined Oxides	181.057	g
Total solids before trim addition	252.6926	g
Predicted total solids at target levels	260.5608	g
Target Ag metal content in trimmed sludge	0.010000	total wt % dry basis
$AgNO_3$ to add (CF=0.682)	0.04103	g
Ag_2O calcined solids added	0.02799	g
Target wt % Hg dry basis	2.500	total w t% dry basis
Total HgO in fresh Sludge	0.000	g
Total HgO in trimmed Sludge	7.03361	g
HgO to add	7.03361	g
HgO calcined solids added	0.00000	g
Target Pd metal content in trimmed sludge	0.0040	total wt % dry basis
wt % Pd in reagent solution	15.2700	wt % in solution
$Pd(NO_3)_2$*H_2O solution to add (CF=0.531)	0.06825	g of solution
Pd(NO3)2 to add	0.02257	g
PdO calcined solids added	0.01198	g
Target Rh metal content in trimmed sludge	0.0160	total wt % dry basis
wt % Rh in reagent solution	4.93	wt % in solution
$Rh(NO_3)_3$*$2H_2O$ (CF=0.439)	0.8456	g of solution
$Rh(NO_3)_3$ to add	0.11705	g
Rh_2O_3 calcined solids added	0.05138	g
Target Ru metal content in trimmed sludge	1.0000	total wt % dry basis
wt % Ru in $Ru(NO_3)$ solution	1.50	wt % in solution
Nitric acid in Ru solution	0.252	mmol/g
Nitric acid in Ru solution	1.5879	wt %
Nitric acid added with Ru solution	0.0035	mols
Nitric acid added with Ru	0.22	g

$Ru(NO)(NO_3)_3$ solution to add (CF=0.4197)	13.8966	g solution
$Ru(NO)(NO_3)_3$ to add	0.6540	g
RuO_2 calcined solids added	0.2745	g
Total mass of trim chemicals added	21.8851	g
Calcined oxides added in trim chemicals	0.3658	g
Total solids after trim addition	260.7815	g
Match of actual to predicted total solids mass	99.92%	
Total Calcined solids after trim	181.4230	g
Water added to dilute and/or rinse trim chemicals	100.0	g
Mass of trimmed sludge	1,771.8851	g
Calculated wt % total solids in trimmed sludge	14.7177	Wt %
Sample mass of trimmed sludge	16.8345	g
Mass of trimmed feeds reacted	1,755.0506	g
Sample removal ratio after trim	0.990	
Mass of PRFT added	767.2948	g
Mass of PRFT flush water added	10.0000	g
Total solids added w/ PRFT	43.8444	g
Calcined solids added w/ PRFT	33.0352	g
Mass of water removed after PRFT addition to return to initial total solids %	**735.0976**	**g**
Mass of slurry after PRFT dewater	1,797.2479	g
Mass of sample after PRFT cycle (before SRAT cycle)	16.8345	g
Mass of slurry going into SRAT cycle	1,780.4134	g
Sample removal ratio after PRFT (for PRFT components only)	0.9906	
Sample removal ratio at start of SRAT (for sludge components only)	0.9812	
Mass at start of SRAT	1,780.4134	g
Total Solids at start of SRAT	299.3181	g
Calcined solids at start of SRAT	210.7418	g
STOICHIOMETRIC ACID CALCULATIONS		
Hsu Stoichiometric Acid Ratios Used		
Acid requirement per mol of Nitrite	0.75	mol H^+/ mol NO_2^-
Acid requirement per mol of Mn	1.20	mol H^+/ mol Mn
Acid requirement per mol of Carbonate	2.00	mol H^+/ mol $CO_3^=$
Acid requirement per mol of Hydroxide	1.00	mol H^+/ mol OH^-
Acid Requirement per mol of H+	-1.00	mol total acid required
Acid requirement per mol of Hg	1.00	mol H^+/ mol Hg^{++}
Acid requirement per mol of Oxalate	0.00	mol H+/ mol $C_2O_4^=$
Koopman Stoichiometric Acid Ratios Used (Min)		
Acid requirement per mol of Nitrite	1.00	mol H^+/ mol NO_2^-
Acid requirement per mol of Mn	1.50	mol H^+/ mol Mn
Acid requirement per mol of Soluble TIC	1.00	mol H+/ mol CO3=
Acid requirement per mol of Hydroxide	1.00	mol H^+/ mol OH^-

Acid requirement per mol of Hg	1.00	mol H^+/ mol Hg^{++}
Acid requirement per mol of Oxalate	0.00	mol H+/ mol $C_2O_4^=$
Acid requirement per mol of Calcium	1.50	mol H^+/ mol Ca
Acid requirement per mol of Mg	1.50	mol H^+/ mol Mg
Cation Stoichiometric Acid Ratios Used (Nominal)		
Glycolic Stoichiometric Acid Ratios Used		
Acid Requirement per mol of Nitrite	0.75	mol H^+/mol NO_2^-
Acid Requirement per mol of Manganese	0.80	mol H^+/mol Mn
Acid Requirement per mol of Mercury	0.33	mol H^+/mol Hg
Acid Requirement per mol of Soluble TIC	1.00	mol H+/mol CO_3^{--}
Acid Requirement per mol of Calcium	1.50	mol H^+/mol Ca
Acid Requirement per mol of Magnesium	1.50	mol H^+/mol Mg
Acid Requirement per mol of OH	1.00	mol H^+/mol OH-
Sludge + PRFT NO_2^-	0.404	mol
Fresh feed insoluble Manganese	0.207	mol
Fresh feed slurry Carbonate	0.349	mol
Fresh feed OH^-	0.757	mol
Fresh Feed Mercury	0.032	mol
Fresh Feed Oxalate	0.016	mol
Fresh Feed Supernate Carbonate	0.349	mol
Fresh Feed Calcium	0.053	mol
Fresh Feed Magnesium	0.062	mol
Fresh Feed Sodium	2.400	mol
Fresh Feed Potassium	0.021	mol
Fresh Feed Cesium	0.000	mol
Fresh Feed Strontium	0.000	mol
Fresh Feed Nickel	0.089	mol
Fresh Feed Nitrate	0.297	mol
Fresh Feed Sulfate	0.024	mol
Fresh Feed Chloride	0.014	mol
Fresh Feed Formate	0.000	mol
Fresh Feed Phosphate	0.000	mol
Hsu Total Stoichiometric Acid required	2.0384	mol
Koopman Minimum Stoichiometric Acid required	2.0246	mol
Glycolic Stoichiometric Acid required	1.7578	mol
Cation Nominal Stoichiometric Acid required	2.7311	mol
Percent Acid in Excess Stoichiometric Ratio	100.00	%
Actual acid to add to SRAT	2.0246	mol
Percent Acid in Excess Stoichiometric Ratio (w/ SEFT)	102.92	%
REDOX CALCULATION (SME PRODUCT REDOX PREDICTION)		
REDOX Target	0.1500	Fe^{+2} / Fe
Predicted REDOX (G=6, Mn=0)	0.1491	

Ratio of glycolic acid to total acid	0.609520	moles glycolic acid / moles total acid
Delta between predicted REDOX and target REDOX	-0.000866	
Activation of SME cycle corrections? (1=SME corrections performed):	1	
Nitric acid density, 20 °C	1.30610	g/mL
Glycolic acid density, 20°C	1.2626	g/mL
Nitric acid amount	0.791	mol
Glycolic acid amount	1.234	mol
Total Manganese in sludge + PRFT	0.207	mol
Manganese added with SEFT (SRAT)	0.000	mol
Manganese removed with SRAT product samples	0.019	mol
Manganese added with SEFT (SME)	0.000	mol
Projected Melter Feed Manganese, total moles	0.188	mol
Formate moles in sludge + PRFT	0.000	mol
Formate generated in SRAT	0.012	mol
Formate moles removed with SRAT product sample	0.001	mol
Formate moles introduced in SME	0.011	mol
Formate moles formed in SME	0.000	mol
Formate Moles after SME	0.011	mol
Projected Melter Feed Formate, total moles	0.011	mol
Trimmed Sludge + PRFT Nitrate	0.308	mol
Nitrate moles from nitric acid	0.791	mol
Nitrate moles from SEFT (SRAT)	0.059	mol
Nitrate from conversion of nitrite to nitrate in SRAT and SME	0.212	mol
Nitrate from minor trim chemicals	0.01113	mol
Nitrate going into SRAT cycle	1.1576	mol
Nitrate into SRAT + nitrate formed by nitrite conversion	1.3698	mol
Nitrate removed with SRAT product sample	0.12668	mol
Nitrate moles from SEFT (SME)	0.00000	mol
Nitrate destroyed in the SME	0.00000	mol
Projected Melter Feed Nitrate, total moles (Sum of inputs - destroyed)	1.243	mol
Glycolate added with acid	1.234	mol
Glycolate moles destroyed in SRAT	0.232	mol
Glycolate moles removed with SRAT product sample	0.093	mol
Glycolate moles destroyed in SME	0.000	mol
Projected Melter Feed Glycolate, total moles	0.909	mol
Oxalate in sludge + PRFT	0.016	mol
Oxalate created from glycolate	0.012	mol
Oxalate removed with SRAT product sample	0.003	mol
Projected Melter Feed Oxalate, total moles	0.025	mol

Carbon from Coal in sludge + PRFT	0.000	mol
Carbon removed in SRAT product Sample	0.000	mol
Projected Melter Feed Carbon from coal, total moles	0.000	mol
Projected Melter Feed Nitrite, total moles	0.0000	mol
Mass of Antifoam Present in Melter Feed (Hypothetical)	0.037	g
Mass % of Carbon in Antifoam	51.280	%
Moles of Carbon from Antifoam in Melter Feed	0.002	mol
Assumed SME density	1.390	g/ml
Projected final SME mass	**1.458**	kg
Manganese concentration in final melter feed	0.129	mol/kg melter feed slurry
Formate concentration in final melter feed	0.008	mol/kg melter feed slurry
Glycolate concentration in final melter feed	0.623	mol/kg melter feed slurry
Oxalate concentration in final melter feed	0.017	mol/kg melter feed slurry
Carbon from coal concentration in final melter feed	0.000	mol/kg melter feed slurry
Nitrate concentration in final melter feed	0.852	mol/kg melter feed slurry
Nitrite concentration in final melter feed	0.000	mol/kg melter feed slurry
Antifoam Carbon concentration in final melter feed	0.001	mol/kg melter feed slurry
Projected final SME volume	**1.049**	**liters**
BENCH SCALE CALCULATIONS		
Bench Scale Operational Setting		
Scaled glycolic acid feed rate	0.9797	ml/min
Scaled nitric acid feed rate	1.1310	ml/min
Prototypical glycolic acid feed time	106.5	min
Prototypical nitric acid feed time	68.2	min
Glycolic acid volume required	104.339	ml
Nitric acid volume required	77.172	ml
Dewatering Calc for Target wt % Total Solids in SRAT Product		
Final SRAT Product Total Solids	25.00	%
Water in Trimmed (and sampled) Sludge (post PRFT, if applicable)	1,481.10	g
Water added with antifoam flush	3.92	g
Water added with glycolic acid	37.89	g
Water added with nitric acid	50.98	g
Water added in acid flushing	0.00	g
Water made during base equiv neutralization	13.64	g
Water made in TIC destruction	6.29	g
Water made in SRAT nitrite destruction	2.42	g
Water made in Mercury Reduction	0.38	g
Water made in Manganese Reduction	6.20	g
Revised water mass in slurry	1,602.82	g
Solids in Trimmed (and sampled) Sludge	299.32	g
Antifoam added	0.04	g

