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SRNL Sludge Batch 10 Qualification SRAT and SME Off-Gas Results

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) completed a small-scale demonstration of the Defense Waste Processing Facility (DWPF) Chemical Process Cell (CPC) utilizing the nitric-glycolic acid (NGA) flowsheet to support Sludge Batch 10 (SB10) qualification. The demonstration utilized a Tank 51 slurry sample washed by SRNL (with added H-canyon material).

The purpose of this document is to report the observed off-gas results from the demonstration. With the NGA flowsheet, DWPF has a CPC hydrogen generation limit of 2.4×10^{-2} lb/h. The peak observed rate was nearly 90 times less than that limit during SRNL testing. Peak observed concentrations and generation rates scaled to 6,000 gallons of DWPF Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) feed are given below.

Peak Off-Gas Concentrations and Generation Rates

Gas	Unit	SRAT Cycle	SME Cycle
Carbon Dioxide	volume %	31	0.43
	lb/h	320	2.1
Nitrous Oxide	volume %	0.67	<0.05
	lb/h	4.5	<0.2
Hydrogen (DWPF limit: 2.4×10^{-2} lb/h)	ppm_v	9.0	12
	lb/h	2.7×10^{-4}	2.7×10^{-4}
Methane	ppm_v	16	110
	lb/h	3.7×10^{-3}	2.0×10^{-2}

Generation rates are scaled to 94 SCFM purge rate for the SRAT cycle and 72 SCFM for the SME cycle.

Methane was sporadically detected at low concentrations in both the SRAT and SME cycle. The source of methane generation has not been identified.

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LIST OF ABBREVIATIONS

CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
LOQ	limit of quantification
μGC	micro gas chromatograph
MWWT	mercury water wash tank
ND	not detected
NGA	nitric-glycolic acid
ppm_v	parts per million by volume
SB10	Sludge Batch 10
SCFM	standard cubic feet per minute
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TTR	technical task request
vol. %	volume percent

1.0 Introduction

Savannah River National Laboratory (SRNL) completed a small-scale demonstration of the Defense Waste Processing Facility (DWPF) Chemical Process Cell (CPC) utilizing the nitric-glycolic acid (NGA) flowsheet to support Sludge Batch 10 (SB10) qualification.[1-5] The demonstration utilized a Tank 51 slurry sample washed by SRNL[6,7]. During washing, material from H-Canyon Tanks 16.3 and 16.4 was also added.

The purpose of this document is to report the hydrogen, nitrous oxide, carbon dioxide, and methane off-gas results specified in the technical task request (TTR).[1]

2.0 Experimental Procedure

2.1 Off-Gas Measurement

Off-gas was quantified using an Agilent model 3000 micro gas chromatograph (μGC). Channel A of the instrument consists of a molecular sieve column with thermal conductivity detector. Gases quantified on channel A are hydrogen, krypton (used as a tracer), and methane. The method was optimized for quantification of small concentrations of hydrogen and methane. Oxygen and nitrogen were also detected on channel A, but cannot be accurately quantified due to saturation of the detector. Qualitative oxygen results are presented for a portion of the testing. Channel B consists of a PoraPLOT Q column with thermal conductivity detector. Gases quantified on this channel are carbon dioxide and nitrous oxide. Argon is used as the carrier gas on both channels. Note that nitric oxide does elute on a molecular sieve column, but nitric oxide readily reacts with oxygen, so any detection would be qualitative at best.

Concentrations were measured in volume % (vol. %) of the gas or parts per million by volume (ppm_v). The μGC was calibrated and checked using a calibration gas containing, nominally, 50 ppm_v hydrogen, 0.5 vol. % krypton, 100 ppm_v methane, 1 vol. % carbon dioxide, 0.5 vol. % nitrous oxide, 20 vol. % oxygen, and the balance nitrogen. This gas was chosen as it represents, approximately, the gas composition when hydrogen and methane are at their projected peaks. Ideally, calibration gas should represent the gas to be analyzed as closely as possible, thus the cal gas has low carbon dioxide. As a result, the peak carbon dioxide concentration encountered in the SB10 qualification test is a significant extrapolation of the calibration and may have a bias.

The experimental apparatus was purged with a gas containing 0.5 vol. % krypton, 20 vol. % oxygen, and the balance nitrogen. The krypton was added as an internal standard to assist in calculating the flow out of the vessel during times of high off-gas generation, may aid in identifying major off-gas in-leakage, and gives an indication that off-gas from the vessel is indeed being sampled and analyzed by the μGC.

Vessel purge rate during the demonstration was determined by scaling the applicable DWPF purge rate [94 standard cubic feet per minute (SCFM) in the Sludge Receipt and Adjustment Tank (SRAT) and 72 SCFM in the Slurry Mix Evaporator (SME)] with a 6,000 gallon sludge volume to the SRNL volume.

2.2 Off-Gas Generation Rate Calculations

Off-gas generation rates for nitrous oxide and hydrogen were calculated and scaled to a DWPF 6,000 gallon SRAT or SME cycle using the following equation.

$$Gen\ Rate_i = F_{out} \times C_i \times \frac{mol}{24.1\ L} \times MW_i \frac{g}{mol} \times \frac{lb}{454\ g} \times \frac{60\ min}{h} \times DWPF\ Scale\ Factor \qquad \text{Eq. 1}$$

where:

F_{out} = flow out of the vessel, L/min. See Equation 2 and following text for explanation.

C_i = concentration of component *i* (hydrogen, methane, nitrous oxide, or carbon dioxide) as mol fraction in the off-gas (vol. %/100 or $ppm_v/10^6$)

24.1 L/mol is the ideal gas molar volume for ideal gas at 70 °F and 1 atm, the reference conditions for the gas flow controller

MW_i = molecular weight of i (hydrogen, methane, nitrous oxide, or carbon dioxide), g/mol

DWPF Scale Factor = ratio of a 6,000 gal SRAT or SME divided by the SRNL SRAT or SME volume, as calculated and published in the respective demonstration run plan[3-5]

For the SRAT cycle, the flow out of the vessel was calculated as follows.

$$F_{out} = F_{in} \times \frac{Kr_{ave}}{Kr_t} \quad \text{Eq. 2}$$

where:

F_{in} = the flow into the vessel, L/min

Kr_{ave} = the average of multiple Kr concentrations during times of low gas generation

Kr_t = the Kr concentration at time *t*

For the SME cycle, the gas generation was minimal. Therefore, the flow out of the vessel was taken as equal to the flow into the vessel without impact, i.e. $F_{out} = F_{in}$.

The molecular weights and scale factors used in the generation rate calculations are given in Table 2-1.

Table 2-1. Molecular Weights and Scaling Factors

Parameter	Units	Value
Nitrous oxide molecular weight	g/mol	44.01
Hydrogen molecular weight	g/mol	2.016
Methane molecular weight	g/mol	16.04
Carbon dioxide molecular weight	g/mol	44.01
SRAT Cycle Scale Factor	6,000 gal/SRNL SRAT cycle starting volume (gal)	7214
SME Cycle Scale Factor	6,000 gal/SRNL SME cycle starting volume (gal)	8538

2.3 Estimation of Limits of Quantification

The limits of quantification (LOQs) for hydrogen and methane were previously estimated to be 3 and 14 ppm_v, respectively.[8] The LOQs for carbon dioxide and nitrous oxide are estimated to be 0.05 vol% and 0.03 vol%, respectively. These LOQs were determined using a method where the t-statistic is applied to the standard deviation of the results of a known concentration, the calibration gas in this case.[9] Equation 1, with $F_{out} = F_{in}$, is used to calculate the limit of quantification (in lb/h on DWPF scale) for hydrogen, nitrous oxide, and methane for the SRAT and SME cycles. Limits of quantification are presented in Table 2-2.

Table 2-2. Limits of Quantification

Gas	Unit	SRAT Cycle	SME Cycle
Carbon Dioxide	volume %	0.05	0.05
	lb/h	0.3	0.2
Nitrous Oxide	volume %	0.03	0.03
	lb/h	0.2	0.2
Hydrogen (DWPF limit: 2.4×10^{-2} lb/h)	ppm_v	3	3
	lb/h	9×10^{-5}	7×10^{-5}
Methane	ppm_v	14	14
	lb/h	4×10^{-3}	3×10^{-3}

2.4 Description of the SRNL CPC Demonstrations

For the SRNL demonstration of the first stage of the CPC process, the SRAT cycle began with mixing, purging, and heating the vessel to 93 °C per an approved run plan.[5] Nitric acid addition was then initiated. After approximately 60% of the nitric acid was added, a foamover event occurred. An attempt to resume nitric acid addition led to another foamover and the run was suspended. Per the run plan, antifoam was not to be added until after nitric acid addition was complete. In the following section, this part of the experiment is designated as the SRAT cycle Part 1.

SRNL, in consultation with Liquid Waste contractor personnel, evaluated the event and proceeded to resume the run. The evaluation and path forward is documented in a revised run plan.[4] At the resumption of the run, antifoam was added, nitric acid addition was completed, additional antifoam was added, and glycolic acid addition was completed.

