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Time Dependence of Methane Generation Rates from Saltstone

M.R. Duignan
C.L. Crawford
M.L. Restivo
M.R. Alexander
K.A. Hill

April 2021
SRNL-STI-2021-00010, Revision 0

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EXECUTIVE SUMMARY

This report documents testing to determine the capacity, and reaction time, for methylmercury (MeHg) contained within Tank 50 salt solution simulant (T50SS) to produce methane when mixed with saltstone dry feed ingredients of cement, slag cement, and fly ash. For those three grout components two mass combinations were used, the current mixture of 10/45/45 and the newly proposed mixture of 0/60/40, respectively[1].

Previously, scoping tests demonstrated that methane is produced when MeHg, which is found in the Tank 50 feed waste to the Saltstone Disposal Facility (SDF), is in the presence of sulfides. When Tank 50 waste is combined with grout premix solids, sulfides are released from the solids from the slag cement component of the premix. The scoping tests were performed in sealed reactors and thus, methane generation was not measured continuously; rather, it was measured after one hour and 24 hours. After 24 hours, a large percentage of the MeHg was converted to methane, but after 1 hour only a small percentage of methane was released, though it is noteworthy that the methane generation rate (MGR) was greater at the one-hour measurement. Furthermore, previous radioactive testing identified the formation of methane with actual Tank 50 waste and methane measurements were performed following 28 days. That test showed long-term methane generation but not what happened near the time of formation.

The current tests expand the scoping work to better demonstrate the dependence of methane generation on time, specifically the quantity and rate of generation from 2 hours to 4 days. By focusing on the period of 4 days, or less, the current tests better show when most of the methane is generated, i.e., shortly after saltstone is manufactured and during its transfer to the SDF.

The testing was performed slightly above room temperature, at 35°C, so the temperature could be maintained constant and not subject to daily room fluctuations. The testing was in three campaigns: methane generation, MeHg destruction, and Hg speciation. The first campaign demonstrates methane generation after multiple time periods from T50SS simulant spiked with 100 mg/L of MeHg, and then with a source of sulfide, i.e., Na_2S or grout. The second campaign used a separate, but similar, set of mixtures from the first campaign to analyze directly for the destruction of MeHg as methane was formed. The final campaign employed Nuclear Magnetic Resonance Spectrometry to better understand which soluble Hg species remain after MeHg is destroyed due to reactions with reduced sulfide.

Conclusions

- Combining MeHg with material containing sulfide, e.g., Na_2S or slag, generated methane gas while MeHg decomposed. This indicates that sulfide in the pH=14 salt solution is causing the destruction of MeHg resulting in methane gas.
- Methane production correlated directly with MeHg concentration, especially from the Na_2S, but less so from the grout mixtures, from which the sulfide release is more complex.
- MGR was highest during the first 4 hours of forming saltstone.
- Methane is released at a faster rate for 0/60/40 grout mixture than the 10/45/45 grout mixture for the first 6 hours, but after 2 days the concentrations of methane are similar.
- For both grout mixtures cumulative average MGR peaks at approximately 4 hours: 1.2×10^{-4} $(ft^3/h)/gal$ for the 10/45/45 grout mixture and 1.9×10^{-4} $(ft^3/h)/gal$ for the 0/60/40 grout mixture, or about 60% larger.

[1] In this report all grout premix solids mixtures will follow the convention of mass ratios of Cement / Slag / Fly Ash, e.g., 10/45/45 or 0/60/40. Each number, e.g., 10, 45, or 45, represent the percent of the total mass of cementitious components.

- For both grout mixtures the average MGR peaks between 2 to 4 hours but in reaching that peak the 0/60/40 grout mixture gets there faster. At 1 hour, the 0/60/40 mixture is almost at its peak while for the 10/45/45 mixture, the MGR at 1 hour is still zero.
- After 18 hours the average interval MGR drops to zero, especially for the 0/60/40 grout mixture. The 10/45/45 grout mixture may still be reacting after 4 days.
- With continuous mixing there is no significant difference for either methane released or MGR between water-to-solids (grout premix additives) mass ratios of 0.59 (non-dilute) and 0.85 (dilute).
- Methane generation and released for solidified grout is 2 to 3 times less than for grout continually mixed.
- As shown in each of the appendices for the test series, the generation of H_2, N_2O, and CO_2 were also detected but at rates of approximately an order of magnitude less than methane.
- A first-order chemical reaction equation based on first 24-hours of results from the Na_2S spiked mixture of T50SS + 100 mgL of MeHg can be used to predict the change in MeHg concentrations in time from mixtures that start with other initial concentrations of MeHg in the presence of excess sulfide.
- Mercury remained soluble in the sulfide-bearing pH=14 solution. That is, the total soluble mercury remained constant at the initial spiked concentrations after methane was produced and MeHg destroyed. Therefore, S^{2-} is not useful to remove Hg (precipitate) from T50SS when pH=14.
- NMR analysis confirmed the presence of primarily MeHg in a control sample of T50SS simulant spiked with 100 mg/L of MeHg, but no sulfide. From a second sample spiked with Na_2S, no MeHg was found, but the full concentration of 100 mg/L of Hg remained in soluble forms. Those forms were in a series of anion groups, tentatively identified as three different soluble Hg-containing species (from ^{199}Hg-NMR) and three other organic species (from H-NMR). These soluble Hg species could indeed account for the analyzed soluble total Hg found in post-reacted samples for this study and previous scoping tests.

Suggestions for future work

- The NMR analysis could potentially be applied to actual radioactive caustic waste-tank samples from SRS Tank Farm to further investigate and understand the various Hg species present.
- All decomposition species identified in the NMR analyses are based on literature information. Further studies with spike additions of some, or all, of the decomposition species into a reacted system would be required to further confirm the presence of these compounds.

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LIST OF ABBREVIATIONS

AR&D	Analytical Research & Development (Group)
AMR	Applied Materials Research (Group)
BFS	Blast Furnace Slag
CAS	Chemical Abstracts Service
CFD	Chemical Flowsheet Development (Group)
CPT	Chemical Processing Technologies (Section)
CY	calendar year
DMA	Direct Mercury Analyzer (to measure total mercury)
ELN	(SRNL) Electronic Notebook [L0833-00239-11, -12]
EM&ES	Environmental, Materials & Energy Sciences (Directorate)
EM&ES O&S	Environmental, Materials & Energy Sciences Operations & Support (Section)
GC	gas chromatograph
GC-CVAFS	Gas Chromatograph – Cold-Vapor Atomic Fluorescence Spectrometer
HGR	hydrogen generation rate
MS&E	Measurement Systems and Equipment
M&TE	Measure and Testing Equipment
MGR	methane generation rate
MeHg	methylmercury
MS&E	Materials Science & Engineering (Section)
N	Number of Samples
N/A	not applicable
ND	not detected
NMR	Nuclear Magnetic Resonance (Spectrometry)
ppm	parts per million (mass, or volume, or hertz)
PSAL	Process Science Analytical Laboratory
RS	Research Support (Group)
SDF	Saltstone Disposal Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SS&E	Separation Sciences & Engineering (Group)
T50SS	Tank 50 Salt Solution
TOC	Total Organic Carbon
XRD	X-ray diffraction

1.0 Introduction

This report documents the tests performed to address the requirements listed in the Technical Request [6.1], which resulted in a Task Technical & Quality Assurance Plan (TTQAP) [6.2] and a Run Plan [6.3] to obtain the required information. The research expands previous scoping work [6.4] to better understand methane generation in the Saltstone Disposal Facility (SDF). That scoping work [6.4] demonstrated that methane is produced when sulfide-containing material is added to methylmercury (MeHg), which is found in the SDF Tank 50 feed waste. When Tank 50 waste is combined with grout premix solids dry feed ingredients of cement, slag cement[2], and fly ash[3], sulfides are released from the slag cement component of the premix.

The prior testing results showed that while the concentration of total mercury was not affected in the pH 14 waste, the MeHg likely reacted with the sulfide contained in the slag [see Appendix A]. The scoping tests were performed in sealed reactors and thus, methane generation was not measured continuously; rather, it was measured after one hour and after 24 hours. After 24 hours, a large percentage of the MeHg was converted to methane, but after 1 hour only a small percentage of methane was released. It is noteworthy that the methane generation rate (MGR) was greater at the one-hour measurement.

The data compiled from the scoping work needed to be expanded to better understand the generation of methane released from grout mixed with Tank 50 waste. This expanded study developed a more extensive knowledge of how and when methane is generated to inform the Documented Safety Analysis (DSA) of the SDF. As such, employing 8 sealed reactors, the methane generation time periods were extended to 2, 4, 6, 18, 30, 48, 72, and 96 hours (4 days). Results are documented herein to determine the capacity for MeHg, contained within Tank 50 salt solution (T50SS) simulant[4], to produce methane when mixed with saltstone dry feed ingredients, i.e., individual components (cement, slag, and fly ash) or a combination of those components.

As per the test Run Plan [6.3], testing was done in three campaigns. The first campaign was to directly measure the release of methane gas from each of the mixtures at 35°C. This campaign was broken into 5 test series shown Table 1. The test mixture for Test Series 1 contained T50SS spiked with 100 mg/L of MeHg and further spiked with Na_2S as a control. The liquid mixture would present sulfide fast to react with MeHg. The kinetics of this mixture were expected to release the most, and fastest amount of, methane as a comparison to all subsequent test series with grout. Test Series 2 and Test Series 3 both contained mixtures of grout with the difference being the mass contributions of grout premix solids. Test Series 2 had the 10/45/45 grout mixture, which is the standard combination currently used for SDF. Test Series 3 had the 0/60/40 grout, cement-less, mixture, which is planned to replace the 10/45/45 mixture. Both test series were to demonstrate the difference of methane generation between the two mixtures. Another feature of these tests was to demonstrate the methane produced especially during the first few hours of grout curing, that is, shortly after saltstone is manufactured and during its transfer to the SDF, while the grout is still a slurry, and then up to 4 days from formation. As such the mass ratio water-to-solids (referred herein as mass ratio) used was a more dilute value of 0.85 instead of the current value of 0.59. This mass ratio is of grout premix of cement, slag, and fly ash. At a 0.85 mass ratio a continually-stirred mixture is maintained as a slurry.

[2] Slag Cement is made of Blast Furnace Slag (BFS) plus trace amounts of gypsum and limestone that are added to enhance the slag properties as it is used in the cement industry. In this report 'slag' will be used in place of Slag Cement.
[3] In this report all grout premix solids mixtures will follow the convention of mass ratios of Cement / Slag / Fly Ash, e.g., 10/45/45 or 0/60/40. Each number represent the percent of the total mass of cementitious components.
[4] Shown as Table 3, which was first used in the final report from previous testing [6.5]. The makeup of the simulant can be found in SRNL Electronic Notebook [6.6].

The last two test series, Test Series 4 and 5, were similar to Test Series 2 and Test Series 3 but were included to demonstrate the effect on methane release by the 0.59 versus the 0.85 mass ratio, and by continually mixed versus solidified grout. Test Series 4 had the 10/45/45 grout mixture with 4 reactors containing the 0.59 mass ratio and 4 reactors with the 0.85 mass ratio. Test Series 5 had the 0/60/40 grout mixture with 4 reactors containing the 0.59 mass ratio and 4 reactors with the 0.85 mass ratio. In both test series the grout mixtures were agitated for only 30 minutes to ensure a good mixture and then agitation was terminated to allow the grout to solidify during the remaining test duration. Those durations were limited to 2, 6, 18, and 30 hours because the purpose was to compare differences between the mixtures rather than the measurement of methane generation out to 4 days.

Besides the gas generation test series of campaign one, two subsequent test campaigns were performed. Campaign 1 was called the MeHg Destruction Test, and Campaign 3 was called the Hg Speciation Test. These tests were included due the recommendations made the previous scoping work [6.4].

The MeHg Destruction Test was performed to analyze the concentration of MeHg as it changed in the release of methane. Pulling samples after methane was generated for subsequent analysis of MeHg proved problematic. Due to the fact that even after filtration, the mixtures continued reacting, so by the time the samples were analyzed all, or most of, the MeHg was destroyed. Therefore, a comparison of the changing MeHg concentration with time could not be made with the methane generation with time. Therefore, a second set of the three main mixtures of Test Series 1, 2, and 3 were made at the location where samples could be analyzed very close to the time they were pulled. These results are used to compare the time of MeHg destruction to the time of methane generation from each of the test series.

The Hg Speciation Test was performed because the scoping work [6.4] elicited results that after MeHg was destroyed in a mixture, the total Hg measurements still indicated that the mixtures continued to have the initial concentration of soluble Hg. That is, the methyl group from MeHg reacted with the excess sulfide and released methane, but the Hg formed unknown groups that remained dissolved in the aqueous phase. This was especially evident in Test Series 1, which did not contain grout, so the mixture was entirely a liquid solution. In fact, samples were analyzed for both MeHg and total Hg and while no, or only insignificant amounts of, MeHg, were detected, all the soluble Hg remained in solution. In those samples no precipitation was evident; therefore, two samples of the T50SS + 100 mg/L of Hg, with and without Na_2S, were subjected to an analysis by Nuclear Magnetic Resonance Spectroscopy in an attempt to better understand what form of Hg existed after methane was generated.

2.0 Experimental Setup

2.1 Sealed Reactor Test Matrix

Table 1 lists the test matrix, which is also described into Run Plan [6.3]. It shows each of the five-test series performed in 8 sealed reactors simultaneously. Each reactor has an internal volume of approximately 200 mL with the wetted surfaces of the test mixtures contained in Teflon inserts. The mixtures were agitated with Teflon-coated stirrers and maintained at 35°C ±5°C. This temperature was chosen to be close to room temperature but slightly above to avoid fluctuations due to ambient changes. An important parameter listed in the table is the molar ratio of sulfur to mercury, which was greater than 300. For Test Series 1 the form of sulfur is sulfide, but for the test series with grout premix additives the sulfide is contained in the slag solids, which contains other sulfur components like sulfate, which will not participate in forming methane gas.

