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Measurement of Hydrogen Generation Rates during Digestion, Neutralization, Transfer, and Storage of Reillex HPQ Resin

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October 2018

Savannah River
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AUTHOR'S NOTE

Due to the nature of the work described in this document and its application to multiple processes across separate programs, different units have been employed to express the same term: Hydrogen Generation Rate, or HGR. This distinction has been made to align with the units commonly used by Savannah River Nuclear Solutions (SRNS) and Savannah River Remediation (SRR) personnel. When referring to resin digestion experiments, the H-Canyon preferred units of "liters of H_2 per liter of solution per hour" are used, whereas the SRR-preferred units of "cubic feet of H_2 per gallon of solution per hour" are used when referring to Concentration, Storage, and Transfer Facilities (CSTF) HGR measurement experiments.

The reader may convert between these two units with the following conversion factors:

$$HGR\left(\frac{L\ H_2}{L\cdot hr}\right) = 7.4805 \times HGR\left(\frac{ft^3 H_2}{gal\cdot hr}\right)$$

$$HGR\left(\frac{ft^3 H_2}{gal\cdot hr}\right) = 0.1337 \times HGR\left(\frac{L\ H_2}{L\cdot hr}\right)$$

The reader will also note that all HGR values presented in this document are reported at standard vapor conditions of 25 °C and 1 atmosphere. No corrections have been applied to the data presented herein to express the volumetric generation rates of hydrogen at process conditions as needed for flammability evaluations. The following conversions are calculated at these Standard Temperature and Pressure (STP) conditions and provided for convenience:

$$1\,ft^3_{STP}\ H_2 = 28.3168\ L_{STP}\ H_2$$

$$1\,L_{STP}\ H_2 = 0.03531\,ft^3_{STP}\ H_2$$

$$1\,mol\ H_2 = 24.46\ L_{STP}\ H_2$$

$$1\,L_{STP}\ H_2 = 0.04087\ mol\ H_2$$

$$1\,mol\ H_2 = 0.8638\,ft^3_{STP}\ H_2$$

$$1\,ft^3_{STP}\ H_2 = 1.1577\ mol\ H_2$$

EXECUTIVE SUMMARY

Non-radioactive simulant testing has been performed to evaluate the risk of hydrogen formation from products of the acidic digestion of Reillex® HPQ ion exchange resin. The testing included two digestions of Reillex® HPQ resin at conditions currently employed in Savannah River Site (SRS) H-Canyon processing facilities.[1] The digestions used the following protocol.

- 6.4 grams of dry Reillex® HPQ resin was combined with 222.7 grams of 8M nitric acid and mixed.
- 700.1 grams of 5.7% potassium permanganate solution was metered in to the mixture at 5 mL per minute.
- The reaction mixture was stirred at ambient conditions for one hour before heating to 71 °C at a rate of 10 °C/min.
- The reaction mixture then held at 71 °C for 15 hours.
- The mixture was cooled to <50 °C and neutralized with 210.9 grams of 50% sodium hydroxide solution.

Following digestion, the digestion product was added to salt solutions designed to simulate conditions in Tanks 39 and 32 within the SRS Concentration, Storage, and Transfer Facility (CSTF). The digestion product was added to the salt solution simulants to simulate the addition of 159 L of equivalent undigested resin (i.e., the total amount of Reillex® HPQ resin theoretically transferred to the CSTF from previous and planned transfers) to a single CSTF waste tank. Testing was also conducted to evaluate the hydrogen generation rates (HGRs) expected during transfer from H-Canyon to CSTF via H-Area Pump Tank (HPT) 5 assuming a transfer of 42 L of equivalent undigested resin to a minimum heel volume of approximately 1,670 gallons.

The testing yields the following conclusions regarding Reillex® HPQ resin digestion.

- Conditions experienced during the acidic digestion of Reillex® HPQ resin are corrosive and may cause pitting in metal.
- Concentrations of hydrogen due to chemical generation during digestion are expected to be less than 40 ppm during regular processing. Concentrations of 40 ppm H_2 were observed during testing with purge rates 163 times lower and headspace residence times 32 times longer than planned in facility operation.
- Hydrogen generation rates during digestion and neutralization are limited to approximately 2.7×10^{-5} L H_2 L^{-1} hr^{-1}.
- Carbon dioxide and oxygen are the primary gaseous products generated during digestion.
- The rates of hydrogen produced during permanganate addition, heat-up, and digestion relative to the rates of other generated gases is too low to generate a flammable concentration of hydrogen, regardless of purge conditions.

Testing also yields the following conclusions concerning HGRs of Reillex® HPQ digestion products in CSTF conditions.

- Hydrogen generation rates in HPT-5 are expected to be less than 3.0×10^{-8} ft^3 H_2 hr^{-1} gal^{-1}.
- Tank 39 testing at conservatively high Total Organic Carbon (TOC) concentrations (i.e., approximately 4x that expected in the proposed future discharge, equivalent to 159 L of undigested resin) yielded an HGR of 4.3×10^{-7} ft^3 H_2 hr^{-1} gal^{-1} at 100 °C and 1.9×10^{-7} ft^3 H_2 hr^{-1} gal^{-1} at 80 °C.

- Tank 32 testing at conservatively high TOC concentrations (approximately 4x that expected in the proposed future discharge, equivalent to 159 L of undigested resin) yielded an HGR of 3.0×10^{-6} ft^3 H$_2$ hr^{-1} gal^{-1} at 100 °C and 8.6×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1} at 80 °C.
- Results from testing with Reillex® HPQ digestion product in Tank 39 simulant at temperatures at or below 100 °C can be described by the following expression:

$$HGR_{TK39}\left(T\right) = 4.3 \times 10^{-7} e^{-\frac{44,700}{R}\left(\frac{1}{T} - \frac{1}{373.15}\right)}$$

- Results from testing with Reillex® HPQ digestion product in Tank 32 simulant at temperatures at or below 100 °C can be described by the following expression (this expression is expected to be representative of the highest hydrogen producing tanks in the CSTF and is expected to bound CSTF operations given the dependence on aluminum concentrations reported in literature[2-4]).

$$HGR_{Tk32}\left(T\right) = 3.0 \times 10^{-6} e^{-\frac{68,400}{R}\left(\frac{1}{T} - \frac{1}{373.15}\right)}$$

The following recommendations are made from the observations and results generated from this testing.

- The risk of corrosion to vessel integrity should be further assessed for process vessels used in the digestion of Reillex® HPQ resin in H-Canyon.
- Additional testing may be warranted to determine the contribution of corrosion to hydrogen generation during Reillex® HPQ digestion in H-Canyon stainless steel vessels.
- Additional HGR testing with Reillex® HPQ digestion product can better elucidate the destruction rates of digestion resin material in tank conditions for extended durations (>30 days) in CSTF. Such testing will allow for reduction of conservative estimates used in the analysis of the data presented in this report.
- Future digestion experiments with polystyrene-based resins (such as IONAC A-641) are in progress and should be completed by SRNL to assess the risk of hydrogen formation from the degradation products of such resins.[5]

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
AD	Analytical Development
CSTF	Concentration, Transfer, and Storage Facility
GC	Gas Chromatography
HGR	Hydrogen Generation Rate
HPT	H-Area Pump Tank
LWO	Liquid Waste Operations
PSAL	Process Science Analytical Laboratory
PTFE	(poly)tetrafluoroethylene
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRR	Savannah River Remediation
SRS	Savannah River Site
STP	Standard Temperature and Pressure
TCD	Thermal Conductivity Detector
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
WAC	Waste Acceptance Criteria

1.0 Introduction

Reillex® HPQ ion exchange resin is a polyvinylpyridine/divinylbenzene copolymer used to separate heavy metals in Savannah River Site (SRS) processing streams.[6] It is used primarily in HB-Line to separate plutonium from process streams. The structure of Reillex® HPQ resin is given in Figure 1-1.[7]
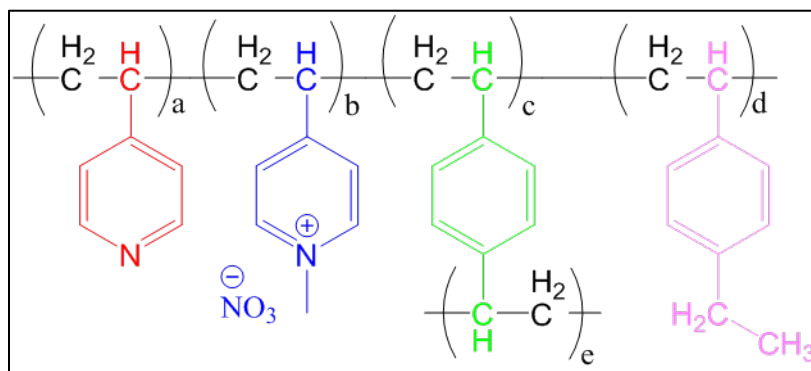
Figure 1-1. Chemical Structure of Reillex® HPQ Ion Exchange Resin.

Although Reillex® HPQ resin is only employed at one process (HB-Line) at SRS, it has the potential to enter several process streams at SRS through its disposition lifecycle. This lifecycle is portrayed in Figure 1-2.
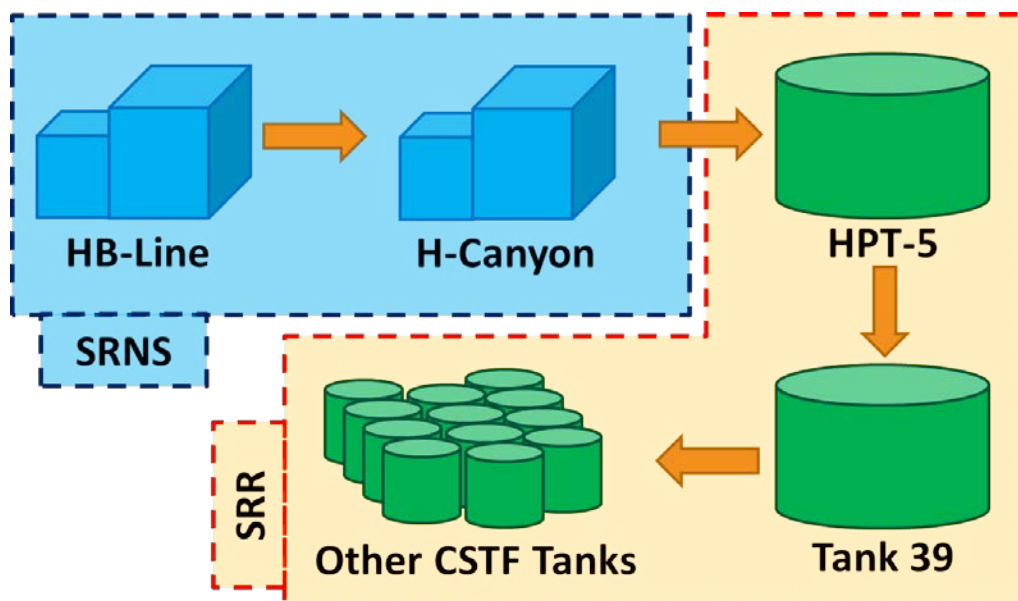
Figure 1-2. Block Flow Diagram of Reillex® HPQ fate at SRS.

