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Antifoam Degradation Products in Off Gas and Condensate of Sludge Batch 9 Simulant Nitric-Formic Flowsheet Testing for the Defense Waste Processing Facility

Tara E. Smith

April 2016

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Savannah River National Laboratory™
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EXECUTIVE SUMMARY

Ten chemical processing cell (CPC) experiments were performed using simulant to evaluate Sludge Batch 9 for sludge-only and coupled processing using the nitric-formic flowsheet in the Defense Waste Processing Facility (DWPF). Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) cycles were performed on eight of the ten. The other two were SRAT cycles only. Samples of the condensate, sludge, and off gas were taken to monitor the chemistry of the CPC experiments. The Savannah River National Laboratory (SRNL) has previously shown antifoam decomposes to form flammable organic products, (hexamethyldisiloxane (HMDSO), trimethylsilanol (TMS), and propanal), that are present in the vapor phase and condensate of the CPC vessels. To minimize antifoam degradation product formation, a new antifoam addition strategy was implemented at SRNL and DWPF to add antifoam undiluted.

During Sludge Batch 9 flowsheet testing, antifoam degradation products were analyzed for in the condensate samples, sludge product samples, and the off gas of select runs. HMDSO is seen in the off gas following each antifoam addition. However, results indicate that HMDSO is formed more significantly during acid addition and the initial boiling period than at other points of the CPC process. Although the release rate is likely influenced by several variables there is a clear influence from the pH of the sludge. At this point in the CPC process acid addition and the formation of NO_x causes the pH to be more acidic. The surface interface is typically more acidic than the bulk of the sludge as a result of the re-condensation of acidic gases. The maximum release rate of HMDSO observed in these runs was 0.0217 mmol/min/gram antifoam in the SRAT and 0.0006 mmol/min/gram antifoam in the SME. Formation of propanal is most probable when the sludge is boiling or after being present in the sludge for an extended amount of time. Both propanal and TMS were seen in the sludge product. TMS appears to readily volatilize and is easily formed throughout CPC processing. In the runs performed the SRAT dewater had an average concentration of 0.34 mg/L, 2.6 mg/L and 12.6 mg/L for HMDSO, propanal and TMS respectively. SME dewater had an average concentration of < 0.25 mg/L, 13.0 mg/L and 9.9 mg/L for HMDSO, propanal and TMS respectively.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technical Laboratory
ARP	Actinide Removal Process
AF	Antifoam
CI	Confidence Interval
CPC	Chemical Processing Cell
DWPF	Defense Waste Processing Facility
FAVC	Formic Acid Vent Condensate
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
HMDSO	Hexamethyldisiloxane
MCU	Modular Caustic Side Solvent Extraction Unit
MS	Mass Spectrometry
MWWT	Mercury Water Wash Tank
LFL	Lower Flammability Limit
LOQ	Limit of Quantification
PPMV	Parts per Million by Volume
SB9	Sludge Batch 9
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SVOA	Semi-Volatile Organic Analysis
TMS	Trimethylsilanol
TTR	Technical Task Request
VOA	Volatile Organic Analysis

1.0 Introduction

Antifoam degradation is of concern to the Defense Waste Processing Facility (DWPF) due to flammable decomposition products in the vapor phase of the Chemical Process Cell (CPC) vessels, as well as the collection of flammable and organic species in the off gas condensate. The Savannah River National Laboratory (SRNL) has previously shown antifoam decomposes to form flammable organic products including hexamethyldisiloxane (HMDSO), trimethylsilanol (TMS), and propanal in the vapor phase and condensate of the Chemical Processing Cell (CPC) vessels [1]. The study found that TMS and propanal are readily removed by the off gas train (i.e. condensers and scrubbers). Further, it was determined that antifoam degradation begins to occur upon dilution with water and a new antifoam strategy was implemented to add antifoam undiluted then flush the line with 100 gallons of process water.

Sludge Batch 9 simulant (SB9A) testing was performed using the nitric-formic flowsheet as requested by the DWPF Technical Task Request (TTR) X-TTR-S-00005, Rev. 2 and as described in SRNL-RP-2014-01059, Rev. 1 [2, 3]. The objective of this work was to perform DWPF CPC Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) simulant flowsheet testing to validate the sludge-only flowsheet and establish a coupled operation flowsheet for use with sludge batch 9 (SB9) and using the new antifoam addition strategy. Objectives were achieved by monitoring the chemistry of the CPC experiments through sampling the condensate, sludge, and off gas. Condensate samples, sludge product samples, and the off gas were used to monitor for antifoam degradation products. This report details the antifoam degradation seen in experimental runs SB9A-1A through SB9A-10A. Additional results and observations associated with the SB9 simulant testing will be presented in subsequent reports.

2.0 Experimental Procedure

Ten lab-scale CPC runs were performed with blended Tank 51 and Tank 40 simulants deemed SB9A. Each CPC run was performed in a clean, empty rig. Glassware is cleaned between runs by soaking in concentrated nitric acid for 8+ hours. The Mercury Water Wash Tank (MWWT) was filled to the reflux overflow (~31-36 mL for the 4 L and ~27-28 mL for the 1 L) with DI water. The ammonia scrubber recycle vessel was filled with 749 mL of DI water and 1 mL of 50 wt% nitric acid. The Formic Acid Vent Condenser (FAVC) started empty. Sludge was added to the vessel then trimmed uniquely for each run with noble metals and mercury. The trimmed SRAT receipt volume was 3.1 L for the 4 L laboratory scale and 1.3-1.4 L for the 1-L laboratory scale. The MWWT and FAVC are drained and not refilled between the SRAT and SME cycles.

Testing was completed at the Aiken County Technology Laboratory (ACTL). Four liter laboratory scaled CPC runs were performed in pairs; all runs were performed using round-the-clock operations. Eight of the ten SB9A experiments were SRAT/SME runs; whereas for the other two were SRAT only. Three of the eight runs were performed in the 1-L laboratory scaled setup instead of the 4-L laboratory scaled setup. One run added the Actinide Removal Process (ARP) simulant without monosodium titanate and also the Modular Caustic Side Solvent Extraction (MCU) simulant. This run was used to validate the coupled operation flowsheet for SB9. Another run was performed at half the DWPF design basis boil-up rate and included six canister decontamination simulant additions. An eleventh run was performed; however, no sample or gas analysis was performed relating to antifoam degradation products. It is thus not included in this report.

2.1 Experimental Run Parameters

Acid stoichiometry of experiments ranged from 105% to 145% of the Koopman minimum acid equation, which is equivalent to a range of 109.7% to 151.5% for the Hsu minimum acid factor. Experiments are summarized in **Table 2-1**. All experiments targeted a REDOX ratio (measured using Fe^{+2}/Total Fe analytical results) of 0.15, 100% destruction of nitrite, SRAT product total solids of 25%, and SME product total solids of 48%. The assumed values for the conversion of nitrite to nitrate, destruction of formic acid, and destruction of nitrate are also listed in **Table 2-1**. Assumptions were adjusted as needed to meet the REDOX target.

Table 2-1. Experimental Matrix

Run ID #	Acid in Excess Stoichiometric Ratio		Vessel Size	Conversion of Nitrite to Nitrate in SRAT	Destruction of Formic acid charged in SRAT	Destruction of Formic acid charged in SRAT	Destruction of Nitrate
	Koopman	**Hsu**			**SRAT Cycle**	**SME Cycle**	**SME Cycle**
SB9A-1A	145%	151.5%	4-L	25%	20%	1.50%	0.50%
SB9A-2A	105%	109.7%	4-L	25%	20%	1.50%	0.50%
SB9A-3A	130%	135.9%	4-L	28.6%	36%	1.50%	0.50%
SB9A-4A	130%	135.9%	1-L	28.6%	36%	1.50%	0.50%
SB9A-5A	125%	130.6%	4-L	25%	20%	1.50%	0.50%
SB9A-6A	120%	125.4%	4-L	25%	20%	1.50%	0.50%
SB9A-7A	120%	125.4%	1-L	25%	20%	N/A	N/A
SB9A-8A	120%	125.4%	1-L	25%	20%	N/A	N/A
SB9A-9A[a]	120%	125.4%	4-L	25%	20%	1.50%	0.50%
SB9A-10A[b]	120%	125.4%	4-L	25%	20%	1.50%	0.50%

[a] Coupled Run
[b] Extended Run

For SB9A-7A and SB9A-8A the SRAT cycle only was performed to compare the ruthenium (Ru) and rhodium (Rh) catalyzed hydrogen off gas in the 1-L and 4-L laboratory scale setup. SB9A-9A, the ARP/MCU coupled run, consisted of adding the ARP simulant scaled to a DWPF volume of 1,250 gallons and a MCU simulant scaled to a DWPF volume of 12,000 gallons [4, 5]. The MCU simulant targeted 0.01 M boric acid titrated with NaOH to a pH of 8.7 (69.5 mg/L Na) and 117.9 mg/L of Blended Solvent (87 mg/L Isopar-L). Solvent was added by a syringe pump immediately before the boric acid was pumped into the SRAT through a port in the lid of the kettle. SB9A-10A, the extended run, was performed at a reduced boil-up rate equivalent to 2,500 lbs/hr of steam and included six canister decontamination simulant additions (water only) added to the SME prior to the two frit additions. All other runs were performed at the DWPF design basis boil-up rate equivalent to 5,000 lbs/hr of steam and canister decontamination simulant additions were not performed [6].

Two 4-L runs are performed at the same time using separate hoods located in 999-W Lab 132, whereas the 1-L run was performed individually in 999-W Lab 134. Lab view was used to automate the CPC experiments and record real time data. Two heating rods were used for each CPC run. During heating to 93°C a PID algorithm is used to reach the temperature set point while limiting the temperature differential between the hottest rod and the sludge to 30°C. Above 93°C, a PID algorithm is used to target a wattage set point. The wattage is adjusted by personnel to target the desired boil-up rate. The pH of the sludge is monitored and the automation temperature corrects the pH to 25°C. Several thermocouples are used to monitor the condensers, laboratory hood temperature, sludge temperature, and ammonia scrubber solution temperature. This data will be presented in a separate report, but some observations are presented in this report that relates to the formation of antifoam degradation products. The 4-L laboratory scale CPC setup is shown in **Figure 2-1** and the l-L laboratory scale is shown in **Figure 2-2**.

Figure 2-1. CPC 4-L setup

Figure 2-2. CPC 1-L setup

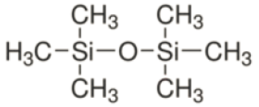
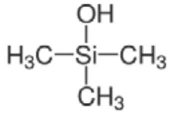
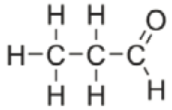
Purge rates, acid addition flow rates, and boil-up rates were scaled based on the DWPF flow rates used for a DWPF SRAT receipt volume of 6,000 gallons. The DWPF scale antifoam additions were scaled to a 6,000 gallon SRAT receipt. Because the work performed is used to develop the SB9 flowsheet, the DWPF SME purge rates, and antifoam additions are scaled to the predicted SME starting volume. The

SME starting volume accounts for the starting mass of the trimmed sludge (scaled to a DWPF SRAT receipt volume of 6,000 gallons) after acid addition, nitrite destruction, conversion of nitrite to nitrate, formic destruction, nitrate destruction, dewatering, and adjusted for sampling. Thus, the predicted SME volume is highly dependent on the experimental inputs.

