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Investigation of Thermolysis Hydrogen Generation Rate in Tank 38 and Tank 50 Waste Samples with Sodium Glycolate

C.J. Martino, J.D. Newell, J.M. Pareizs, M.R. Duignan, and M.L. Restivo

February 2019

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February 2019

Savannah River
National Laboratory ™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

This report contains hydrogen generation rate (HGR) measurements of Tank 38 and Tank 50 radioactive samples with and without added glycolate as a function of temperature. The objective of the Tank 38 and Tank 50 HGR measurements is to extend the knowledge from previous sample thermolysis HGR measurements and augment simulant testing for developing an equation for the Savannah River Site (SRS) Concentration, Storage, and Transfer Facility (CSTF) thermolysis HGR with and without added glycolate. Tank 38 testing is applicable to the 2H-Evaporator System and associated CSTF waste tanks. Tank 50 HGR measurement is applicable to CSTF tanks and the Saltstone Production Facility (SPF). The glycolate concentration used is based on what would be expected to be near the high-end concentration of glycolate (1570 mg/L in Tank 38 and 350 mg/L in Tank 50). The radioactive dose rate of the Tank 38 material was high enough to require use of the flow system in the Shielded Cells. Tank 50 material was less radioactive, so the higher temperatures were investigated in the flow system while the lower temperatures were investigated in the sealed system contained within a radiological hood.

The following are key results from the Tank 38 HGR testing:

- Based on conservative assumptions, 1570 mg/L of glycolate was added to the Tank 38 material as a high projection of future evaporator drop tank glycolate concentration. The HGR with 1570 mg/L of added glycolate at 80, 95 and 111.5 °C were 9.99×10^{-7} ft^3 h^{-1} gal^{-1}, 3.08×10^{-6} ft^3 h^{-1} gal^{-1}, and 1.04×10^{-5} ft^3 h^{-1} gal^{-1}, respectively. The reproducibility of HGR measurements from two successive periods at boiling (111.5 °C) were within the experimental uncertainty of the measurements (9.99×10^{-6} ft^3 h^{-1} gal^{-1} and 1.07×10^{-5} ft^3 h^{-1} gal^{-1}, respectively). As seen in the following figure, at temperatures of 80 °C and above, the HGR measurements with 1570 mg/L of added glycolate were more than an order of magnitude greater than the HGR measurements without added glycolate.
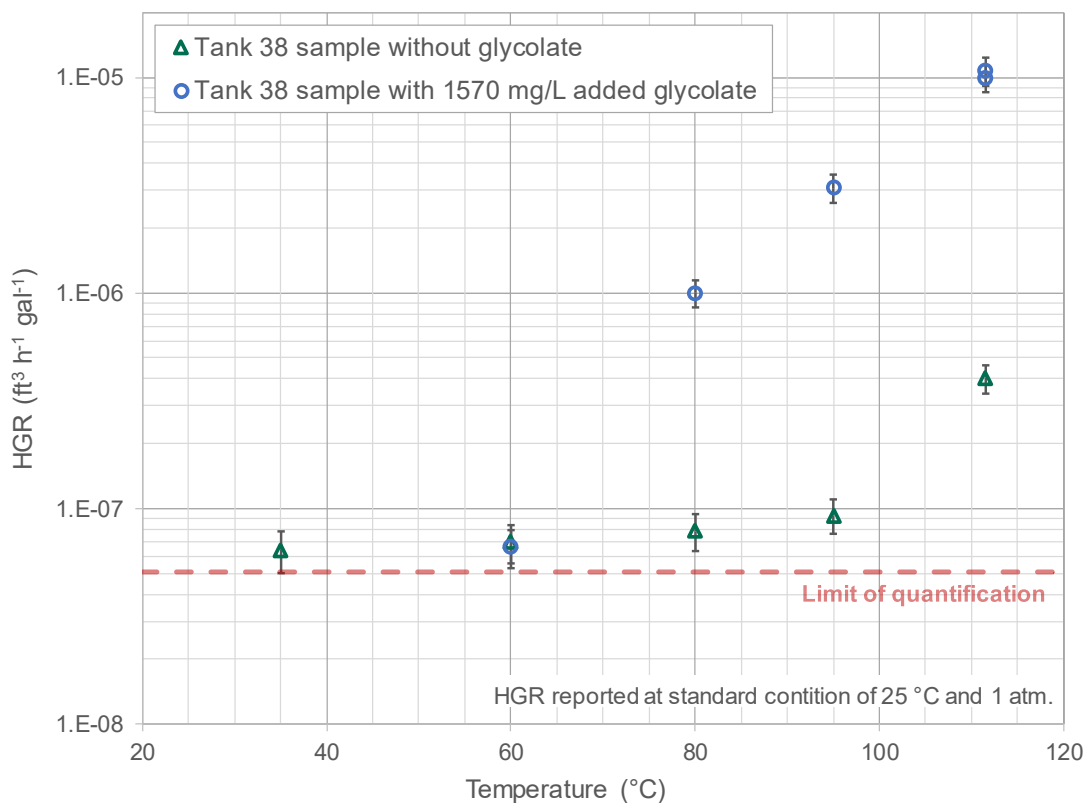
- Using the measurements at 80, 95, 111.5 °C, the activation energy for hydrogen generation from thermolysis in Tank 38 with 1570 mg/L of added glycolate is 84.1 ± 8.3 kJ/mol.

- Methane was generated at levels near or below the 14 ppmv (3.1×10^{-7} ft^3 h^{-1} gal^{-1}) Limit of Quantification (LOQ) during boiling of Tank 38 without added glycolate. The methane generated during the boiling condition of Tank 38 with 1570 mg/L of added glycolate, when above the LOQ, averaged 18 and 22 ppmv (4×10^{-7} and 5×10^{-7} ft^3 h^{-1} gal^{-1}). The June 2018 Tank 38 test with 1570 mg/L of added glycolate remained within the methane generation noted for the August 2017 test performed without glycolate, which averaged approximately 45 ppmv (approximately 1×10^{-6} ft^3 h^{-1} gal^{-1}).

- For all temperatures examined except for the ambient condition, the HGR measurements without added glycolate from the current (June 2018) test are lower than the HGR measurements from the August 2017 test performed on a different aliquot of the same sample (HTF-38-17-60). Although some hypotheses are provided in this report, the specific cause of the decrease is not known. In the June 2018 test, the HGR measurements for Tank 38 sample without added glycolate at 35, 60, 80 and 95 °C are similar to each other, ranging from 6.43×10^{-8} ft^3 h^{-1} gal^{-1} to 9.28×10^{-8} ft^3 h^{-1} gal^{-1}. The HGR of Tank 38 material without glycolate at boiling (111.5 °C) was 4.03×10^{-7} ft^3 h^{-1} gal^{-1} (95% confidence interval ± 15%).

The following are key results from the Tank 50 HGR testing:

- The sealed-system HGR measurements of Tank 50 sample with 350 mg/L of added glycolate at 43, 58, and 73 °C were 1.36×10^{-9}, 1.29×10^{-8}, and 3.70×10^{-8} ft^3 h^{-1} gal^{-1}, respectively. Tank 50 flammability is evaluated at a maximum of 43 °C, but HGR measurements at higher temperatures were performed to support SPF.

- The flow system HGR measurements of Tank 50 sample with 350 mg/L of added glycolate at 85 and 100 °C are 2.46×10^{-7} ft^3 h^{-1} gal^{-1} and 6.69×10^{-7} ft^3 h^{-1} gal^{-1}, respectively. The result measured in the flow system at 70 °C (2.09×10^{-7} ft^3 h^{-1} gal^{-1}) appears biased high with respect to the entire set (i.e., flow and sealed system), suggesting either the release of dissolved hydrogen or a short-lived thermolysis reaction.

- The data from the flow system under oxic conditions at higher temperatures (85 to 100° C) and the data from the sealed system under anoxic conditions at lower temperatures (43 to 73 °C) provide a consistent estimate of activation energy for hydrogen generation from glycolate. Excluding the 70 °C flow-system test, the activation energy for Tank 50 sample with 350 mg/L of added glycolate is 106 ± 21 kJ/mol.

- Comparing to previous sealed-system testing of Tank 50 without added glycolate, the overall set of data demonstrates that HGR of Tank 50 with 350 mg/L of added glycolate is on the same order as HGR without glycolate. Excluding the flow-system test at 70 °C, the HGR measurement results for Tank 50 with 350 mg/L glycolate were near to or less than the prediction of the Hu expression. For sealed-system tests near 70 °C, differences between tests with and without glycolate were not statistically significant.

- No methane was detected in the testing of Tank 50 with 350 mg/L of glycolate.

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LIST OF ABBREVIATIONS

CI	Confidence Interval
CPC	Chemical Processing Cell
CSTF	Concentration, Storage, and Transfer Facility
DAC	Data Acquisition and Control system
DC	Direct Current
DSA	Documented Safety Analysis
DWPF	Defense Waste Processing Facility
EPA	Environmental Protection Agency
GC	Gas Chromatograph
HGR	Hydrogen Generation Rate
ICA	Ion Chromatography for Anions
ICP-AES	Inductively Coupled Plasma – Atomic Emissions Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
LOD	Limit of Detection
LOQ	Limit of Quantification
LTAD	Low Temperature Aluminum Dissolution
M&TE	Measuring and Test Equipment
MS&E	Measurement Systems and Equipment
PID	Proportional-Integral-Differential controller
PISA	Potential Inadequacy in the Safety Analysis
RCT	Recycle Collection Tank
SME	Slurry Mix Evaporator
SPF	Saltstone Processing Facility
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SS	Stainless Steel
SVOA	Semivolatile Organics Analysis
TIC	Total Inorganic Carbon
TMS	trimethylsilanol
TOC	Total Organic Carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VOA	Volatile Organics Analysis
WTP	Waste Treatment Plant

1.0 Introduction

In February 2017, Savannah River Remediation (SRR) declared a Potential Inadequacy in the Safety Analysis (PISA) in each of three Savannah River Site (SRS) Liquid Waste facilities: Concentration, Storage, and Transfer Facility (CSTF),[1] Saltstone Processing Facility (SPF),[2] and the Defense Waste Processing Facility (DWPF).[3] The PISAs relate to how organics can impact the radiolytic and thermolytic production of hydrogen, which is a flammable gas.

With the implementation of the Nitric-Glycolic Acid (NGA) flowsheet at DWPF, small amounts of glycolate will be transferred into the SRS CSTF from the DWPF recycle stream. A literature survey indicated that glycolate can produce hydrogen via thermolytic reactions.[4] Work performed for the Hanford Reservation tank waste programs indicated that glycolate decomposition in high pH solutions containing soluble aluminum generates hydrogen.[5-6] A prior analysis of this literature data predicted the expected influence of glycolate on radiolytic and thermolytic hydrogen generation in the SRS CSTF, SPF, and DWPF.[7]

Savannah River National Laboratory (SRNL) previously conducted research to determine the thermolytic Hydrogen Generation Rate (HGR) with simulated and actual waste. Gas chromatography methods were developed and used with air-purged flow systems to quantify hydrogen generation from heated simulated and actual waste at rates applicable to the CSTF Documented Safety Analysis (DSA). Testing included a measurement of HGR on waste from Tank 38 and simulated waste with the most common SRS CSTF organics at temperatures up to 140 °C.[8] HGR measurements of Tank 50 samples with and without additives (not including glycolate) were performed using a sealed measurement system.[9] Subsequent measurement with Tank 22 samples with and without 120 mg/L of added glycolate showed none to minimal thermolytic HGR in that dilute sample matrix with the higher detection limits of the flow system.[10]

This report contains HGR measurements of Tank 38 and Tank 50 radioactive samples with and without added glycolate. The primary goal for Tank 38 and Tank 50 HGR measurements is to extend the knowledge from the previous sample measurements[8, 10] and augment simulant testing for developing an equation for CSTF HGR with and without added glycolate. Tank 38 testing is applicable to the 2H-Evaporator System and associated waste tanks in the CSTF. Tank 50 HGR measurement is applicable to CSTF tanks and SPF. The glycolate concentration used is based on what would be expected to be near the high end if no mitigation is employed in the NGA flowsheet to prevent glycolate from entering CSTF via DWPF recycle stream.

SRNL has two systems installed for testing HGR on radioactive samples: a gas-purged flow system in the Shielded Cells and a sealed system in a radiological hood. The flow system has the advantages of having been adapted for testing in the Shielded Cells (allowing for use for more highly radioactive samples) and providing for continuous time-dependent measurements. The sealed system has the advantage of having a lower achievable detection limit for hydrogen generation rate but is limited to cumulative (or average) measurements over longer periods of time. The radiation dose rate of the Tank 38 material was high enough to require testing within the Shielded Cells and thus the flow system was used. Tank 50 material had a lower radiation dose rate, so lower temperatures were investigated in the sealed system contained in a radiological hood because it had the ability to measure lower rates of hydrogen generation. The higher temperatures of HGR Tank 50 were investigated in the flow system because it was available for use for this purpose prior to the sealed system being available. The driver for examining temperatures above 50 °C for Tank 50 is that higher temperatures can be attained during grout curing in SPF.

To address these needs, SRR issued a Technical Task Request (TTR) requesting that SRNL perform simulant and actual waste testing to support thermolysis HGR determination for CSTF processes.[11] This report covers a portion of the data gathered as Task 2 of the TTR, specifically addressing data from actual waste spiked with glycolate. A Task Technical and Quality Assurance Plan (TTQAP) further defines the actual-waste and simulated-waste testing.[12] Finally, three Run Plans give test details specific to the HGR testing of radioactive waste samples from Tank 38,[13] Tank 50 (flow system),[14] and Tank 50 (sealed system).[15] As specified by the TTR and TTQAP and as detailed in the Run Plans, a basis for glycolate concentration was developed for use in Tank 38 and Tank 50 testing and subsequent testing was performed in flow and sealed systems as deemed most appropriate for use with these samples.

1.1 Thermolytic Hydrogen Generation

A background of thermolytic hydrogen generation applicable to current CSTF organic compounds and future additions of glycolate are detailed elsewhere and is summarized here.[7-8]

Thermolytic production of hydrogen from organic compounds was also described by Hu in 2004.[16] In work designed to support flammability calculations at the Hanford Waste Treatment Plant (WTP), Hu developed an empirical model (Equation 1) describing the thermolytic production of H_2 from organic molecules as a function of temperature, organic carbon content, and aluminum content.

$$HGR_{thm} = a_{thm} \cdot r_f \cdot [TOC] \cdot [Al]^{0.4} \cdot L_f \cdot e^{-E_{thm}/RT}$$

Equation 1

where,

HGR_{thm} = thermolytic hydrogen generation rate, mole kg^{-1} day^{-1}
a_{thm} = pre-exponential factor, 3.94×10^9 mol kg^{-1} day^{-1}
r_f = reactivity factor
$[TOC]$ = concentration of total organic carbon in the liquid, wt%
$[Al]$ = concentration of aluminum, wt%
L_f = mass fraction of waste present as liquid
E_{thm} = thermolytic activation energy, 89,600 J mole^{-1}
R = gas constant, 8.314 J mole^{-1} K^{-1}
T = temperature, K

Both the activation energy and the pre-exponential factor are values regressed from hydrogen generation measurements specific to Hanford actual waste samples at temperatures between 60 and 120 °C. Thus, the values are representative of the specific blend of organics present in that waste. The reactivity factor was used to improve the fit of the data, with recommended values varying between 0.15 and 1. Data generated in this report is compared to the most conservative recommendation, using Equation 1 and a reactivity factor value of $r_f = 1$. Note that the use of a reactivity factor equal to 1 is more conservative than the values recommended by Hu for Hanford waste tanks (0.3 or 0.6).[16]

Being empirical, Equation 1 does not describe the precise mechanisms of hydrogen generation from tank waste. The advantage of the model developed by Hu, however, is that exact knowledge of the concentrations for each organic species present is not needed. Rather, a composite measurement (i.e., Total Organic Carbon, TOC) is employed such that hydrogen generation from organic thermolysis can be predicted within a factor of 3 for Hanford organics without the need for extensive sampling and characterization campaigns. This approach is especially useful in the context of evaluating SRS wastes, where hundreds of organics are known to exist in trace amounts.[17]

In 2017, Crawford and King used observations and data generated by Ashby et al.[5] to develop a rate expression for hydrogen generation due to glycolate thermolysis.[7] This rate equation was generated by assuming that one mole of glycolate makes one mole of hydrogen. Using this assumption, the kinetic data for glycolate degradation from Ashby et al., and an observed hydrogen generation activation energy (113,000 J/mol),[5] Crawford and King developed a rate expression for thermolytic HGR from glycolate, as given in Equation 2:

$$HGR_{thm}^{gly} = k \frac{[Al]\left[NO_2^-\right][gly]}{[OH^-]} e^{\frac{-E_A}{R}\left(\frac{1}{T} - \frac{1}{393.15}\right)}$$
Equation 2

where,

HGR_{thm}^{gly} = rate of hydrogen production by glycolate thermolysis, moles L^{-1} h^{-1}

k = rate constant for glycolate degradation at 120 °C, 4×10^{-4} L mol^{-1} h^{-1}

$[Al]$ = aluminum concentration, M

$\left[NO_2^-\right]$ = nitrite concentration, M

$[gly]$ = glycolate concentration, M

$[OH^-]$ = hydroxide concentration, M

E_A = activation energy for hydrogen generation, 113,000 J mol^{-1}

R = gas constant, 8.314 J mol^{-1} K^{-1}

T = temperature, K

The analyses and kinetic studies performed by Ashby et al. comprise a matrix of tests to benchmark simulant experimental data generated at SRNL.

There are significant differences between the solution compositions used by Hu and that of SRS waste. Substantive differences also exist between the experiments performed by Ashby et al. and compositions of SRS waste. Simulant work to gather information more appropriate to SRS CSTF conditions is underway.[12, 18]

1.2 Glycolate Concentration Applicable to HGR Testing

From previous testing, the Run Plan for Tank 22 testing defined the typical glycolate concentration of 120 mg/L for Tank 22, the receipt tank for DWPF recycle.[19] This analysis was partially based on flowsheet and qualification testing showing that future glycolate concentrations in the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) would be approximately 65% of the historic formate concentrations in the SRAT and SME. This percentage provides an estimated upper bound on the future glycolate to be sent to CSTF via the Recycle Collection Tank (RCT) in relation to the historic formate sent to CSTF via the RCT.[19]

With continuous processing of DWPF recycle through the 2H-Evaporator System, the formate concentration in the 2H-Evaporator System tanks (Tank 38 and Tank 43) has increased, with the highest formate concentration measured in these tanks at 2.42 g/L.[20] Using the approach described for Tank 22, taking 65% of the formate value, an expected high-end concentration of glycolate in Tank 38 is 1.57 g/L. There is added conservatism in this approach because glycolate is expected to decompose faster than

formate at CSTF conditions. Therefore, the glycolate concentration is not expected to reach the concentration levels of formate.

Tank 50 samples from recent salt processing (third quarter of 2009 through first quarter of 2017) showed the highest formate concentration measured for the third quarter 2015 sample at 536 mg/L.[21] Using the approach described for Tank 22, taking 65% of the formate value, an expected high-end concentration of glycolate in Tank 50 is 350 mg/L. As mentioned previously, there is added conservatism in this approach because glycolate is expected to decompose faster than formate at Tank 50 conditions. In addition, a portion of the formate in the historical Tank 50 value results from sources other than DWPF recycle (e.g., decomposition of legacy organics from Canyon and other site operations). Therefore, the glycolate concentration is not expected to reach the concentration levels based on a proportion to the formate. This approach has the underlying assumption that future salt processing will use similar ratios of 2H-Evaporator salt material (Tank 38 and 43) to the other CSTF salt material as the salt processing performed between 2009 and 2017.

2.0 Experimental

2.1 Shielded Cells Flow System Apparatus

2.1.1 *Description of Apparatus*
The flow-system apparatus used in the Tank 38 and Tank 50 thermolytic HGR testing in the Shielded Cells is identical to the system used for Tank 22 thermolytic HGR testing.[10] The apparatus was based on the simulant testing flow system being used for Task 1 of the TTR and TTQAP.[11-12] The apparatus combined design elements from equipment used for previous one liter and four liter sludge batch qualification Chemical Processing Cell (CPC) testing.[22-23] The vessel holding the radioactive waste sample and the sealing lid assuring capture of gases during testing was made of Teflon®, with an internal volume of approximately 1.2 liters. Use of a flow-through system with minimal headspace is consistent with the HGR measurement apparatus recommended and developed for qualification of radioactive-waste feeds at the Hanford WTP, although dimensions are larger for this application.[24-25] Teflon® fluoropolymer was chosen for HGR measurements with the flow system based on recommendations from simulant testing.[18] Teflon® was used to minimize potential interferences from performing tests in glass or stainless-steel vessels.