At the conclusion of glycolic acid addition, another antifoam addition was made, and the vessel was taken to boiling under reflux. The purpose of this added reflux period (planned and documented in the revised run plan[4]) was to remove sludge in the off-gas line. During this cleaning reflux period, the purge rate was lowered for a brief six-minute period to prevent loss of water from the manometer. Following the cleaning reflux period, testing continued, but with removal of water to concentrate the SRAT product to the targeted weight percent total solids. After water removal, the material was boiled under reflux, as planned, to steam strip mercury. At the conclusion of the cycle a sample was taken and characterized in preparation for the SME cycle.

The SME cycle was completed per an approved SME cycle run plan.[3] The addition and removal of five canister decontamination waters, two frit additions (with rinse water), and finally water removal to concentrate the SME product were completed without incident.

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. This document, including all calculations, was reviewed by Design Verification by Document Review. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. All work, analysis, and documentation were performed with quality assurance methods commensurate with the Safety Class data requirements.

3.0 Results and Discussion

Following are subsections describing the SRAT and SME cycles with applicable off-gas plots. Each plot contains the temperature profile as the temperature is an indicator of the state of processing. For example, 93 °C indicates acid addition, and drops in temperature indicate activities such as water or frit addition.

The final subsection has a discussion on overall gas generation observations and a table with peak concentrations and generation rates.

3.1 SRAT Cycle Part 1

SRNL began purging and mixing the washed SB10 Tank 51 qualification sample per an approved run plan.[5] The material was idled at 40 °C for several hours as acid addition bottles, acid addition lines, dewater bottles, etc., were staged. The slurry was heated to 93 °C and nitric acid addition was initiated per the run plan. Plots of the carbon dioxide concentration, carbon dioxide generation rate, hydrogen concentration, and hydrogen generation rate are given in Figure 3-1, Figure 3-2, Figure 3-3, and Figure 3-4, and , respectively. Time is shown from initiating of heating from 40 °C. The qualitative measurements for oxygen concentration appeared relatively constant and are therefore not plotted. No nitrous oxide or methane was detected during this stage of processing.

During the initial nitric acid addition step of the SB10 SRAT cycle, a foamover resulted in carryover of sludge from the SRAT to the Mercury Water Wash Tank (MWWT) via the off-gas line. The event occurred after approximately 60% of the nitric acid had been added, with the sludge temperature at 93 °C and agitator set at 600 rpm. Acid addition and heating were immediately stopped. The event can be seen on the SRAT Part 1 off-gas figures at the approximately 1.75 hour time (just before the CO_2 and H_2 peaks). Upon observing the liquid level in the manometer continually increasing (approaching ~1 inch from the top, or approximately 7 inches of water pressure), the purge rate was set to zero (approximately two minutes) until the pressure stabilized. At this point, the purge was resumed, and a time out was called. SRNL management and Liquid Waste contractor personnel were notified and consulted. The decision was made to resume the demonstration (i.e., resume heating and acid addition). Heating and nitric acid addition were resumed concurrently (vessel temperature had dropped to 83 °C). Within seven minutes, a second foamover occurred resulting in additional sludge being transferred to the MWWT via the vessel off-gas line/condenser. See elevated CO_2 and H_2 at approximately 2.5 hours. Heating and acid addition were halted, and the purge rate was reduced (approximately four minutes) to prevent loss of water from the manometer. Another time out was called, with SRNL management and Liquid Waste contractor personnel notifications.

The experiment was placed in a safe configuration. After internal SRNL discussions and discussions with Liquid Waste contractor personnel, the run was resumed 22 days later. See the next section for a description of the continuation of the run.

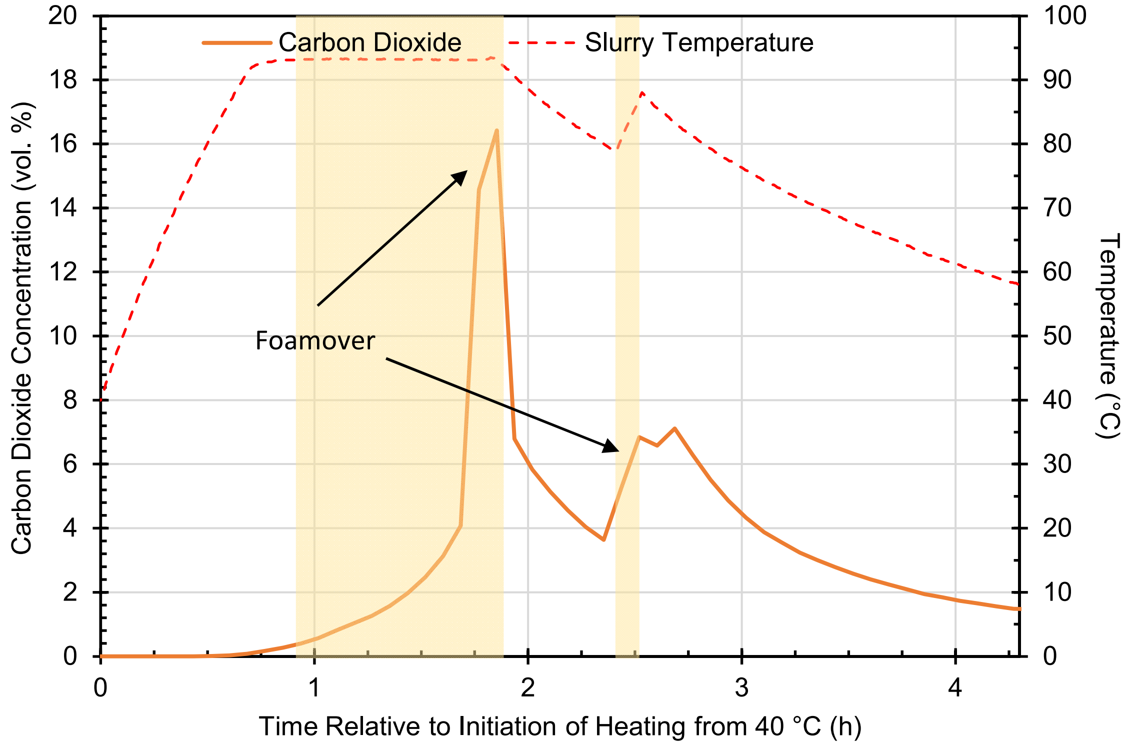

Figure 3-1. SRAT Part 1 Carbon Dioxide Concentration (shaded areas show nitric acid addition)

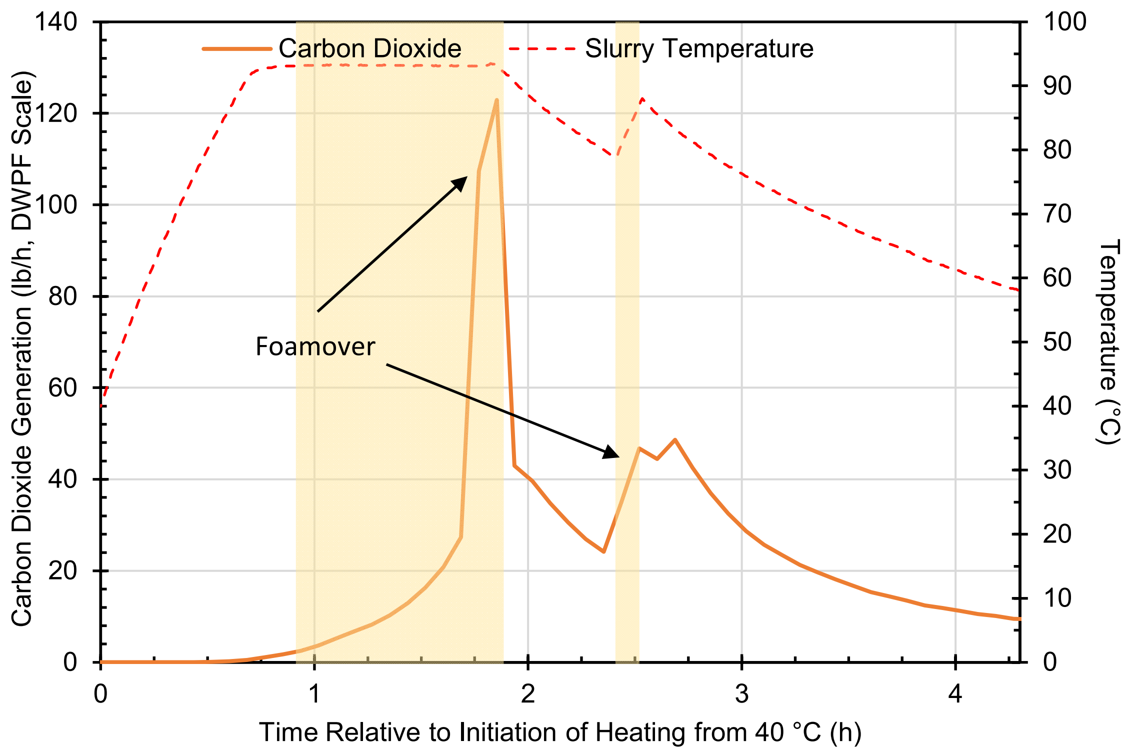

Figure 3-2. SRAT Part 1 Carbon Dioxide Generation (shaded areas show nitric acid addition)

