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Assessing First-Order Dependence of Thermolytic HGR on Glycolate at Low Glycolate Concentrations

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EXECUTIVE SUMMARY

This report describes the results of testing performed to investigate the assumed first-order behavior of glycolate at low concentrations in the current Glycolate Thermolytic Hydrogen Generation Rate (HGR) expression. Four experiments were performed at 100 °C using a simulant based on a Tank 28 supernate sample, and the glycolate concentration in the experiments ranged from 5 - 175 mg/L. The thermolytic HGR results from all tests were well-described by the current Glycolate Thermolytic HGR Model. A linear fit of the Ln(HGR) and Ln(Gly) gave a suggested reaction order of 1.15. Additionally, by taking into account prior knowledge on how varying chemistry impacts the HGR, a reaction order of 0.99 was obtained. Both cases suggest that the data validates the assumed first-order dependence of HGR on glycolate.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Center
CSTF	Concentration, Storage, and Transfer Facilities
DAC	Data Acquisition and Control
DI	deionized
GC	Gas Chromatograph
HGR	Hydrogen Generation Rate
M&TE	Measuring and Test Equipment
PTFE	polytetrafluroethylene
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TTR	Technical Task Request

1.0 Introduction

Testing to determine the thermolytic Hydrogen Generation Rate (HGR) of organics expected in the Savannah River Site (SRS) Concentration, Storage, and Transfer Facilities (CSTF) including glycolate has been requested via Technical Task Request (TTR) by Savannah River Remediation (SRR).[1-2] To date, Savannah River National Laboratory (SRNL) personnel have performed several series of tests to measure the thermolytic production of hydrogen gas from organics including glycolate dissolved in caustic tank waste media.[3-4] These HGR measurements performed by SRNL have led to the generation of model expressions for the thermolytic production of hydrogen from glycolate.[3] The model is shown below in Equation [1],

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

where,

HGR_{GLY} is the hydrogen production rate from the thermolysis of glycolate in $ft^3 \, h^{-1} \, gal^{-1}$,
$[OH]$ is the concentration of hydroxide in mol L^{-1},
$[Na]$ is the concentration of sodium in mol L^{-1},
$[C_{GLY}]$ is the concentration of carbon from glycolate in mol L^{-1},
$[NO_3]$ is the concentration of nitrate in mol L^{-1},
R is the ideal gas constant, 8.314 J $mol^{-1} \, K^{-1}$, and
T is the temperature in K.

The model expression given in Equation [1] assumes that the impact of glycolate on HGR is linear. In other words, an increase in glycolate causes a proportional increase in HGR. The experimental data used to build the model included glycolate concentrations of around 2000, 1000, and 500 mg/L. In more recent testing to expand the range of applicability of the model to higher temperature and hydroxide concentrations, a glycolate concentration of 150 mg/L was targeted.[4] SRR has requested further testing to determine or confirm the first-order behavior of glycolate at very low glycolate concentrations.

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.[3] 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 consists of a 1.2L polytetrafluroethylene (PTFE) vessel and lid. Fitted to the center of the lid was a Parr® high-torque magnetic drive connected to a PTFE agitator impeller and shaft used to mix the simulant inside the vessel. The speed of the agitator was 200 rpm. Surrounding the magnetic drive were eight ports with stainless-steel fittings used for the following: temperature control within the vessel by two Incoloy® 800 heating rods, monitoring liquid temperature within the vessel with an Inconel® 600 thermocouple, providing purge gas to continuously sweep the vapor space of the vessel, connecting the headspace of the vessel to a glass condenser, providing a route for reflux from the condenser back to the reaction vessel, and for adding sodium glycolate. Upstream from the reaction vessel, two MKS® mass flow controllers were used to supply CO_2-free compressed air or N_2 cylinder gas containing 0.5 vol % Kr and 20 vol % O_2. Downstream from the reaction vessel, a glass condenser was employed to remove condensable gases from the gas before proceeding to analysis. After passing through the condenser, the gas was sampled and quantified for hydrogen content by an Inficon Micro Gas Chromatograph (GC) Fusion before being vented to a chemical hood.