Mass of pure nitric acid (HNO_3) added	49.82	g
Mass of pure glycolic acid ($HOCH_2COOH$)	93.85	g
Solids lost during base equiv neutralization	13.64	g
Solids lost in TIC destruction	21.67	g
Solids lost in SRAT nitrite destruction	5.61	g
Solids made in SRAT formate formation	0.57	g
Solids made in SRAT oxalate formation	1.11	g
Solids lost in SRAT glycolate destruction (glycolic acid)	17.66	g
Solids lost in Mercury Stripping	6.90	
Revised solids mass in slurry	379.22	g
Target final water mass in slurry to hit total solids target	1,137.67	g
Total water to remove in SRAT dewater	**465.15**	g
Mass of SEFT added to slurry	3,668.14	g
Mass of solids added with SEFT	0.00	g
Mass of Slurry after SEFT Addition	5,185.03	g
Solids in slurry after SEFT Addition	379.22	g
Mass of Water to remove during SEFT dewater	**3,668.14**	g
SEFT Addition Rate	1.72	mL/min
SEFT Addition Time	2,142.86	min
SEFT Dewater Time	1,499.18	min
Mass of carbonate lost as CO_2	15.37	g
Mass of nitrite lost as N_yO_x	3.19	g
Glycolate converted to CO_2 in SRAT	18.27	g of CO2
SRAT Product Mass (neglecting intermediate and product samples)	1516.89	g
Mass of SRAT cycle samples (Product and Intermediate, excluding SRAT Receipt)	140.29	g
Mass of treated sludge going into SME cycle	1376.61	g
Fraction of SRAT product going into SME Cycle	0.9075	
Calcined Solids going to SME	191.25	g
DWPF SCALE TO BENCH SCALE		
DWPF Scale SRAT cycle		
density estimate =	1.122	
Volume based scale factor 6000 gal starting SRAT	15448.6	
Minimum SRAT conflux time	1473.6	min
Bench Scale SRAT cycle		
99.5% of scaled air purge	7.0773	mmol/min
Helium purge rate at 0.5 vol%	0.0356	mmol/min
Scaled boil up rate	2.45	g/min
Required dewatering time at above rate (PRFT and after acid)	190.1	min

Required time for SEFT addition and dewater	2142.9	min
DWPF Scale SME cycle		
Bench Scale SME cycle		
SME scale factor (Assuming 6000 gallons of SME receipt)	19248.5	
99.5% scaled SME air purge	4.4	mmol/min
Helium purge rate at 0.5 vol %	0.02	mmol/min
Solids remaining at start of SME	344.2	g
SRAT product Calcine Factor (calculated)	0.556	g oxide/g dry SRAT Product
Sludge calcined solids - based on SRAT product	191.25	g
Sludge oxide contribution in SME	38.00	%
Frit oxide contribution	62.00	%
Frit slurry wt % solids	50.00	wt%
Mass of SEFT added to SME receipt	0.00	g
Mass of Solids added with SEFT	0.00	g
Mass of Slurry after SEFT Addition	1376.61	g
Solids in slurry after SEFT Addition	344.15	g
Mass of Water to remove during SEFT dewater	0.00	g
SEFT Addition Rate	0.00	mL/min
SEFT Addition Time	0.00	min
SEFT Dewater Time	0.00	min
Mass of Calcined Solids in SME cycle (with SEFT addition)	191.25	g
Added water simulating decontamination of canisters	1,179.8	g
SME cycle antifoam addition (cylinder decon + frit addition)	0.00	g
Water Added with Antifoam during cylinder decon	0.00	g
Frit solids (total)	312.0	g
Acid added with frit	0.00	g
Water Added with Frit	312.0	g
Water added with antifoam during frit addition	0.0	g
Total frit slurry water	312.0	g
Total mass of frit slurry	624.1	g
Number of equal SME frit slurry additions	2	
Water added with each frit addition	156.0	g
Scaled SME boil up rate	1.96	g/min
Approximate time to remove water from each frit addition (not last frit addition)	79.5	min
Final solids content in SME	656.2	g
Target SME solids total wt %	45.0	%
Target Water in SME product	802.0	g

Mass of water in SME before dewatering FINAL frit addition	1188.5	g
Mass of water to boil off for final SME concentration	386.5	g
Scaled boil up rate	1.96	g/min
Approximate time to reach solids target concentration.	196.8	min

Table A-2. Acid Calculation for Nitric-Formic Acid Flowsheet Experiments

SRNL SRAT Acid, Trim Chemical, Dewater and Redox Calc Revised:	*1/12/2017*	
Experiment Description:	**SRAT/SME run with Nitric/Formic Flowsheet Testing**	
Total nitrite	0.404	mol
Total Mn minus soluble Mn	0.207	mol
Total carbonate	0.349	mol
Total hydroxide	0.757	mol
Total mercury	0.032	mol
Total oxalate	0.016	mol
Trim Chemicals Calculations		
Fresh Sludge Calcine Factor (1100°C), g oxide/g dry solids (calculated)	0.7165	g/g
Fresh Sludge Calcined Oxides	181.057	g
Total solids before trim addition	252.6926	g
Predicted total solids at target levels	260.3278	g
Target Ag metal content in trimmed sludge	0.010000	total wt % dry basis
$AgNO_3$ to add (CF=0.682)	0.04100	g
Ag_2O calcined solids added	0.02796	g
Target wt % Hg dry basis	2.500	total wt % dry basis
Total HgO in fresh Sludge	0.000	g
Total HgO in trimmed Sludge	7.02732	g
HgO to add	7.02732	g
HgO calcined solids added	0.00000	g
Target Pd metal content in trimmed sludge	0.0040	total wt % dry basis
wt % Pd in reagent solution	15.2700	wt % in solution
$Pd(NO_3)_2{*}H_2O$ solution to add (CF=0.531)	0.06819	g of solution
$Pd(NO_3)_2$ to add	0.02255	g
PdO calcined solids added	0.01197	g

Target Rh metal content in trimmed sludge	0.0160	total wt % dry basis
wt % Rh in reagent solution	4.93	wt % in solution
$Rh(NO_3)_3$*$2H_2O$ (CF=0.439)	0.8449	g of solution
Rh(NO3)3 to add	0.11694	g
Rh2O3 calcined solids added	0.05134	g
Target Ru metal content in trimmed sludge	1.0000	total wt % dry basis
wt % Ru in $RuCl_3$ solids	48.73	wt % in solution
Nitric acid in $RuCl_3$ solids	0.000	mmol/g
Nitric acid in $RuCl_3$ solids	0.0000	wt %
Nitric acid added with Ru	0.0000	mols
Nitric acid added with Ru	0.00	g
$RuCl_3$ Solids to add (CF=0.6415)	0.4274	g solution
$RuCl_3$ to add	0.4274	g
RuO_2 calcined solids added	0.2742	g
Total mass of trim chemicals added	8.4088	g
Calcined oxides added in trim chemicals	0.3655	g
Total solids after trim addition	260.3278	g
Match of actual to predicted total solids mass	100.00%	
Total Calcined solids after trim	181.4226	g
Water added to dilute and/or rinse trim chemicals	100.0	g
Mass of trimmed sludge	1,758.4088	g
Calculated wt% total solids in trimmed sludge	14.8047	wt %
Sample mass of trimmed sludge	16.8345	g
Mass of trimmed feeds reacted	1,741.5743	g
Sample removal ratio after trim	0.990	
Mass of PRFT added	767.2948	g
Mass of PRFT flush water added	10.0000	g
Total solids added w/ PRFT	43.8444	g
Calcined solids added w/ PRFT	33.0352	g
Mass of water removed after PRFT addition to return to initial total solids %	**735.0976**	**g**
Mass of slurry after PRFT dewater	1,783.7716	g
Mass of sample after PRFT cycle (before SRAT cycle)	16.8345	g
Mass of slurry going into SRAT cycle	1,766.9371	g
Sample removal ratio after PRFT (for PRFT components only)	0.9906	
Sample removal ratio at start of SRAT (for sludge components only)	0.9811	
Mass at start of SRAT	1,766.9371	g
Total Solids at start of SRAT	298.8328	g
Calcined solids at start of SRAT	210.7133	g
STOICHIOMETRIC ACID CALCULATIONS		
Hsu Stoichiometric Acid Ratios Used		
Acid requirement per mol of Nitrite	0.75	mol H^+/ mol NO^{2-}

Acid requirement per mol of Mn	1.20	mol H^+/ mol Mn
Acid requirement per mol of Carbonate	2.00	mol H^+/ mol $CO^{3=}$
Acid requirement per mol of Hydroxide	1.00	mol H^+/ mol OH^-
Acid Requirement per mol of H^+	-1.00	mol total acid required
Acid requirement per mol of Hg	1.00	mol H^+/ mol Hg^{++}
Acid requirement per mol of Oxalate	0.00	mol H^+/ mol $C^2O^{4=}$
Koopman Stoichiometric Acid Ratios Used (Min)		
Acid requirement per mol of Nitrite	1.00	mol H^+/ mol NO^{2-}
Acid requirement per mol of Mn	1.50	mol H^+/ mol Mn
Acid requirement per mol of Soluble TIC	1.00	mol H^+/ mol $CO^{3=}$
Acid requirement per mol of Hydroxide	1.00	mol H^+/ mol OH^-
Acid requirement per mol of Hg	1.00	mol H^+/ mol Hg^{++}
Acid requirement per mol of Oxalate	0.00	mol H^+/ mol $C^2O^{4=}$
Acid requirement per mol of Calcium	1.50	mol H^+/ mol Ca
Acid requirement per mol of Mg	1.50	mol H^+/ mol Mg
Cation Stoichiometric Acid Ratios Used (Nominal)		
Glycolic Stoichiometric Acid Ratios Used		
Acid Requirement per mol of Nitrite	0.75	mol H^+/mol NO_2-
Acid Requirement per mol of Manganese	0.80	mol H^+/mol Mn
Acid Requirement per mol of Mercury	0.33	mol H^+/mol Hg
Acid Requirement per mol of Soluble TIC	1.00	mol H^+/mol CO_3^{--}
Acid Requirement per mol of Calcium	1.50	mol H^+/mol Ca
Acid Requirement per mol of Magnesium	1.50	mol H^+/mol Mg
Acid Requirement per mol of OH	1.00	mol H^+/mol OH^-
Sludge + PRFT NO_2^-	0.404	mol
Fresh feed insoluble Manganese	0.207	mol
Fresh feed slurry Carbonate	0.349	mol
Fresh feed OH^-	0.757	mol
Fresh Feed Mercury	0.032	mol
Fresh Feed Oxalate	0.016	mol
Fresh Feed Supernate Carbonate	0.349	mol
Fresh Feed Calcium	0.053	mol
Fresh Feed Magnesium	0.062	mol
Fresh Feed Sodium	2.400	mol
Fresh Feed Potassium	0.021	mol
Fresh Feed Cesium	0.000	mol
Fresh Feed Strontium	0.000	mol
Fresh Feed Nickel	0.089	mol
Fresh Feed Nitrate	0.297	mol
Fresh Feed Sulfate	0.024	mol
Fresh Feed Chloride	0.014	mol
Fresh Feed Formate	0.000	mol
Fresh Feed Phosphate	0.000	mol
Hsu Total Stoichiometric Acid required	2.0382	mol
Koopman Minimum Stoichiometric Acid required	2.0243	mol
Glycolic Stoichiometric Acid required	1.7576	mol