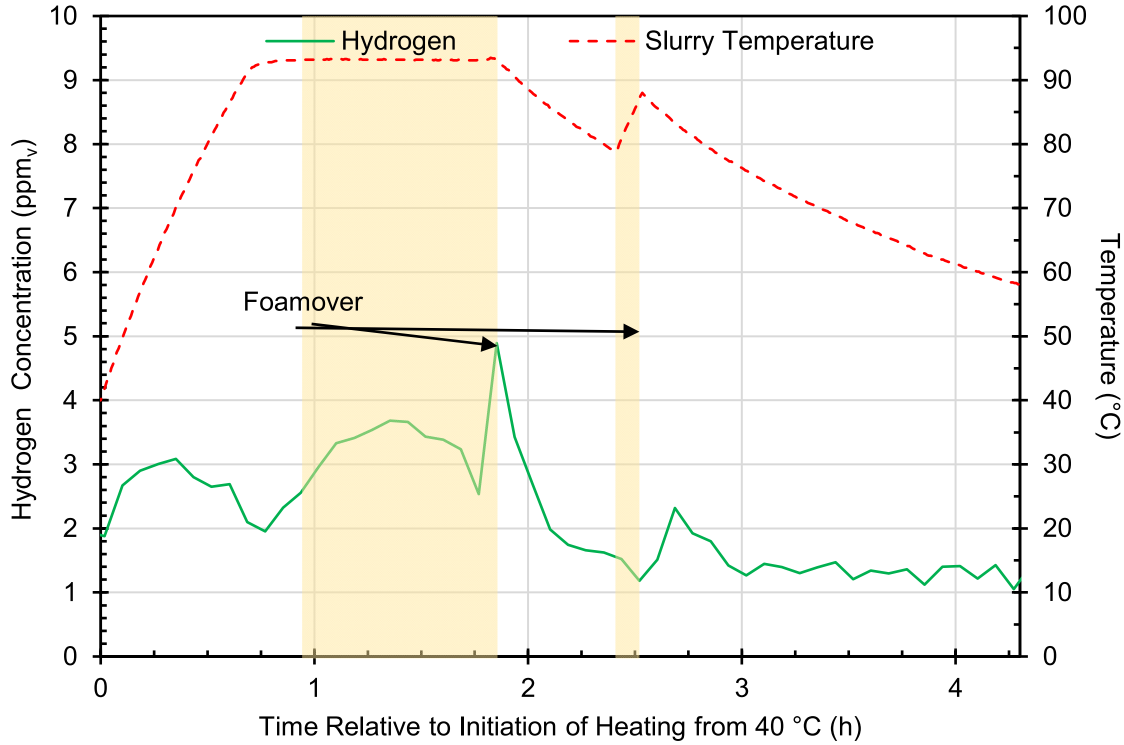

Figure 3-3. SRAT Part 1 Hydrogen Concentration (shaded areas show nitric acid addition)

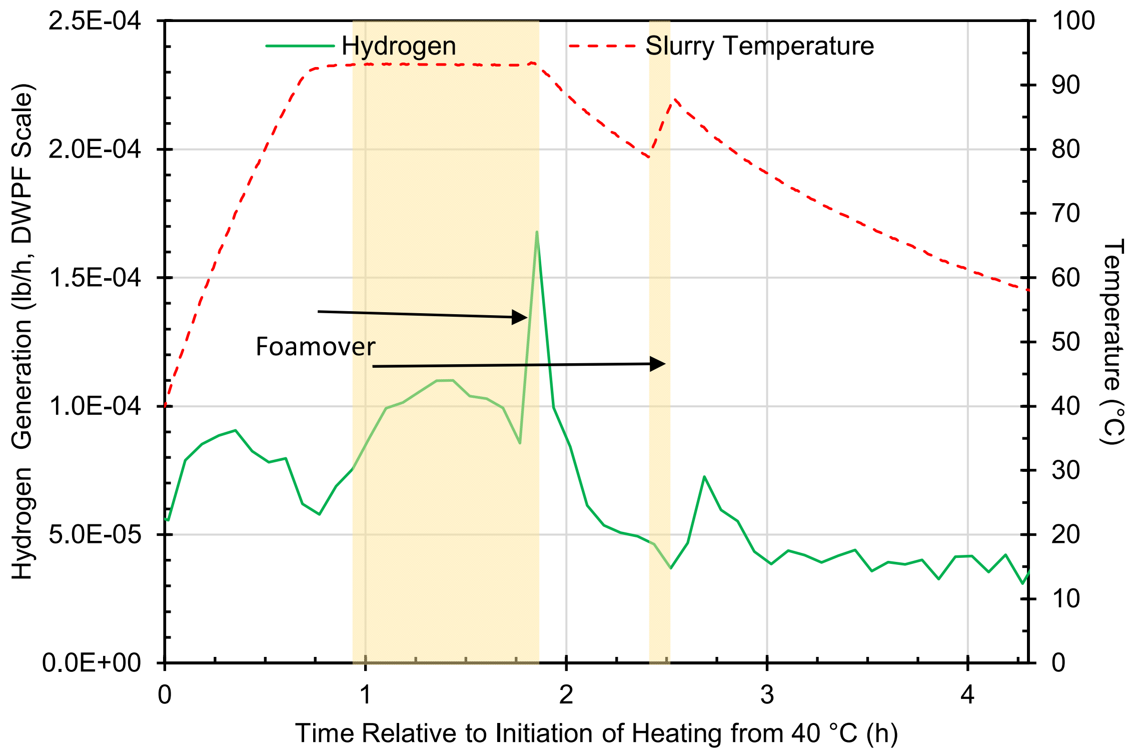

Figure 3-4. SRAT Part 1 Hydrogen Generation Rate (shaded areas show nitric acid addition)

3.2 SRAT Cycle Part 2

The SRAT cycle was resumed per a revised run plan.[4] Prior to resumption, various mixing rates were evaluated and it was determined from both visual observations and off-gas measurements (no difference in off-gas between mixing rates) that 600 rpm provided adequate mixing. Also, sludge from the MWWT was drained and added back to the vessel. The run began with the addition of antifoam, followed by heating, nitric acid addition, glycolic acid addition, boiling under reflux to "clean" the off-gas line, removal of water, and finally boiling under reflux. Because of the foamover (see above) the decision was made to add acid at a reduced rate, targeting 50% of the DWPF prototypic rate. In evaluating when each acid addition began and ended, it appears the acid addition rates were much lower than 50%. The lower addition rates may have spread out the carbon dioxide and nitrous oxide generation (i.e., lowering the peak concentrations and generation rates, as these gases are generated during acid addition and are limited by the acid reactant concentration). Hydrogen, however, is produced after nitrite destruction and thus the peak hydrogen concentration and generation rate was likely not impacted by the acid addition rate. The timeline is presented in Table 3-1.

Table 3-1. SRAT Cycle Part 2 Timeline

Elapsed Time (h)	Activity
0.0	Began heating Added Momentive™ Y-17112 antifoam during heating
1.1	Began the resumption of nitric acid addition
4.7	Completed nitric acid addition
5.2	Added Momentive™ Y-17112 Began glycolic acid addition
11.6	Completed glycolic acid addition
12.2	Added Momentive™ Y-17112 Began boiling under reflux to "steam clean" off-gas line
13.0	Purge reduced, heating paused as vessel pressure increased, sludge visible in off-gas
13.2	Purge and heating resumed, no additional pressure or visible sludge (continued to "steam clean off-gas line")
16.3	Began dewatering
19.9	Completed Dewatering
39.7	Completed reflux, thus completing the SRAT cycle

Carbon dioxide, nitrous oxide, hydrogen, and methane plots (both concentrations and generation rates) are presented in Figure 3-5, Figure 3-6, Figure 3-7, Figure 3-8, Figure 3-9, Figure 3-10, Figure 3-11, and Figure 3-12.

As can be seen in the plots, carbon dioxide was produced during acid addition. Nitrous oxide, occurring at the latter part of acid addition and into boiling, shows nitrite was being destroyed.

Hydrogen generation peaked after nitrous oxide peaked and then declined. Note that the peak in hydrogen concentration at the approximate 13 hour mark was due to reducing the purge from 368 sccm to 50 sccm for approximately six minutes during initial reflux to clean the off-gas line of sludge from the foamover described in the previous section. When the reduced purge is accounted for in the calculation, the hydrogen generation is in line with the calculated generation before and after the high concentration. See Figure 3-9 (concentration) and Figure 3-10 (generation rate).