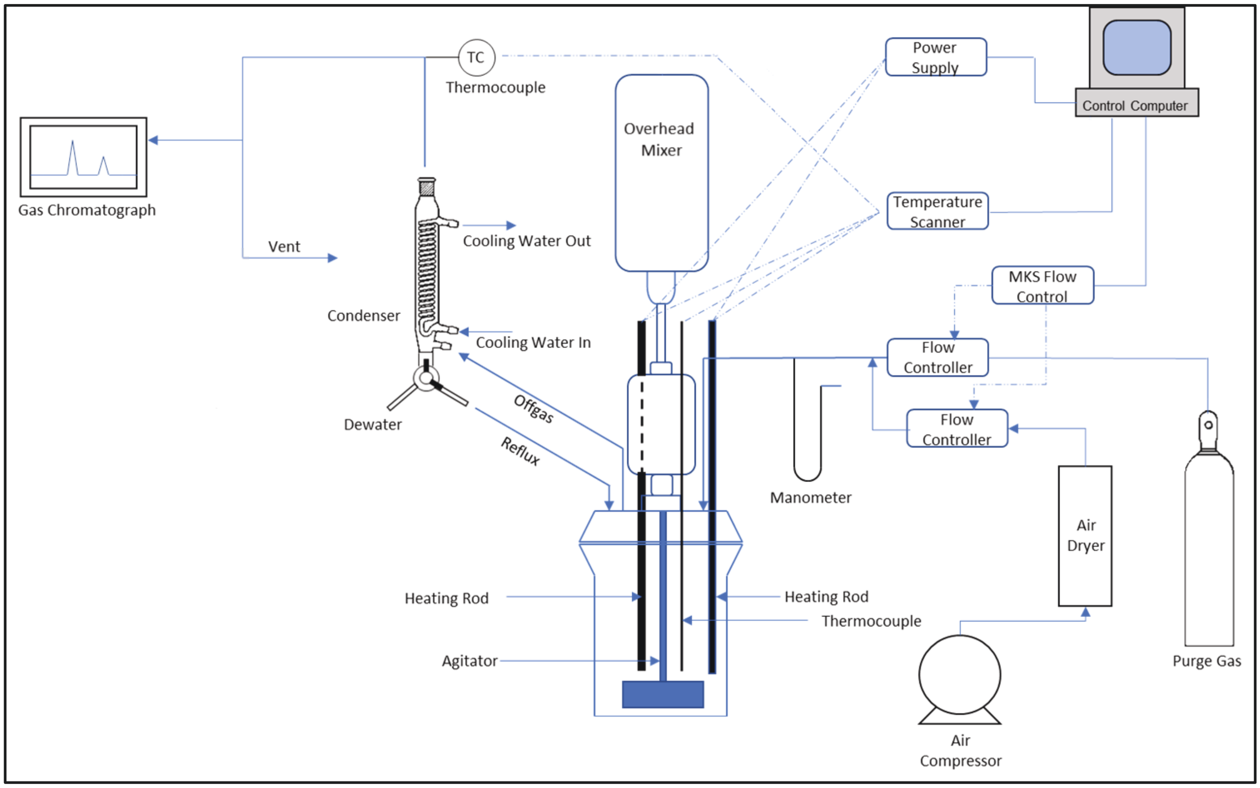


Figure 2-1. Schematic of HGR Measurement Apparatus.

2.2 Simulant Preparation

All testing was performed using a simple salt simulant based on a Tank 28 supernate sample[5], as shown in Table 2-1. The simulant was chosen due to its high salt concentration, which was expected to give measurable HGR readings at the desired low glycolate concentrations. The high salt concentration of the simulant is also representative of the 3H-Evaporator System. It should be noted that the simulant has a reduced aluminum concentration in comparison to the actual waste sample to allow for the use of aluminum nitrate as a source rather than sodium aluminate, which in turn leads to lower trace organic content in the simulant. Reagent grade sodium nitrite and a 50 wt% sodium hydroxide solution were purchased from Fisher Chemical and used as received. Reagent grade aluminum trinitrate nonahydrate was purchased from Sigma-Aldrich and used as received. The reagents were added directly to the reaction vessel before sealing. The order of addition to the vessel was as follows: sodium hydroxide and half of the deionized (DI) water prior to the aluminum trinitrate, then sodium nitrite and remaining DI water.

Table 2-1. Targeted Tank 28 Simulant Composition.