Each reactor contained T50SS simulant spiked with MeHg and material and ratios listed below.

a. Single solids of cement, slag, or fly ash

b. Mixtures of 10%, 45%, 45%; and 0%, 60%, 40% by weight (generally noted as 10/45/45 and 0/60/40 in the order of cement, slag, fly ash, respectively)
c. Mass ratios of 0.59 and 0.85 of water-to-solids of grout premix
d. Na_2S (A control to determine the theoretical reaction kinetics of mercury immobilization.)

Table 1. Test matrix for methane testing of T50SS simulant with 100 mg/L MeHg at 35°C

Test Series	Cement g/L (2)	Slag (1) g/L (2)	Fly Ash g/L (2)	Na_2S g/L	Sulfur M (3)	MeHg mg/L	MeHg M (3)	Hg M (3)	S/Hg molar ratio (3)	Comments
1	0	0	0	12	1.54E-01	100	4.64E-04	4.64E-04	332	Na_2S will be used as a control to determine the theoretic reaction kinetics of mercury immobilization.
2 & 4 (4)	104	466	466	0	1.45E-01	100	4.64E-04	4.64E-04	313	10/45/45 (2QCY2019): 0.85 water to grout premix mass ratio.
3 & 5 (4)	0	621	414	0	1.94E-01	100	4.64E-04	4.64E-04	418	0/60/40 (2QCY2019): 0.85 water to grout premix mass ratio.
4	148	671	671	0	2.09E-01	100	4.64E-04	4.64E-04	451	10/45/45 (2QCY2019): 0.59 water to grout premix mass ratio.
5	0	895	597	0	2.79E-01	100	4.64E-04	4.64E-04	602	0/60/40 (2QCY2019): 0.59 water to grout premix mass ratio.

Notes:
(1) Slag = Blast Furnace Slag + Gypsum + Limestone
(2) Amount of grout premix components are based on a sealed reactor head space of approximately 120 mL. Volume of 1 Liter is of Tank 50 Salt Solution.
(3) Test Series 1 contains sodium sulfide. For Test Series 2, 3, 4 and 5 the sulfur is contained in the slag, which was measured to be approximately 1 wt%. Slag contains approximately 2 wt% of gypsum that contains sulfate, which is a non-reduced from of sulfur. However, the majority of the sulfur in slag is in reduced forms of sulfide and other sulfur species. For this task all the sulfur in slag was assumed to be sulfide. MW: 200.59 (Hg), 215.62 (MeHg), 78.05 (Na_2S), 32.07 (S).
(4) Test Series 4 and 5 contain both the non-dilute and dilute grout mixtures of 0.59 and 0.85 mass ratio of water-to-grout premix solids (referred to as mass ratio), respectively. All other test series contain the dilute 0.85 mass ratio to have a continuosly stirred slurry.

The results from each mixture in Table 1 will be discussed later, but the important aspect of the information in the table is to show that the number of moles of sulfur, or sulfide, was much larger than the moles of mercury for the reactors that contain mercury. The grout pre-mix batch indicated in 2QCY19 in Table 1 and listed in Table 2, was being used by SDF when this work commenced and one of the batches used in the scoping work [6.4].

Table 2. Grout pre-mix batches

Grout Pre-Mix	Manufacturer	Batch	Date Obtained	P.O. Number
Cement	Holcim	2QCY19	27-Jun-19	2019-IR-05-0487
Slag	Lehigh	2QCY19	27-Jun-19	2019-IR-05-01040
Fly Ash	SEFA	2QCY19	27-Jun-19	2019-IR-05-0714

2.2 Tank 50 Simulant

The T50SS makeup, shown in Table 3, was similar to that made for past tests [6.4-6.5]. This T50SS simulant was the base material to spike with 100 mg/L of MeHg, and then with either Na_2S or grout premix solids to demonstrate the potential to generate methane. Note that the estimated sodium molarity based on the ion balance is shown as 5.0 M, which is slightly lower that a previous value of 5.21 M [6.4-6.5]. The previous calculation for Na included a term for the aluminate, whereas a non-Na containing chemical, (aluminum nitrate nonahydrate ($AL(NO_3)_3\ 9H_2O$)) was used in the simulant preparation.

Table 3. Simulant of Tank 50 waste

Component Name	Mol. Wt. g/mol	Actual M (1, 2)	Simulant M (2)
Total Sodium	22.99	5.77 ±0.5%	5.0 ±5% (3)
Aluminate	95.00	0.18 ±0.7%	0.14 ±1.5%
Free Hydroxide	17.01	1.99 ±1.3%	1.92 ±0.7%
Nitrate	62.00	1.92 ±1.5%	1.74 ± 0.0%
Nitrite	46.01	0.57 ±0.7%	0.64 ±1.7%
Oxalate	88.02	0.006 ±0.4%	(4)
Carbonate	60.01	0.27 ±1.2%	0.28 ±0.0%
Sulfate	96.06	0.05 ±0.1%	0.05 ±3.5%
Density	g/mL	1.237	1.219 ±0.6% (5)

(1) Waste sample of 2nd Quarter Calendar Year 2018 (SRNL-STI-2018-00499)
(2) Uncertainties are %RSD of repeated samples (N=3).
(3) Na concentration is based on the ion balance of the other components. Its uncertainty is based on that of those components.
(4) No oxalate was added to simulant. As an original recipe for HGR testing oxalate was not expected to produce H_2; therefore, not included.
(5) Three T50SS batches were made. This is the average.

2.3 MeHg

To the T50SS was added enough MeHg, using a 1M MeHgOH solution[5], to target a concentration of 100 mg/L. The available source is MeHg used was 1 M methylmercury (II) hydroxide dissolved in H_2O, with a molecular weight of 232.62 g/mole. The amounts needed per liter are shown in Table 4. Several spike batches of target concentration were made, as needed, which were then mixed with the material to be tested in each reactor.

Table 4. Concentrations of MeHg

Supply of MeHg Hydroxide (1 M)		
MW =	232.62	g/gmole (CH_3HgOH)
MW =	215.62	g/gmole (CH_3Hg^+)
Water % =	80.60	wt%
CH_3HgOH =	19.40	wt%
Density =	1.20	g/mL
need		
100	ppm (mg/L) of CH_3Hg^+	
0.0004638	M of 1 M CH_3HgOH in H_2O	
0.4638	mL from the 1 M stock	
0.557	grams per liter of Tank 50 SS	

[5] Chemical source: 50-mL bottle of Alfa Aesar™ Methylmercury(II) hydroxide, 1M in H2O, Lot: M28C026, CAS: 1184-57-2

Due to concern over stability of mercury species, the method of handling and storing was important [6.6]. After the T50SS was spiked with MeHg, and before adding the source of sulfide, liquid samples, pulled before filling the first reactor and after filling the last reactor, were analyzed for total Hg and MeHg. Those samples were then refrigerated to ≤ 4°C, while waiting to be analyzed for a period of much less than the 52-week maximum storage time the handling procedure [6.6] recommends.

2.4 Test Series 1 Used as a Control

The rate of methane generated from Test Series 2, 3, 4, and 5 that contained grout was not known; therefore, Test Series 1, which contained no grout, was included as a control. The mixture for Test Series 1 also contained T50SS with 100 mg/L of MeHg, but then it was spiked with enough sodium sulfide to have more moles of sulfide than mercury. With a readily available source of sulfide, the MeHg-sulfide reaction was to demonstrate the bounding kinetic reaction rate. The Na_2S has a molecular weight of 78.05 g/mole and the 12 g/L used of this chemical added 12 g/L / 78 g/mole ~ 0.15 M of sulfide to the T50SS. This amount was more than 300 times the number of moles of mercury in the reactor based on the intended concentration of Hg of 0.0005 M shown in Table 1. In contrast, in the other test series with grout, for sulfide to become available the slag in the grout premix solids would need to dissolve first; therefore, the rate of methane generation from grout mixtures was expected to be less.

2.5 Mercury Needed

Radioactive Tank 50 waste is the salt solution source, but it is the mercury contained in that waste which is of concern for generation of methane. Table 5 shows the mercury species measured concentrations from 2019 sample(s) and the mercury target. The amount of mercury used was 100 mg/L, which is larger than what existed in the available Tank 50 waste samples, to provide conservatism, and because this concentration was used in the previous scoping study [6.4]. It was also important to know the amount of sulfide expected in the grout premix materials, specifically slag. Table 6 shows that a sulfide concentration of 0.1 g/L has 6 times the number of moles of sulfide to the moles of mercury. If only 50% of the sulfide in slag is active, then there were still 3 moles of sulfide to 1 mole of mercury. Table 1 shows the mass of slag used for the 10/45/45 grout premix is 466 g/L and for the 0/60/40 grout premix it is 621 g/L, so an excess of sulfide is expected. For this T50SS simulant test the assumption was that Hg + S => HgS is the sole reaction which is expected to differ from radioactive waste where sulfide can react with other compounds like chromium.

Table 5. Mercury in Tank 50 Salt Solution

Category	Mass	Unit	Species	MW	M
Hg in Tank 50 Waste (1)	82.5	mg/L	Hg	200.59	0.00041
MeHg in Tank 50 Waste (1)	37.6	mg/L	CH_3Hg^+	215.62	0.00017
MeHg to use	100	mg/L	CH_3Hg^+	215.62	0.00046
(1) The values were taken from [6.7]. From 2QCY19 results total Hg was 63.0 mg/L and MeHg was 19.3 mg/L in Tank 50. The values in the table are averages over 5 years, from 4QCY14 to 2QCY19, during which the highest value of MeHg was 61.6 mg/L, measured in the 4QCY16 sample.					

Once the amounts of the slag and other solids were determined, based on the amount of T50SS in each reactor, then those quantities of solids determined the minimum sulfide concentration required. Two mixtures of grout premix solids were tested to demonstrate the potential of generating methane, the mixture

currently in use, i.e., 10/45/45, and a mixture that contains no cement, i.e., 0/60/40. Besides these two mixtures, it was of interest to understand the methane released as the grout cures and is transported to the vault, that is, while it is a slurry. Therefore, an initial part of the testing was to determine a water-to-grout mass ratio that would not completely solidify. To solidification, several dilute mixtures were made until the grout mixture would remain liquid with continuous mixing of the 4-day duration for the last reactor. The standard mixture to make Saltstone grout has a water-to-grout premix mass ratio of 0.59. Successively more dilute mixtures were tried starting with mass ratios of 0.65. These pretest trials demonstrated that for a mixture > 0.80 water-to-grout premix mass ratios the grout remained in a liquid stated for at least 24 hours. The mass ratio used was 0.85 and after 4 days the mixtures became quite viscous; however, the stirrer bar movement could still be detected as the mixture pulsed.

Table 6. Sulfur in slag (1)

S in Slag (1,2) wt%	Slag (3) g slag/L	Sulfur (3) g/L	Sulfur (4) M	S/Hg (5) ratio	S/Hg (6) ratio
1	1000	10	0.311867	626	313
1	100	1	0.031187	63	31
1	10	0.1	0.003119	6	3

(1) Sulfur is assumed to be in the form of sulfide
(2) Measured total sulfur in 2018 Lehigh Slag (see Appendix A)
(3) Based on liter of T50SS simulant
(4) MW = 32.065
(5) Ratio if 100% of sulfide is active, based on 0.0005 M Hg
(6) Ratio if 50% of sulfide is active, based on 0.0005 M Hg

Table 7 shows the resulting mixtures for a combination of weight percent of 10/45/45 and 0/60/40 for cement, slag, and fly ash, respectively, at a water-to-grout premix ratio of 0.85. However, the masses shown in the table, of the small batches tested, were increased so that they displayed on a 1-Liter basis to be consistent. The actual amounts used in each of the 200 mL-sized sealed reactors were much smaller and differ slightly for each reactor. These results also allow one to determine the solids that were used for all the individual reactors.

Table 7. Grout Premix

Material	Premix (1) 10/45/45		Premix (1) 0/60/40	Unit
T50SS Density	1.219		1.219	g/mL
T50SS Volume	1000		1000	mL
T50SS Mass	1219		1219	g
T50SS Solids (2)	27.5		27.5	wt%
T50SS Solids	335.2		335.2	g
T50SS Water	883.8		883.8	g
Premix	1035.3		1035.3	g
Mass Cement	103.5		0.0	g
Mass Slag	465.9		621.2	g
Mass Fly Ash	465.9		414.1	g
Total Mass	2254.3		2254.3	g
Water to Premix %	85		85	%

(1) Percentages of Cement, Slag, and Fly Ash. Mixtures shown are for values based on 1 Liter of T50SS that were obtained from small batches with a total mass of 148 grams to determine mixtures that do not solidify when mixing is maintained. Standard water-to-premix mass ratio for Saltstone is 0.59. The actual total masses expected were closer to 60 grams, which allowed a head space of ~120 mL in the 200 mL sealed reactors.

(2) The total dissolved solids of 27.5 wt% shown was of the simulant batch made for the scoping work, when all the grout values were determined. For the current study, 3 more batches were made and the total dissolved solids varied slightly. For all four batches 15 solids analyses were made with an average of 26.8 ±7 wt% at the 95% confidence level.

