**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).

**Disclaimer:**

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1 ) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2 ) representation that such use or results of such use would not infringe privately owned rights; or
3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

# Impacts to H₂ Generation Rates from Glycolate in Radioactive Waste in Grout - 21087

M. R. Duignan, C. A. Nash, C. L. Crawford, and M. L. Restivo
Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

## ABSTRACT

At the Savannah River Site tests were performed with simulant and radioactive salt solution immobilized in grout to measure the hydrogen generation rate (HGR) after the addition of glycolate. Sealed reactors were employed because the HGR was expected to be very low, on the order of $2.2 \times 10^{-11}$ (m³/h)/L. [that is, cubic feet of $H_2$ generated per hour per gallon of radioactive liquid waste, or $3 \times 10^{-9}$ (ft³/h)/gal.] An open, continuous flow, system could only measure rates as low as $4.5 \times 10^{-10}$ (m³/h)/L, i.e., $6 \times 10^{-8}$ (ft³/h)/gal. By accumulating generated gases 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.

Savannah River Remediation declared a Potential Inadequacy in the Safety Analysis, which was concerned with the generation of hydrogen from the decomposition of organics in facilities, which include the Saltstone Production Facility (SPF). The paper discusses the experiments performed to demonstrate hydrogen generation from low activity waste, which feeds the SPF, with a specific focus on the impact of glycolate in the waste on the generation of hydrogen.

Approximately 50 mL of Tank 50 waste, which is a 5-molar sodium salt solution and spiked with glycolate, was mixed with grout to make approximately 100-mL samples that were sealed in 200-mL stainless steel reactors. The grout was held at varying temperatures, e.g., 64°C, 82°C, and 112°C, to demonstrate the effect of glycolate decomposition on $H_2$ generation. Radioactive tests were preceded by non-radioactive simulant testing to measure if hydrogen generation was a function of exposed grout surface areas. In addition, the experiments evaluated the pre-mix grout solids used to stabilize waste in grout, e.g., grout-premix solids of Portland cement, slag cement, and fly ash, to determine if any solid phase reactions are present, which would accelerate or inhibit the generation of $H_2$ at these temperatures.

The simulant tests demonstrated that for a 10-fold increase of exposed surface areas the HGR does not change significantly. The radioactive tests showed that HGR does not change significantly from Tank 50 waste at 82°C for glycolate concentration of < 350 mg/L. Over the test range of temperatures from 64°C up to 112°C, the results showed that to accurately estimate HGR it is necessary to consider the total organic carbon contained in additives in grout pre-mix materials which contain relatively small, but measurable amounts of organic compounds due to primarily the grinding agents added during processing the materials.

## INTRODUCTION

Savannah River Remediation (SRR) at the Savannah River Site (SRS) needed to evaluate the influence of organics on the generation of flammable gases in the vapor space within SRS High-Level Waste (HLW) waste tanks and evaporator systems [1-6]. This paper focuses on testing for one of those waste tanks, Tank 50, and related downstream processing from that tank which is mixed with grout solid in the Saltstone Disposal Facility (SDF).

Studies for waste tanks at another DOE site, Hanford, indicate chemical decomposition by radiolysis and 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 the absence of a prior evaluation of thermolysis occurring within the SRS waste tanks, the testing described in this paper is intended to determine the thermolytic contribution to flammable gases in the Tank 50 matrix with grout.

Testing involved samples from Tank 50 held at varying temperatures, i.e., nominally 60°C, 80°C, and 110°C, to determine if organic compounds are decomposing into $H_2$ and other flammable gases such as methane. Testing also included preparing grout using a non-radioactive salt solution simulant of Tank 50 waste spiked with glycolate. Glycolate is known to be present in either Tank 50 or downstream process operations after the pending introduction of glycolic acid (to replace formic acid) in the SRS Defense Waste Processing Facility (DWPF) flowsheet for vitrification of HLW.

The test needed limit of detection (LOD) for $H_2$ to be as low as reasonably achievable; therefore, a sealed reactor system was designed because the HGR LOD for an open, continuous flow system is approximately $4.5 \times 10^{-10}$ $(m^3/h)/L$ [$6 \times 10^{-8}$ $(ft^3/h)/gal$] [7]. Quantification of HGR below this limit, like the estimated rate of $2.2 \times 10^{-11}$ $(m^3/h)/L$ [$3 \times 10^{-9}$ $(ft^3/h)/gal$] for Tank 50 waste [8], required an alternate measurement system. By accumulating generated gases in a sealed, closed, system and avoiding use of a continuous purge gas, the $H_2$ concentration increases thus improving the sensitivity of measurement, while sacrificing time resolution. Design of a sealed system implies obtaining no or very low permeability and was based in part on successful past designs [9-11]. 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 using a 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.

## 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 hotplates, measurement and data acquisition and control system (DAC), gas and liquid sampling equipment, and safety equipment, e.g., overtemperature control. Further information on the design and operation of the sealed reactors and instrumentation has already been published [12].

*Sealed Reactors*
For previous work [7] reactors, HGV-2 to HGV-8, were constructed of 304 stainless steel, which is impermeable to $H_2$ below 150°C (13); more so than 316 SS [14-15]. They had an internal volume of approximately 200 mL. The reactors were checked for leaks with helium to 150 psig and 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 picture and sketch of the finished reactor with two control valves installed, a pressure transducer, and sampling port in the center. Further details of the reactor construction, evaluation, and operation can be found in a previous report [7].
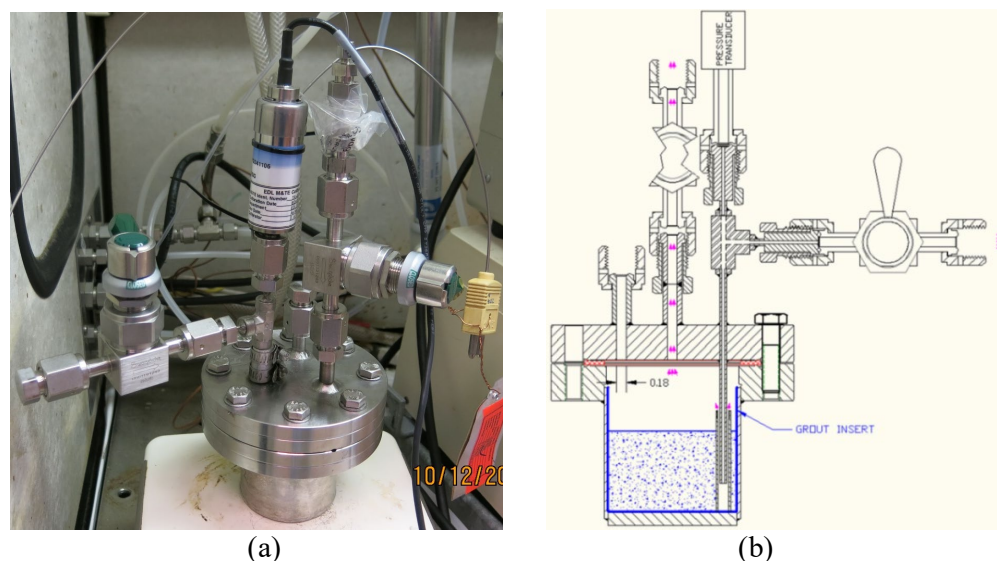
<div align="center">(a)                                          (b)</div>