Analyte	Concentrations (M)
[OH]	8.23E+00
[NO_2]	1.99E+00
[NO_3]	1.85E+00
[Al]	6.17E-01
[Na]	1.27E+01

2.3 Experimental Procedure

The full test plan outlined in the run plan is shown in Table 2-2.[6] Only experiments LGE-2, LGE-3, LGE-6, and LGE-7 were performed. These tests made up the initial testing to determine if further tests would be necessary.

Table 2-2. Full Test Plan for Low Glycolate Testing.

Test ID	Glycolate Concentration (mg/L)	Temperature (°C)	Model Predicted HGR ($ft^3\ hr^{-1}\ gal^{-1}$)
LGE-1	300	100	1.78E-05
LGE-2*	175	100	1.04E-05
LGE-3*	70	100	4.15E-06
LGE-4	50	100	2.97E-06
LGE-5	30	100	1.78E-06
LGE-6*	15	100	8.9E-07
LGE-7*	5	100	2.97E-07
LGE-8	2	100	1.19E-07
LGE-9	300	60	7.36E-07
LGE-10	175	60	4.29E-07
LGE-11	70	60	1.72E-07
LGE-12	50	60	1.23E-07
LGE-13	15	125	4.71E-06
LGE-14	5	125	1.57E-06

* Actual tests performed.

After the addition of all chemicals, the vessel was sealed and checked for leaks by mass balance of air flow through the process headspace. Once leak-free conditions had been confirmed, stirring was initiated and a purge flow of dried air was applied to the process to sweep residual CO_2 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 30 °C. In the experiments with very low glycolate concentrations, LGE-6 and LGE-7, the process fluid was first brought to boiling (~125 °C) to lessen the impact of background hydrogen from reagent impurities. The vessel was then cooled to 100 °C, at which point a blank was collected prior to the addition of sodium glycolate. For LGE-2 and LGE-3, the process fluid was brought to 100 °C and sodium glycolate was added. The purge gas was then switched to the typically lower-purge process gas stream (0.5 vol % Kr and 20 vol % O_2 in N_2). This point was designated as the start of the experiment.

The experiment continued while monitoring for hydrogen concentration via GC. The experiment duration was planned such that at a minimum, the vessel headspace could undergo approximately three vapor space-volume turn-overs (achieving 99.7% of pseudo steady-state, assuming continuously-stirred reactor dynamics; note that this time is volume- and purge rate-dependent). Once this time was reached and hydrogen measurements by GC stabilized or began to decrease, the heating rod power was turned off and the experiment was stopped. The higher-purge air was then reapplied to the vessel to sweep residual hydrogen from the system. 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 a Measuring and Test Equipment (M&TE) autopipette and an M&TE balance.

2.4 Offgas Analyses

An Inficon Micro GC Fusion was used to analyze offgas content for all experiments. The GC was equipped with two analysis channels: one using a Molsieve 5A column for H_2, O_2, N_2, CH_4, and Kr analysis, and a second using a PoraPLOT Q column for N_2O and CO_2 analysis. Each column employed a thermal conductivity detector which measured against the background of pure argon (also used as a carrier gas). The GC calibration was verified before each experiment using a calibration gas with a composition of 50 ppmv H_2, 101 ppmv CH_4, 0.5 vol % Kr, 0.503 vol % N_2O, 1.01 vol % CO_2, and balance air.

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

2.5 Quality Assurance

The customer-identified functional classification for these tasks is Safety Class.[1] Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. This document, including all calculations, was reviewed by Design Verification by Document Review. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Data was recorded in the electronic laboratory notebook system.[7] The use of M&TE or Measurement Systems and Equipment was recorded in these notebooks. Measurements, analysis, documentation, and technical review comply with the customer required quality assurance level to support Safety Class use of information contained in this report.[2]

The Data Acquisition and Control (DAC) software employed in this testing was used to control mass flow controllers and electric heating rods as well as to record data taken from thermocouples and the GC. This software is classified as level D.[8] 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 M&TE 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.

Analytical measurements of the gas stream were made using a GC. The GC is in the Measurement Systems and Equipment program and the software is controlled under the requirements of the program. The statistical software package JMP 14 has undergone verification and validation[9] and is classified as level D software.

