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# Evaluation of Thermolytic Hydrogen Generation Rate Models at High-Temperature/High-Hydroxide Regimes

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July 2020

SRNL-STI-2020-00274, Revision 0



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**Printed in the United States of America**

**Prepared for  
U.S. Department of Energy**

**Keywords:** *Hydrogen, Thermolysis*

**Retention:** *Permanent*

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.



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## **ACKNOWLEDGEMENTS**

The authors wish to acknowledge the efforts of all of those involved in the planning, design, performance, analysis, and documentation of this research. Meagan Kinard expertly performed the experiments described herein. John Pareizs served invaluablely as the process expert for the gas chromatography columns employed during these tests. Holly Hall served as the facility coordinator, ensuring that the increasing demand for resources could always be supplied. Amy Blunt managed the samples and materials generated in the course of this research.

## EXECUTIVE SUMMARY

This report describes the results of testing performed to extend the applicable ranges of temperature and hydroxide concentration for use within the Glycolate and Global Total Organic Carbon (TOC) Hydrogen Generation Rate (HGR) expressions. Seven experimental conditions (six simulants of the 242-25H Evaporator system chosen as a D-optimal set of experiments and a single test conducted at an elevated boiling point of 170 °C) were investigated in the presence of sodium glycolate and Xiameter™ AFE-1010. Glycolate was employed to study the extension of the Glycolate Thermolytic HGR expression while Xiameter™ AFE-1010 was employed to study the extension of the Global TOC Thermolytic HGR expression.

The following conclusions were derived from this testing.

- The Glycolate Thermolytic HGR expression may be confidently used to predict thermolytic HGRs from glycolate at temperatures as high as 170 °C and hydroxide concentrations as high as 23 M.
- The hydroxide and temperature-dependence predicted by the Global TOC Thermolytic HGR expression has been confirmed at temperatures as high as 170 °C and hydroxide concentrations as high as 23 M, suggesting that the Global TOC Thermolytic HGR expression may be used at these ranges.
- Methane was observed from tests with Xiameter™ AFE-1010 at production rates higher than those observed for hydrogen. These rates were observed at temperatures higher than 100 °C.
- Preliminary models suggest that increasing hydroxide/temperature causes an increase in Methane Generation Rate (MGR) from Xiameter™ AFE-1010.

The following recommendations are based on this testing.

- The existing equations for thermolytic HGR from glycolate and non-glycolate organics should be used at Concentration, Storage, and Transfer Facilities (CSTF) storage and evaporation conditions, including temperatures and hydroxide concentrations exhibited in the 242-25H Evaporator.
- Further investigation should be made into the influence of methylsilanes on CSTF flammability. This investigation should include: determination of the types of methylsilanes historically added to the CSTF, determination of methane formation rates from each type of methylsilane, and determination of the extent of degradation of methylsilanes in CSTF waste.
- Characterization techniques should be developed by Savannah River National Laboratory (SRNL) to assist in the speciation of methylsilane-containing waste in the CSTF.
- Additional testing with radioactive waste should be performed to determine the MGRs possible in radioactive waste and better inform model predictions made from testing with simulants.

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## LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
BDL	below detection limit
CSTF	Concentration, Storage, and Transfer Facilities
DAC	Data Acquisition and Control
DI	deionized
GC	Gas Chromatograph(y)
HBP	High Boiling Point
HGR	Hydrogen Generation Rate
M&TE	Measuring and Test Equipment
MGR	Methane Generation Rate
OMCTS	octamethylcyclotetrasiloxane
PDMS	polydimethylsiloxane
PISA	Potential Inadequacies in the Safety Analyses
PTFE	polytetrafluoroethylene
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TCD	thermal conductivity detector
TOC	Total Organic Carbon

## 1.0 Introduction

In 2017, three Potential Inadequacies in the Safety Analyses (PISAs) were declared by Savannah River Remediation (SRR) in which no allowance had been made for the impacts (radiolytic and thermolytic) of trace organic compounds on the generation of flammable gases in the Savannah River Site (SRS) Liquid Waste system.<sup>1-3</sup> Savannah River National Laboratory (SRNL) was tasked by SRR to study the thermolytic generation of hydrogen by organics in waste media.<sup>4-5</sup>

To date, SRNL personnel have performed several series of tests on both radioactive and simulated caustic waste to measure the thermolytic production of hydrogen gas from organics, including glycolate.<sup>6-9</sup> These hydrogen generation rate (HGR) measurements performed by SRNL have led to the generation of model expressions for the thermolytic production of hydrogen from glycolate and non-glycolate organics in caustic waste.<sup>9</sup> The HGR expression for glycolate thermolysis is derived from simulant testing and confirmed with radioactive waste testing with added glycolate. The non-glycolate organic HGR expression is based on simulant tests with the most reactive CSTF organics that followed a similar thermolytic mechanism (hydroxide dependence and Arrhenius behavior), and a correction for the observed thermolytic reactivity of organics in radioactive waste. The models are shown below in Equations [1] and [2],

$$HGR_{GLY} = 6.262 \times 10^5 [Na]^{1.520} [NO_3]^{0.282} [OH]^{1.441} [C_{GLY}] e^{-82,300/RT} \quad [1]$$

$$HGR_{TOC} = 2.45 \times 10^6 [OH]^{0.925} [C_{TOC}] e^{-82,900/RT} \quad [2]$$

where,

$HGR_{GLY}$  is the hydrogen production rate from the thermolysis of glycolate in  $\text{ft}^3 \text{ h}^{-1} \text{ gal}^{-1}$ ,