Once a column of Reillex® HPQ resin is ready for disposition, it is transferred from HB-Line to H-Canyon (specifically Tank 5.2) for digestion by potassium permanganate under acid conditions. H-Canyon is currently operated by Savannah River Nuclear Solutions (SRNS) and adheres to a flowsheet designed by Savannah River National Laboratory (SRNL) for digestions of Reillex® HPQ resin.[1] Once the resin has been sufficiently digested, it is neutralized to 1.2 M excess hydroxide by SRNS personnel to meet Waste Acceptance Criteria (WAC) requirements of the SRS Liquid Waste Operations (LWO), Savannah River

Remediation (SRR).[8] Once the neutralization is complete, the waste is accepted by SRR and transferred to HPT-5, an H-area pump tank. Following transfer to HPT-5, the digested resin material will be pumped to Tank 39 before subsequent distribution and dilution to other Concentration, Storage, and Transfer Facilities (CSTF) tanks through normal operations. Throughout HB-Line operation, 117 L of Reillex® HPQ has been digested, neutralized, and transferred to the CSTF, with an additional 42 L planned for digestion and disposition in 2018.

Previous, unpublished Hydrogen Generation Rate (HGR) measurement experiments performed by SRNL demonstrated that compounds with a methylpyridinium functionality (such as Reillex® HPQ) may exhibit high HGRs at elevated temperatures in CSTF conditions at low loadings of organic carbon. Given this finding, it became important to understand the potential for hydrogen generation of Reillex® HPQ after it has been digested.

SRNL was tasked by SRR to investigate and quantify the contributions of organic molecules (including Reillex® HPQ digestion products) toward hydrogen production by non-radiolytic chemical reaction (hereafter referred to as "thermolysis").[9] SRNL was further tasked by SRNS to investigate HGRs exhibited during the digestion of Reillex® HPQ resin.[10] SRNL developed a Run Plan in collaboration with SRR and SRNS to conduct the testing necessary to meet these criteria.[5] The results of the tests proposed in that plan are described and discussed in this report.

2.0 Experimental Procedure

The experimental work described herein was performed by SRNL personnel at the Aiken County Technology Laboratory (ACTL).

2.1 Simulant Preparation

Two simulant mixtures were prepared for this testing; a mixture to represent Tank 39 salt concentrations and a mixture to represent Tank 32 salt concentrations.[11] Tank 39 was used to evaluate the HGR expected upon preliminary transfer of Reillex® HPQ resin digestion product to Tank 39. Tank 32 was used to evaluate the HGR at concentrations that are expected to represent one of the highest hydrogen-producing conditions in the CSTF based on Hu equation projections. The concentrations of salt species in Tank 39 and Tank 32 simulants were based on samples taken from each respective tank on May 29th, 2015 and February 27th, 2018, respectively. The composition of Tank 32 includes elevated aluminum, hydroxide, and nitrate concentrations. Prior literature[2-4] and work in progress implicate these species as promoting higher HGRs from thermolysis. Hence, Tank 32 represents conservative waste conditions to assess hydrogen generation contribution from the discharged Reillex® digestion products.

The target concentrations for each tank are given below in Table 2-1.

Table 2-1. Target Concentrations of Simulants for HGR Experiments

Analyte	Tank 39, M	Tank 32, M
Al	0.118	0.769
NO_2^-	0.315	2.58
NO_3^-	1.98	2.31[a]
OH^-	1.23	7.41

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[a] The nitrate concentration of the Tank 32 simulant has been artificially increased from 1.99 M to 2.31 M to allow for the use of aluminum trinitrate as a source of aluminum during testing. Recent unpublished results from HGR testing performed at SRNL suggest that this increase in NO_3 will increase the conservatism in the Tank 32 HGR experiments.

Sodium nitrate, sodium nitrite, 50 wt% sodium hydroxide solution, and aluminum trinitrate nonahydrate were purchased from Fisher Chemicals and used as received. Deionized water was prepared in-house (>18 MΩ·cm) and used to prepare all simulant solutions.

2.1.1 Tank 39 Simulant Solutions

Tank 39 simulant was expected to be reasonably dilute with no concern for solid precipitation. Therefore, a single 5-L batch of Tank 39 simulant was prepared and used as needed throughout testing. Details concerning the preparation of this simulant follow:

1. 680.8 g of 50 wt% NaOH solution was added to 250 g of deionized water.
2. 221.3 g of aluminum trinitrate nonahydrate was added to the sodium hydroxide solution.
3. 691.0 g of sodium nitrate was added to the mixture.
4. 108.7 g of sodium nitrite was added to the mixture.
5. The mixture was diluted to 5 L with deionized water.

One liter of Tank 39 simulant was subsampled from the master batch and used for each Tank 39 HGR experiment.

2.1.2 Tank 32 Simulant Solutions

Tank 32 material is significantly more concentrated in salt species than Tank 39. Given the possibility of undissolved solids at this higher loading of salt, Tank 32 simulant solutions were prepared in individual 1-L batches for use in HGR testing. The general protocol for production of this material follows:

1. 838.8 g of 50 wt% NaOH solution was added to 50 g of deionized water.
2. 288.5 g of aluminum trinitrate nonahydrate was added to the sodium hydroxide solution.
3. 178 g of sodium nitrite was added to the mixture.
4. The mixture was diluted to 1 L with deionized water.

The contents of a 1-L batch of Tank 32 simulant were transferred to an HGR rig for each test at Tank 32 conditions. This approach resulted in a transfer of solids along with liquid solution into each Tank 32 test.

2.2 Digestion Apparatus

The apparatus used for the digestion of Reillex® HPQ resin was similar in design to those used in previous HGR testing.[12] The apparatus consisted of a 1.2 L reaction vessel equipped with overhead mixing. Heating was provided via two Incoloy® 800 heating rods controlled by an independent control computer. Purge gas was used to sweep the headspace of the vessel. The purge gas (consisting of either building air or 0.5 vol% Kr and 20 vol% O_2 in N_2) was controlled by MKS Instruments mass flow controllers and introduced directly into the vessel headspace via Swagelok® National Pipe Thread fittings. Liquid temperature was monitored using an Inconel® 600-clad thermocouple and read using a Digi-Sense scanning thermometer. Liquids were metered into the vessel using a piston pump at a maximum flow rate of 5 mL/min. Generated gases were swept from the headspace with the purge gas and flushed into a condenser set at 10 °C. Condensate was returned to the reaction vessel while non-condensed gases flowed downstream for analysis by Gas Chromatography (GC) using an Inficon 3000 MicroGC. Gas streams were then exhausted to the hood. The MicroGC was calibrated using a specialty gas mixture generated by MESA Specialty Gases & Equipment (50 ppm H_2, 0.5 vol% Kr, 1 vol% CO_2, 0.5 vol% N_2O in air) and certified within 2% accuracy.