Cation Nominal Stoichiometric Acid required	2.8420	mol
Percent Acid in Excess Stoichiometric Ratio	110.00	%
Actual acid to add to SRAT	2.2268	mol
Percent Acid in Excess Stoichiometric Ratio (w/ SEFT)	112.92	%
REDOX CALCULATION (SME PRODUCT REDOX PREDICTION)		
REDOX Target	0.1500	Fe^{+2} / Fe
Predicted REDOX (G=6, Mn=0)	0.1500	
Ratio of formic acid to total acid	0.937591	moles formic acid / moles total acid
Delta between predicted REDOX and target REDOX	0.000031	
Activation of SME cycle corrections? (1=SME corrections performed):	1	
Nitric acid density, 20 °C	1.30611	g/mL
Formic acid density, 20°C	1.2050	g/mL
Nitric acid amount	0.139	mol
Formic acid amount	2.088	mol
Total Manganese in sludge + PRFT	0.207	mol
Manganese added with SEFT (SRAT)	0.000	mol
Manganese removed with SRAT product samples	0.020	mol
Manganese added with SEFT (SME)	0.000	mol
Projected Melter Feed Manganese, total moles	0.186	mol
Formate moles in sludge + PRFT	0.000	mol
Formate added with acid	2.088	mol
Formate destroyed in SRAT	0.418	mol
Formate moles removed with SRAT product sample	0.163	mol
Formate moles introduced in SME	1.507	mol
Formate moles destroyed in SME	0.000	mol
Formate Moles after SME	1.507	mol
Projected Melter Feed Formate, total moles	1.507	mol
Trimmed Sludge + PRFT Nitrate	0.304	mol
Nitrate moles from nitric acid	0.139	mol
Nitrate moles from SEFT (SRAT)	0.059	mol
Nitrate from conversion of nitrite to nitrate in SRAT and SME	0.101	mol
Nitrate from minor trim chemicals	0.00768	mol
Nitrate going into SRAT cycle	0.5025	mol
Nitrate into SRAT + nitrate formed by nitrite conversion	0.6034	mol
Nitrate removed with SRAT product sample	0.05906	mol
Nitrate moles from SEFT (SME)	0.00000	mol
Nitrate destroyed in the SME	0.00000	mol
Projected Melter Feed Nitrate, total moles (Sum of inputs - destroyed)	0.544	mol

Glycolate added with acid	0.000	mol
Glycolate moles destroyed in SRAT	0.000	mol
Glycolate moles removed with SRAT product sample	0.000	mol
Glycolate moles destroyed in SME	0.000	mol
Projected Melter Feed Glycolate, total moles	0.000	mol
Oxalate in sludge + PRFT	0.016	mol
Oxalate created from glycolate	0.000	mol
Oxalate removed with SRAT product sample	0.002	mol
Projected Melter Feed Oxalate, total moles	0.014	mol
Carbon from Coal in sludge + PRFT	0.000	mol
Carbon removed in SRAT product Sample	0.000	mol
Projected Melter Feed Carbon from coal, total moles	0.000	mol
Projected Melter Feed Nitrite, total moles	0.0000	mol
Mass of Antifoam Present in Melter Feed (Hypothetical)	0.037	g
Mass % of Carbon in Antifoam	51.280	%
Moles of Carbon from Antifoam in Melter Feed	0.002	mol
Assumed SME density	1.390	g/ml
Projected final SME mass	**1.413**	kg
Manganese concentration in final melter feed	0.132	mol/kg melter feed slurry
Formate concentration in final melter feed	1.066	mol/kg melter feed slurry
Glycolate concentration in final melter feed	0.000	mol/kg melter feed slurry
Oxalate concentration in final melter feed	0.010	mol/kg melter feed slurry
Carbon from coal concentration in final melter feed	0.000	mol/kg melter feed slurry
Nitrate concentration in final melter feed	0.385	mol/kg melter feed slurry
Nitrite concentration in final melter feed	0.000	mol/kg melter feed slurry
Antifoam Carbon concentration in final melter feed	0.001	mol/kg melter feed slurry
Projected final SME volume	**1.017**	**liters**
BENCH SCALE CALCULATIONS		
Bench Scale Operational Setting		
Scaled formic acid feed rate	0.4901	mL/min
Scaled nitric acid feed rate	0.4901	mL/min
Prototypical formic acid feed time	180.7	min
Prototypical nitric acid feed time	27.7	min
Formic acid volume required	88.579	mL
Nitric acid volume required	13.566	mL
Dewatering Calc for Target wt % Total Solids in SRAT Product		
Final SRAT Product Total Solids	23.00	%
Water in Trimmed (and sampled) Sludge (post PRFT, if applicable)	1,468.10	g
Water added with antifoam flush	3.92	g

Water added with formic acid	10.65	g
Water added with nitric acid	8.96	g
Water added in acid flushing	0.00	g
Water made during base equiv neutralization	13.64	g
Water made in TIC destruction	6.29	g
Water made in SRAT nitrite destruction	2.42	g
Water made in Mercury Reduction	0.57	g
Water made in Manganese Reduction	3.72	g
Revised water mass in slurry	1,518.28	g
Solids in Trimmed (and sampled) Sludge	298.83	g
Antifoam added	0.04	g
Mass of pure nitric acid (HNO_3) added	8.76	g
Mass of pure formic acid (HCOOH)	96.09	g
Solids lost during base equiv neutralization	13.64	g
Solids lost in TIC destruction	21.67	g
Solids lost in SRAT nitrite destruction	12.62	g
Solids made in SRAT formate formation	0.00	g
Solids made in SRAT oxalate formation	0.00	g
Solids lost in SRAT formate destruction (formic acid)	19.22	g
Solids lost in Mercury Stripping	6.89	
Revised solids mass in slurry	329.69	g
Target final water mass in slurry to hit total solids target	1,103.73	g
Total water to remove in SRAT dewater	**414.55**	g
Mass of SEFT added to slurry	3,668.14	g
Mass of solids added with SEFT	0.00	g
Mass of Slurry after SEFT Addition	5,101.56	g
Solids in slurry after SEFT Addition	329.69	g
Mass of Water to remove during SEFT dewater	**3,668.14**	g
SEFT Addition Rate	1.72	mL/min
SEFT Addition Time	2,142.86	min
SEFT Dewater Time	1,499.18	min
Mass of carbonate lost as CO_2	15.37	g
Mass of nitrite lost as N_yO_x	10.20	g
Formate converted to CO_2 in SRAT	18.38	g of CO_2
SRAT Product Mass (neglecting intermediate and product samples)	1433.42	g
Mass of SRAT cycle samples (Product and Intermediate, excluding SRAT Receipt)	140.29	g
Mass of treated sludge going into SME cycle	1293.13	g
Fraction of SRAT product going into SME Cycle	0.9021	
Calcined Solids going to SME	190.09	g
DWPF SCALE TO BENCH SCALE		
DWPF Scale SRAT cycle		

density estimate =	1.122	
Volume based scale factor 6000 gal starting SRAT	15448.6	
Minimum SRAT conflux time	1540.2	min
Bench Scale SRAT cycle		
99.5% of scaled air purge	17.3723	mmol/min
Helium purge rate at 0.5 vol %	0.0873	mmol/min
Scaled boil up rate	2.45	g/min
Required dewatering time at above rate (PRFT and after acid)	169.4	min
Required time for SEFT addition and dewater	2142.9	min
DWPF Scale SME cycle		
Bench Scale SME cycle		
SME scale factor (Assuming 6000 gallons of SME receipt)	20202.9	
99.5% scaled SME air purge	4.3	mmol/min
Helium purge rate at 0.5 vol %	0.02	mmol/min
Solids remaining at start of SME	297.4	g
SRAT product Calcine Factor (calculated)	0.639	g oxide/g dry SRAT Product
Sludge calcined solids - based on SRAT product	190.09	g
Sludge oxide contribution in SME	38.00	%
Frit oxide contribution	62.00	%
Frit slurry wt % solids	50.00	wt %
Mass of SEFT added to SME receipt	0.00	g
Mass of Solids added with SEFT	0.00	g
Mass of Slurry after SEFT Addition	1293.13	g
Solids in slurry after SEFT Addition	297.42	g
Mass of Water to remove during SEFT dewater	0.00	g
SEFT Addition Rate	0.00	mL/min
SEFT Addition Time	0.00	min
SEFT Dewater Time	0.00	min
Mass of Calcined Solids in SME cycle (with SEFT addition)	190.09	g
Added water simulating decontamination of canisters	936.7	g
SME cycle antifoam addition (cylinder decon + frit addition)	0.00	g
Water Added with Antifoam during cylinder decon	0.00	g
Frit solids (total)	310.1	g
Acid added with frit	0.00	g
Water Added with Frit	310.1	g
Water added with antifoam during frit addition	0.0	g
Total frit slurry water	310.1	g
Total mass of frit slurry	620.3	g
Number of equal SME frit slurry additions	2	
Water added with each frit addition	155.1	g

Scaled SME boil up rate	1.87	g/min
Approximate time to remove water from each frit addition (not last frit addition)	82.9	min
Final solids content in SME	607.6	g
Target SME solids total wt %	43.0	%
Target Water in SME product	805.4	g
Mass of water in SME before dewatering FINAL frit addition	1150.8	g
Mass of water to boil off for final SME concentration	345.4	g
Scaled boil up rate	1.87	g/min
Approximate time to reach solids target concentration.	184.6	min

Appendix B. RC1 Data

These experiments were the first use of the Mettler Toledo RC1 for SRAT and SME testing. The RC1 records about 100 records per second during the experiment. The data is stored in the eNotebook for this experiment.[29] A few summary tables and graphs are included in this appendix.