3.0 Results and Discussion

The conditions used to evaluate first-order behavior of the HGR model down to low glycolate concentrations and the results of each test are given in Table 3-1.

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

Run Name	Temp (°C)	Targeted Glycolate (mg/L)	$[C_{Gly}]$ (M)	[Al] (M)	$[NO_2]$ (M)	$[NO_3]$ (M)	[OH] (M)	[Na] (M)	HGR ($ft^3\ hr^{-1}\ gal^{-1}$)
LGE-2	100	175	4.63E-03	6.09E-01	1.97E+00	1.83E+00	8.13E+00	1.25E+01	1.41E-05
LGE-3	100	70	1.86E-03	6.09E-01	1.96E+00	1.83E+00	8.12E+00	1.25E+01	5.09E-06
LGE-6	100	15	3.74E-04	6.10E-01	1.97E+00	1.83E+00	8.13E+00	1.25E+01	7.03E-07
LGE-7	100	5	1.32E-04	6.12E-01	1.97E+00	1.84E+00	8.16E+00	1.26E+01	2.46E-07

The targeted glycolate concentration ranged from 5 - 175 mg/L. The HGR given is the thermolytic HGR attributable to glycolate following subtraction of background HGR. The HGRs reported in Table 3-1 were evaluated against the predictions made from the Glycolate Thermolytic HGR Model (Equation [1]).[3] The results of this evaluation are displayed in Figure 3-1 as green diamonds overlaid with previous high hydroxide/temperature data (yellow diamonds), model generation data (black diamonds), and the results from Tank 28 real waste testing with 500mg/L glycolate (red circles). All four measurements for the low glycolate test fall near the model prediction line, showing that the experiments are well-described by the Glycolate Thermolytic HGR Model. The Tank 28 real waste testing has been previously plotted to the Glycolate model;[3] as can be seen, the real waste results fall below the model prediction but within the lower bound of the 95% confidence limit, showing that the model is not overly conservative in predicting thermolytic HGR for glycolate. An additional, perhaps easier, way to compare the actual measurements from the Tank 28 simulant low glycolate experiment HGR measurements and the real waste Tank 28 HGR measurements is given in Table 3-2. The thermolytic HGR measurements for LGE-2 and LGE-3 are approximately 140% to 130% of their model predictions, while LGE-6 and LGE-7 are approximately 90% of their model predictions. The three real waste Tank 28 results that straddle the lower bound are ~25% of their model predictions, while Tk28-124.8°C is approximately ~90% of its model prediction.