2.6 Measurement Uncertainties

Besides the analytical measurements made on liquid samples, e.g., total dissolved solids, MeHg, total mercury, etc., the principal measurements were gas concentrations, temperature, pressure, reactor head space volume, masses added, and time. This was a Safety Significant task; therefore, the M&TE equipment connected to the sealed reactors was recalibrated with the results shown in Appendix B to the 95% confidence level. All results related to the measurement of gas concentrations and the calculations of gas generation rates were statistically analyzed, with the results discussed in Appendix C and the uncertainties for the individual component to generate rates listed in Table 14, the uncertainties of MGR listed in Table 15, and the uncertainties of HGR listed in Table 16 given to a 95% confidence level. The focus of this study is on CH_4, including its measurement uncertainty, but measurements were also made for H_2, N_2O and CO_2 but the generation rates of these gases were one order, or several orders, of magnitude less than for CH_4. Often the results for those gases are barely detectable, especially for CO_2. Detailed statistical analyses for CH_4 and H_2, are shown in Appendix C. Note that the calculated uncertainties for each of the 40 tests,

which make up all of the test series of the first campaign, are different, but throughout the discussion of the results the maximum uncertainty is used for each test series. These are shown as error bars on select graphs of data. For all other analytical data, the standard measurement certainty is ±20% at the 95% confidence level. Another contribution to gas measurement uncertainty is any gas absorbed into the mixtures, which is discussed below.

2.6.1 Gas Absorption

A concern in determining gas generated is if generated gases become dissolved in the simulant before even entering the reactor head space. That is, it is important to know how much of the gases of concern is retained in the T50SS simulant. To estimate gas solubility in the simulant it was necessary to know Henry's law gas constants and fortunately, a previous work [6.8] has measured the constants for a Hanford waste simulant, which was very similar to T50SS with respect to density, pH, and simulant components. Furthermore, it appears that the gases of concern[6] are considerably less soluble in salt solutions than in pure water [6.9]. While the Hanford study [6.8] states that the gases shown in Table 8 are 5 to 10 times less soluble in salt solution than in water, it compares experimental results to several models.

Table 8. Solubility of gases in T50SS simulant for the 10/45/45 grout premix mixture

Material	Chemical Symbol	Henry's Constant (1) Pure Water H_{H2O} at 25°C mol / (kg-water x atm)	Henry's Constant (2) Salt Solution (SS) H_{SS} at 25°C mol / (kg-water x atm)	H_{H2O} versus H_{SS} H_{H2O}/H_{SS}	Gas Dissolved in T50SS (3) vs. Gas in Head Space (4) %
Hydrogen	H_2	7.80E-04	3.85E-04	2.0	0.27
Oxygen	O_2	1.22E-03	9.97E-04	1.2	0.69
Nitrogen	N_2	6.38E-04	3.17E-04	2.0	0.22
Methane	CH_4	1.22E-03	9.87E-05	12.3	0.07
Nitrous Oxide	N_2O	1.82E-02	1.18E-02	1.5	8.15

(1) Values are from a literature reference [6.9], which is a compilation of Henry Law's constants from many sources at 25°C, which is close to the average temperatures when the GC measured gas concentrations. This is a lower temperature than the test temperature 35°C, so the values of gas dissolution are more conservative.

(2) A Hanford Report [6.8] contains Henry's Law constants of a salt solution similar (see note 3) to T50SS. Constants for H_2, N_2, and N_2O came from the more conservative Table 4.8 of that reference. O_2 and CH_4 are not listed in Table 4.8; therefore, they were taken from the less conservative Table 4.7 of the reference. The constants for those gases were made more conservative by interpolating between the two tables with values for N_2 and H_2, respectively.

(3) The Hanford SS simulant (pH=14, density 1.18 g/mL) from the PNNL source [6.8] was very similar to the T50SS SRS simulant (pH=14, density 1.21 g/mL). It was made up with the same 6 components of Na+, OH^-, AlO_2^-, NO_3^-, NO_2^-, and CO_3^{2-}; therefore, $H_{T50SS} \sim H_{SS}$ is assumed.

(4) Calculations for these values can be found in Appendix of this report on *Solubility of Gases in Salt Solution*.

For the current study the most conservative values from the Hanford study were chosen. Table 8 shows that Henry's constants at 25°C for pure water to be 2 times larger for hydrogen, and 6 times larger for methane, than for salt solution. The last column of Table 8 calculates the mass percentage of the measured reactor head space gas that is retained in the simulant and the values are based on the conditions of a reactor with the 10/45/45, as an example. Besides N_2O, which is the most soluble gas of the group at less than 9%, all the gases are fractions of a percent; therefore, insignificant. This is especially true for methane which

[6] The Hanford reference [6.8] does not mention CO_2.

is retained in the simulant by less than 0.1% of the methane in the headspace. The calculations in the table for the percentage of gases dissolved in the T50SS simulant can be found in Appendix D. Therefore, all gas generation results in this study neglect the insignificant amount of the gas retained in the mixtures.

2.6.2 Sealed Reactor Headspace

An important factor to calculate the gas generation rate is an accurate volume of the headspace. To determine the head-space volume entails an accurate knowledge of the internal volume of each sealed reactor and the material that occupies that volume while a test is ongoing. Some of that material includes the Teflon insert that contains the mixtures, the mixtures themselves, the stir bar, and the pipe used to sample the gas, like with sampling with the GC. Each sealed reactor is slightly different but roughly the head spaces were on the order of 120 mL in the ~200 mL sealed reactors. A detailed discussion of head-space volume determination is given in Appendix E along with the head-space volume for each reactor. The exact volumes used, and their uncertainties, are listed in Table 14 the statistical analysis located in Appendix C. As summary of those volumes are given in Table 9.

Table 9. Sealed reactor fill volumes and headspaces

Sealed Reactor Head Volume							
HGV	**Reactor Vol.**	**Teflon**	**Insert Vol.**	**Mixture**	**Headspace**	**Mixture**	**Headspace**
No.	**mL (1)**	**Insert (2)**	**mL (3)**	**mL (4)**	**mL (5)**	**mL (6)**	**mL (5)**
7	192.01	A	22.22	55.74	**114.05**	56.39	**113.40**
8	194.96	B	21.13	55.74	**118.09**	56.39	**117.44**
9	194.44	C	21.46	55.74	**117.24**	56.39	**116.59**
10	194.37	D	21.49	55.74	**117.14**	56.39	**116.49**
11	193.29	E	21.84	55.74	**115.71**	56.39	**115.06**
12	193.09	F	21.66	55.74	**115.68**	56.39	**115.03**
13	196.64	G	21.26	55.74	**119.64**	56.39	**118.99**
14	195.02	H	21.65	55.74	**117.63**	56.39	**116.98**
15	193.94	I	21.86	55.74	**116.34**	56.39	**115.69**

(1) Measured at 22°C.
(2) The Teflon inserts are in alphabetical order for this table, but when an test was performed the insert employed was noted to obtain the accurate head-space volume.
(3) Based on a measurement of mass and a standard room temperature density of 2.20 g/mL for Teflon.
(4) All mixtures introduced into each sealed reactor were measured during a pretest evaluation to fill all the Teflon cup inserts to the same level which turned out to be a volume of 55.74 mL for the 0.85 water-to-solids grout premix mass ratio. This volume includes the 1.69 mL volume of the stir bar.
(5) To this reactor head space is added 2.576 mL for the internal volume of the piping connecting a reactor to the GC. For Test Series 3, 4, and 5, and the subsequent Redo tests, another 2.121 mL is added to the head space due to the removal of the purge tube, which became plugged with grout during Test Series 2.
(6) This note is the same as for note (4) except the mixture fill volume was 56.39 mL for the 0.59 water-to-solids grout premix mass ratio.

2.7 Gas and Liquid Measurements

Besides methane, the gas headspace in each reactor was measured for hydrogen, nitrous oxide, and carbon dioxide. Methane will be discussed later in the Results and Discussion Section; however, all gases measured are discussed in each of the appendices for each test series.

There were three groups of liquid measurements. The first group was of T50SS simulant that filled sealed reactors. The 100 mg/L spiked concentration of MeHg was confirmed after MeHg was added to batches of T50SS simulant, but before introducing the source of sulfide. Samples were pulled before filling the first reactor and before filling the last reactor for each test series. Those liquid samples were analyzed for both total Hg and MeHg. These results will be discussed in the appendices for each test series, but generally, the spiked concentration was shown to be within measurement uncertainty for all tests. The second group was for the MeHg destruction test, which will be discussed later, but in that test the three test mixtures, i.e., Na_2S, 10/45/45 grout, and 0/60/40 grout were periodically sampled and analyzed to determine the change in MeHg concentration after the source of sulfide was introduced. The last group was for the NMR test which evaluated two samples of T50SS simulant containing 100 mg/L of MeHg, one spiked with Na_2S and one with no source of sulfide, as a control. Those results will be discussed later in Section 3.3.

2.8 Subsequent Test

The first campaign of Test Series 1 to Test Series 5 was the principal set of tests performed, as shown in Table 1; however, those tests were followed by two separate test campaigns. One was performed to analyze the MeHg concentration changing in time with a Gas Chromatograph – Cold-Vapor Atomic Fluorescence Spectrometer (GC-CVAFS), which was done immediately after spiking the simulant with a source of sulfide. This was done to better understand how the production of methane related to the destruction of MeHg. The results of this test are highlighted in the Results and Discussion Section with details given in Appendix K. The last test campaign was performed on T50SS simulant samples the contained 100 mg/L with and without a source of sulfide, to better understand the results obtained from previous work [6.5] where the total Hg was shown not to be affected after MeHg is destroyed. That is, soluble Hg concentration did not change but remained soluble in some unknown form, or forms, which is known to happen but not well understood [6.10]. The samples were analyzed using NMR Spectrometry and the results of this campaign are summarized at the end of the Results and Discussion Section with details given in Appendix L.

2.9 Sealed Reactor Equipment

The primary equipment for this testing includes 9 sealed stainless-steel reactors having nickel flange seals. For each test, 8 reactors were used with one as a spare. The materials of construction were found to not interfere with previous hydrogen generation rate measurements down to 10^{-9} (ft^3/h) / gal [6.11] in testing with T50SS, samples, and various additives. The initial set of reactors were used for radioactive work [6.5] so a new set of reactors were made using the same design. Those reactors were again used to capture and measure methane generation rates. The equipment includes heated aluminum blocks placed on top of multiple and individual heating/stirring plates with temperatures controlled separately. The blocks help to keep the reactors stable and the temperature uniform.

The internal volume of each reactor is nominally 200 mL. The reactors have (1) gas purge capability, (2) a pressure transducer, and (3) a thermocouple attached to the outside reactor wall. The reactor discharge fitting allows venting to a gas chromatograph (GC) for the gas composition measurements. Each reactor also has a purge fitting to introduce gas to each vessel through a dip tube. Before sealing the reactors, a Teflon insert, which contains a Teflon-coated stir bar, is filled with the appropriate amount of dry grout pre-mix solids and installed within the appropriate reactor so the reactor flange can be sealed. The stir bar is actuated after the T50SS is slowly introduced so that the mixture remains a slurry and does not solidify for Test Series 1 to Test Series 3. For the remaining two test series the stir bar agitation is stopped after 30

minutes to allow the grout to solidify. When finally sealing the reactors with a mixture it is very important to complete the seal within minutes to minimize any loss of generated methane. Once sealed, the reactors were not purged with gas so that any generated gases would not escape. The reactors were simply pressurized with pure nitrogen to have sufficient gas to feed the GC at the end of each test. This means any existing atmosphere of air in the reactor after it was sealed mixed with the nitrogen and then the generated gases. Each test mixture, which contained MeHg, was only to be in contact with a Teflon cup. The filled cups were inserted into the sealed reactors to hold the T50SS and other test materials.

Figure 1 shows a schematic of a sealed reactor. Figure 2 shows the reactors in place after receiving the appropriate test mixture and sealed. In the forefront of Figure 2 HGV-7 is shown being pressurized with nitrogen. After all reactors were pressurized, they were insulated and heated to 35°C. What is not seen is the fume hood in front of the table to where each reactor was brought when it was time to sample, and then vent, the gas.