Figure 2-1 contains two photographs of the HGR measurement system. The photograph on the left is the system with the stainless-steel pot prior to its use in the Low Temperature Aluminum Dissolution (LTAD) tests).[26] The photograph on the right is the same system but with a Teflon® pot installed in SRNL Shielded Cells, A Block Cell 2. A separate Teflon® pot is installed for each tank sample to be tested.

Heating was provided using two 0.375-inch diameter Alloy 800 heating rods powered by an automated direct current (DC) power supply (TDK-Lambda Genesys, GEN150-10). Mixing was controlled using a mixer system consisting of a Servodyne mixing head coupled to an agitator shaft via a Parr high torque magnetic drive. Two 1-inch diameter, 4-blade, 45° pitched turbine stainless steel impellers were welded to the stainless-steel agitator shaft. The slurry was continually stirred over the course of the testing. Purge gas was controlled using an MKS Model 647 Multi Gas Controller and MKS Model 1179 Flow Controller. An offgas condenser allowed condensate to reflux into the reactor containing the sample material. Non-condensable gas exiting the condenser was sampled by a dedicated Agilent 3000A dual column micro gas chromatograph (GC), as described in further detail in a later subsection. A data acquisition and control system (DAC) was utilized for control of the heating rods, mixing, and purge gas flow and for automated data logging. A schematic depicting integration of the primary components of the HGR measurement flow system apparatus is given in Figure 2-2.

Additional details about the flow-system apparatus and its use is contained in the Tank 22 thermolytic HGR testing report.[10]
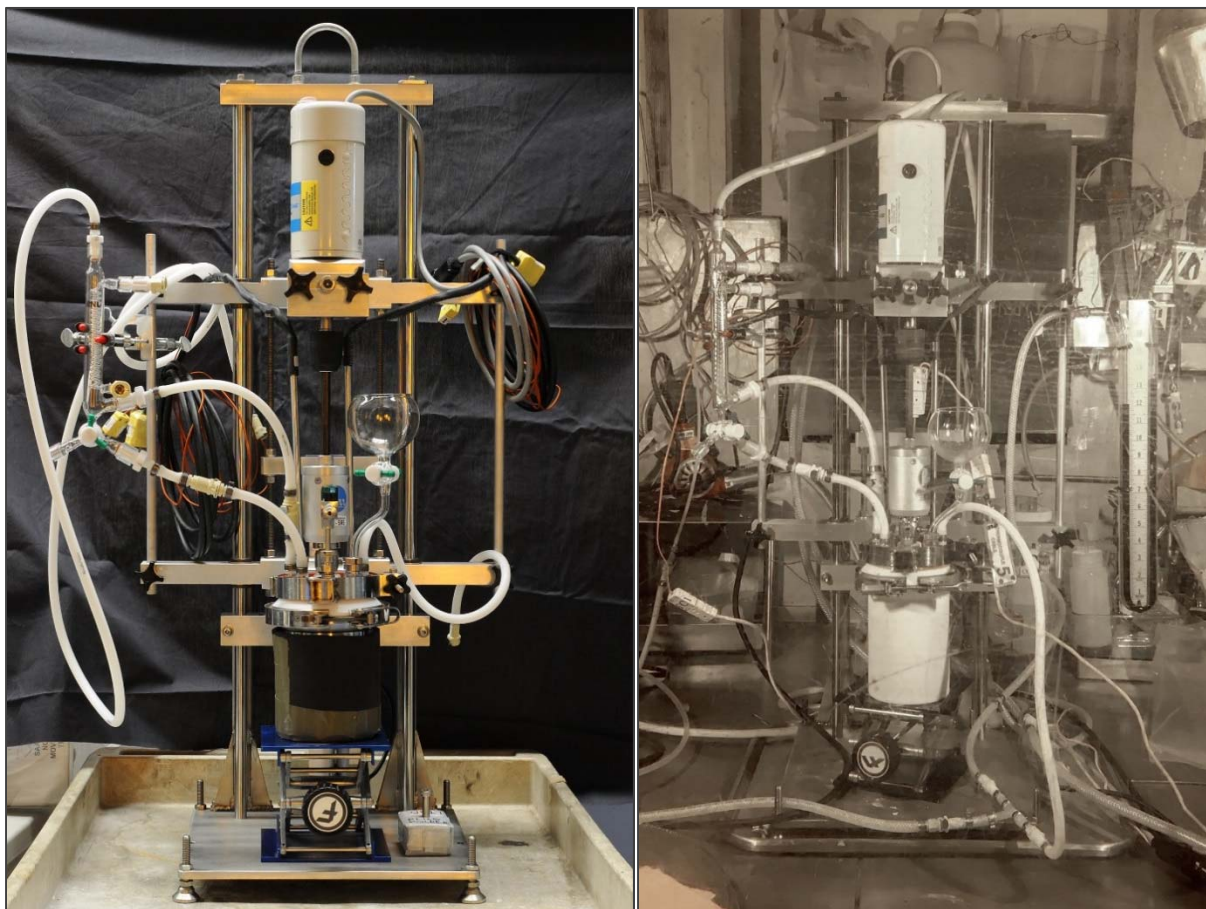
Figure 2-1. HGR measurement flow system prepared for installation (left) and in operation (right)
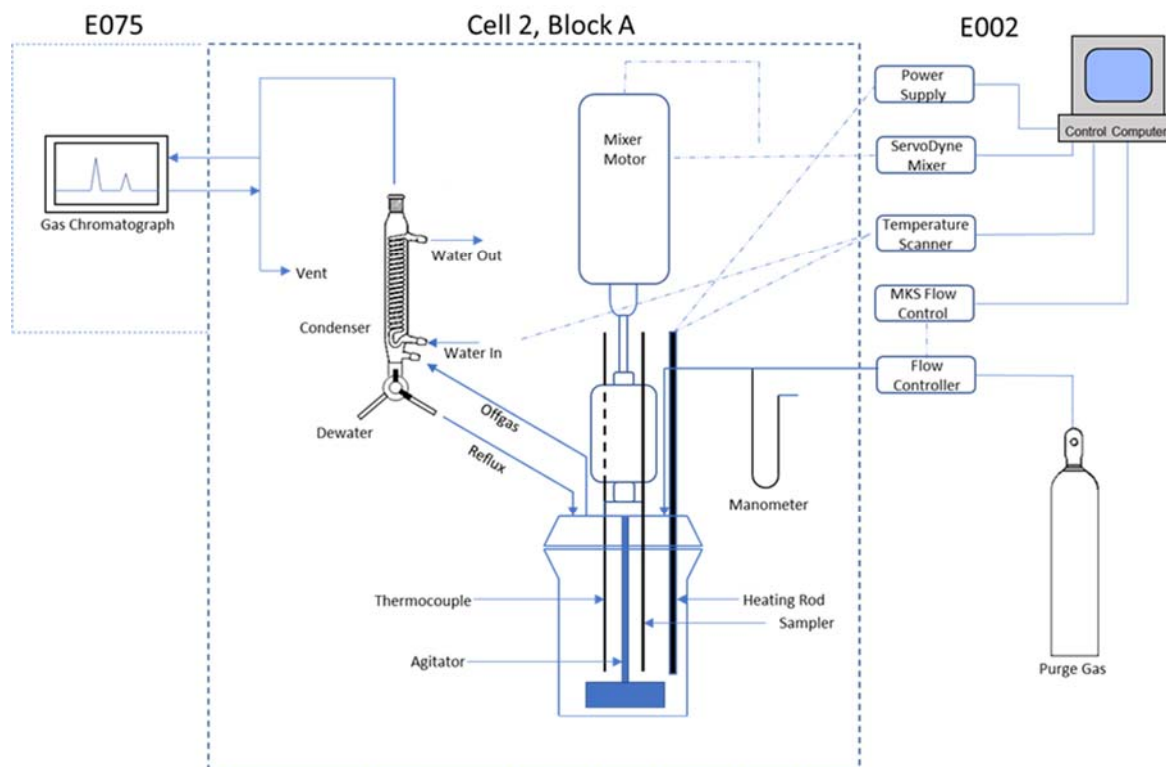
Figure 2-2. HGR measurement flow system used in Tank 38 and Tank 50 testing

2.2 <u>Radiological Sealed-System Apparatus</u>

2.2.1 *Description of Apparatus*

Sealed-system reactors were designed because the HGR Limit of Quantification (LOQ) for an open, continuous-flow system is just below 6×10^{-8} ft^3 h^{-1} gal^{-1}. Quantification of HGR below this limit, like the estimated rate of 3×10^{-9} ft^3 h^{-1} gal^{-1} for Tank 50 waste, requires an alternate measurement system. By accumulating generated gasses in a sealed system and avoiding use of a continuous purge gas, the hydrogen concentration increases thus improving the sensitivity of measurement. Design of a sealed system implies obtaining no or very low permeability and was based in part on successful past designs.[27-29] The selection of sealing surfaces and material is important to minimize the loss of generated gasses. The sealed system allows placing a measured sample mass inside a robust vessel of known volume. Testing held the apparatus at temperature for a measured duration and stirred continuously using a stirrer/hotplate. At the end of a selected period, the headspace of the reactors was sampled, utilizing a GC to measure the hydrogen. From the concentration of hydrogen and elapsed time, one determines the average combined thermolytic and radiolytic HGR for the sample over the test period. Tests were performed at multiple temperatures to calculate an activation energy of the thermolytic HGR assuming a first-order Arrhenius equation.

Figure 2-3 shows a schematic of the finished reactor with two control valves installed, a pressure transducer, and the liquid introduction and sampling port sealed. The thermocouples were secured to the outside of the reactor walls using pipe clamps, as shown in Figure 2-4 taken before the reactor was insulated. A DAC was utilized for or automated logging of pressure and temperature data. Details of reactor design and use are contained in the earlier report on sealed-system testing of Tank 50 sample material without the addition of glycolate.[9]
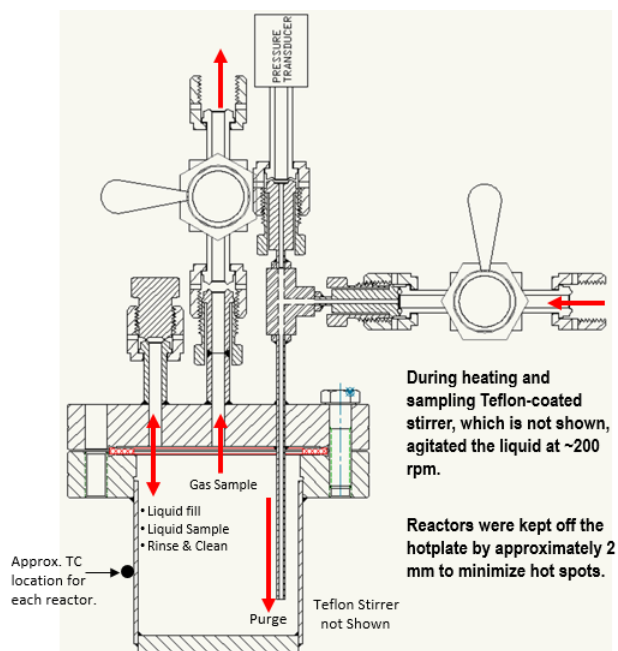
Figure 2-3. Schematic of a sealed-system reactor

Figure 2-4. Single reactor on hotplate (with thermocouple placements) prior to adding insulation

2.3 Test Protocol

2.3.1 *Sample Description*

Tank 38 waste sample HTF-38-17-60 was taken using a three-liter sampler and delivered to SRNL on July 10, 2017. This supernate sample was slightly hazy due to the sample containing a small quantity (<1 wt%) of solids that were insoluble in the supernate. A 1466.44 g portion of HTF-38-17-60 was used in previous HGR test of Tank 38 without added glycolate.[8] Characterization of sample HTF-38-17-60 was also performed at that time.[8] The flow system HGR testing of Tank 38 described in this report used a separate 1465.79 g portion of sample HTF-38-17-60 that was retained for potential future testing. The sample material had been stored in a poly bottle for approximately one year at ambient Shielded Cells conditions prior to initiating this testing; the composition may have shifted during the interval by various mechanisms (e.g., precipitation of salts, radiolysis, or sorption of organics into the storage bottle).

The Tank 50 HGR measurements with both the flow and sealed systems used portions of the 3 L first quarter 2018 Tank 50 sample HTF-50-18-12. This sample received extensive characterization for comparison with the SPF Waste Acceptance Criteria (WAC).[30] The sample material had been stored in a polymer bottle for approximately 5 months at Shielded Cells conditions prior to use in this testing. Thus, minor changes in composition between characterization and use in this test may have occurred. Based on a previous sample, a separate report determined the amount of radiation energy retained within the liquid applicable to the sealed-system testing.[31]

The samples did not contain glycolate, so sodium glycolate (Alfa Aesar, 99.1 wt%) was added to the sample material to the desired level of glycolate, where applicable.

2.3.2 *Flow System Testing Parameters*

The parameters for flow-system testing of Tank 38 were as follows.
- Measurement apparatus: nominally 1 L flow system, fluoropolymer vessel with fluoropolymer lid. Total volume (liquid and gas) of approximately 1.2 L.
- Test sample: Tank 38 sample HTF-38-17-60
- Sample density: approximately 1.32 g/mL at 27 °C
- Sample volume: approximately 1.1 L
- Sample mass: approximately 1465 g
- Glycolate addition: 1.57 g/L of glycolate (as sodium glycolate)
- Equipment total gas volume: approximately 100 mL
- Target measurement purge rate: 3 mL/min at standard conditions (1 atm and 21.1 °C). Higher rates of air without Kr tracer (10 to 40 sccm) were used during periods of temperature adjustment. Lower rate of purge gas with Kr tracer (3 mL/min) was applied once the measurement temperature is attained.
- Expected minimum time to equilibrate for HGR measurement: It required approximately 2 hours to achieve three vapor space volume turn-overs at standard conditions and 3 mL/min purge rate. Due to water vapor and increased gas temperature, this period appears to shorten significantly for tests equilibrating at the boiling point temperature.
- Condenser cooling water set point: 10 °C
- Condenser gas output temperature target: 10 to 30 °C (influenced by ambient shielded cell temperature)
- Heating rod temperature target: less than 20 °C above solution temperature when equilibrating at measurement temperature, less than 30 °C above solution temperature when heating to measurement temperature

- Mixer rate: nominally 100 to 300 rpm, or as needed for liquid mixing and foam control. Note that there was not visual confirmation of mixing.

The testing parameters for flow-system testing of Tank 50 were as follows.
- Measurement apparatus: nominally 1 L flow system, fluoropolymer vessel with fluoropolymer lid. Total volume (liquid and gas) of approximately 1.2 L.
- Test sample: first quarter 2018 Tank 50 sample HTF-50-18-12.
- Sample density: approximately 1.24 g/mL at 23.9 °C
- Sample volume: approximately 1.0 L
- Sample mass: approximately 1240 g
- Glycolate addition: 350 mg/L of glycolate (as sodium glycolate)
- Equipment total gas volume: approximately 200 mL
- Target measurement purge rate: 3 mL/min at standard conditions (1 atm and 21.1 °C). Higher rates of air without Kr tracer (e.g., 10 to 40 sccm) were used during periods of temperature adjustment. Lower rate of purge gas with Kr tracer (3 mL/min) was applied once the measurement temperature is attained and the Kr measurement provided an indication that the test has proceeded for at least three vapor space volume turn-overs.
- Expected minimum time to equilibrate for HGR measurement: It requires approximately 3.3 hours to achieve three vapor space volume turn-overs at standard conditions and 3 mL/min purge rate.
- Condenser cooling water set point: 10 °C
- Condenser gas output temperature target: 10 to 30 °C (influenced by ambient shielded cell temperature)
- Heating rod temperature target: less than 20 °C above solution temperature when equilibrating at measurement temperature, less than 30 °C above solution temperature when heating to measurement temperature
- Mixer rate: nominally 100 to 300 rpm, or as needed for liquid mixing and foam control. Note that there was not visual confirmation of mixing.

2.3.3 *Flow System Testing Process*

HGR measurements at a series of temperatures were performed on a single aliquot of the Tank 38 sample without and with the addition of sodium glycolate. The measurement was performed by holding the Tank 38 material in a fluoropolymer vessel that allows for mixing, heating, temperature measurement, and gas measurement. Hydrogen, methane, and tracer in the offgas were measured by a GC system. The offgas was carried to the GC by purge gas, which is a mixture containing 20 vol% oxygen, 0.5 vol % krypton tracer, and the balance nitrogen. The measurements of Tank 38 material without glycolate occurred at near ambient temperature, followed by a series of increasing temperatures, culminating with testing at the atmospheric pressure boiling point of the material. The material was cooled to below 50 °C and sodium glycolate was added. The series of increasing temperatures (up to the atmospheric pressure boiling point) was repeated for the material with added glycolate. At the conclusion of testing, the material was cooled to below 50 °C and again heated to boiling to investigate differences in the HGR for repeated boiling periods.

Similarly, HGR measurements at a series of temperatures were performed on a single aliquot of the Tank 50 material with the addition of sodium glycolate in the SRNL Shielded Cells. The measurements were performed by holding the Tank 50 material and sodium glycolate in a fluoropolymer vessel that allowed for mixing, heating, temperature measurement, and gas measurement. Hydrogen, methane, and tracer in the offgas were measured by a GC system. The offgas was carried to the GC by purge gas, which is a mixture containing 20 vol% oxygen, 0.5 vol % krypton tracer, and the balance nitrogen. The measurements of Tank 50 material with added glycolate occurred at a series of elevated temperatures: 70, 85, and 100 °C. These

temperatures were selected because it is expected that at least two of the three HGR measurements will be above the target LOQ for the flow system of approximately 6×10^{-8} ft^3 h^{-1} gal^{-1}. HGR measurements at lower temperatures are more suitable for the sealed system.

For each measurement condition, time zero of the measurement is when the target temperature has been reached and the measurement purge flow has been established. At time zero, it is assumed that the thermolytic reactions in the liquid phase generating hydrogen and the release of the hydrogen into the vapor phase are constant. In that case, the minimum time for the experiment after time zero is the sum of three components: 1) the time required for three vapor space volume turn overs in the flow system vessel, 2) the amount of time required to displace gas from the volume of the line to the GC instrument, and 3) the time required to obtain eight to ten valid gas concentration measurements by GC. The ratio of the krypton concentration in the offgas (Kr) to the krypton concentration in the purge gas (Kr$_0$) is monitored to assist in determining when this minimum time has been met. If the assumption of a constant formation and release of hydrogen at time zero is not valid (e.g., HGR increasing due to accumulation of a reactive intermediate or HGR decreasing due to depletion of a reactant), the experiment time is extended from the minimum time that was targeted. In those cases, the measurement time was extended while monitoring hydrogen concentration until the change in hydrogen concentration was less than 10% over the final hour of measurements.

Analysis of the flow-system data assumes the equipment functions like a classic continuous stirred tank reactor. Hence, until sufficient purge gas has been supplied to provide ~3 full vapor space turnovers, the test is still in a transition period approaching a pseudo steady-state. Until $Kr/Kr_0 \geq 0.8$, the HGR is in transition (i.e., having achieved only 1-2 vapor space turnovers). Although hydrogen concentration measurements are valid during transition, the HGR values during transition are less reliable for projecting the pseudo steady-state HGR. During the early period of data collection, the purge rate is altered to allow for quantifying the degree of approach to steady-state conditions. Hence, values before $Kr/Kr_0 \approx 0.8$ are not useful in determining the pseudo steady-state HGR. The report only provides HGR values adjusted for measured tracer in the non-condensable offgas when $Kr/Kr_0 \geq 0.8$ in the flow system. The target of three vapor space turnovers corresponds to $Kr/Kr_0 \approx 0.99$. Requiring measured attainment of $Kr/Kr_0 \geq 0.99$ is impractical due to flow controller uncertainty, GC analysis uncertainty, uncondensed water vapor, and possible trace production of gasses such as N_2.