$HGR_{TOC}$  is the hydrogen production rate from the thermolysis of other organics in  $\text{ft}^3 \text{ h}^{-1} \text{ gal}^{-1}$ ,

$[OH]$  is the concentration of hydroxide in  $\text{mol L}^{-1}$ ,

$[Na]$  is the concentration of sodium in  $\text{mol L}^{-1}$ ,

$[C_{GLY}]$  is the concentration of carbon from glycolate in  $\text{mol L}^{-1}$ ,

$[C_{TOC}]$  is the concentration of organic carbon not attributable to formate, oxalate, or glycolate in  $\text{mol L}^{-1}$ ,

$[NO_3]$  is the concentration of nitrate in  $\text{mol L}^{-1}$ ,

$R$  is the ideal gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ , and

$T$  is the temperature in K.

The model expressions given in Equations [1] and [2] were generated from testing within a specific range of salt concentrations and temperatures. The limits of applicability of these HGR rate expressions are given in Table 1-1.

**Table 1-1. Previous Limits of Applicability for Total Organic Carbon (TOC) and Glycolate Thermolysis Model Expressions**

Parameter	Glycolate Thermolysis		TOC Thermolysis	
	Minimum	Maximum	Minimum	Maximum
Aluminum (M)	9.64E-04 M	2.49E+00 M	1.29E-03 M	1.98E+00 M
Nitrite (M)	2.21E-01 M	2.78E+00 M	2.21E-01 M	2.74E+00 M
Nitrate (M)	6.55E-02 M	6.34E+00 M	6.75E-02 M	5.58E+00 M
Hydroxide (M)	4.66E-02 M	1.22E+01 M	1.58E-01 M	1.25E+01 M
Sulfate (M)	4.94E-04 M	2.50E-01 M	4.94E-04 M	2.05E-01 M
Carbonate (M)	2.38E-03 M	6.54E-01 M	8.14E-03 M	7.23E-01 M
Sodium (M)	3.40E-01 M	2.56E+01 M	4.65E-01 M	2.47E+01 M
Temperature (°C)	60 °C	134 °C	70 °C	130 °C

SRR requested SRNL to perform testing to expand the parameter applicability range for hydroxide and temperature to include historical 242-25H Evaporator operating conditions. Specific conditions of interest to SRR were hydroxide concentrations as high as 16.3 M and temperatures as high 164 °C. The testing described herein was governed by two Run Plans that 1) identified a matrix of test conditions to fully evaluate chemical space of expected 242-25H Evaporator operations, and 2) identified a single test condition for testing at 170 °C and was undertaken to determine the applicability of the glycolate and non-glycolate organic HGR models at these expanded regions of high hydroxide and temperature.<sup>10-11</sup>