2.2 Antifoam Additions

Previous work by SRNL determined that the antifoam degradation products, seen in **Table 2-2**, exist in both the vapor space and the condensate [1].

Table 2-2. Antifoam Degradation Products

Compound	Formula	Structure	Molar Mass, g/mol	Solubility in water	Lower Flammability Limit, vol %	Boiling Point
Hexamethyl disiloxane (HMDSO)	$C_6H_{18}OSi_2$		162.38	0.933 mg/L @ 23 °C	0.8	100 °C
Trimethyl silanol (TMS)	$C_3H_{10}OSi$		90.20	35 g/L @ 25 °C	1.45	99 °C
Propanal	C_3H_6O		58.08	310 g/L @ 25 °C	2.6 -2.9	46-50 °C

As part of the study, SRNL found that degradation was partially caused by the dilution of antifoam with water before the addition of the diluted mixture to the CPC vessel. A new antifoam addition strategy was developed to add antifoam undiluted and then flush the line with 100 gallons of process water at DWPF.

Antifoam 747 manufactured by Siovation on April 13th, 2011 (Lot # 110684-0413) was used for all additions. SRAT antifoam additions were scaled from the DWPF addition size for a 6,000 gallon SRAT receipt to the starting mass of the material in the laboratory scaled setup. The DWPF 100 gallon antifoam flush that follows the antifoam addition was also scaled to the laboratory size. SME antifoam additions and the associated flush water were scaled to the predicted SME starting volume. Fewer samples were planned for the 1-L lab scale setup during the SRAT cycle to ensure the heating rods stay covered. The planned antifoam additions during the SRAT and SME cycle are detailed in **Table 2-3**.

Table 2-3. Planned Antifoam Additions

		Antifoam Addition					
Addition Timing	**Temperature, °C**	**DWPF Scale, gal**		**Approximate 4-L Lab Scale, g**		**Approximate 1-L Lab Scale, g**	
		Antifoam	Flush	Antifoam	Flush	Antifoam	Flush
ARP Addition	93	0.5		0.28	44.1	N/A	
Post Nitric Acid Addition	93	1.5	100	0.77	51.4	0.32	21.5
Post Formic Addition	93	1.5		0.77	51.4	0.32	21.5
12-Hour/Emergency Addition	Boiling (~102)	1		0.52	51.4	0.11	21.5
Frit Cycle Addition	95	1		0.43	44.1	0.17	16.9
Addition prior to SME Boiling	93	0.5		0.22	44.1	N/A	
Canister Decontamination Addition	Boiling (~102)	0.5		0.22	44.1		

Typically two 12 hour additions were expected to be added based on the predicted run time of the CPC experiments. Two frit additions each containing frit 803, formic acid, and water were performed during the SME. Antifoam was added prior to going to boiling in the SME cycle. Six simulated canister decontamination additions were performed scaled to a DWPF volume of 1,000 gallons.

2.3 Off-Gas

Off gas passes through the SRAT/SME vessel then passes through a condenser operated at 25°C that drops any SRAT/SME condensate vertically into the mercury water wash tank (MWWT). This design significantly reduced the hold-up of mercury and antifoam degradation products in the condenser drain leg that had been seen in prior test programs. The MWWT is filled with ~30 mL of DI water (for both the 1-L and 4-L) prior to starting the run. For the 4-L laboratory scale setup, off gas flows from the condenser through the ammonia scrubber. The reservoir below the ammonia scrubber was charged with a solution of 749 g of de-ionized water and 1 mL of 50 wt% nitric acid. The dilute acid reservoir solution was recirculated by a MasterFlex driven Micropump gear pump at 120 mL per minute to a spray nozzle at the top of the packed section. The lab-scale ammonia scrubber collects ammonia vapor in the SRAT/SME condenser off-gas for quantification of ammonia generation. For both the 4-L and 1-L laboratory scale setups the off gas next passes through the formic acid vent condenser (FAVC), which is operated at 4°C. The off gas then passes through the Nafion dryer after which the gas is sampled for analysis before exhausting to the hood. Off gas is analyzed by gas chromatography (GC) for all runs, mass spectrometry (MS) for all 4-L laboratory scale setups, and Fourier Transform Infrared (FTIR) spectroscopy for half of the 4-L laboratory scale setups. The FTIR was switched from SB9A-9A to SB9A-10A, after SB9A-9A completed. FTIR and MS were used to monitor for antifoam degradation products. This report will only present off gas results of antifoam degradation species.

The Extrel Core MS samples chilled off-gas leaving the FAVC that was passed through the Nafion dryer in counter-current flow with a dried air stream to reduce the moisture. MS measures the abundance of ions and fragments based on their mass. A single MS is used to monitor off gas data from the pair of CPC runs performed simultaneously with an automated sampling system. The MS sampler cycles back and forth between the off gas streams from the two hoods taking reading every 6-7 seconds. The MS is set to scan for specific molecular weights associated with the fragments of antifoam degradation products and off gas compounds resulting from the CPC chemistry. HMDSO fragments are associated with mass 73 and mass 147.

A MKS FTIR is manually valved into one or the other CPC off gas systems for the duration of the run. Since two CPC runs occurred in parallel, the FTIR was used on typically the higher acid stoichiometry run of the pair. The FTIR gives CO_2, NO, NO_2, N_2O, H_2O, and HMDSO concentrations as currently configured. HMDSO is a volatile marker for decomposed antifoam. Although the GC detects water, the FTIR gives a quantitative concentration for moisture in the chilled off-gas leaving the Nafion drier. The FTIR obtained data roughly every 19 seconds (about 7400 data sets for SB8-D4 vs. 600 GC data sets).

The purge gas for the SRAT and SME was 99.5vol% air and a 0.05vol% helium (He) tracer. The helium was used to compare between the GC and MS readings and correct for instrument drift during the experiment. The purge rate was scaled to a DWPF SRAT purge rate of 230 scfm for 6,000 gallons of SRAT receipt and a DWPF SME purge of 74 scfm.

The FTIR was used for runs SB9A-1A, SB9A-3A, SB9A-5A, SB9A-9A (SRAT cycle), and SB9A-10A (SME cycle). The MS was used for all runs, but HMDSO cannot be quantified by the current MS method.

2.4 Analytical Samples

Condensate samples were taken from the MWWT, FAVC, and ammonia scrubber, and the SRAT/SME dewater material in addition to the SRAT/SME product to detect HMDSO, TMS, and propanal. The samples were analyzed by volatile organic analysis (VOA) and semi-volatile organic analysis (SVOA) to look for antifoam degradation products. VOA is performed using purge and trap. The trap was loaded by sparging a water diluted sample with helium gas at room temperature. The trap is then heated, desorbing constituents and purging them into a heated gas chromatography column for analysis. VOA is used to detect HMDSO and propanal. SVOA is used to detect HMDSO and TMS. For SVOA, the constituents are extracted from the sample using methyl chloride. The organic is then injected into a gas chromatography mass spectrometer. Preparation of condensate and slurry samples was the same. No samples were filtered.

All samples taken to specifically analyze for antifoam degradation products are presented in this report. Additional samples were taken to monitor other CPC chemistry during the SB9 simulant testing and will be presented in subsequent reports.

2.5 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.

3.0 Results and Discussion

Ten CPC runs were completed and analyzed to qualify Sludge Batch 9 using the new antifoam addition strategy. During the SRAT and SME cycles, samples were pulled (see **Table 3-1**) to evaluate antifoam degradation products, in addition to using the FTIR and MS to monitor off gas species. TMS and propanal are readily soluble in the condensate and thus have lower concentrations in off gas that has been processed through the condensers and ammonia scrubber.

Table 3-1. Standard Condensate Sample Plan

Sample Name	Vessel	Sample Description	Analysis
Initial MWWT	MWWT	Flush of MWWT Prior to Run	SVOA, VOA
MWWT Post Formic	MWWT	MWWT Condensate Post Acid Addition	SVOA, VOA
SRAT Dewater	SRAT Dewater	SRAT Dewater Condensate (Pulled from dewater bottle upon completion)	SVOA, VOA
SRAT Product	SRAT	Final SRAT Product	SVOA, VOA
MWWT Post SRAT Cycle	MWWT	MWWT Condensate Post SRAT Cycle	SVOA, VOA
FAVC	FAVC	FAVC Condensate Post SRAT Cycle	SVOA, VOA
Scrubber Solution Post SRAT Cycle	Scrubber	Ammonia Scrubber Solution Post SRAT Cycle	SVOA, VOA
SME 1st Frit Dewater	SME Dewater	SME 1st Frit Dewater	SVOA, VOA
SME 2nd Frit Dewater	SME Dewater	SME 2nd Frit Dewater	SVOA, VOA
SME Product	SME	Final SME Product	SVOA, VOA
FAVC Post SME Cycle	FAVC	FAVC Post SME Cycle	SVOA, VOA
End SME Scrubber Solution	Scrubber	Ammonia scrubber Post SME Cycle	SVOA, VOA

During runs SB9A-1A and SB9A-2A a sample was taken from the MWWT post nitric addition as well. The sample weight was added back to the MWWT using DI water. The FTIR data indicated that antifoam degradation products come off continuously during all of acid addition, thus to ensure that antifoam degradation products in the condensate were detectable it was decided to take future samples at the end of acid addition only. Runs SB9A-4A, SB9A-7A, and SB9A-8A were performed using the 1-L setup, which does not have an ammonia scrubber in the flow path. Further, for the 1-L laboratory scale product samples were not taken due to material constrains. There was not a significant buildup of condensate during the SME cycle because less time is spent at boiling and the MWWT and FAVC are completely drained after the SRAT cycle. The minimum amount of FAVC material caused the sample to not be collected after SB9A-3A. Samples taken are summarized in **Table 3-2**.

Table 3-2. Summary of Samples Pulled

Sample Name	**SB9A-1A**	**SB9A-2A**	**SB9A-3A**	**SB9A-4A**	**SB9A-5A**	**SB9A-6A**	**SB9A-7A**	**SB9A-8A**	**SB9A-9A**	**SB9A-10A**
Initial MWWT	X	X	X	X	X	X	X	X	X	X
MWWT Post Nitric	X	X								
MWWT Post Formic	X	X	X	X	X	X	X	X	X	X
SRAT Dewater	X	X	X	X	X	X	X	X	X	X
MCU Dewater[c]									X	
SRAT Product	X	X	X		X	X			X	X
MWWT Post SRAT Cycle	X	X	X	X	X	X	X	X	X	X
FAVC	X	X	X	X	X	X			X	X
Scrubber Solution Post SRAT Cycle	X	X	X		X	X			X	X
Canister Decontamination Dewater[c]										X
SME 1st Frit Dewater	X	X	X		X	X			X	
SME 2nd Frit Dewater	X	X	X		X	X			X	
SME Combined Dewater	X			X						X
SME Product	X	X	X		X	X			X	X
FAVC Post SME Cycle	X	X	X							
End SME Scrubber Solution	X	X	X		X	X			X	X

[c] Multiple Samples taken at different periods of the activity

SB9A-7A had equipment issues causing a significant delay after acid addition. Upon successful restart of SB9A-7A the SRAT cycle was cut short after dewater to repeat the experiment, i.e. SB9A-8A. SB9A-8A was stopped after viewing the Ru and Rh hydrogen peaks evolve. During SB9A-9A there was an equipment issue with the syringe pump that caused less solvent to be added than expected during the first four hours. Therefore, the total blended solvent concentration in the MCU simulant was actually 88.8 mg/L (65.5 mg/L Isopar-L).

