Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

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SRNL-STI-2018-00470

Measurements of Hydrogen Generation Rates using a Sealed Reactor System - 19428

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ABSTRACT

Sealed reactor tests were performed to measure the hydrogen generation rate (HGR) from stored radioactive waste at the Savannah River Site. HGR may be very low, on the order of 7.5 x 10^{-13} (m^3/h)/L [that is, cubic meters of H_2 generated per hour per liter of radioactive liquid waste, or 10^{-10} (ft^3/h)/gal]. Because the estimated HGR limit of detection for an open, continuous flow, system is approximately 7.5 x 10^{-10} (m^3/h)/L [or 10^{-7} (ft^3/h)/gal], a more sensitive method was needed. By accumulating generated gasses in a sealed system without a continuous purge gas, the resulting concentrations can increase the sensitivity of measurement, which is based on time of heating.

In 2017, Savannah River Remediation declared a Potential Inadequacy in the Safety Analysis related to the potential thermal decomposition of organics that generate hydrogen in each of three Liquid Waste facilities: Concentration, Storage and Transfer Facility, Saltstone Production Facility, and the Defense Waste Processing Facility. The research for this study concerns low activity waste of Tank 50, which feeds the Saltstone Production Facility. This study evaluated the impact of organics including formate on the generation of H_2.

Samples of SRS Tank 50 waste, which is a nominal 5 molar sodium salt solution, were sealed in stainless steel reactors and held at varying temperatures, e.g., 50°C, 75°C, 100°C, and 120°C, to determine if organic compounds are decomposing into H_2. The experiments included trace solids used to stabilize waste in grout, e.g., grout-premix and Blast Furnace Slag, to determine if any solid phase reactions are present, which would accelerate or inhibit the generation of H_2 at these temperatures.

This paper describes the sealed reactors designed and constructed at Savannah River National Laboratory and the radioactive tests that were performed to measure HGR in both oxic and anoxic atmospheres. The shakedown tests showed the sealed reactors to be leak tight and hydrogen concentrations from calibrated standards could be accurately measured. Previous simulant tests helped to perfect the test methods and better design the radioactive tests. The radioactive results showed that the rate of hydrogen generated from Tank 50 waste, over a range of temperatures from 30°C up to 120°C, is bounded by an empirical relation (Hu Equation) that can be used to approximate HGRs in Tank 50 radioactive waste.

INTRODUCTION

In February 2017, Savannah River Remediation (SRR) declared a Potential Inadequacy in the Safety Analysis (PISA) in several Liquid Waste facilities. The PISA relate to how organics can impact the radiolytic and thermolytic production of H_2, which is a flammable gas. Parallel studies are evaluating the impact of organics on the generation of flammable gases in the vapor space within Savannah River Site (SRS) High-Level Waste (HLW) waste tanks and evaporator systems [1-6]. The impact of organics on radiolysis in SRS Defense Waste Processing Facility (DWPF) is currently addressed using a combination of previous testing and revised calculation methods [7-8]. This paper focuses on testing for Tank 50 waste that was recently completed [9].

Radioactive samples were used for the testing, allowing for a measurement of thermolytic Hydrogen Generation Rate (HGR) with the mixture of organics present in the radioactive waste. Studies for Hanford Site waste tanks indicate chemical decomposition by radiolysis and/or thermolysis as important

mechanisms for the generation of H_2 in the Hanford Site HLW system. There are significant differences in the composition of waste between the Hanford Site and SRS. Because of those differences and no prior evaluation of thermolysis occurring within the SRS waste tanks, the testing described in this paper intended to determine the thermolytic contribution to flammable gases in the Tank 50 matrix. Testing included the addition of pre-mix grout materials, which are comprised of Blast Furnace Slag (BFS), Cement, and Fly Ash to determine if any solid phase reactions are present which would accelerate or inhibit the generation of H_2 at the temperatures of interest.