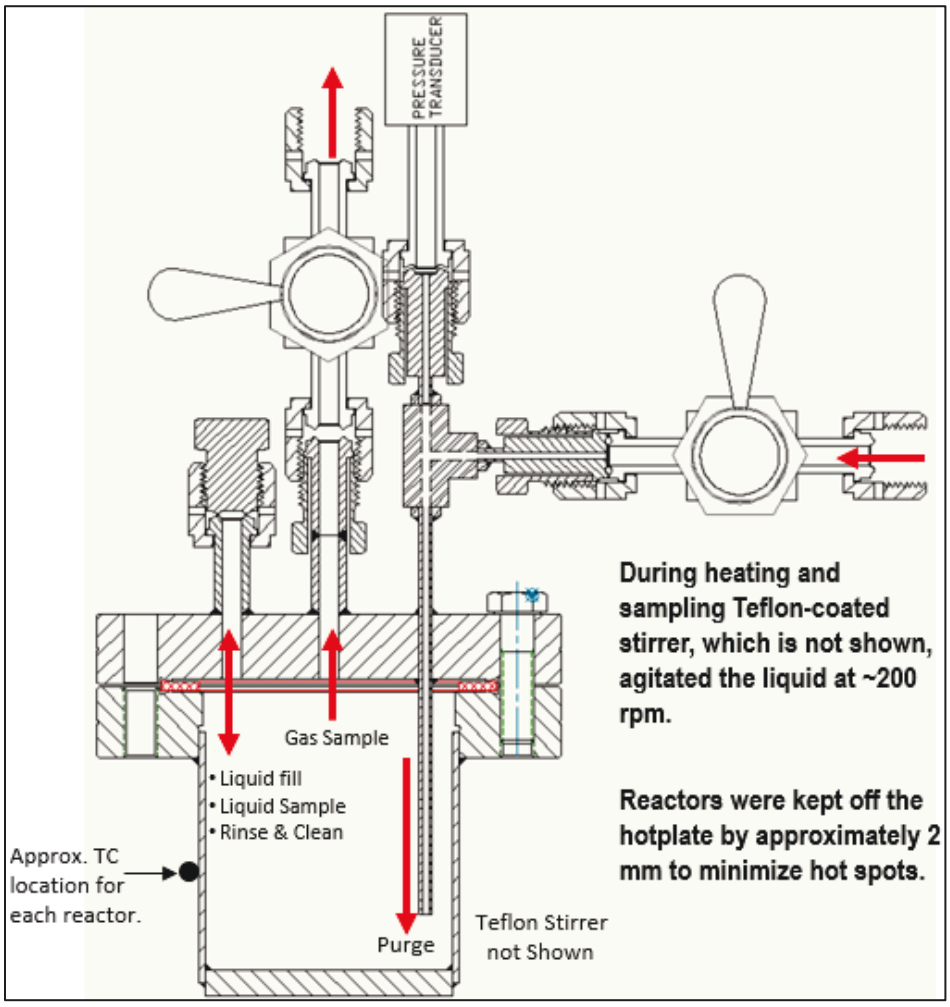

Figure 1. Sealed Reactor without Teflon Cup Insert

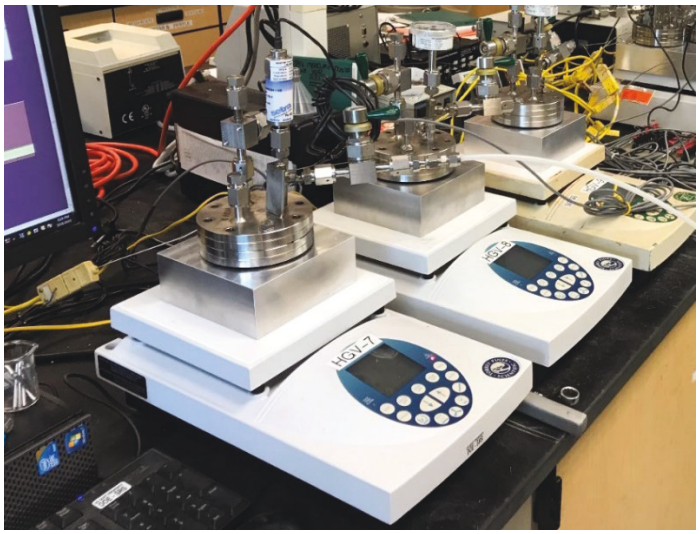

Figure 2. Test setup shows three of the four sealed reactors on mixing/heating plates

2.10 Highlights of the Method of Operation

The principal steps for carrying out each test series were very similar and are listed below.

Prior to test day

1. Prepare T50SS at least 2 days before the test so it can be filtered, sampled, and determined stable.
2. Fill Teflon inserts for the sealed reactors with dry mixtures of grout solids one day before, or the day of a test. The exception is for Test Series 1, which used the anhydrous form of Na_2S; therefore, hygroscopic. It needed to be mixed with the T50SS immediately to minimize water absorption from the air.
3. Seal the reactors, except for the liquid fill port, which is generally done the day before testing.

Test day

4. Spike T50SS with 100 mg/L of MeHg. (This could be done the day before testing if kept refrigerated.)
5. Fill each reactor with the required amount of T50SS and completely seal reactor. As this, and each of the other reactors, are slowly filled, the Teflon mixing agitator is turned on to approximately 200 rpm, but not to exceed 250 rpm, to mix the contents and prevent them from solidifying.
6. After all reactors are sealed and mixing, they are pressurized with pure nitrogen to approximately 12 to 14 psig[7], after which all valves are tightly closed, and valve stems are sealed.
7. All reactors are insulated and heated to 35°C for the test duration.
8. At the end of a reactor's test period, it is moved to a fume hood to sample the gas, where a reactor is connected to a GC by a stainless-steel tube that runs to the measurement equipment. The gas is principally measured for methane, but also for hydrogen, nitrous oxide, and carbon dioxide.
9. After gas sampling all reactors each reactor is vented in the fume hood and then opened to photograph the state of the mixture.

2.11 Quality Assurance

As required [6.1], a Functional Classification of Safety Significant applies to this work. Equipment with a General Service functional classification comprises the analytical measurement systems used to collect data

[7] Any pressure was acceptable as long as it did not exceed the GC limit of 20 psig, to protect the equipment, and it was known in order calculate MGR.

for this testing. Standards used to calibrate these systems are purchased at Level 2 with a certificate of analysis. Chemicals and reagents used in testing and sample preparation are purchased at levels 2 or 3. Standards shall be uniquely identified and traceable to NIST or equivalent per 1Q, 2-7 section 5.2.3.

To match the requested functional classification, the reports, calculations, and technical memoranda issued from this testing received technical review by design verification (E7 Manual Procedure 2.60, Section 5.3). A design verification report will be generated with a unique ID and transmitted to SRS Document Control, using form OSR 19-196 or equivalent. Signature of E7 technical reviewer on this final report signifies completion of the design verification review. Record keeping of the review on form WSRC-IM-2002-00011, Rev. 2 and retention in ELN [6.12] is considered equivalent to OSR 19-196.

Several software packages were utilized in the performance of this study. Those packages are described below.

A Data Acquisition and Control System (DAC) software package was used to display and log test readings from pressure transducers and thermocouples. The software name is Labview, Version 2014, HGSDAS HGR Data Acquisition System from National Instruments, and its classification is Level D. The approved classification Document No. is B-SWCD-A- 00737 [6.13]. The DAC software displays the temperature and pressure and records a data file for later use. The thermocouples and pressure transducers are in the M&TE program; therefore, the pressure and temperature measurements meet the requirements for Safety Significant application.

Uncertainty analyses for gas generation measurements were performed using two commercially available statistical software packages, GUM Workbench and JMP® Pro. For these packages, the software classification is Level D, as described in the approved software classification documents (B-SWCD-W-00022 and B-SWCD-W-00023, respectively) [6.14-6.15]. Both statistical packages have undergone verification and validation per the software qualification procedure (Manual 1Q, Procedure 20-1, Revision 14) [6.16]. Calculations performed by these software packages are subjected to the technical review process (Manual E7, Procedure 2.60). Therefore, the calculation of uncertainties meets the requirements for Safety Significant application. The scoping data [6.4] were not included in the uncertainty analyses and not used in rate expressions discussed in this report. However, those scoping data are included in this report for comparison purposes. Furthermore, the M&TE instrumentation used for the present work was the same used for the scoping work was properly calibrated.

Analytical measurements for gas streams were made with a GC made by INFICON, and the model is Micro GC Fusion® Gas Analyzer. The GC has its own software and is not part of operation of any of the preceding tasks. The GC is in the Measurement Systems & Equipment (MS&E) program and thus the software is controlled under the requirements of Manual 1Q Procedure 2-7. The reprocessed data from the GC software are used in the gas generations calculations; therefore, the GC measurements of the gas stream meet the requirements for Safety Significant application. The calibration-gas standards used are listed in Appendix B in Table 13.

The TTR [6.1] designates the work as requiring Safety Significant pedigree with no waste form affecting (RW-0333P) provisions.

3.0 Results and Discussion

The results are comprised of three campaigns: gas generation in sealed reactors, MeHg destruction to demonstrate the changing MeHg concentration with time, and Hg speciation analysis after MeHg destruction, to show the soluble forms Hg after MeHg reacts with sulfide to produce methane. Details of each campaign are discussed in the appendices, but highlights of each are discussed in this section. The results of the first campaign on gas generation are located in Appendix F, Appendix G, Appendix H, Appendix I, and Appendix J for Test Series 1, 2, 3, 4, and 5, respectively. Details of the second campaign on MeHg destruction Test are located in Appendix K and details of the last campaign on the Hg Speciation Test are in Appendix L.

The principal focus for this study was the demonstrate methane generation and generation rate from grout in time, but especially when grout was still in a slurry after the grout is formed and transported to the Saltstone Disposition Facility (SDF) for storage. Along with CH_4 gas, a few other gases were measured, i.e., H_2, N_2O, and CO_2; however, those other gases were secondary and information on those are limited to the appropriate appendix. For this section the principle gas, CH_4, is discussed for each test series and the entire set of results is listed in Table 10. The statistical analysis for all gas generation results is discussed in Appendix C, but select graphical figures show error bars for which quantitative statistical information can be found in Table 14, Table 15, and Table 16 of that appendix.

Table 10 is broken into four sections and it contains all the CH_4 results for the first two campaigns. The first three sections are for the results of the gas generation campaign and the last section lists the results for MeHg destruction campaign. Both campaigns were of tests with time as the independent variable. The data for last test campaign on Hg Speciation are omitted because for that test time was not the focus, so they will be discussed later. Some other important features of Table 10 are as follows.

Header: The table header columns list each of 10-time intervals from 1 to 96 hours, but only 8 of those intervals were performed for this current study. The other two intervals, i.e., 1 and 24 hours, are from previous scoping tests [6.4] and are included to compare with the current results. Each time duration is from a different reactor; however, information on specific reactors is given in the appropriate appendix because for the comparisons made here knowledge of an individual reactor is not necessary, unless something unique occurred.

Rows: The table rows list each of the Test Series 1-5. For Test Series 1, 2, and 3, all 10-time durations have data; however, for each of Test Series 4 and 5, the 8 reactors were split so that 4 reactors contained the 0.85 mass ratio and 4 reactors contained the 0.59 mass ratio. Those two groups of 4 reactors had the same time intervals of 2, 6, 18, and 30 hours. The principal difference between Test Series 1-3 and Test Series 4-5 is the first set of test series had continuous mixing and the second set of test series allowed the grout mixtures to solidify after by mixed for 30 minutes.

Sections: The top section of Table 10 lists the CH_4 results. The second section from the top of the table lists the CH_4 generation rate results. The third section from the top of the table lists the fraction of CH_4 moles released normalized by the total number of MeHg moles available that could be converted to CH_4. The bottom section is slightly different from the other sections because the time intervals were different as those different times durations were more convenient for personnel shift work

Other Columns: The second column indicates the specific mixture used in each reactor. The third column shows the concentration of MeHg in the simulant that analyzed by GC-CVAFS before spiking with a source of sulfide. The fourth column shows the concentration of total Hg in the simulant that was analyzed by DMA before spiked with a source of sulfide. The target concentration of initial MeHg was 100 mg/L and results from the data in columns 3 and 4 indicate the target was attained for all the gas generation tests

within the measurement uncertainty of ±20% at the 95% confidence level. Other details of the information in Table 10 are given in the notes to that table and in the appropriate appendix for each test series and MeHg Destruction test.

Table 10. Methane results at 35°C

CH_4 Results				Target Test Duration, h >>>	1 (5)	2	4	6	18	24 (5)	30	48	72	96
				Average Actual Test Duration, h >>>	0.99 (6)	2.14	4.02	6.02	18.2	26.6	30.1	48.4	72.1	95.9
Test (1) Series Name	Reactor Mixture (2) Name (3)	Avg MeHg Spike (4) mg/L	Avg Total Hg mg/L (4)	Avg. Test Temp. °C	CH_4 Generation [ppm]									
TS 1	Na_2S	84	97 (6)	34 ±3	945	1416	1814	1779	1054	2574	1126	2617	2597	2520
TS 2	10/45/45-0.85-SL	105	100	34 ±4	0	83	430	416	650	990	781	974	1054	1065
TS 3	0/60/40-0.85-SL	103	99	35 ±2	142	339	645	729	923	442	892	780	963	963
TS 4	10/45/45-0.85-SO	134	120	33 ±4		8		141	277		293			
TS 4	10/45/45-0.59-SO	same	same	33 ±3		83		212	367		204			
TS 5	0/60/40-0.85-SO	109	109	32 ±2		62		220	294		378			
TS 5	0/60/40-0.59-SO	same	same	32 ±4		18		87	169		287			
					CH_4 Generation Rate [(ft³/h) / gal]									
TS 1	Na_2S	84	97	34 ±3	5.30E-04	3.61E-04	2.49E-04	1.62E-04	8.46E-05	5.25E-05	5.13E-05	2.95E-05	1.87E-05	1.42E-05
TS 2	10/45/45-0.85-SL	105	100	34 ±4	0.00E+00	4.22E-05	1.21E-04	7.47E-05	4.07E-05	3.66E-05	2.75E-05	2.21E-05	1.62E-05	1.23E-05
TS 3	0/60/40-0.85-SL	103	99	35 ±2	1.53E-04	1.57E-04	1.86E-04	1.38E-04	5.54E-05	1.97E-05	3.36E-05	1.76E-05	1.46E-05	1.03E-05
TS 4	10/45/45-0.85-SO	134	120	33 ±4		4.82E-06		2.66E-05	2.00E-05		1.08E-05			
TS 4	10/45/45-0.59-SO	same	same	33 ±3		3.82E-05		3.99E-05	2.32E-05		7.51E-06			
TS 5	0/60/40-0.85-SO	109	109	32 ±2		3.50E-05		4.09E-05	1.79E-05		1.36E-05			
TS 5	0/60/40-0.59-SO	same	same	32 ±4		9.82E-06		1.68E-05	1.058E-05		1.062E-05			
					Moles CH_4 Generated Versus Moles MeHg Available [fraction]									
TS 1	Na_2S	84	97	34 ±3	0.34	0.51	0.62	0.61	0.95	0.94	0.89	0.89	0.84	0.85
TS 2	10/45/45-0.85-SL	105	100	34 ±4	0.00	0.06	0.29	0.27	0.45	0.64	0.49	0.65	0.71	0.74
TS 3	0/60/40-0.85-SL	103	99	35 ±2	0.10	0.22	0.44	0.48	0.59	0.35	0.63	0.53	0.61	0.57
TS 4	10/45/45-0.85-SO	134	120	33 ±4		0.01		0.09	0.21		0.19			
TS 4	10/45/45-0.59-SO	same	same	33 ±3		0.04		0.14	0.24		0.13			
TS 5	0/60/40-0.85-SO	109	109	32 ±2		0.04		0.14	0.19		0.23			
TS 5	0/60/40-0.59-SO	same	same	32 ±4		0.01		0.06	0.11		0.18			
					MeHg Destruction [T = 23°C ±2°C] (7)									
		Target Test Duration, h >>>			0	2	4	6	24	29	48	53	72	77
TS 1	Na_2S	Actual Test Duration, h >>>			0.0	2.4	4.4	6.1	23.6	28.0	46.5	51.6	73.6	77.0
TS 1	same	108		mg/L >	112	16.3	27.8	16.1	3.77	2.71	1.99	2.19	2.02	1.71
TS 1	same			fraction >	0	0.85	0.75	0.86	0.97	0.98	0.98	0.98	0.98	0.98
TS 2	10/45/45-0.85-SL	Actual Test Duration, h >>>			0.0	2.4	3.4	5.1	22.4	26.8	NM (8)	NM	NM	NM
TS 2	same	334		mg/L >	383	315	187	145	288	114				
TS 2	same			fraction >	0	0.18	0.51	0.62	0.25	0.70				
TS 3	0/60/40-0.85-SL	Actual Test Duration, h >>>			0.0	1.2	3.3	5.0	22.4	26.8	NM	NM	NM	NM
TS 3	same	119		mg/L >	80.4	33.5	75	98.3	53.8	20.4				
TS 3	same			fraction >	0	0.58	0.07	-0.22	0.33	0.75				