A schematic of the apparatus used for Reillex® HPQ digestions is shown in Figure 2-1.
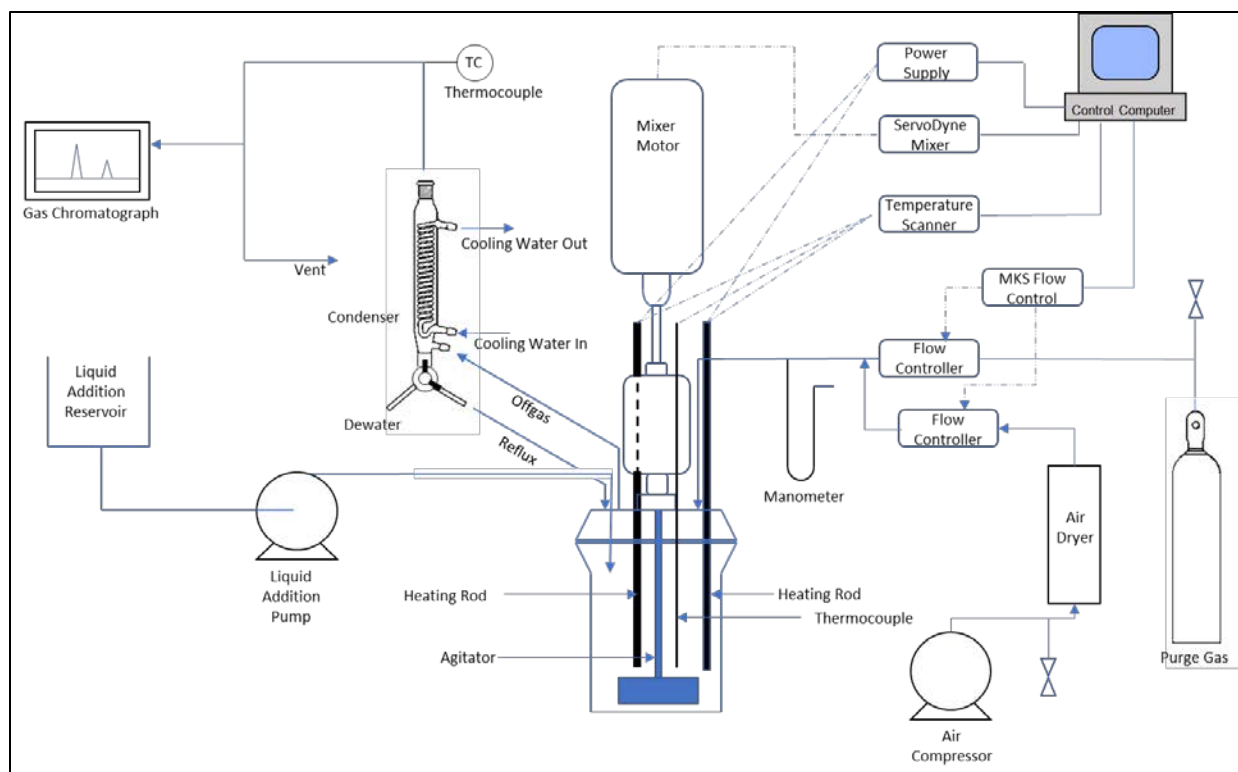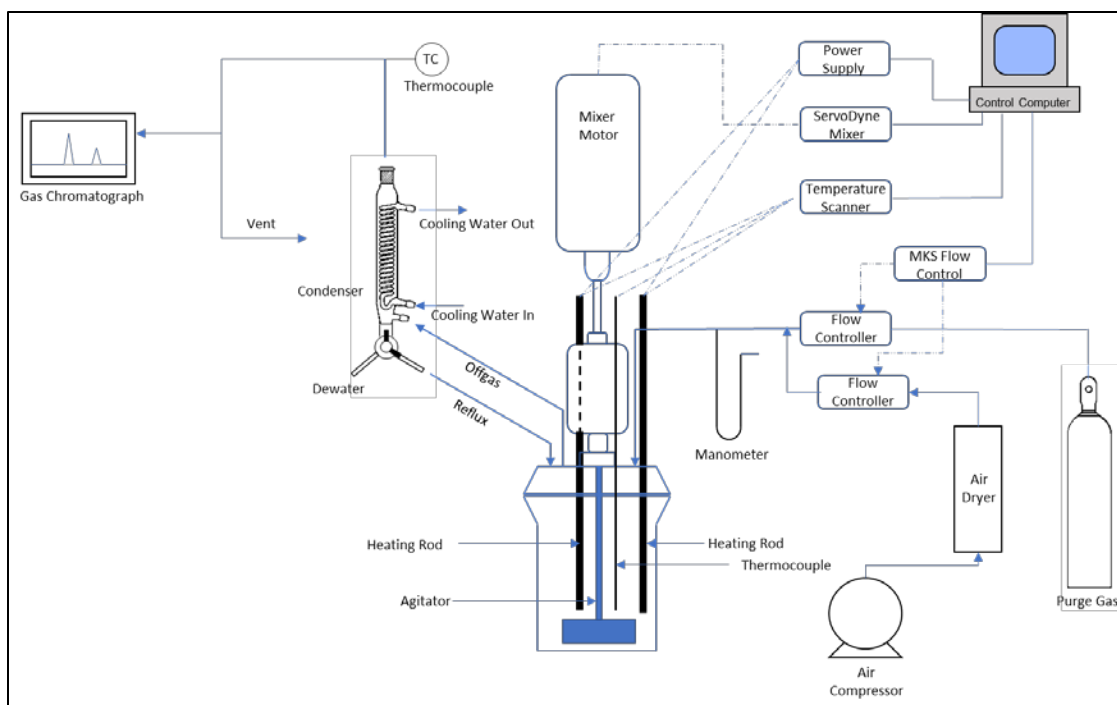
Figure 2-1. Schematic of Resin Digestion Apparatus Used in Reillex® HPQ Digestion Testing.

For the purposes of these experiments, two digestions of Reillex® HPQ resin were performed: the first using all metal wetted components (stainless-steel pot and agitator, Incoloy® heating rods and Inconel® thermocouple) and the second using (poly)tetrafluoroethylene (PTFE) and Inconel wetted components (PTFE pot and agitator, Inconel heating rods and thermocouple). Aggressive corrosion was observed in the first experiment, which is why a second experiment with PTFE was performed. Both experiments are explained in more detail in Section 3.1 of this report.

2.3 Hydrogen Generation Rate (HGR) Measurement Apparatus

The apparatus used to measure HGRs was identical to that used in previous HGR testing.[12] A 1.2 L PTFE reaction vessel was equipped with overhead mixing via a PTFE agitator. Purge gases (either building air or 0.5 vol% Kr and 20 vol% O_2 in N_2) was supplied via MKS Instruments mass flow controllers and controlled by an independent control computer. Heating was provided by 3/8" Incoloy® heating rods controlled by computer. A borosilicate glass condenser (set at 10 °C) was used to condense water vapor from the offgas stream before downstream GC analysis and subsequent exhaust to the hood. A schematic of the apparatus used for HGR testing is shown in Figure 2-2.

Figure 2-2. Schematic of Apparatus Used in HGR Measurement Testing.

2.4 Resin Digestion Experiments

Resin digestion experiments were performed to simulate the digestion of Reillex® HPQ in Tank 5.2 Experiments were performed by charging 6.4 g of dried Reillex® HPQ resin (10 mL, approximately 2100 times less than the planned transfer volume of 21 L) to the digestion vessel and combining it with 222.7 g of 8 M HNO_3. The vessel was then sealed and purged with carrier gas consisting of 0.5 vol% Kr and 20 vol% O_2 in N_2. The vessel was mixed at 200 rpm and purged at ambient conditions until Kr could be detected at 90% of its expected value (0.45 vol%). The purge gas flow rate was then decreased to 3 sccm for the duration of the experiment. Following purge gas adjustment, 700.1 g of 5.7 wt% $KMnO_4$ solution was added at a rate of 5 mL/min to the vessel. Once the permanganate had been added, the vessel mixed without heating for 1 hour. Following the 1-hour incubation period, the reaction mixture was heated to 71 °C at a rate of approximately 10 °C/min, while stirring. Upon reaching 71 °C, the reaction mixture continued digesting for 15 hours with stirring.

At the completion of the 15-hour digestion cycle, the reaction mixture was cooled to below 50 °C. Once below 50 °C, 210.9 g of 50 wt% NaOH was metered in to the reaction mixture. The flow rate of NaOH solution was controlled such that the exothermic acid-base neutralization never caused the liquid to increase above 50 °C, with a maximum flow rate of 5 mL/min. Once the NaOH solution had been introduced to the kettle, the reaction was allowed to cool to 40 °C and monitored for hydrogen production for 4 hours.

2.5 Vapor and Liquid Sampling

Liquid samples were drawn from each digestion experiment for chemical analysis. Product densities were measured at the point of generation via micropipette and laboratory balance. Anion content was determined by ion chromatography at the SRNL Process Science Analytical Laboratory (PSAL). Total Inorganic Carbon (TIC), Total Organic Carbon (TOC) and free hydroxide content were determined by SRNL's Analytical Development (AD) laboratory.

Gas composition measurements of the experiment effluent were made using an Inficon MicroGC. A Molsieve 5 column was employed to detect H_2, Kr, N_2, O_2, and CH_4. A QPlot column was employed to detect N_2O and CO_2. Each column was equipped with a Thermal Conductivity Detector (TCD) to quantify gaseous concentrations. A calibration gas consisting of 50 ppm H_2, 100 ppm CH_4, 0.5% Kr, 0.5% N_2O, and 1% CO_2 in air was employed to calibrate the TCD response factors between experiments.

2.6 Hydrogen Generation Experiments

Nine HGR measurement experiments were proposed in the Run Plan.[5] These tests were proposed to evaluate the HGR due to Reillex® HPQ digestion products at five conditions: 1) HGR in Tank 39 at 100 °C, 2) HGR in Tank 39 at 80 °C, 3) HGR in Tank 32 at 100 °C, 4) HGR in Tank 32 at 80 °C, and 5) HGR in HPT-5 during transfer from H-Canyon to CSTF. The nine tests and their experimental conditions are given in Table 2-2.

Table 2-2. Conditions Employed in Reillex® HPQ Digestion Product HGR Testing.

Test ID	Simulant	Amount of Digestion Product Added	Temperature
REI-1	Tank 39	0 g	100 °C
REI-2	Tank 32	0 g	100 °C
REI-3	Tank 39	17.4 g	100 °C
REI-4	Tank 32	17.4 g	100 °C
REI-5	Tank 39	17.4 g	80 °C
REI-6	Tank 32	17.4 g	80 °C
REI-7	Tank 39	0 g	80 °C
REI-8	Tank 32	0 g	80 °C
REI-9	Tank 39	400 mL	55 °C

As may be seen in Table 2-2, experiments REI-1 through REI-8 as test and control experiments and are paired such that a thermolytic HGR due only to the presence of digestion product may be extracted. REI-1 and REI-3 are the control and test (respectively) evaluating the thermolytic HGR from Reillex® digestion product at 100 °C in Tank 39 conditions, while REI-2 and REI-4 are the control and test (respectively) evaluating the same thermolytic HGR at the same temperature in Tank 32 conditions. Similarly, REI-5 through REI-8 are tests designed to measure the same thermolytic HGR contributions in the same tank conditions at 80 °C. Test REI-9 was performed to evaluate the expected HGR at HPT-5 conditions and is therefore markedly different from tests REI-1 through REI-8. The conservatisms in these test conditions are explained fully in the Run Plan and are repeated in Section 3.0 of this report.

Tests REI-1 through REI-8 were performed by first charging 1 L of the specified salt simulant to the HGR apparatus. Following salt simulant addition, either 0 or 17.4 g of digestion product (depending on the specifications of the test) were added to the HGR apparatus before sealing the vessel (the addition of 17.4 g of digestion product simulates the addition of 159 L of equivalent undigested resin to Tank 39 and represents a bounding concentration of organic material). Mixing was initiated at 200 rpm, and a purge gas of building air was introduced to the headspace at a rate of 20 sccm. Power was then supplied to the heating rods and the reaction mixture was heated to the desired temperature (80 °C or 100 °C). Once the target temperature was achieved, the purge gas was changed to 0.5 vol% Kr and 20 vol% O_2 in N_2 and reduced to 3 sccm. Each experiment proceeded for ≥4 hours (roughly equivalent to 3 headspace turnovers).