Step-by-step details of the flow system testing process are included in Appendix A.

2.3.4 *Sealed System Testing Process*

Approximately 0.6 L of the Tank 50 sample HTF-50-18-12, density of 1.237 g/mL, was used for sealed system radioactive testing, including analysis samples and contingency. For four of five reactors (HGV-3, -4, -5, and -6), the waste material was spiked with 350 mg/L of glycolate in the form of sodium glycolate. For HGV-2 no glycolate was added as a control.

For HGV-2, -3, -4, and -5, the head spaces were set at 100 mL and the reactors were maintained at their target temperature for 6 days. For the low-temperature reactor (HGV-6 at 40 °C), the head space was set to 20 mL to increase sensitivity and it was held at temperature for 27 days to accumulate more hydrogen.

In the sealed-system testing, the reactor vapor space was filled with nitrogen. Each reactor vapor space was sampled and characterized using an Inficon series 3000 micro GC.[a] The GC has an on-board sample pump that can draw gas samples with pressures as low as atmospheric. For the sealed-system tests, the vapor/head space was filled with gas up to 20 psig to allow for multiple gas samples per reactor per test. The GC was configured with a Molsieve 5A column. The instrument was optimized to quantify low quantities of H_2, as

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[a] The Agilent and Inficon Series 3000 GCs are essentially the same. Inficon purchased the 3000 series product line from Agilent.

this was the primary flammable gas of interest. When little or no H_2 generation was expected the GC was calibrated with a nominal 10 ppm H_2, 20% oxygen, balance nitrogen gas standard. From the calibrations, the limit of detection (LOD) for H_2 was determined to be 1 ppm, with the LOQ as 3 ppm.

Step-by-step details of the sealed system testing process are included in Appendix A.

2.4 <u>Data Collection</u>

2.4.1 *Gas Handling and Analysis (flow system)*

Offgas from the tests was characterized using an Agilent series 3000 micro GC. Column-A collected data related to He, H_2, O_2, N_2, Kr, and CH_4, while column-B collected data related to CO_2 and N_2O. Due to limited GC sensitivity when using argon carrier gas (needed for hydrogen quantification), it was not possible to identify other oxides of nitrogen and carbon. The GC method was modified to quantify low quantities of hydrogen. The instruments have previously been used to quantify offgas from DWPF CPC demonstrations which generally have significantly higher gas generation rates. To quantify the low concentrations of hydrogen, sample injection times were increased by a factor of three relative to DWPF simulations. To improve sensitivity, the GC sensitivity mode was changed from normal to high. Because of these changes, the ability to accurately quantify oxygen and nitrogen has been sacrificed, although even with previous settings, the nitrogen results were of limited usefulness, due to low consistency. Raw chromatographic data were acquired by the GC from the offgas stream samples using a separate computer interfaced to the data acquisition computer. Sampling frequency was approximately one chromatogram every eight minutes.

The GC was calibrated with a gas mixture containing 50 ppmv hydrogen, 100 ppmv methane, 20.0 vol% oxygen, 0.5 vol% krypton, 1.0 vol% carbon dioxide, 0.5 vol% nitrous oxide, and the balance nitrogen. It was assumed that the GC response (peak area) was linear and proportional to the gas concentration. This assumption was demonstrated to be appropriate for hydrogen with several other hydrogen-bearing gas standards.[8] The calibrations were verified prior to and after completing the week of flow-system testing.

The primary purge gas contained 0.5 vol% krypton, 20.0 vol% oxygen, and 79.5 vol% nitrogen. Air purge was also available and used to partially flush the system between measurement conditions. The Kr-bearing purge gas (as compared to air) served several purposes. First, by using the measured krypton concentration, one could determine if the headspace of the reaction vessel had been purged of air. Second, unlike air, the purge had no helium and hydrogen, which could interfere with quantification of hydrogen produced from radiolysis or thermolysis. Third, Kr measurements were used to adjust for bulk gas generation from the sample, air leakage into the system, and back-mixing at the GC.

The relationship identified in Equation 3 was used to calculate the HGRs. With this equation, it was assumed that flow out of the vessel was equal to flow into the vessel. The validity of this assumption was confirmed by checking that the measured Kr concentration was the same as the Kr concentration in the purge gas fed to the reaction vessel.

$$HGR = H2_{area} \times \frac{H2_{stdconc}}{H2_{stdarea}} \times \frac{Kr_{stdarea}}{Kr_{stdconc}} \times \frac{Kr_{purgegas}}{Kr_{area}} \times F_{in} \times \frac{\rho}{m} \times 8.020 \times 10^{-6}$$

Equation 3

where,

HGR = H_2 generation rate, $ft^3 \cdot h^{-1} \cdot gal^{-1}$

$H2_{area}$ = GC H_2 response for a gas sample

$H2_{stdconc}$ = Concentration of H_2 calibration gas, ppmv

$H2_{stdarea}$ = Average of five GC responses from the H_2 calibration gas

F_{in} = flow of Kr-bearing purge gas into the reaction vessel, sccm

ρ = density of sample, g·mL^{-1}

m = mass of sample, g

8.020×10^{-6} = conversion factor, ft^3·min·mL·cc^{-1}·gal^{-1}·ppmv^{-1}·hr^{-1}

$Kr_{purgegas}$ = Concentration of Kr in the purge gas, not including any supplemental air, vol%

Kr_{area} = GC Kr response for a gas sample

$Kr_{stdconc}$ = Concentration of Kr calibration gas, vol%

$Kr_{stdarea}$ = Average of five GC responses from the Kr calibration gas

The gas volume basis of the HGR measurements reported in this document is at a standard condition of 25 °C and 1 atm to match the CSTF HGR calculation standard condition. Purge rates quoted in this document are at a standard condition of 21.1 °C and 1 atm to match the standard condition of the HGR measurement apparatus.

The software package GUM workbench[32] was used to determine the partial derivatives used to calculate the overall uncertainty for the above equations. The overall uncertainty (using these derivatives) and one sigma uncertainties in the variables was then used to calculate uncertainties for all the data points using the software package JMP Pro Version 11.2.1.[33]

Based on current and previous GC calibration data,[8] the LOQ for hydrogen was determined to be 2.3 ppmv. Using a simplified version of Equation 3,[b] the LOQ corresponds to 5.1×10^{-8} ft^3 h^{-1} gal^{-1} at the sample volume and purge rate used for Tank 38 flow-system testing and 5.6×10^{-8} ft^3 h^{-1} gal^{-1} for Tank 50 flow-system testing. The LOD was determined to be 1.2 ppmv, which corresponds to 2.6×10^{-8} and 2.8×10^{-8} ft^3 h^{-1} gal^{-1} for Tank 38 and Tank 50 testing, respectively. Measurements below the LOQ are semi-quantitative and should only be applied in a qualitative manner, such as representing general trends (i.e., increasing or decreasing with time). Measurements above the LOD but below the LOQ should be interpreted as positive indications of the presence of hydrogen as distinguishable from the GC baseline measurement. However, measurement uncertainty and bias are greatly increased when below the LOQ, and thus measurement values below the LOQ should not be used in calculations and comparisons.

Since the Tank 38 and Tank 50 flow-system experiments, SRNL evaluated the GC with 2 ppmv and 10 ppmv methane standards (balance air in both cases). The GC was unable to detect 2 ppmv methane. The 10 ppmv methane gas could be detected and quantified. Ten runs of this calibration gas yielded a relative standard deviation of 15%. Based on the 10 ppm methane calibration gas, the GC's LOD is less than 10 ppmv. Using an Environmental Protection Agency (EPA)[34] and Taylor[35] based methodology, the methane LOQ is approximately 14 ppmv.

2.4.2 *Analytical Methods for Sample Analysis*

The feeds of the Tank 38 and Tank 50 (without the addition of glycolate) were analyzed previously.[8, 30] The products after the conclusion of the flow-system HGR tests were analyzed by the following methods. Methods included Inductively Coupled Plasma – Atomic Emissions Spectroscopy (ICP-AES); Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS); Ion Chromatography for Anions (ICA); titration for total

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[b] In Equation 3, the first three terms involving hydrogen simplify to the hydrogen measurement concentration in ppm. The four terms involving krypton simplify to unity.

base, free hydroxide, and other base excluding carbonate; and Total Inorganic Carbon/Total Organic Carbon (TIC/TOC). Additionally, the product from the Tank 38 HGR test was analyzed by Volatile Organics Analysis (VOA) and Semivolatile Organics Analysis (SVOA). The ICA analysis for glycolate and other organic acid anions used an OnGuard II column to remove transition metals to improve the peak shape and ultimately the quantification of these anions.

Tank 50 post-HGR flow-system test product supernate generated from the heated flow-system test with 350 mg/L of glycolate added was also used in a special analysis for technetium to determine the percentage of technetium that was not in oxidation state VII. As-received Tank 50 sample material[30] and material from previous sealed-system heated HGR tests without added glycolate[9] were also used in technetium oxidation state measurements for comparison. The results of the technetium oxidation state measurements are not included in this report. Those results will be included in a separate document.

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.[36] This document, including all calculations (e.g., hydrogen generation rates and uncertainties), 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.[37] Data are recorded in the electronic laboratory notebook system as notebook/experiment numbers A6583-00142-21 and 22, L0833-00239-09, and other associated notebooks/experiments.

For the flow system, the DAC software package used to control, display, and log test parameters is software classification level D.[38] The DAC software controls the heating, mixing, and gas purge flow; displays the test measurements to the user; and records a data file for later use. The DAC software does not perform calculations that are used in this report. The logged data that contributes to HGR calculations are the purge gas flows and the reaction temperature. The purge gas flow instruments are in the Measurement Systems and Equipment (MS&E) program and the thermocouples and temperature scanner are in the Measuring and Test Equipment (M&TE) program. Each of these instruments has an alternative reading outside of the DAC software. Data is periodically recorded manually (e.g., every 20 or 30 minutes) to supplement the files generated by the DAC software. Hence, the temperature and flow measurements meet the requirements for Safety Class application.

For the sealed system, the DAC software package used to display and log test readings from pressure transducers and thermocouples is software classification level D.[39] The thermocouples and pressure transducers are in the M&TE program, satisfying the requirements for Safety Class application.

As described previously, two commercially available statistical software packages (GUM Workbench and JMP® Pro) are utilized for uncertainty analyses for HGR measurements. For these packages, the software classification is level D.[40-41] Both statistical packages have undergone verification and validation.[42] Calculations performed by these software packages are subjected to the technical review process to satisfy the requirements for Safety Class application.

Analytical measurements for gas streams were made with GCs. The GCs are in the MS&E program and thus their software is controlled under the requirements of the MS&E program, satisfying the requirements for Safety Class application. The reprocessed data from the GC software is used in the HGR calculations.

3.0 Results and Discussion

3.1 Results for Tank 38 Actual Waste without Added Glycolate

The full measurement profile including HGR, temperature, purge rates, and tracer measurements is contained in Appendix A.

3.1.1 *Hydrogen Generation Rate Measurements*

Figure 3-1 and Figure 3-2 display HGR data for the June 2018 Tank 38 sample tests without added glycolate. The data reported for each test starts when $Kr/Kr_0 \geq 0.8$, which corresponds to between one and two vessel headspace turn-overs. The earliest time that measurements were concluded was the time required for three vessel headspace turn-overs plus allowing the time for air to reach the GC, which totals approximately 2.5 hours for the Tank 38 test conditions. Tests at most temperatures were extended slightly and the test at boiling was extended significantly for the trend in hydrogen concentration to stabilize. For all measurement temperatures, HGR was evaluated based on the average of the final 10 gas measurements (i.e., the final 80 minutes). Time zero on Figure 3-1 and Figure 3-2 corresponds to the time that the target temperature was attained. As seen in Appendix A, for each test, the measurements were performed in series from lowest to highest temperature on the same sample aliquot. The LOQ value is an approximate minimum value for the LOQ (calculated for $Kr/Kr_0 = 1$, which is applicable only near the end of each test condition). Although the LOQ for hydrogen concentration is constant, the LOQ for HGR decreases with testing time as Kr/Kr_0 increases toward one. The error bars seen in Figure 3-1 and Figure 3-2 represent the 95% confidence intervals (CI) on individual HGR measurements and indicate the points used to calculate the average HGR measurement for each temperature. The HGR results at several of the temperatures showed decreasing trends with measurement time. Thus, some of the HGR results may contain additional bias not represented by the reported CI.

The original intent was to use a heated near-ambient condition of 30 °C for the Tank 38 HGR measurements with and without glycolate. This temperature was chosen to be slightly above the expected ambient temperature in the SRNL Shielded Cells so that it could be controlled by adding a small amount of heat. However, the ambient condition in the Shielded Cells during the week prior to testing was above 30 °C. Thus, the ambient measurements were performed at 35 °C to retain the ability to control this temperature.

As can be seen in Figure 3-1, the HGR measurements at 35, 60, 80 and 95 °C are nearly the same, ranging from 6.43×10^{-8} ft^3 h^{-1} gal^{-1} to 9.28×10^{-8} ft^3 h^{-1} gal^{-1}. At each of those conditions, there was a general decrease in the HGR measurement with time. While the equilibrium condition met the criteria for completing each measurement outlined in Section 2.3.3, the observed continued decrease indicated that 1) the HGR evaluated for these temperatures may have been lower if the measurement was performed over a longer period of time, 2) the HGR measurement at each subsequent temperature is likely dependent on the stopping point of the measurement of the prior temperature, and 3) the order of the measurement temperatures likely influenced the HGR results. Although each increasing temperature increased the HGR, the lack of strong temperature dependence would be indicative of hydrogen production that includes a significant contribution (e.g., radiolysis) not due to thermolysis over the temperature range of 35 to 95 °C for the Tank 38 sample. The decreasing trend in each HGR measurement is consistent with a small amount of a trace component being responsible for thermolytic hydrogen generation, and that component being slowly depleted during testing.
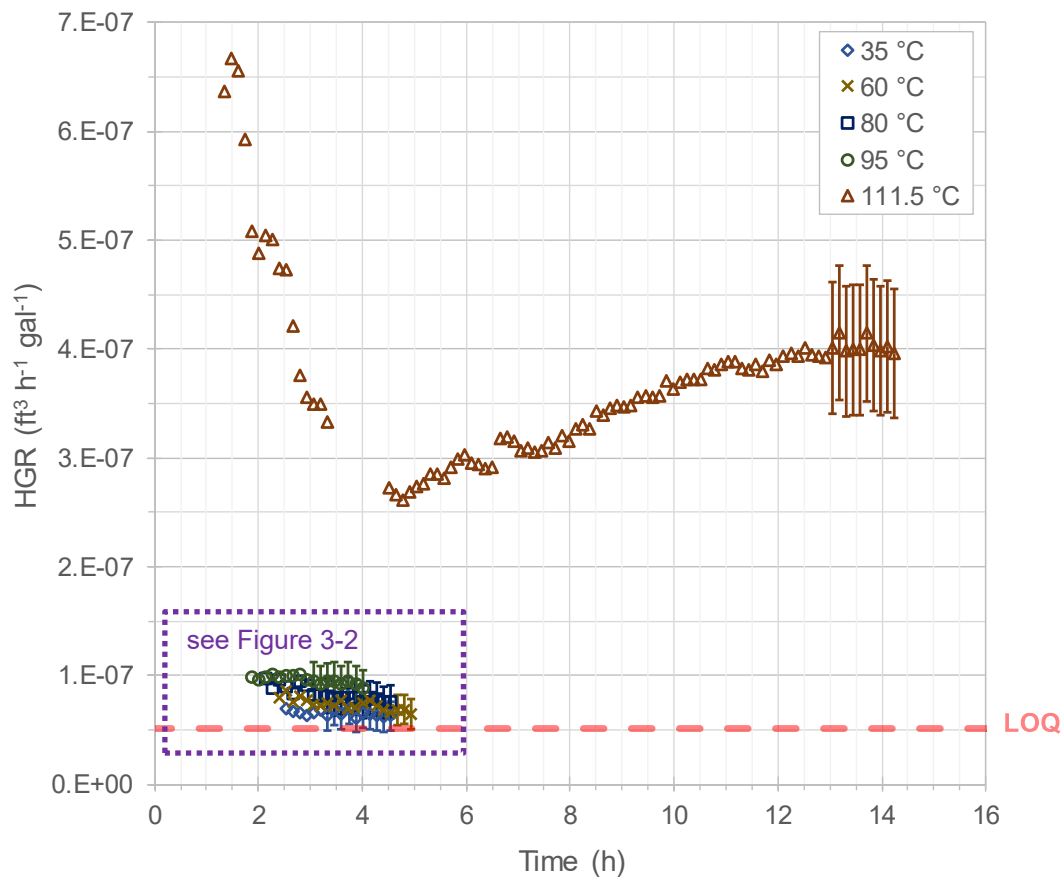
Figure 3-1. HGR measurements for Tank 38 sample without glycolate at a series of increasing temperatures
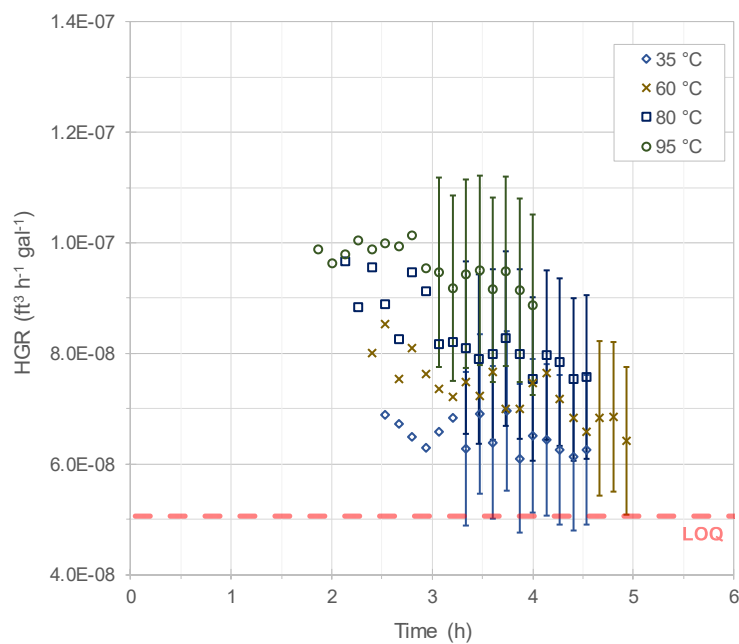

Figure 3-2. Detail of HGR measurements for Tank 38 sample without glycolate focusing only the sub-boiling temperatures

The atmospheric pressure boiling point condition (111.5 °C) displayed a greater HGR and a different time-dependent behavior than observed for the measurements at lower temperatures. The measurements initially decreased at a rate faster than the criteria for completing the HGR measurements. Once a minimum in HGR was observed, however, an increasing trend in HGR was encountered. Ultimately, HGR of Tank 38 material without glycolate at 111.5 °C appeared to plateau at 4.03×10^{-7} ft^3 h^{-1} gal^{-1} (95% CI of $\pm$15%) after 13 hours of measurement. From this observation, the time required to establish liquid phase reaction steady state in the Tank 38 HGR measurement at boiling was considerably longer than the time required to establish gas phase equilibration. This observation is consistent with a small concentration of a compound of higher reactivity being rapidly consumed, followed by more persistent thermolysis of a less reactive compound.

Table 3-1 contains the tabulated results of the June 2018 HGR measurements for Tank 38 sample HTF-38-17-60 without added glycolate. The standard condition for the HGR measurement is 25 °C and 1 atm. All HGR measurements were greater than the approximate LOQ of 5.1×10^{-8} ft^3 h^{-1} gal^{-1}. The reported uncertainty is the 95% CI. Additionally, Table 3-1 contains the tabulated results of the previous August 2017 HGR measurements for a different 1.1 L aliquot of the same actual-waste Tank 38 sample HTF-38-17-60.[8] The August 2017 measurements were performed in the order 27, 110.5, 90, 80, and 100 °C. The June 2018 HGR Tank 38 sample HGR measurements are detailed below.