Figure 1. (a) Photograph of a sealed reactor during sampling and (b) a sketch showing a monolith of grout

*Grout Preparation*

The making of spiked grout samples was a three-step process. The first step was to make the Tank 50 simulant, or secure the radioactive Tank 50 waste sample, well in advance of the test date. The second step entailed measuring the mass of each of the three needed pre-mix grout solids and blending/mixing them together to be ready for use. Finally, the simulant, or radioactive waste, was spiked with the target concentrations of glycolate. The grout solids were pre-weighed, and the spiked simulant was prepared one day before grout was to made and sealed in the reactors and heated to obtain the target temperatures. To make the grout the spiked simulant, or radioactive waste, was added to the pre-weighed solids and mixed until all the solids were fully incorporated, and the grout readily flowed as it was transferred to the reactors.

Table 1 lists the pre-mix grout components of cement, slag, and fly ash, added to the simulant, or radioactive waste, along with the mixture mass ratios and total organic carbon (TOC) values measured.

Table 1. Grout premix solids added to Tank 50 simulated and radioactive waste[1]

| Grout Mixture | | | | |
|---|---|---|---|---|
| Grout Pre-Mix Solids | ~ 55 wt% | | | |
| Tank 50 Waste | ~ 45 wt% | | | |
| Pre-Mix 4th Quarter 2016 Batch | | | | |
| Component of Grout Pre-Mix Solids | Vendor Name | % in Mixture | TOC in solid (2) wt% | TOC Addition mg-C/L |
| Cement | HOLCIM | 10 | 0.017 | 25 |
| Slag (1) | LeHigh | 45 | 0.0134 | 88 |
| Fly Ash | SEFA | 45 | < 0.0089 | < 62 |
| TOC from grout pre-mix additives = | | | | < 175 |
| (1) Slag Cement (Slag) is made of Blast Furnace Slag plus trace amounts of Gypsum and Limestone that are added to enhance the slag properties as it is used in the cement industry. | | | | |
| (2) Analytical results are from mixing each dry component in ultra-pure water and then filtered. TOC is only from what dissolves in the water. | | | | |

---

[1] Hydrogen generation from tank waste is significantly increased by grout additives (by ~1 order of magnitude), which include grinding aids that contain water soluble organics [16]. The additives increase the TOC to approximately 270% above the concentration of the adjusted TOC of Tank 50 waste alone.

*Added Glycolate*
The only organic deliberately added to the mixtures was glycolate.  The planned spike concentrations were 120 and 350 mg/L, prior to the pre-mix grout additions.  To obtain those concentrations either the waste simulant, or radioactive waste salt solution, was spiked with the appropriate amount of sodium glycolate.  The batch of sodium glycolate available had an assay of 99.1wt% pure.

*Simulant Grout Monolith and Pellet Tests*
The very first test series was with simulated waste to evaluate how surface area affected gas generation.  Table 2 presents a set of 4 tests using grout made with a caustic simulant.  The simulant recipe was derived from Tank 50 salt solution quarterly sample analyses [17].  Grout monoliths were formed by pouring a fresh grout mixture into a Teflon® insert (cup) that was then placed in the Sealed Vessel, Figure 2.

Table 2. Simulant Tests

| Test (1) | Glycolate Concentration, mg/L | Grout Form |
|---|---|---|
| 1 | 350 | Monolith |
| 2 | 120 | Monolith |
| 3 | 350 | Pellets |
| 4 | 120 | Pellets |

(1) Target reactor head-space was 100 mL, with a fill gas of $N_2$, and the tests duration was 6 days.

(2) The target temperature was 75°C, but the actual reactor temperatures were 82°C ±5°C (2 sigma).
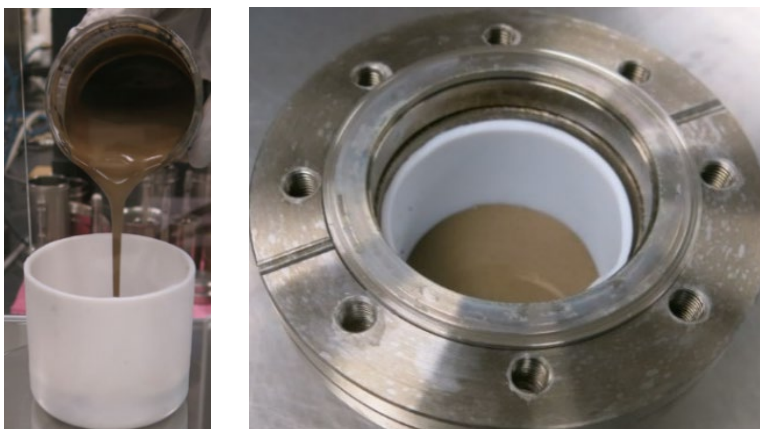


Figure 2. Filling reactor Teflon® insert with fresh grout and placement into a sealed reactor

The fresh grout mixture was made in the same manner as routine quarterly radioactive saltstone samples [18].  The grout contains approximately 55 wt% of premix solids which are comprised of 10% cement, 45% blast furnace slag, and 45% fly ash, with an overall water-to-solids grout premix mass ratio of 0.59.  A stainless-steel tube with a closed bottom was placed in the grout to protect the gas purge dip tube in the Sealed Vessel lid so that grout does not plug the purge tube.  See the sketch of Figure 1b and the photograph of Figure 3.  The photograph shows the grout as it appeared after overnight curing in a vacuum.