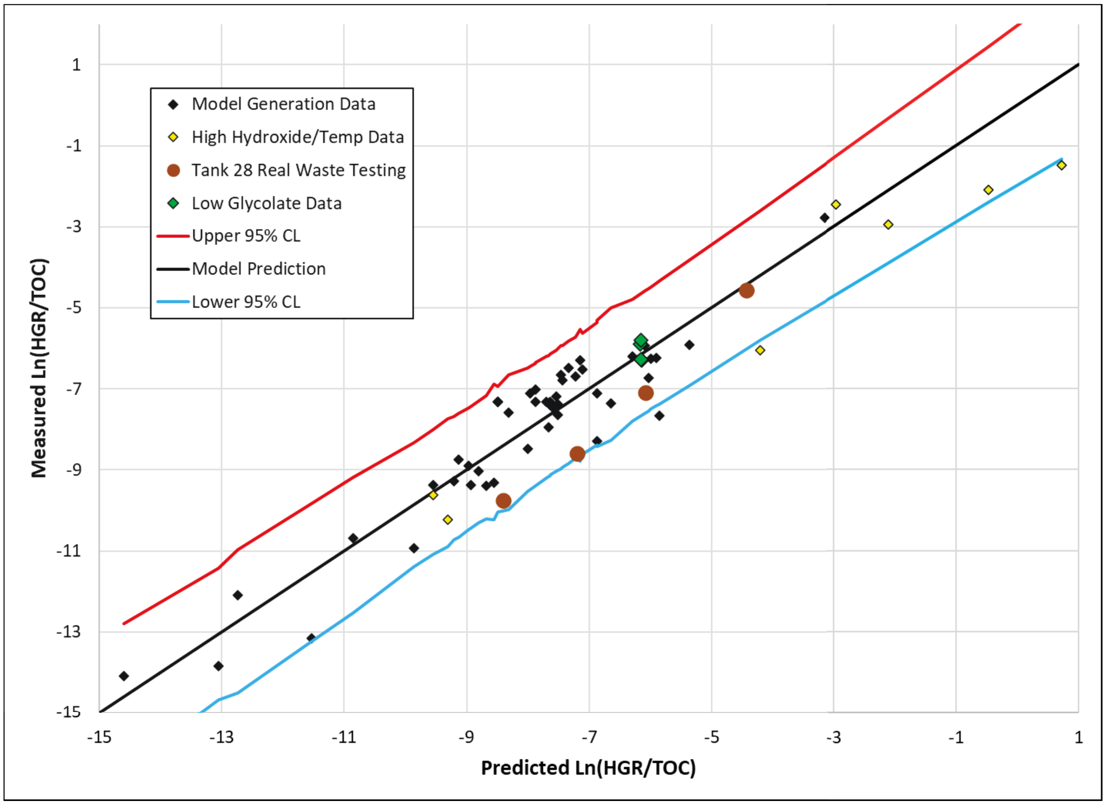
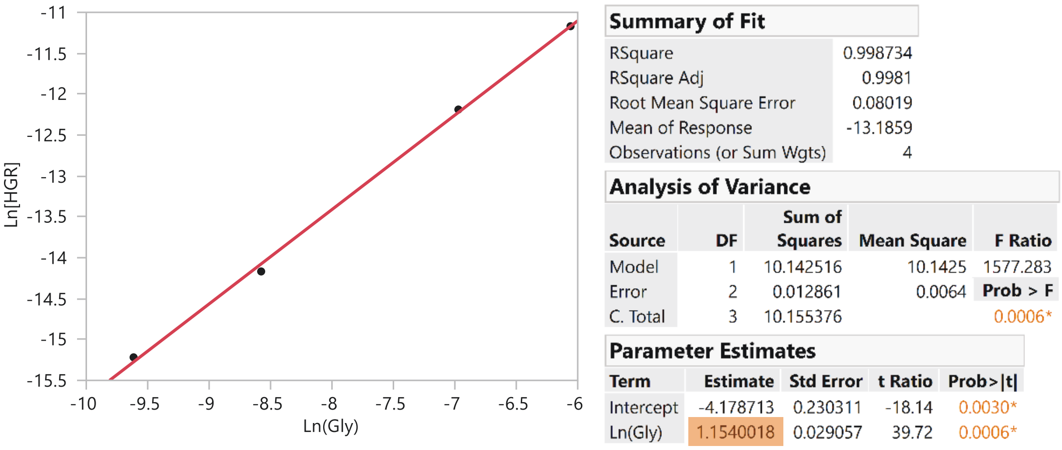


Figure 3-1. Model Evaluation of Glycolate HGR Data.

Table 3-2. Comparison of Model Prediction and Measured Results.

Test	Model Predicted Thermolytic HGR	Thermolytic HGR Measured	Percent of Model Predicted HGR
TK28-70°C	2.95E-06	7.50E-07	25%
TK28-85°C	9.88E-06	2.41E-06	24%
TK28-100°C	3.00E-05	1.09E-05	36%
TK28-124.8°C	1.57E-04	1.35E-04	86%
LGE-2	9.92E-06	1.41E-05	142%
LGE-3	3.96E-06	5.09E-06	129%
LGE-6	8.00E-07	7.03E-07	88%
LGE-7	2.87E-07	2.46E-07	86%

To show the impact of glycolate on HGR is linear, the results of Ln(HGR) vs. Ln(Gly) can be plotted, as shown in Figure 3-2. Doing this gives a good fit with a suggested reaction order of 1.15.