Methane was detected for approximately one hour at near its limit of quantification of 14 ppm. The limit of quantification was determined in previous testing.[8]

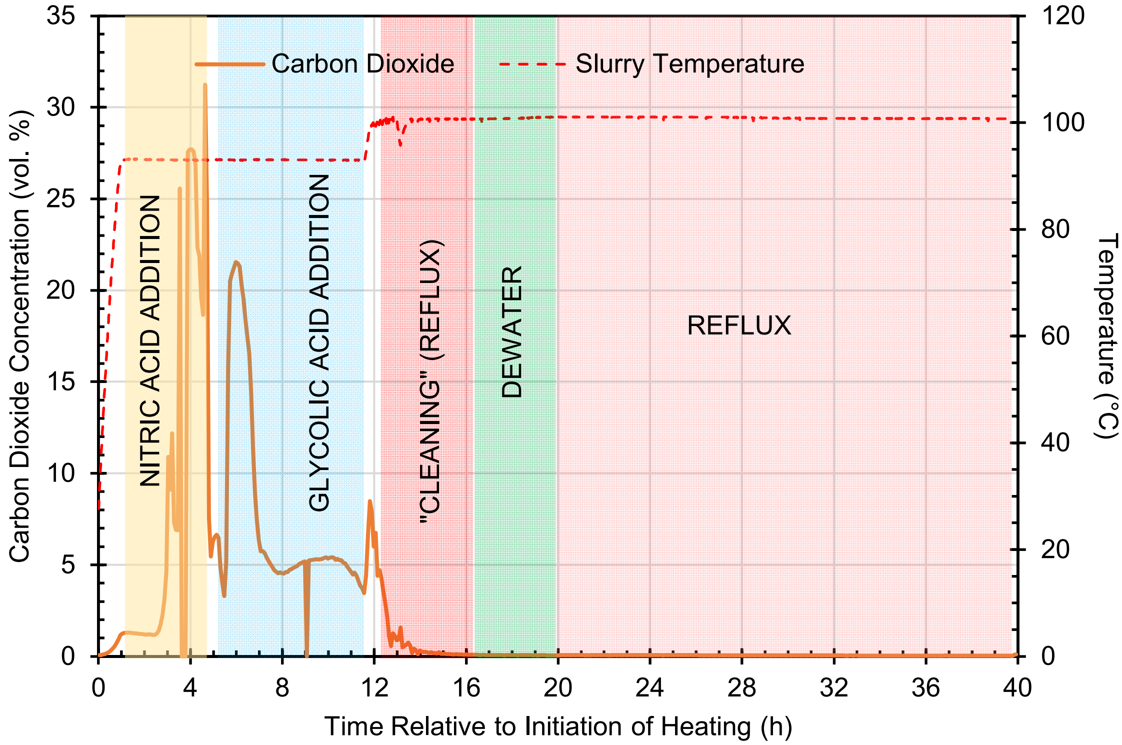

Figure 3-5. SRAT Part 2 Carbon Dioxide Concentration

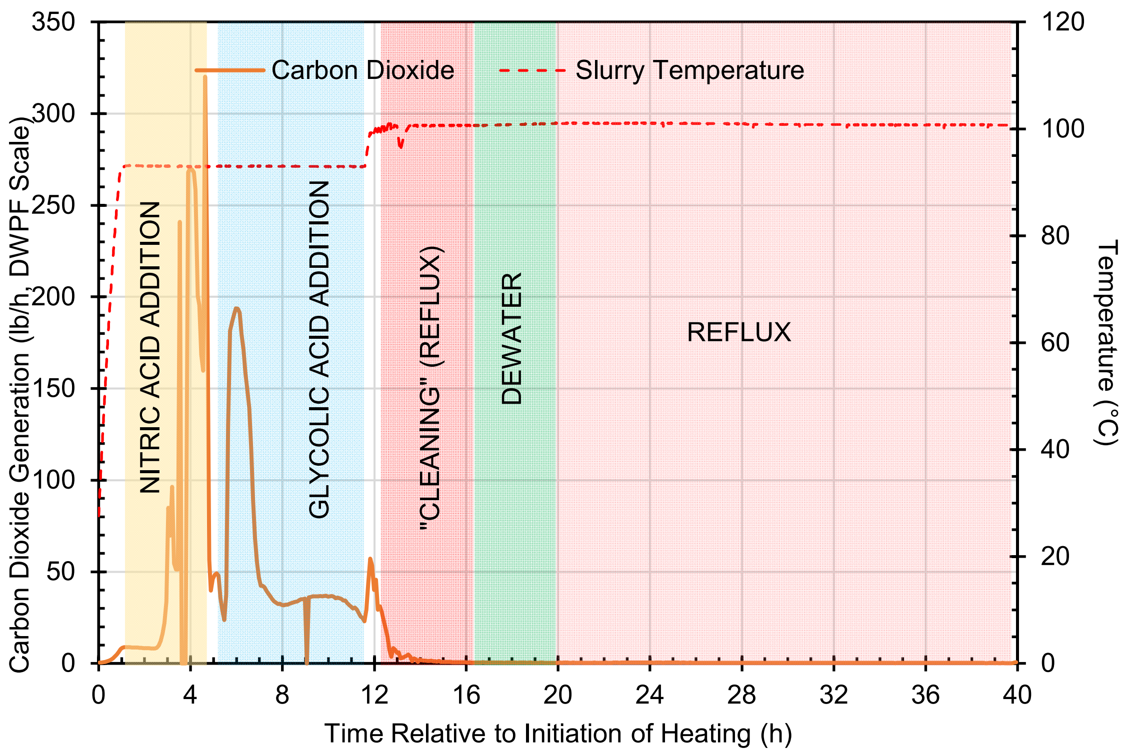

Figure 3-6. SRAT Part 2 Carbon Dioxide Generation Rate

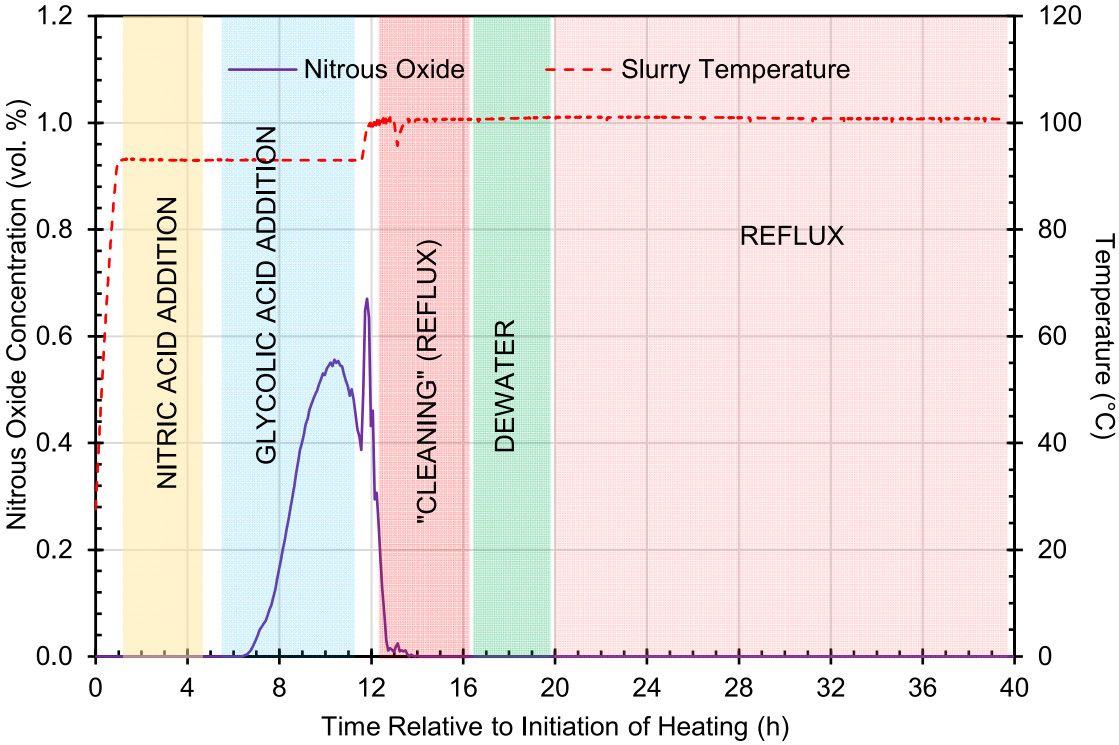

Figure 3-7. SRAT Part 2 Nitrous Oxide Concentration

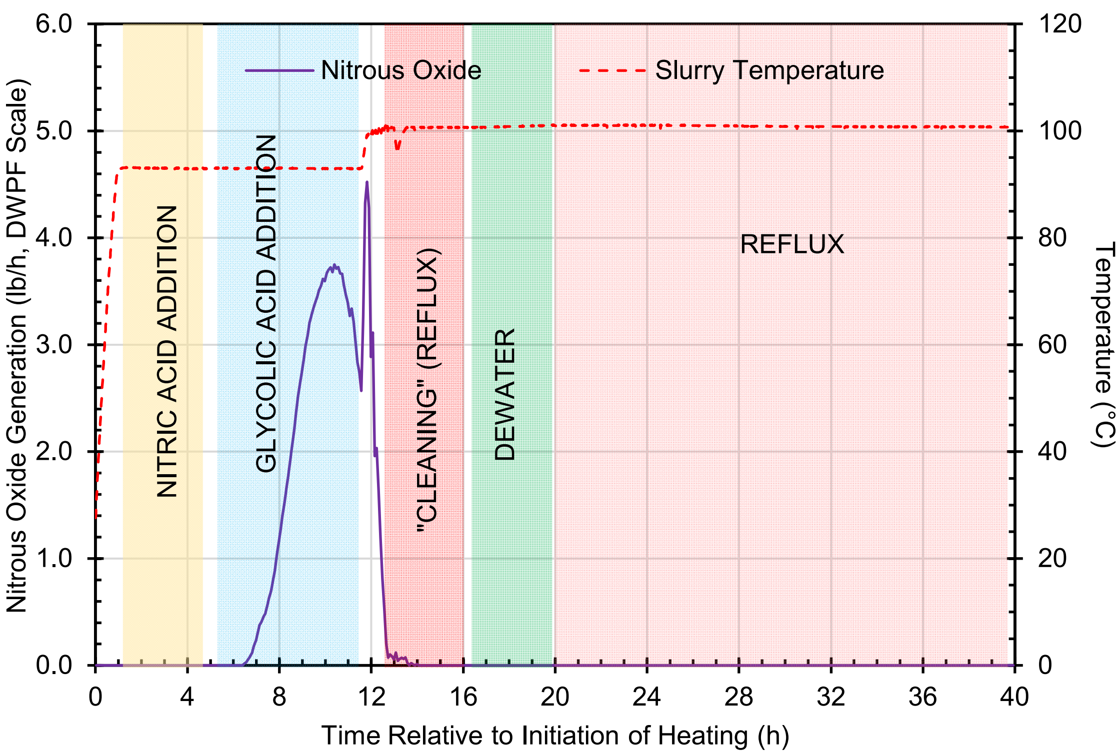

Figure 3-8. SRAT Part 2 Nitrous Oxide Generation Rate

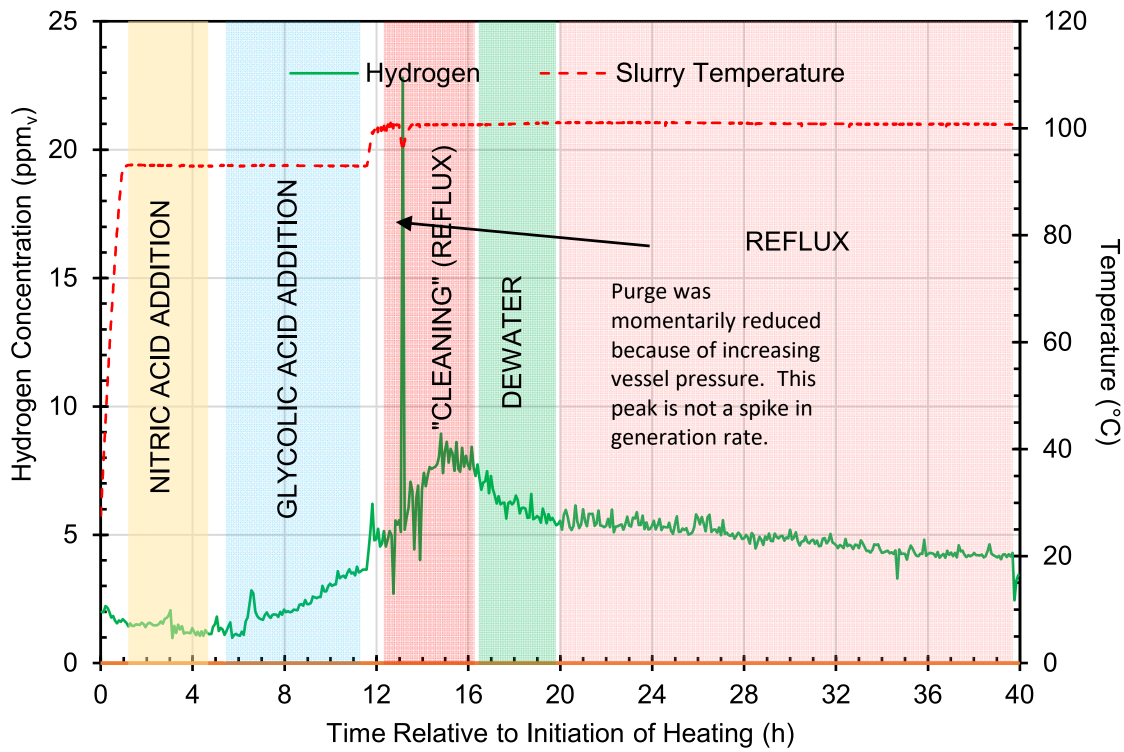

Figure 3-9. SRAT Part 2 Hydrogen Concentration

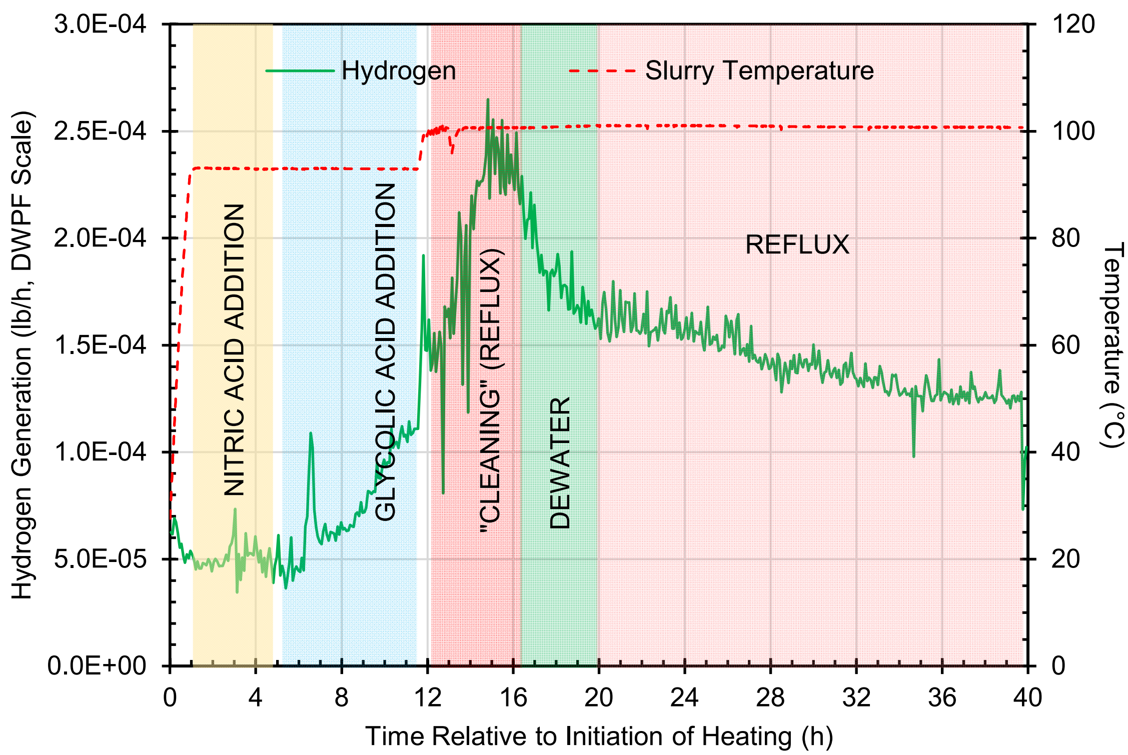

Figure 3-10. SRAT Part 2 Hydrogen Generation Rate

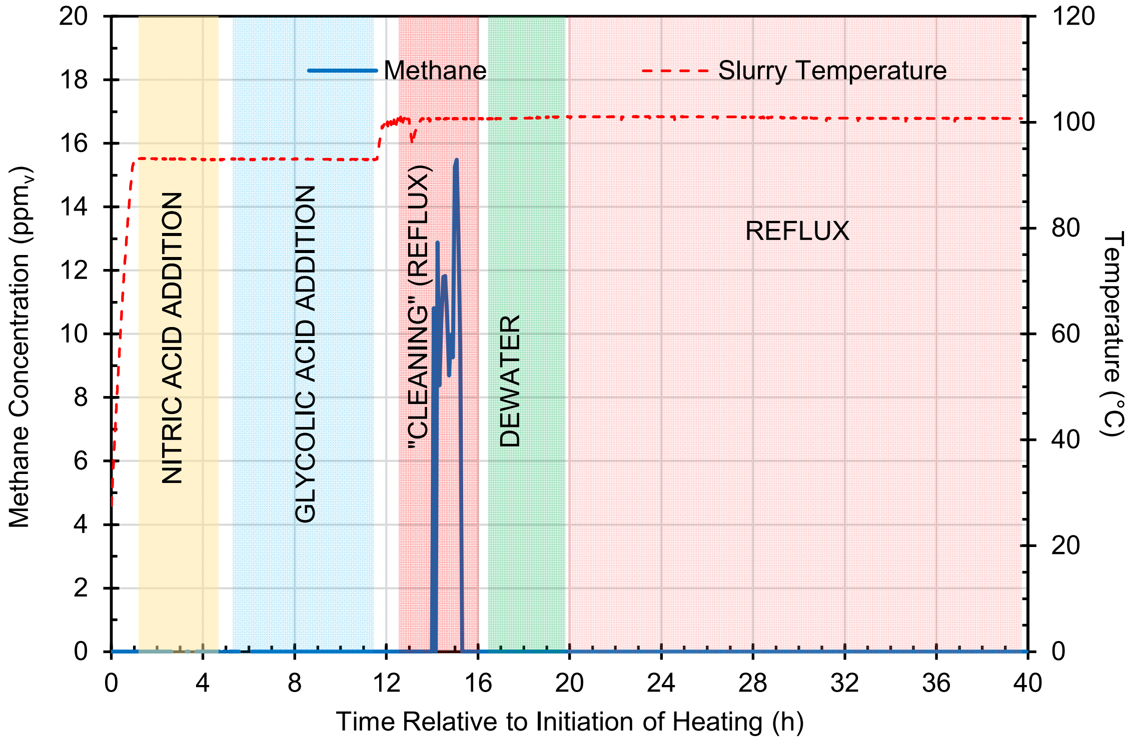

Figure 3-11. SRAT Part 2 Methane Concentration

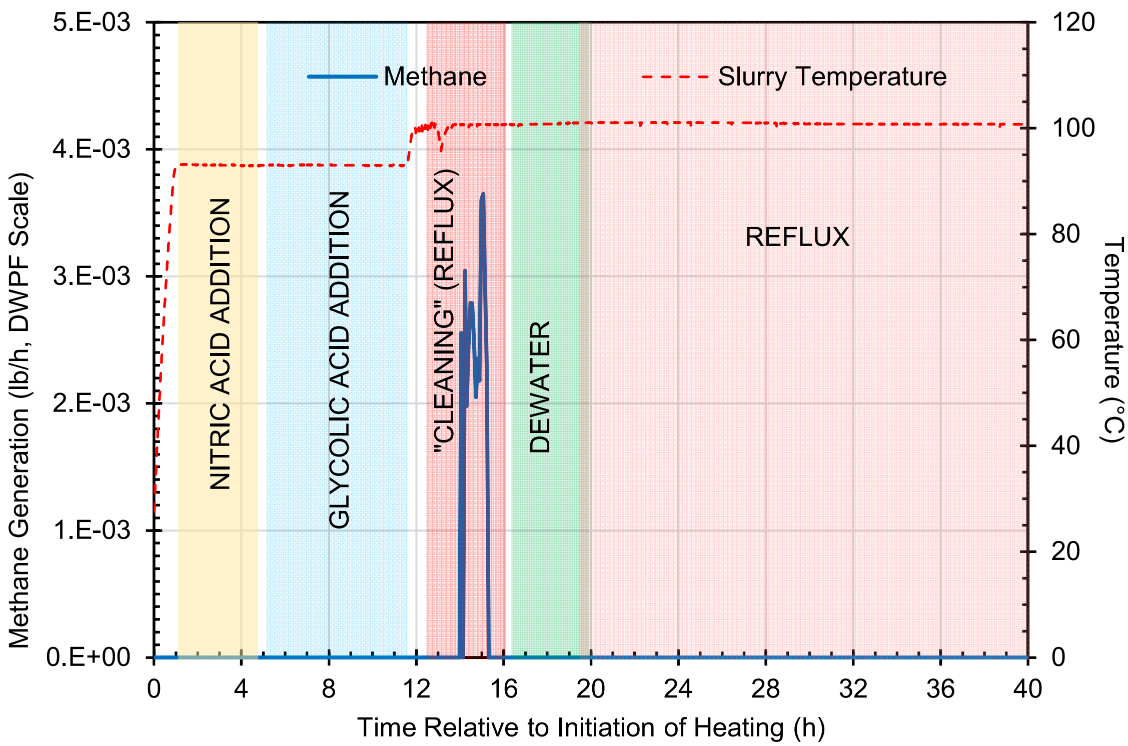

Figure 3-12. SRAT Part 2 Methane Generation

Oxygen results are presented in Figure 3-13. As stated in Section 2.1, the µGC method was optimized to quantify low concentrations of hydrogen and methane. Thus, the detector was saturated with oxygen and nitrogen and could not be reliably calibrated for those gasses. As a result, the oxygen results should be considered qualitative. No detectible drop in oxygen during peak carbon dioxide generation (nitric acid addition) is evidence of this. A drop in oxygen during glycolic acid addition is discernable, and the oxygen concentration is likely lower than the ~15 vol% shown in the figure.

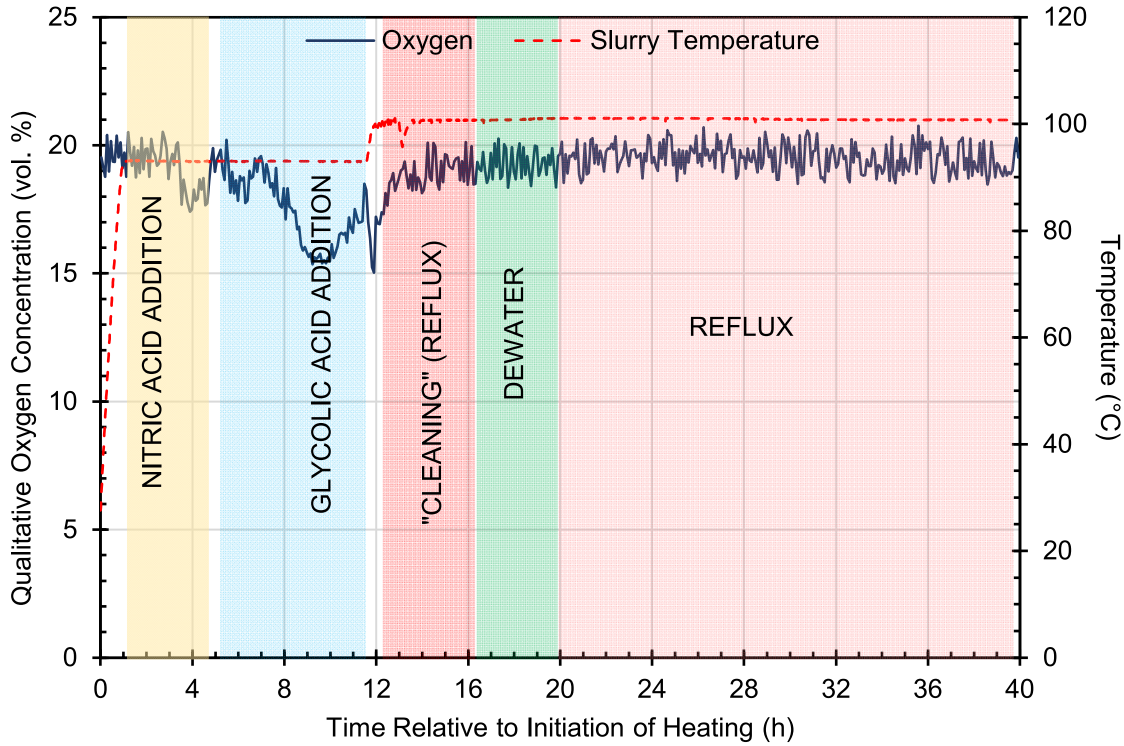

Figure 3-13. SRAT Part 2 Qualitative Oxygen Concentration

3.3 <u>SME Cycle</u>