Figure 3. Filling reactor Teflon® insert with grout and placement into a sealed reactor

To increase the surface-area of the grout, pellets were made by a molding process using a customized stainless-steel cheese mold. A molding process was used to minimize grout handling to avoid contamination of the grout. As soon as the grout was hard enough the pellets were removed from the mold to fill the reactors. Fabrication of the grout samples was not prototypic of plant operation, but an attempt was made to make sure the grout remained either free of oxygen, or wet during the initial curing process, just before they were sealed in the reactors and heated to the target temperatures. The time involved from production of the post-molded and cured pellets to loading/sealing in the test vessels, with subsequent nitrogen purge, was controlled to minimized excessive air contact and potential oxidation with the surface area of the pellets. The curing time was the same for both the monoliths and the pellets, approximately 20 hours, to allow sufficient structure to build, so the pellets could be handled to fill the reactors. For both the making of monoliths and pellets the grout was exposed to air for approximately 1 hour during mixing, pouring, and reactor purging, and then the grout was held in a moist environment to remain wet. The stainless-steel tube shown in Figure 3 was still used with the pellets but it was held in place by a stainless still mesh that was also used to support several layers of grout pellets, seen in Figure 4.
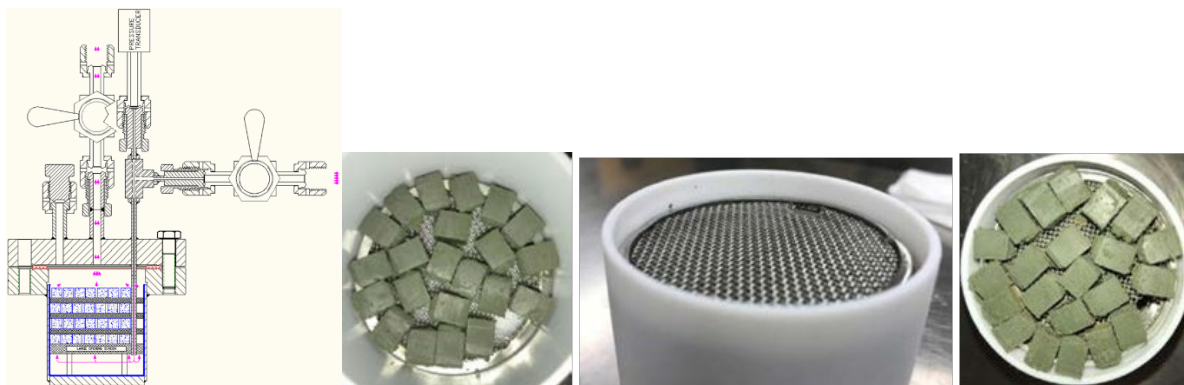


Figure 4. Filling reactor Teflon® insert with grout pellets and placement into a sealed reactor

After the filled reactors were sealed and heated to a target temperature, the heating was discontinued on the last day so that reactors to cool overnight before sampling. That is, one day after heating was de-energized head space of each reactor was sampled for hydrogen and methane, as measured by gas chromatograph. Each sampling event included multiple, usually seven, GC measurements. These multiple measurements were found to be essentially equal in testing.

*Radioactive Grout Monolith Test*
Radioactive grout testing with Tank 50 samples followed the simulant work once there was a clear understanding of test operations with sealed reactors.

Table 3 covers the use of five sealed reactors for radioactive grout monoliths.  A large hotplate with an aluminum block (Al Block) allowed multiple vessels at one temperature.  Single hotplates accommodate one vessel each and operate at independently set temperatures.  Radioactive work used a nominal 28-day full-cure time with one sampling event on the 29th days after reactors cooled overnight.

Table 3. Radioactive Grout Monolith Tests

| Test (1) | Location | Glycolate Concentration, mg/L | Target Temperature, °C (2) |
|---|---|---|---|
| 1 | Al Block | none | 75 |
| 2 | Al Block | 120 | 75 |
| 3 | Al Block | 350 | 75 |
| 4 | Hot Plate 1 | 350 | 95 |
| 5 | Hot Plate 2 | 350 | 55 |
| (1) Target reactor head-space was 100 mL, with a fill gas of $N_2$, and the tests duration was 28 days. |||||
| (2) The actual reactor temperatures were to 82°C, 112°C, and 64°C, respectively, ±5°C (2 sigma). |||||

**RESULTS AND DISCUSSION**

The data for each test, i.e., Temperature History, Pressure History, and the $H_2$, which were obtained during the gas sampling of each reactor after it returned to room temperature, are presented in the following sections.  This information, along with reactor specifics, is used to determine the HGR.  That calculation is adjusted to a pressure of 1 atmosphere (14.7 psia) and a temperature of 25°C.  That is, for the HGR calculation, the sampling initial pressure, which was usually close to 20 psig, and temperature, which was usually between 22°C to 25°C, so all the graphical data are adjusted to 1 atm and 25°C.  Equation (1) is used for to determine HGR.

HGR =

[[(Head Space Volume, $ft^3$) • **A** • $H_2$ Measured, ppm / 1000000] / (Test Time, hours)] / Volume Liquid, gal   (Eq. 1)

Where **A** = Adjustment factor to 25°C and 1 atm = [$P_{initial\ sample}$ / $P_{standard}$] [$T_{standard}/T_{sampling}$] =

[(Initial Sample Head Pressure, psig + 14.7 psia) / 14.7 psia] [298 K / (T°C at sampling + 273 K)]

With $P_{standard}$ = 1 atm = 14.7 psia and $T_{standard}$ = 25°C

**Simulated Waste Tests**
Two tests were done with simulant, one with grout in the form of a monolith and one with grout in the form of many pellets.  The purpose of the different forms was to demonstrate the effect of increased surface area on HGR.  The goals of these simulant tests were: (1) to develop protocols before starting radioactive work, (2) have a good idea of HGR at two difference concentrations of glycolate, and (3) to determine the effect of increased surface area.