(1) TS = Test Series
(2) Grout batch used was 2QCY2019
(3) Name for grout tests = X/Y/Z-AA-BB: X=mass% of cement, Y=mass% of slag, Z= mass% of fly ash, AA=water-to-solids grout premix mass ratio, BB=SL (slurry) or SO (solid).
(4) Samples were pulled before and after filling all reactors to measure MeHg and Total Hg concentrations, before adding sulfide. The measurement uncertainty is given as ±20% (2 sigma).
(5) The data for the 1-hour duration and the 24-hour durations came from the preceding scoping test for comparison [SRNL-STI-2020-00013].
(6) Each reactor had a slightly different duration. The times listed are the average for all test series. The exact times are list the appendices for each test series.
(7) The MeHg destruction test differed from the Methane-Generation Test Series in two ways: (1) Times were different for convenient shift work and (2) no attempt was made to heat mixtures to 35°C, which required equipment for heating, monitoring, and over-temperature control in a Radiological Buffer Area. The difference between 35°C and the room temperature (in this case 23°C ±2°C) did not expect to have a significant impact on MeHg destruction. All other aspects were the same, e.g., mixing, masses, vessel geometry, etc.
(8) NM = Not Measured because after the 29-h tests the grout was too viscous to retrieve any liquid to analze; therefore, those tests were terminated.

3.1 Effect of Time: CH_4 production and generation from 1 hour to 4 days of gas generation at 35°C

To expand on the scoping data [6.4] for two test durations of 1 and 24 hours, eight more duration were added of 2, 4, 6, 18, 30, 48, 72, and 96 hours. Furthermore, it was important to demonstration methane generation during the first few hours of grout production, that is, shortly after saltstone is manufactured and during its transfer to the Saltstone Disposition Facility (SDF), while the grout is still a slurry, and then up to 4 days from formation. This is the reason Test Series 2 and Test Series 3 were performed with grout

mixture with a slightly dilute water-to-solids grout premix of 0.85 instead of the standard 0.59 so the grout could remain a slurry while being continuously mixed for the duration of the test periods. The results are shown in Figure 3 as squares and triangles. Also included in the figure are the results of the mixture that did not contain grout solids but only a source of sulfide, i.e., Na_2S, that would react faster and more completely with the 100 mg/L of MeHg to demonstrate the limit for the production of methane. It is important to remember that these results of absolute methane concentrations are only for the small-scale sealed reactors; however, since all tests were from reactors of the same size, comparisons between test series are appropriate and elicit important information. As expected, the Na_2S of Test Series 1 generated more methane than either of the test with grout and it was on the order of 2.5 times greater. The error bars show the 95% confidence level and is discussed in detained in Appendix C.

All three mixtures reached an asymptote after 1 or 2 days. In all cases the mixtures had an excess of sulfide, see Table 1, to react with MeHg to produce methane, but only the T50SS simulant with 100 mg/L spiked with Na_2S converted most, or all, of the MeHg to methane. This fact can be better seen in Figure 4, which depicts the results from the MeHg destruction test for Test Series 1, with Na_2S.

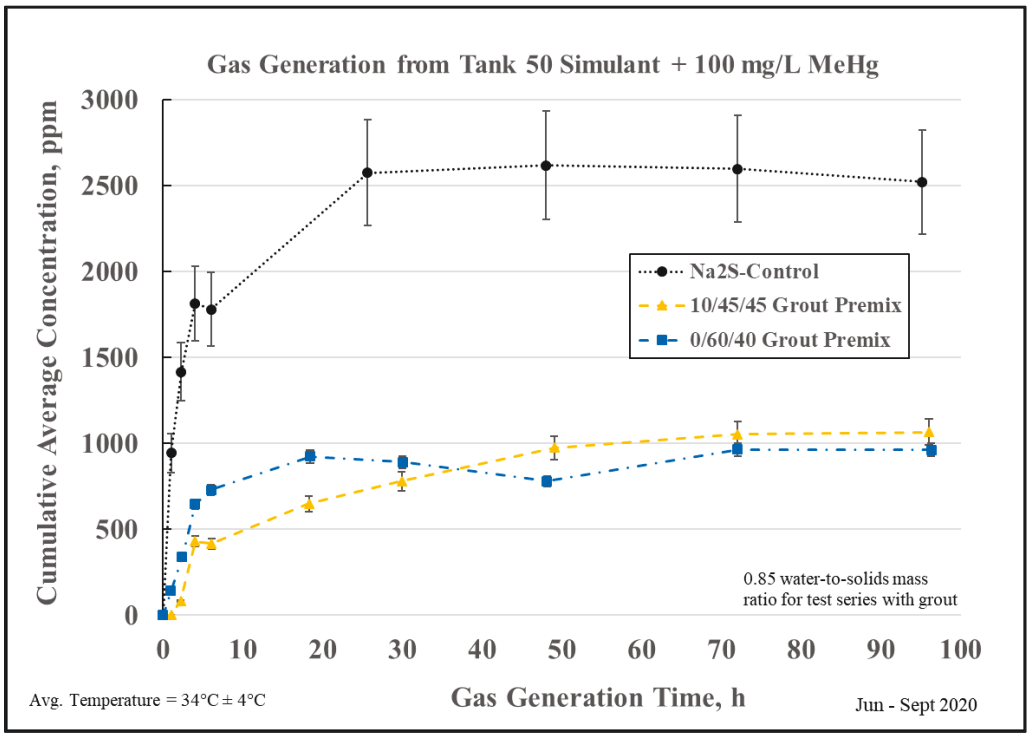

Figure 3. Comparison of Test Series 1-3 of methane concentrations up to 4 days

To compare Test Series 1 results of the first campaign to those of the second campaign, a separate but similar mixture of T50SS + 100 mg/L + Na_2S was made, see Appendix K for a detailed discussion. For this second campaign, instead of measuring the methane off-gas, the mixture was periodically sampled to measure the diminishing concentration of MeHg by a GC-CVAFS analysis. The triangles in Figure 4 indicate how much of the MeHg was destroyed relative to the starting concentration of 100 mg/L, while the circles, from Test Series 1, indicate the increasing fraction of methane produced relative to the total moles of methane that would be produced if 100% of the MeHg reacted with the reduced sulfide available from Na_2S. Within a measurement uncertainty at the 95% confidence level both data sets correlate well, which implies a one-to-one relationship. That is, as a mole of MeHg is destroyed as it reacts with reduced sulfide to produce a mole of methane, and the reaction is between 95% and 100% complete after approximately 24 hours. For the two grout mixtures the comparison from the two campaigns is more complex so they will

be discussed in each of the appropriate appendices, but their molar conversion fractions are closer to 60% to 70%, which is probably due to the more complex mechanism to release several forms of reduced sulfide from slag.

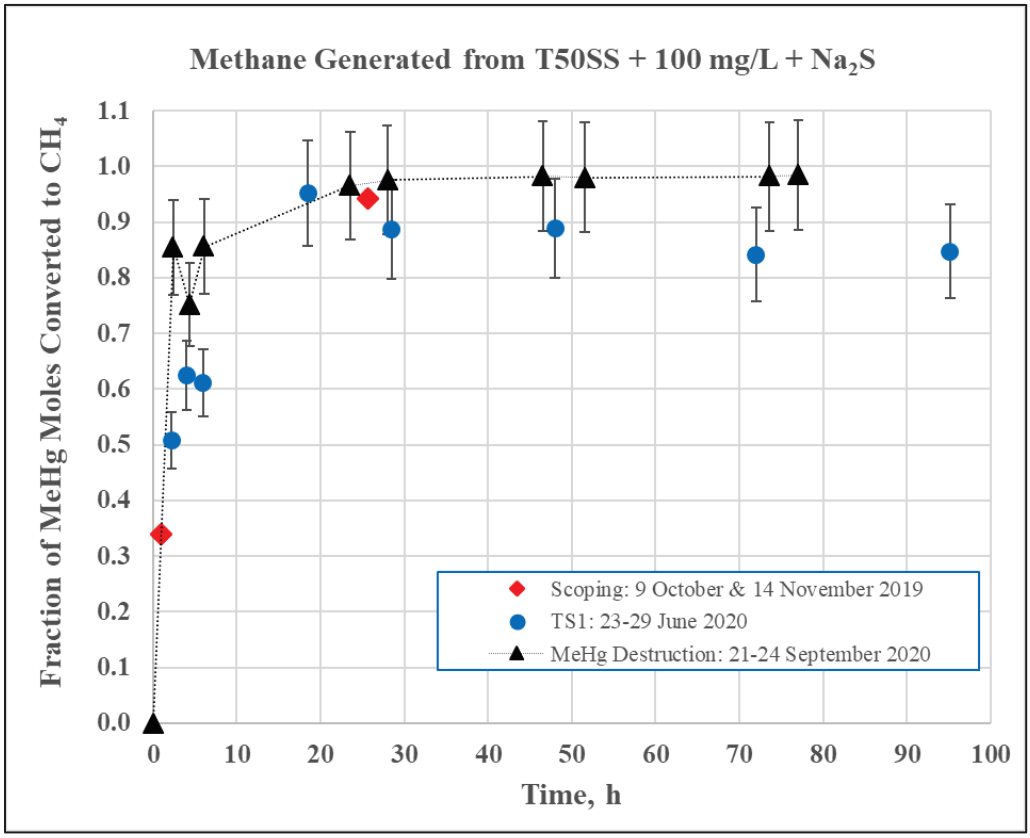

Figure 4. Comparison of Test Series 1 conversion of moles of MeHg to moles of CH_4 destruction of moles of MeHg relative to the initial concentration

One of the goals of this study was to better understand methane generation during the first few hours of grout production, and as can be seen from Figure 3 that while both mixtures of 10/45/45 and 0/60/40 of grout premix solids reach approximately the same asymptote of approximately 1000 ppm after more than 2 days, the rise of the 10/45/45 is slower. That is, the increase of methane of the 0/60/40 appears to be faster and attains the asymptote in less than 24 hours. To better see these results the first six hours after grout was formed is shown in Figure 5. Once again, the methane generation from the mixture with Na_2S is well above both grout mixtures by several factors. However, between the two grout mixtures the 0/60/40 increases to the asymptote faster. The major differences between the two grout mixtures is that the 0/60/40 mixture has 15% more slag than the 10/45/45 mixture and has no cement. Because both mixtures had an excess of sulfide to react with available MeHg, Table 1, it is not clear that the higher concentration of sulfide, due to having more slag, is the cause. Furthermore, the presence of cement, containing Ca^{2+}, may play a role that may slow down the release of S^{2-}, but this hypothesis is not proven by these data. What is known [6.22] is that the sulfur breakdown from slag is complex and produces polysulfides, which will probably have an impact on its availability to react with MeHg to produce methane. However, after 2 days it appears the methane released is similar for both mixtures, Figure 3.