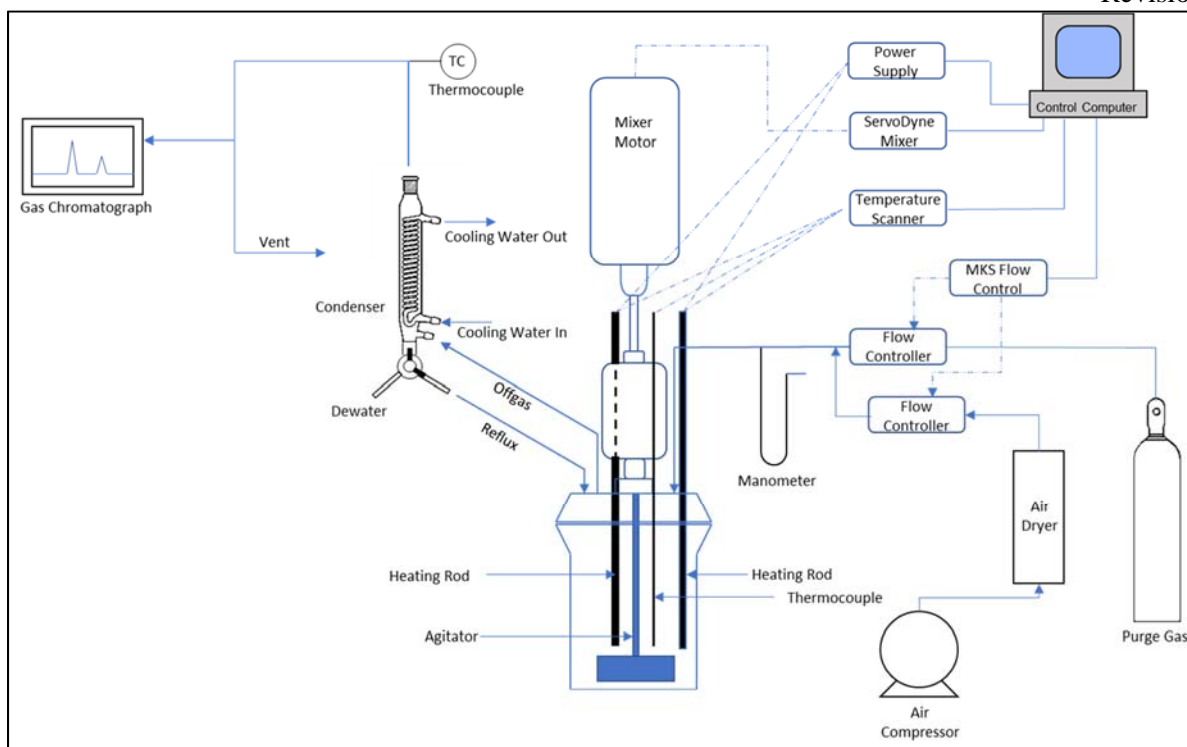
## 2.0 Experimental Procedure

### 2.1 Experimental Apparatus

The work described herein was performed using the same custom-designed reaction apparatus used in previous testing.<sup>9</sup> All testing was conducted at SRNL facilities within the Aiken County Technology Laboratory (ACTL). A schematic of the apparatus is shown in Figure 2-1. The apparatus consisted of a 1.2 L polytetrafluoroethylene (PTFE) vessel sealed with a PTFE lid. The solution inside the vessel was mixed by a PTFE agitator impeller and shaft connected to a Parr® high-torque magnetic drive fitted to the center of the lid. Eight ports with stainless-steel fittings surrounded the magnetic drive. The ports were used for the following.

- Controlling temperature within the vessel by two Incoloy® 800 heating rods
- Monitoring liquid temperature within the vessel using an Inconel® 600 thermocouple
- Providing a purge gas to continuously sweep the vapor space of the vessel
- Connecting the headspace of the vessel to a glass condenser
- Providing a route for reflux from the condenser back to the reaction vessel
- Adding organic species
- Sampling by a stainless-steel J-Loop during high boiling point (HBP) testing

Upstream from the reaction vessel, two Measuring and Test Equipment (M&TE) MKS® mass flow controllers were used to supply CO<sub>2</sub>-free compressed air or N<sub>2</sub> cylinder gas containing 0.5 vol % Kr and 20 vol % O<sub>2</sub>. Downstream from the reaction vessel, a glass condenser was employed to remove condensable gases from the gas before proceeding to analysis. After passing through the condenser, the gas was sampled and quantified for hydrogen content by either an Inficon Micro 3000 GC-TCD (gas chromatograph – thermal conductivity detector) or an Inficon Micro GC Fusion before being vented to a chemical hood.



**Figure 2-1. HGR Process Schematic**

## 2.2 Sample Preparation

Reagent grade sodium nitrate, sodium nitrite, and a 50 wt % reagent grade sodium hydroxide solution were purchased from Fisher Chemical and used as received. In the case where the targeted hydroxide concentration precludes the use of 50 wt % sodium hydroxide solution, reagent grade sodium hydroxide pellets were used as the hydroxide feedstock. Reagent grade aluminum trinitrate nonahydrate was purchased from Sigma-Aldrich and used as received. For the test condition where the target nitrate-to-aluminum ratio would not permit the use of aluminum trinitrate, technical grade (>85%) sodium aluminate was used as the source of aluminum. OLI<sup>12</sup> was used to predict simulant densities; these densities were then used to calculate the desired amounts of salts and water needed to achieve the targeted molarities in test conditions. The reagents were added directly to the reaction vessel before sealing. The order of addition to the vessel was as follows: sodium hydroxide and half of the deionized (DI) water prior to the aluminum source, then the remaining species (sodium nitrate and sodium nitrite) and remaining DI water.

## 2.3 Experimental Procedure

After the addition of all chemicals, the vessel was sealed and checked for leaks by mass balance of air flow through the process headspace. Once leak-free conditions had been confirmed, stirring was initiated and a purge flow of dried air was applied to the process to sweep residual CO<sub>2</sub> out of the vessel. The system controls were then set to apply heat via two electric heating rods such that the difference between the process (fluid) temperature and that of the heating rod interior could not exceed 40 °C. For the blank tests, the process fluid was brought to its boiling point. In all other tests, the process fluid was brought to within approximately 10 °C of its boiling point, at which point the organic additive was added and subsequently brought to boiling. In all tests, the purge gas was then switched to the typically lower-purge process gas stream (0.5 vol % Kr and 20 vol % O<sub>2</sub> in N<sub>2</sub>). This point was designated as the start of the experiment.

The experiment continued while monitoring for hydrogen concentration via GC. To ensure hydrogen and methane concentrations stayed below their flammability limits, the purge rate was increased using both the air purge and the Kr tracer-containing gas stream as needed. The experiment duration was planned such that at a minimum, the vessel headspace could undergo approximately three vapor space volume turnovers

(achieving 99.7% of pseudo steady-state, assuming continuously-stirred reactor dynamics; note that this time is volume and purge rate dependent). Once this time was reached and hydrogen measurements by GC stabilized or began to decrease, heating rod power was turned off and the experiment was stopped. The higher-purge air was then reapplied to the vessel to sweep out residual hydrogen. The simulant mixture was then removed from the vessel and subsampled as needed for product analyses. Density of the simulant was checked by weighing a known volume of the simulant using an M&TE autopipette and an M&TE balance.

The HBP test differed from above as follows: 1) the simulant was heated to its boiling point and excess water was removed until the desired boiling point (170 °C) was reached. At this point, a blank measurement was performed. Heating was then stopped, and the solution allowed to cool by approximately 10 °C before adding the organic species. It was then brought back to boiling and hydrogen concentration monitored by GC as above. 2) After the experiment was stopped and the vessel had cooled to approximately 160 °C, the simulant was sampled. The solution conformity was also confirmed by removing the lid and visually determining that solids were not present at the end of the experiment.