The test required that the H_2 Limit of Detection (LOD) be as low as reasonably achievable to allow measurement of the predicted low HGR. A Sealed Reactor System was designed because the HGR LOD for an open, continuous flow system, is approximately 7.48 x 10^{-10} (m^3/h)/L [or 1 x 10^{-7} (ft^3/h)/gal]. Quantification of HGR below this limit, like the estimated rate of 2.2 x 10^{-11} (m^3/h)/L [or 3 x 10^{-9} (ft^3/h)/gal] for Tank 50 waste; therefore, requires an alternate measurement system. By accumulating generated gasses in a sealed, closed, system and avoiding use of a continuous purge gas, the H_2 concentration increases thus improving the sensitivity of measurement. Design of a sealed system implies obtaining no or very low permeability and was based in part on successful past designs [10-12]. The selection of sealing surfaces and material is important to minimize the loss of generated gasses. The sealed system allows placing a measured sample mass inside a robust vessel of known volume. Testing held the apparatus at temperature for a measured duration and stirred continuously using a stirrer/hotplate. At the end of a selected period, the headspace of the reactors was sampled, utilizing a gas chromatograph (GC) to measure the H_2. From the concentration of H_2, and elapsed time, one determines the average thermolytic HGR for the sample over the test period. Tests were performed at multiple temperatures to calculate an activation energy of the thermolytic HGR assuming a first-order Arrhenius equation [13].

EXPERIMENTAL EQUIPMENT

Besides the test solutions and gases, the principal part of the experimental setup was the sealed reactor to contain the evolution of H_2 from a test solution. The supporting equipment included heating and stirring plates, measurement and data acquisition system (DAS), gas and liquid sampling equipment, safety equipment, e.g., over-temperature control.

Sealed Reactors

Eight reactors were constructed of 304 stainless steel, which is impermeable to H_2 below 150°C [14]; more so than 316 SS [15-16]. Only five reactors were used because per procedural requirements, one reactor was subjected to burst testing to establish the maximum allowable operating pressure. It held leak tight until 19,406 kPa [2800 psig] when the large conflat seal began to slowly leak. The remaining seven reactors, equipped with purging and sample valves, but without the pressure transducers, were leaked check with helium to 1136 kPa [or 150 psig]. They were shown to have a leak rate of less than 10^{-9} cc/sec He, which implies a lower rate for H_2 due to being a larger molecule. Figure 1 shows a schematic of the finished reactor with two control valves installed, a pressure transducer, and the liquid introduction and sampling port sealed. Of the seven reactors only five used so that two could stay clean in the event of other testing or as a backup of those in radioactive service.

Reactor Preparation and Volume Calibration

The reactors were built for sealed operation and the first steps needed before testing was to prepare the vessels so that the vessels themselves would not lead significant uncertainty in the H_2 results. They were cleaned, passivated in 20 vol% nitric acid (4.8 M), and baked at 315°C for > 4 hours under vacuum to remove residual H_2 from the steel. On completion of reactor preparations all the reactors were checked to confirm they met ASME B31.3 code specifications for Pressure Protection.

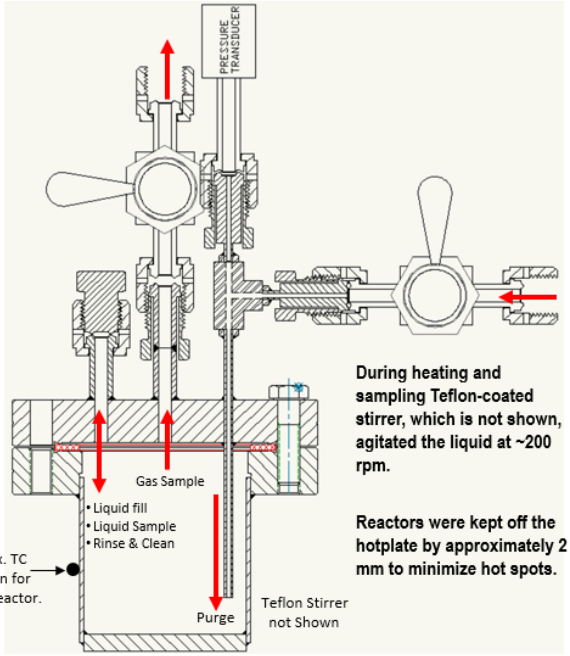

Figure 1. Sealed Reactor

Figure 2 shows a reactor during several stages of its preparation, including after machining and welding. Figure 2(a) show the reactor before being cleaning (to remove organics), after passivating in nitric acid (to build an oxide coat to minimize permeability), then baking in an inert atmosphere (to remove any H_2 within the steel), and pressure testing (to determine sealability). Figure 2(b) shows one vessel fully assembled and ready for a pressure test.

(a) (b)

Figure 2. (a) shows the top and bottom inside of a reactor and the conflat seal, (b) shows the closed reactor ready for testing.