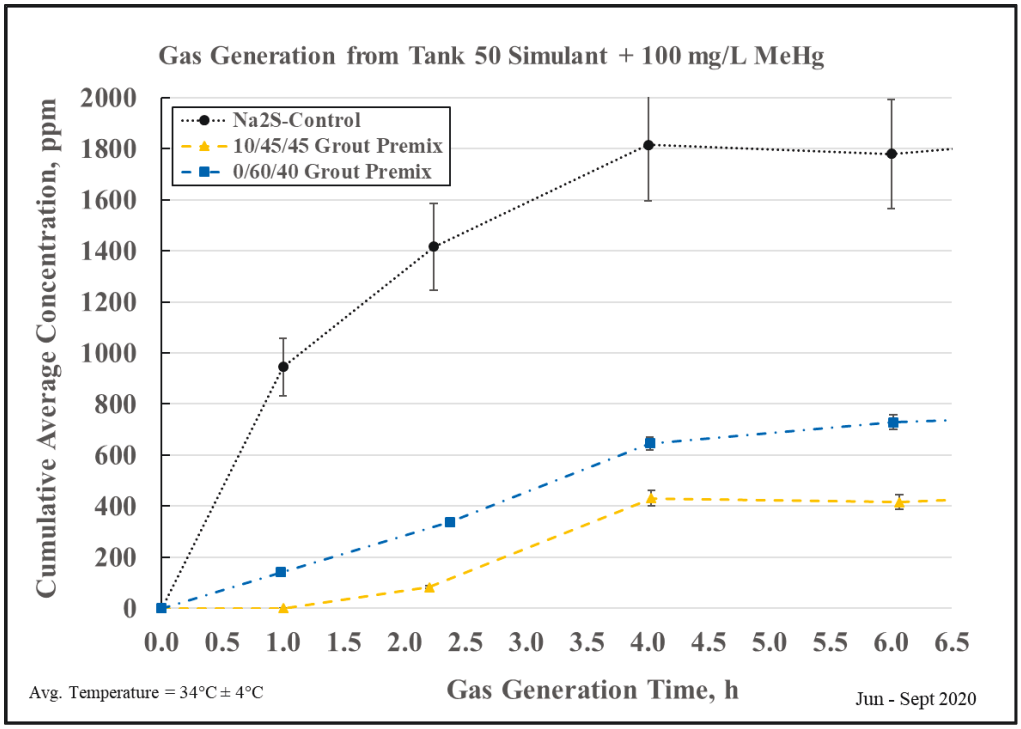

Figure 5. Comparison of Test Series 1-3 of methane concentrations for the first 6 hours

A similar set of results can be seen more comprehensively as methane gas generation rate (MGR) since they are relative to the volume of simulated waste, i.e. T50SS, and adjusted to 25°C and 1 atm. Figure 6 shows the results and it is important to remember that each successive reactor with longer time durations show the average cummulative rates and not instantaneous rates. That is, the MGR for the last reactor at 4 days has accumulated all the methane generated over the 4-day period and the MGR is not an instantaneous rate at 4 days, but the average rate for the period of 4 days. As just discussed with the concentration results, the larger difference occurs during the first couple of days, but with time the curves begin to merge as MGR becomes successively smaller. The data points include the calculation uncertainties for a 95% confidence level and as time continues the curve begin to merge.

To better see the trends all the data in Figure 6 for each test series have been fit to power law models which show good correlations with correlation coefficients of better than $R > 0.99$. Only data recorded from the peak generation rate onward for a given data set, see Table 10, were included in those curve fits and not those data for the increasing MGR. Because the reactor accumulates the generated methane with time the curves begin to merge within measurement uncertainty. That is, the rate tapers off for all the mixtures; however, the MGRs for the Na_2S mixture appear to bound the other two mixtures across all time intervals for the 4 days.

Another way to observe the results is from the changing MeHg concentrations, based on the methane measured. In Figure 7 a logarithmic display of concentration with time is depicted. It appears that for the control mixture with Na_2S, circles, and for the grout without cement, squares, after 24 hours reactions have stopped because the slope of the curves are no longer descending. For the 10/45/45 mixture, triangles, the reactions are slowing but since the slope of the curve is still descending this implies the reactions may still be continuing; however, differences among the curves at 4 days are statistically insignificant.

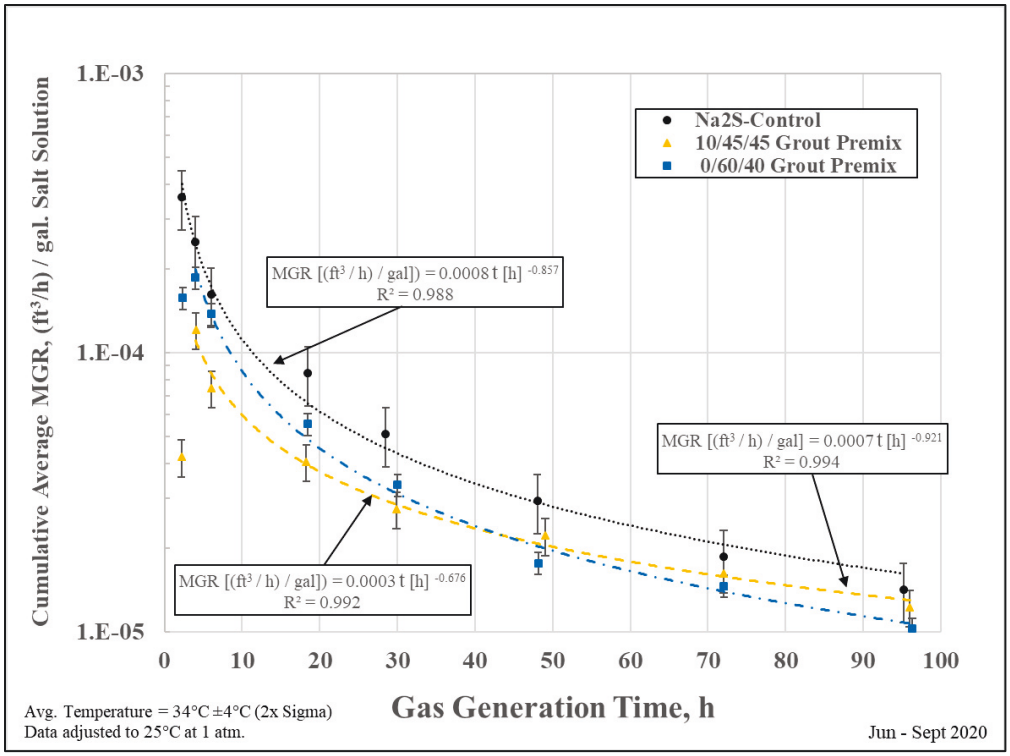

Figure 6. Comparison of Test Series 1-3 of the cumulative average MGR up to 4 days

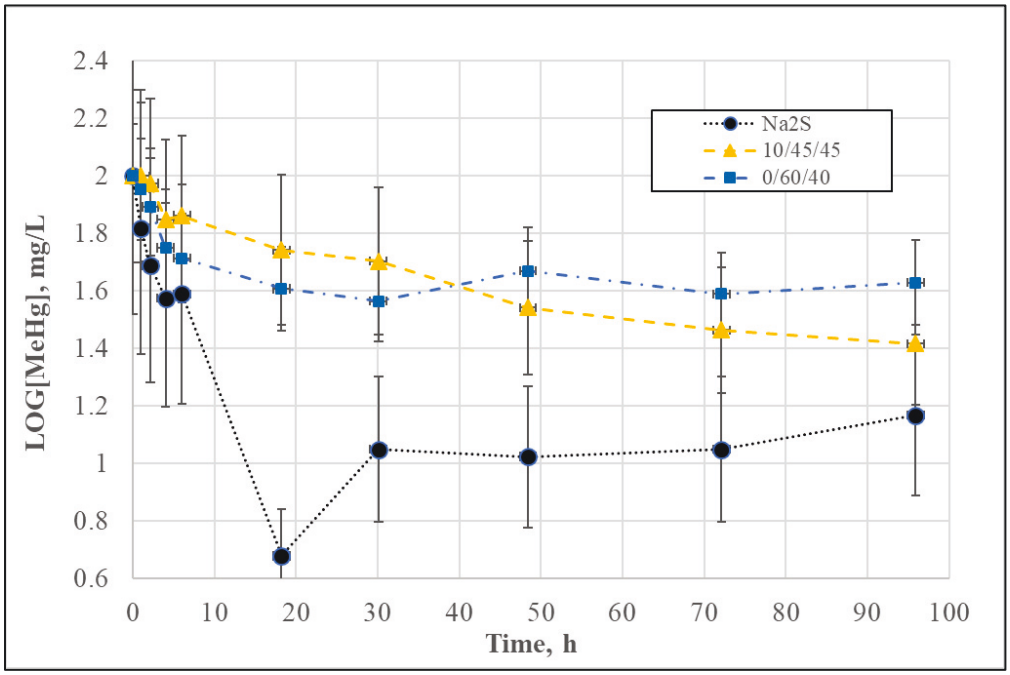

Figure 7. Comparison of Test Series 1-3 of the Log[MeHg] versus time. Note, concentrations were based on the moles of CH_4 released

Focusing in on the first six hours, Figure 8, MGR peaks the fastest for the Na_2S mixture within the first hour. Even though the two grout mixtures are being continually stirred their MGRs are lower and they peak at four hours. As seen for methane concentration, the MGR for the 0/60/40 mixture increases during

the first hour while no methane for the 10/45/45 was detected. As previous explained, the 0/60/40 mixture has 15% more slag than the 10/45/45 mixture and has no cement.

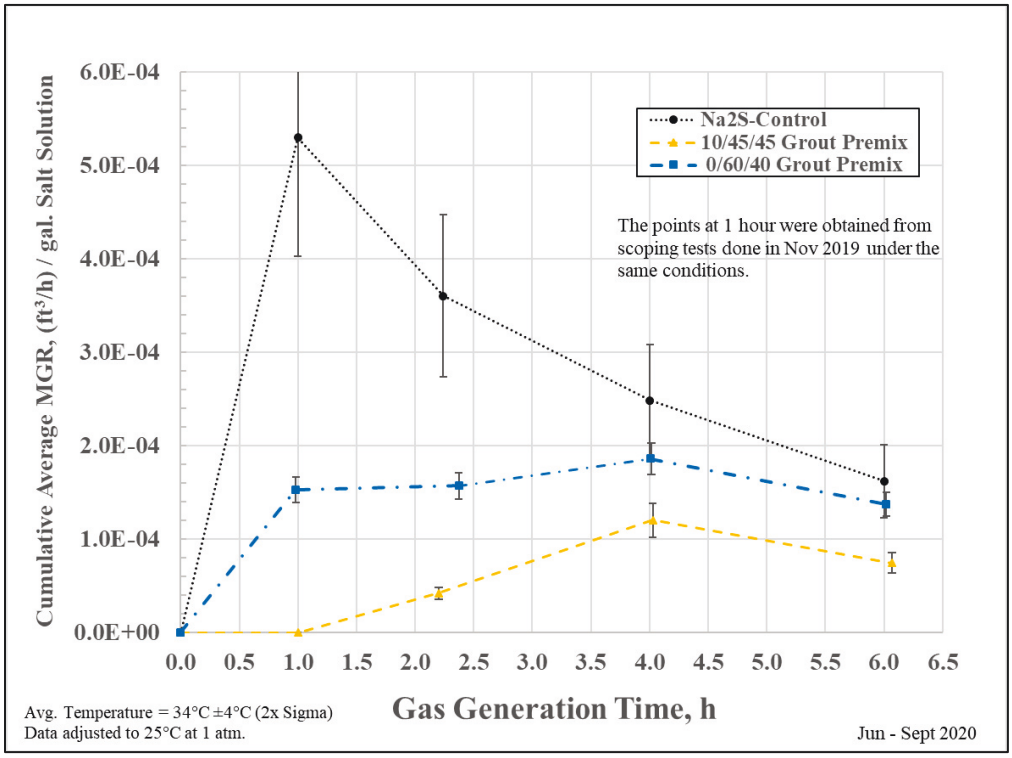

Figure 8. Comparison of Test Series 1-3 of the cumulative average MGR for the first 6 hours

A weakness of using sealed reactors, which accumulate gas over time, is that making measurements of instantaneous MGR is not possible. However, an attempt was made to look at the average MGR over the intervals between the 9 test durations from the first interval, 0-1 hour, to the last interval, 72-96 hours. Employing the 1-hour duration from the previous scoping study [6.4], the 0-1 hour interval was obtained and shown in Figure 9 as the open symbols. All other intervals were obtained from the results from the current study and shown in the figure with closed symbols. The symbol shapes relate to each Test Series as indicated in the figure legend. Figure 9 shows the results and the 9 intervals, which are also listed on the figure. It appears 1st interval produced the peak MGR for the control, Na_2S, mixture, which means it occurred during that first hour of operation. For both the grout mixtures the peak MGR occurred during the 3rd interval, i.e., 2 to 4 hours; however, both mixtures did not travel the same path. As shown in Figure 8, the grout without cement produced methane during the first hour, and then idled for the 2nd interval, i.e., from 1 to 2 hours, to then peak during the 3rd interval, i.e., from 2 to 4 hours. For the 10/45/45 grout mixture nothing happened until after the first hour and then slowly increased to peak during the 3rd interval, i.e., between 2 to 4 hours. These differing grout results are probably due the complex process which sulfides are leached from the mixtures. For all three mixtures it appears that during the 4th or 5th intervals, i.e., less than 18 hours, the MGR for all three mixtures drops to markedly lower levels. Methane is probably still being generated after 18 hours, but at a rate no longer detectable for this study.

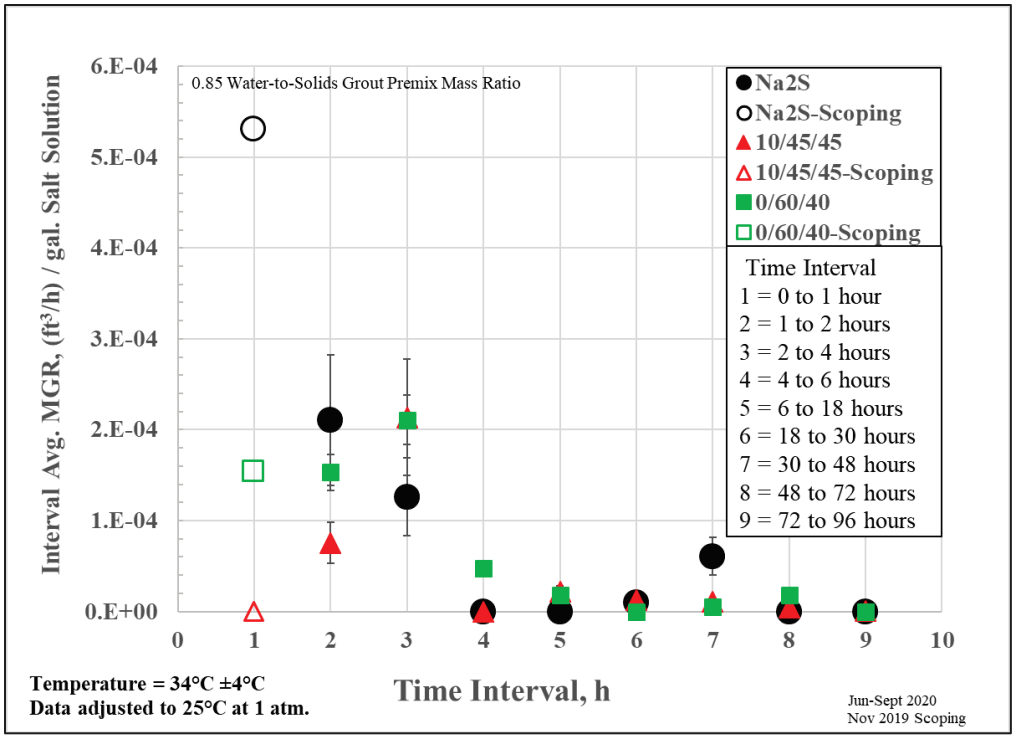

Figure 9. MGR at each time interval from T50SS with 100 mg/L MeHg

So far, all the results discussed concern the three main mixtures of Na_2S, 10/45/45 grout, and 0/60/40 grout under continual stirred conditions. There are two more test series that involve the two grout mixtures that were not stirred after being mixed for 30 minutes in the sealed reactors. Those were Test Series 4 and 5. These last test series were performed to demonstrate if the gas generation results differ from the stirred, more dilute mixtures and if there is a difference between the more dilute mass ratio of 0.59 and 0.85 of water-to-solids grout premix. The results of Test Series 4 and Test Series 5 are discussed in detail in Appendix I and Appendix J, respectively.