## 2.4 Offgas Analyses

Either an Inficon Micro 3000 GC or an Inficon Micro Fusion GC was used to analyze offgas content for all experiments. The GCs were equipped with two analysis channels: one using a Molsieve 5A column for H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and Kr analysis, and a second using a PoraPLOT Q column for N<sub>2</sub>O and CO<sub>2</sub> analysis. Each column employed a thermal conductivity detector which measured against the background of pure argon (also used as a carrier gas). The GC calibration was verified before each experiment using a calibration gas with a composition of 50 ppm<sub>v</sub> H<sub>2</sub>, 100 ppm<sub>v</sub> CH<sub>4</sub>, 0.5 vol % Kr, 1 vol % N<sub>2</sub>O, 1 vol % CO<sub>2</sub>, and 20 vol % O<sub>2</sub> in N<sub>2</sub>. The GCs were also used to qualitatively track the concentrations of He and H<sub>2</sub>O.

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

## 2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. This document, including all calculations (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.<sup>13</sup> Data was recorded in the electronic laboratory notebook system as notebook/experiment numbers K7482-00430-1 through K7482-00430-19.<sup>14</sup> The use of any Measuring and Test Equipment or Measurement Systems and Equipment is recorded in these notebooks. Measurements, calculations, documentation, and technical review comply with the customer-required quality assurance level to support Safety Class use of information contained in this report.<sup>4,5</sup>

The Data Acquisition and Control (DAC) software employed in this testing was used to control mass flow controllers, overhead mixers, and electric heating rods as well as record data taken from thermocouples and GC-TCD stations. This software is classified as level D.<sup>15</sup> 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, thermocouples, and temperature scanner are in the Measurement and Test Equipment program. Each of these instruments has an alternative reading outside of the DAC software. Data is periodically recorded manually (e.g., every 30 minutes) to supplement the files generated by the software.

Additionally, the statistical software package JMP 14 was used for the evaluation and regression of linear models developed in this report. JMP 14 has undergone verification and validation<sup>16</sup> and is classified as level D software.

### 3.0 Results and Discussion

#### 3.1 HGR Testing with Glycolate

The conditions used to evaluate HGRs from glycolate at elevated temperatures and hydroxide concentrations and the results of each test are given in Table 3-1.

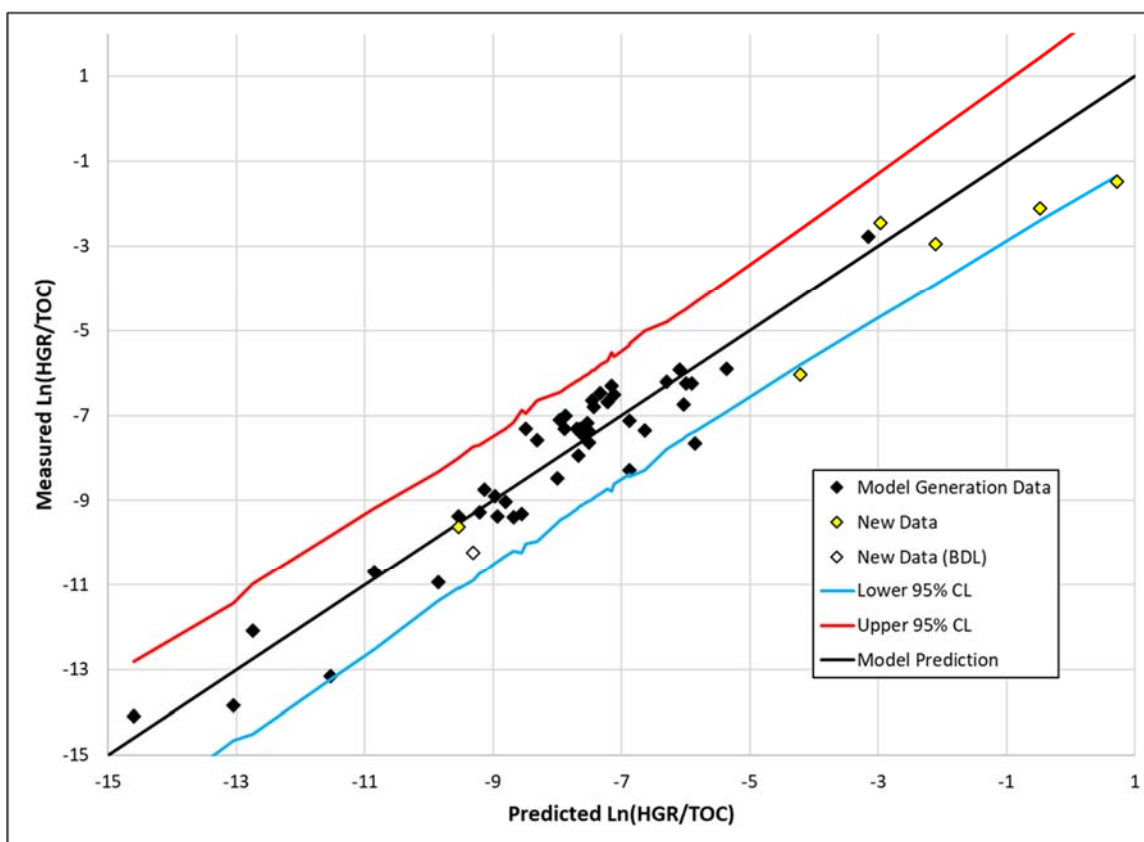
**Table 3-1. Conditions and Results of HGR Testing with Glycolate.**