Test REI-9 was performed in a method like that of tests REI-1 through REI-8 except for digestion product concentration and temperature. In Test REI-9, 400 mL of digestion product was added to 600 mL of Tank 39 simulant (representing the addition of 42 L of equivalent, undigested resin to a minimum HPT-5 heel of

1,670 gallons and therefore a bounding concentration of organic material from resin) and heated to 55 °C rather than 80 °C or 100 °C.

2.7 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60.[13] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[14]

3.0 Results and Discussion

3.1 Resin Digestion Results

As previously mentioned, two digestions of Reillex® HPQ resin were performed: the first using a stainless-steel pot and agitator, and the second using a PTFE pot and agitator. Several differences exist between these two experiments and are described here.

The first resin digestion experienced complications due to incomplete dissolution of $KMnO_4$ in water. The presence of solids in the $KMnO_4$ addition stream (i.e., partially-dissolved permanganate) necessitated a change in the addition method, which included troubleshooting the experiment and opening the vessel to add permanganate solids directly to the vessel. This opening introduced air to the vapor headspace and therefore increased the uncertainty associated with offgas measurements during the early segment of digestion. The delays associated with the troubleshooting required to employ a solid addition method also significantly increased the duration of the potassium permanganate addition stage of the first digestion experiment.

Approximately 2 hours after the end of caustic addition, significant hydrogen generation was observed. These relatively high rates of hydrogen production appeared to be correlated with the power supplied to the heating rods, suggesting that the hydrogen being produced was formed by electrolysis from the current being supplied to the heating rods. This was further confirmed after the first digestion finished when, upon opening the digestion vessel, severe pitting and corrosion was observed on all surfaces, including the heating rods. The pitting on the heating rods appeared by visual observation to penetrate the Incoloy® cladding at the approximate level of the liquid-vapor interface (Figure 3-1 and 3-2).

Figure 3-1. Picture of Inside of 304L Stainless Steel Vessel Used in First Digestion Experiment. Pitting can be seen along the weld line, coincident with the liquid-vapor interface.

Figure 3-2. Picture of Incoloy® 800 Heating Rod Used in First Digestion Experiment. Pitting can be seen at the height of the liquid-vapor interface.

Given the complications with permanganate addition, temporary opening of the vessel headspace, longer exposure times, and probable contributions of corrosion to measured hydrogen, it was decided to perform a second digestion using PTFE equipment in place of stainless-steel and ensuring complete dissolution of the KMnO$_4$ solution. The offgas from the second experiment is therefore expected to be more representative of the generation rates expected from chemical reaction during Reillex® HPQ digestion and is therefore the only offgas data presented in this report.

Figure 3-3 gives the profile of hydrogen concentration as a function of time during the second Reillex® HPQ digestion. Gray hashed lines separate the profile into four segments: 1) permanganate addition, 2) heat-up, 3) digestion, and 4) cooldown and neutralization.
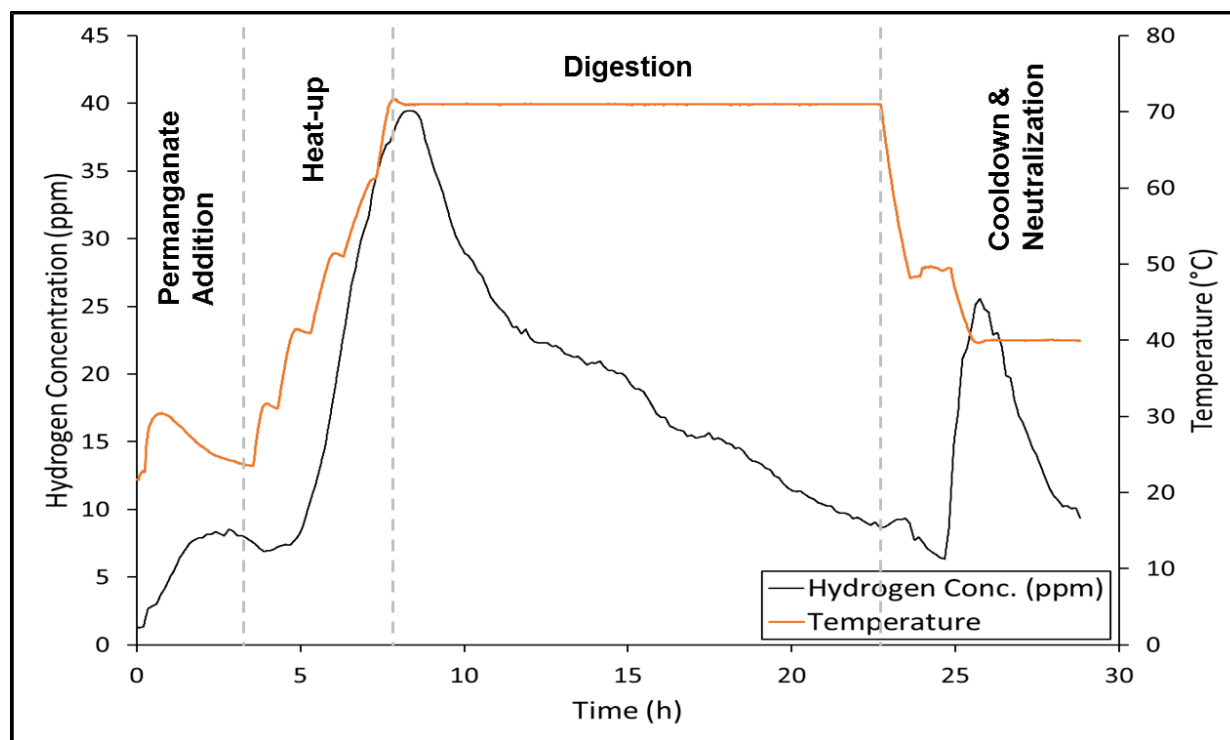
Figure 3-3. Hydrogen Concentration (in ppm) as a Function of Time during Reillex® HPQ Digestion Experiments.

It is clear from Figure 3-3 that the concentration of hydrogen in the headspace due to thermolysis never exceeded 40 ppm. The concentration of hydrogen in the vapor space is conservative with respect to normal facility processing conditions. H-Canyon performs digestion in Tank 5.2, which typically has a purge of 50 scfm. This flow rate, scaled to SRNL experimental conditions, is approximately equal to 490 sccm. As stated earlier, all SRNL experiments were performed at purge rates of 3 sccm, indicating a decrease in purge rate of a factor of 163. It should be noted that the experiment performed by SRNL did not employ the same vapor-liquid ratio as that used in H-Canyon; the vapor space residence time is therefore not directly related to the experimental residence time by a factor of 163. Note that while the purge rate employed in testing was approximately 163 times lower that that used in facility processing, the headspace residence time was not 163 times longer than that seen in the facility. After neutralization, Tank 5.2 typically holds 2,900 L of neutralized material (approximately half of its 5,880 L total volume). This leads to a liquid-to-vapor ratio of 1:1, much lower than the 5:1 ratio employed in testing (1 L of neutralized material in a 1.2 L pot). Therefore, though the purge rate employed in testing was 163 times lower than that used in the facility, the vapor space residence time is only ~32 times longer. These differences should be considered for flammability evaluations.

The highest concentration observed during testing was measured immediately after heat-up finished, reaching as high as 40 ppm H_2. After this peak, hydrogen concentration decreased to approximately 10 ppm by the end of digestion, suggesting a continually-decreasing rate of hydrogen generation. A second peak of hydrogen concentration was observed during cooldown and neutralization (25 ppm), which rapidly decreased to approximately 10 ppm.

The time-dependent hydrogen concentration (shown in Figure 3-3) may be used along with the supplied purge gas flow rate, the measured Kr concentration, and the time-dependent liquid volume to calculate the

HGR (in units of L H_2 L^{-1} hr^{-1}). This conversion is applied to the experimental data to show the volumetric HGR graphically in Figure 3-4.
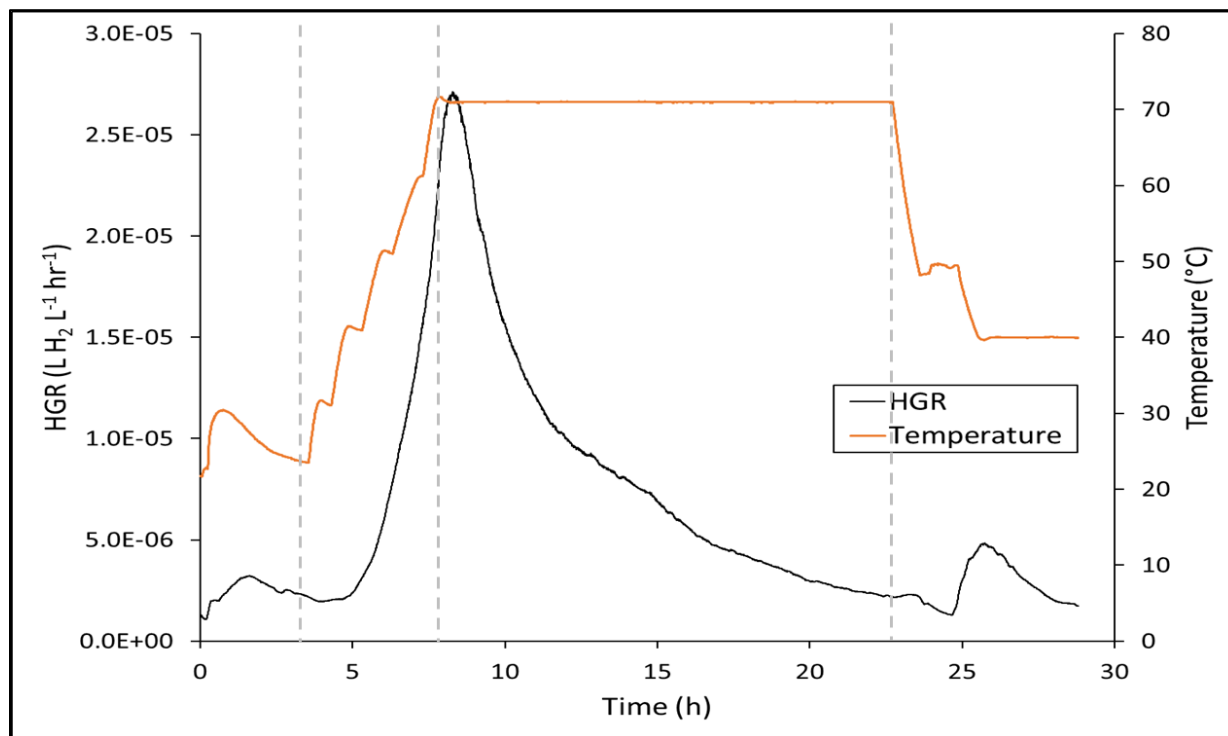
**Figure 3-4. HGR (in L H_2 L^{-1} hr^{-1}) as a Function of Time during Reillex® HPQ Digestion Experiments.**