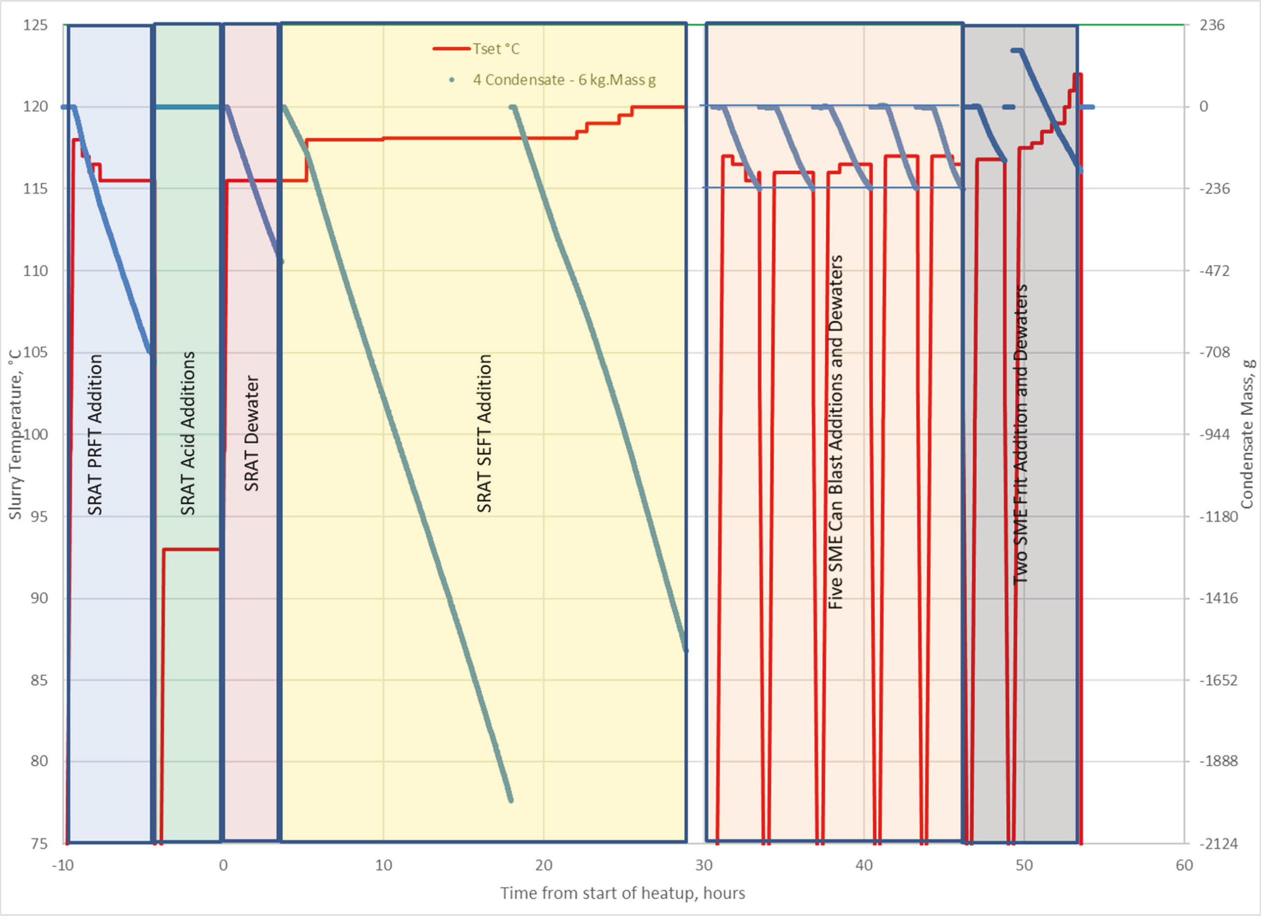

Figure B-1 Nitric-Formic Acid Flowsheet MD20 Condensate Generation

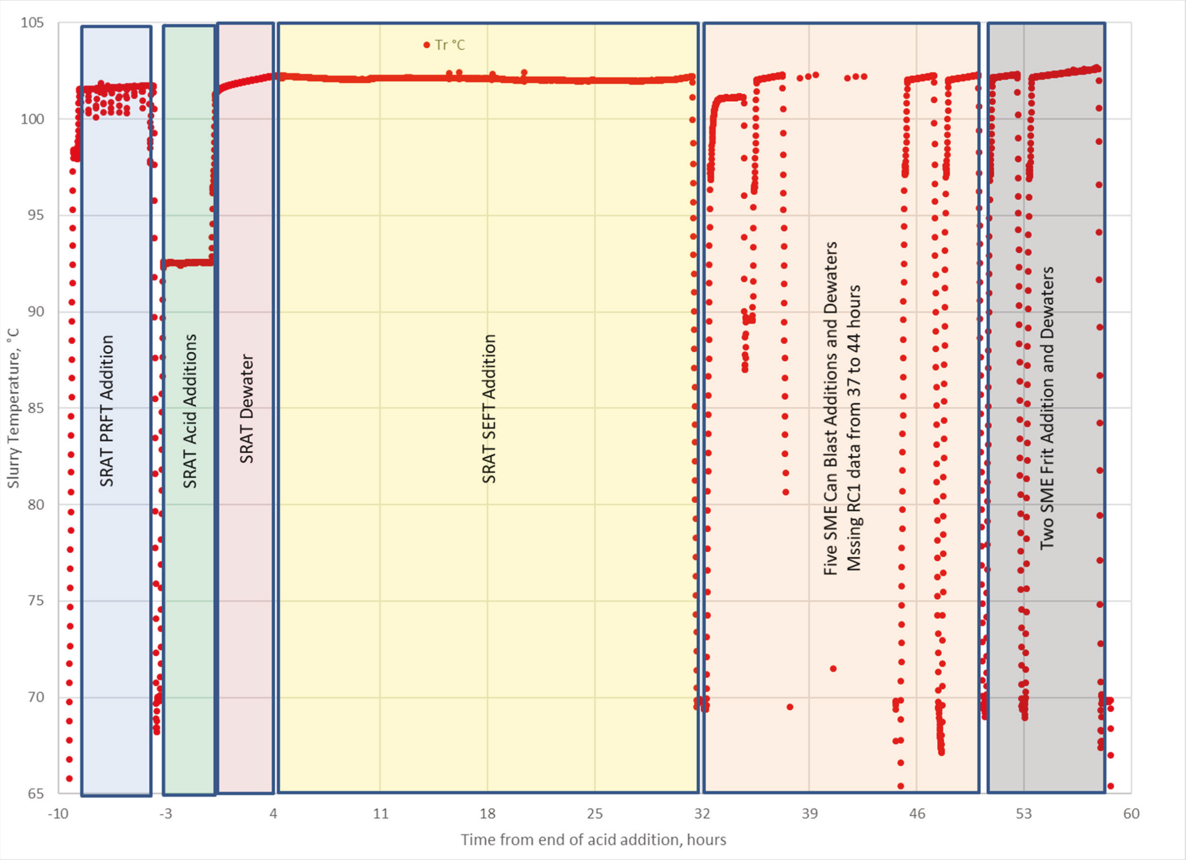

Figure B-2. Nitric-Glycolic Acid Flowsheet Momentive™ Y-17112 Temperature Profile

Note: Data loss for Reactor Temperature from 37 to 44 hours. Data from data sheets was added during this time (approximately every 30 min)

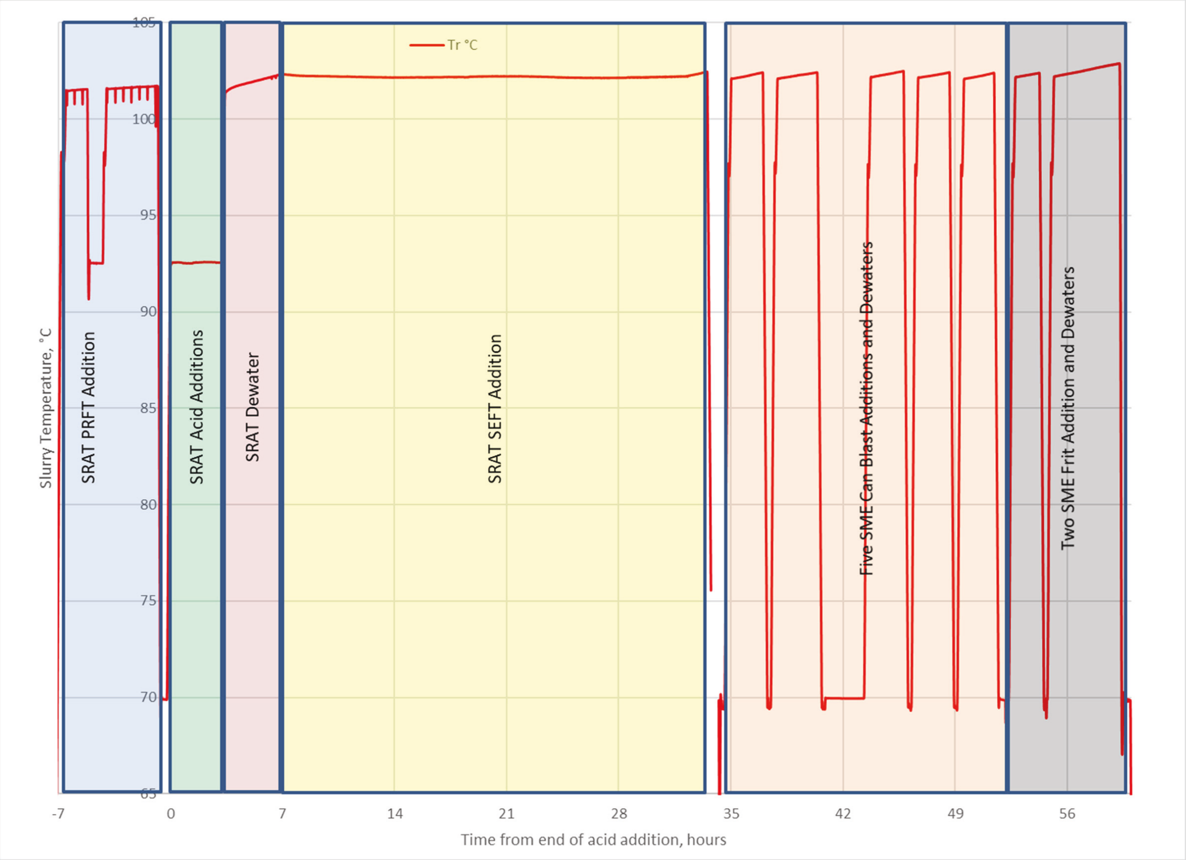

Figure B-3. Nitric-Glycolic Acid Flowsheet Evonik Surfynol® MD20 Temperature Profile