Figure 10 depicts the results of both mass ratio mixtures and the error bars shown indicated the statistical uncertainty at the 95% confidence level that can be found in Appendix C. Because these test series were done to compare to each other and to the mixed grout mixtures there were only done for periods of up to 30 hours, which allowed all 8 reactors to be used for each series so that four reactors contained the 0.59 mass ratio and four reactors contained the 0.85 mass ratios. The difference between the two test series is that TS4 used the 10/45/45 grout mixture and TS5 contained the 0/60/40 grout mixture. From the results three comparisons that can be made for these solid grout analyses.

The open symbols represent the standard mass ratio of 0.59 and the closed symbol represents the dilute mass ratio of 0.85. Within the 95% confidence level there is no significant difference. A statisical comparison is shown in Exhibits 4 and 5. Appendix C confirms there is no significant difference. The conclusion is the results from either mass ratio should accurately demonstrate gas generation and gas generation rates.

The triangles symbols represent the current grout premix make-up of 10/45/45 and the diamonds symbols represent the proposed new grout premix make-up of 0/60/40, or the cement-less mixture. Once again, within the 95% confidence level there is no significant difference. The conclusion is the results from either mass ratio should accurately demonstrate gas generation and gas generation rates. This result for solidified grout is slightly different from the continually-mixed grout. It appears that as the grout solidifies the gas

generation is similar, probably due to the fact that leaching the sulfide from the slag solids become more difficult that when the solids are in continual motion that can enhance leaching.

The last comparison is between the results for solid grout, Figure 10, and continually mixing grout, Figure 3. There is a significant difference with the mixing grout, generating aproximately 800 ppm at 30 hours, while the solidified grout ranging between 200 ppm to below 400 ppm. As mentioned in the preceding paragraph, the solidified grout probably makes it more difficult for methane to be released. This difficulty may be the solidified grout preventing the release of formed methane or the grout hindering sulfide availability to react with MeHg to create methane. It is possible that both mechanisim exist.

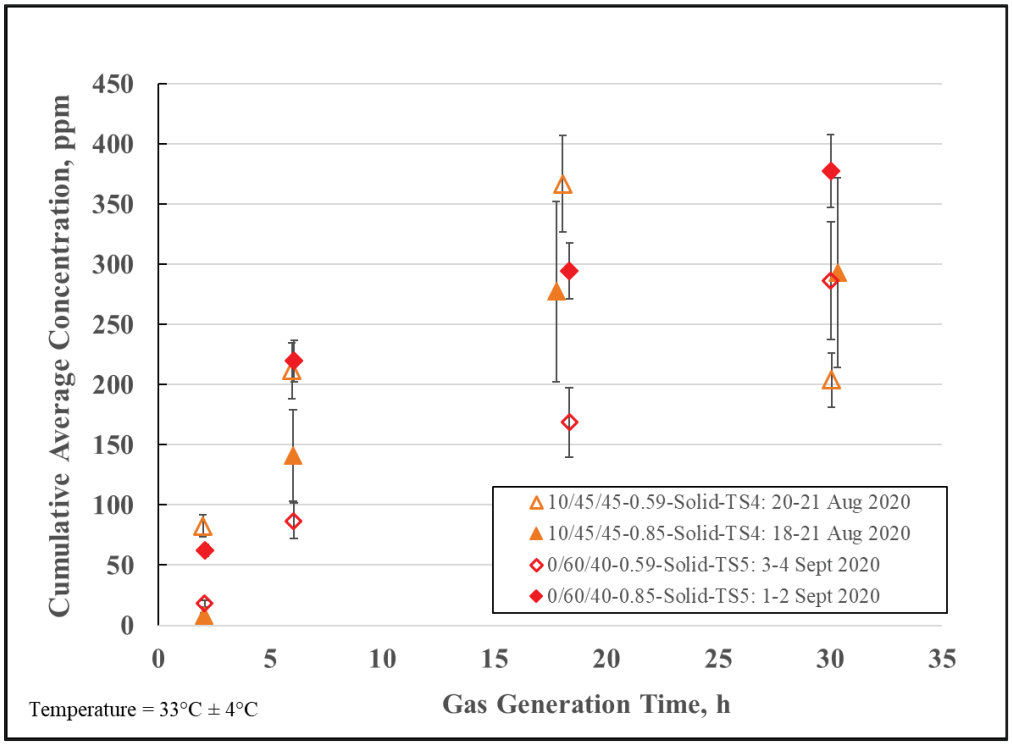

Figure 10. Comparison of Test Series 4 to Test Series 5 of methane concentrations to 30 hours

The rate of methane gas release, MGR, is shown in Figure 11 for both mixtures of solidified grout, which like for methane concentration basically indicate the data sets are statistically the same, Figure 10. Comparing the rates for mixing to solidified grout, the peak MGR is higher and faster with the continually stirred mixtures reaching 1 to 2 x 10^{-4} (ft^3/h)/gal after 4 hours, Figure 8, while the solidified grout reaching its MGR peak at 1 to 4 x 10^{-5} (ft^3/h)/gal at approximately 6 hours, Figure 11. That is, the MGR from solidified grout appears to be approximately an order of magnitude lower.

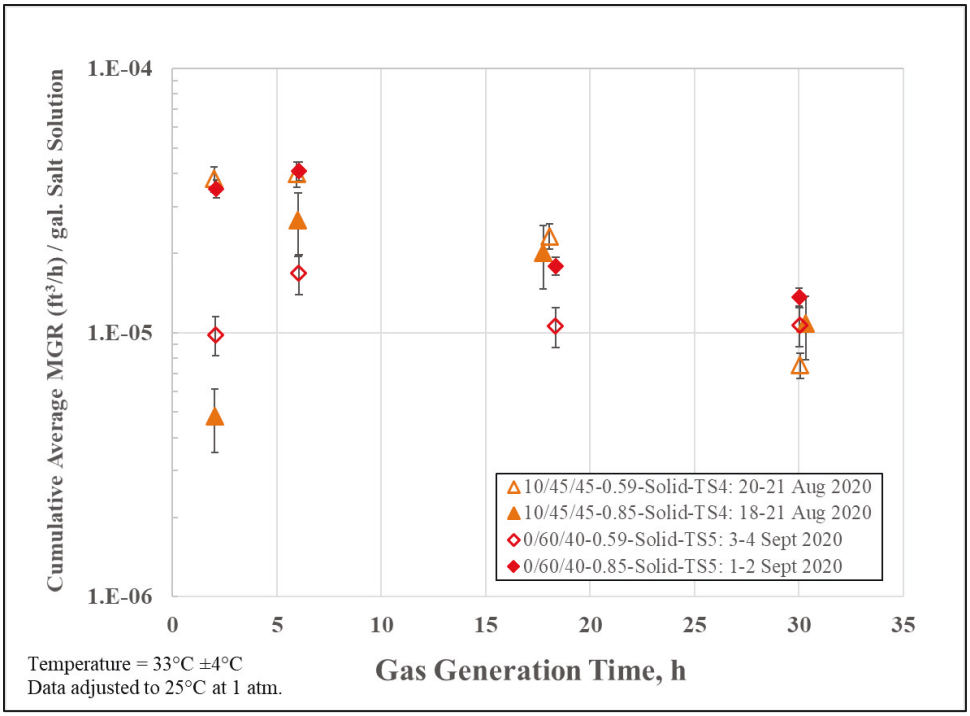

Figure 11. Comparison of MGR between Test Series 4 and Test Series 5 to 30 hours

Finally, the MeHg results for all five test series can be compared in many ways, but they are shown in Figure 12 in a similar fashion as depicted in Figure 4, i.e., depicting the moles of methane released relative to the moles of available MeHg.

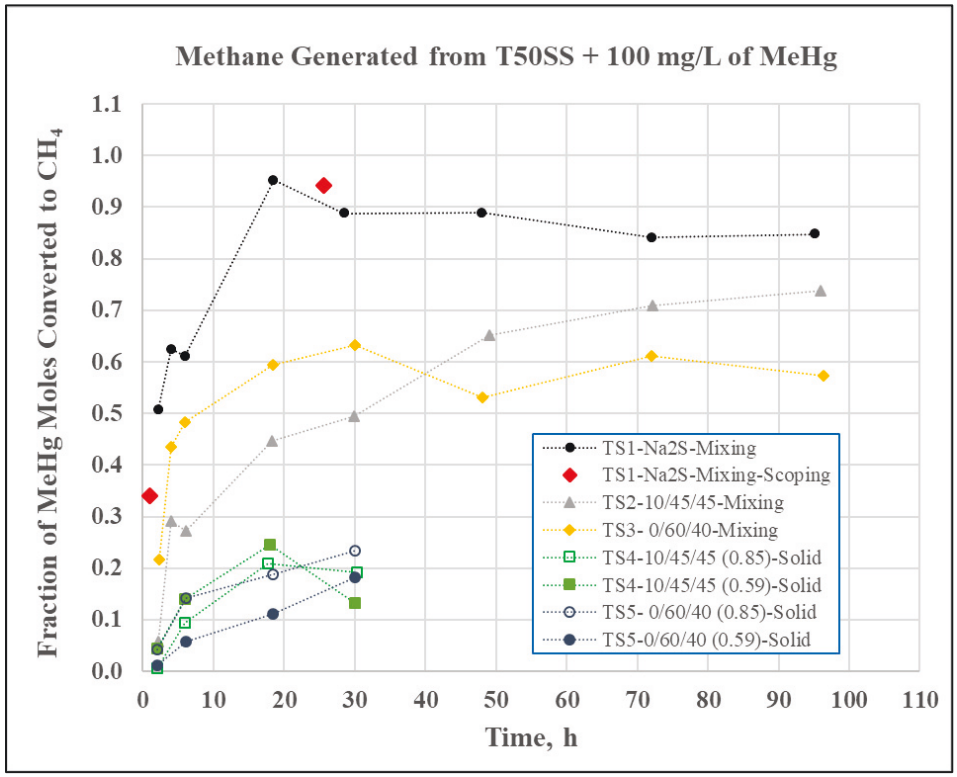

Figure 12. Fraction of methane moles released normalized to initial moles of MeHg

As shown in Figure 4, for Test Series 1, the mixture with Na_2S, which is the top set of data points, produces methane the fastest of all the mixtures and converts at least 90% of the MeHg to methane in less than 24 hours. For Test Series 2, the 10/45/45 grout mixture, which is the triangle set of data points in Figure 12, the data slowly increases to a peak at 96 hours converting just above 70% of the MeHg to methane. It appears that this grout mixture may still be reacting as implied by the information shown in Figure 7 or the 10/45/45 mixture. For Test Series 3, the 0/60/40 grout mixture, which is the diamond set of data points in Figure 12, the methane concentration increases rapidly during the first 6 hours, then increases at a slower rate to a peak at 30 hours at which point appears to have reached an asymptote of converting MeHg to methane at around the 60% level. After 4 days both the 10/45/45 and the 0/60/40 behave similarly. The remaining two data sets, i.e., Test Series 4 and 5, which are from both grout mixtures that were allowed to solidify, are not significantly distinct and both appear to reach a peak at approximately 20% of converting MeHg to methane or a factor of 3 less than the same mixtures that were maintained in slurry state.

3.2 First Order Chemical Reaction Kinetics

This section is a revision of a similar discussion made for the previous scoping work [6.4] to show increased prediction accuracy with the current larger data sets. For the previous study only data at 1-hour and 24-hours were available for the MeHg concentrations calculated from the methane gas measurements. This current study includes a larger data set to 96 hours of MeHg, also calculated from methane gas measurements, but also includes data to 77 hours from direct measurements of MeHg in the mixtures themselves. This analysis is only done for the Na_2S mixture because those with grout are more complex for which a 1st-order chemical reaction to release methane is not expected.