*Typical Temperature and Pressure Profiles*
The simulant tests were performed over two sequential 6-days periods; starting with grout monoliths and ending with pellets. Once the grout was made and allowed to cure overnight in a moist environment, the reactors were sealed, purged with nitrogen, and pressurized to ~240 kPa (~20 psig). Heating was initiated and once the target temperatures were constant, the vessels were held at temperature for 6 days. After the sixth day the reactors cooled overnight and were sampled with a GC. The temperature, Figure 5, and pressure, Figure 6, histories show fairly steady results. Those histories were during the grout monolith tests but those for the grout pellets were similar, so they are not shown.
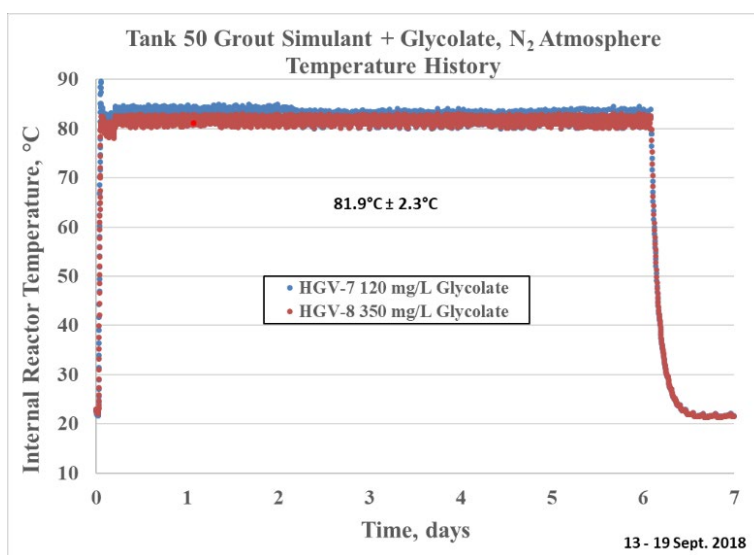
Figure 5. Pre-Radioactive simulant test Temperature history

However, on the second day the insulation on the reactors was slightly adjusted to plug some small gaps, allowing the pressures to stabilize better. The average temperature of both reactors over the test period is shown to be 82°C, which is higher than the target of 75°C. For the pressures, the two reactors were slightly different because the starting pressures were slightly different. However, the pressures held steady once they increased from ~240 kPa to ~325 kPa due to the temperature increase.
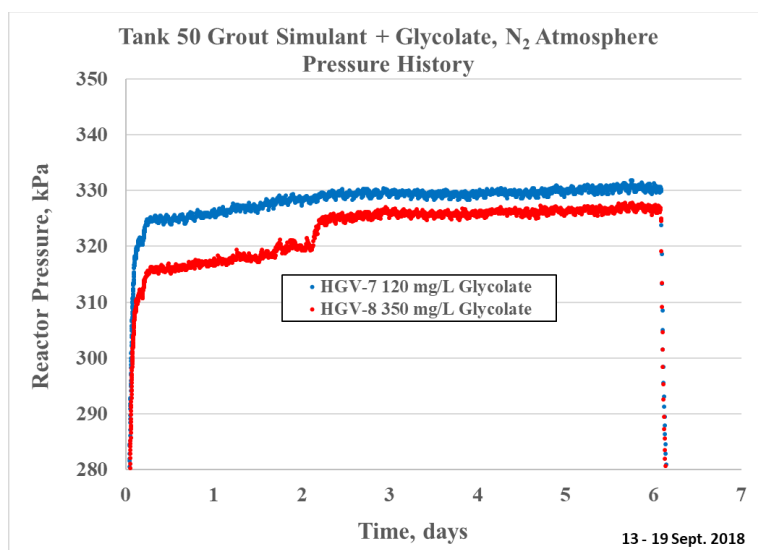
Figure 6. Pre-Radioactive simulant test pressure history

*Hydrogen test results from grout pellets versus grout monolith made with Tank 50 salt solution simulant*
Immediately following the simulant grout monolith test, simulant grout pellet test was performed to determine if increased grout surface area would impact hydrogen production rate (HGR). Table 4, for the grout monoliths, and Table 5, for the grout pellets, show the mass of grout used and exposed surface areas of the tests. The grout mass, of which about 45% is made of Tank 50 simulant salt solution are on the same order. That is, the 88 to 92 pellets had approximately the same mass as the single grout monoliths. However, the 6-sided pellets increased the exposed grout surface area by more than an order of magnitude. It was expected if there was an effect of surface area on hydrogen production, this would determine the impact. Note that exposed area is the surface area of grout exposed to the head space, i.e., for the monolith only its upper surface would be in intimate contact with that gases in the head space, whereas most of each the pellets 6 sides would be exposed.

Table 4. Parameters used for first simulant test with grout monoliths

| Reactor | Grout (1) Volume | Grout Mass | Exposed Surface Area | Head (1) Space | Mass Loss (2) After Test | Height Loss After Test |
|---------|---------|---------|---------|---------|---------|---------|
| No | mL | g | cm$^2$ | mL | % | % |
| HGV-7 | 61 | 102 | 22.66 | 97.07 | 2.1 | 0.0 |
| HGV-8 | 40 | 68 | 22.66 | 121.25 | 3.6 | 0.0 |
| (1) The grout volume and head space for HGV-8 are different than those of HGV-7 due underestimating the grout density; however, the values used are accurate, which allowed an accurate determination of HGR. | | | | | | |
| (2) Some of this loss was due to the condensed liquid found on opening the reactors. | | | | | | |

Table 5. Parameters used for first simulant test with grout pellets

| Reactor | Grout (1) Volume | Grout Mass | Exposed Surface Area (2) | Head (3) Space | Mass Loss (4) After Test | Pellets Used |
|---------|---------|---------|---------|---------|---------|---------|
| No. | mL | g | cm$^2$ | mL | % | # |
| HGV-7 | 45 | 75 | 340.1 | 118.20 | 4.1 | 88 |
| HGV-8 | 46 | 75 | 352.0 | 119.20 | 0.9 | 92 |
| (1) Volumes are based on mass and density (~1.66 g/mL) measured, but rounded off. | | | | | | |
| (2) Areas are based on average of a 10% sample of pellets before test, but a post-test check on the pellets found no significant change:  Pre-test average = 3.87 ±0.10 cm$^2$   Post-test average = 3.97 ±0.11 cm$^2$ | | | | | | |
| (3) Head spaces are based on internal reactor volume less volume of the grout, the Teflon inserts, and the stainless steel meshes used to support the grout pellets. | | | | | | |
| (4) Some of this loss was due to the condensed liquid found on opening the reactors. | | | | | | |