Following the SRAT cycle, SRNL completed a demonstration of the SME cycle per an approved run plan.[3] The demonstration included the addition and removal of water representing five canister decontamination waters, addition of frit with an equal mass of water, removal of the added water, addition of a second batch of frit with equal mass of water, removal of that water, and finally removal of water to attain a pre-defined target weight percent total solids in the SME product. A timeline is given in Table 3-2.

Table 3-2. SME Cycle Timeline

Elapsed Time (h)	Activity
Prior to heating	Added canister decontamination water-1 Added Momentive™ Y-17112 antifoam
0.0	Began heating
1.0	Began boiling, dewatered the added water
2.6	Stopped heating
3.2	Added canister decontamination water-2, Began heating
3.7	Began boiling, dewatered the added water
5.3	Stopped heating
5.5	Added canister decontamination water-3, Began heating
5.9	Began boiling, dewatered the added water
7.5	Stopped heating
7.7	Added canister decontamination water-4, Began heating
7.9	Began boiling, dewatered the added water
9.6	Stopped heating
9.8	Added canister decontamination water-5, Began heating
10.1	Began boiling, dewatered the added water
11.8	Stopped heating, allowed vessel to cool below 80 °C, Added Momentive™ Y-17112 antifoam Added frit addition-1 and equal mass of water
13.5	Started heating
14.3	Began boiling, dewatered the added water
15.5	Stopped heating, allowed vessel to cool to below 60 °C, added frit addition-2 and equal mass of water (Note that frit became damp and did not flow well in the first addition, thus the contents were allowed to cool more before the second addition)