Table 3-1. HGR measurements for Tank 38 sample without glycolate

June 2018 Measurement			August 2017 Measurement [a]		
T (°C)	HGR (ft^3 h^{-1} gal^{-1})	95% C.I.	T (°C)	HGR (ft^3 h^{-1} gal^{-1})	95% C.I.
35	6.43E-08	± 21%	27	~ 4.8E-08 [b]	N/A
60	6.98E-08	± 20%	80	1.7E-07	± 10%
80	7.87E-08	± 19%	90	4.7E-07	± 10%
95	9.28E-08	± 18%	100	5.9E-07	± 10%
111.5	4.03E-07	± 15%	110.5	2.6E-06	± 10%

[a] from SRNL-STI-2017-00611, Rev. 0
[b] This value is below the LOQ but above the LOD

For all temperatures except for the ambient condition, the HGR measurements from the June 2018 test are lower than the HGR measurements from the August 2017 test performed on a different aliquot of the same sample (HTF-38-17-60). There are several differences in the testing, each of which could account for differences between the two sets of test results:
1. Greater than 11 months had passed between sampling and performance of the June 2018 test while less than two months had passed between sampling and the August 2017 test.
2. The June 2018 flow system uses a Teflon® vessel and lid while the August 2017 flow system used a borosilicate glass vessel and lid.
3. The June 2018 test was performed over a series of increasing temperatures (35, 60, 80, 95, and 111.5 °C) while the August 2017 test was performed in a different sequence of temperatures (27, 110.5, 90, 80, and 100 °C).

The first two test differences have the potential to account for most of the difference between the results while the third test difference is likely a minor contributor to results at different temperatures. First, it is plausible that the most reactive organic species in the Tank 38 sample would continue to react while the

sample is in storage in SRNL and become significantly depleted after a year. Supposing that the organic species that contribute to hydrogen generation in Tank 38 waste are present in small quantities and are only replenished by transfers into Tank 38, storage of a sample could contribute to significant reduction in hydrogen generation with time. The Cs-137 activity in the sample would be reduced by less than 2% over this period, so the decrease in water radiolysis over this period is insignificant. Second, the work of Ashby et al. suggested that experiments where glass is in contact with the waste causes faster reaction of hydroxyethylethylenediamine triacetic acid and possibly glycolate.[5] Such an increased rate of organic depletion might have a corresponding increase in the rate of hydrogen production if the experiments are performed in glass. Neither of these hypothesized causes of the differences in HGR between the June 2018 and August 2017 measurements have been confirmed as the specific cause.

3.1.2 *Other Gas Generation*

Methane generation was noted at levels both above and below the LOQ of 14 ppmv for the boiling condition of Tank 38 without added glycolate. No methane was noted at the other measurement temperatures. Most of the measurements at boiling were below the LOQ, with only three of the 89 measurements being above the methane LOQ. Figure 3-3 shows the measured methane concentration for the Tank 38 sample at boiling without added glycolate and includes the measured hydrogen concentration for comparison. As will be discussed in Section 3.2.2, the methane generated during the June 2018 testing was much lower than the methane generated during the boiling condition of the August 2017 Tank 38 testing.
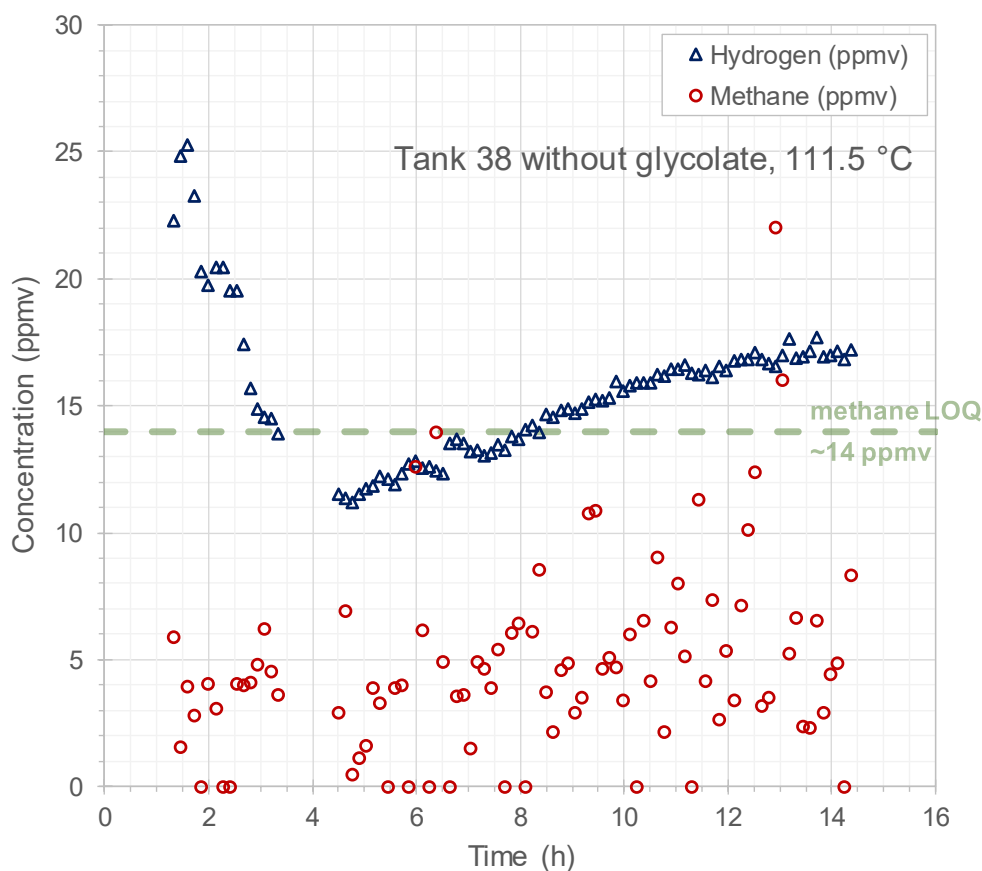

Figure 3-3. Methane and hydrogen concentration measurements in Tank 38 sample at boiling (111.5 °C) without added glycolate

3.2 Results for Tank 38 Waste with Added Glycolate

The full measurement profile including HGR, temperature, purge rates, and tracer measurements is contained in Appendix A.

3.2.1 *Hydrogen Generation Rate Measurements*

Figure 3-4 contains a summary of the Tank 38 sample HGR measurements after the addition of 1570 mg/L of glycolate. Sodium glycolate (2.28 g) was dissolved in 53 g of Tank 38 sample and added to the same Tank 38 sample aliquot that was used immediately prior for HGR measurements without glycolate (Figure 3-1). The data reported for each test is when $Kr/Kr_0 \geq 0.8$, which corresponds to between one and two vessel headspace turn-overs. The earliest time that measurements were assessed for steady-state behavior was the time required for three vessel headspace turn-overs plus allowing the time for air to reach the GC, which will total approximately 2.5 hours for the Tank 38 test conditions. Tests at most temperatures were extended slightly for the trend in hydrogen concentration to stabilize. For all cases, HGR was evaluated based on the average of the final 10 gas measurements (i.e., the final 80 minutes). Time zero on Figure 3-4 corresponds to the time that the target temperature was attained. As seen in Appendix A, for each test, the measurements were performed in series from lowest to highest temperature on the same sample aliquot. The LOQ value is an approximate minimum value for the LOQ (calculated for $Kr/Kr_0 = 1$, which is applicable only near the end of each test condition). Although the LOQ for hydrogen concentration is constant, the LOQ for HGR decreases to its minimum as Kr/Kr_0 increases toward one as the test progresses. The error bars seen in Figure 3-4 represent the 95% CI on individual HGR measurements and indicate the points used to calculate the average HGR measurement for each temperature. The error bars on the 80 °C data are approximately the height of the symbols on the graph.

As with the HGR test without glycolate, the HGR measurements of Tank 38 with 1570 mg/L of glycolate were performed at a series of temperatures, starting with the near ambient temperature (35 °C) and continuing to subsequent temperatures of 60, 80, 95, and boiling (111.5 °C). The sodium glycolate was added as the sample material from the previous experiment cooled below 40 °C. The initial temperature of 35 °C was below both the LOQ ($<5.1\times10^{-8}$ ft^3 h^{-1} gal^{-1}) and LOD ($<2.6\times10^{-8}$ ft^3 h^{-1} gal^{-1}). Even with the addition of 1570 mg/L of glycolate, the 35 °C non-detect result was lower than both the June 2018 and August 2017 tests without glycolate (6.43×10^{-8} ft^3 h^{-1} gal^{-1} and $<4.8\times10^{-8}$ ft^3 h^{-1} gal^{-1}, respectively).

In Figure 3-4 and Table 3-2, the subsequent results at a series of increasing temperatures (60, 80, 95, and 111.5 °C) resulted in progressively increasing HGR measurements. The 60 °C HGR measurement of Tank 38 with 1570 mg/L glycolate was 6.63×10^{-8} ft^3 h^{-1} gal^{-1}, which was near the LOQ and within the value, when considering the uncertainty of the 60 °C HGR result for Tank 38 without added glycolate. Although the 60 °C measurement attained the criteria for completion of the test condition after approximately 6 hours, the 60 °C HGR measurement may be biased low when compared to the other glycolate HGR results at higher temperatures. A recent simulant HGR test with glycolate at the relatively low flow-system temperature of 60 °C demonstrated that the HGR can continue to slowly increase before appearing to plateau after approximately 36 hours of testing.[43] Testing at 60 °C involves a relatively low temperature for short term glycolate thermolysis, as it appears that liquid phase steady state may take significant time for the specific thermolysis reactions involved. It is not known whether a higher HGR result would have been measured for 60 °C if the solution would have been held at a higher temperature for a period of time to allow reactive intermediates to accumulate. Thus, because the measurement at 60 °C may be biased low, the data at 60 °C should be given less regard than the measurements at the higher temperatures for Tank 38 tests with glycolate.
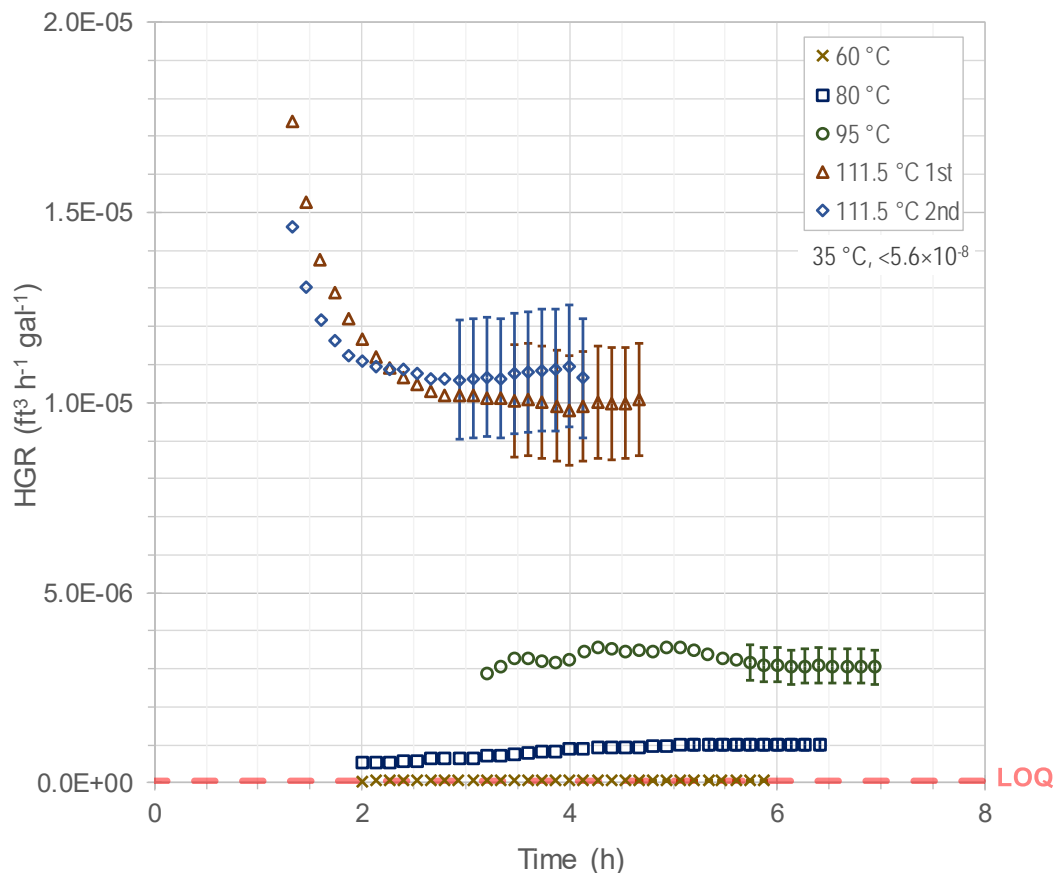
Figure 3-4. HGR measurements for Tank 38 sample with 1570 mg/L of added glycolate at a series of increasing temperatures

After gas phase equilibration the HGR measurement at 80 °C had a period of increase before appearing to plateau at 9.99×10^{-7} ft^3 h^{-1} gal^{-1}. The HGR measurement at 95 °C had short periods of increase and decrease before appearing to stabilize at 3.08×10^{-6} ft^3 h^{-1} gal^{-1}. The first period at boiling resulted in a stable HGR at 9.99×10^{-6} ft^3 h^{-1} gal^{-1} and the second period at boiling resulted in a slightly higher HGR of 1.07×10^{-5} ft^3 h^{-1} gal^{-1}, for an average HGR of 1.04×10^{-5} ft^3 h^{-1} gal^{-1} at 111.5 °C. This reproducibility of the two periods at boiling is within the experimental uncertainty of the measurements, as shown on Figure 3-4.

Table 3-2. HGR measurements for Tank 38 sample with 1570 mg/L of added glycolate

T (°C)	HGR (ft^3 h^{-1} gal^{-1})	95% C.I.
35	<5.1E-08 [a]	--
60	6.63E-08	± 20%
80	9.99E-07	± 15%
95	3.08E-06	± 15%
111.5	9.99E-06	± 15%
111.5	1.07E-05	± 15%

[a] No hydrogen detected with a LOD of 2.6×10^{-8} ft^3 h^{-1} gal^{-1}

Figure 3-5 contains a summary of HGR data from the June 2018 measurements of Tank 38 sample without and with 1570 mg/L of added glycolate. At 60 °C, the HGR with added glycolate, which may be biased low as discussed previously, matched the HGR without added glycolate within the experimental uncertainty. At 80 °C and higher temperatures, the HGR measurements with 1570 mg/L of added glycolate were more than an order of magnitude greater than the HGR measurements without added glycolate.
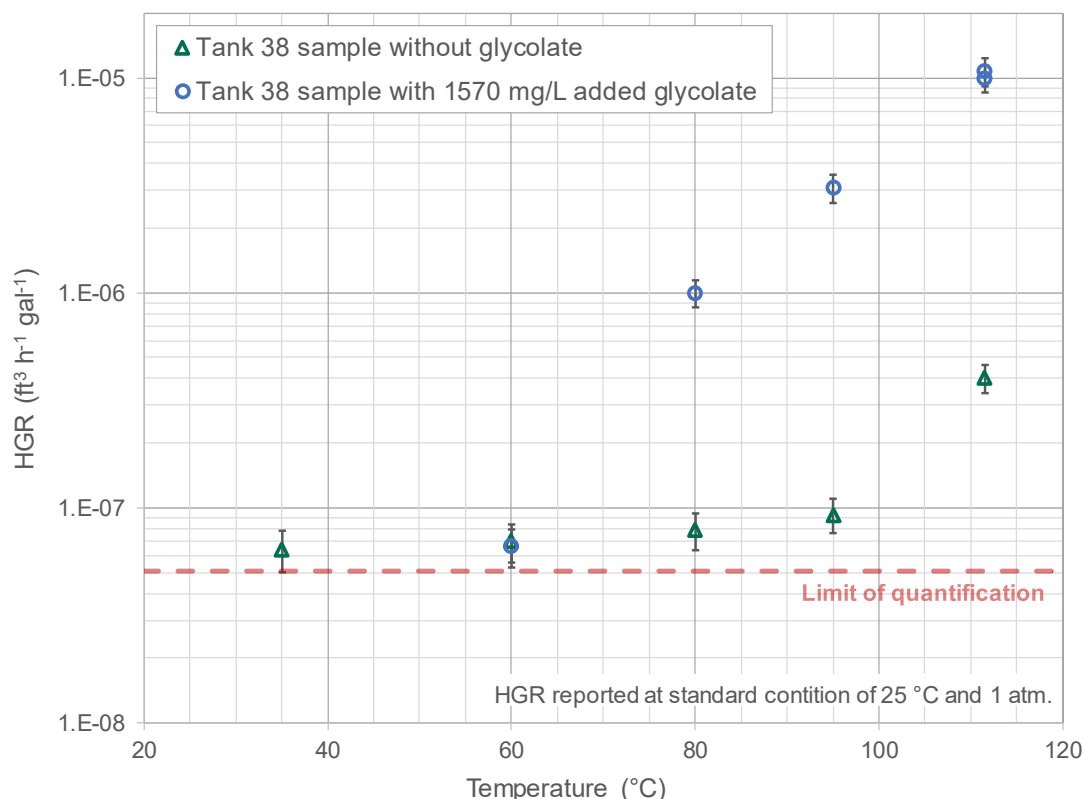
Figure 3-5. Comparison of June 2018 HGR measurements of Tank 38 sample without and with 1570 mg/L of added glycolate

Table 3-3 contains predictions for the thermolytic HGR for the Tank 38 sample material with the addition of 1570 mg/L of glycolate compared with the HGR measurement results. In evaluating the Hu expression for organics (Equation 1) and the Crawford/King expression for glycolate (Equation 2), the following inputs are used. Concentrations for aluminum (9.42×10^{-2} M), nitrite (2.37 M), and hydroxide (2.85 M) are based on the previously measured values[8] for Tank 38 sample HTF-38-17-60, although using the post-HGR test analysis would result in similar predictions. The TOC used in the evaluation of the Hu expression was the average "Adjusted TOC (TOC – formate – oxalate)" of the original sample HTF-38-17-60 analysis (136 mg C/L) plus the 502 mg C/L of added TOC from the 1570 mg/L of glycolate, for a total of 638 mg C/L (or 0.0481 wt%). For the Crawford/King expression, the glycolate value used was the amount added to the experiment (2.09×10^{-2} M).

Table 3-3. Comparison of the measurement test of Tank 38 sample with 1570 mg/L of added glycolate compared with evaluated Hu (r_f=1) and Crawford/King relationships

Tank 38 T (°C)	measured HGR (ft^3 hr^{-1} gal^{-1})	95% CI	Hu HGR (ft^3 hr^{-1} gal^{-1})	Crawford/King HGR (ft^3 hr^{-1} gal^{-1})	measured / Hu
111.5	9.99E-06	15%	5.61E-06	1.19E-06	1.8
	1.07E-05	15%			1.9
95	3.08E-06	15%	1.60E-06	2.45E-07	1.9
80	9.99E-07	15%	4.61E-07	5.11E-08	2.2
60	6.63E-08	20%	7.38E-08	5.07E-09	0.90
35	<5.1E-08	--	5.35E-09	1.85E-10	--

The HGR measurement results for Tank 38 with 1570 mg/L glycolate at boiling was higher than indicated by both the Hu and Crawford/King expressions. The measured HGR at 80, 95, and 111.5 °C were approximately 2 times that of the Hu expression evaluated with r_f = 1. At 60 °C, however, the Hu expression was within the experimental uncertainty of the measured HGR result. The Crawford/King prediction, which considers only thermolytic HGR from glycolate, yielded results that were consistently low for all temperatures for Tank 38 with added glycolate when compared with the measured HGR and the Hu prediction.

Figure 3-6 is an Arrhenius plot for the temperature relationship of the measured HGR for Tank 38 with 1570 mg/L of added glycolate. From the plot, the four higher temperature HGR measurements (80, 95, and two measurements at 111.5 °C) are very close to linear (R^2=0.999). The HGR measurement at 60 °C appears low when compared with the linear fit of the other temperatures. As mentioned previously, this may be due to the need to accumulate a reactive intermediate that forms slowly at the lower temperature before the maximum HGR at 60 °C is reached. The HGR for 35 °C were not included in the Arrhenius plot because the hydrogen results were below the LOQ.