3.1 FTIR Off Gas Data

The FTIR was used to monitor the off gas for HMDSO for SB9A-1A, SB9A-3A, SB9A-5A, and parts of SB9A-9A AND SB9A-10A. The FTIR signal for TMS and propanal are below the quantifiable limit because the compounds are significantly more soluble than HMDSO and the off gas is sampled downstream of the condensers. Propanal and TMS were expected to collect in the condensers and scrubber. MS was used to monitor for HMDSO fragments corresponding to mass 73 and mass 147. Off gas results are displayed in **Figure 3-1** though **Figure 3-6** below. The timing of the antifoam additions is denoted by the pink squares and is not quantitative. The actual mass of antifoam added to the FTIR monitored runs can be seen in **Table 3-3**, **Table 3-4,** and **Table 3-5**.

Table 3-3. Conditions of Actual Antifoam Addition for FTIR Analyzed Runs: SB9A-1A, SB9A-3A, SB9A-5A

Run	**Post Nitric Acid Addition**			**Post Formic Acid Addition**			**Conflux Addition 1**			**Conflux Addition 2**			**SME #1 Addition**			**SME #2 Addition**		
	Antifoam, g	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*
SB9A-1A	0.7871	7.87	92.9	0.7856	3.9	93.1	0.5598	5.73	101.9	0.5254	6.55	101.7	0.4307	6.54	38.0	0.4361	5.88	94.7
SB9A-3A	0.7785	8.49	92.9	0.7814	4.1	95.1	0.5212	4.97	101.7	0.5223	5.97	101.7	0.4367	6.05	101.1	0.4444	5.84	97.8
SB9A-5A	0.7822	8.53	89.7	0.7833	4.09	93.1	0.52	5.38	102.2	0.5272	6.43	101.8	0.4373	6.31	57.9	0.4394	6.38	66.7

Table 3-4. Conditions of Actual Antifoam Addition for FTIR Analyzed Runs: SB9A-9A

Run	**ARP**			**Post Nitric Acid Addition**			**Post Formic Acid Addition**			**Conflux Addition**				**SME #1 Addition**			**SME #2 Addition**		
	Antifoam, g	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*		*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*
SB9A-9A	0.2877	10.7	92.1	0.5607	10.1	94.0	0.8409	4.1	94.0	1st Addition	0.8499	5.20	101.7	0.622	6.65	52.7	0.2079	5.81	60.4
										2nd Addition	0.8413	6.02	101.8						

Table 3-5. Conditions of Actual Antifoam Addition for FTIR Analyzed Runs: SB9A-10A

Run	**Post Nitric Acid Addition**			**Post Formic Acid Addition**			**Conflux Addition**			**Canister Decon. Addition**			**SME #1 Addition**			**SME #2 Addition**		
	Antifoam, g	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*	*Antifoam, g*	*pH*	*Temperature, °C*
SB9A-10A	0.7732	8.87	93.9	0.7839	3.82	92.6	0.5259 (emergency)	5.09	101.7	0.2209 (1st)	5.82	93.0	0.4435	5.85	94.5	1.770	5.67	92.2
							0.5215 (12 hr)	5.70	100.3	0.218 (2nd)	6.04	99.5						
							0.524 (24 hr)	5.99	100.3	0.223 (3rd)	6.16	91.1						
							0.5238 (36 hr)	6.06	99.7	0.2212 (4th)	6.22	94.0						
										0.2212 (5th)	6.41	85.4						
										0.8895 (6th)	6.44	99.7						

Prior to nitric acid addition in SB9A-1A the antifoam was added a bit earlier than intended, which is why the temperature is a bit lower than all other runs. As expected, HMDSO is seen immediately after each antifoam addition in **Figure 3-1** through **Figure 3-6**. The antifoam addition does not correlate with a y-axis. The pH data is temperature corrected. MS measures the abundance of ions and fragments based on their mass. The intensity of the signal for mass 147 and 73 (i.e. HMDSO found during a MS scan) is plotted below on the right y-axis.

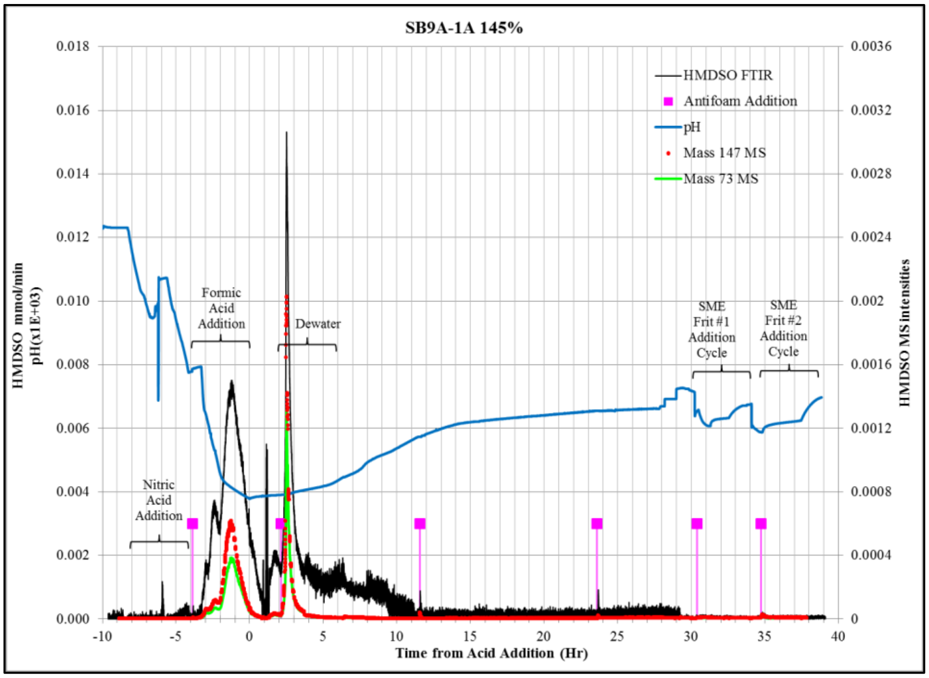


Figure 3-1. SB9A-1A HMDSO Concentration in Off Gas

During SB9A-1A, equipment issues caused a delay after acid addition delaying the time boiling was reached. The maximum HMDSO released correlates to reaching boiling, thus the peak is seen later after completing acid addition than in other runs.