17.4	Started heating
18.2	Began boiling. Dewatered the added water and the amount of water needed to reach target wt% total solids
22.6	Stopped heating, ending the SME cycle

Off-gas plots for carbon dioxide, hydrogen, and methane (concentration and generation rates) are given in Figure 3-14, Figure 3-15, Figure 3-16, Figure 3-17, Figure 3-18, and Figure 3-19. The temperature profile clearly shows when additions were made (the dips in temperature). Nitrous oxide was detected as purging, mixing, and heating began and then the concentration dropped to less than detect. Therefore, a nitrous oxide plot is not shown. The qualitative measurements for oxygen concentration appeared relatively constant and are therefore not plotted.

The relatively high concentrations of carbon dioxide, nitrous oxide, hydrogen, and methane during heat-up are likely retained gases being released. Thus, the concentrations are not considered in determining the demonstration maximum concentrations and generation rates.

All three gases – carbon dioxide, hydrogen, and methane – showed relatively high concentrations as vessel contents were brought back to boiling. This suggests that when not boiling, generated carbon dioxide, hydrogen, and methane are being retained.

The peak methane concentration was 110 ppm_v, which is 0.22% of the methane lower flammability limit in air of 50,000 ppm_v.[10]

There is a slight "bump" of carbon dioxide and methane as the vessel began cooling. This is likely a result of the unsteady state of the vessel during cooling –a slight initial vacuum.