As seen in Figure 3-4, the peak HGR observed during Reillex® HPQ digestion is approximately 2.7×10^{-5} L H_2 L^{-1} hr^{-1}. This peak generation rate occurs immediately following heat-up and diminishes to 2.2×10^{-6} L H_2 L^{-1} hr^{-1} by the end of digestion. A second HGR peak is observed during caustic neutralization. This second peak reaches 4.7×10^{-6} L H_2 L^{-1} hr^{-1} before decreasing to 1.8×10^{-6} L H_2 L^{-1} hr^{-1} by the end of the experiment. These HGRs may be used to evaluate vapor space flammability during Reillex® HPQ resin digestion without consideration of dilution from other gases being generated.

It should be noted that the relative peak heights in concentration space (40 ppm vs 25 ppm) are not equivalent to the relative peak heights in HGR space (2.7×10^{-5} L H_2 L^{-1} hr^{-1} vs 4.7×10^{-6} L H_2 L^{-1} hr^{-1}). The reason for this discrepancy is the normalization by liquid volume when converting to HGR units. The theoretical volume of liquid present during the digestion cycle (~880 mL) is less than that present after caustic neutralization (~1000 mL). Note that these volumes are calculated based on the masses added and predicted densities without consideration of lost mass due to vapors. The higher production rate of hydrogen (40 ppm) generated from a smaller volume of solution suggests a disproportionately higher HGR when normalized on a solution volume basis.

Gases other than hydrogen were expected from the digestion of Reillex® HPQ resin. Figure 3-5 gives the profiles of other gases measured during the digestion experiments (for O_2, CO_2, N_2, and Kr). Note that CO and NH_3 concentrations were not determined with the equipment used during testing.
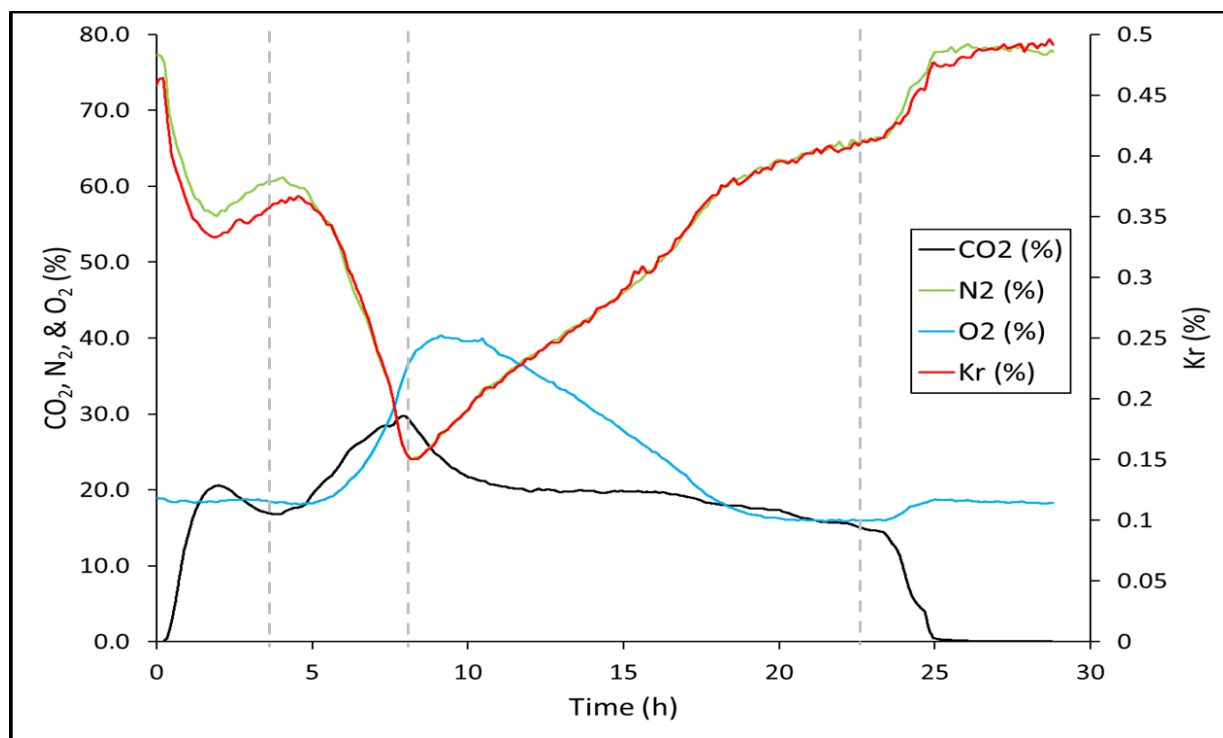
Figure 3-5. Concentrations of CO₂, O₂, N₂, and Kr (in vol%) during Digestion Testing.

The CO_2 concentrations vary between 15 and 30 vol% for most of the digestion experiment, corresponding to the breakdown of Reillex® HPQ resin. A sharp decrease in CO_2 concentration to 0 vol% is observed shortly after the beginning of caustic neutralization, which is consistent with the notion of alkaline retention of CO_2 as carbonate anion, as shown in Equation (1).

$$CO_{2(g)} + NaOH_{(l)} \rightarrow NaHCO_{3(l)} \tag{1}$$

Note that the CO_2 values measured (15-30 vol%) exceed the concentration used in the calibration gas (1 vol%); a linear response is assumed in the GC TCDs to calculate concentrations above the calibration gas concentration. Note also that neither CH_4 nor N_2O were observed during digestion, suggesting that the concentrations of each gas are below the calibration values of 100 ppm and 0.5 vol%, respectively. N_2 and Kr were added as purge gas components throughout the experiment. The fact that both gases follow the same trend suggests that neither gas is being produced during the digestion experiment. It is also important to note that both gases exhibit a global minimum in concentration during the experiment at the end of heat-up and the start of the digestion (i.e. ~ 8.5 hours), suggesting that the purge gas is most heavily diluted at the start of digestion equating to large amounts of offgas being generated. Peak dilution appeared to occur at the completion of heat-up, indicating dilution of Kr from an expected concentration of 0.5 vol% to 0.15 vol%.

Interestingly, O_2 exhibits a significant increase around the same time as peak dilution, reaching as high as 40 vol %. Given that O_2 was added at a concentration of 20 vol% in the purge gas, a significant fraction of the offgas being generated consists of O_2 and CO_2 (rather than only CO_2).

Given the relatively low concentrations of hydrogen observed (<40 ppm) and the relatively high concentrations of non-flammable offgas species, CO_2 and O_2 (30 vol% and 40 vol%), it is expected that

hydrogen will be a small component of the offgas being generated during digestion. Using the measured Kr concentration, the concentration of hydrogen in the generated gas stream can be calculated using Equation (2),

$$y_{H_2}^{generated} = \frac{y_{H_2}^{measured}}{1 - \left(y_{Kr}^{measured} \middle/ y_{Kr}^{purge} \right)} \tag{2}$$

where,

$y_{H_2}^{generated}$ is the concentration of hydrogen in the generated gas stream,

$y_{H_2}^{measured}$ is the concentration of hydrogen measured by GC,

$y_{Kr}^{measured}$ is the concentration of krypton measured by GC, and

y_{Kr}^{purge} is the concentration of krypton in the pure purge gas.

The calculation described in Equation (2) is applied to the resin digestion experimental data and shown in Figure 3-6.
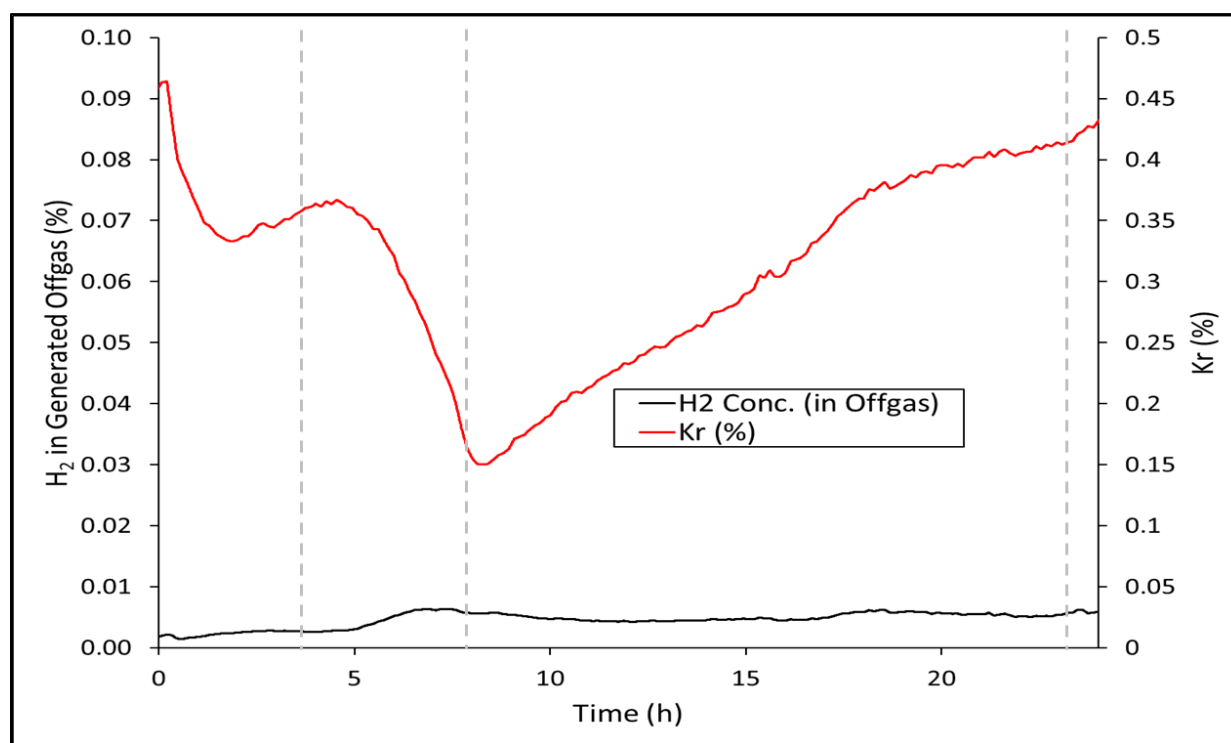
Figure 3-6. Concentration of H₂ (in vol%) Present in Generated Offgas as a Function of Time during Resin Digestion Experiments.