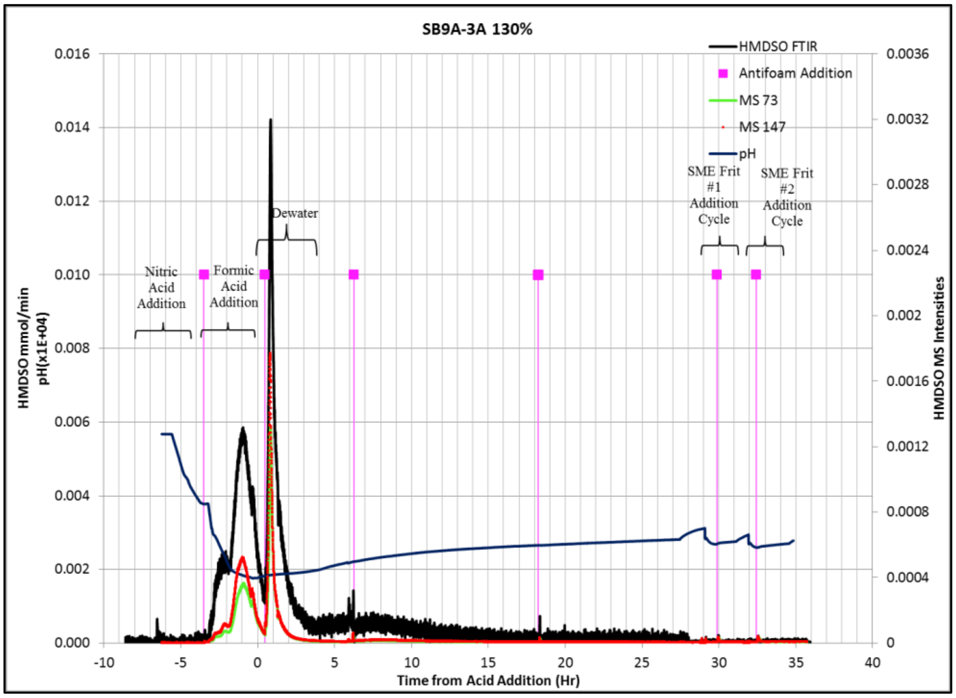


Figure 3-2. SB9A-3A HMDSO Concentration in Off Gas

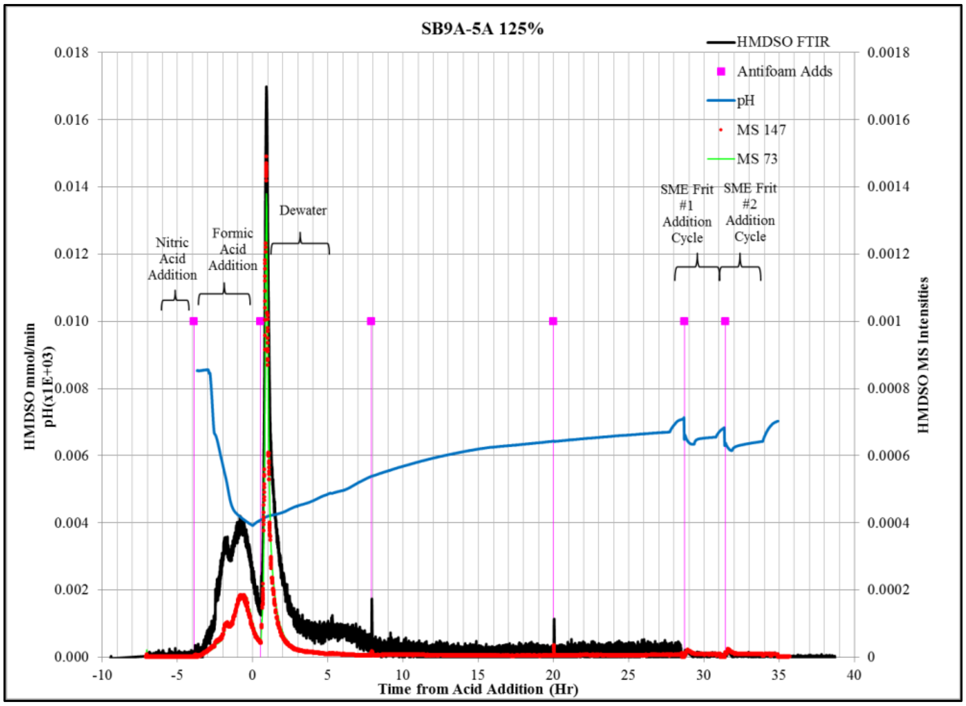


Figure 3-3. SB9A-5A HMDSO Concentration in Off Gas

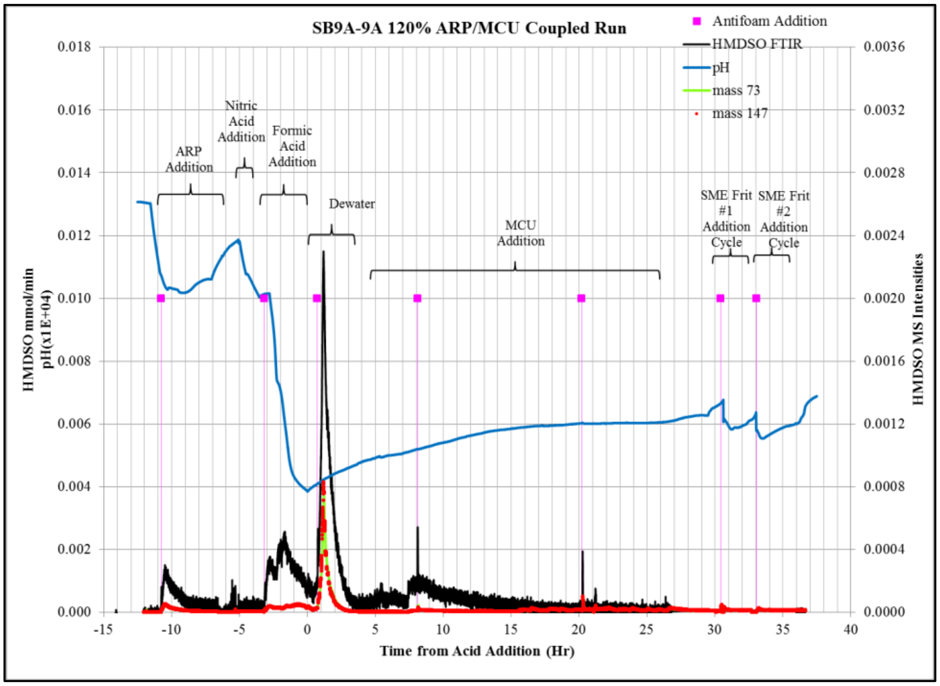


Figure 3-4. SB9A-9A HMDSO Concentration in Off Gas

During SB9A-10A two antifoam additions were made at 4x the DWPF scaled amount. The increased additions are noted by higher antifoam addition markers in **Figure 3-5** and **Figure 3-6**.

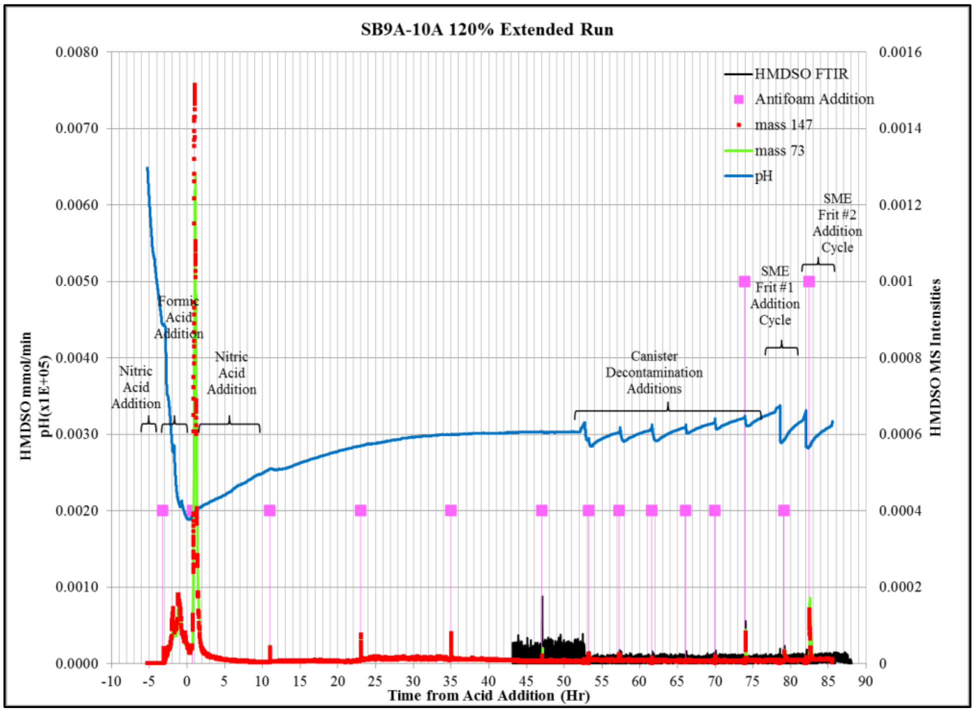


Figure 3-5. SB9A-10A HMDSO Concentration in Off Gas

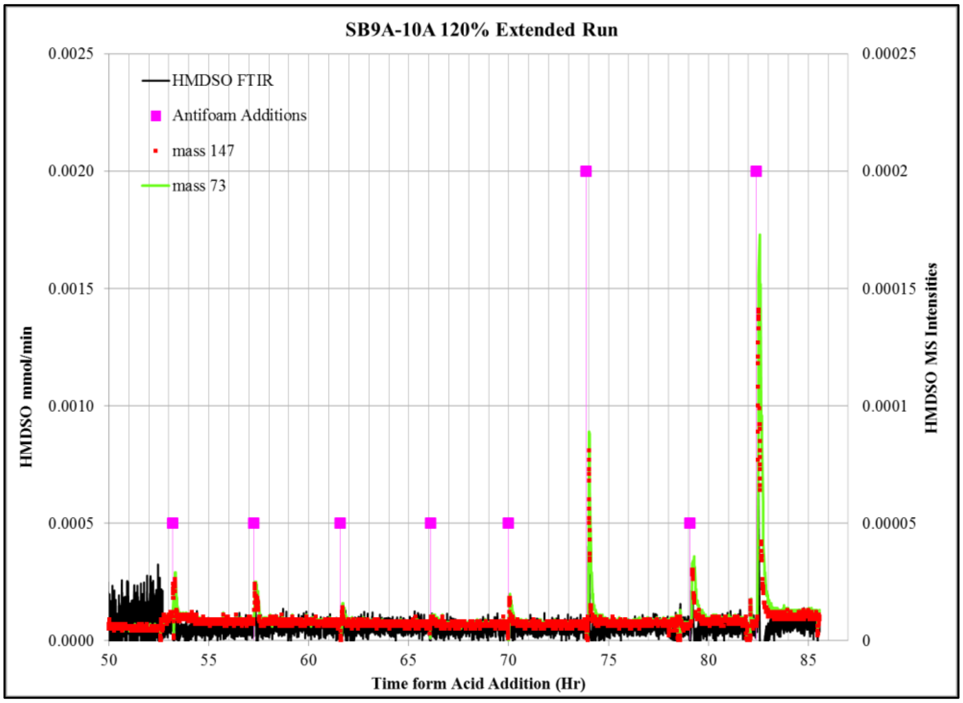


Figure 3-6. SB9A-10A SME HMDSO Concentration in Off Gas

Using the actual antifoam additions seen in **Table 3-3** through **Table 3-5** the peak release rate of HMDSO per gram of antifoam can be determined.

Table 3-6. Peak Release Rates of HMDSO for Antifoam Additions at Different Stages of Processing

	SB9A-1A, mmol/min/g AF	SB9A-3A, mmol/min/g AF	SB9A-5A, mmol/min/g AF	SB9A-9A, mmol/min/g AF
ARP	N/A	N/A	N/A	0.0052
Post Nitric Acid Addition	0.0180	0.0075	0.0054	0.0046
Post Formic Acid Addition	0.0195	0.0182	0.0217	0.0137
Conflux Addition 1	0.0016	0.0016	0.0033	0.0032
Conflux Addition 2	0.0017	0.0014	0.0022	0.0023
SME #1 Addition	0.0003	0.0005	0.0006	N/A
SME #2 Addition	0.0005	0.0004	0.0006	N/A

Table 3-7. Peak Release Rates of HMDSO for Antifoam Additions at Different Stages of SME Processing in SB9A-10A

	Canister Decon. #1	Canister Decon. #2	Canister Decon. #3	Canister Decon. #4	Canister Decon. #5	Canister Decon. #6	SME #1 Addition	SME #2 Addition
SB9A-10A, mmol/min/g AF	0.0007	0.0008	0.0007	0.0007	0.0008	0.0006[d]	0.0005	0.0004[d]

[d] The antifoam addition was added at 4x the scaled antifoam mass.

Measurements that were not taken because either the FTIR was not utilized during that portion of the run or the activity was not performed are denoted by none associated (N/A). The total quantifiable HMDSO released between antifoam additions can be seen in **Table 3-8** and **Table 3-9**. The limit of quantification (LOQ) for each run is equivalent to the confidence interval (CI) associated with the run. The CI is also listed in ppmv in **Table 3-10** and **Table 3-11** below. The FTIR measurement CI values included in this report are half-widths of the intervals at the 95% confidence level. Measurements below the LOQ are within the noise of signal and were not included in the integration.

Table 3-8. Total HMDSO Released between Antifoam Additions during SRAT Processing

	CI, mmol/min	**Starting, mmol**	**ARP, mmol**	**Post Nitric Acid Addition, mmol**	**Post Formic Acid Addition, mmol**	**1st Conflux Addition, mmol**	**2nd Conflux Addition, mmol**
SB9A-1A	3.59E-04	0.001	N/A	1.079	0.689	0.002	0.003
SB9A-3A	2.29E-04	0.000	N/A	0.637	0.612	0.157	0.008
SB9A-5A	3.59E-04	0.000	N/A	0.563	0.838	0.021	0.0011
SB9A-9A	3.18E-04	0.000	0.088	0.309	0.598	0.174	0.006

Table 3-9. Total HMDSO Released between Antifoam Additions in SME

Run	**CI, mmol/min**	**Canister Decon. #1, mmol**	**Canister Decon. #2, mmol**	**Canister Decon. #3, mmol**	**Canister Decon. #4, mmol**	**Canister Decon. #5, mmol**	**Canister Decon. #6, mmol**	**SME #1 Addition, mmol**	**SME #2 Addition, mmol**	**Cooling Down from 70 °C, mmol**
SB9A-1A	1.03E-04	N/A						0.001	0.002	0.000
SB9A-3A	6.88E-05							0.001	0.003	0.000
SB9A-5A	9.65E-05							0.006	0.007	0.001
SB9A-10A	6.53E-05	0.003	0.006	0.006	0.004	0.005	0.007[e]	0.006	0.016[e]	0.005

[e] This antifoam addition was added 4x the scaled antifoam mass

The ‘starting’ column in **Table 3-8** denotes the sum of the quantifiable HMDSO released prior to acid addition. No antifoam has been added to the sludge before or during this point in the CPC experiment; therefore, the FTIR signal associated with this stage is considered the background. The ‘cooling down from 70 °C’ column in **Table 3-9** denotes the sum of the quantifiable HMDSO released once the sludge temperature is cooled below 70 °C at the end of the run and until the experiment was shut down or the vessel was opened to sample the sludge. There was some variance as to what temperature the integration is stopped at. The maximum concentration of HMDSO released during the SRAT and SME are detailed in **Table 3-10** and **Table 3-11**. The peak times were included to better correlate to the off gas graphs presented. The FTIR was used for the SRAT cycle of SB9A-9A and then switched to collect date from SB9A-10A SME cycle.