Run Name	Temp (°C)	[Al] (M)	[NO <sub>2</sub> ] (M)	[NO <sub>3</sub> ] (M)	[OH] (M)	[C <sub>Gly</sub> ] <sup>†</sup> (M)	HGR (ft <sup>3</sup> h <sup>-1</sup> gal <sup>-1</sup> )
HTH-1	138.3	9.90E-01	1.20E+00	7.90E-01	1.30E+01	4.20E-03	3.60E-04
HTH-2	107.4	4.30E-01	8.60E-01	3.40E+00	1.10E+00	4.30E-03	2.90E-07
HTH-3	105.4	9.50E-02	6.00E-01	7.80E-01	2.70E+00	4.20E-03	<1.5E-07
HTH-4	142.2	1.30E-02	4.30E+00	5.00E+00	1.10E+01	5.20E-03	2.70E-04
HTH-5	157.1	3.80E-01	1.90E+00	1.60E+00	1.90E+01	4.80E-03	5.90E-04
HTH-6	124.8	4.00E-01	1.70E+00	2.20E+00	9.00E+00	4.50E-03	1.10E-05
HBP	170.2	4.50E-01	2.20E+00	1.90E+00	2.30E+01	5.60E-03	1.30E-03

<sup>†</sup>Glycolate concentrations varied between 158 and 210 mg/L.

The highest temperature explored in this set of tests was recorded at  $170.2 \pm 2$  °C in the HBP experiment. Similarly, the HBP experiment yielded the highest observed hydroxide concentration (23 M). These values fall far outside of the original bounds placed on the Glycolate Thermolytic HGR model.

The HGRs reported in Table 3-1 were evaluated against the predictions made from the Glycolate Thermolytic HGR model (Equation [1]).<sup>9</sup> The results of this evaluation are displayed in Figure 2-1.



**Figure 3-1. Model Evaluation of Glycolate HGR Data.**

The results displayed in Figure 3-1 indicate that the Glycolate Thermolytic HGR model well describes the HGRs observed in high temperature/high hydroxide environments. Of the seven experiments performed, all seven fall below the upper 95% confidence limit for a prediction made with the model expression. Six of the seven points fall below the model prediction line, suggesting further that the model expression provides a measure of conservatism when predicting HGRs from glycolate at high temperatures and hydroxide concentrations. It should be noted that a single data point is reported as a “BDL”, or “below detection limit” measurement. In this case, the hydrogen produced from glycolate could not be adequately differentiated from that of the glycolate-free experiment due to purge rates and GC limitations. The true value of this data point is expected to fall lower than that shown by the empty diamond in Figure 3-1, and is therefore not expected to be problematic.

From the results above, it may be concluded that the Glycolate Thermolytic HGR expression may be safely used to predict glycolate in conditions with temperatures as high as 170 °C and hydroxide concentrations as high as 23 M. These new bounds are expected to completely include 242-25H Evaporator operations.

### 3.2 HGR Testing with Xiameter™ AFE-1010

The conditions and results of testing used to investigate HGRs from Xiameter™ AFE-1010 are given in Table 3-2.

**Table 3-2. Conditions and Results of HGR Testing with Xiameter™ AFE-1010.**

Run Name	Temp (°C)	[Al] (M)	[NO <sub>2</sub> ] (M)	[NO <sub>3</sub> ] (M)	[OH] (M)	[TOC] (M)	HGR (ft <sup>3</sup> h <sup>-1</sup> gal <sup>-1</sup> )
HTH-1	138.8	9.47E-01	1.13E+00	7.50E-01	1.20E+01	4.25E-04	<7.0E-4
HTH-2	107.5	4.30E-01	8.60E-01	3.44E+00	1.07E+00	4.51E-04	9.52E-07
HTH-3	105.2	9.37E-02	5.87E-01	7.73E-01	2.63E+00	4.21E-04	5.10E-07
HTH-4	142.7	1.26E-02	4.26E+00	4.97E+00	1.04E+01	5.10E-04	1.34E-05
HTH-5	156.6	3.51E-01	1.73E+00	1.46E+00	1.79E+01	4.51E-04	7.54E-06
HTH-6	125	4.14E-01	1.74E+00	2.33E+00	9.39E+00	4.76E-04	6.64E-06
HBP	170.5	4.43E-01	2.18E+00	1.85E+00	2.26E+01	5.89E-04	2.48E-05

The highest temperature and hydroxide recorded in this set of tests is similar to those seen in testing with glycolate (170.2 °C and 23 M).