The data shown in Figure 3-6 suggests that the hydrogen concentration of the gases being generated during the permanganate addition, heat-up, and digestion sections of the experiment never exceeds 0.1 vol%. Given that the lower flammability limit of H_2 is 4 vol% in air, it may be concluded that the gases produced during permanganate addition, heat-up, and digestion of Reillex® HPQ resin are incapable of producing a flammable concentration of hydrogen from thermolysis, regardless of purge gas conditions. No such

conclusion can be made for the caustic neutralization stage of the experiment due to the large increase in uncertainty stemming from decreased gas generation rates.

At the conclusion of each digestion experiment, both digestion products were sampled and analyzed for chemical composition. The results of chemical analysis are given in Table 3-1.

Table 3-1. Chemical Analysis of Reillex® HPQ Digestion Products.

Analyte	Digestion Product #1 (304L SS)	Digestion Product #2 (PTFE)
Glycolate (mg/L)	14.6	23.7
Formate (mg/L)	32.7	26.3
Chloride (mg/L)	185	142
Nitrite (mg/L)	< 10.0	< 10.0
Nitrate (mg/L)	55,800	65,000
Sulfate (mg/L)	61.1	77.8
Oxalate (mg/L)	10.4	14.6
Phosphate (mg/L)	< 10.0	< 10.0
Total Inorganic Carbon, TIC (mg/L)	83.2	114
Total Organic Carbon, TOC (mg/L)	229	500
Free Hydroxide (M)	1.07	1.22
Density (g/mL)	1.1435	1.1475

Trace amounts of organic anions (formate and oxalate) were observed in each product and are likely the products of resin digestion. Nitrate (added with nitric acid and formed from digestion) and hydroxide (resulting from caustic neutralization) concentrations seems to have decreased in the first digestion when compared to the concentrations observed in the second digestion product. It is currently unknown if these differences were caused by changes in nitrogen oxide chemistry from corrosion of the stainless steel vessel. TIC measurements of each product are relatively low (83 and 114 mg/L, respectively), which is consistent with acidic treatment before neutralization. TOC measurements between the two experiments are varied (229 mg/L in the first digestion, 500 mg/L in the second digestion). However, this difference is similar to the range of the variations in post-digestion TOC measurements made previously (between 234 and 443 mg/L reported by Kyser in 2009).[1]

3.2 <u>HGR Measurement Results</u>

The HGR experiments described herein were performed using the digestion product from the first digestion of Reillex® HPQ resin. It was hypothesized that the deviations that influenced off gas results in the first digestion would not have a significant impact on liquid-phase chemistry and therefore would have no appreciable impact on HGR experiments. A confirmatory test was performed with the second digestion product at 100 °C using Tank 39 simulant to test this hypothesis (conditions identical to test REI-3). Results from these identical test conditions returned HGRs of 5.0×10^{-7} ft^3 hr^{-1} gal^{-1} for the first digestion product and 5.6×10^{-7} ft^3 hr^{-1} gal^{-1} for the second digestion product. The difference of 11% is within the experimental error of HGR measurement. It is therefore concluded that both digestion products were equivalent for the purposes of HGR testing.

3.2.1 Tank 39 Results

HGR testing in Tank 39 conditions was performed at a digestion product concentration of 17.4 g of product per liter of simulant. This concentration corresponds to the transfer of 159 L of undigested resin to a waste tank containing 284,000 gallons of material following digestion. Figure 3-7 gives the results of HGR testing in Tank 39 simulant at 100 °C with added digestion product as well as the results of a control experiment without added digestion product.
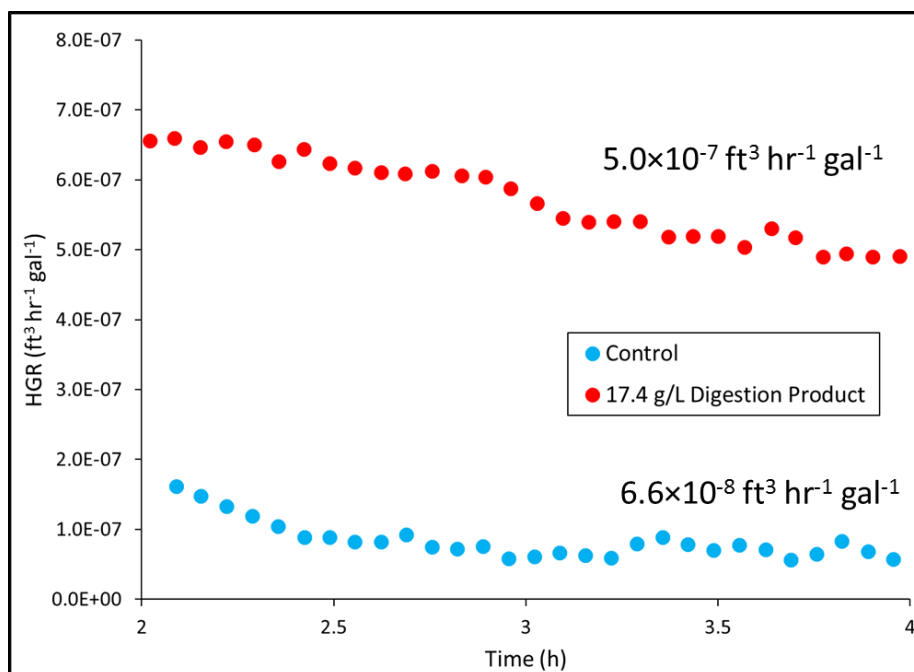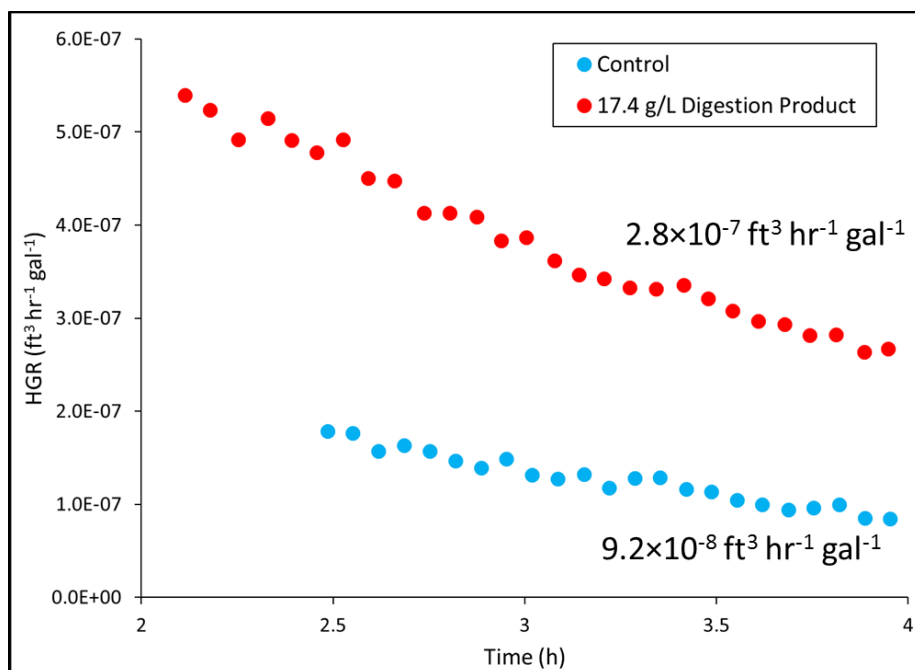
Figure 3-7. HGRs Observed in the Presence and Absence of Digestion Product at 100 °C in Tank 39 Simulant.

Tank 39 simulant at 100 °C with no added digestion product was observed to produce 6.6×10^{-8} ft^3 H$_2$ hr^{-1} gal^{-1} after 4 hours of reaction, likely from thermolysis of organic impurities in simulant ingredients, while the same mixture with 17.4 g of added digestion product produced 5.0×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1} at the same time. Four hours is chosen as the time of quantification based on the anticipated time to equilibrate the reactor vessel headspace (200 mL) at the purge rates employed (3 sccm). These results suggest that the HGR from Reillex® HPQ digestion product thermolysis at 100 °C in Tank 39 conditions is approximately 4.3×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1}. Note that the difference of HGR measurements between the control experiment and the test experiment is reported as the thermolytic contribution from Reillex® HPQ digestion products. This is because contributions to thermolytic HGR from organic impurities in the salt solution simulant are expected to be identical in both the test and control experiments. Note also that a more conservative estimation may be made by using the HGR measured in the presence of added digestion product without subtracting the contributions observed in the control experiment.

The same experiments were performed at 80 °C to examine the effect of temperature on Reillex® HPQ digestion product thermolysis. Figure 3-8 gives the results of these 80 °C tests.

Figure 3-8. HGRs Observed in the Presence and Absence of Digestion Product at 80 °C in Tank 39 Simulant.