To better show the grout pellet results, it is illustrative to contrast those data with the grout monolith data. Figure 7 show both sets of data considering the temperatures were similar, as well as the test period of 6 days. Overall, surface area does not seem to be a factor. With respect to glycolate, the HGR dropped with increased concentration, which was the opposite realized from the grout monolith. It appears there is little to no effect on the rate of hydrogen production. The measurement uncertainty with 95% confidence was ±10% relative standard deviation, which is smaller than the size of the black circles on Figure 7.
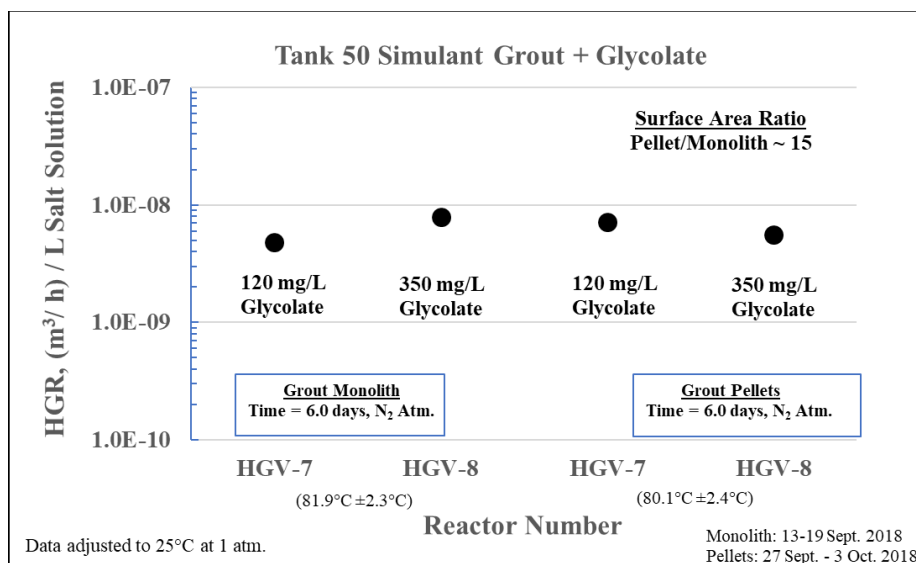
Figure 7. HGR in sealed reactor head space from the grout pellets and the grout monolith

## Radioactive Waste Tests

Unlike the simulant tests that had a test period of 6 days, the nominal period for the radioactive tests was 28 days. This period is normally considered the time necessary for the grout to reach is maximum compressive strength[19]. Furthermore, from the results of the simulant work the grout form was limited to monolith, which can be seen in Figure 2 and Figure 3. After the grout was made, cured overnight in a moist atmosphere of water vapor, sealed in the reactors, purged with nitrogen, and pressurized to approximately 20 psig, the reactors were insulated and heated to the appropriate target temperatures. The temperature and pressure histories are shown in Figure 8 and Figure 9, respectively
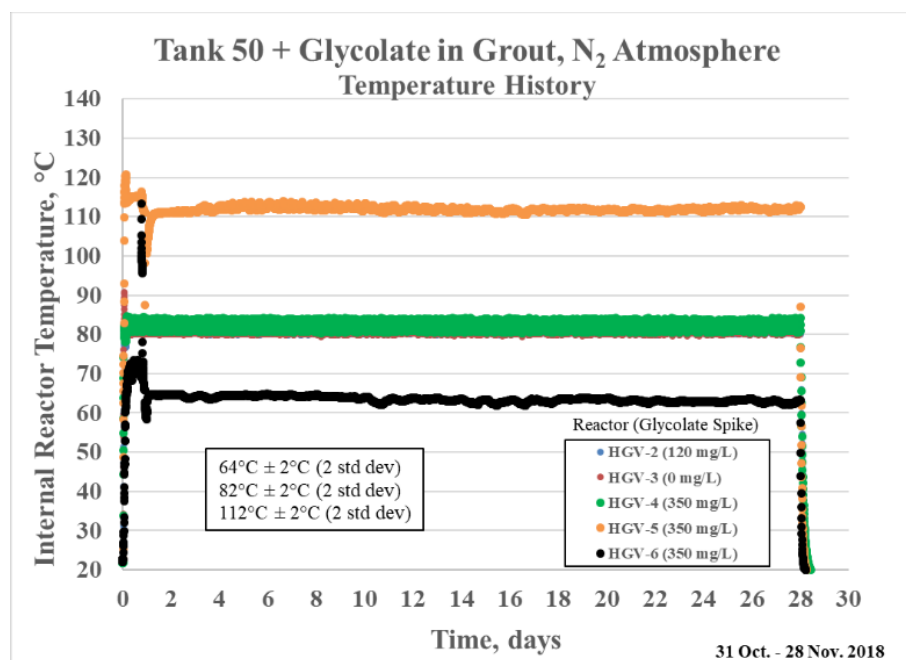


Figure 8. Temperatures during the 28-day radioactive grout + glycolate test
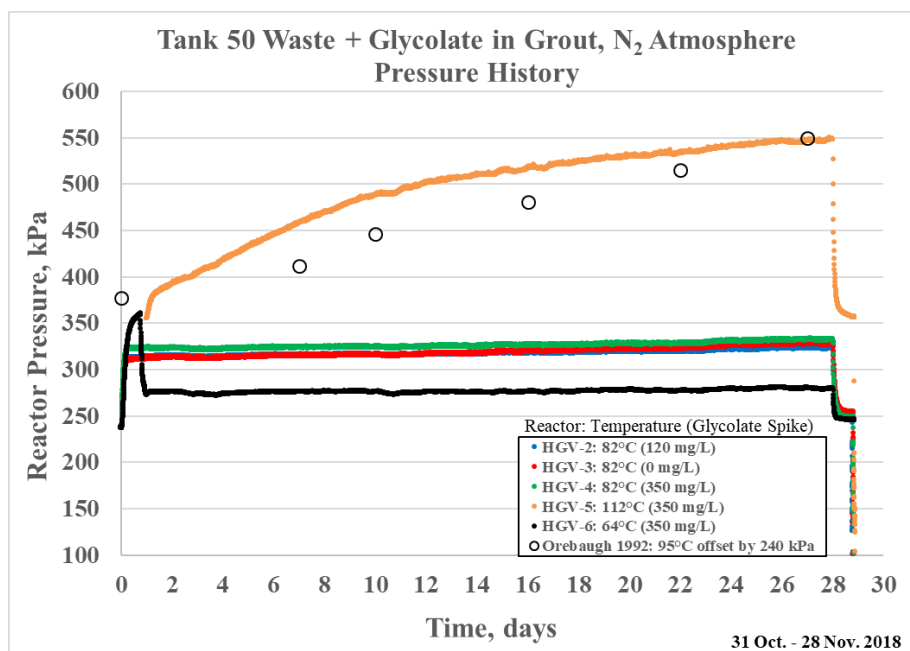
Figure 9. Pressures during 28-day radioactive grout + glycolate test