After the preparation, each reactor was calibrated for its internal volume with water so the liquid added and gas head space could be accurately known for testing. The reactors were design to have 200 mL of internal volume they were closer to 195 mL when measured and a Teflon-coated magnetic stirrer was added to each before being sealed. The volume of each 9.52-mm diameter by 381-mm long stirrer is 2.715 mL. The head space volume is reduced by the stirrer volume when calculating the HGR.

Overall Sealed Reactor System

The basic arrangement for all tests was the same. To fill a reactor, it is removed from its stirrer/hotplate, then the liquid port is slowly opened. A funnel is inserted after a custom-made fitting is installed to secure the funnel and prevent leaks. Of the 5 reactors, three, i.e., HGV-2, 3, and 4 were placed on a single large stirrer/hotplate for one temperature. The remaining reactors were placed on two individual stirrer/hotplates, i.e., HGV-5 and HGV-6, to obtain different temperatures and heating periods.
Once the reactors were filled with test solution and purged with a test gas, they were fully connected to the DAS and insulated to minimize heat loss. Because the waste was radioactive the equipment was in a radioactive hood shown in Figure 3, which shows the sealed reactors enclosed with insulation. The GC is visible to the left.

Figure 3. The overall sealed reactor setup for radioactive tests with the GC to the left.

Test Operation

The operation for the radioactive tests is summarized below:

1. Start with clean reactors.
2. Fill with test solution and spike material.
3. Seal reactors, purge with either nitrogen or hydrogen-free air, as required, then pressurize to 239 kPa [or 20 psig].
4. Heat reactors to target temperature and mix solution with Teflon magnetic stirrer.
5. Maintain at the target temperature for required period.
6. De-energize reactors and allow to cool overnight.
7. Sample for H_2 and then pull liquid sample for analyses.

Pressure

To maintain the leak integrity of the vessel, a specific VCR® compatible pressure transducer was chosen to measure 0-1136 kP [or 0-150 psig] pressure. The chosen model was the Setra® 225G-150P-G-D4-11-06. It had all 316L SS wetted parts, with an output of 4-20 mADC. It provided a less than $1x10^{-9}$ cc/sec leak rate. The stated accuracy was ±0.25% Full Scale, with a temperature compensated range of -9 to 66°C.

Gas Flow

The purge gas flow was measured with a rotameter was used with a range of 51.8 to 517.8 sccm of air. Its stated accuracy was ± 25 sccm. Because it is a rotameter, the value indicated on the scale must be corrected for pressure and temperature in the metering tube. Since it was calibrated at atmospheric conditions, and its use in the lab required positive pressure in the tubing, i.e., pressure losses downstream of rotameter always caused greater than atmospheric pressure in the metering tube, then the indicated mass flow rate value was always conservative. That is, the value indicated was always less than the actual mass flow rate. This was deemed acceptable, as the rotameter was used to meet the minimum number of volume changes in the head space required by the procedure. Volume changes were determined by flow rate multiplied by the time interval, indicating volume of gas displaced in head space as a multiple of head space volumes.

GC - H_2 Measurement

In the sealed system testing, the reactor vapor space was filled with either nitrogen or a hydrogen-free air mixture of 20% oxygen, 0.5% krypton, balance nitrogen gas. The krypton was a tracer to periodically check the GC operation. Nitrogen was initially used for some testing in cases where high H_2 generation was postulated. The remaining tests used the H_2-free mixture of oxygen/krypton/nitrogen with no detectible helium, which can interfere with low level H_2 quantification. Both helium and H_2 in air can be detected with the micro GC.

Each reactor vapor space was sampled and characterized using an Agilent series 3000 micro GC. The GC has an on-board sample pump that can draw gas samples with pressures as low as atmospheric. For the sealed reactor tests the vapor/head space was filled with gas up to 239 kPa [or 20 psig] to allow for multiple gas samples per reactor per test. The GC was configured with a Molsieve 5A column, which can be used to collect data related to helium, H_2, oxygen, nitrogen, krypton, and methane. However, the instrument was optimized to quantify low quantities of H_2, as this was the primary flammable gas of interest.

When little or no H_2 generation was expected, then the GC was calibrated with a nominal 10 ppm H_2, 20% oxygen, balance nitrogen gas standard. Due to the high sensitivity settings to quantify H_2, concurrent quantification of oxygen and nitrogen was not possible. From the calibrations, the LOD for H_2 was determined to be 1 ppm, but the limit of quantification (LOQ) was 3 ppm.