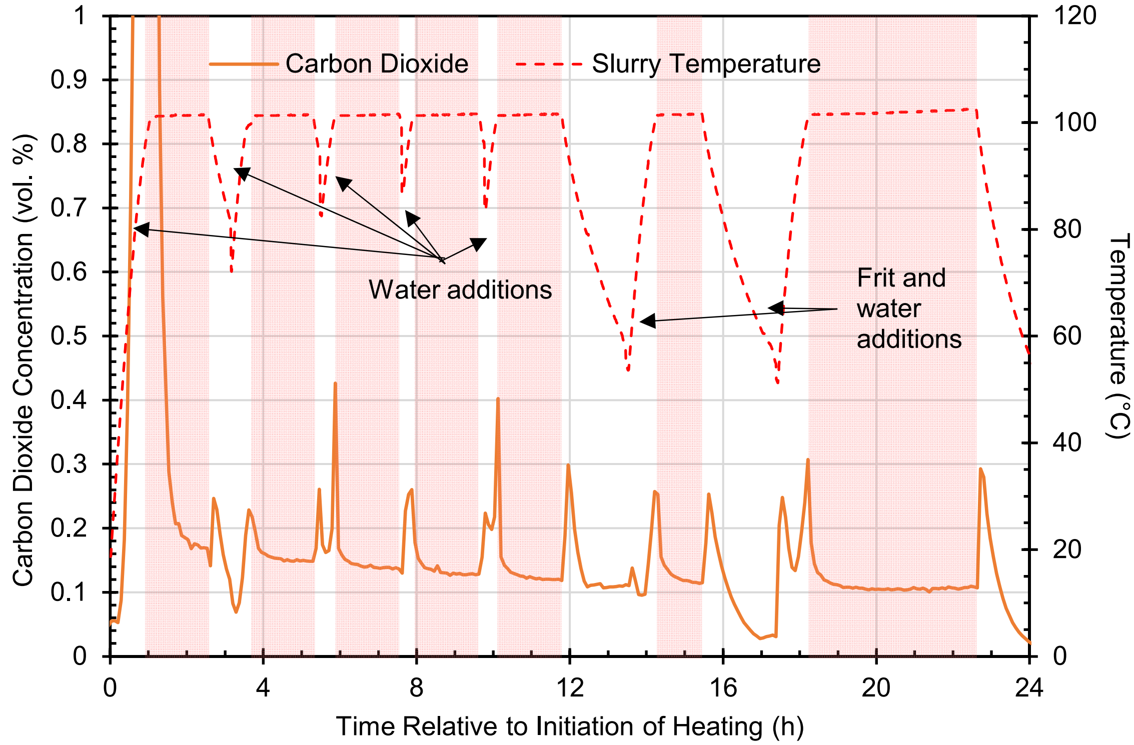

Figure 3-14. SME Cycle Carbon Dioxide Concentration (shaded areas represent boiling)

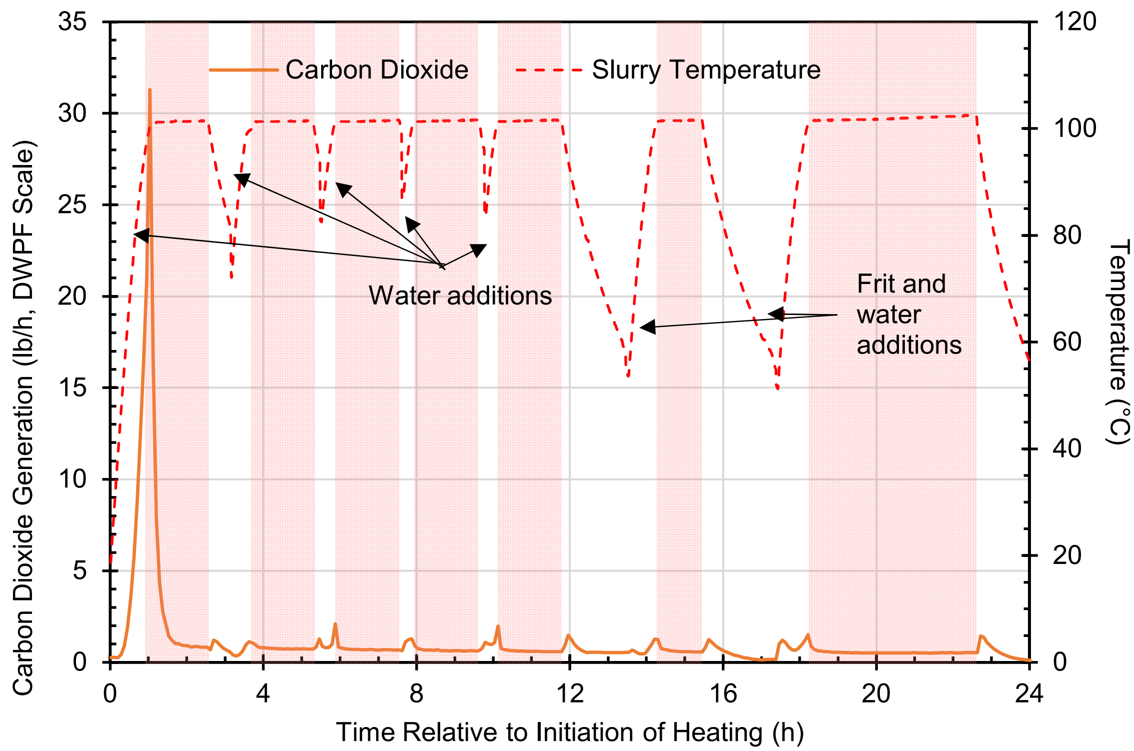

Figure 3-15. SME Cycle Carbon Dioxide Generation (shaded areas represent boiling)

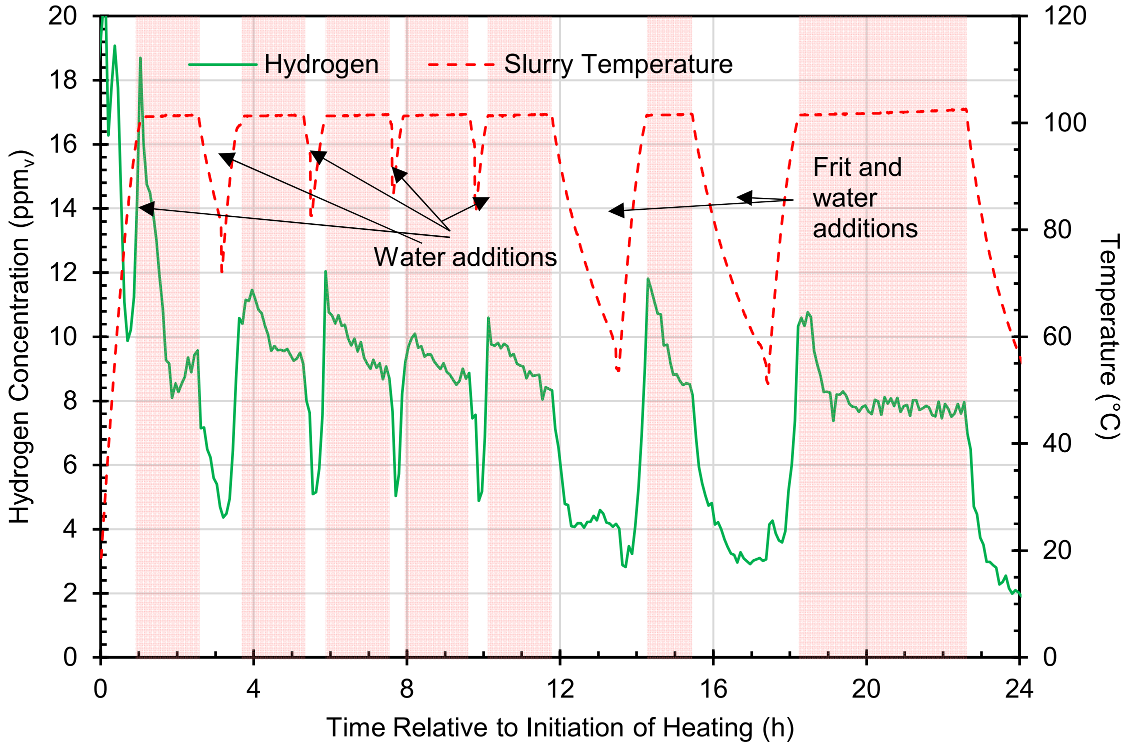

Figure 3-16. SME Cycle Hydrogen Concentration (shaded areas represent boiling)