The temperatures held well over the entire test period; however, during the first day the thermocouples on the reactors on the individual heaters, i.e., HGV-5 and HGV-6, were loose.  On inspection the thermocouples, normally held on the reactor side wall with a pipe clamp, were found to be away from the reactor wall.  They were reading lower than expected, see the first hour in Figure 8 for the pressures being measured, Figure 9.  The insulation was removed for a short time to re-seat the thermocouple, which then showed the constant reactor-wall temperatures.  The temperatures were then readjusted and stabilized to the targets.

What was surprising over the test period was the large increase in the internal reactor pressure for reactor HGV-5, which was at the highest temperature of approximately 112°C.  Subsequently, it was determined that for grout above approximately 85°C nitrous oxide is generated at an accelerated pace.  A close look at the pressure history of all the reactors shown in Figure 9 indicates a slight increase in the pressures, but for HGV-5 it is much more significant.  A 1992 report [20], which measured gas generation from DWPF simulated waste supernatant in grout, found similar results at 95°C.  The open circles on Figure 9 shows the increase of nitrous oxide measured from that 1992 study.  Those earlier data were adjusted to begin at 35°C because that previous test pressure started closer to atmospheric pressure, i.e., 101 kPa, instead of this study's initial pressure of 240 kPa.  $N_2O$ was measured[2] to be approximately 32% of the entire head-space gas composition, as shown in Figure 10.  To be able to put the measured value of $N_2O$ on the same scale as the $H_2$ measured the concentration was divided by a factor of 100.

---

[2] In fact, the mass of $N_2O$ was too large for the GC to give an accurate measure; therefore, the values shown in Figure 10 are only qualitative.
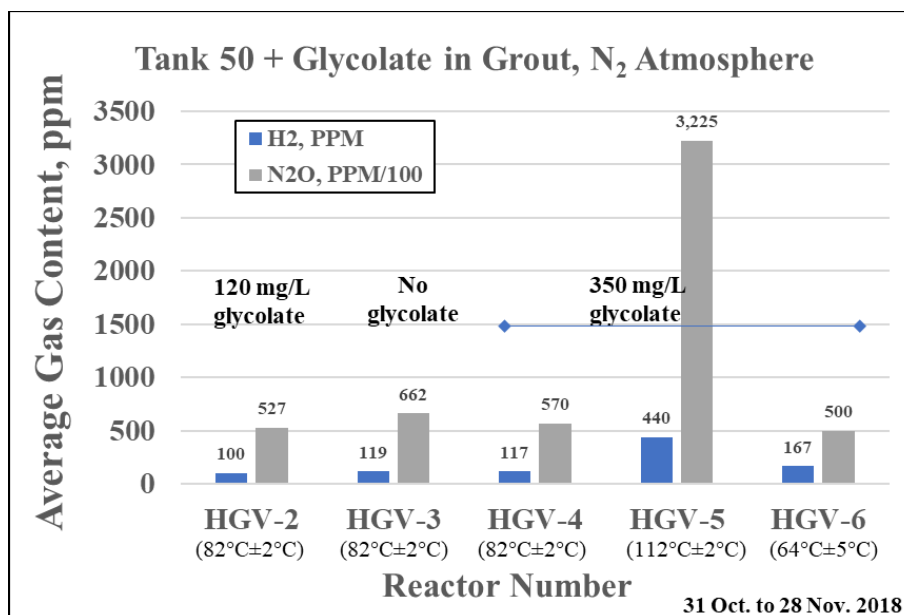
Figure 10. Concentration of $H_2$ and $N_2O$ generated from Tank 50 radioactive grout

*Hydrogen Production*

Figure 11 depicts measurements made from all the sealed reactors on the 29th day after the reactors cooled overnight. There does seem to be an effect of temperature because at the highest temperature of 112°C, $H_2$ is more than double that at the lower temperatures of 64°C and 82°C, but for unknown reasons the $H_2$ decreased as the temperature increased from 64°C to 82°C. One possibility may be the large increase in the production of $N_2O$ above 85°C, just discussed; however, whether the $N_2O$ production is affecting the $H_2$ production is not known.
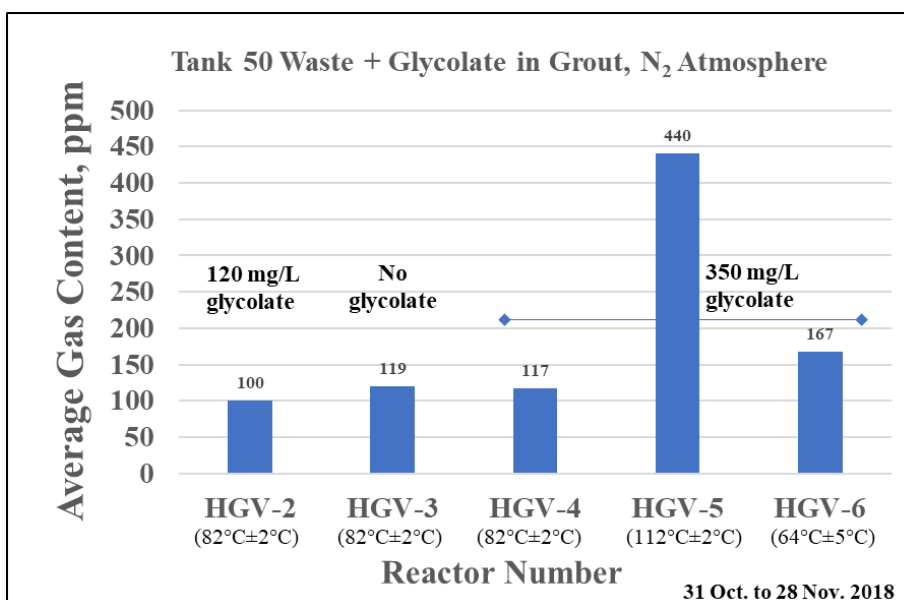