The control experiment (no added digestion product) yielded an HGR of 9.2×10^{-8} ft^3 H$_2$ hr^{-1} gal^{-1}, while the experiment with added digestion product yielded an HGR of 2.8×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1}. The difference in these values suggests that the HGR expected from Reillex® HPQ digestion product in Tank 39 conditions at 80 °C would be roughly equal to 1.9×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1}. This value is lower than the value obtained at 100 °C and is therefore consistent with the expected temperature effects on thermolytic HGR. Note that the control experiment at 80 °C returned a higher value for HGR ($\sim9\times10^{-8}$) than was observed for the control experiment at 100 °C ($\sim7\times10^{-8}$). This difference is likely due to increased error of hydrogen measurement near the limit of detection (3×10^{-8}). This impact is small with respect to the larger order-of-magnitude increases seen when adding digestion material. Note also that the HGR appears to be decreasing at 4 hours rather than approaching a stable value. This suggests that the value of 1.9×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1} is conservative with respect to the actual steady-state HGR.

Given the HGR values measured at 100 °C and 80 °C, it is possible to calculate an activation energy for thermolysis of Reillex® HPQ resin digestion product in Tank 39 conditions (assuming Arrhenius behavior). This can be done by calculating the response (or slope) of the natural logarithm of HGR against the inverse of temperature in K. Note that the use of only two points limits the capability of such an expression to account for multiple reaction pathways, as may be experienced in resin digestion products.

Calculation of the activation energy returns a value of 44.7 kJ/mol. This activation energy can then be used to construct an expression for digestion product thermolytic HGR in Tank 39 at any temperature, as shown in Equation (3).

$$HGR_{TK39}\left(T\right) = 4.3\times10^{-7}\, e^{-\frac{44,700}{R}\left(\frac{1}{T}-\frac{1}{373.15}\right)} \tag{3}$$

where,

$HGR_{Tk39}(T)$ is the HGR expected in Tank 39 conditions in ft^3 hr^{-1} gal^{-1},

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

T is the temperature in K.

3.2.2 Tank 32 Results

In addition to Tank 39 testing, HGR experiments were also performed using Tank 32 simulants. Figure 3-9 gives the result of HGR testing with and without added digestion product in Tank 32 simulant at 100 °C.
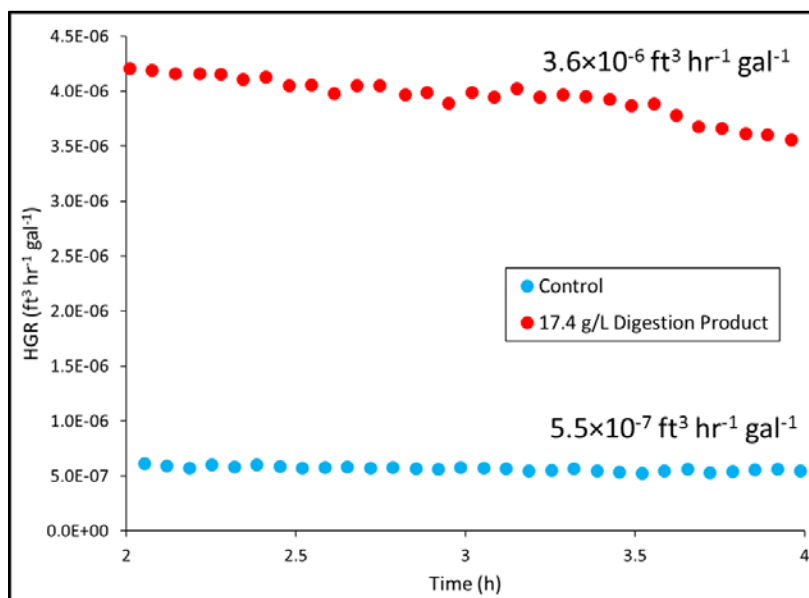
Figure 3-9. HGRs Observed in the Presence and Absence of Digestion Product at 100 °C in Tank 32 Simulant,

The 100 °C Tank 32 control experiment exhibited an HGR of 5.5×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1}, measurably higher than that observed in the 100 °C Tank 39 control experiment (6.6×10^{-8} ft^3 H$_2$ hr^{-1} gal^{-1}). This is consistent with the prediction offered by the Hu thermolytic HGR expression[4] that the increased aluminum loading of Tank 32 would yield a higher HGR than that of Tank 39. The HGR observed from Tank 32 simulant at 100 °C in the presence of digestion product was 3.6×10^{-6} ft^3 H$_2$ hr^{-1} gal^{-1}. The results suggest that the thermolytic HGR due to Reillex® HPQ digestion product at 100 °C in Tank 32 conditions is about 3.0×10^{-6} ft^3 H$_2$ hr^{-1} gal^{-1}.

HGR measurements at 80 °C in Tank 32 conditions exhibited behavior atypical to that generally seen in simulant work and complicates quantification of a bounding value for hydrogen generation. Unlike all other HGR measurements performed in this testing, REI-6 (testing at 80 °C in Tank 32 simulant with added digestion product) exhibited continually increasing hydrogen concentrations (rather than the decreasing concentrations seen in other tests). This behavior is postulated to be due to the slow dissolution of salt components (e.g., aluminum, nitrate, nitrite, etc.) in Tank 32 simulant that affect the thermolysis of digestion product organics at 80 °C. Since HGR is known to increase with these species, delayed dissolution may result in later increases in reaction rate. Figure 3-10 gives the hydrogen concentration of REI-6 as a function of time throughout the duration of the experiment.
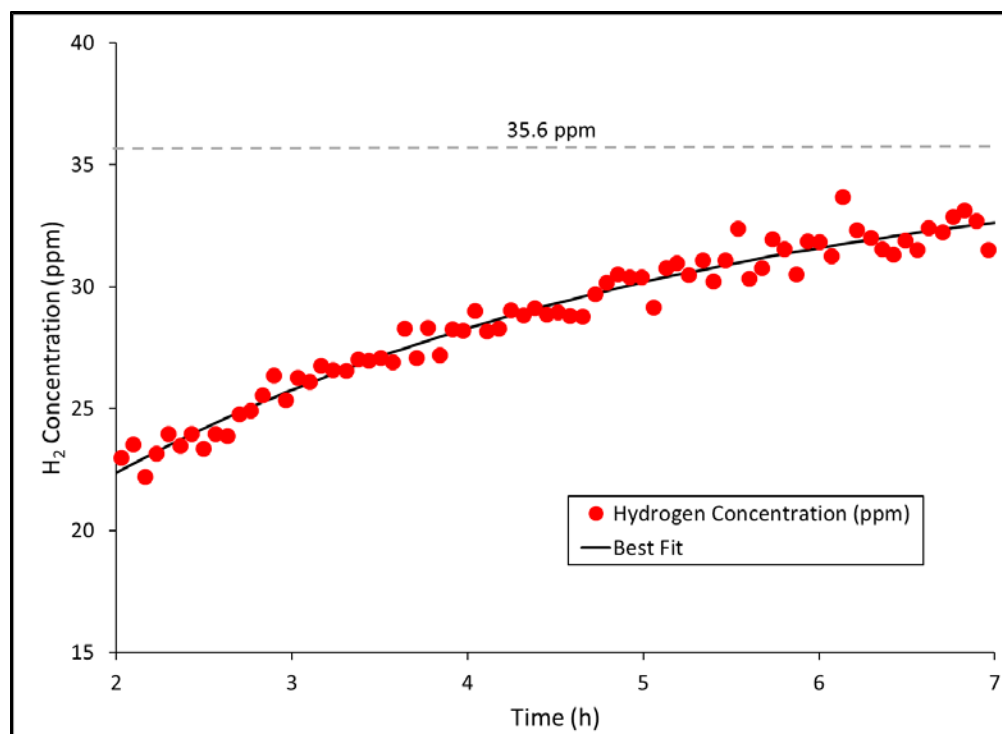
Figure 3-10. Hydrogen Concentration (in ppm) Observed during Test REI-6 (17.4 g of Digestion Product in Tank 32 Simulant at 80 °C).

Although the hydrogen concentration in REI-6 exhibited continual increase for the duration of the test, the rate of change of HGR decreased as a function of time. This behavior may be fit with an exponential curve to predict the final "steady-state" hydrogen concentration. Such a fit, when applied to REI-6 data, suggests a final, steady hydrogen concentration of 35.6 ppm. This concentration of hydrogen corresponds to an HGR value of 9.2×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1}.

A similar procedure can be applied to a control experiment to better estimate the contribution of non-Reillex® HPQ organic impurities to the measured thermolytic HGR at 80 °C in Tank 32 conditions. Figure 3-11 gives the hydrogen concentration measured for REI-8 (control experiment with Tank 32 simulant at 80 °C) as a function of time throughout the duration of the test.
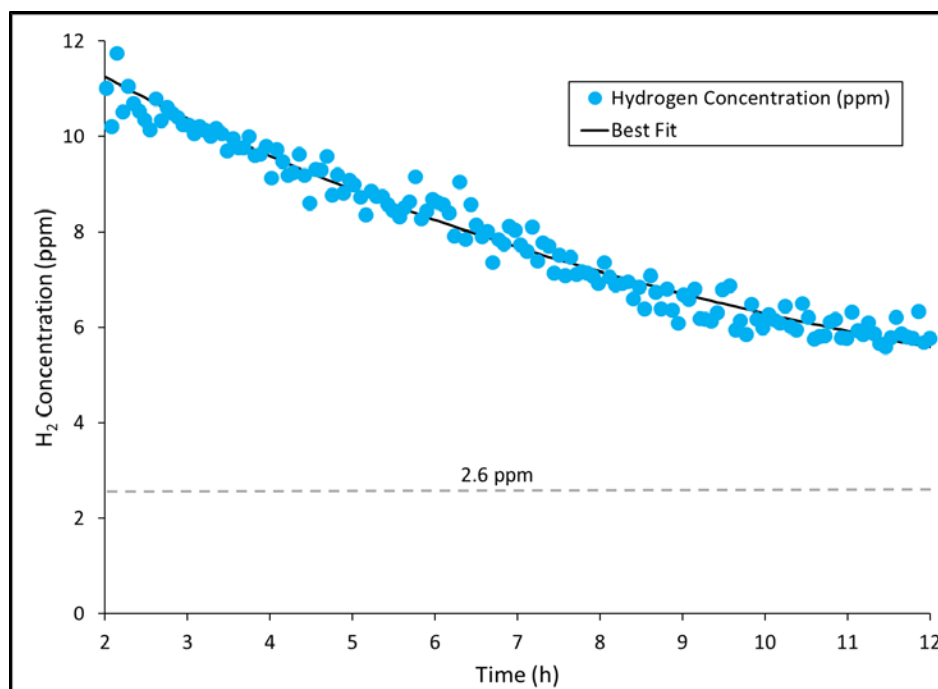
Figure 3-11. Hydrogen Concentration (in ppm) Observed during Test REI-8 (Tank 32 Simulant at 80 °C with no Added Digestion Product).