Table 3-10. Maximum Peak HMDSO in SRAT

Run	**Percent Acid Stoichiometry**	**Max Peak, ppmv**	**Antifoam Added, g**	**Peak time, hr after acid addition**	**Peak HMDSO, mmol/min**	**Peak, mmol/min/g AF**	**CI, ppmv**	**CI, mmol/min/g AF**
SB9A-1A	145%	375	0.7856	2.511	0.0153	0.0195	8.78	0.0005
SB9A-3A	130%	347	0.7814	0.849	0.0142	0.0182	5.57	0.0003
SB9A-5A	125%	381	0.7822	0.906	0.0170	0.0217	8.05	0.0005
SB9A-9A	120%	257	0.8409	1.178	0.0115	0.0137	7.12	0.0004
SB9A-10A	120%	N/A						

The maximum peak in the SRAT consecutively occurred after acid addition and upon starting boiling. Equipment issues after completing acid addition caused delay in reaching boiling SB9A-1A and SB9A-9A. It is unknown if the equipment issues have influenced HMDSO release concentration.

Table 3-11. Maximum Peak HMDSO in SME

Run	Percent Acid Stoichiometry	Max Peak, ppmv	Antifoam Added, g	Peak time, hr after acid addition	Peak HMDSO, mmol/min	Peak, mmol/min/g AF	CI, ppmv	CI mmol/min/g AF
SB9A-1A	145%	18.5	0.4361	34.830	0.0002	0.0005	8.78	0.0002
SB9A-3A	130%	17.4	0.4367	29.970	0.0002	0.0005	5.57	0.0002
SB9A-5A	125%	21.6	0.4394	27.525	0.0003	0.0006	8.05	0.0002
SB9A-9A	120%	N/A						
SB9A-10A	120%	64.1	1.7706	82.490	0.0007	0.0004	5.93	0.00004

SB9A-10A contained the six canister decontamination additions and dewaters prior to the two frit additions. The maximum peak in the SME is independent of the frit addition timing. The first frit addition resulted in the maximum peak in the SME for runs SB9A-3A and SB9A-5A, the second frit addition resulted in the maximum peak for SB9A-1A. The 4x the scaled amount of antifoam added in SB9A-10A resulted in the second fit addition being the maximum peak.

3.2 SVOA and VOA Results and Discussion

The results of the antifoam degradation products found in condensate and product material can be seen in Table 3-12 through Table 3-16. The total actual quantity of antifoam added between samples is also listed. The method detection limit for both VOA and SVOA is 0.25 mg/L. The measurement analytical uncertainty is 20%.

Table 3-12. SB9A-1A through SB9A-3A Antifoam Degradation Product Results in Condensate and Product Samples

Run		Initial MWWT	MWWT Post Nitric	MWWT Post Formic	SRAT Dewater	SRAT Product	MWWT Post SRAT Cycle	FAVC Post SRAT Cycle	Scrubber Solution Post SRAT Cycle	SME 1st Frit Dewater	SME 2nd Frit Dewater	SME Combined Dewater	SME Product	FAVC Post SME Cycle	Scrubber Solution Post SME Cycle
SB9A-1A	Antifoam, g	N/A	N/A	0.787	0.786	1.085	N/A	N/A	N/A	0.867	N/A	N/A	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	< 0.25	0.7	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
	HMDSO (SVOA), mg/L	< 0.25	< 0.25	1.4	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
	Propanal (VOA), mg/L	< 0.25	< 0.25	< 0.25	3.85	< 0.25	0.8	< 0.25	0.9	5.6	9.1	7.5	0.45	3.9	1.3
	TMS (SVOA), mg/L	1.5	13	31	30	< 0.25	18	18	18	18	15	19	< 0.25	25	24
SB9A-2A	Antifoam, g	N/A	N/A	0.781	0.782	1.030	N/A	N/A	N/A	0.419	0.449	N/A	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	N/A	< 0.25	< 0.25	< 0.25
	HMDSO (SVOA), mg/L	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	N/A	< 0.25	< 0.25	< 0.25
	Propanal (VOA), mg/L	0.47	0.4	< 0.25	1.4	0.35	2.5	< 0.25	< 0.25	2.5	2.5	N/A	2.2	2.4	0.31
	TMS (SVOA), mg/L	5.9	10	58	17	< 0.25	18	26	24	15	13	N/A	13	14	20
SB9A-3A	Antifoam, g	N/A	N/A	0.779	0.781	1.044	N/A	N/A	N/A	0.437	0.444	N/A	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	N/A	0.87	< 0.25	0.35	< 0.25	< 0.25	0.25	< 0.25	< 0.25	N/A	< 0.25	< 0.25	< 0.25
	HMDSO (SVOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	N/A	< 0.25	< 0.25	< 0.25
	Propanal (VOA), mg/L	< 0.25	N/A	0.23	3.1	1.7	< 0.25	< 0.25	0.45	9.2	14	N/A	< 0.25	8.5	0.45
	TMS (SVOA), mg/L	11	N/A	26	23	12	17	20	16	16	16	N/A	< 0.25	15	12

Table 3-13. SB9A-4A through SB9A-6A Antifoam Degradation Product Results in Condensate and Product Samples

Run		Initial MWWT	MWWT Post Nitric	MWWT Post Formic	SRAT Dewater	SRAT Product	MWWT Post SRAT Cycle	FAVC Post SRAT Cycle	Scrubber Solution Post SRAT Cycle	SME 1st Frit Dewater	SME 2nd Frit Dewater	SME Combined Dewater	SME Product	FAVC Post SME Cycle	Scrubber Solution Post SME Cycle
SB9A-4A	Antifoam, g	N/A	N/A	0.344	0.343	0.486	N/A	N/A	N/A	N/A	N/A	0.366	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	N/A	0.7	0.25	N/A	< 0.25	< 0.25	N/A	N/A	N/A	< 0.25	N/A	N/A	N/A
	HMDSO (SVOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	N/A	< 0.25	< 0.25	N/A	N/A	N/A	< 0.25	N/A	N/A	N/A
	Propanal (VOA), mg/L	< 0.25	N/A	< 0.25	1.9	N/A	1.6	< 0.25	N/A	N/A	N/A	16	N/A	N/A	N/A
	TMS (SVOA), mg/L	11	N/A	18	16	N/A	14	15	N/A	N/A	N/A	15	N/A	N/A	N/A
SB9A-5A	Antifoam, g	N/A	N/A	0.782	0.783	1.05	N/A	N/A	N/A	0.4373	0.4374	N/A	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	N/A	< 0.25	N/A	0.5
	HMDSO (SVOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	N/A	< 0.25	N/A	< 0.25
	Propanal (VOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	0.5	1.2	0.5	0.63	9.5	10	N/A	3.0	N/A	< 0.25
	TMS (SVOA), mg/L	0.77	N/A	14	0.49	7.0	11	9.7	13	4.8	4.6	N/A	< 0.25	N/A	13
SB9A-6A	Antifoam, g	N/A	N/A	0.780	0.783	1.043	N/A	N/A	N/A	0.443	0.444	N/A	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	N/A	1.9	2.0	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	N/A	< 0.25	N/A	< 0.25
	HMDSO (SVOA), mg/L	< 0.25	N/A	0.27	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	N/A	< 0.25	N/A	< 0.25
	Propanal (VOA), mg/L	0.45	N/A	0.96	4.2	0.5	< 0.25	< 0.25	< 0.25	1.0	2.4	N/A	1.0	N/A	0.7
	TMS (SVOA), mg/L	< 0.25	N/A	22	< 0.25	0.5	6.2	8.8	3.9	5.7	6.2	N/A	< 0.25	N/A	4.1

Table 3-14. SB9A-7A through SB9A-8A Antifoam Degradation Product Results in Condensate and Product Samples

Run		**Initial MWWT**	**MWWT Post Nitric**	**MWWT Post Formic**	**SRAT Dewater**	**SRAT Product**	**MWWT Post SRAT Cycle**	**FAVC Post SRAT Cycle**	**Scrubber Solution Post SRAT Cycle**	**SME 1st Frit Dewater**	**SME 2nd Frit Dewater**	**SME combined Dewater**	**SME Product**	**FAVC Post SME Cycle**	**Scrubber Solution Post SME Cycle**
SB9A-7A	Antifoam, g	N/A	N/A	0.322	0.328	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	N/A	< 0.25	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	HMDSO (SVOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	N/A	< 0.25	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Propanal (VOA), mg/L	0.31	N/A	0.3	1.0	N/A	0.85	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	TMS (SVOA), mg/L	0.29	N/A	8.7	5.3	N/A	9.3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
SB9A-8A	Antifoam, g	N/A	N/A	0.326	0.443	N/A	0.229	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	N/A	< 0.25	0.55	N/A	< 0.25	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	HMDSO (SVOA), mg/L	< 0.25	N/A	< 0.25	< 0.25	N/A	< 0.25	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Propanal (VOA), mg/L	0.28	N/A	0.34	4.8	N/A	1.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	TMS (SVOA), mg/L	< 0.25	N/A	16	6.0	N/A	3.7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table 3-15. SB9A-9A Antifoam Degradation Product Results in Condensate and Product Samples

Run		**Initial MWWT**	**MWWT Post Formic**	**SRAT Dewater**	**MCU Dewater Bottle 1**	**MCU Dewater Bottle 2**	**SRAT Product**	**MWWT Post SRAT Cycle**	**FAVC Post SRAT Cycle**	**Scrubber Solution Post SRAT Cycle**	**SME 1st Frit Dewater**	**SME 2nd Frit Dewater**	**SME Product**	**Scrubber Solution Post SME Cycle**
SB9A-9A	Antifoam, g	N/A	0.8484	0.8409	N/A	0.8499	0.8413	N/A	N/A	N/A	0.622	0.2079	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	<0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
	HMDSO (SVOA), mg/L	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
	Propanal (VOA), mg/L	< 0.25	< 0.25	3.3	2.6	2.9	11	0.93	1.2	0.95	21	5.5	11	0.81
	TMS (SVOA), mg/L	< 0.25	0.4	14	4.9	2.5	< 0.25	5.6	8.5	9.2	4.3	4.7	< 0.25	5.3

In SB9A-9A, two 3.5 L vessels were used to collect the MCU dewater, both were sampled. During canister decontamination in SB9A-10A, each canister was dewatered into a 500 mL bottle before being added to a 3.5 L vessel. A sample was taken from the 500 mL bottle after dewatering canister 3 and canister 6. At the end of the canister decontamination additions, a sample was pulled from the 3.5 L vessel containing the composite dewaters.