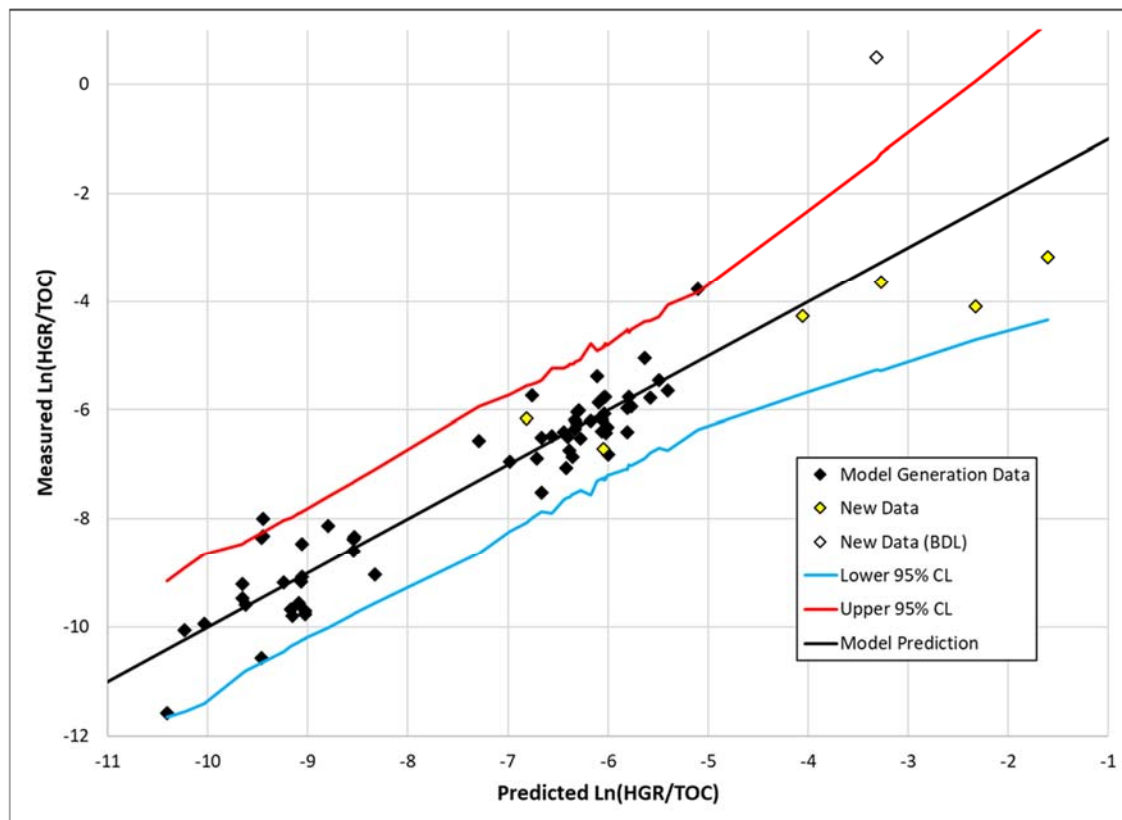
From previous testing Xiameter™ AFE-1010 was found to be one of the most reactive organic species towards hydrogen production.<sup>9</sup> It is important to recognize that antifoam components like Xiameter™ AFE-1010 have not been directly added to CSTF material in >15 years.<sup>9</sup> After years of exposure to caustic environments and radiation fields, one can expect that the most reactive organic species have degraded in CSTF and have depreciated in reactivity (compared to that expected from the addition of “fresh” organic material). In earlier studies, it was determined that the kinetic behavior of the most reactive CSTF organics follows a single profile characterized by 1) positive hydroxide dependence, and 2) Arrhenius-type temperature dependence. In earlier testing, it was shown that the same hydroxide and temperature-dependent behavior was observed with Xiameter™ AFE-1010, Reillex® HPQ, and IONAC A-641 ion exchange resin degradation products. It is therefore expected that hydroxide and temperature changes would impact these reactive organics in a similar way. It follows, then, that only one of these species needed further evaluation in the expanded hydroxide and temperature regimes investigated in this study. Xiameter™ AFE-1010 was chosen for 1) material availability, and 2) similarity to organics expected in CSTF waste.

It should be noted that the Global TOC model was derived by assessing the difference in apparent reactivity of “fresh organics” and those found in the CSTF (presumably due to aging). Therefore, to evaluate the ability of the Global TOC Thermolytic HGR model to be applied to regions of higher temperature and



hydroxide concentration, it is only necessary to verify that the same hydroxide dependence and Arrhenius behavior is observed in testing with fresh Xiameter™ AFE-1010 (i.e., absolute magnitude of HGRs measured from tests with freshly-added Xiameter™ AFE-1010 would not be expected to fall within global TOC HGR predictions developed for aged waste, but should exhibit the same kinetic profile).

The results of testing with Xiameter™ AFE-1010 are evaluated against the kinetic model derived from freshly-added organics (performed in previous studies)<sup>9</sup> and displayed graphically in Figure 3-2. The previous data taken from testing with Xiameter™ AFE-1010 as well as digestion products from IONAC A-641 and Reillex® HPQ ion exchange resins are indicated with black diamonds. New data taken with Xiameter™ AFE-1010 (tests described in Table 3-2) are indicated with yellow diamonds and empty diamonds (when hydrogen could not be detected).



**Figure 3-2. Model Evaluation of Xiameter™ AFE-1010 HGR Data.**

As is shown in Figure 3-2, the new data points taken with Xiameter™ AFE-1010 at elevated temperature and hydroxide agree nicely with the kinetic model predicted and described in previous testing. Of the seven experiments performed, all measurable HGRs fall within the 95% confidence limit for a single prediction, and five of those six measurable HGRs fall below the kinetic model prediction. It should be noted that the single point plotted above the upper 95% confidence limit in Figure 3-2 has been determined as a “BDL” measurement. This test exhibited a relatively large detection limit due to 1) a greatly increased presence of hydrogen in the Xiameter-free and Xiameter-added tests (likely from the high TOC impurities in sodium aluminate (only available as Technical Grade, 85%), the source of aluminum in this test), and 2) an elevated purge rate required to control the flammability of methane being simultaneously produced from the thermolysis of Xiameter™ AFE-1010. Given that this point is reported as a “BDL” measurement, it does not provide evidence of failure to fit within the kinetic model derived in earlier testing.