Figure 11. Concentration of $H_2$ generated from Tank 50 radioactive grout spiked with glycolate

The HGR results are shown in Figure 12, which includes the effect of time and mass of salt solution used, demonstrates the same lack of dependency on glycolate concentration. All the HGR values were adjusted to the conditions of 25°C and 1 atm. When comparing the HGR at ~82°C from the 28-day radioactive

11

waste tests to the 6-day simulated waste tests shown in Figure 7 the HGR is lower by an order of magnitude.   This may indicate that most of the hydrogen is formed early in the curing process, i.e., during the first few days, but tests with difference intervals are needed to resolve this.
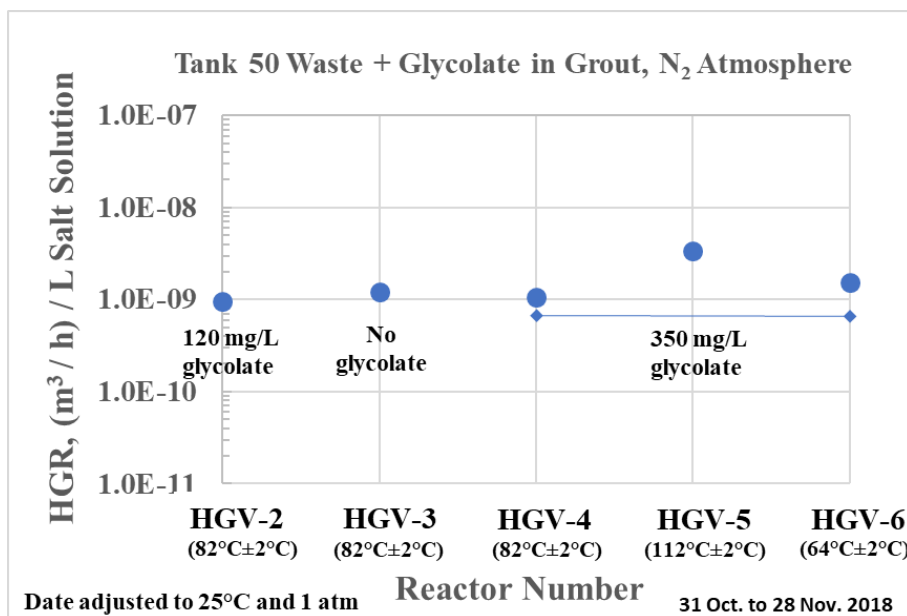


Figure 12. HGR from Tank 50 radioactive grout spiked with glycolate

*Tank 50 Grout Waste Arrhenius Analysis*
The experimental data from the radioactive test contain both the radiolytic and thermolytic effects but at the relatively high-test temperatures, i.e., > 50°C (or 1/T < 0.003K) the radiolytic component has been found [8] to be insignificant.  Therefore, the HGR results may be primarily due to thermolytic effects.

On Figure 13 there are two lines overlaid along with the experimental data.  The dotted line was taken from previous work [8] which measured the HGR from the supernatant of Tank 50 waste with glycolate, but with no grout.
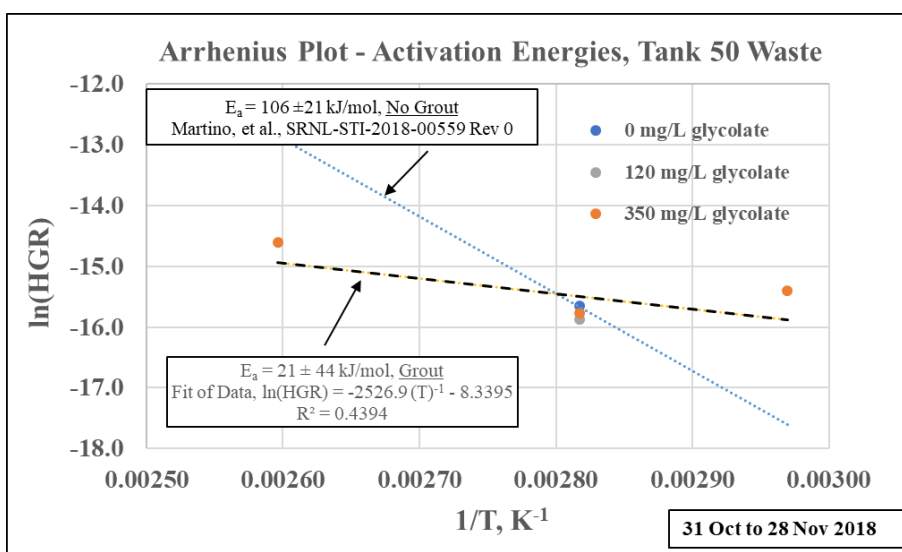


Figure 13. Arrhenius model of HGR versus temperature

The resulting activation energy, $E_a$, is $106 \pm 21$ kJ/mol as obtained from the Arrhenius Equation (2).

$$k = A \cdot e^{-\frac{E}{RT}} \qquad\qquad \text{(Eq. 2)}$$

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 (2) can be written as:

$$\ln(HGR) = -\frac{E}{RT} + \ln(A) \qquad\qquad \text{(Eq. 3)}$$

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.  In using a least-square fit of the current data of Tank 50 waste with glycolate in grout with using Equation (3) the resulting activation energy is $21 \pm 44$ kJ/mol (95% confidence level), which means that zero activation energy cannot be ruled out.  Because the $E_a$/T is the slope of the Arrhenius empirical model, the lower activation energy implies that rate of $H_2$ generation is smaller than for when no grout is present.  Moreover, it appears that for temperatures > 85°C (~1/T < 0.00280 K$^{-1}$) the HGR is lower for grout waste and for temperatures < 85°C (~1/T > 0.00280 K$^{-1}$) the HGR is higher for grout waste.  It may be coincidental but, as previously discussed at greater than approximately 85°C the generation of $N_2O$ increases significantly [20].  If there is a relation between the generation of $H_2$ and $N_2O$, it is currently unknown.

**Measurement Uncertainties**
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 was estimated at approximately 10 %RSD[3] for a confidence level of 95%.  The largest contributor to the HGR uncertainty was from the $H_2$ gas chromatograph measurement, followed by temperature.  However, the HGR are reported with $\pm 2$ standard deviations in the variability of the $H_2$ measurements.  For all the $H_2$ and HGR results discussed in this report the size of the symbols for the data points generally is larger than the uncertainty.