Simulant testing is in progress to develop a model for the thermolytic HGR of glycolate over a range of temperatures and salt component concentrations applicable to CSTF.[18, 43] The Tank 38 HGR results will be compared to the model developed through simulant testing, and that comparison will be contained in a separate report.

Using only the measurements at 80, 95, 111.5 °C, the activation energy (E_A) is 84.1 ± 8.3 kJ/mol where the uncertainty is the 95% CI. This is consistent with the E_A from the Hu relationship (Equation 1, 89.6 kJ/mol) but is lower than the E_A from the Crawford/King relationship (Equation 2, 113.0 kJ/mol). Including the 60 °C measurement in the analysis, the E_A is 101.7 ± 22.3 kJ/mol. The uncertainty of this relationship using all our measurement data is large enough to be consistent with both the Hu and Crawford/King relationships.
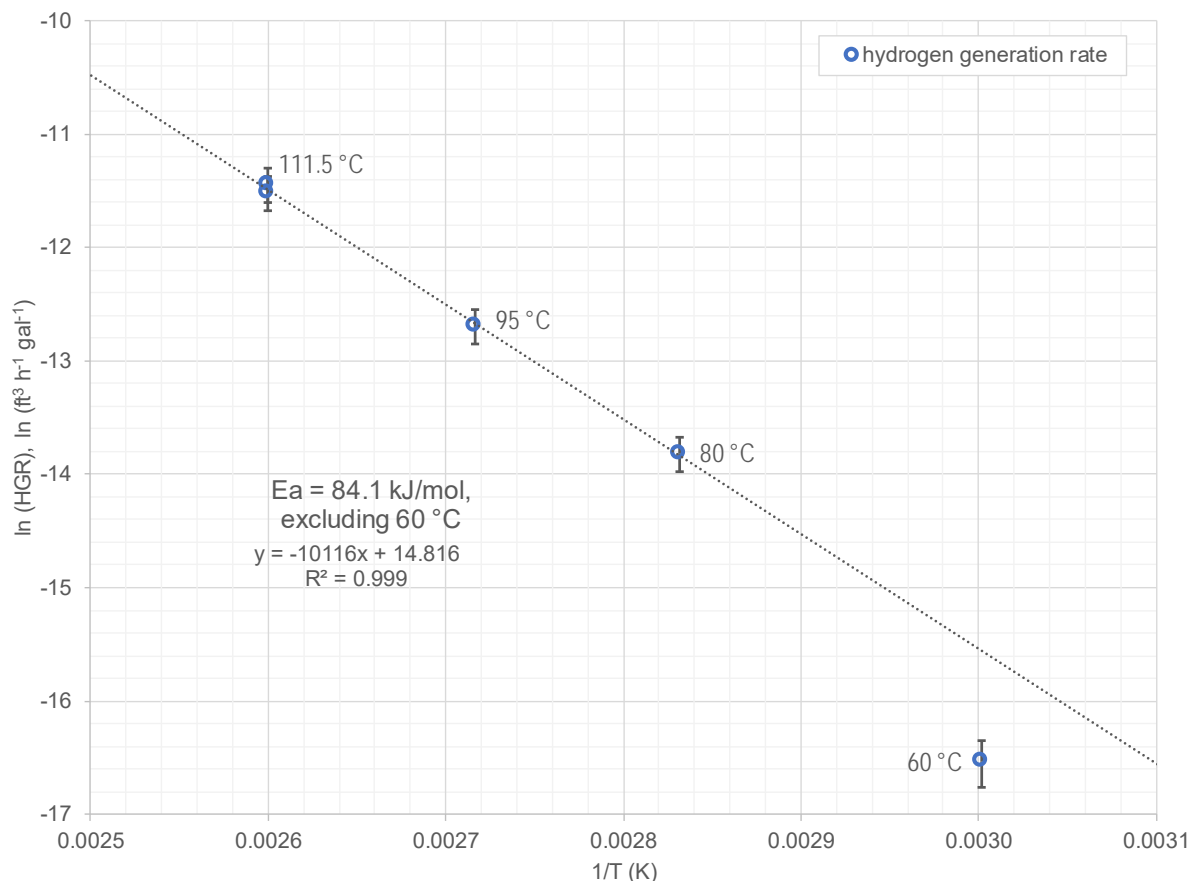
Figure 3-6. Arrhenius plot for hydrogen generation of Tank 38 sample with 1570 mg/L of added glycolate

3.2.2 *Other Gas Generation*

Methane generation was noted at levels both above and below the LOQ of 14 ppmv for the boiling condition of Tank 38 with 1570 mg/L of added glycolate. No methane was noted at the other measurement temperatures. After equilibration, 37 of the 49 methane measurements at boiling were above the LOQ. Figure 3-7 shows the measured methane concentration for the Tank 38 sample at boiling with 1570 mg/L of added glycolate and includes the measured hydrogen concentration for comparison. The concentration of methane produced in the June 2018 with glycolate is greater than the methane produced for the June 2018 Tank 38 test without glycolate. However, the concentration methane produced in the June 2018 with glycolate is much lower than the hydrogen produced for the same test. Methane measured in the June 2018 Tank 38 test with glycolate was in the range of 15 to 30 ppmv while hydrogen measured for the same test was in the range of 400 to 500 ppmv. The measurement of methane, though scattered, was repeatable when the Tank 38 sample with 1570 mg/L of added glycolate was brought back to boiling for a second period.

Figure 3-8 compares the methane concentrations from the four Tank 38 measurements at boiling conditions (August 2017 without added glycolate, June 2018 without added glycolate, and two measurements for June 2018 with 1570 mg/L of added glycolate). The highest methane after test equilibration was encountered for the August 2017 test without added glycolate, which averaged approximately 45 ppmv of methane, or approximately 1×10^{-6} ft^3 h^{-1} gal^{-1}. The methane generated during the boiling condition of the June 2018 testing without added glycolate averaged below the LOQ of 14 ppmv of methane (or 3.1×10^{-7} ft^3 h^{-1} gal^{-1}),

which is much lower than the methane generated during the comparable August 2017 test. The methane results above the LOQ for the Tank 38 testing with glycolate averaged 18 and 22 ppmv (4×10^{-7} and 5×10^{-7} ft^3 h^{-1} gal^{-1}) for the repeated test at boiling. While the glycolate appeared to increase the methane generation in the Tank 38 material at boiling looking only at the June 2018 test, the test with glycolate remained within the methane generation noted for the test performed without glycolate in August 2017.
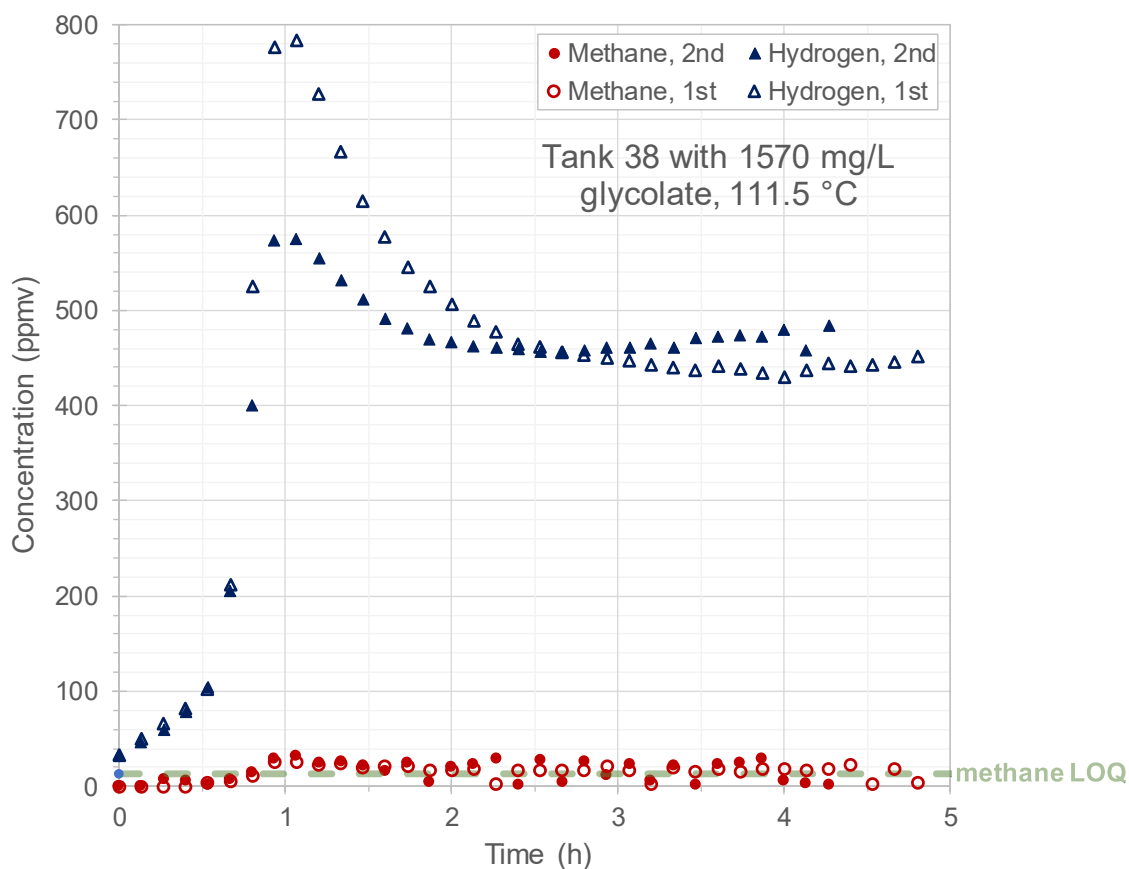
Figure 3-7. Relative methane and hydrogen concentration during thermolysis experiments at boiling created from Tank 38 sample material with 1570 mg/L added glycolate
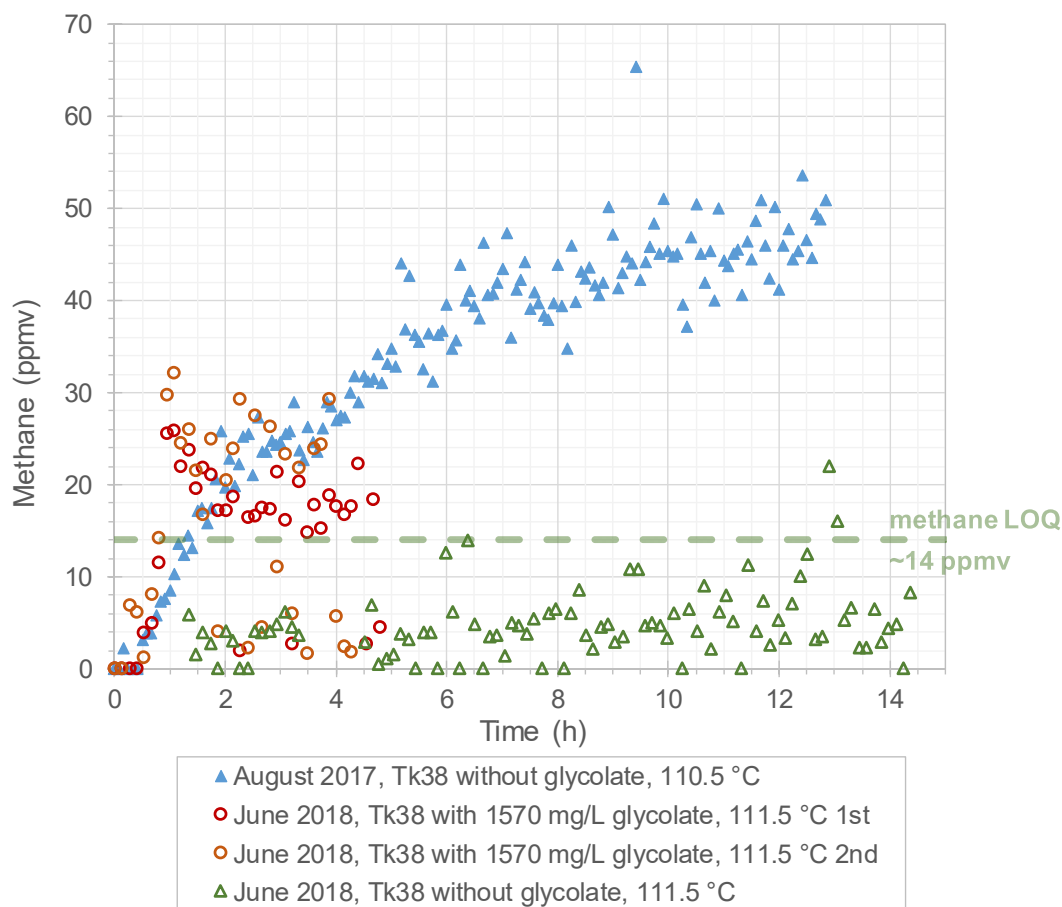
Figure 3-8. Comparison of methane measurements in Tank 38 sample tests from multiple steady state periods at boiling

The source of the methane generation was not determined. Because methane was observed without the addition of glycolate to the Tank 38 sample, glycolate cannot be the sole contributor to methane generation. However, based on the comparison of the June 2018 results at boiling with and without glycolate, glycolate may contribute to the generation of methane. The DWPF antifoam degradation product trimethylsilanol (TMS) and legacy antifoam used in the 2H-Evaporator are other potential candidates for the source of methane, although it is unknown at what levels those were present in the sample used in testing. Unpublished results for CSTF supernate simulant testing identified methane as a thermolysis product from TMS.[44] Methylmercury is also a suspected path to the generation of methane.[45] Tank 38 has had a relatively high concentration of methylmercury, with the Tank 38 subsurface samples from 2015 and 2016 having approximately 160 mg/L of methylmercury.[46-47] The methylmercury content of the HST-38-17-60 could not be confirmed, likely due to the method of storage and analytical preparation.

Nitrous oxide (N_2O) and carbon dioxide (CO_2) were not detected during Tank 38 sample HGR testing without and with added sodium glycolate.

3.2.3 *Tank 38 Sample Analysis*

Table 3-4 contains the results of the analyses of the Tank 38 post-HGR flow-system sample as compared with the feed analysis from sample HTF-38-17-60.[8] Other analysis results that were below the detection limit are tabulated in Appendix A.

Table 3-4. Analysis of post-HGR flow system Tank 38 material

analyte	method	units	1σ (%)	post-HGR average	RSD	n	feed [a]	RSD	% change [c]
density	gravimetric	g/mL		1.332	0.6%	4	1.327	0.7%	0.4%
Na^+	ICP-ES	M	10	7.89E+00	2.7%	2	7.79E+00	0.4%	1%
OH^-	titration	M	10	3.00E+00	0.2%	2	2.85E+00	3.5%	5%
NO_3^-	IC	M	10	1.22E+00	0.8%	2	1.27E+00	0.6%	-4%
NO_2^-	IC	M	10	2.33E+00	1.3%	2	2.37E+00	0.8%	-2%
CO_3^{2-}	TIC/TOC	M	10	6.86E-01	0.7%	2	6.27E-01	0.4%	9%
$Al(OH)_4^-$	ICP-ES	M	10	8.49E-02	1.9%	2	9.40E-02	0.8%	-10%
SO_4^{2-}	IC	M	10	7.37E-02	0.7%	2	6.08E-02	2.2%	21%
PO_4^{3-}	IC	M	10	4.80E-03	0.3%	2	3.98E-03	6.5%	21%
Cl^-	IC	M	10	7.32E-03	1.4%	2	6.90E-03	0.3%	6%
CHO_2^-	IC	M	10	4.21E-02	3.2%	2	3.49E-02	0.6%	21%
$C_2O_4^{2-}$	IC	M	10	3.90E-03	0.2%	2	5.01E-03	0.8%	-22%
$C_2H_3O_3^{2-}$	IC	M	10	2.08E-02	1.8%	2	2.09E-02 [b]	--	-1% [b]
TOC	TIC/TOC	mg C/L	10	1.19E+03	0.6%	2	6.76E+02	--	75%
B	ICP-ES	mg/L	10	1.68E+02	2.5%	2	1.82E+02	1.1%	-8%
Cr	ICP-ES	mg/L	11	9.79E+01	1.3%	2	1.04E+02	0.8%	-6%
Li	ICP-ES	mg/L	10	8.57E+01	4.0%	2	9.44E+01	3.8%	-9%
Si	ICP-ES	mg/L	20	9.17E+01	16%	2	1.56E+02	2.8%	-41%

[a] from SRNL-STI-2017-00611 Revision 0[8]
[b] not analyzed, based on the targeted 1570 mg/L addition of glycolate
[c] (Post-HGR concentration – feed concentration) / (feed concentration) × 100%

Notable analytical results are the reasonably good matches between the expected (feed) and the post-HGR measurements of glycolate, sodium, and many of the anions thought to be important to HGR (nitrite, hydroxide, and aluminate). Any glycolate decomposition during the period of the HGR measurement was too small to be quantified by comparison to the glycolate added to the Tank 38 sample. An addition of 0.0209 M of sodium glycolate was targeted and 0.0208 M of glycolate was measured in the post-HGR sample analysis. The difference in the TOC measurements is mostly due to the addition of glycolate, which was not present in feed measurement but present in post-HGR measurement. Based on analysis, it appears that oxalate may be consumed or decomposed and formate is formed. It is uncertain whether there was an actual change in these values or whether these ~20% changes in oxalate and formate are due to experimental uncertainty.

Additionally, SVOA and VOA was performed on the Tank 38 post-HGR test material, with results below the detection limit. The detection limit was 0.1 mg/L for hexamethyldisiloxane, 1 mg/L for other SVOA analytes, and 0.25 mg/L for VOA analytes (including trimethylsilanol and propanal).

3.3 <u>Results for Tank 50 Actual Waste with Added Glycolate</u>

3.3.1 *Hydrogen Generation Rate Measurements*

Previous sealed-system HGR measurement testing with Tank 50 radioactive sample material was completed over a range of nominally 30 to 120 °C.[9] The sealed-system HGR tests were performed with and without added materials (such as Isopar® L and saltstone premix), but glycolate was not one of the additives used in the previous testing. This report details flow-system and sealed-system tests of Tank 50 material with 350 mg/L of added glycolate. The flow system was used for higher temperature conditions because at least the two upper temperatures of 85 and 100 °C were expected to produce HGR results above the LOQ for the flow system. The sealed system needed to be used at the lower temperatures (40, 55, and 70 °C) to assure measurable HGR results. The flow-system tests were performed with an air (oxic) atmosphere while the sealed-system tests were performed with a nitrogen (anoxic) atmosphere due to safety requirements for pressurized radioactive testing at SRNL.

3.3.1.1 Flow System

The full measurement profile for the flow-system test, including HGR, temperature, purge rates, and tracer measurements, is contained in Appendix A.