The conclusion from the results described is that the kinetic behavior expressed in the Global TOC Thermolytic HGR expression (Equation [2]) may be safely extrapolated to temperatures as high as 170 °C

and hydroxide concentrations as high as 23 M. This conclusion supports the use of the Global TOC Thermolytic HGR expression to predict non-glycolate thermolysis in the 241-25H Evaporator system.

### 3.3 Methane Generation Observations from Xiameter™ AFE-1010 Testing

It should be noted that significant evolution of methane was observed during HGR testing with Xiameter™ AFE-1010. No such observation was made with glycolate or in the absence of added organics, suggesting that this phenomenon is unique to testing with chemicals similar to those found in Xiameter™ AFE-1010. While the GCs used during these experiments were calibrated for methane measurement, the experimental setup used for testing was optimized for hydrogen measurement at the cost of suboptimal methane measurements. Therefore, the observations and measurements presented here should be viewed as preliminary; testing with an optimized apparatus would be expected to yield values with a higher degree of precision.

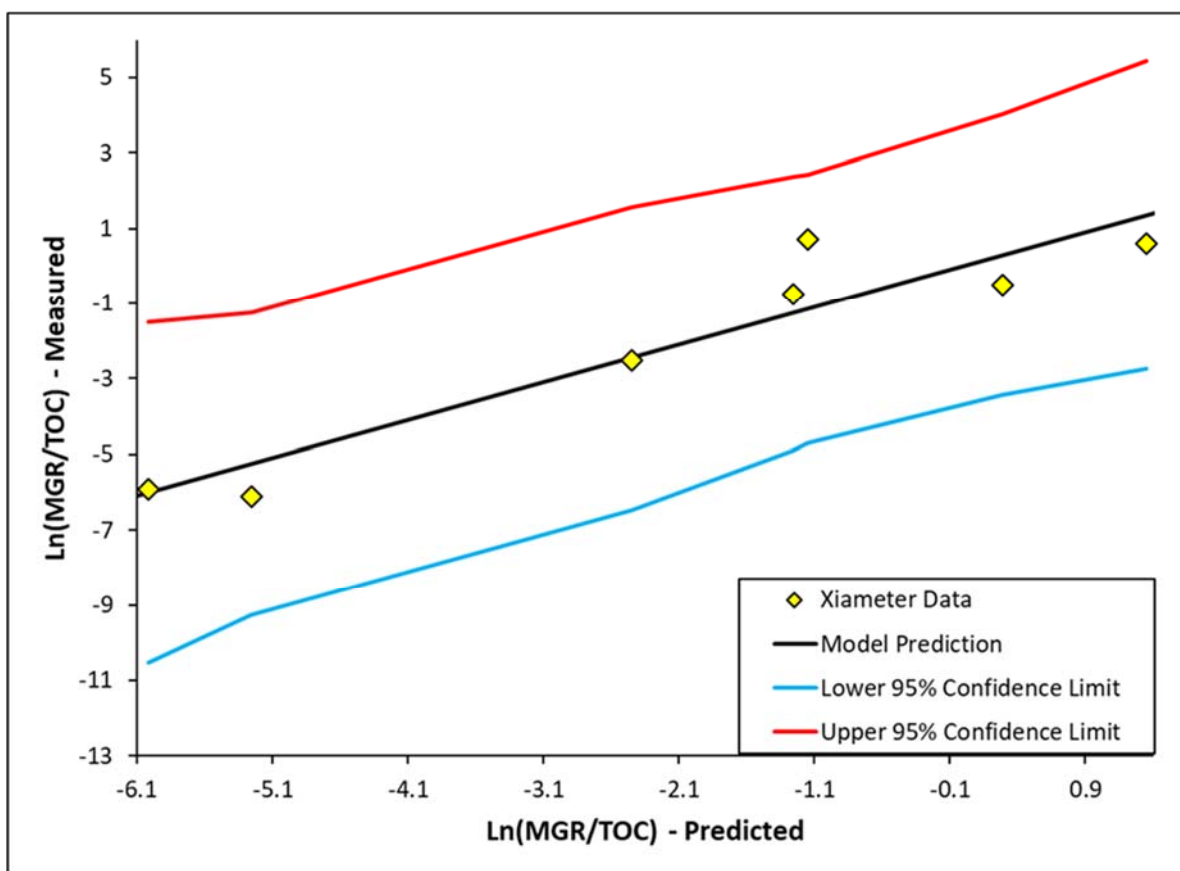
Table 3-3 lists the conditions and observed methane generation rates (MGRs) from the tests performed with Xiameter™ AFE-1010. The respective HGRs and the observed CH<sub>4</sub>:H<sub>2</sub> ratio is reported as well for convenient review.

**Table 3-3. Methane Generation Results from Testing with Xiameter™ AFE-1010.**

Run Name	Temp (°C)	[OH] (M)	[TOC] (M)	HGR (ft <sup>3</sup> h <sup>-1</sup> gal <sup>-1</sup> )	MGR (ft <sup>3</sup> h <sup>-1</sup> gal <sup>-1</sup> )	CH <sub>4</sub> :H <sub>2</sub>
HTH-1	138.8	1.20E+01	4.25E-04	<7.0E-4	2.0E-04	>0.3:1
HTH-2	107.5	1.07E+00	4.51E-04	9.52E-07	1.2E-06	1:1
HTH-3	105.2	2.63E+00	4.21E-04	5.10E-07	9.3E-07	2:1
HTH-4	142.7	1.04E+01	5.10E-04	1.34E-05	1.0E-03	78:1
HTH-5	156.6	1.79E+01	4.51E-04	7.54E-06	2.7E-04	36:1
HTH-6	125	9.39E+00	4.76E-04	6.64E-06	3.9E-05	6:1
HBP	170.5	2.26E+01	5.89E-04	2.48E-05	1.1E-03	43:1

Almost universally, the MGRs observed during testing with Xiameter™ AFE-1010 met or exceeded the HGRs observed, with the single exception (HTH-1) yielding an undetermined ratio of >0.3:1 for CH<sub>4</sub>:H<sub>2</sub>. This suggests that methane is more easily formed from Xiameter™ AFE-1010 than hydrogen at the conditions employed during this testing (i.e., temperatures greater than 100 °C).