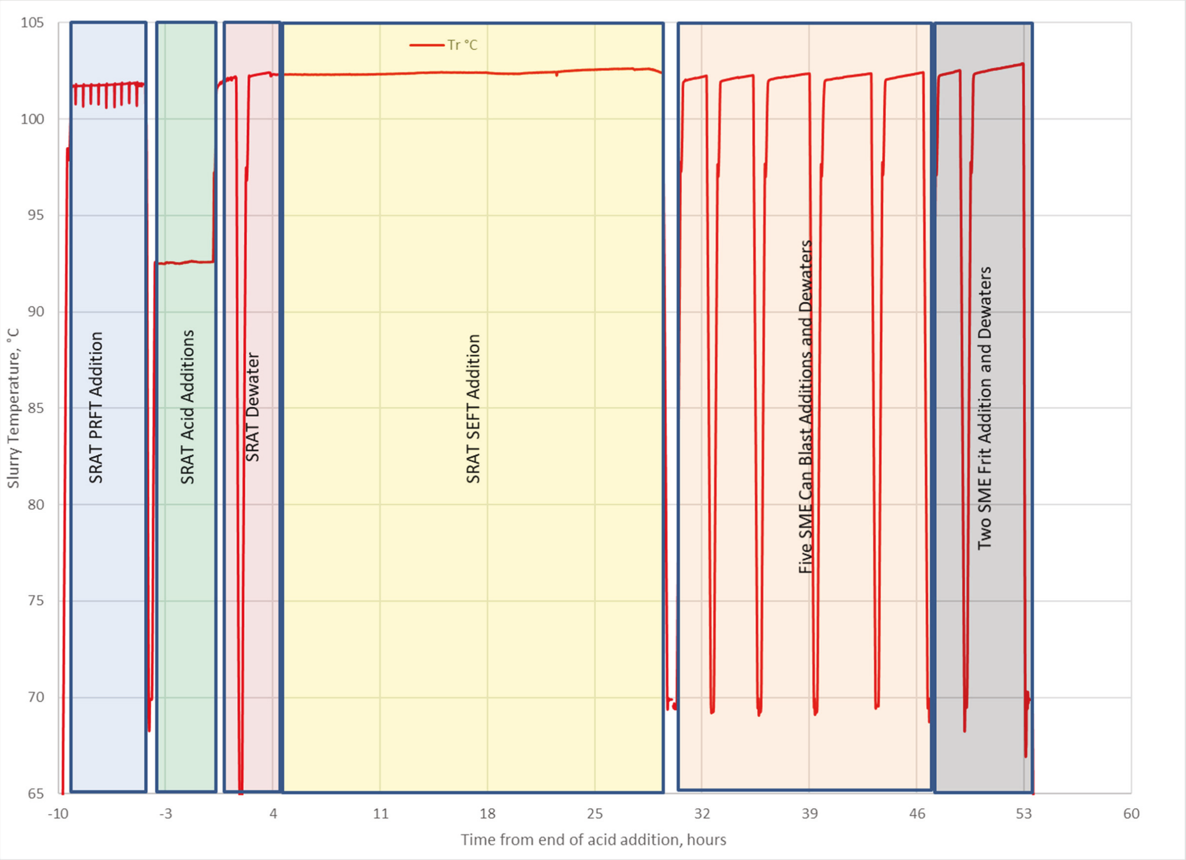

Figure B-4. Nitric-Formic Acid Flowsheet Momentive™ Y-17112 Temperature Profile

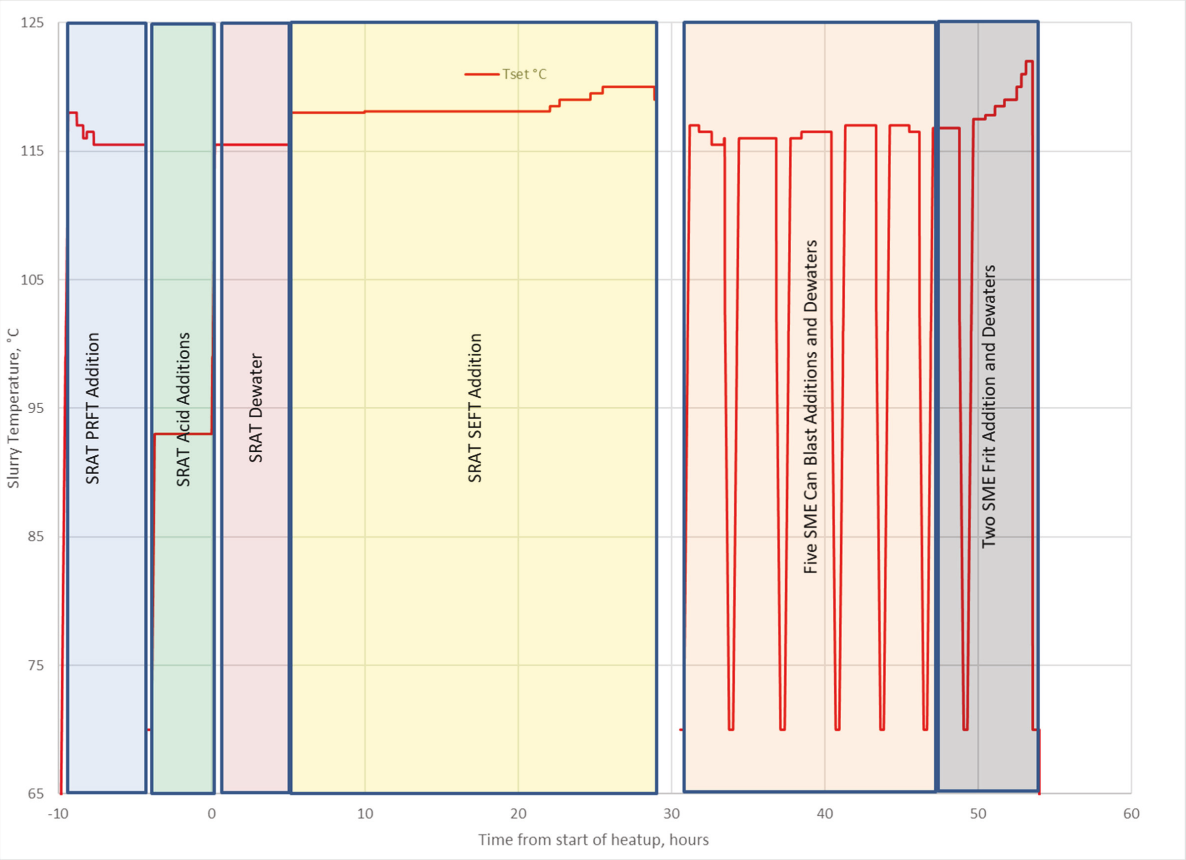

Figure B-5. Nitric-Formic Acid Flowsheet Evonik Surfynol® MD20 Temperature Profile

Note: No Reactor Temperature data is available until the SME cycle. Plotted the setpoint temperature as that data is available.

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Appendix C. Offgas Results

The identified gases are summarized in a series of graphs. For the nitric-glycolic acid flowsheet experiments, the major species (CO_2, NO, NO_2 and N_2) are summarized in Figure C-1 and Figure C-2 The minor species (H_2, N_2O, NO_2 and He) are summarized in Figure C-3 and Figure C-4. For the nitric-formic acid flowsheet experiments, the major species (CO_2, NO, NO_2 and N_2) are summarized in Figure C-5 and Figure C-6. The minor species (H_2, N_2O, NO_2 and He) are summarized in Figure C-7 and Figure C-8.

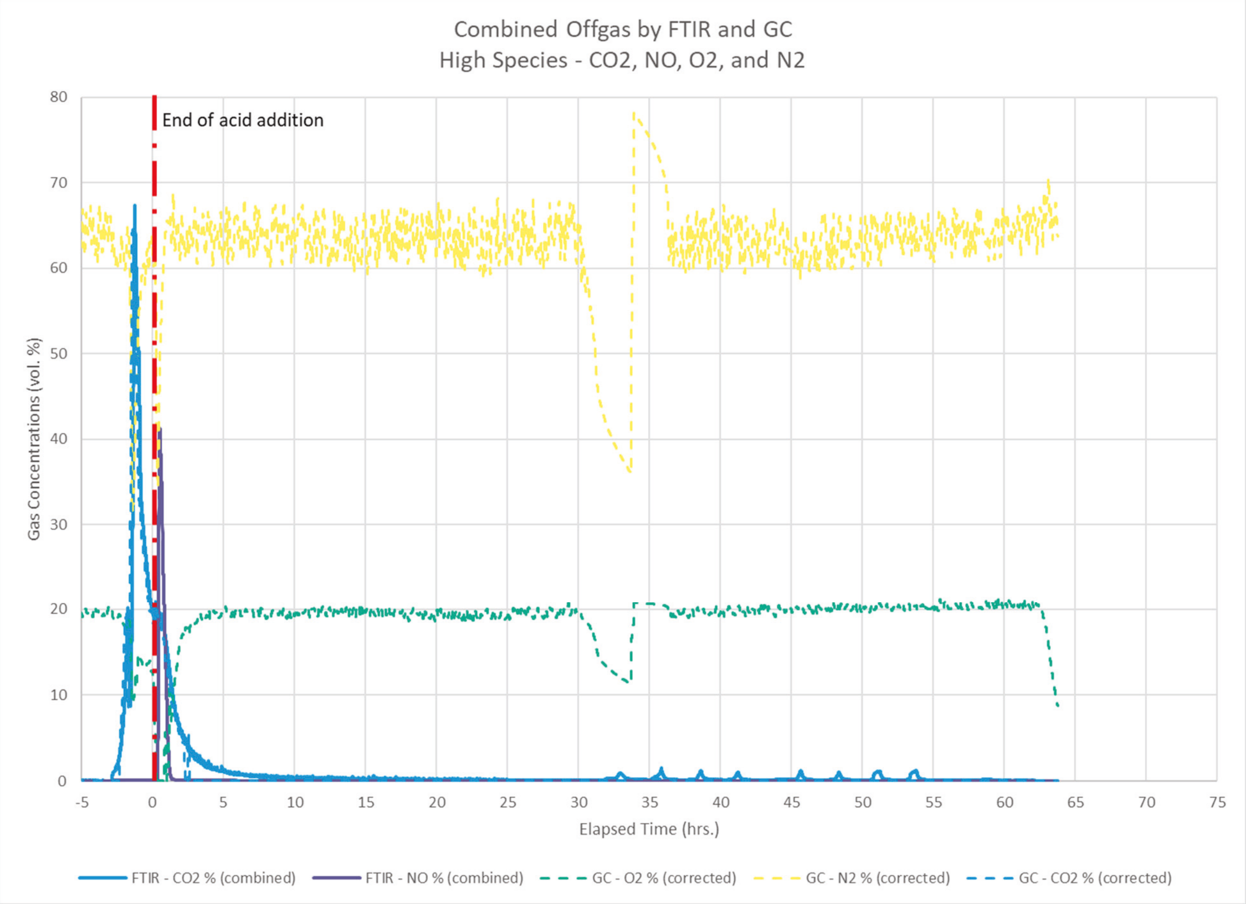

Figure C-1. Combined Offgas by FTIR and GC for CO_2, NO, O_2 and N_2 Momentive™ Y-17112 Nitric-glycolic acid flowsheet