Figure 3-9 contains a summary of the flow system Tank 50 sample HGR measurements after the addition of 350 mg/L of glycolate. As seen in Appendix A, the HGR measurements were performed at a series of increasing temperatures of 70, 85, and 100 °C using the same 1 L sample aliquot. The data reported for each test is when $Kr/Kr_0 \geq 0.8$, which corresponds to between one and two vessel headspace turn-overs. The target is to reach at least three vessel headspace turnovers by the completion of the HGR measurement, which occurs after approximately 3.3 hours. HGR was evaluated based on the average of 8 gas measurements for the 70 and 85 °C conditions and 10 gas measurements for the 100 °C condition. The equilibration period of the 70 °C test unintentionally had GC measurements every 4 minutes instead of every 8 minutes. Thus, the time period of data used in the condition averages are approximately 30 minutes for 70 °C, 60 minutes for 85 °C, and 80 minutes for 100 °C. Time zero on Figure 3-9 corresponds to the time that the target temperature was attained. The LOQ value is an approximate minimum value for the LOQ (calculated for $Kr/Kr_0 = 1$, which is applicable only near the end of each test condition). The error bars seen in Figure 3-9 represent the 95% CI on individual HGR measurements and indicate the points used to calculate the average HGR measurement for each temperature.
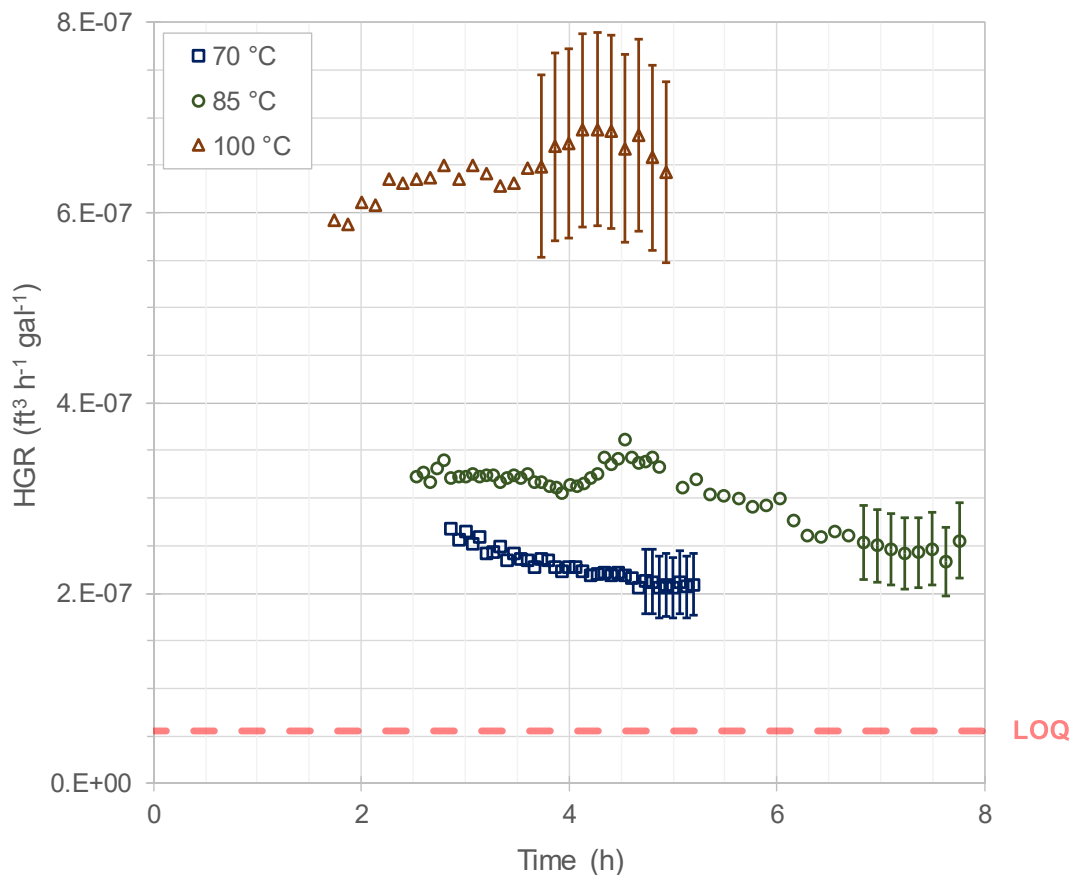
Figure 3-9. HGR measurements for flow-system testing of Tank 50 sample with 350 mg/L of added glycolate at a series of increasing temperatures

The HGR result at 70 °C showed a decline, though the decline was gradual enough to be within the criteria established prior to testing for determining the ending point of the test. The subsequent 85 °C temperature result showed a net decrease before apparently converging on a stable value; and the 100 °C possibly showed an increase before converging on a stable value. The decrease evident in the 85 °C HGR measurement supports the conclusion that the 70 °C HGR measurement would have continued to decrease if the measurement would have been extended to a longer period. The similarity between the 70 and 85 °C measurements gives an indication that there was a temporally inconsistent hydrogen generation (or release) during this testing. The 70 °C measurement is likely biased high due to a combination of two factors. First, as seen with Tank 22 thermolysis HGR tests with the flow system,[10] the release of soluble hydrogen may impact the initial HGR measurements at lower temperatures.[c] Second, there may have been a transient

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[c] In Tank 22 HGR testing, initial peaks were seen at the start of tests at the initial temperature of 30 °C. These peaks were hypothesized to be due to the release of hydrogen that was produced slowly by radiolysis during the sample storage period. There are differences between the Tank 50 testing and the previous Tank 22 testing that calls into question the applicability of this mechanism in accounting for the Tank 50 HGR measurement at 70 °C. First, Tank 50 supernate has a lower potential for radiolytic hydrogen production than Tank 22 supernate or slurry, which would require longer storage to get the same impact from hydrogen produced by radiolysis on Tank 50 measurements. Second, due to the higher salt content, the solubility of hydrogen in Tank 50 supernate should be significantly lower than in Tank 22 supernate, thus reducing the potential for this effect. Third, for Tank 38 and Tank 50 HGR testing, a longer period of a higher purge rate at the initiation of testing was used to flush the reactor headspace of released dissolved hydrogen to avoid the measurement delays caused by the initial peaks encountered in the Tank 22 HGR testing.

(short term) reaction contributing to thermolysis HGR due to a reactant other than glycolate that was already contained in the Tank 50 sample material. Because of the decreasing trend at 70 and 85 °C, the short-term HGR seen in Tank 50 flow-system testing was less likely to be observed in the sealed system due to the difference in time scales between the two measurement methods. Thus, more weight should be given to the longer-term sealed-system tests at 70 °C than the flow-system test at 70 °C when considering the contribution of glycolate to the thermolysis HGR. Table 3-5 contains a tabulation of the HGR measurements and the associated CI for Tank 50 sample flow-system tests with 350 mg/L of added glycolate. The 85 and 100 °C HGR measurements are 2.46×10^{-7} ft^3 h^{-1} gal^{-1} and 6.69×10^{-7} ft^3 h^{-1} gal^{-1}, respectively.

Table 3-5. HGR measurements for flow-system testing of Tank 50 sample with 350 mg/L of added glycolate

T (°C)	HGR (ft^3 h^{-1} gal^{-1})	95% C.I.
70	2.09E-07	± 16%
85	2.46E-07	± 15%
100	6.69E-07	± 15%

3.3.1.2 Sealed System

The radioactive tests used 5 sealed reactors. Three reactors, HGV-2, HGV-3, and HGV-4 were on a single large stirring/hotplate at an average of temperature 73 °C for 6 days and had a nitrogen (anoxic) head space of 100 mL. Two of those reactors, HGV-3 and HGV-4, were duplicate tests spiked with 350 mg/L of glycolate, and the third reactor, HGV-2, served as a control with no glycolate added. HGV-5 and HGV-6 were spiked with 350 mg/L glycolate and were tested at different temperature, head space and duration. HGV-5 was maintained at an average temperature of 58 °C for 6 days and had an anoxic head space of 100 mL. HGV-6 was maintained at an average temperature of 43 °C for 27 days and had an anoxic head space of 20 mL. The lower temperature was expected to produce less hydrogen then the higher temperatures; therefore, a longer test duration was used to allow more hydrogen to accumulate.

The test data are shown in Figure 3-10. With an LOD for hydrogen of 1 ppm and an LOQ of 3 ppm, the hydrogen concentration of 5.2 ppm from the sealed reactor at 58 °C (HGV-5) was just barely quantifiable. The same can be stated for HGV-2 tested at 73 °C without glycolate. The corresponding pressure and temperature data are in Appendix C.

The HGR from this set of five sealed system Tank 50 tests is shown in Figure 3-11. At 73 °C, HGV-2 with no glycolate, has an HGR of about one half of that from the two reactors with 350 mg/L glycolate, i.e., 1.8×10^{-8} ft^3 h^{-1} gal^{-1} versus 3.7×10^{-8} ft^3 h^{-1} gal^{-1} (the average of HGV-3 and HGV-4). The statistical significance of the apparent effect of glycolate addition is evaluated later in this section. When comparing the results from HGV-3/4 (73 °C), HGV-5 (58 °C), and HGV-6 (43 °C), which all have the same glycolate concentration of 350 mg/L, the HGR shows an expected effect from temperature.
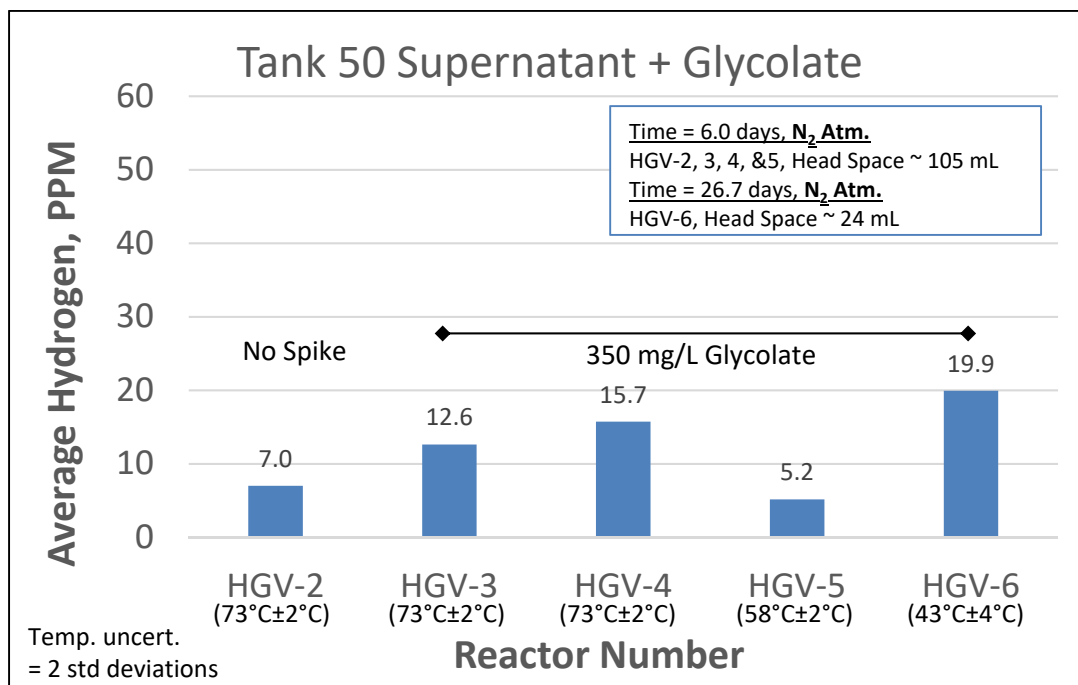
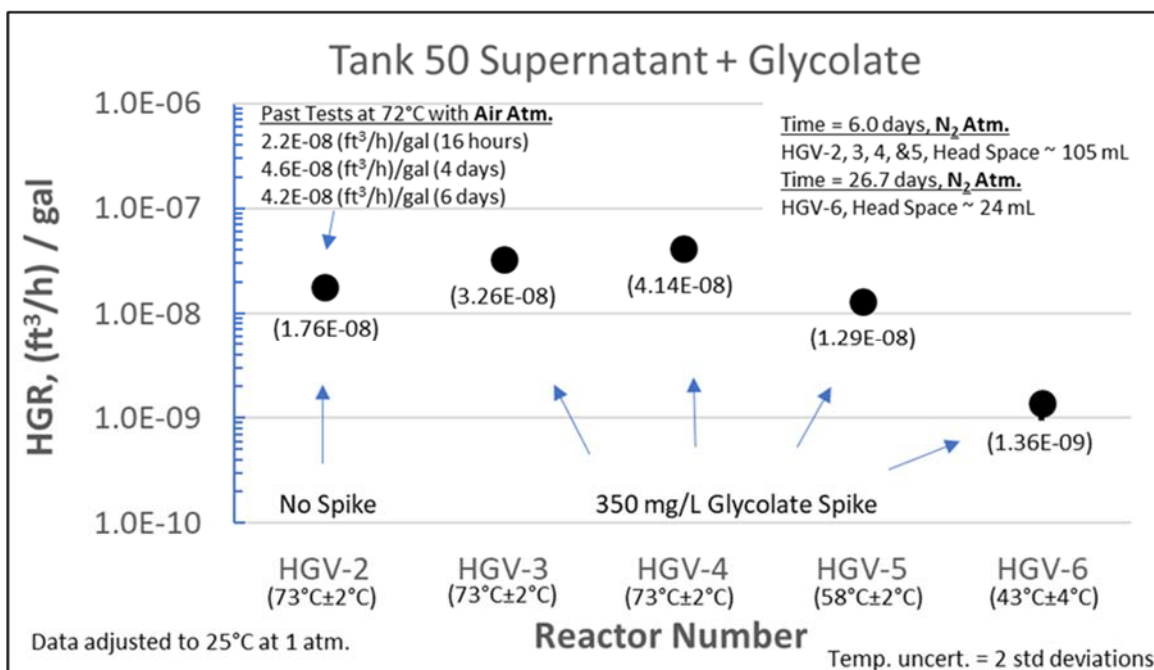**Figure 3-10. Sealed system hydrogen measurements from Tank 50 samples**

Figure 3-11. Sealed system HGR measurements from radioactive Tank 50 samples

Results from previous work[9] from Tank 50 waste (fourth quarter 2017 sample) at 72 °C with no glycolate added are included in a table at the top of Figure 3-11. The test durations ranged from 16 hours to 6 days with a headspace of hydrogen-free air (oxic). The 6-day value was about twice than that obtained for the 6-day value with a nitrogen (anoxic) atmosphere.

Using the Tank 50 thermolysis HGR results from Figure 3-11 at the single temperature of approximately 70 °C, the effects of glycolate and anoxic versus oxic atmospheres were investigated using a statistical construct, which is shown in Figure 3-12. Figure 3-12 contains a plot of means diamonds for three sets of Tank 50 thermolysis HGR results. The solid circles represent the measurements, the top and bottom of the diamonds represent the 95% CIs, and the horizontal line through the center of the diamonds represent the group means. All results for ln(HGR) have units of $\ln(ft^3\ h^{-1}\ gal^{-1})$. From left to right, the first diamond represents HGR for the prior two tests of Tank 50 fourth quarter 2017 sample with no glycolate and an air atmosphere.[9] A third 4 day duration HGR result is not included because the measurement was performed on the same aliquot as the 16 hour test and thus was not a true repeated test. The second diamond represents HGR from HGV-2, with no glycolate and a nitrogen atmosphere. The third diamond represents HGR from HGV-3 and HGV-4, with 350 mg/L added glycolate and a nitrogen atmosphere. Two of the three sets of tests included a repeated test. A pooled standard deviation was developed from these results by considering four additional sets of measurements form repeated tests (which were at different temperatures and/or included different additives).[9] The pooled standard deviation allowed for a better understanding of test reproducibility and contributed to the calculation of the confidence intervals.
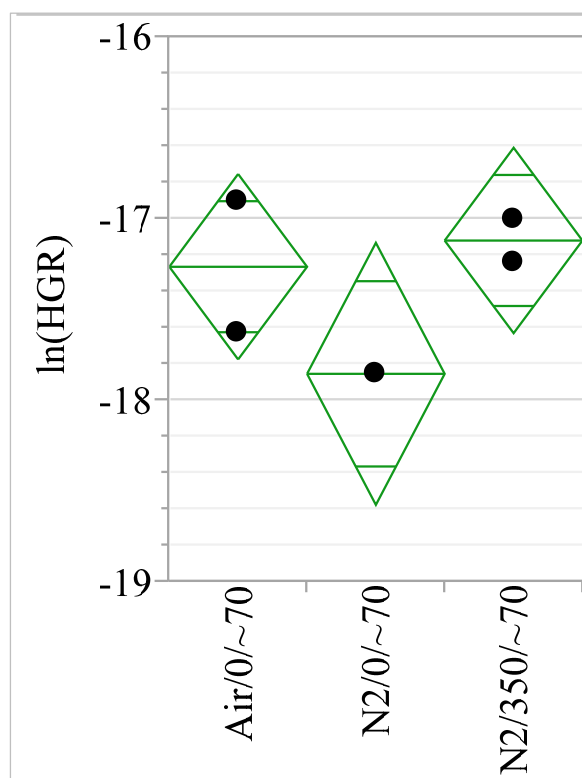
Figure 3-12. Means diamonds plot of Tank 50 of select sealed system HGR data at ~70 °C

A Tukey-Kramer "honestly significant difference" test was applied to the limited set of data available from the sealed system at approximately 70 °C. The analysis failed to show statistically significant differences in the three cases (i.e., no added glycolate with air atmosphere, no added glycolate with nitrogen atmosphere, and 350 mg/L added glycolate with nitrogen atmosphere). Therefore, the null hypothesis that there is no difference between the thermolytic HGR of these three cases has not been rejected. From Figure 3-12, this failure to reject the null hypothesis is consistent with the large overlap in the CIs of ln(HGR) for the three cases.

3.3.1.3 Overall

An Arrhenius plot for Tank 50 flow system and sealed-system tests is shown in Figure 3-13. The E_A is plotted for the tests in this report for Tank 50 material with 350 mg/L of added glycolate. From the Arrhenius expression, it is evident that the result of the flow system test at 70 °C, which was performed first in the series of temperatures, appears to be an outlier. Inclusion or elimination of the 70 °C flow-system test point does not impact the activation energy but does impact the uncertainty and intercept. Including the 70 °C flow-system test, the E_A is 106 ± 45 kJ/mol. Excluding the 70 °C flow-system test, the E_A is 106 ± 21 kJ/mol. The trendline and linear regression displayed in Figure 3-13 includes the 70 °C flow-system test.

Figure 3-13. Arrhenius Plot for Tank 50 HGR

The E_A of 106 ± 21 kJ/mol for Tank 50 testing with 350 mg/L glycolate overlaps the E_A based on the models of Equations 1 and 2. The E_A is greater than but has overlap with the E_A for previous Tank 50 sealed-system testing with no additives, with blast furnace slag, and with grout premix. The E_A for Tank 50 testing with 350 mg/L glycolate is very close to the E_A for previous Tank 50 sealed-system testing with additives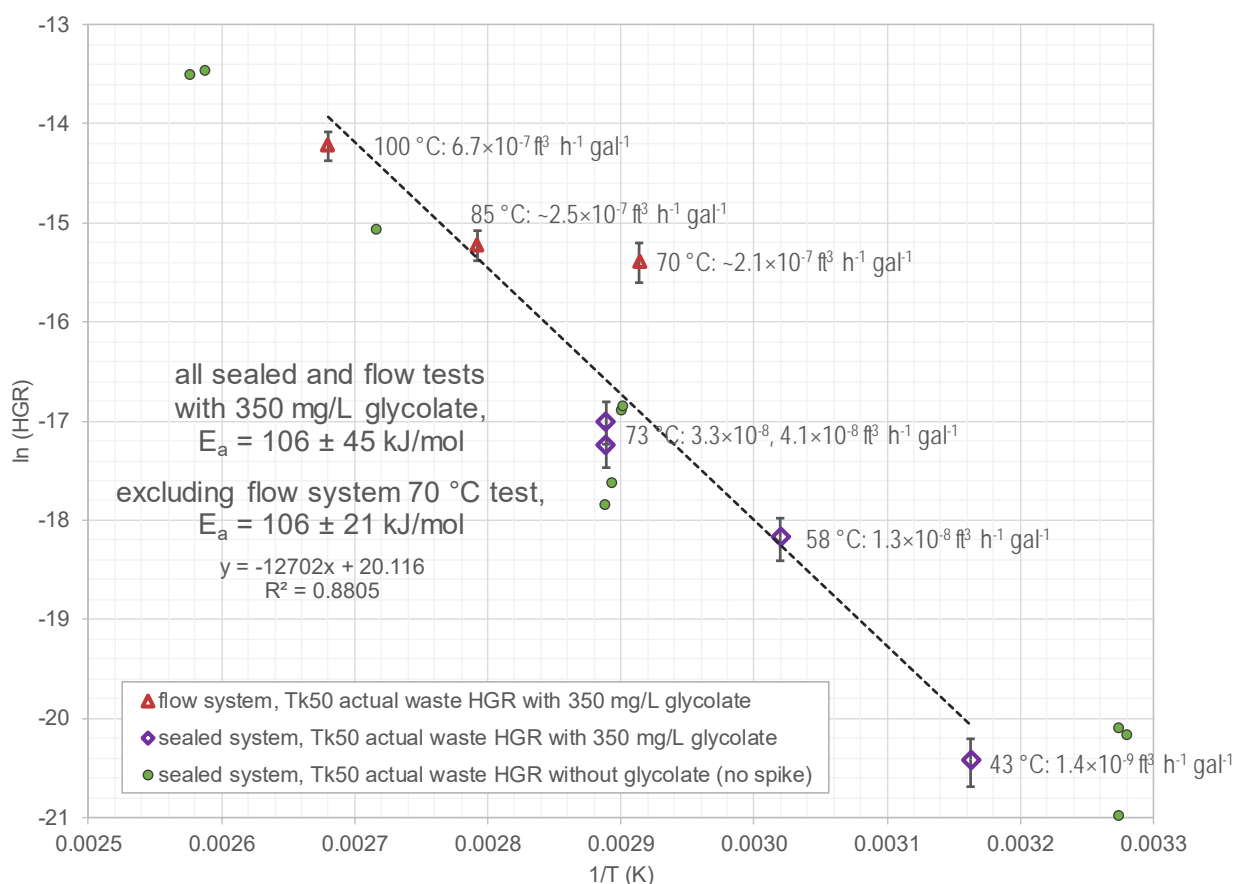 of 98 ± 37 kJ/mol, but that CI is large. The E_A for Tank 50 testing with 350 mg/L glycolate is also in reasonable agreement with the E_A developed from the Tank 38 tests with 1570 mg/L glycolate presented in Section 3.2.1 (i.e., 84.1 ± 8.3 kJ/mol).