The data in Figure 3-11, when fit with an exponential decay curve, suggests a final, "steady-state" hydrogen concentration of approximately 2.6 ppm. The concentration corresponds to an HGR value of 6.4×10^{-8} ft^3 H$_2$ hr^{-1} gal^{-1}.

The calculated HGR values for REI-6 and REI-8 suggest an approximate contribution from Reillex® HPQ digestion product to thermolytic HGR at 80 °C in Tank 32 conditions of 8.6×10^{-7} ft^3 H$_2$ hr^{-1} gal^{-1}.

Given the HGR values measured in Tank 32 conditions at 100 °C and 80 °C (reported above), it is possible to calculate an activation energy for thermolysis of Reillex® HPQ resin digestion product at conditions that are representative of the highest hydrogen producing tanks in CSTF (assuming Arrhenius behavior). Note again that the use of two points to calculate an activation energy precludes the evaluation of effects from multiple reaction pathways, as may be expected in resin digestion product-containing mixtures.

Calculation of this value returns an activation energy of 68.4 kJ/mol. This activation energy can then be used to construct an expression for digestion product thermolytic HGR in Tank 32 (which may be extended to provide an upper bound to other tanks) at any temperature, as shown in Equation (4).[a]
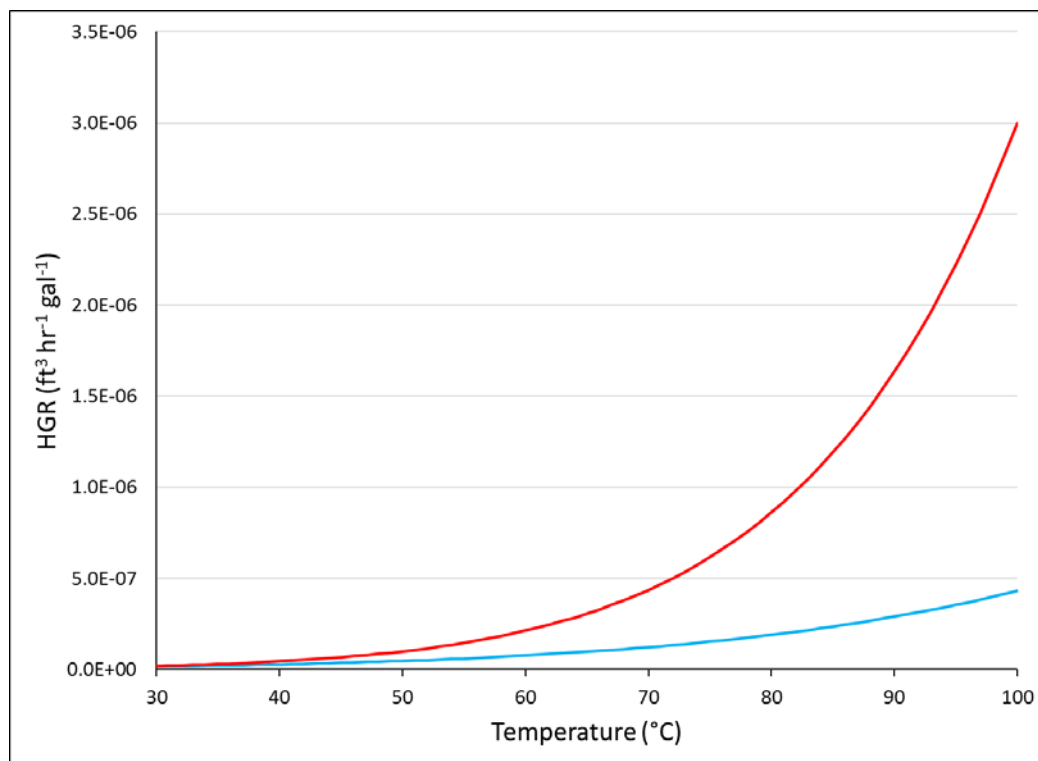
$$HGR_{Tk\,32}\left(T\right) = 3.0 \times 10^{-6}\, e^{-\frac{68,400}{R}\left(\frac{1}{T} - \frac{1}{373.15}\right)} \tag{4}$$

where,

   $HGR_{Tk\,32}\left(T\right)$ is the HGR expected at bounding Tank 32 conditions in ft^3 hr^{-1} gal^{-1}.

The HGRs predicted by Equations (3) and (4) are given as a function of temperature in Figure 3-12.

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[a] This expression will be used to evaluate hydrogen flammability in X-CLC-A-00112 by T. Smith (currently unpublished).

Figure 3-12. Predicted HGRs from Tank 39 (blue) and Tank 32 (red) Data as a Function of Temperature.

As is shown, the HGRs predicted from the Tank 32 expression exceed that expected from Tank 39 at all temperatures of interest.

3.2.3 HPT-5 Results

Test REI-9 was performed to simulate conditions expected in HPT-5 after a transfer of digested resin material from H-Canyon. During this test, 400 mL of digestion product were added to 600 mL of Tank 39 simulant. This represents a transfer of 1,110 gallons of digestion product (42 L of resin $\times$ 100 L of digested material/L resin) to a heel of 1,670 gallons in HPT-5. Note that the assumption of 42 L of resin is conservative in organic concentration with respect to the planned transfers of 21 L. This condition is expected to be a bounding concentration of organic material for the planned discharge since the discharge will likely include added flush liquid and may occur at a larger heel volume. The temperature employed in REI-9 was 55 °C, 5 °C higher than the solution temperature prior to transfer from H-Canyon to HPT-5. This temperature is also viewed as a bounding condition.

Test REI-9 yielded HGR results below the established hydrogen limit of detection for the apparatus (3×10^{-8} ft^3 hr^{-1} gal^{-1}) at the tested conditions (i.e., 1 L of tested material, 3 sccm purge rate, 1 ppm H_2 by GC). Therefore, the HGR value for REI-9 is reported as 3×10^{-8} ft^3 hr^{-1} gal^{-1} to provide a conservative estimate of HGR for HPT-5 conditions.

4.0 Conclusions

The following conclusions concerning Reillex® HPQ resin digestion can be drawn from these test results.

- Conditions experienced during the acidic digestion of Reillex® HPQ resin are corrosive and may cause pitting in surfaces composed of metal.
- Hydrogen concentrations during digestion are expected to be less than 40 ppm during regular processing in H Canyon. 40 ppm H_2 was observed during testing with 163x lower purge rates and 32x longer headspace residence times.
- Hydrogen generation rates during digestion and neutralization are limited to approximately 2.7×10^{-5} L H_2 L^{-1} hr^{-1}.
- Carbon dioxide and oxygen are the primary gaseous products from digestion with 40 vol% O_2 and 30 vol% CO_2 observed at testing with lower purge rates.
- The amount of hydrogen produced during permanganate addition, heat-up, and digestion relative to other gases is too low to generate a flammable concentration of hydrogen, regardless of purge conditions.

The following conclusions concerning HGRs of Reillex® HPQ digestion products in CSTF conditions can be drawn from these test results.

- Hydrogen generation rates in HPT-5 are expected to be less than 3.0×10^{-8} ft^3 H_2 hr^{-1} gal^{-1}.
- Tank 39 testing at conservatively high TOC concentrations (i.e., approximately 4x that expected in the proposed future discharge) yielded an HGR of 4.3×10^{-7} ft^3 H_2 hr^{-1} gal^{-1} at 100 °C and 1.9×10^{-7} ft^3 H_2 hr^{-1} gal^{-1} at 80 °C.
- Tank 32 testing at conservatively high TOC concentrations (i.e., approximately 4x that expected in the proposed future discharge) yielded an HGR of 3.0×10^{-6} ft^3 H_2 hr^{-1} gal^{-1} at 100 °C and 8.6×10^{-7} ft^3 H_2 hr^{-1} gal^{-1} at 80 °C. This is expected to represent and bound the highest hydrogen-producing conditions in the CSTF due to the high aluminum and the importance of those species predicted in literature.
- Results from testing with Reillex® HPQ digestion product in Tank 39 simulant between 80 °C and 100 °C can be described by the following expression.

$$HGR_{TK39}(T) = 4.3 \times 10^{-7} e^{-\frac{44,700}{R}\left(\frac{1}{T} - \frac{1}{373.15}\right)}$$

- Results from testing with Reillex® HPQ digestion product in Tank 32 simulant between 80 °C and 100 °C can be described by the following expression (this is expected to be representative of the highest hydrogen producing tanks in the CSTF).

$$HGR_{Tk32}(T) = 3.0 \times 10^{-6} e^{-\frac{68,400}{R}\left(\frac{1}{T} - \frac{1}{373.15}\right)}$$

5.0 Recommendations

The following recommendations are made considering the observations and results generated from the testing.

- The risk of corrosion to vessel integrity should be assessed for process vessels used in the digestion of Reillex® HPQ resin in H-Canyon.
- The contribution of corrosion to hydrogen generation during Reillex® HPQ digestion in H-Canyon stainless steel vessels may warrant further investigation.
- Additional HGR testing with Reillex® HPQ digestion product can better elucidate the destruction rates of digestion resin material in tank conditions for extended durations in CSTF. This testing could be performed by evaluating the HGR from Reillex® HPQ digestion product in simulant

solutions at varied durations of dissolution (0-30 days). Such testing would allow for reduction of conservative estimates used in the analysis of the data presented in this report.

- Digestion experiments with polystyrene-based resins (such as IONAC A-641) are in progress and should be completed by SRNL to assess the risk of hydrogen formation from the degradation products of such resins.

6.0 References

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