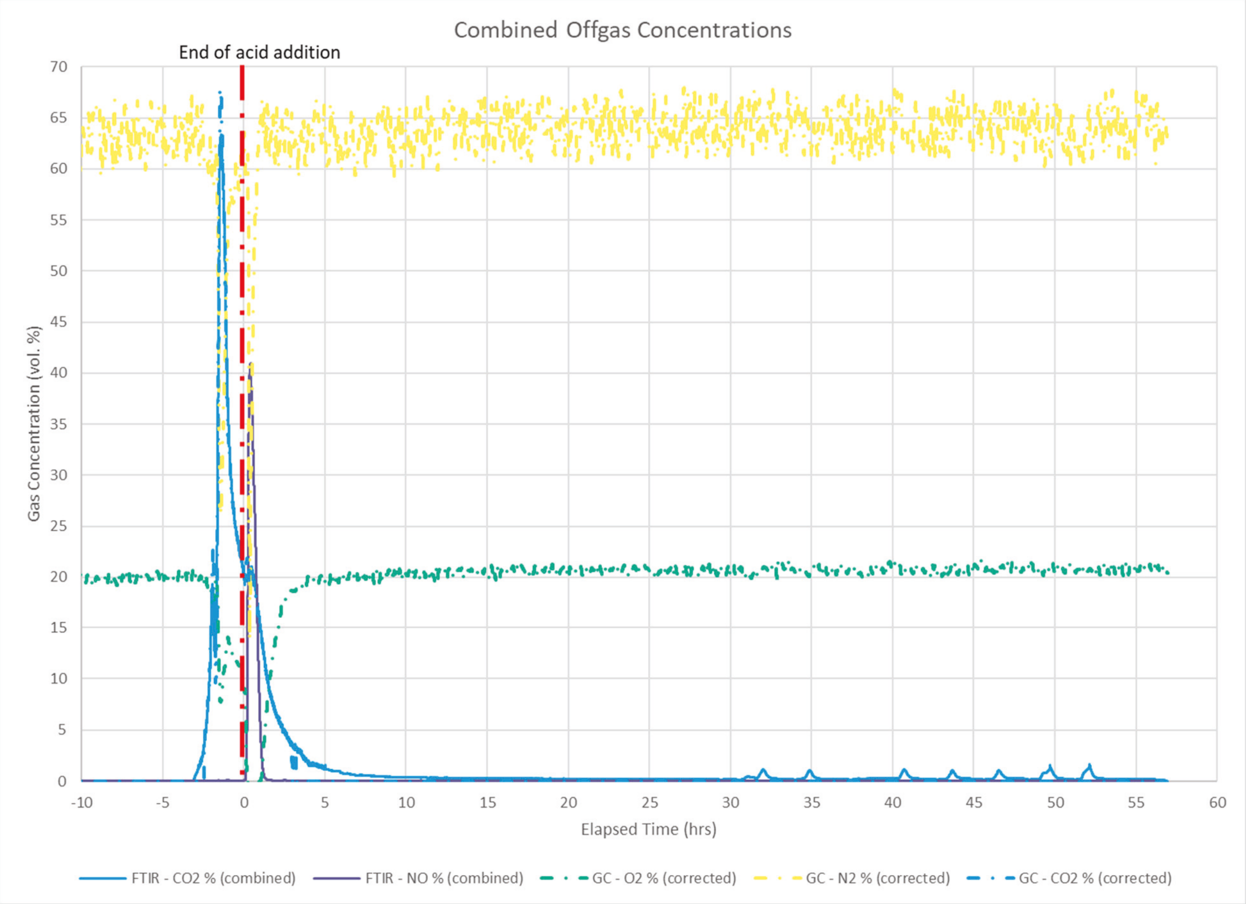

Figure C-2. Combined Offgas by FTIR and GC for CO_2, NO, O_2 and N_2 Surfynol® MD20 Nitric-glycolic acid flowsheet

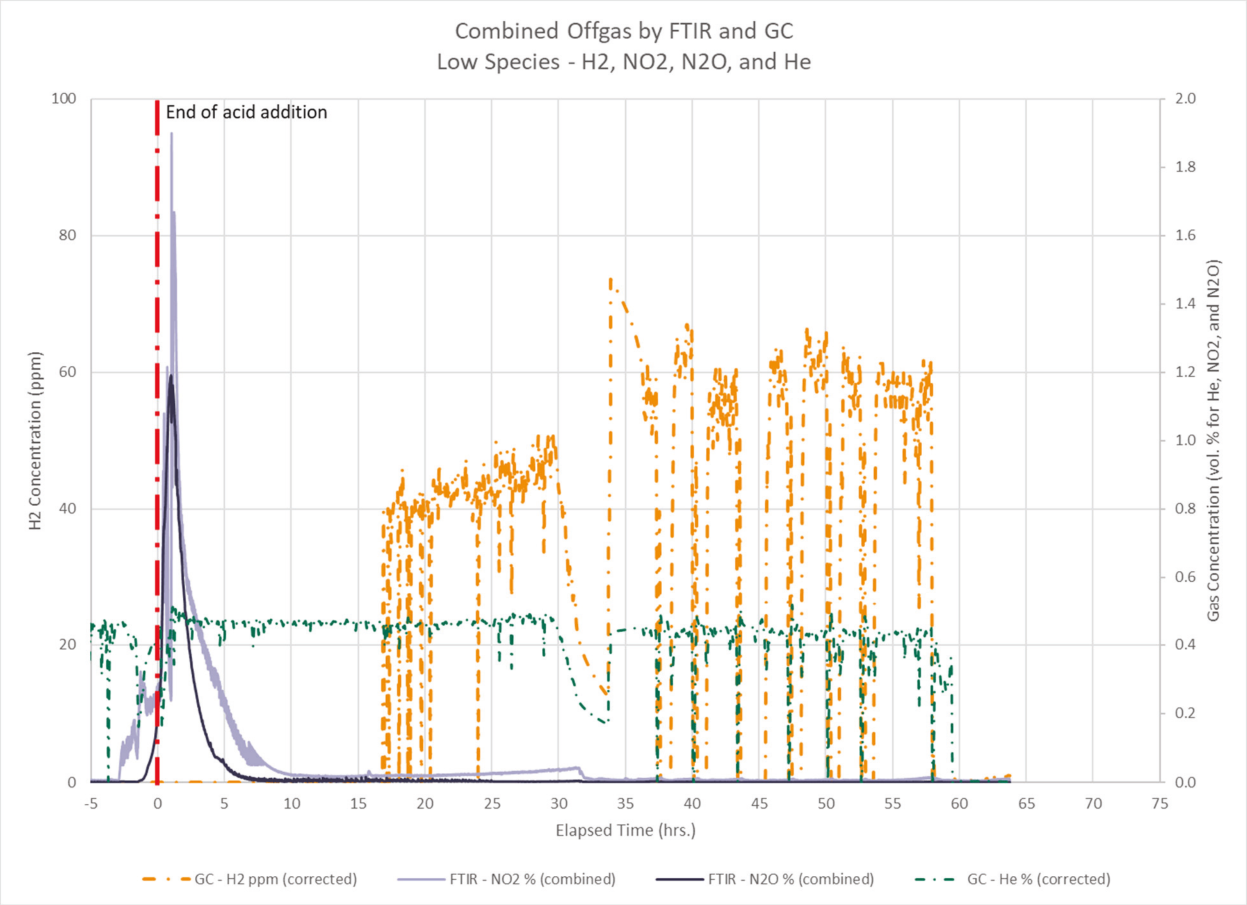

Figure C-3. Combined Offgas by FTIR and GC for H_2, N_2O, NO_2 and He Momentive™ Y-17112 Nitric-glycolic acid flowsheet

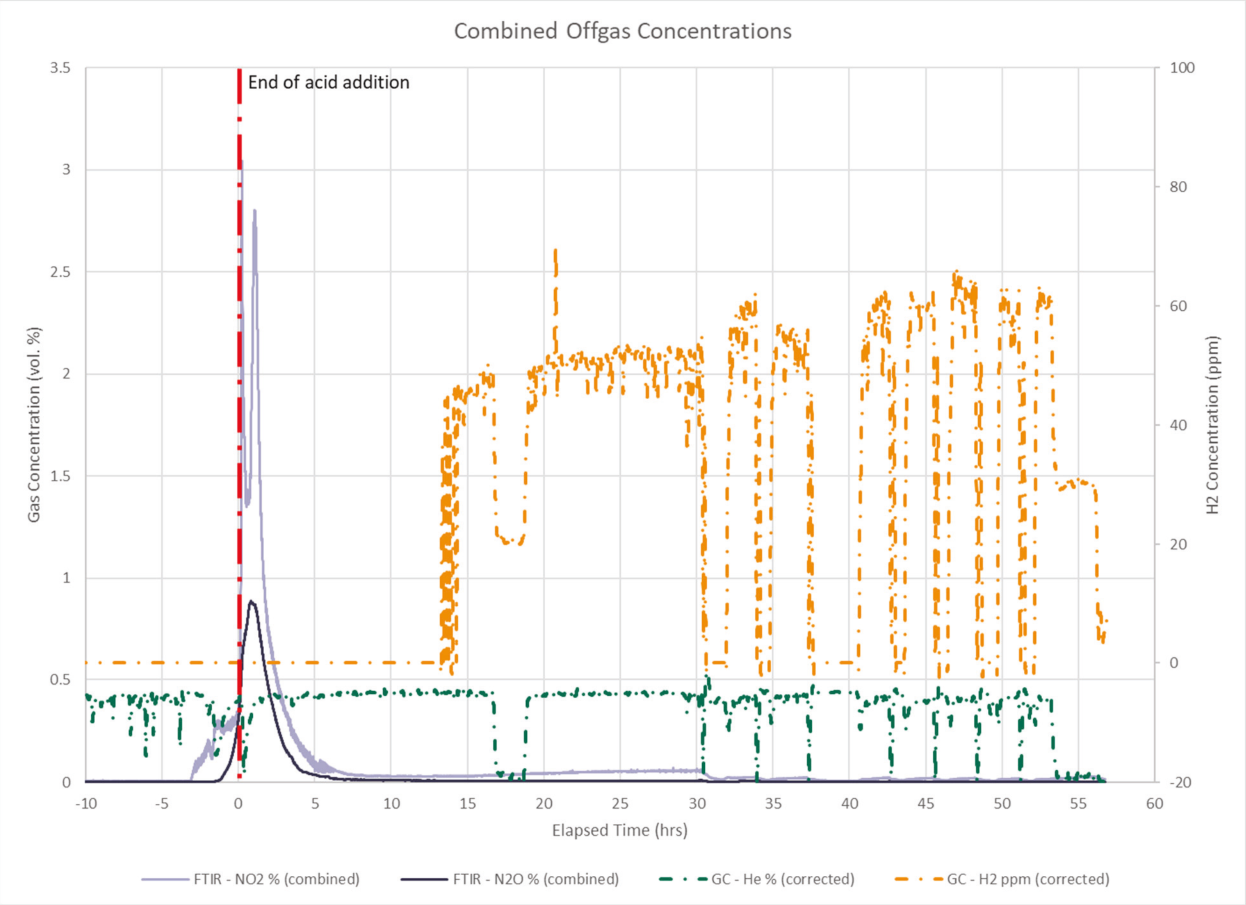

Figure C-4. Combined Offgas by FTIR and GC for H_2, N_2O, NO_2 and He Surfynol MD20 Nitric-glycolic acid flowsheet