A preliminary model for methane formation may be derived from the data given in Table 3-3. This model is displayed graphically in Figure 3-3.



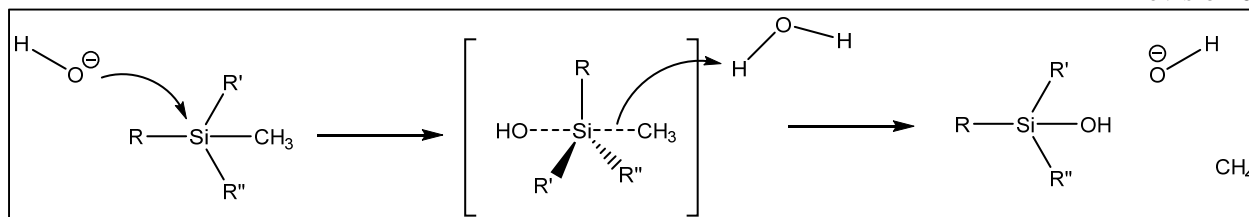
**Figure 3-3. Preliminary Model Fit for Methane Generation from Xiameter™ AFE-1010 Testing.**

The model shown in Figure 3-3 is derived using JMP 14 to fit the data in Table 3-3. The derived model is given in Equation [3].

$$MGR_{Xia} = 1.35 \times 10^{10} [OH]^{1.046} [C_{Xia}] e^{-93,100/RT} \quad [3]$$

The model derived using JMP suggests a positive influence of hydroxide concentration on methane generation. This dependency is similar to the hydroxide influence observed on hydrogen generation.

While the source of methane in Xiameter™ AFE-1010 testing is uncertain, a preliminary assessment can be made based on a literature review conducted by Hunter and Woodham.<sup>17</sup> It is known that polydimethylsiloxane (PDMS) is the antifoaming agent in Xiameter™ AFE-1010. Furthermore, oligomers of PDMS (such as octamethylcyclotetrasiloxane, or OMCTS) are known to exist in trace amounts in Xiameter™ AFE-1010. Methylsilanes and methylsiloxanes (such as PDMS and OMCTS) have been known to produce methane at elevated temperatures in the presence of hydroxide and water.<sup>17</sup> Given these observations, a simple hydroxide-catalyzed hydrolytic mechanism may be proposed for the formation of methane from methylsilanes (such as those found in Xiameter™ AFE-1010). This mechanism is displayed in Figure 3-4.



**Figure 3-4. Proposed Mechanism of Methane Formation from Methylsilanes.**

The conclusion drawn from these results is that methane may be produced at rates higher than hydrogen from specific organics that may or may not exist in the CSTF today. The preliminary model in Equation [3] is presented here for reference in future testing and investigation. It is not recommended for use in predicting MGRs from CSTF waste as a function of organic content. The mechanism proposed in Figure 3-4 is recommended for further evaluation in parallel with the preliminary model expression in Equation [3] in additional MGR testing, as was recommended in earlier SRNL studies.<sup>9</sup> Ideally, this testing should identify 1) the types of organic compounds capable of producing methane that are present in CSTF material, 2) the kinetics of methane production from these organics, and 3) an acceptable model that well-predicts methane observed in experiments performed with radioactive waste.

#### 4.0 Conclusions

In summary, the following conclusions have been made as a result of this testing.

- The Glycolate Thermolytic HGR expression may be confidently used to predict thermolytic HGRs from glycolate at temperatures as high as 170 °C and hydroxide concentrations as high as 23 M.
- The hydroxide- and temperature-dependence predicted by the Global TOC Thermolytic HGR expression has been confirmed at temperatures as high as 170 °C and hydroxide concentrations as high as 23 M, suggesting that the Global TOC Thermolytic HGR expression may be used at these ranges.
- Methane was observed from tests with Xiameter at production rates higher than those observed for hydrogen. These rates were observed at temperatures higher than 100 °C.
- Preliminary models suggest that increasing hydroxide/temperature causes an increase in MGR from Xiameter™ AFE-1010.

#### 5.0 Recommendations

The following recommendations are made as a result of this testing.

- The existing equations for thermolytic HGR from glycolate and non-glycolate organics should be used at CSTF storage and evaporation conditions, including temperatures and hydroxide concentrations exhibited in the 242-25H Evaporator.
- Further investigation should be made into the influence of methylsilanes on CSTF flammability. This investigation should include: determination of the types of methylsilanes historically added to the CSTF, determination of methane formation rates from each type of methylsilane, and determination of the extent of degradation of methylsilanes in CSTF waste.
- Characterization techniques should be developed by SRNL to assist in the speciation of methylsilane-containing waste in the CSTF.
- Additional testing with radioactive waste should be performed to determine the MGRs possible in radioactive waste and better inform model predictions made from testing with simulants.

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