Radioactive Tank 50 Waste Used

Approximately two liters of the Tank 50 sample, obtained in October of 2017, were used for radioactive testing. The sample was taken at a height of 1.7 m from the tank bottom after the tank had been agitated using a single slurry pump for ~ 4.4 hours on Wednesday, October 18, 2017. Using a mixed sample obtained below the surface reduces the potential of collecting a surface layer of immiscible organic from the tank.

Spike Material

TABLE I highlights the materials used to spike the test solutions to demonstrate the effect of those materials on the HGR. The spike materials are pre-mix grout solids and Blast Furnace Slag (BFS) solids. BFS is one of the components of the pre-mix material, i.e., BFS, Fly Ash, and Cement, which is used to make grout for Saltstone at SRS. BFS was used separately to demonstrate if it alone with accelerate the production of H_2.

TABLE I. Spike Materials for Both Simulant and Radioactive Tests

Organic Spike Material	Added Reagent	TOC Contribution mg/L	Target for Test mg	Approx. in Test mg
Blast Furnace Slag	1000 mg/L BFS	Trace [a]	Trace [a]	Trace [a]
Grout-premix	2222 mg/L grout-premix	Trace [a]	Trace [a]	Trace [a]

[a] The organic content of these additions was not measured.

RESULTS AND DISCUSSION

Initially the radioactive testing only included the use of an oxic head space; however, after evaluating the safety documentation it was necessary to include an initial test with an anoxic head space to quantify the H_2 produce to demonstrate that the lower flammability level (LFL) would not be exceeded. When the anoxic test was added a final test was added to repeat some important tests over a longer period (6 days) then the 16 hours that most of the radioactive tests utilized.

To reiterate, the radioactive tests were limited to 5 sealed reactors because two were held in reserve in case non-radioactive testing would be necessary. Of the seven-planned radioactive tests, the first five only used three reactors because two reactors were used for a sixth, long-term, test, i.e., 26 days, that continued while all other tests were ongoing. To have a better comparison for the added spikes, the first five tests had the same operating parameters except the temperature, which ranged from 120°C down to 50°C. When the long-term test was completed a final, seventh, test was performed with all five reactors at the important temperature point of 75°C for the SRS facility. Before discussing the H_2 generation results, the analytical data from all the liquid samples pulled from the reactors after each test are discussed.

Radioactive Tank 50 Waste Analytical Data

TABLE II shows the analytical results from the radioactive waste samples. The most distinctive aspect of the results is the absence of trend in the chemical make-up of the waste despite the variation in testing parameters be it, spike material: none, BFS, or grout-premix, temperature: 50°C to 120°C, duration: 16 hours to 6 days, etc. The highest silicon concentration occurred at a lower temperature of 50°C for BFS and grout-premix, additives which contain silicon, as may be expected since higher temperatures promote silicate formation. However, the spread in the data indicates no statistically significant claim for that suspected behavior. In summary, none of the temperatures, spikes, or durations had a statistically discernible impact of the chemical make-up of the waste.