Figure 3-13 also contains comparison points for the Tank 50 data without added glycolate from the previous sealed-system test[9] and the one additional point without glycolate gathered during the current sealed-system test. The preponderance of the data (excluding the 70 °C flow system test point) show that the addition of 350 mg/L of added glycolate does not greatly increase the HGR in Tank 50 material. The data from the flow system under oxic conditions and at higher temperatures (85 to 100° C) were able to be merged satisfactorily with the data from the sealed system under anoxic conditions and at lower temperatures (43 to 73 °C).

Table 3-6 contains predictions for the thermolytic HGR for the Tank 50 sample material with the addition of 350 mg/L of glycolate compared with the HGR measurement results. In evaluating the Hu expression (Equation 1), the following inputs are used. Concentrations for aluminum (1.60×10^{-1} M), nitrite (5.50×10^{-1} M), and hydroxide (1.96 M) are based on the previously measured values[8] for Tank 50 sample HTF-50-18-12. The TOC was the average "TOC minus formate and oxalate" of the original sample HTF-50-18-12 analysis (70 mg C/L) plus the 112 mg C/L of added TOC from the 350 mg/L of glycolate, for a total of 182 mg C/L (or 0.0146 wt%). The activation energy and pre-exponential factor was used as shown in Equation 1.

Table 3-6. Comparison of the measurement test of Tank 50 sample with 350 mg/L of added glycolate compared with evaluated Hu relationship (r_f=1)

System/ Atmosphere	Tank 50 T (°C)	measured HGR (ft³ hr⁻¹ gal⁻¹)	95% CI	Hu HGR (ft³ hr⁻¹ gal⁻¹)	measured / Hu
flow/ oxic	100	6.69E-07	15%	9.14E-07	0.73
	85	2.46E-07	15%	2.73E-07	0.90
	70	2.09E-07	16%	7.32E-08	2.9
sealed/ anoxic	73	3.26E-08	21%	9.61E-08	0.34
		4.14E-08	21%		0.43
	58	1.29E-08	21%	2.35E-08	0.55
	43	1.36E-09	24%	5.01E-09	0.27

Except the flow-system test at 70 °C, the HGR measurement results for Tank 50 with 350 mg/L glycolate were near or below the prediction of the Hu expression (evaluated with $r_f = 1$).

The previously discussed analysis of the approximately 70 °C data from the sealed system showed that the increase in thermolysis HGR due to the addition of glycolate was not statistically significant. Overall, due to unknowns in comparing the tests with the two different systems, it was difficult to evaluate whether the increase in thermolysis HGR due to glycolate is statistically significant. By qualitative comparison, the Tank 50 results with 350 mg/L of added glycolate, the impact of the added glycolate appears to be similar to or less severe than the impact of 2.22 g/L of grout premix or 1 g/L of blast furnace slag.[9]

Flammability in Tank 50 is evaluated at a supernate temperature of 43 °C,[48] while HGR measurements at higher temperatures were performed to support SPF. Tank 50 HGR with 350 mg/L glycolate was measured as $1.36 \times 10^{-9} \pm 3.2 \times 10^{-10}$ ft^3 h^{-1} gal^{-1} at a direct comparison temperature of 43 ± 2 °C. Evaluating the linear regression shown in Figure 3-13, Tank 50 HGR with 350 mg/L glycolate at 43 °C is 1.94×10^{-9} ft^3 h^{-1} gal^{-1} based on data at all temperatures measured.

3.3.2 *Other Gas Generation*

In the Tank 50 flow system and sealed-system testing, methane (CH_4) concentration was below the LOQ and LOD. The flow system LOQ of 14 ppmv of methane corresponds to 3.1×10^{-7} ft^3 h^{-1} gal^{-1} of methane. Nitrous oxide (N_2O) and carbon dioxide (CO_2) were also not detected during Tank 50 sample HGR testing.

3.3.3 *Tank 50 Sample Analysis*

3.3.3.1 *Flow System Tank 50 Sample Analysis*

Table 3-7 contains the results of the analyses of the Tank 50 Post-HGR flow-system sample as compared with the feed analysis from the first quarter 2018 Tank 50 sample HTF-50-18-12.[30] Other analysis results that were below the detection limit are tabulated in Appendix B.

Initial analysis for the glycolate concentration in the post-HGR sample was 0.00621 M (466 mg/L), which was 33% higher than the 0.00467 M (350 mg/L) targeted glycolate concentration via sodium glycolate addition to the Tank 50 sample. With the known components in Tank 50, it was not anticipated that glycolate could be produced during HGR testing. Thus, glycolate analysis of the post-HGR sample was repeated along with a portion of the first quarter 2018 Tank 50 sample freshly spiked with 350 mg/L of glycolate. The results of the glycolate re-analysis are shown in Table 3-7. The post-HGR sample glycolate was 0.00451 M (339 mg/L) glycolate. Similarly, to investigate matrix impacts, Tank 50 first quarter 2018 material spiked with 350 mg/L glycolate and was measured to contain 0.00449 M (337 mg/L) glycolate.[d] By comparison of these results, no significant depletion of glycolate was detected in the post-HGR Tank 50 material. It is recommended that the glycolate analysis continue to be examined in the Tank 50 matrix and other CSTF sample matrixes to improve the reliability of future analyses in these samples with higher concentrations of anionic species that complicate the analysis.

The sodium, hydroxide, nitrite, and aluminum differences between the post-HGR measurement and the Tank 50 WAC analyses are reasonable, typically 11% or less. There was a large formate increase of 266% when comparing the post-HGR material with the WAC analysis. The formate in the product is likely an anomalous result; it was not reanalyzed when glycolate measurements were repeated.

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[d] This spike was performed specifically for ICA analysis. The Tank 50 material with 350 mg/L of added glycolate that was used in the flow system test was not sampled prior to the test.

Table 3-7. Analysis of post-HGR flow system Tank 50 material

analyte	method	units	1σ (%)	average	RSD	n	feed [a]	RSD	% change [c]
density	gravimetric	g/mL		1.239	0.6%	4	1.2369	0.01%	0.2%
Na^+	ICP-ES	M	10	5.42E+00	0.6%	2	5.26E+00	0.6%	3%
OH^-	titration	M	10	1.98E+00	0.0%	2	1.98E+00	1.7%	0%
NO_3^-	IC	M	10	2.01E+00	0.6%	2	1.87E+00	23%	7%
NO_2^-	IC	M	10	6.13E-01	2.5%	2	5.50E-01	1.4%	11%
CO_3^{2-}	TIC/TOC	M	10	2.34E-01	0.3%	2	2.60E-01	0.5%	-10%
$Al(OH)_4^-$	ICP-ES	M	10	1.78E-01	4.7%	2	1.60E-01	0.02%	11%
SO_4^{2-}	IC	M	10	4.92E-02	0.9%	2	3.78E-02	4.3%	30%
PO_4^{3-}	IC	M	10	3.93E-03	0.0%	2	1.64E-03	2.3%	139%
Cl^-	IC	M	10	1.46E-02	0.3%	2	1.34E-02	2.4%	9%
$C_2O_4^{2-}$	IC	M	10	6.64E-03	0.6%	2	6.11E-03	2.7%	9%
CHO_2^-	IC	M	10	1.69E-02	0.9%	2	4.62E-03	2.4%	266%
$C_2H_3O_3^{2-}$	IC	M	10	4.51E-03	1.0%	3	4.67E-03 [b]	--	-3% [b]
TOC	TIC/TOC	mg C/L	10	3.80E+02	0.2%	2	2.72E+02	2.5%	40%
B	ICP-ES	mg/L	10	5.10E+01	6.2%	2	4.52E+01	1.3%	13%
Ba	ICP-ES	mg/L	10	2.40E-01	--	1	6.33E-01	9.9%	-62%
Ca	ICP-ES	mg/L	10	7.73E+00	65%	2	--	--	--
Cr	ICP-ES	mg/L	10	6.06E+01	6.2%	2	5.10E+01	1.0%	19%
Fe	ICP-ES	mg/L	10	8.38E+00	31%	2	1.72E+01	63%	-51%
K	ICP-ES	mg/L	10	4.48E+02	6.9%	2	4.16E+02	1.6%	8%
Li	ICP-ES	mg/L	10	1.02E+01	11%	2	<8.9E+00	--	14%
P	ICP-ES	mg/L	10	1.84E+02	7.7%	2	--	--	--
Si	ICP-ES	mg/L	10	2.56E+01	13%	2	2.26E+01	13%	13%
Zn	ICP-ES	mg/L	10	8.61E+00	8.0%	2	7.45E+00	0.7%	16%

[a] from SRNL-STI-2018-00204, Revision 0[30]
[b] based on the targeted 350 mg/L addition of glycolate
[c] (post-HGR concentration – feed concentration) / (feed concentration) × 100%

3.3.3.2 Sealed System Tank 50 Sample Analysis

Table 3-8 shows the analytical results from the post-HGR radioactive waste samples. Other analysis results that were below the detection limit are tabulated in Appendix B. There is an absence of trend in the chemical composition of the waste despite the variation in testing parameters, with post-HGR test glycolate concentrations averaging 399 mg/L for the tests where 350 mg/L of glycolate was added. This corresponds to an average 14% positive bias in the post-HGR test glycolate versus the glycolate concentration added in the tests. The highest silicon measurement occurred for the sample from reactor HGV-6 and may be an outlier; the value is well outside the 95% confidence interval for the other 4 measurements. The TOC concentration for that same sample is ~27% higher than the average for the other three experiments with a comparable glycolate addition.

Table 3-8. Analytical results of Tank 50 sealed system post-HGR test samples

Test name (GLYC-S-T50-)				1	2	3	4	5	
Sealed-system reactor				HGV-2	HGV-3	HGV-4	HGV-5	HGV-6	
Glycolate addition (mg/L)				none	350	350	350	350	
Headspace volume (mL)				100	100	100	100	20	
Temperature (°C)				73	73	73	58	43	
Test duration (days)				6	6	6	6	27	
analyte	method	units	1σ (%)	HGV-2	HGV-3	HGV-4	HGV-5	HGV-6	feed [a]
Na^+	ICP-ES	M	10	5.13E+00	5.26E+00	5.22E+00	5.87E+00	5.09E+00	5.26E+00
OH^-	titration	M	10	1.87E+00	2.13E+00	1.86E+00	1.87E+00	1.90E+00	1.98E+00
NO_3^-	IC	M	10	2.00E+00	2.60E+00	2.00E+00	2.02E+00	1.97E+00	1.87E+00
NO_2^-	IC	M	10	6.02E-01	7.69E-01	5.89E-01	5.96E-01	5.69E-01	5.50E-01
CO_3^{2-}	TIC/TOC	M	10	2.60E-01	2.58E-01	2.56E-01	2.56E-01	2.76E-01	2.60E-01
$Al(OH)_4^-$	ICP-ES	M	10	1.65E-01	1.68E-01	1.66E-01	1.90E-01	1.83E-01	1.60E-01
SO_4^{2-}	IC	M	10	4.70E-02	6.17E-02	4.64E-02	4.65E-02	4.90E-02	3.78E-02
PO_4^{3-}	IC	M	10	3.69E-03	4.75E-03	3.72E-03	3.83E-03	4.27E-03	1.64E-03
Cl^-	IC	M	10	1.40E-02	1.84E-02	1.40E-02	1.42E-02	1.46E-02	1.34E-02
F^-	IC	M	10	<5.3E-03	<5.3E-03	<5.3E-03	5.32E-03	<5.3E-03	<5.3E-04
CHO_2^-	IC	M	--	<2.2E-03	<2.2E-03	<2.2E-03	<2.2E-03	<2.2E-03	6.11E-03
$C_2O_4^{2-}$	IC	M	10	6.18E-03	8.09E-03	6.15E-03	6.16E-03	6.53E-03	4.62E-03
$C_2H_3O_3^{2-}$	IC	M	10	<1.3E-03	5.37E-03	5.44E-03	5.45E-03	5.02E-03	4.67E-03 [b]
TOC	TIC/TOC	mg C/L	10	2.48E+02	3.52E+02	3.55E+02	3.55E+02	4.48E+02	2.72E+02
B	ICP-ES	mg/L	12	5.27E+01	5.00E+01	4.89E+01	4.91E+01	5.69E+01	4.52E+01
Ca	ICP-ES	mg/L	10	3.99E+00	1.97E+01	1.50E+00	2.74E+00	3.41E+00	--
Cr	ICP-ES	mg/L	10	5.82E+01	5.42E+01	5.02E+01	4.89E+01	5.31E+01	6.06E+01
Fe	ICP-ES	mg/L	10	4.09E+00	6.60E+00	6.12E+00	8.22E+00	8.33E+00	8.38E+00
K	ICP-ES	mg/L	10	4.78E+02	4.36E+02	4.62E+02	4.61E+02	4.61E+02	4.48E+02
Li	ICP-ES	mg/L	13	7.72E+00	7.59E+00	7.19E+00	7.58E+00	<2.0E+01	1.02E+01
Mg	ICP-ES	mg/L	10	3.20E-01	2.30E+00	<2.2E-01	<2.2E-01	3.50E-01	--
Mo	ICP-ES	mg/L	11	2.08E+01	1.98E+01	2.00E+01	2.05E+01	1.80E+01	1.81E+01
P	ICP-ES	mg/L	10	1.59E+02	1.52E+02	1.54E+02	1.53E+02	1.58E+02	1.84E+02
Si	ICP-ES	mg/L	10	4.37E+01	4.56E+01	3.25E+01	3.83E+01	1.31E+02	2.56E+01
Zn	ICP-ES	mg/L	10	8.45E+00	7.84E+00	7.66E+00	7.89E+00	7.27E+00	8.61E+00

[a] from SRNL-STI-2018-00204, Revision 0[30]

4.0 Conclusions

The following are key results from the Tank 38 HGR testing:

- Based on conservative assumptions, 1570 mg/L of glycolate was added to the Tank 38 material as a high projection of future evaporator drop tank glycolate concentration. The HGR with 1570 mg/L of added glycolate at 80, 95 and 111.5 °C were 9.99×10^{-7} ft^3 h^{-1} gal^{-1}, 3.08×10^{-6} ft^3 h^{-1} gal^{-1}, and

1.04×10^{-5} ft^3 h^{-1} gal^{-1}, respectively. The reproducibility of HGR measurements from two successive periods at boiling (111.5 °C) were within the experimental uncertainty of the measurements (9.99×10^{-6} ft^3 h^{-1} gal^{-1} and 1.07×10^{-5} ft^3 h^{-1} gal^{-1}, respectively). At temperatures of 80 °C and above, the HGR measurements with 1570 mg/L of added glycolate were more than an order of magnitude greater than the HGR measurements without added glycolate.

- Using the measurements at 80, 95, 111.5 °C, the activation energy for hydrogen generation from thermolysis in Tank 38 with 1570 mg/L of added glycolate is 84.1 ± 8.3 kJ/mol.

- Methane was generated at levels near or below the 14 ppmv (3.1×10^{-7} ft^3 h^{-1} gal^{-1}) LOQ during boiling of Tank 38 without added glycolate. The methane generated during the boiling condition of Tank 38 with 1570 mg/L of added glycolate, when above the LOQ, averaged 18 and 22 ppmv (4×10^{-7} and 5×10^{-7} ft^3 h^{-1} gal^{-1}). The June 2018 Tank 38 test with 1570 mg/L glycolate remained within the methane generation noted for the August 2017 test performed without glycolate, which averaged approximately 45 ppmv (approximately 1×10^{-6} ft^3 h^{-1} gal^{-1}).

- For all temperatures examined except for the ambient condition, the HGR measurements without added glycolate from the June 2018 test are lower than the HGR measurements from the August 2017 test performed on a different aliquot of the same sample (HTF-38-17-60). Although some hypotheses are provided in this report, the specific cause of the decrease is not known. In the June 2018 test, the HGR measurements for Tank 38 sample without added glycolate at 35, 60, 80 and 95 °C are similar to each other, ranging from 6.43×10^{-8} ft^3 h^{-1} gal^{-1} to 9.28×10^{-8} ft^3 h^{-1} gal^{-1}. The HGR of Tank 38 material without glycolate at boiling (111.5 °C) was 4.03×10^{-7} ft^3 h^{-1} gal^{-1} (95% CI ± 15%).

The following are key results from the Tank 50 HGR testing:

- The sealed-system HGR measurements of Tank 50 sample with 350 mg/L of added glycolate at 43, 58, and 73 °C were 1.36×10^{-9}, 1.29×10^{-8}, and 3.70×10^{-8} ft^3 h^{-1} gal^{-1}, respectively. Tank 50 flammability is evaluated at a maximum of 43 °C, but HGR measurements at higher temperatures were performed to support SPF.

- The flow system HGR measurements of Tank 50 sample with 350 mg/L of added glycolate at 85 and 100 °C are 2.46×10^{-7} ft^3 h^{-1} gal^{-1} and 6.69×10^{-7} ft^3 h^{-1} gal^{-1}, respectively. The result measured in the flow system at 70 °C (2.09×10^{-7} ft^3 h^{-1} gal^{-1}) appears biased high with respect to the entire set (i.e., flow and sealed system), suggesting either the release of dissolved hydrogen or a short-lived thermolysis reaction.

- The data from the flow system under oxic conditions at higher temperatures (85 to 100° C) and the data from the sealed system under anoxic conditions at lower temperatures (43 to 73 °C) provide a consistent estimate of activation energy for hydrogen generation from glycolate. Excluding the 70 °C flow-system test, the activation energy for Tank 50 sample with 350 mg/L of added glycolate is 106 ± 21 kJ/mol.

- Comparing to previous sealed-system testing of Tank 50 without added glycolate, the overall set of data demonstrates that HGR of Tank 50 with 350 mg/L of added glycolate is on the same order as HGR without glycolate. Excluding the flow-system test at 70 °C, the HGR measurement results for Tank 50 with 350 mg/L glycolate were near to or less than the prediction of the Hu expression. For sealed-system tests near 70 °C, differences between tests with and without glycolate were not statistically significant.

- No methane was detected in the testing of Tank 50 with 350 mg/L of glycolate.

5.0 Recommendations

Improvements to glycolate analysis in CSTF sample matrices for glycolate concentrations below 1570 mg/L (specifically needed for 350 mg/L and below) should be pursued since the projected concentration of glycolate in the DWPF falls below this range. Feedback from these HGR measurement test should be evaluated and incorporated as appropriate into the planning of subsequent HGR tests.

6.0 Acknowledgements

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Appendix A. Test Process

The flow system testing process for the Tank 38 waste sample was as follows.