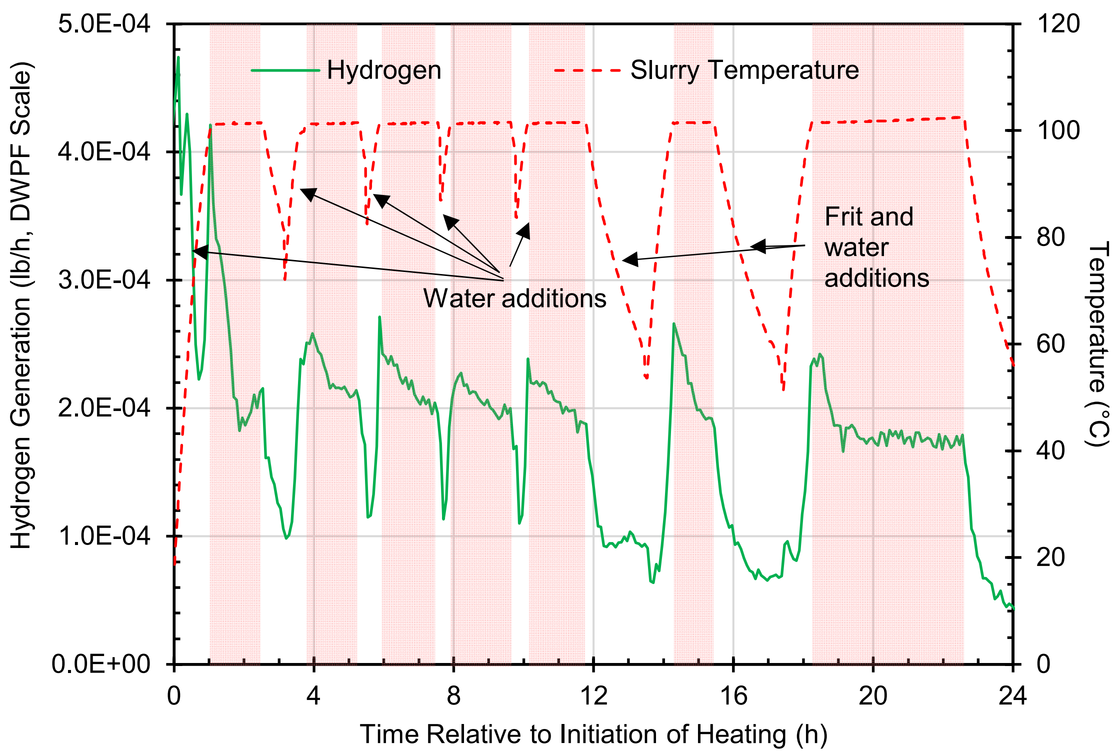

Figure 3-17. SME Cycle Hydrogen Generation Rate (shaded areas represent boiling)

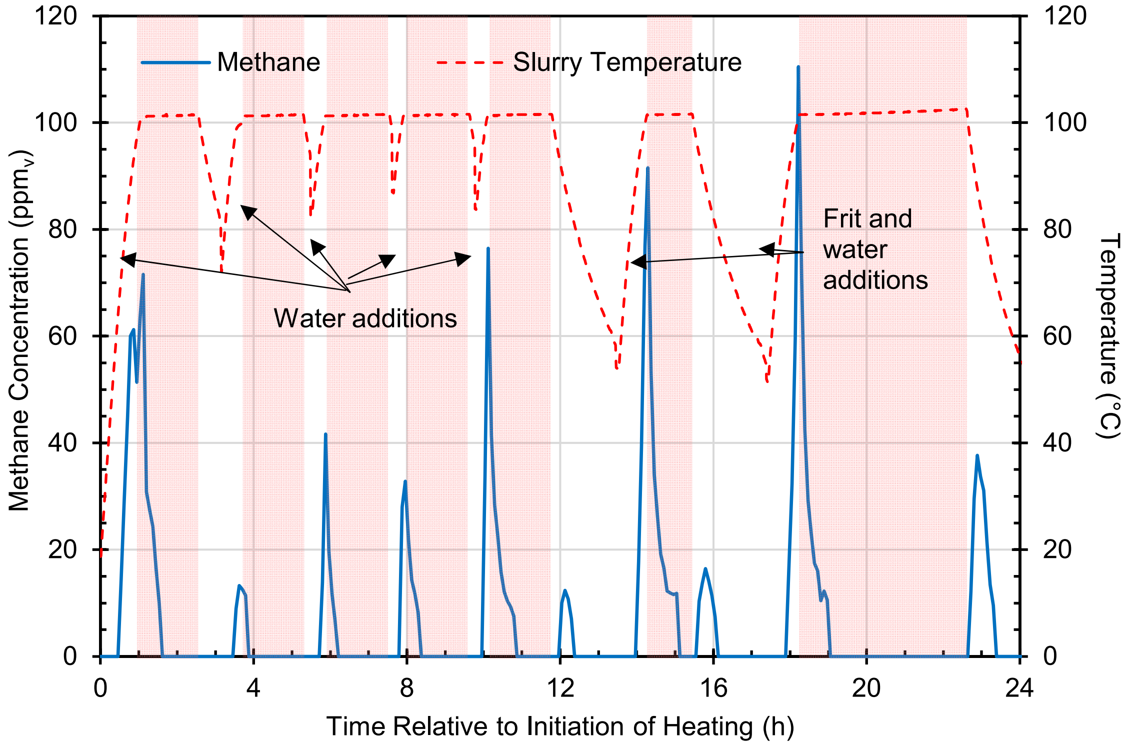

Figure 3-18. SME Cycle Methane Concentration (shaded areas represent boiling)

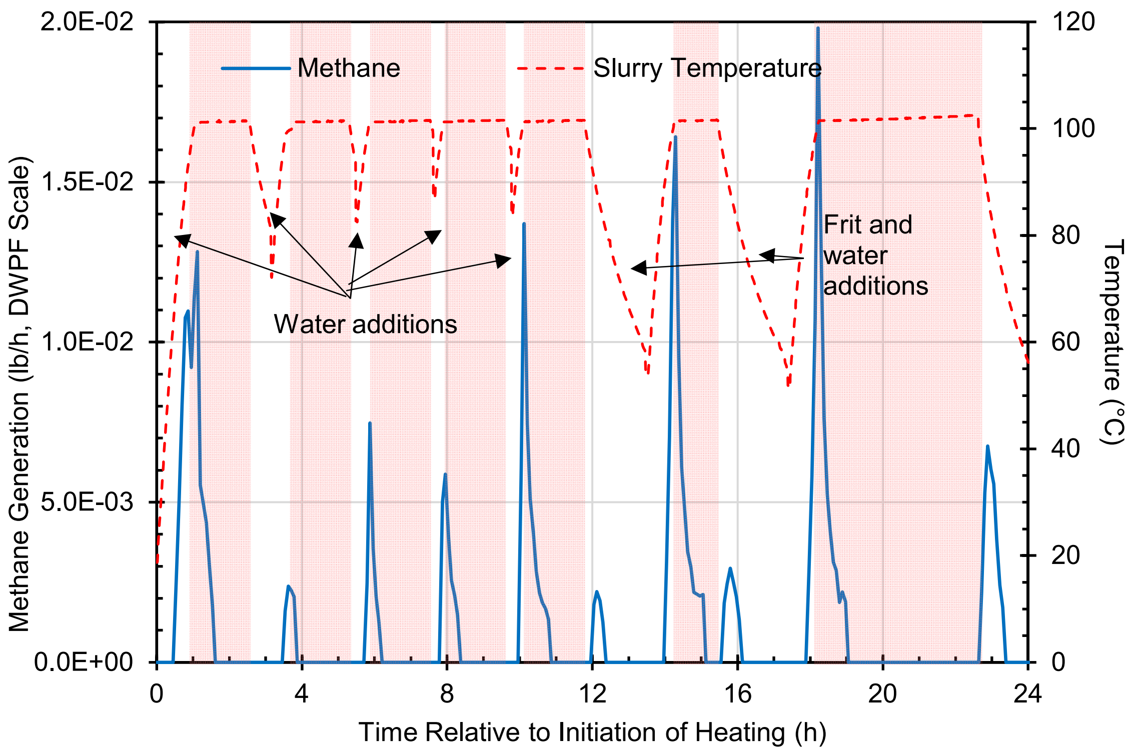

Figure 3-19. SME Cycle Methane Generation (shaded areas represent boiling)

3.4 Peak Off-gas Concentration and Generation

Presented in Table 3-3 are peak carbon dioxide, nitrous oxide, hydrogen, and methane concentrations for the SRAT and SME cycles. The TTR[1] also specifies generation rates for nitrous oxide and hydrogen, which are also included in the table. The DWPF does not have a concentration or generation rate limit for carbon dioxide, nitrous oxide, or methane. With the NGA flowsheet, the DWPF limit for hydrogen generation is 2.4×10^{-2} lb/h in the SRAT and the SME. The maximum SRNL-observed hydrogen generation rates were ~1/90th of this limit.

Table 3-3. Peak Off-Gas Concentrations and Generation Rates

Gas	Unit	SRAT Cycle	SME Cycle
Carbon Dioxide	volume %	31	0.43
	lb/h	320	2.1
Nitrous Oxide	volume %	0.67	<0.05
	lb/h	4.5	<0.2
Hydrogen (DWPF Limit: 2.4×10^{-2} lb/h)	ppm_v	9.0	12
	lb/h	2.7×10^{-4}	2.7×10^{-4}
Methane	ppm_v	16	110
	lb/h	3.7×10^{-3}	2.0×10^{-2}

Generation rates are scaled to 94 SCFM purge rate for the SRAT cycle and 72 SCFM for the SME cycle.

4.0 Conclusions

SB10 with washed Tank 51 sludge (and added H-Canyon material) was processed through SRAT and SME cycles of the NGA flowsheet in the shielded cells without approaching the DWPF hydrogen generation rate limit.

Methane was sporadically detected at low concentrations in both the SRAT and SME cycle. The source of methane generation has not been identified.

5.0 References

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