TABLE II. Analytical Data From Each Reactor After Each Test

Test #	Reactor	Tank 50H Waste	(A)noxic	Target	TIC	TOC	Free OH	Oxalate	Nitrite	Nitrate	Sulfate	Formate	Al	Cr	K	Na	Si
New	#	Spike Type	(O)xic	Temp./Dur.	mg/L	mg/L	M	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	HGV-2	Control - None	A	120°C / 16 h	3180	268	2.33	473	27800	117000	4590	241	4270	43.5	773	91500	85.3
1	HGV-3	BFS	A	120°C / 16 h	3200	268	1.98	467	26500	111000	4440	235	3950	34.6	653	87300	62
1	HGV-4	Grout	A	120°C / 16 h	3220	268	2	480	27400	115000	4510	241	3940	24.5	780	88100	74.3
2	HGV-2	Control - None	O	120°C / 16 h	3140	252	2.03	470	27400	115000	4440	235	4380	98.4	725	87300	57.6
2	HGV-3	BFS	O	120°C / 16 h	3140	252	1.93	492	28300	119000	4600	247	4300	68.7	739	88000	57.7
3	HGV-4	Grout	O	120°C / 16 h	3100	252	1.92	439	25100	105000	4040	220	4170	86.3	775	87400	56.5
3	HGV-2	Control - None	O	120°C / 16 h	3060	267	1.92	615	26600	111000	4360	235	4490	62.2	450	123000	61.1
3	HGV-3	BFS	O	120°C / 16 h	3090	254	1.98	585	26400	110000	4370	225	4090	55.8	503	122000	60.5
3	HGV-4	Grout	O	120°C / 16 h	3140	262	1.97	602	26700	111000	4330	231	4230	55.1	559	123000	60.7
4	HGV-2	Control - None	O	75°C / 16 h	3060	248	1.96	895	26200	110000	4220	190	4760	52.9	434	123000	118
4	HGV-3	BFS	O	75°C / 16 h	3060	248	1.95	557	26300	109000	4210	216	4400	49.3	434	114000	116
4	HGV-4	Grout	O	75°C / 16 h	3060	248	1.94	542	25900	107000	4100	212	4320	53	520	116000	128
5	HGV-2	Control - None	O	50°C / 16 h	3370	158	1.89	513	27200	123000	4360	218	4430	49.7	501	116000	77.1
5	HGV-3	BFS	O	50°C / 16 h	3370	142	1.83	515	27100	122000	4320	217	4460	49.8	563	116000	155
5	HGV-4	Grout	O	50°C / 16 h	3360	142	1.91	519	26800	120000	4250	217	4520	50.4	618	118000	159
6	HGV-5	Control - None	O	35°C / 26 days	3390	251	1.93	245	27500	116000	4540	234	4670	57.2	437	125000	31.6
6	HGV-6	Control - None	O	35°C / 26 days	3410	254	1.87	233	27000	114000	4380	234	4350	53.2	432	119000	27.9
7	HGV-2	BFS	O	75°C / 6 days	3330	140	1.89	521	27900	125000	4370	219	4580	68.7	473	126000	35.1
7	HGV-3	Grout	O	75°C / 6 days	3370	143	1.84	524	27400	117000	4370	219	4290	57.4	511	122000	85.3
7	HGV-4	Control - None	O	75°C / 6 days	3380	146	1.89	524	27400	122000	4250	218	4460	64.7	511	118000	30.7
7	HGV-5	BFS	O	75°C / 6 days	3380	142	1.84	523	27600	123000	4290	223	4390	60.7	519	116000	30.5
7	HGV-6	Grout	O	75°C / 6 days	3390	142	1.86	522	26400	121000	4270	219	4170	57.4	521	125000	30.5
(1) NA - Not Applicable. TOC was changed as part of the testing.				Average =	3236	NA(5)	1.9	512	26950	115591	4346	225	4346	57	565	111436	73
				Stand. Dev =	137	NA	0.1	126	743	5787	142	13	207	15	121	14915	40
				%rsd =	4	NA	5.3	25	3	5	3	6	5	27	22	13	55
				Minimum =	3060	140	1.83	233	25100	105000	4040	190	3940	24.5	432	87300	27.9
				Maximum =	3410	268	2.33	895	28300	125000	4600	247	4760	98.4	780	126000	159

Overall Tank 50 Test Results

The data are graphically depicted in Figure 4. As the uncertainty analysis determined, the addition of solids (i.e., BGS or grout-premix) increases the H_2 production. Within statistical uncertainty (at 95% confidence) there is no discernible difference between the increase due to BGS or grout-premix. This can be better seen in the HGR results shown in Figure 5. To illustrate the impact of the ±7 %RSD uncertainty, discussed later, the error bars are shown on both graphs, but only for the no-spike (Oxic) data so that all the data can be clearly seen. Note that for the HGR calculation, the sampling initial pressure (usually close to 239 kPa [or 20 psig]), and temperature (usually between 22°C to 28°C) were adjusted to 101.35 kPa (14.7 psia) and 25°C.