Summary of Fit

RSquare	0.998734
RSquare Adj	0.9981
Root Mean Square Error	0.08019
Mean of Response	-13.1859
Observations (or Sum Wgts)	4

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	10.142516	10.1425	1577.283
Error	2	0.012861	0.0064	**Prob > F**
C. Total	3	10.155376		0.0006*

Parameter Estimates

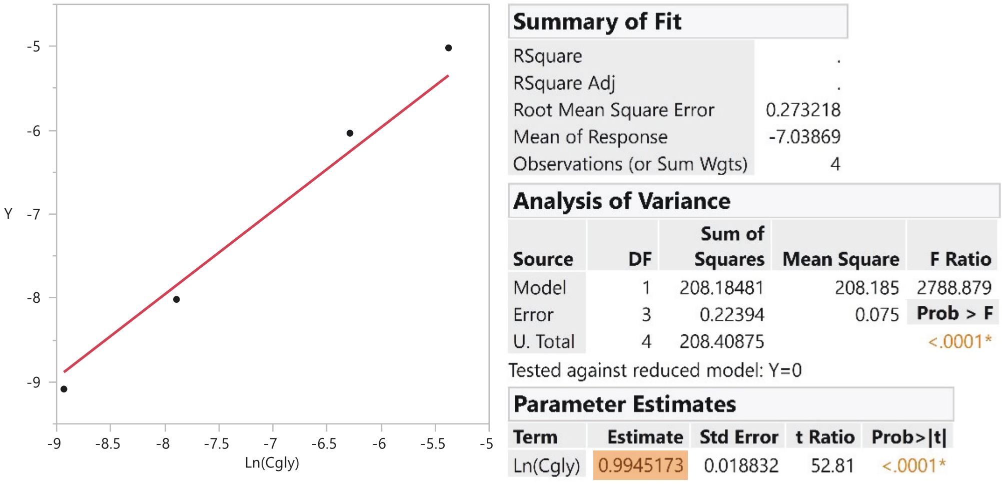
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-4.178713	0.230311	-18.14	0.0030*
Ln(Gly)	1.1540018	0.029057	39.72	0.0006*

Figure 3-2. Linear Fit on Ln(HGR) vs. Ln(Gly) using JMP 14.

The above fit adequately shows the near first-order behavior of glycolate. As seen in Table 3-1, there is some slight variation in the salt concentrations between tests. Using current knowledge from previous HGR testing with glycolate, a more accurate picture can perhaps be surmised by taking into account these slight changes in the salt composition between experiments. The Glycolate Thermolytic HGR Model can be rearranged, as shown in Equation [2].

$$\ln\left(\frac{HGR_{GLY}}{6.262\times10^{5}[NO_3]^{0.282}\,[OH]^{1.441}\,[Na]^{1.520}e^{\frac{-82,300}{RT}}}\right)=\alpha\ln[C_{GLY}] \qquad [2]$$

A best fit line of the left side of Equation [2] against the natural log of glycolate carbon is shown in Figure 3-3. This leads to an adequate fit of the data with good statistics around fit parameters, indicating a reaction order of 0.99. A near first-order result is obtained in either case, suggesting that this data validates the current assessment that glycolate concentration is linearly proportional to the HGR.



Summary of Fit

RSquare	.
RSquare Adj	.
Root Mean Square Error	0.273218
Mean of Response	-7.03869
Observations (or Sum Wgts)	4

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	208.18481	208.185	2788.879
Error	3	0.22394	0.075	**Prob > F**
U. Total	4	208.40875		<.0001*

Tested against reduced model: Y=0

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Ln(Cgly)	0.9945173	0.018832	52.81	<.0001*

Figure 3-3. Fitting using Glycolate Thermolytic HGR Model with JMP 14.

4.0 Conclusions

SRNL investigated the assumed first-order behavior of glycolate in the current Glycolate Thermolytic HGR Model at very low glycolate concentrations. Experiments were performed using a simulant based on a Tank 28 supernate sample with glycolate concentrations ranging between 5 - 175 mg/L. The thermolytic HGR results from all tests were well-described by the current Glycolate Thermolytic HGR Model. Additionally, Tank 28 real waste thermolytic HGR results from previous testing were compared to the Glycolate Thermolytic HGR Model, which showed that all four measurements were above the lower limit of the 95% confidence interval and one of the thermolytic HGR measurements was approximately 90% of the model prediction, showing that the model is not overly conservative in predicting thermolytic HGR for glycolate in real waste. A good linear fit of Ln(HGR) and Ln(Gly) gave a suggested reaction order of 1.15. Additionally, by taking into account prior knowledge on how salt composition impacts the chemistry, a reaction order of 0.99 was obtained. Both cases suggest that the data validates the assumed first-order dependence of HGR on glycolate.

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