Table 3-16. SB9A-10A Antifoam Degradation Product Results in Condensate and Product Samples

Run		**Initial MWWT**	**MWWT Post Formic**	**SRAT Dewater**	**SRAT Product**	**MWWT Post SRAT Cycle**	**FAVC Post SRAT Cycle**	**Scrubber Solution Post SRAT Cycle**	**3rd Canister Dewater**	**6th Canister Dewater**	**Composite Canister Decon. Dewater**	**SME Combined Dewater**	**SME Product**	**Scrubber Solution Post SME Cycle**
SB9A-10A	Antifoam, g	N/A	0.7732	0.7839	2.0952	N/A	N/A	N/A	0.6619	1.3319	N/A	2.2135	N/A	N/A
	HMDSO (VOA), mg/L	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
	HMDSO (SVOA), mg/L	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
	Propanal (VOA), mg/L	< 0.25	< 0.25	2.4	11	1.2	2.2	1.2	3.7	4.4	0.86	42	11	19
	TMS (SVOA), mg/L	< 0.25	13	14	0.58	5.9	12	2.1	2	10	< 0.25	< 0.25	0.93	1.6

MWWT condensate material was refluxed before ‘MWWT Post Nitric,’ ‘MWWT Post Formic,’ and ‘MWWT Post SRAT Cycle’ samples were taken.

Antifoam degradation products are plotted based on when the sample was pulled (see **Figure 3-7** through **Figure 3-10**). The error bars denote the analytical uncertainty of the measurement (i.e. 20%). Measurements under the limit of quantification (< 0.25 mg/L) are plotted as zero.

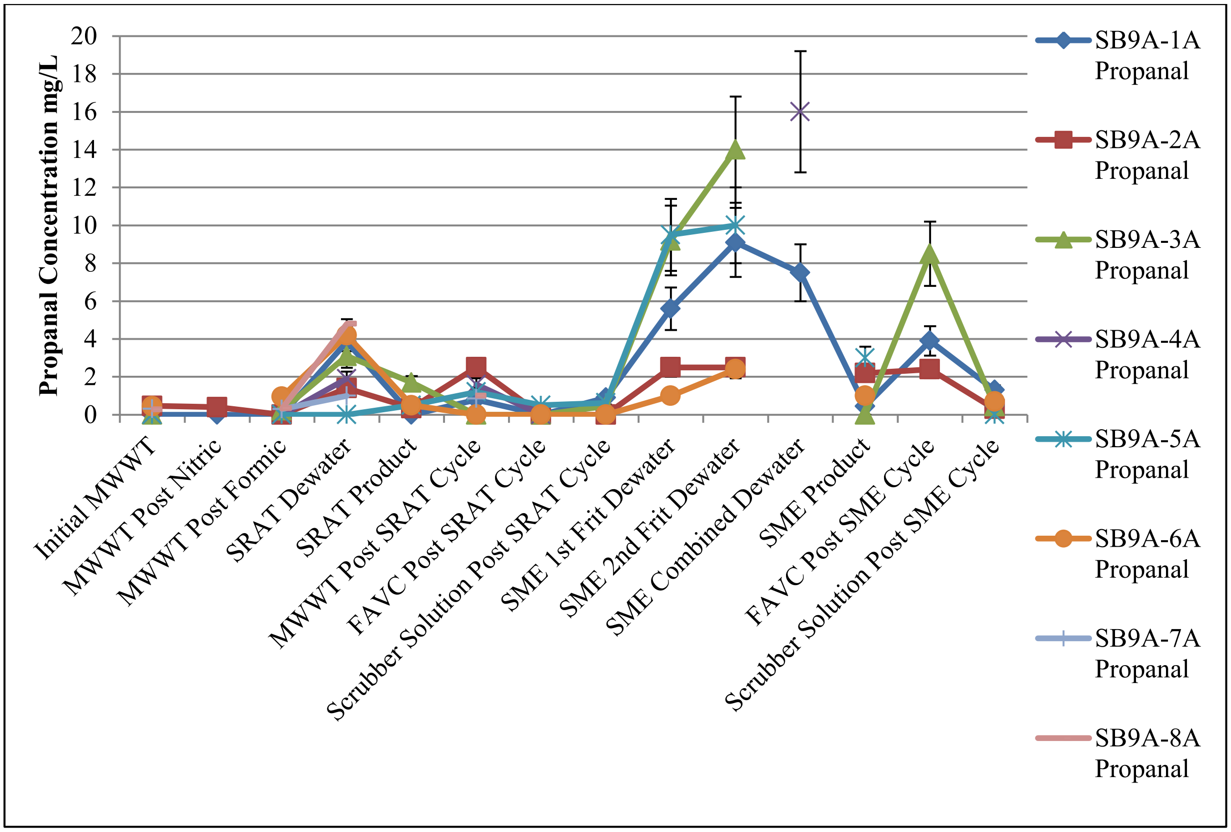


Figure 3-7. Propanal Concentration in Condensate and Slurry Samples

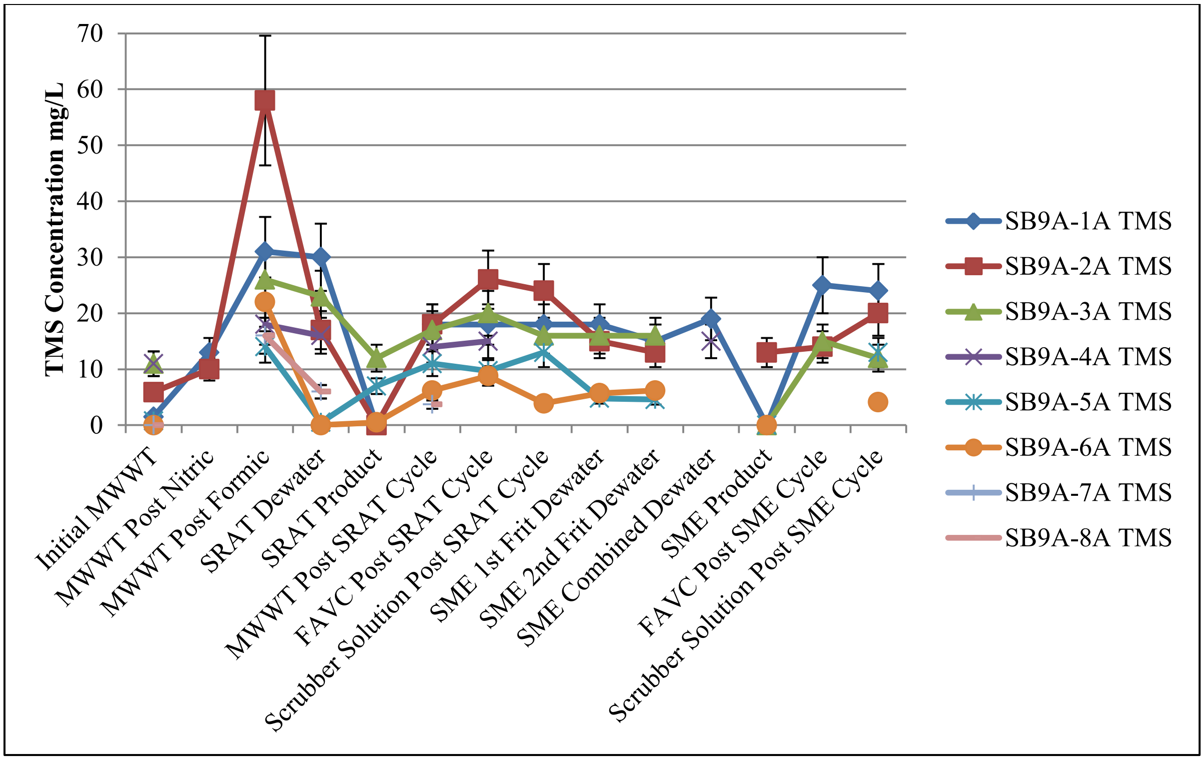


Figure 3-8. TMS Concentration in Condensate and Slurry Samples

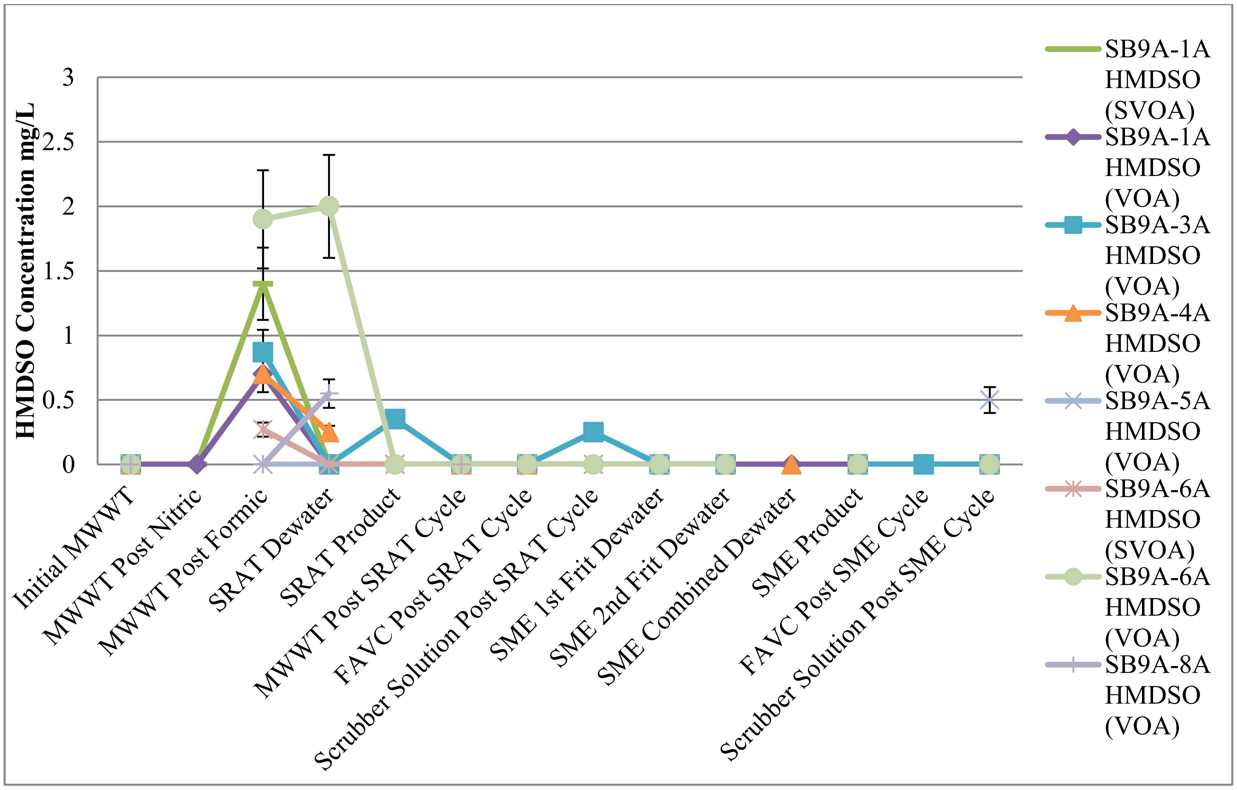


Figure 3-9. HMDSO Concentration in Condensate and Slurry Samples

As seen in **Table 3-3**, HMSDO was not detected above the limit of quantification for runs SB9A-2A, SB9A-4A, and SB9A-7A. Thus the trends were not plotted in **Figure 3-9**. HMDSO was primarily seen in the sample taken from the MWWT post formic acid addition. The average concentration was 0.47 mg/L (max 1.9 mg/L). Additionally HMDSO was detected in the SRAT Dewater for runs SB9A-4A, SB9A-6A, and SB9A-8A. The average concentration was 0.34 mg/L with a maximum concentration of 2 mg/L detected in SB9A-6A.