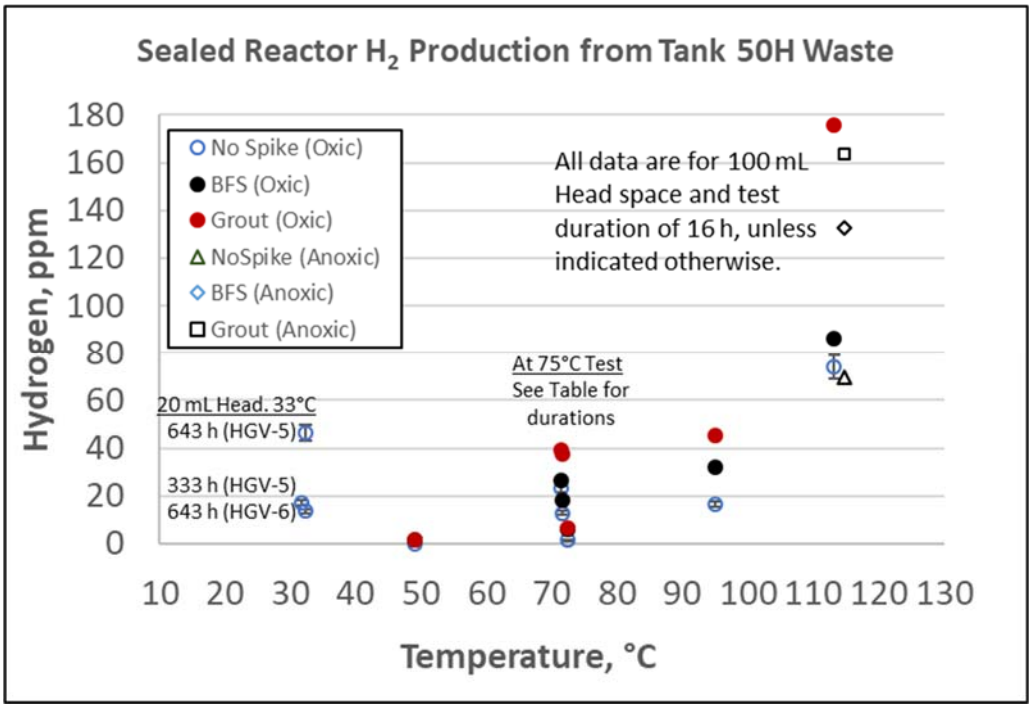

Figure 4. H_2 measurements from radioactive-waste Tests 1-7

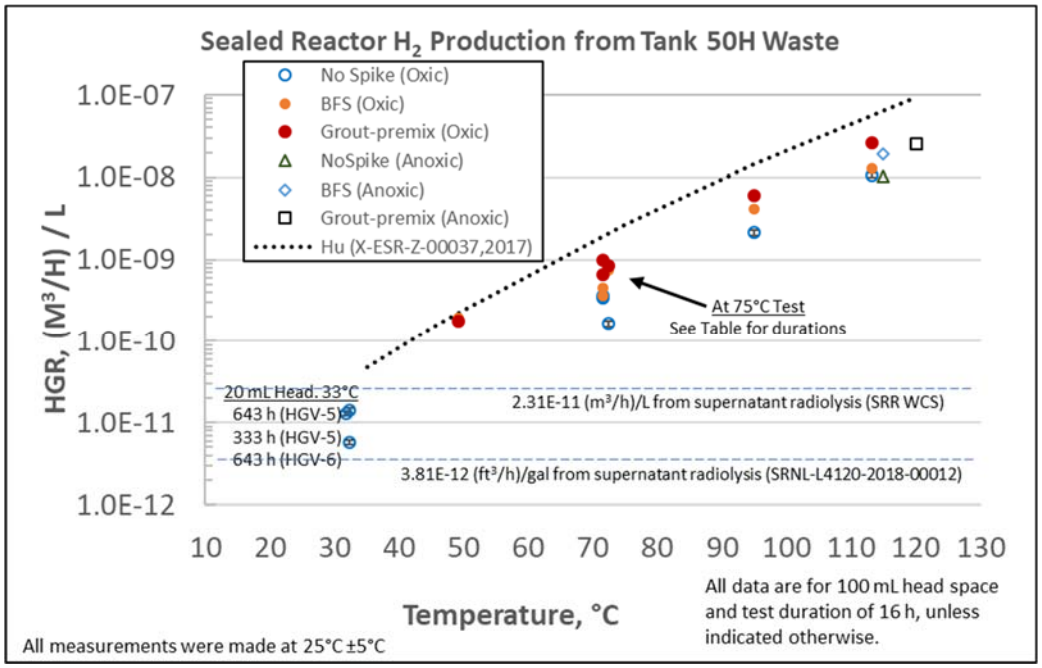

Figure 5. HGR measurements from radioactive-waste Test 1-7

From these 7 tests, the difference in the rate of production of H_2 for an overlaying oxic or anoxic atmosphere is statistically insignificant. Figure 5 shows that the HGR production is exponential with temperature and appears linear on a logarithmic scale. When considering the presence of BFS and grout-premix, the HGR increases, with the grout-premix test at 115°C having the largest rate of 7.48 x 10^{-9} (m^3/h)/L [or 1.0 x 10^{-6} (ft^3/h)/gal]. The statistical analysis performed indicates no significant discernible difference in rates between BFS and grout-premix. Furthermore, all the experimental HGR results are

bounded by the calculated HGR based on the Hu equation adjusted to a 25°C [17]. As was previously done (see Equation 3 of reference [18]), the TOC and Al values from the radioactive Tank 50 characterization were input into the Hu equation and the resulting HGR was calculated at various temperatures in units of mol/day/kg. These results were then converted to units of $(m^3/h)/L$ at 25°C (the nominal sampling temperature for these experimental tests). The TOC value used 273 mg/L carbon which gives a TOC of 2.21 x 10^{-2} wt% using a density of 1.237 g/mL; the Al value used is 5,040 mg/L which gives an Al of 0.407 wt% using a density of 1.237 g/mL.