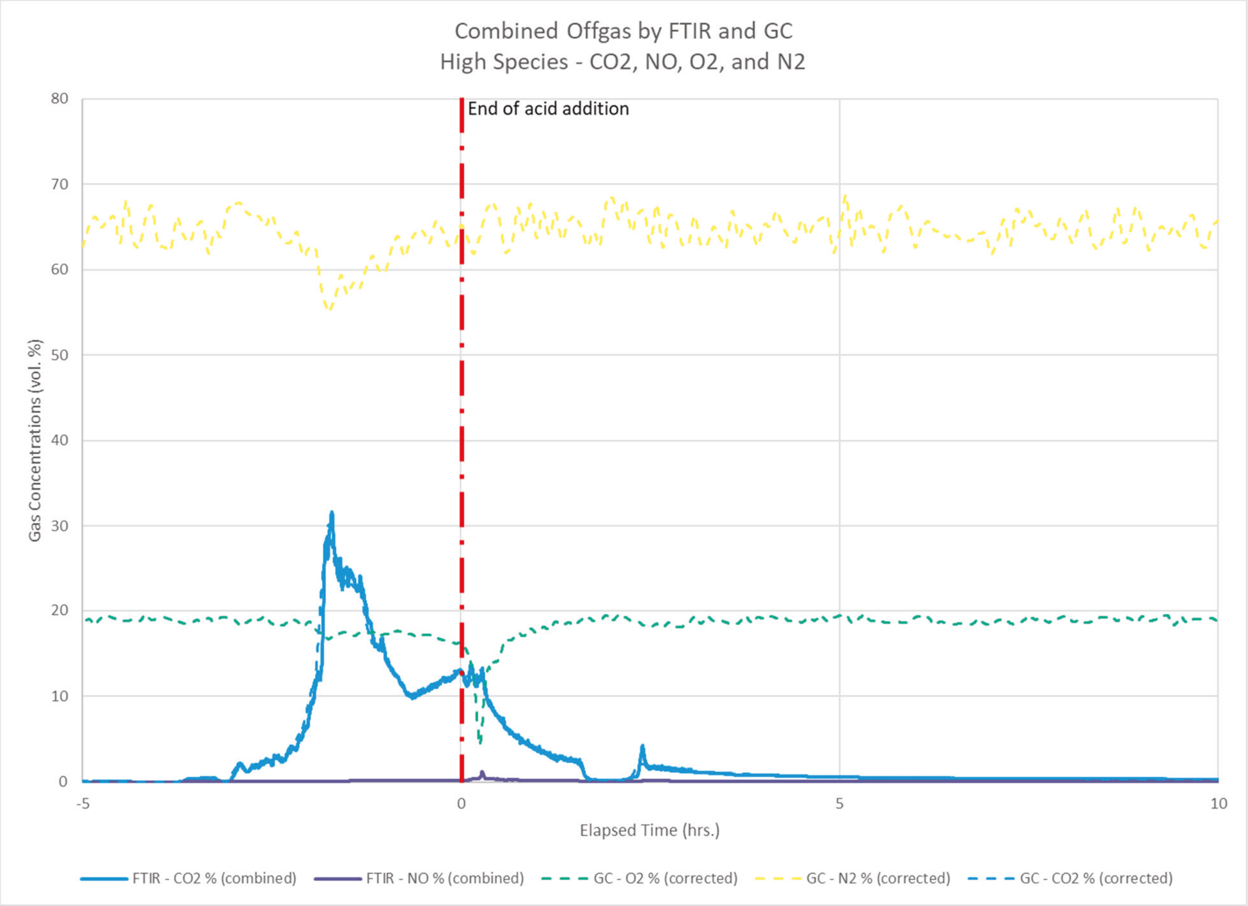

**Figure C-5. Combined Offgas by FTIR and GC for CO_2, NO, O_2 and N_2
Momentive™ Y-17112 Nitric-formic acid flowsheet**

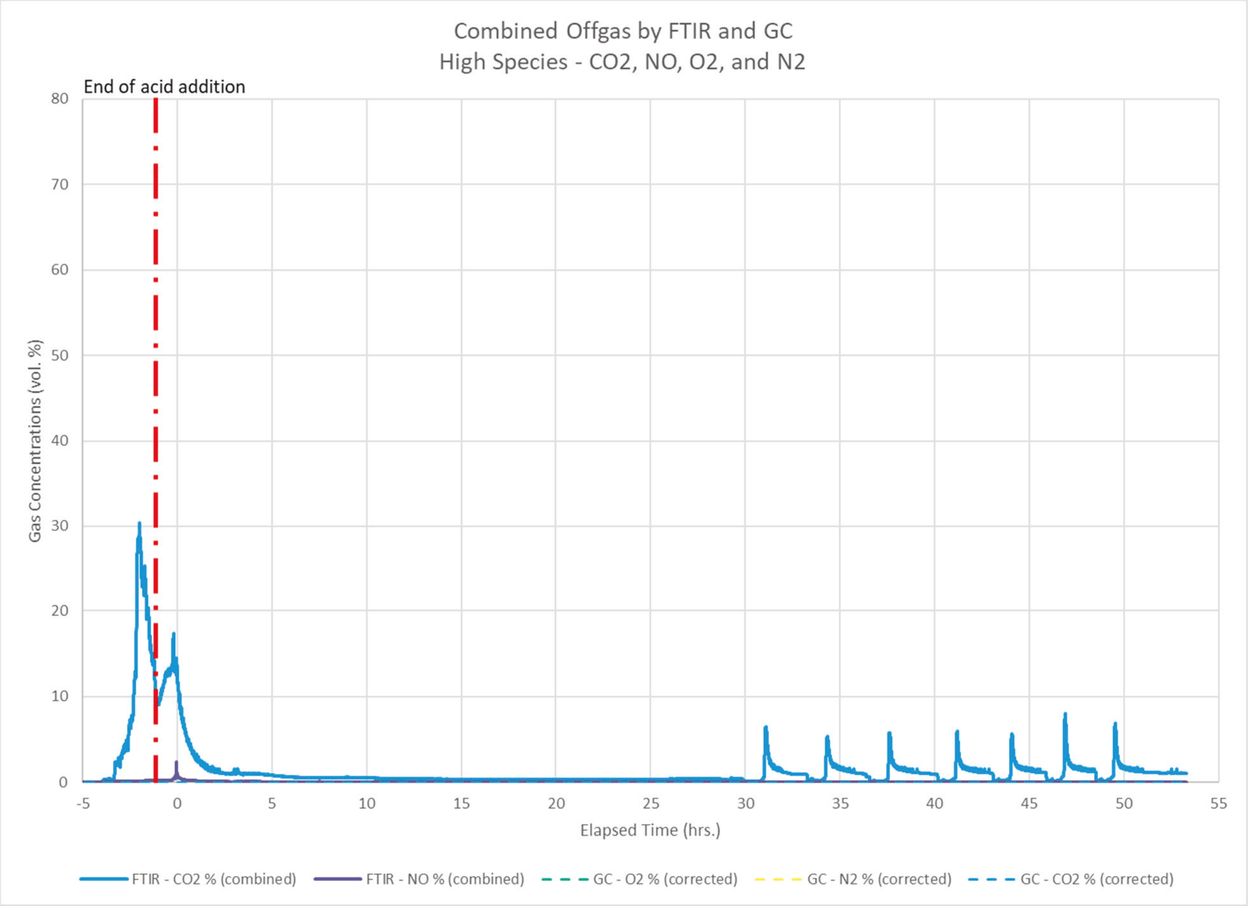

Figure C-6. Combined Offgas by FTIR and GC for CO_2, NO, O_2 and N_2 Surfynol® MD20 Nitric-formic acid flowsheet

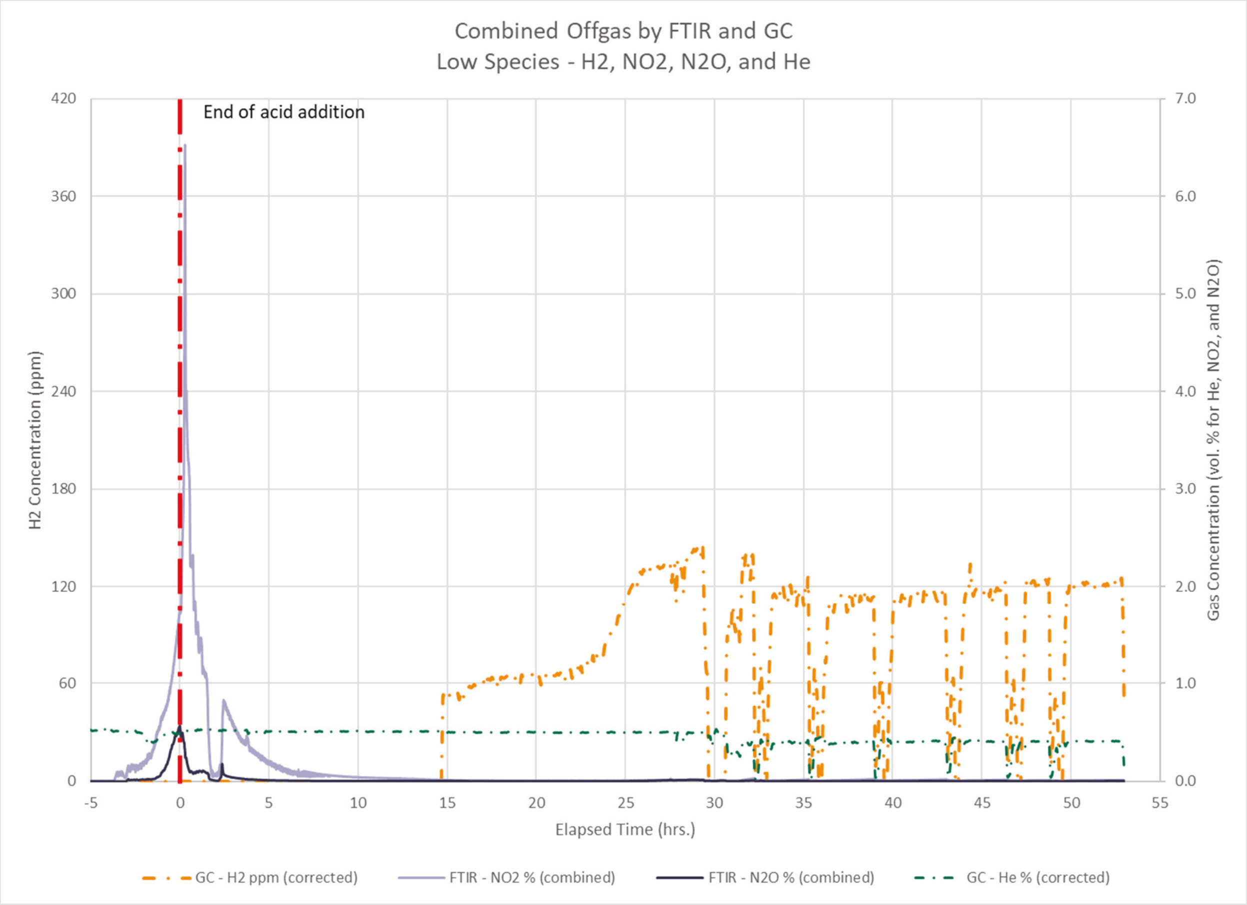

Figure C-7. Combined Offgas by FTIR and GC for H_2, N_2O, NO_2 and He Momentive™ Y-17112 Nitric-formic acid flowsheet