SB9A-9A was run at 120% minimum acid stoichiometry coupled with the ARP and MCU additions. SB9A-10A was also performed at 120%, but included six canister decontamination additions and was performed at half the DWPF design basis boil-up rate, 2500 lbs/hr steam. Antifoam degradation products for SB9A-9A and SB9A-10A can be seen in **Figure 3-10**. HMDSO was not seen above the detection limit.

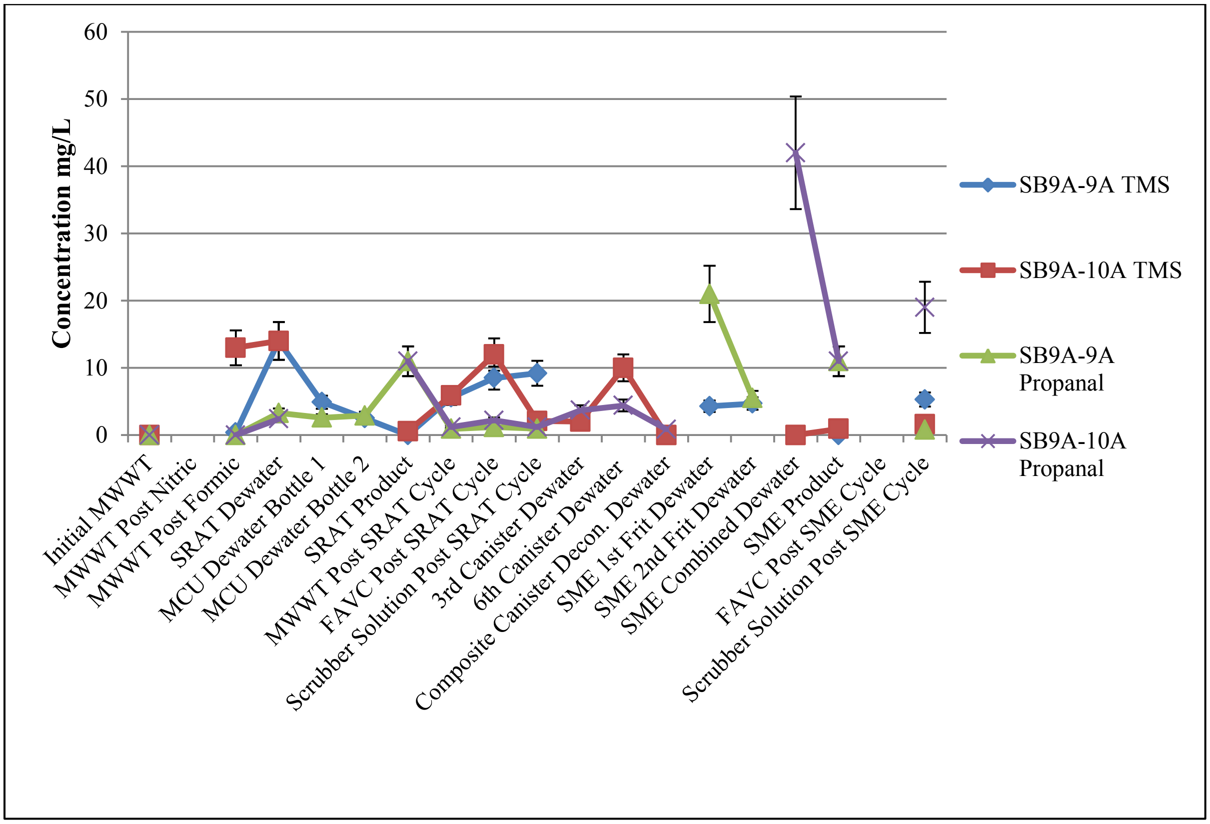


Figure 3-10. SB9A-9A and SB9A-10A Antifoam Degradation Concentration in Condensate and Slurry Samples

The maximum propanal concentration in the SRAT dewater was 4.8 mg/L (SB9A-8A), whereas the average was 2.6 mg/L. For the SME dewater the maximum propanal was 42 mg/L (SB9A-10A) and the average was 13.0 mg/L. SB9A-10A SME dewater propanal was significantly higher than all other runs. The next highest concentration was 16 mg/L in SB9A-4A. Rerunning the same SB9A-10A sample returned a similar concentration. Because the sample was taken from a container holding the total dewater it is not clear at this time why this number is an outlier.

3.3 Discussion of Results

The first large peak seen in the off gas results (**Figure 3-1** through **Figure 3-4**) occurs prior to the sampling of the MWWT Post Formic Addition, which correlates well to the HMDSO condensate trends. The next condensate sample was of the SRAT dewater, which occurs during the second large peak seen in off gas data. For some runs elevated levels of HMDSO are seen in the dewater condensate, but they are not as significant as the levels of HMDSO seen in the MWWT Post Formic Addition sample because of the dilution effects of the dewater. The smaller off gas peaks seen later in the SRAT and SME cycles indicate HMDSO is likely present in the condensate at points after antifoam addition has occurred; however, since it is sparingly soluble in water (0.933 mg/L at 23°C) it is likely not above the VOA and SVOA LOQ (0.25 mg/L) [1].

Previous antifoam degradation studies show sharp, instantaneous HMDSO peaks immediately after antifoam addition similar to the HMDSO peaks seen in this study immediately after the antifoam additions made during dewater, reflux, and the SME cycle. It is well documented in literature that this antifoam is most stable at neutral pHs [7-11]. Results of Knoche et. al demonstrate degradation rates of the primary antifoam component increases as the solution becomes more basic and especially more acidic [9]. In the study, degradation was not significant at a pH between 6 and 8 at 24 +/- 1 °C [9]. Degradation was seen during all other pHs studied; however, the degradation in acidic pHs was more significant than when exposed to alkaline conditions [9]. The same study also evaluated the effect of temperature, between 25 and 35 °C, on degradation. A slight increase in degradation rate was seen at higher temperatures, but the change in kinetics was not impacted as much as by pH. During CPC processing, as acid addition proceeds there is a significant pH change.

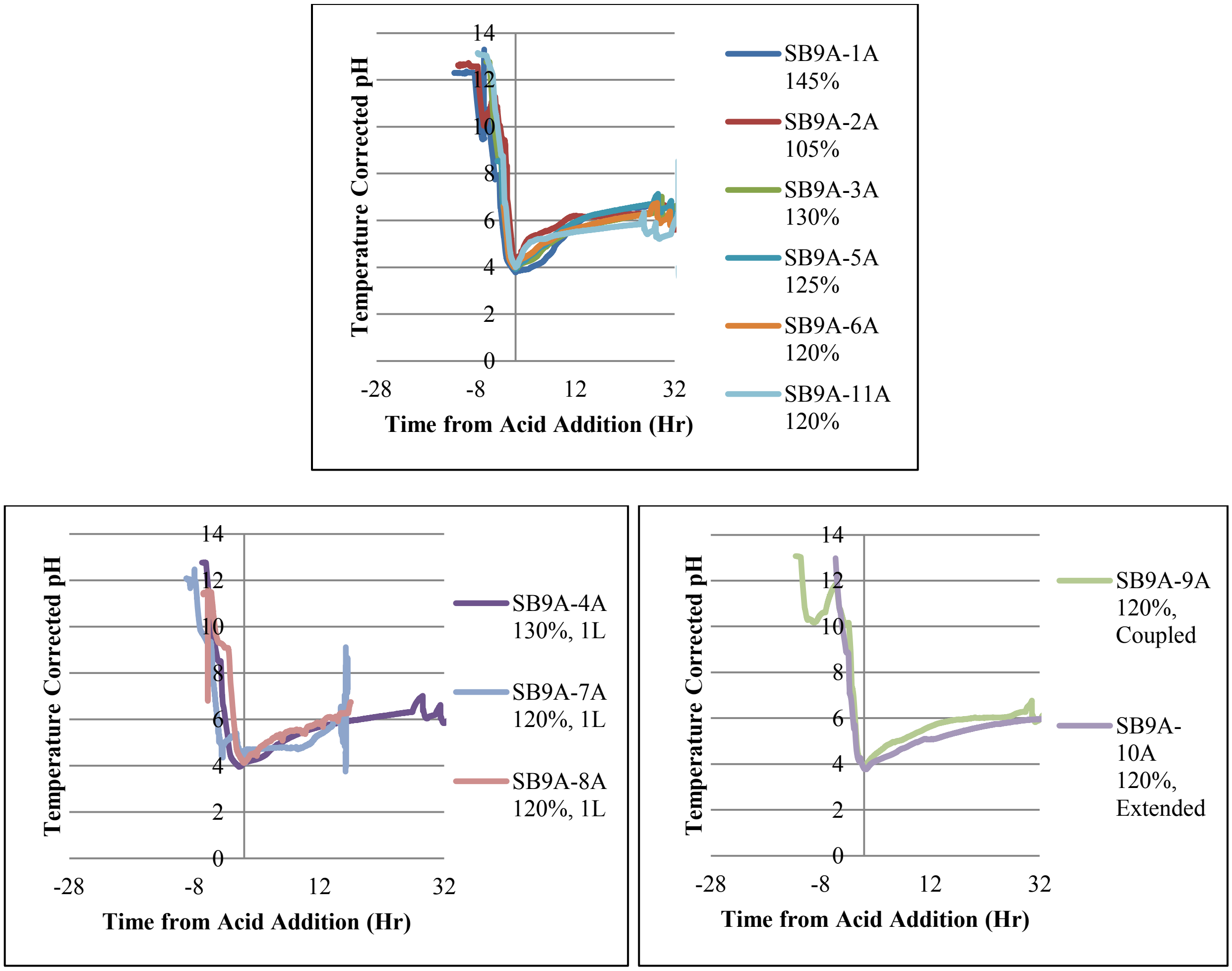


Figure 3-11. Temperature Corrected pH during CPC Runs

During nitric acid addition there is a significant pH drop and little off gas is produced. In runs without added ARP, the first antifoam addition was made after nitric acid addition is complete. During formic acid addition, the pH of the sludge drops even further to the minimum. The release of HMDSO seen in the off gas results post nitric acid addition is not as immediate as the release upon achieving boiling post formic addition. During formic acid addition, NO and NO_2 are generated, which reacts with water to form nitric acid near the liquid surface and can accelerate the antifoam degradation. The pH shift over time likely is a primary driver causing the extended release of HMDSO seen after the first antifoam addition is made. The below boiling temperature also is expected to impacts the degradation rate of the antifoam. The second antifoam addition made after formic acid addition (time after acid addition ~0-1 hour) occurs near the pH minimum (average pH minimum = 4.0). Shortly after the antifoam addition the sludge temperature is increased about 8-10°C to boiling, which would also contribute to the increased degradation. The combination of higher temperature, low pH and high NO_2 concentration combine to quickly decompose the antifoam addition post formic acid leading to the high release of HMDSO. The HMDSO concentration measured by FTIR for the post formic acid addition is consistently the maximum release observed.