**CONCLUSIONS**

HGR does not appear to correlate to exposed grout surface area because for a 10-fold increase in surface area there was no significant increase of HGR.  That is, grout does not appear to provide mass transfer resistance to hydrogen in these small-scale tests.  Furthermore, for low concentrations of up to 350 mg/L of glycolate this organic did not appear to have a significant impact on steady-state HGR in grout and is consistent with previous Tank 50 waste testing with no grout.  These results imply that other organics appears to dominate the HGR.  The HGR for simulant and radioactive waste testing is significantly increased by grout ad ditives (by ~1 order of magnitude), which include grinding aids that contain water soluble organics.  The additives increase the TOC between 30 to 60% above the concentration of TOC of just Tank 50 waste.  Finally, HGR from grout is larger at the highest temperature tested, i.e., 112°C, but below ~80°C the dependence of HGR on temperature appears insignificant.  The higher HGR measured from 6-day tests than for the 28-day test may indicate that most hydrogen is formed early in the curing process, during the first few days, but tests with difference intervals are needed to resolve this doubt.

---

[3] RSD = Relative Standard Deviation

**REFERENCES**

1.  W. H. WOODHAM, "Run Plan for Testing to Screen and Assess the Hydrogen Generation Rates Evolved from the Thermolysis of Glycolate and Other Prominent Tank Farm Organics," SRNL-L3300-2018-00004, Rev. 0, 2018.
2.  W. H. WOODHAM, "Run Plan for Testing to Evaluate Importance of Major Salt Species on Thermolytic Production of Hydrogen from Glycolate," SRNL-L3300-2018-00011, Rev. 1, 2018.
3.  W. H. WOODHAM, "Run Plan for Testing to Assess the Risk of Hydrogen Formation from Resin Digestion Products," SRNL-L3300-2018-00037, Rev. 0, 2018.
4.  C. J. MARTINO and T. B. EDWARDS, "Run Plan for Tank 22 Sample Thermolysis Tests," SRNL-L3300-2018-00001, Rev. 0, 2018.
5.  J. D. NEWELL and C. J. MARTINO, "Run Plan for Tank 38 Sample Thermolysis Test with Sodium Glycolate," SRNL-L3300-2018-00015, Rev. 0, 2018.
6.  C. J. MARTINO, "Run Plan for Tank 50 Sample Thermolysis Test with Sodium Glycolate Using a Flow System," SRNL-L3300-2018-00024, Rev. 1, 2018.
7.  C. J. MARTINO, J. D. NEWELL, J. M. PAREIZS, M. R. DUIGNAN, and M. L. RESTIVO, "Investigation of Thermolytic Hydrogen Generation Rate in Tank 38 and Tank 50 Waste Samples with Sodium Glycolate," SRNL-STI-2018-00559, Rev.0, 2019.
8.  M. R. DUIGNAN, C. A. NASH, J. M. PAREIZS, M.R. RESTIVO, C. L. CRAWFORD, and T. B. EDWARDS, "Hydrogen Generation Rates for Tank 50 and Saltstone Related Samples Using a Sealed Reactor System," SRNL-STI-2018-00238, Rev.0, 2018.
9.  M. E. STONE, "Evaluation of Methods to Measure Hydrogen Generation Rate in a Shielded Cell Environment and Method Recommendation," SRNL-STI-2012-00511, Rev. 0, 2012.
10. D. T. HERMAN, B. J. WIERSMA, F. F. FONDEUR, J. C. WITTKOP, J. M. PAREIZS, K. P. CRAPSE, M. S. HAY, M. R. POIREIR, and S. D. FINK, "Investigating Hydrogen Generation and Corrosion in the Treatment Tank and the Potential Formation of a Floating Layer in Neutralization Tank During Waste Tank Heel Chemical Cleaning," WSRC-STI-2007-00209, Rev. 0, 2007.
11. B. J. WIERSMA, "Treatment Tank Off-Gas Testing for the Enhanced Chemical Cleaning Process," SRNL-STI-2011-00444, Revision 0, 2011.
12. M. R. DUIGNAN, C. A. NASH, C. L. CRAWFORD, M. L. RESTIVO, and T. B. EDWARDS, "Measurements of Hydrogen Generation Rates Using a Sealed Reactor System," Proc. of WM2019, Paper 19428, 2019.
13. D. M. GRANT, D. L. CUMMINGS, and D A. BLACKBURN, "Hydrogen in 304 Steel – Diffusion, Permeation and Surface Reaction," *J. Nuclear Materials*, 149 (2), pp. 180-191, 1987.
14. M., TEZUKA, T. MIZUNO, and S. SATO, "Study of Hydrogen Permeation through the Stainless Steels," *The Electrochemical Society*, https://www.electrochem.org/dl/ma/203/pdfs/1273.pdf.
15. D. M. GRANT, D. L. CUMMINGS, and D. A. BLACKBURN, "Hydrogen in 316 Steel – Diffusion, Permeation and Surface Reaction," *J. Nuclear Materials*, 152 (2-3), pp. 139-145, 1988.
16. C. BEHELER, "Grinding Aids Used in the Production of Cement and Slag Dry Materials for the Saltstone Facility," LWO-WSE-2008-00230, Rev. 0, 2008.
17. C. L. CRAWFORD, "Results for the Second Quarter Calendar Year 2018 Tank 50H Salt Solution Sample," SRNL-STI-2 018-00499, Rev. 0, 2018.
18. K. A. HILL, "Saltstone Third Quarter Calendar Year (3QCY17) Toxicity Characteristic Leaching Procedure (TCLP) Results", SRNL-L3300-2017-00046, Rev. 0, December 2017.
19. ACI Standard, *Building Code Requirements for Reinforced Concrete*, ACI 318-63, 1963. (Section 301, p. 11.)
20. E. G. OREBAUGH, "DWPF Saltstone Study: Effects of Thermal History on Leach Index and Physical Integrity – Part II – Final Report (U)," WSRC-RP-92-568, Rev. 1, 1992.
21. D. E, GREEN and R. H. PERRY, *Perry's Chemical Engineers' Handbook*, 8th Ed., McGraw-Hill, New York, 2008 [Reaction Kinetics].