Also shown on Figure 5 is the result for the long-term test that lasted over 26 days (643 hours). The temperature was held at 33°C to obtain a radiolytic result and the Tank 50 Waste averaged HGR of 9.87 x 10^{-12} $(m^3/h)/L$ [or 1.32 x 10^{-9} $(ft^3/h)/gal$]. This HGR result is significantly below the estimated SRR Waste Characterization System radiolytic values of 2.31 x 10^{-11} $(m^3/h)/L$ [or 3.09 x 10^{-9} $(ft^3/h)/gal$] for Tank 50 supernatant and 3.80 x 10^{-11} $(m^3/h)/L$ [or 5.08 x 10^{-9} $(ft^3/h)/gal$] for Tank 50 slurry, which means the estimates are conservative. Furthermore, this HGR result matches, within uncertainty, the Monte Carlo n-Particle Code [19] estimate of radiolytic rate of 3.82 x 10^{-11} $(m^3/h)/L$ [or 5.1 x 10^{-10} $(ft^3/h)/gal$] from a 180-mL batch of waste, as used for this 26-day test.

Another way of looking at the HGR data is by using the Arrhenius methodology to obtain the activation energy, E. Equation (1) is referred to as the Arrhenius equation [13]

$$k = A \cdot e^{-\frac{E}{RT}} \qquad \text{(Eq. 1)}$$

where k = Rate Constant, i.e., HGR, A = frequency factor constant, E = Activation Energy, R = Universal Gas Constant, and T = Absolute Temperature.

In logarithmic space Equation (1) can be written as:

$$\ln(HGR) = -\frac{E}{RT} + \ln(A) \qquad \text{(Eq. 2)}$$

Thus, plotting the log of HGR versus the reciprocal of temperature provides a slope of -E/R and thereby the activation energy, *E,* can be determined from the slope. When putting the HGR data into the form of Equation (2) the results are shown in Figure 6.

Only an average slope is shown in in Figure 6, because of the three sets of data (BFS spike, grout-premix spike, and no spike), the slopes are indistinguishable when considering a 95% confidence level. Note that this average slope excluded data from Test 6, which was done at 33°C to measure the radiolytic HGR. That is, the slope of the line shown in Figure 6 is for the thermolytic HGR as well as the value of activation energy shown, i.e., 83 kJ/mol. Furthermore, a linear slope on an Arrhenius plot implies the reaction is not complex, in this case, the release of H_2 from the liquid waste. However, while the slopes are the same for results of the individual spike data, note that all the no-spike data fall <u>below</u> the other two sets of spiked data. The statistics indicate that while the slope of the no-spike data is not different from that of BFS or grout-premix many of the intercepts of those data, i.e., ln[A], are different. This implies that the addition of either BFS or grout-premix does increase H_2 production.