Hydrolysis of the Si-O bond as a result of the free protons, H^+, has been proposed in literature studying the effects of acidity on antifoam degradation as the primary mechanism of antifoam degradation [8, 10]. It has also been proposed that antifoam could be hydrolyzed by free hydroxide, OH^-, by Snow et. al in an alkaline environment [11]. As seen in **Figure 3-12**, during acid addition H^+ becomes more available as noted by the pH change. Again, the change in pH is a result of the addition of nitric acid, formic acid, and also the CPC chemistry occurring. Some metal hydroxides and carbonates are becoming solubilized during acid addition [12]. Nitrite is being converted to N_2O and also being reduced to NO by formic acid prior to the completion of acid addition [12]. Further, the oxidation of formic acid causes the evasion of CO_2. Future study could evaluate the effects of sludge pH independent of CPC chemistry to further revise the antifoam addition strategy in an effort to minimize degradation.

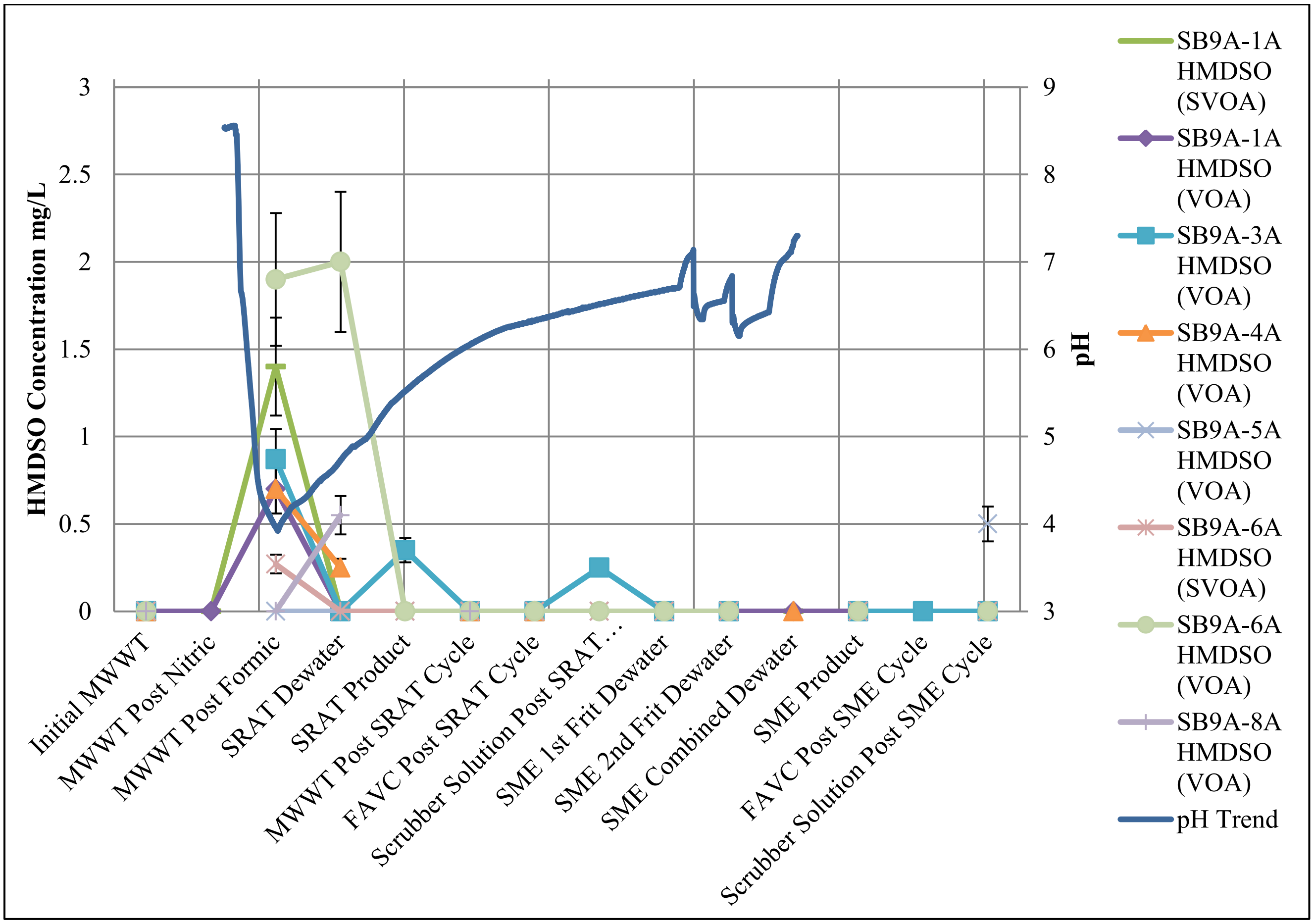


Figure 3-12. pH Trend and HMDSO Concentration

The maximum HMDSO release rate per mass of antifoam occurred as a result of the post formic acid addition in the SRAT cycle. The highest rate of HMDSO release, 0.0217 mmol/min/gram antifoam was observed in the SRAT cycle of SB9A-5A. The highest release rate of HMDSO in the SME was 0.0006 mmol/min/gram antifoam in SB9A-5A.

During the experiments, significant avulsion of hydrogen was not observed during the first two substantial HMDSO releases. HMDSO and hydrogen are flammable constituents in the off gas. Thus under the process conditions evaluated the peak contribution of HMDSO does not have to be compounded with the peak contribution of hydrogen when assessing the contribution to the LFL.

The peak release rate per gram of antifoam added data presented in this report assumes all HMDSO generated is a result of the most immediate add. Although conservative, it neglects residual antifoam that is causing sustained release of HMDSO. A slight increase in the FTIR measurement is seen between the start and end of the runs. Increase in the FTIR measurements is best seen in **Figure 3-6**. The amount of residual antifoam in the sludge is likely higher in SB9A-10A than other runs due to the 4x antifoam additions made later in the process. The 'starting' and 'cooling down from 70 °C' columns in **Table 3-8** and **Table 3-9** can be used to compare the sustained release of degradation products as a result of residual antifoam in the sludge. Temperature effects during heating were not expected because no antifoam had been added. A sludge temperature below 70 °C was chosen to ensure enough data points were available, although it was expected that the temperature effects could bias the release higher than measurements taken at room temperature. The release rate was also determined (see **Table** 3-17). Calculations indicate that residual antifoam in the sludge will cause a minimal avulsion of HMDSO over time. The sustained release rates could be better defined by performing additional experiments at a lower purge rate.

Table 3-17. Background HMDSO

Run	Starting, mmol	Starting, mmol/min	Cooling Down from 70 °C, mmol	Cooling Down from 70 °C, mmol/min	Total AF Added during the Run, g
SB9A-1A	0.001	1.54E-06	0.002	4.29E-05	3.525
SB9A-3A	0.000	1.20E-06	0.000	9.80E-06	3.4845
SB9A-5A	0.000	0.00E+00	0.001	4.31E-05	3.489
SB9A-9A	0.000	0.00E+00	N/A		4.210
SB9A-10A	N/A		0.005	5.21E-05	7.860

Propanal results indicate that it is preferentially released during dewater for both the SRAT and SME cycles (see **Figure 3-7**). Propanal requires breaking C-C bonds, which have a higher bonding enthalpy than Si-C or Si-O. During dewater and reflux the sludge is boiling. The additional latent energy could aid in overcoming the bonding enthalpy allowing propanal to be formed in higher concentrations than at lower system energies. Further, formation of propanal is more likely in residual antifoam within the sludge or as other antifoam degradation products fragments are formed. This is would explain why propanal was seen in some of the SRAT and SME products. In all cases except for SB9A-3A there is a higher concentration of propanal in the SME product than that in the SRAT product.

TMS appears to volatilize consistently throughout the CPC run and is collected in the condensate. TMS was detected in the sludge in SB9A-2A (SME Product), SB9A-3A (SRAT Product), SB9A-5A (SRAT Product), SB9A-6A (SRAT Product), and SB9A-10A (SRAT Product). The average TMS in the SRAT Product was 2.9 mg/L and the maximum was 12 mg/L (SB9A-3A). The average TMS concentration in the SRAT and SME Dewater was 12.6 mg/L and 9.9 mg/L, respectively. The maximum concentrations were 30 mg/L and 19 mg/L in the SRAT and SME Dewater respectively. The higher levels of TMS seen in Table 3-12 through Table 3-16 are consistent with the properties of TMS being both volatile and water soluble, and thus TMS has a more significant build up in the condensate. The ammonia scrubber recirculates condensate downstream of the MWWT in the 4-L laboratory scale setup. TMS, average concentration of 14.0 mg/L, was significantly greater than propanal (avg. 0.57 mg/L) and HMDSO (< 0.25 mg/L) in the ammonia scrubber solution sampled after the SRAT cycle. TMS is a small fraction of the head of the antifoam chain, and is thus most easy to break off.

TMS and propanal were detected in some of the initial MWWT samples, which are pulled before the runs start. Although glassware is soaked in concentrated nitric acid overnight, residual antifoam degradation products can occur. TMS especially in known to be difficult to remove from glassware.

It is important to note that the laboratory scale condensate system is more efficient than the one in DWPF. The lab scale condensers are oversized, the gas flow path is smaller, and the system is tested each run to ensure leaks are minimized.

In future study, the combination of off gas and sample results collected over the course of the runs could be used to evaluate the percent conversion to antifoam degradation products by attempting to resolve the antifoam mass balance. Due to the multitude of formation pathways for antifoam fragments it was beyond the scope of this report, but could be attempted in a Phase II.

4.0 Conclusions

Results indicate the highest concentration of antifoam degradation products in the off gas likely occurs as a result of antifoam additions made during acid addition and shortly after while the pH is well below 6. The maximum release rate of HMDSO in the SRAT was 0.0217 mmol/min/g antifoam and 0.0006 mmol/min/gram antifoam in the SME. Both occurred in run SB9A-5A. Propanal and TMS were detected in the sludge product. Formation of propanal is most likely to occur when boiling and appears to be slightly less volatile than HMDSO or TMS. The average propanal concentration in the SRAT and SME dewater was 2.6 mg/L and 13 mg/L, respectively. TMS is most likely to build up in the condensate. The average TMS concentration in the SRAT and SME dewater was 12.6 mg/L and 9.9 mg/L; however, TMS was observed in higher concentrations in condensate samples where antifoam degradation products could build up during the run.

Future work could be done to perform a mass balance to evaluate degradation percentages and conversations. Also, additional experiments varying the sludge pH more independent of CPC chemistry could be performed to further revise the antifoam addition strategy in an effort to minimize degradation.

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