1. Load the system with approximately 1.1 L (1465 g) of the Tank 38 material. A small amount of material corresponding to approximately 40 mL (53 g) was held back from this stage of testing to aid in eventual addition of sodium glycolate.
2. Agitate sample and initiate purge gas flow
3. Heat to the near-ambient temperature of 35 °C
4. Adjust purge gas flow to the measurement purge rate
5. Allow the system to equilibrate and measure the HGR at 35 °C
6. Increase purge and heat to the first elevated temperature of 60 °C
7. Adjust purge gas flow to the measurement purge rate
8. Allow the system to equilibrate and measure the HGR at 60 °C
9. Increase purge and heat to the second elevated temperature of 80 °C
10. Adjust purge gas flow to the measurement purge rate
11. Allow the system to equilibrate and measure the HGR at 80 °C
12. Increase purge and heat to the third elevated temperature of 95 °C
13. Adjust purge gas flow to the measurement purge rate
14. Allow the system to equilibrate and measure the HGR at 95 °C
15. Increase purge and heat to the atmospheric pressure boiling point of the mixture, which is expected to be approximately 110 °C
16. Adjust purge gas flow to the measurement purge rate
17. Allow the system to equilibrate and measure the HGR at boiling
18. Increase purge and allow the system to cool to below 50 °C
19. Temporarily suspend purge and add 2.28 g of 99.1 wt% sodium glycolate (corresponding to 1.73 g or 1.57 g/L of glycolate) and the approximately 40 mL (53 g) of Tank 38 material that was held back from the initial addition.
20. Agitate sample and initiate purge gas flow
21. Heat to the near-ambient temperature of 35 °C
22. Adjust purge gas flow to the measurement purge rate
23. Allow the system to equilibrate and measure the HGR at 35 °C
24. Increase purge and heat to the first elevated temperature of 60 °C
25. Adjust purge gas flow to the measurement purge rate
26. Allow the system to equilibrate and measure the HGR at 60 °C
27. Increase purge and heat to the second elevated temperature of 80 °C
28. Adjust purge gas flow to the measurement purge rate
29. Allow the system to equilibrate and measure the HGR at 80 °C
30. Increase purge and heat to the third elevated temperature of 95 °C
31. Adjust purge gas flow to the measurement purge rate
32. Allow the system to equilibrate and measure the HGR at 95 °C
33. Increase purge and heat to the atmospheric pressure boiling point of the mixture, which is expected to be approximately 110 °C
34. Adjust purge gas flow to the measurement purge rate
35. Allow the system to equilibrate and measure the HGR at boiling
36. Increase purge and allow the system to cool to below 50 °C
37. Heat to the atmospheric pressure boiling point of the mixture, which is expected to be approximately 110 °C
38. Adjust purge gas flow to the measurement purge rate
39. Allow the system to equilibrate and measure the HGR at boiling
40. Increase purge and allow the system to cool to below 50 °C
41. Shutdown the system and unload the Tank 38 material after the contents have cooled

42. Subsample the Tank 38 material for post-HGR chemical analysis

The flow system testing process for the Tank 50 waste sample was as follows.
1. Load the system with approximately 1.0 L (1240 g) of the Tank 50 material and 0.462 g of 99.1 wt% sodium glycolate (corresponding to 350 mg/L of glycolate).
2. Agitate sample and initiate purge gas flow
3. Increase purge and heat to the first elevated temperature of 70 °C
4. Adjust purge gas flow to the measurement purge rate
5. Allow the system to equilibrate and measure the HGR at 70 °C
6. Increase purge and heat to the second elevated temperature of 85 °C
7. Adjust purge gas flow to the measurement purge rate
8. Allow the system to equilibrate and measure the HGR at 85 °C
9. Increase purge and heat to the third elevated temperature of 100 °C
10. Adjust purge gas flow to the measurement purge rate
11. Allow the system to equilibrate and measure the HGR at 100 °C
12. Increase purge and allow the system to cool to below 50 °C
13. Shutdown the system and unload the Tank 50 material after the contents have cooled
14. Subsample the Tank 50 material for post-HGR chemical analysis

The sealed-system testing process for the Tank 50 waste sample was as follows.
1. Have cleaned and ready the five reactors as well as all the supporting equipment, including the DAC, tools, seal, liquid, test solutions, spike materials, etc. Note that a Teflon®-coated stir bar was already introduced into each reactor when they were sealed.
2. Fill clean reactors with test solution (first quarter 2018 Tank 50 sample HTF-50-18-12) and spike material (350 mg/L glycolate as sodium glycolate)
3. Purge head space in each reactor with nitrogen gas of at least 15 times the internal volume of the space, then pressurize to 20 psig, and seal. This pressure was chosen because it was the highest acceptable by the GC and it provided sufficient gas in the smallest head space used of ~20 ml to be able to draw 5 or more gas samples. The purge is introduced under the liquid in the reactor, which agitates liquid; therefore, the purge rate is low (~200 cc/min) to not cause splashing.
4. Place reactors on the stirrer/hotplates, insulate, energize both the stirrers and heat to reach the target temperature (70 °C, 55 °C, and 40 °C). Stirring is done gently, e.g., 200 rpm, to minimize splashing. When the target temperature was attained and steady to within ±5°C, the clock was started.
5. After the target temperature is held for the target heating period, the stirrer/hotplates are de-energized and the reactors allowed to cool overnight, before measurement.
6. Measure hydrogen by GC, (typically, 5 to 7 replicates for each vessel).
7. Pull a liquid sample from each reactor.
8. Thoroughly drain, rinse, and dry all the reactors.
9. Filter liquid samples if solids were present before submission for analyses.

Appendix B. Additional Analytical Results

The three tables in this Appendix document the below detection limit values that were not included in tables of analytical results in the body of the report.

Table B-1. Below detection limit values for post-HGR flow system Tank 38 material

analyte	method	units	average	feed [a]
F⁻	IC	M	<5.3E-03	2.97E-02
Br⁻	IC	M	<1.3E-03	<1.3E-03
Ag	ICP-ES	mg/L	<1.8E+01	<7.7E+00
Ba	ICP-ES	mg/L	<1.2E+01	<5.9E-01
Be	ICP-ES	mg/L	<7.9E-01	<2.4E-01
Ca	ICP-ES	mg/L	<1.9E+01	<6.3E+00
Cd	ICP-ES	mg/L	<1.5E+01	<7.6E+00
Ce	ICP-ES	mg/L	<4.2E+01	<2.0E+01
Co	ICP-ES	mg/L	<2.3E+01	<8.2E+00
Cu	ICP-ES	mg/L	<5.5E+01	<2.8E+01
Fe	ICP-ES	mg/L	<2.4E+01	<1.0E+01
Gd	ICP-ES	mg/L	<1.2E+01	<5.8E+00
K	ICP-ES	mg/L	<2.9E+02	4.39E+02
La	ICP-ES	mg/L	<1.2E+01	<4.6E+00
Mg	ICP-ES	mg/L	<2.4E+00	<1.1E+00
Mn	ICP-ES	mg/L	<2.1E+00	<1.1E+00
Mo	ICP-ES	mg/L	<4.7E+01	<2.4E+01
Ni	ICP-ES	mg/L	<1.1E+02	<1.3E+01
P	ICP-ES	mg/L	<2.1E+02	<2.3E+02
Pb	ICP-ES	mg/L	<2.1E+02	<1.1E+02
S	ICP-ES	mg/L	<1.3E+04	<6.6E+03
Sb	ICP-ES	mg/L	<4.3E+02	<1.1E+02
Sn	ICP-ES	mg/L	<1.3E+02	<6.6E+01
Sr	ICP-ES	mg/L	<1.1E+00	<2.1E-01
Th	ICP-ES	mg/L	<9.9E+01	<6.0E+00
Ti	ICP-ES	mg/L	<9.0E+01	<2.3E+01
U	ICP-ES	mg/L	<4.4E+02	4.12E+01
V	ICP-ES	mg/L	<7.0E+00	<3.1E+00
Zn	ICP-ES	mg/L	<2.0E+01	1.27E+01
Zr	ICP-ES	mg/L	<7.1E+00	<3.6E+00

[a] from SRNL-STI-2017-00611 Revision 0 (Ref. 8)

Table B-2. Below detection limit values for post-HGR flow system Tank 50 material

analyte	method	units	average	feed [1]
F $^-$	IC	M	<5.3E-03	<5.3E-04
Br $^-$	IC	M	<1.3E-03	
Ag	ICP-ES	mg/L	<3.7E+00	
Be	ICP-ES	mg/L	<1.6E-01	
Cd	ICP-ES	mg/L	<3.0E+00	
Ce	ICP-ES	mg/L	<4.2E+01	
Co	ICP-ES	mg/L	<4.5E+00	<3.0E-02
Cu	ICP-ES	mg/L	<1.1E+01	<1.3E+01
Gd	ICP-ES	mg/L	<2.3E+00	
La	ICP-ES	mg/L	<2.3E+00	
Mg	ICP-ES	mg/L	<4.8E-01	
Mn	ICP-ES	mg/L	<4.2E-01	<5.1E-01
Mo	ICP-ES	mg/L	<4.7E+01	1.81E+01
Ni	ICP-ES	mg/L	<2.1E+01	<2.6E+01
Pb	ICP-ES	mg/L	<4.2E+01	
S	ICP-ES	mg/L	<2.6E+03	
Sb	ICP-ES	mg/L	<8.5E+01	
Sn	ICP-ES	mg/L	<2.6E+01	
Sr	ICP-ES	mg/L	<2.1E-01	<2.6E-01
Th	ICP-ES	mg/L	<2.0E+01	
Ti	ICP-ES	mg/L	<1.8E+01	
U	ICP-ES	mg/L	<8.8E+01	
V	ICP-ES	mg/L	<1.4E+00	
Zr	ICP-ES	mg/L	<1.4E+00	

[1] from SRNL-STI-2018-00204 Revision 0 (Ref. 30)

Table B-3. Below detection limit values for post-HGR sealed system Tank 50 material

| analyte	method	units	HGV-2	HGV-3	HGV-4	HGV-5	HGV-6
Br⁻	IC	M	<1.3E-03	<1.3E-03	<1.3E-03	<1.3E-03	<1.3E-03
Ag	ICP-ES	mg/L	<1.8E+00	<1.8E+00	<1.8E+00	<1.8E+00	<2.6E-01
Ba	ICP-ES	mg/L	<3.8E-01	<3.8E-01	<3.8E-01	<3.8E-01	<6.8E-02
Be	ICP-ES	mg/L	<7.9E-02	<7.9E-02	<7.9E-02	<7.9E-02	<1.0E+00
Cd	ICP-ES	mg/L	<1.5E+00	<1.5E+00	<1.5E+00	<1.5E+00	<8.6E-02
Ce	ICP-ES	mg/L	<4.2E+00	<4.2E+00	<4.2E+00	<4.2E+00	<9.8E-01
Co	ICP-ES	mg/L	<2.3E+00	<2.3E+00	<2.3E+00	<2.3E+00	<1.8E-01
Cu	ICP-ES	mg/L	<1.0E+01	<1.0E+01	<1.0E+01	<1.0E+01	<4.8E-01
Gd	ICP-ES	mg/L	<3.5E+00	<3.5E+00	<3.5E+00	<3.5E+00	<2.8E-01
La	ICP-ES	mg/L	<1.2E+00	<1.2E+00	<1.2E+00	<1.2E+00	<1.8E-01
Mn	ICP-ES	mg/L	<2.1E-01	<2.1E-01	<2.1E-01	<2.1E-01	<2.5E-02
Ni	ICP-ES	mg/L	<6.0E+00	<6.0E+00	<6.0E+00	<6.0E+00	<5.0E+00
Pb	ICP-ES	mg/L	<2.1E+01	<2.1E+01	<2.1E+01	<2.1E+01	<3.0E+01
S	ICP-ES	mg/L	<2.0E+03	<2.0E+03	<2.0E+03	<2.0E+03	<2.0E+03
Sb	ICP-ES	mg/L	<2.2E+01	<2.2E+01	<2.2E+01	<2.2E+01	<2.5E+00
Sn	ICP-ES	mg/L	<5.9E+01	<5.9E+01	<5.9E+01	<5.9E+01	<5.5E+00
Sr	ICP-ES	mg/L	<1.1E-01	<1.1E-01	<1.1E-01	<1.1E-01	<2.1E-02
Th	ICP-ES	mg/L	<2.9E-01	<2.9E-01	<2.9E-01	<2.9E-01	<1.8E+00
Ti	ICP-ES	mg/L	<5.1E+00	<5.1E+00	<5.1E+00	<5.1E+00	<1.6E-01
U	ICP-ES	mg/L	<5.2E+01	<5.2E+01	<5.2E+01	<5.2E+01	<7.6E+00
V	ICP-ES	mg/L	<7.0E-01	<7.0E-01	<7.0E-01	<7.0E-01	<1.0E+00
Zr	ICP-ES	mg/L	<7.2E-01	<7.2E-01	<7.2E-01	<7.2E-01	<8.4E-02

Appendix C. Test Plots
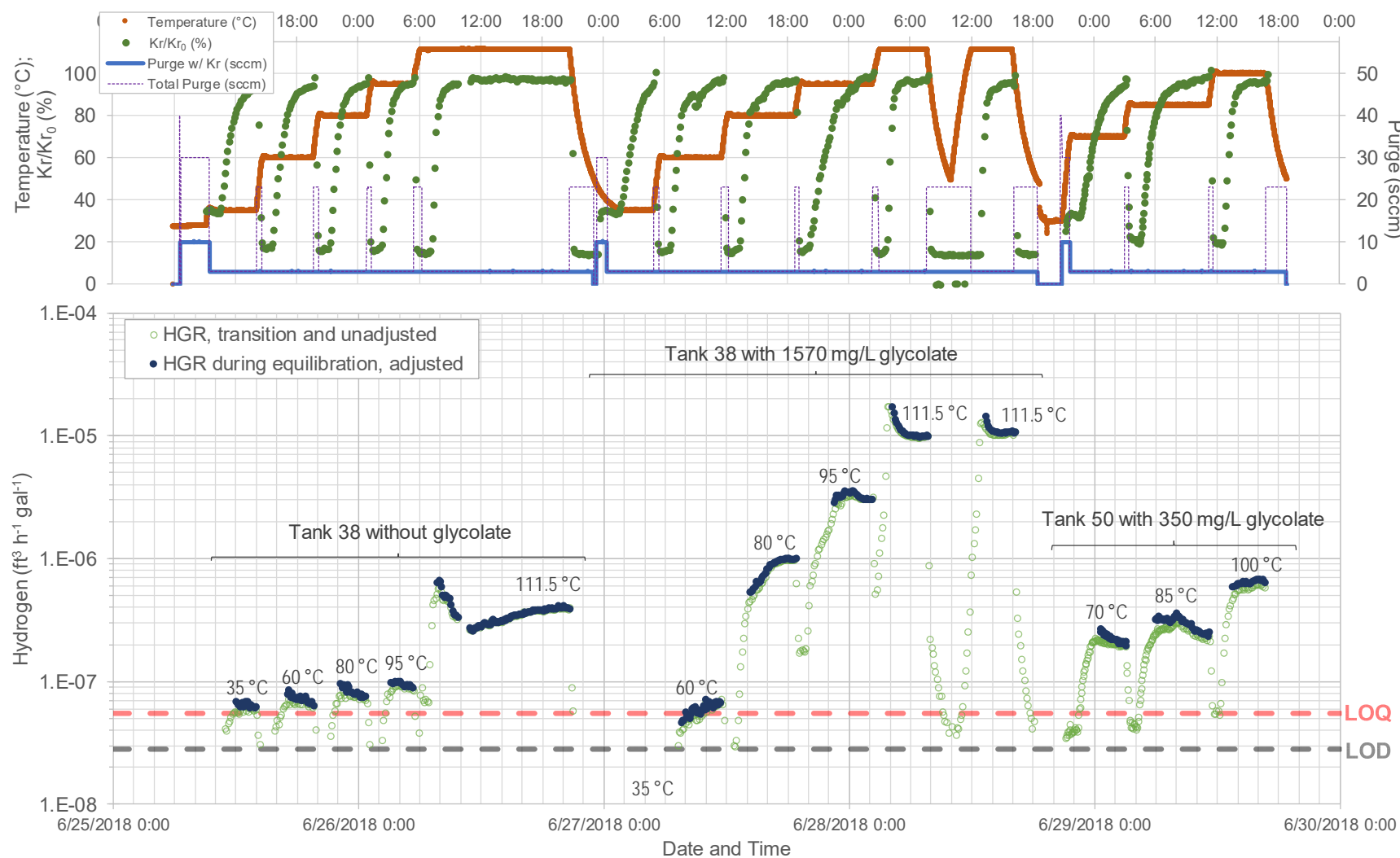
Figure C-1. Test profile of Tank 38 and Tank 50 flow-system test
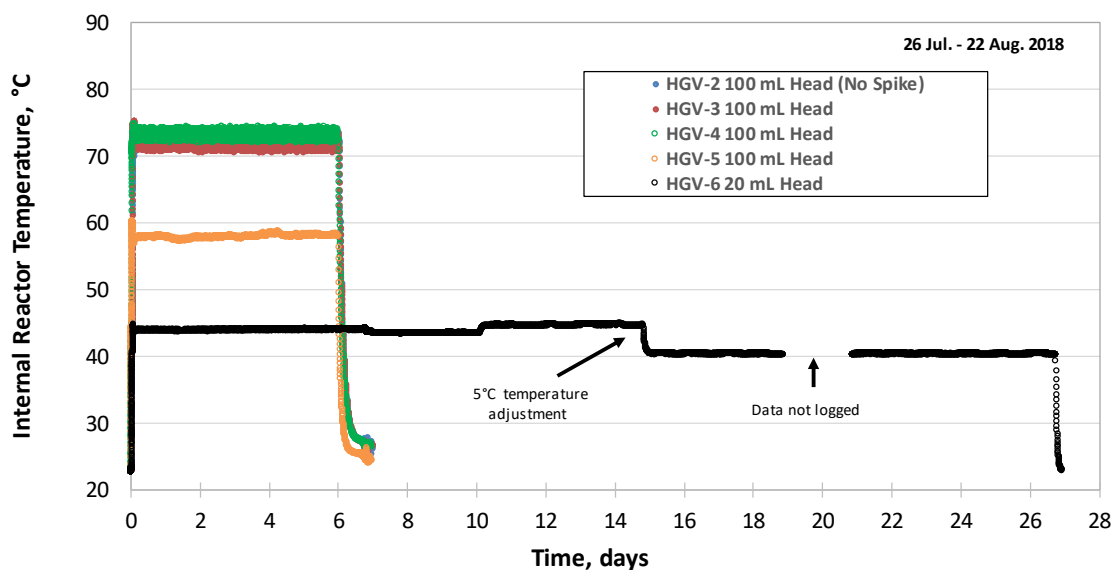
Figure C-2. Temperature history for Tank 50 sealed-system test with 350 mg/L of added glycolate (except HGV-2) in a nitrogen atmosphere
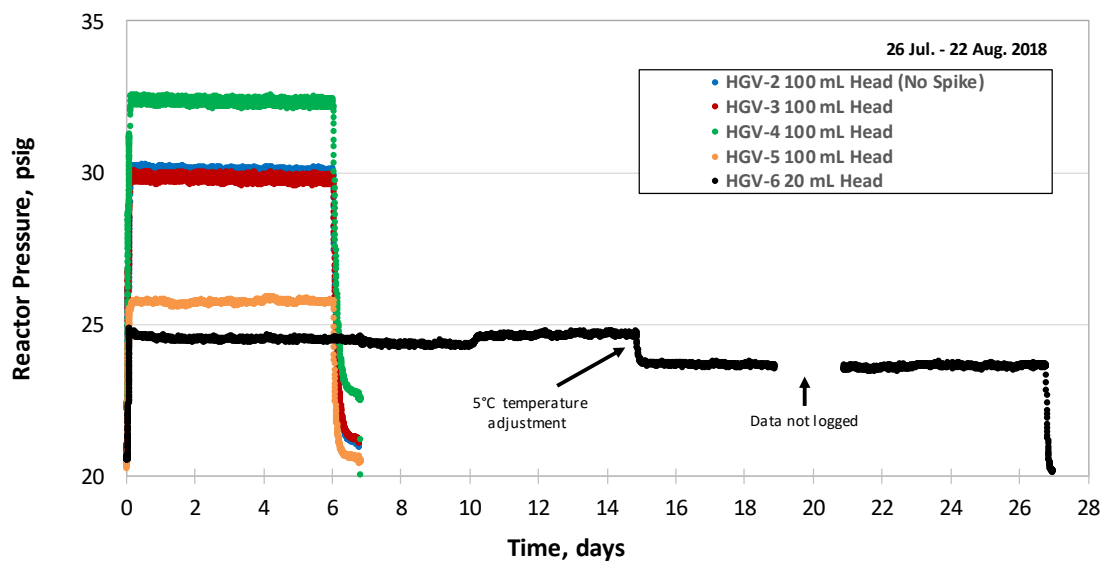

Figure C-3. Pressure history for Tank 50 sealed-system test with 350 mg/L of added glycolate (except HGV-2) in a nitrogen atmosphere

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