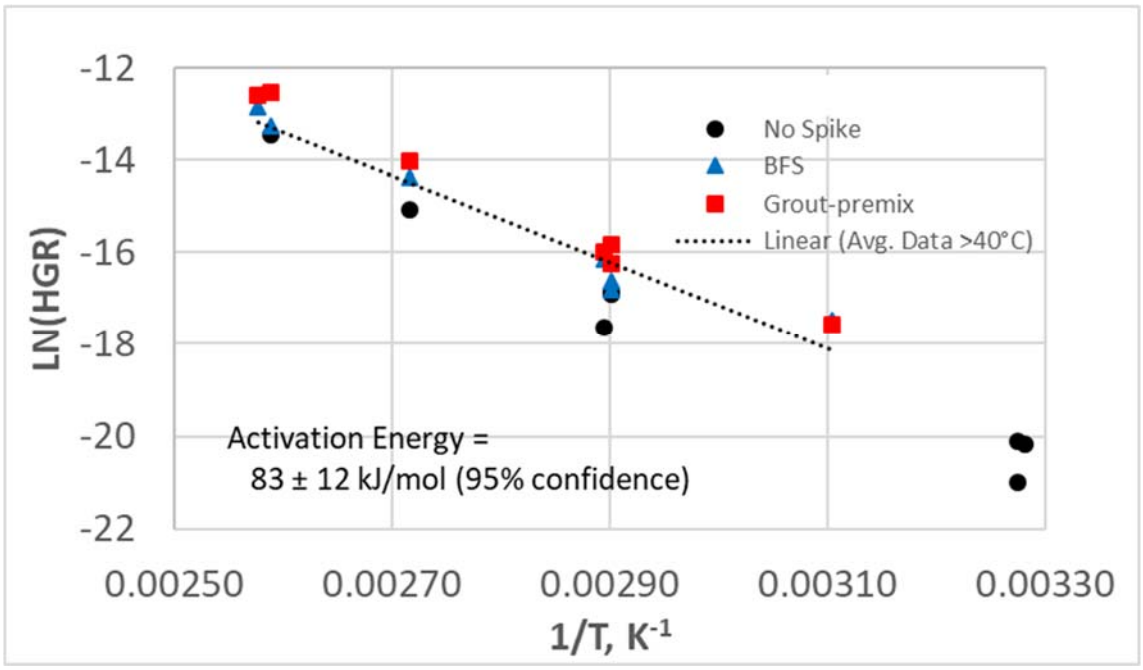

Figure 6. HGR measurements from radioactive-waste Test 1-7

H_2 Generation from Oxic Versus Anoxic Atmospheres

A single radioactive test, Test 1, using an anoxic head space implies there is a difference in H_2 generation when waste contains BFS and grout-premix. However, the data are challenging to interpret. They show that between the grout-premix and no-Spike results there was *no significant difference* in the HGR; however, there *was a significant difference* between both BFS and grout-premix HGRs, and the BFS and No-Spike HGRs. Because there was only a single test performed with an anoxic atmosphere, then that test would have to be repeated to confirm the results.

Measurement Uncertainties

An uncertainty analyses for the measurements and calculations made for the radioactive tests. Besides the analytical measurements made on liquid samples, the principal measurements were temperature, pressure, reactor waste volume, reactor head space volume, masses added, and time. The uncertainty of the principal calculation of HGR ranged from 3 to 10 %RSD, for a confidence level of 95%. The average %RSD = 4.3 for the entire set of radioactive waste tests. The largest contributor to the HGR uncertainty was from the GC H_2 measurement followed by temperature. However, the HGR are reported with ±2 standard deviations in the variability of the H_2 measurements, which is generally larger that ±4.3 %RSD and closer to ±7 %RSD.

CONCLUSION

The tests examined radioactive Tank 50 samples with either grout-premix or BFS added. It was found that the difference in the rate of production of H_2 for an overlaying air or nitrogen atmosphere appears insignificant and the presence of BFS and grout-premix increases the HGR with a maximum measured rate of approximately 7.48 x 10^{-9} (m^3/h)/L [or 1.0 x 10^{-6} (ft^3/h)/gal] at ~115°C, but the difference between BFS and grout-premix was not significantly different within a 95% confidence level.

When assuming a first order Arrhenius dependency the results provided an average activation energy of 82 ± 25 kJ/mol (95% confidence level) for all the Tank 50 samples, as well as for Tank 50 samples with added grout-premix or BFS. However, when excluding room-temperature, 33°C, in order to just consider the effect of thermolysis, then the average activation energy becomes 87 ± 30 kJ/mol (95% confidence level). This value is comparable to that derived for thermolysis of organic constituents in Hanford Site waste of 89.6 kJ/mol [17].

The experimental HGR results are bounded by calculated values based on the Hu equation adjusted to a 25°C following the literature protocol and the characterization data for the Tank 50 samples. Furthermore, testing of Tank 50 samples at 33°C (for 26 days) showed an average HGR of 5.8 x 10^{-12} (m^3/h)/L [or 7.8 x 10^{-10} (ft^3/h)/gal]. This result matches, within uncertainty, the Monte Carlo n-Particle Code estimate of radiolytic rate of 3.82 x 10^{-12} (m^3/h)/L [or 5.1 x 10^{-10} (ft^3/h)/gal]. This result is conservatively bounded by the estimated SRR Waste Characterization System radiolytic value for supernatant of 2.92 x 10^{-11} (m^3/h)/L (m^3/h)/L and 3.80 x 10^{-11} (m^3/h)/L [or 3.09 x 10^{-9} (ft^3/h)/gal and 5.08 x 10^{-9} (ft^3/h)/gal] for slurry.

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