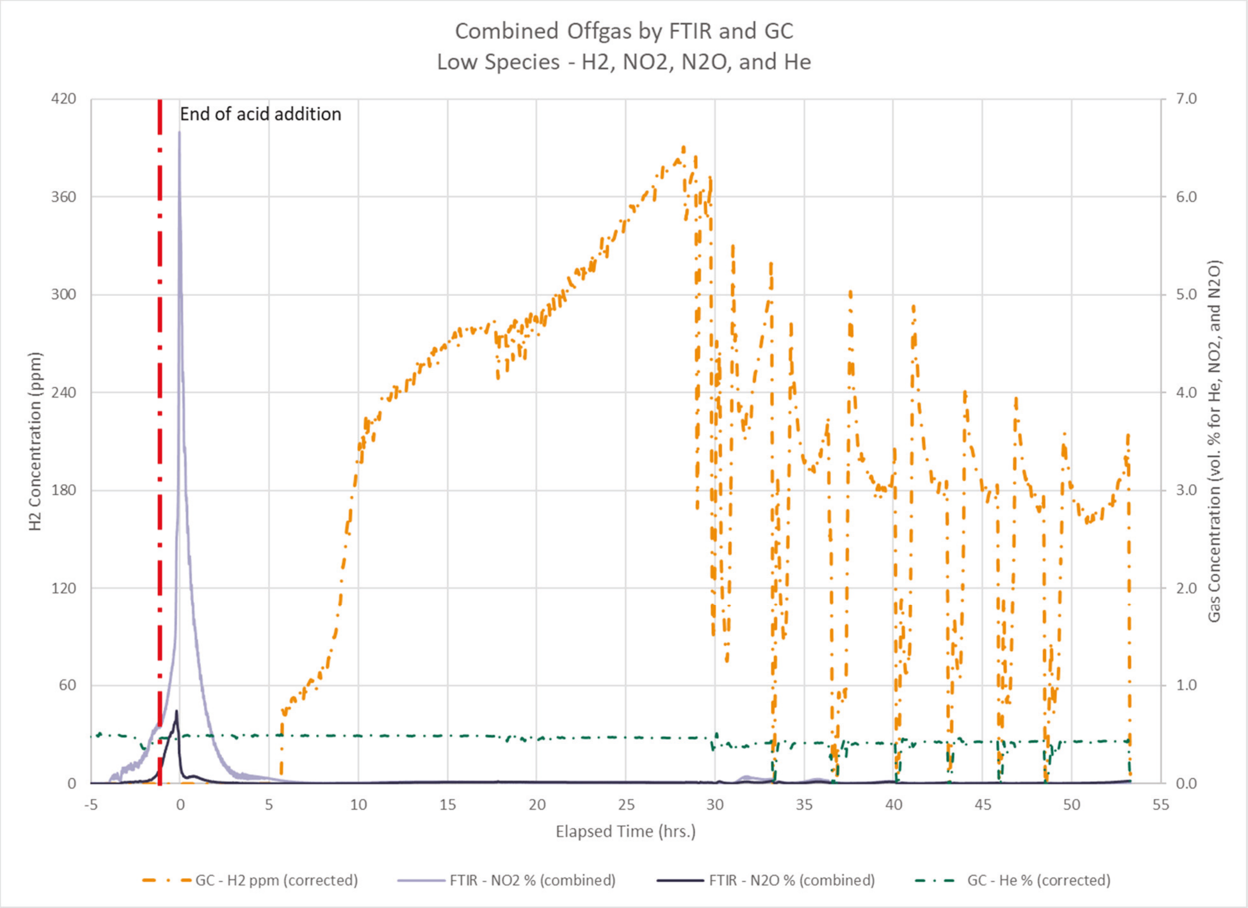

**Figure C-8. Combined Offgas by FTIR and GC for H_2, N_2O, NO_2 and He
Surfynol® MD20 Nitric-formic acid flowsheet**

Appendix D. Liquid Samples

A number of liquid and slurry samples were analyzed by AD, PSAL and for Rheology. The Sample numbers and their corresponding Projects are summarized in Table D-1 and Table D-2.

AD sample are summarized in Table D-1.

Table D-1. AD samples

Run	Nitric-Glycolic Y-17112	Nitric-Formic Y-17112	Nitric-Glycolic MD20	Nitric-Formic MD20
PRFT Dewater	15939	16043	15659	16091
	15278			
	(PROJ-190917-5)	(PROJ-191209-1)	(PROJ-191014-1)	(PROJ-191213-1)
SRAT Dewater	15940	16044		16092
	15278			
	(PROJ-190917-5)	(PROJ-191209-1)		(PROJ-191213-1)
SEFT Dewater	15941	16045		16093
	15278			
	(PROJ-190917-5)	(PROJ-191209-1)		(PROJ-191213-1)
SME Dewater	15942	16046	15661	16094
	15280			
	(PROJ-190917-5)	(PROJ-191209-1)	(PROJ-191014-1)	(PROJ-191213-1)
Pre-PRFT	15275	16047	15656	16095
	(PROJ-190917-5)	(PROJ-191209-1)	(PROJ-191014-1)	(PROJ-191213-1)
Post-PRFT	15726	16048	15657	16096
	(PROJ-190917-5)	(PROJ-191209-1)	(PROJ-191014-1)	(PROJ-191213-1)
Post-SRAT	15277	16049	15658	16097
	(PROJ-190917-5)	(PROJ-191209-1)	(PROJ-191014-1)	(PROJ-191213-1)

Table D-2. PSAL samples

Run	Nitric-Glycolic Y-17112	Nitric-Glycolic MD20	Nitric-Formic Y-17112	Nitric-Formic MD20
PRFT Dewater	S-10824 S-10801	S-10742	S-10750	S-10746
SRAT Dewater	S-10825 S-10802	S-10743	S-10751	S-10747
SEFT Dewater	S-10826 S-10803	S-10744	S-10752	S-10748
SME Dewater	S-10827 S-10804	S-10745	S-10753	S-10749
Post-SRAT	S-9962	S-9964	S-10451	S-10454
Post-SME	S-9963 S-10826	S-9965 S-10824	S-10452 S-10827	S-10455 S-10825

Appendix E. SRAT and SME Product Analytical Results

SRAT and SME Product Sample results are summarized in Table E-1, Table E-2, and Table E-3.

Table E-1. PSAL SRAT Product Analyses

Run	**Nitric-Glycolic Y-17112**	**Nitric-Glycolic MD20**	**Nitric-Formic Y-17112**	**Nitric-Formic MD20**
Sample #	**S-9962**	**S-9964**	**S-10451**	**S-10454**
Al, Wt % Calcined Solids	12.0	11.7	13.3	13.1
Ba, Wt % Calcined Solids	0.114	0.110	0.142	0.136
Ca, Wt % Calcined Solids	1.02	1.06	1.173	1.161
Cr, Wt % Calcined Solids	0.158	0.147	0.1799	0.1895
Cu, Wt % Calcined Solids	0.0931	<0.100	0.0754	0.0792
Fe, Wt % Calcined Solids	16.3	15.4	18.57	18.15
K, Wt % Calcined Solids	0.205	0.225	0.566	0.574
Mg, Wt % Calcined Solids	0.300	0.718	0.833	0.839
Mn, Wt % Calcined Solids	7.57	5.62	5.70	5.64
Na, Wt % Calcined Solids	17.5	17.7	17.0	17.6
Ni, Wt % Calcined Solids	2.43	2.24	2.542	2.560
P, Wt % Calcined Solids	<0.100	0.0997	0.116	0.118
S, Wt % Calcined Solids	0.375	0.219	3.76	3.82
Si, Wt % Calcined Solids	1.67	1.16	1.3	1.3
Sn, Wt % Calcined Solids	<0.100	<0.100	0.0987	0.1002
Ti, Wt % Calcined Solids	4.37	4.23	4.54	4.55
Zn, Wt % Calcined Solids	<0.100	<0.100	0.1017	0.1012
Zr, Wt % Calcined Solids	0.228	0.193	0.1564	0.1558
Glycolate, mg/kg	51,150	67,150	<100	<100
Formate, mg/kg	724	659	46,250	61,350
Chloride, mg/kg	327	334	457	578
Nitrite, mg/kg	<100	<100	<100	<100
Nitrate, mg/kg	47,650	48,850	24,400	27,900

Table E-1. PSAL SRAT Product Analyses

Run	**Nitric-Glycolic Y-17112**	**Nitric-Glycolic MD20**	**Nitric-Formic Y-17112**	**Nitric-Formic MD20**
Sample #	**S-9962**	**S-9964**	**S-10451**	**S-10454**
Nitrite, mg/kg	<100	<100	<100	<100
Nitrate, mg/kg	47,650	48,850	24,400	27,900
Sulfate, mg/kg	1,310	1,500	1,570	1,755
Oxalate, mg/kg	2,135	2,605	550	570
Phosphate, mg/kg	<100	106	<100	<100
pH	5.98	5.82	8.18	8.05
slurry density g/mL	1.2005	1.2273	1.2059	1.2379
filtrate density g/mL	1.1002	1.1114	1.0829	1.1008
total Solids	26.47%	26.97%	25.83%	29.21%
insoluble Solids	13.28%	12.25%	14.80%	16.69%
calcined solids	14.93%	14.85%	17.12%	19.31%
soluble Solids	13.19%	14.71%	11.03%	12.52%

Table E-2. PSAL SME Product Analyses

Run	**Nitric-Glycolic Y-17112**	**Nitric-Glycolic MD20**	**Nitric-Formic Y-17112**	**Nitric-Formic MD20**
Sample #	**S-9963**	**S-9965**	**S-10452**	**S-10455**
Al, Wt % Calcined Solids	5.70	5.30	5.05	5.15
Ba, Wt % Calcined Solids	0.113	<0.100	0.0513	0.0530
Ca, Wt % Calcined Solids	1.01	0.46	0.528	0.517
Cr, Wt % Calcined Solids	0.156	<0.100	0.0737	0.0731
Cu, Wt % Calcined Solids	0.0953	<0.100	0.0406	0.0364
Fe, Wt % Calcined Solids	7.42	6.99	6.79	7.00
K, Wt % Calcined Solids	0.234	0.121	0.564	0.560
Mg, Wt % Calcined Solids	0.329	0.317	0.341	0.341
Mn, Wt % Calcined Solids	2.41	2.29	2.12	2.18
Na, Wt % Calcined Solids	10.8	10.35	10.3	10.4
Ni, Wt % Calcined Solids	1.01	1.01	0.946	0.953
P, Wt % Calcined Solids	<0.100	<0.100	0.116	0.115
S, Wt % Calcined Solids	<0.100	<0.100	3.75	3.72
Si, Wt % Calcined Solids	21.6	22.5	23.7	23.1
Sn, Wt % Calcined Solids	<0.100	<0.100	0.0984	0.0977
Ti, Wt % Calcined Solids	1.96	1.84	1.68	1.76
Zn, Wt % Calcined Solids	<0.100	<0.100	0.0381	0.0380
Zr, Wt % Calcined Solids	0.127	0.110	0.0994	0.100
Glycolate, mg/kg	49,950	70,400	<100	<100
Formate, mg/kg	885	822	46,250	56,100
Chloride, mg/kg	341	374	457	554
Nitrite, mg/kg	<100	<100	<100	<100
Nitrate, mg/kg	45,800	53,450	21,900	26,550
Sulfate, mg/kg	1,280	1,610	1,380	1,700

Table E-2. PSAL SME Product Analyses

Run	Nitric-Glycolic Y-17112	Nitric-Glycolic MD20	Nitric-Formic Y-17112	Nitric-Formic MD20
Sample #	**S-9963**	**S-9965**	**S-10452**	**S-10455**
Oxalate, mg/kg	2,315	3,055	475	571
Phosphate, mg/kg	483	135	<100	<100
pH	6.07	5.99	7.95	8.23
slurry density g/mL	1.3470	1.4103	1.4013	1.4774
filtrate density g/mL	1.1174	1.1422	1.1032	1.1273
total solids	41.72%	48.18%	47.91%	52.99%
insoluble solids	29.17%	34.07%	38.01%	42.00%
calcined solids	31.06%	36.50%	40.23%	44.26%
soluble solids	12.54%	14.10%	9.89%	10.99%

Table E-3 SRAT and SME Product Rheology Results

Flowsheet	Nitric-Glycolic	Nitric-Glycolic	Nitric-Formic	Nitric-Formic
Antifoam	**Y-17112**	**MD20**	**Y-17112**	**MD20**
SRAT Product target wt % solids*	27	27	25	25
SME Product target wt % solids*	48	48	45	45
SME Product measured wt % solids*	47.1	47.5	44.6	45.5
SRAT Product Consistency, cP	4.8	5.7	8.6	7.1
SRAT Product Yield Stress, Pa	0.58	0.88	2.51	2.29
SME Product Consistency, cP	25.2	25.3	29.1	30.7
SME Product Yield Stress, Pa	4.68	4.69	6.92	15.3

* SRAT and SME product samples were diluted with water to the wt % targets in the table above prior to rheology measurements