The proposed general chemical reaction to produce methane from the reaction of MeHg and excess reduced sulfide (S^{2-}) in the caustic Tank 50 aqueous simulant solution is shown in Equation (2).

$$MeHg + Na_2S(excess) \rightarrow methane(gas) + mercury\ species(soluble) \quad (2)$$

The rate equation for this reaction can be written in the form shown in Equation (3).

$$Rate = k[MeHg]*[Na_2S] \quad (3)$$

Since the sulfide concentration in Equation (3) is in high excess relative to the MeHg concentration, see the S/Hg column in Table 1, Equation (3) can be written as a 'pseudo-first order' expression shown in Equation (4)

$$Rate = k'[MeHg], \text{ with } k' = k[Na_2S] \quad (4)$$

The 100-mg/L data shown in Table 10 (Moles CH_4 Generated from Versus Moles MeHg Available, with attention to Na_2S) can be used to calculate the concentrations of MeHg. Furthermore, the 100 mg/L data shown in Table 10 (MeHg Destruction Test, with attention to Na_2S) the measured concentration are also given. Both sets of data are depicted in Figure 13. Logarithmically, the results are shown to be approximately linear over the first 24 hours and for this first-order reaction. From the trend line values of k' can be obtained from the Equation (5) [6.18].

$$Log[MeHg]_t = (-(k'/2.3))*t + Log[MeHg]_0 \quad (5)$$

The value of k' is calculated to be 0.0386 x 2.3 = 0.08878 h^{-1}, for MeHg data calculated from methane measurements, those data have an uncertainty of ±24% at the 95% confidence level, and is calculated to be 0.0468 x 2.3 = 0.10764 hr^{-1}, for MeHg data measured directly from the GC-CVAFS analysis for which have a measurement uncertainty of ±20% at the 95% confidence level.

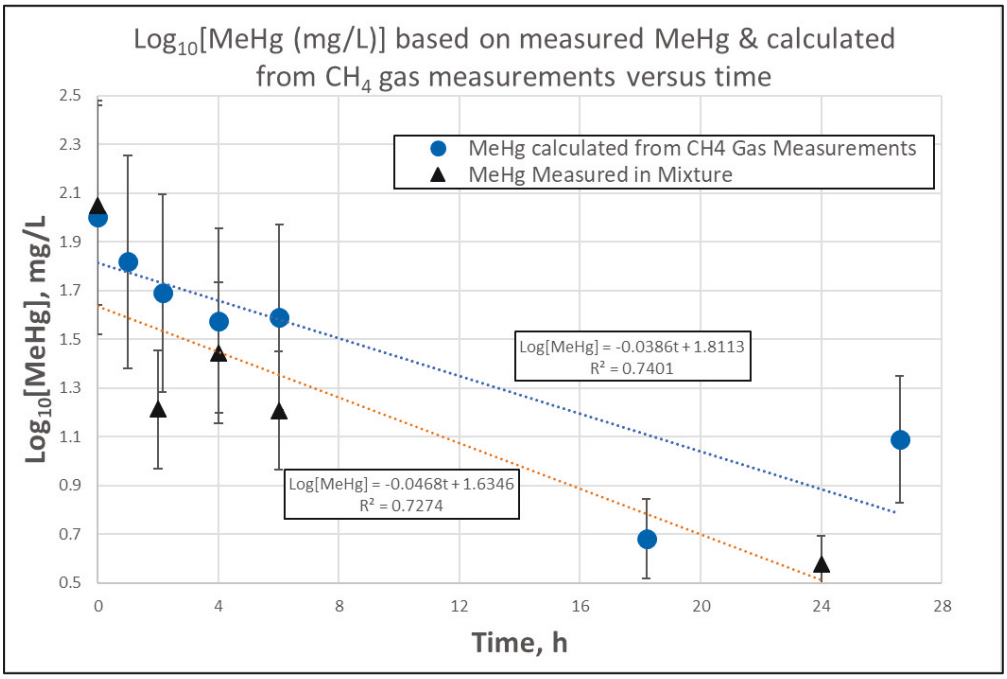

Figure 13. 1st order reaction with starting mixture of T50SS + 100 mg/L of MeHg + 12 g/L Na_2S

Assuming that the MeHg reaction is pseudo-first order at any concentration of MeHg, as long as soluble sulfide is in high excess, one can use the rate constants derived from the testing with 100 mg/L of MeHg at 35°C to calculate the amount of MeHg that would remain at 35°C at varying MeHg starting concentrations. For instance, from the previous scoping study [6.4] for one test the T50SS simulant was spiked with 200 mg/L and with 12 g/L of Na_2S. After 26.8 h the results showed that 91.5% of the available MeHg moles were converted to methane; therefore, after 26.8 h the MeHg remaining can be estimated to be 200 mg/L x (1 - 91.5/100) = 17 mg/L. Now, Equation (5) with the calculated rate constants, k', the remaining MeHg can be predicted for the starting concentration of 200 mg/L. For the first rate constant the remaining MeHg concentration after 26.8 h is predicted as 10^(-((0.08878 h^{-1} / 2.3)*26.8 h)+Log[200 mg/L]) = 18.5 mg/L, and for the second rate constant the MeHg is predicted to be 10^(-((0.10764 h^{-1} / 2.3)*26.8 h)+Log[200 mg/L]) = 11.1 mg/L. The predicted values of 11.1 to 18.5 mg/L of MeHg at 26.8 hours bound the estimated value from the previous study. This is a significant improvement from the original prediction [6.4] of 27 mg/L of MeHg. Note that for the current study the MeHg measurement continued on past 24 hours to 4 days; however, after 24 hours the methane production from the control mixture of MeHg and Na_2S was shown to be complete, see Figure 4, so the first-order reaction no longer applied from then to 4 days.

Test Series 2-5, which contained various mixtures of grout premix additives, were not used for the first-order chemical reaction kinetics because those reactions are complex and may not be first order. The sulfur contained in the slag solids of grout needs to leach into the T50SS and the sulfur will be in both reduced, i.e., S^{4-}, S^{3-},S^{2-}, and non-reduced, i.e., SO_4, forms, so the reactions are more complex [6.22].

3.3 Hg Speciation after Sulfide Reacts with MeHg to produce CH_4

The third campaign of this study was to investigate Hg speciation. During previous scoping work [6.4] to demonstrate methane generation and rates in sealed reactors after 1 hour and 24 hours, the mixtures were filtered and sampled to analyze for the total Hg [by a Direct Mercury Analyzer (DMA)]. For that work, the mixtures of the pH~14 Tank 50 salt solution simulant were spiked with 0, 100, and 200 mg/L of soluble MeHg. For this study only 100 mg/L was used. The mixtures were tested in the "as is" condition, or further spiked with sources of sulfide, i.e., Na_2S or grout solids, which contained sulfur in the slag solids that

release sulfides. The results showed that for the samples with sulfide, the MeHg was destroyed, but total soluble Hg concentration did not change in these filtered, strongly alkaline mixtures. This was surprising; therefore, in the Run Plan [6.3] stated that samples with depleted MeHg would be analyzed by Nuclear Magnetic Resonance Spectroscopy to try to understand what forms of soluble groups of Hg exist after MeHg is destroyed. Appendix L contains a detailed discussion of the results for the summary give here.

The NMR spectrometer was used at two frequencies, one to focus on atoms of mercury, referred to as ^{199}Hg-NMR and one to focus on atoms of hydrogen, referred to as H-NMR. H-NMR was used because its detection capabilities are more than an order of magnitude more sensitive than ^{199}Hg-NMR. Two samples were made for this analysis. The first was a 5-mL sample of T50SS simulant + 100 mg/L of MeHg and no sulfide, to be a control, which would retain its concentration of MeHg. The second was a 20-mL sample of T50SS simulant + 100 mg/L of MeHg + 12.6 g/L of Na_2S, which is the same as the mixture made for Test Series 1 for the current study. Samples with grout were not made and analyzed because the sulfides released from the slag in grout would result in a complex solution that would be harder to analyze and understand.

After both samples were spiked with 100 mg/L of MeHg, they were measured for total Hg. The control sample had a total Hg of 113 mg/L. For the second sample the total Hg was 112 mg/L This second sample was spiked with sulfide and measured several days after spiking to ensure all the MeHg was destroyed, as shown in Figure 4. This is consistent with the previous study [6.4].

From the ^{199}Hg-NMR analysis the following was found.

1. The control sample without the Na_2S spike maintained the full 100 mg/L of MeHg species in the cation. form of $(CH_3Hg)_3O^{1+}$. No other compounds containing Hg were identified.
2. The second sample with the Na_2S spike there was no presence of $(CH_3Hg)_3O^{1+}$, which helped to generate methane, while the full concentration of 100 mg/L of Hg remained in soluble forms. Those Hg forms were:
   a. 60% of $(S\text{-}Hg_2\text{-}S)^{2-}$,
   b. 32% of $(Hg(NO_3)_2$, and
   c. 8% of $(R\text{-}Hg\text{-}S)^{1-}$, with 'R' possibly representing $-CH_2-OH$ or $-COO^-$ (carboxylate).

These assignments were made using literature discussed in Appendix L. The sources of carboxylate could possibly be:

- Partial oxidation of carbon sourced from MeHg in the sample spiked with Na_2S, or
- Organic contamination. However, the control sample without the Na_2S spike showed very little evidence of contamination. However, the base simulant, which used the same reagents for a similar simulant in a previous study [6.5], was found to have tramp organic compounds at trace concentrations.

From the H-NMR analysis the following was found.

1. In the control sample, the full 100 mg/L of MeHg remained in the form of CH_3HgOH. This is the chemical used to spike all samples with MeHg.
2. In the second sample species tentatively identified showed:
   a. formate, $H\text{-}COO^-$ with could be connected to either Na^+ or Hg^+,
   b. methanol, CH_3OH,
   c. acetate, CH_3COO^-, and
   d. dimethylmercury ($(CH_3)_2Hg$), but its intensity peak was very small.

In conclusion, the NMR analysis was used to confirm presence of primarily MeHg in the control sample and to identify three different soluble Hg-containing species (from ^{199}Hg-NMR) and three other organic species (from H-NMR) that result from the reaction of MeHg and soluble sulfide in the Na_2S spiked salt solution. These soluble Hg species could indeed account for the analyzed soluble total Hg found in post-reacted samples for this study and previous scoping tests [6.4]. The NMR analysis and results presented here suggest that this technique could be applied to radioactive caustic tank waste samples from SRS Tank Farm to further investigate and understand the various Hg species present.

4.0 Conclusions

The testing occurred three campaigns: methane generation, MeHg destruction, and Hg speciation. For the results from all three campaigns the conclusions follow.

- Combining MeHg with material containing sulfide, e.g., Na_2S or slag, generated methane gas while MeHg decomposed. This finding indicates that sulfide in the pH=14 salt solution is causing the destruction of MeHg resulting in methane gas.
- Methane production correlated directly with MeHg concentration, especially from the Na_2S, but less so from the grout mixtures, from which the sulfide release is more complex.
- MGR was highest during the first 4 hours of forming saltstone.
- Methane is generated at a faster rate for 0/60/40 grout mixture than the 10/45/45 grout mixture for the first 6 hours, but after 2 days the concentrations of methane are similar.
- For both grout mixtures cumulative average MGR peaks at approximately 4 hours: 1.2 x 10^{-4} (ft^3/h)/gal for the 10/45/45 grout mixture and 1.9 x 10^{-4} (ft^3/h)/gal for the 0/60/40 grout mixture, or about 60% larger.
- For both grout mixtures the average MGR peaks between 2 to 4 hours but in reaching that peak the 0/60/40 grout mixture gets there faster. At 1 hour the 0/60/40 mixture is almost at its peak while for the 10/45/45 mixture the MGR at 1 hour is still zero.
- After 18 hours the average interval MGR drops to zero, especially for the 0/60/40 grout mixture. The 10/45/45 grout mixture may still be reacting after 4 days.
- With continuous mixing there is no significant difference for either methane generation or MGR between grout water-to-solids (grout premix additives) mass ratios of 0.59 (non-dilute) and 0.85 (dilute).
- Methane net generation and release for solidified grout is 2 to 3 times less than for grout continually mixed.
- As shown in each of the appendices for the test series, the generation of H_2, N_2O, and CO_2 were also detected but at rates of approximately an order of magnitude less than methane.
- A first-order chemical reaction equation based on first 24-hours of results from the Na_2S spiked mixture of T50SS + 100 mgL of MeHg can be used to predict the change in MeHg concentrations in time from mixtures that start with other initial concentrations of MeHg in the presence of excess sulfide.
- Mercury remained soluble in the sulfide-bearing pH=14 solution. That is, the total mercury remained constant at the initial spiked concentrations after methane was produced and MeHg destroyed. Therefore, S^{2-} is not useful to remove Hg (precipitate) from T50SS when pH=14.
- NMR analysis confirmed the presence of primarily MeHg in a control sample of T50SS simulant spiked with 100 mg/L of MeHg, but no sulfide. From a second sample spiked with Na_2S, no MeHg was found, but full concentration of 100 mg/L of Hg remained in soluble forms. Those forms were in a series of anion groups, tentatively identified as three different soluble Hg-containing species (from ^{199}Hg-NMR) and three other organic species (from H-NMR). These soluble Hg species could indeed account for the analyzed soluble total Hg found in post-reacted samples for this study and previous scoping tests.

5.0 Recommendation for Future Work

- The NMR analysis could potentially be applied to radioactive caustic waste-tank samples from SRS Tank Farm to further investigate and understand the various Hg species present.
- All decomposition species identified in the NMR analyses are based on literature information. Further studies with spike additions of some, or all, of the decomposition species into a reacted system would be required to further confirm the presence of these compounds.

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Appendix A: Slag Analyses

SRNL was directed to perform analysis of various slags related to toxicity testing associated with the Saltstone Disposition Facility (SDF) [6.19]. Various slags were analyzed by X-ray Diffraction (XRD) and dissolution followed by chemical analysis. [6.18]. The XRD shown in Figure 14 of Holcim slag indicates an amorphous material with no peaks due to any crystalline phase present. However, crystal patterns associated with both gypsum ($CaSO_4 \cdot 2H_2O$) and limestone ($CaCO_3$) are shown in both the 2016 Lehigh slag, Figure 15, and the 2018 Lehigh slag, Figure 16. These crystalline materials are known to be additives with slag at nominally 2 wt% mass content.

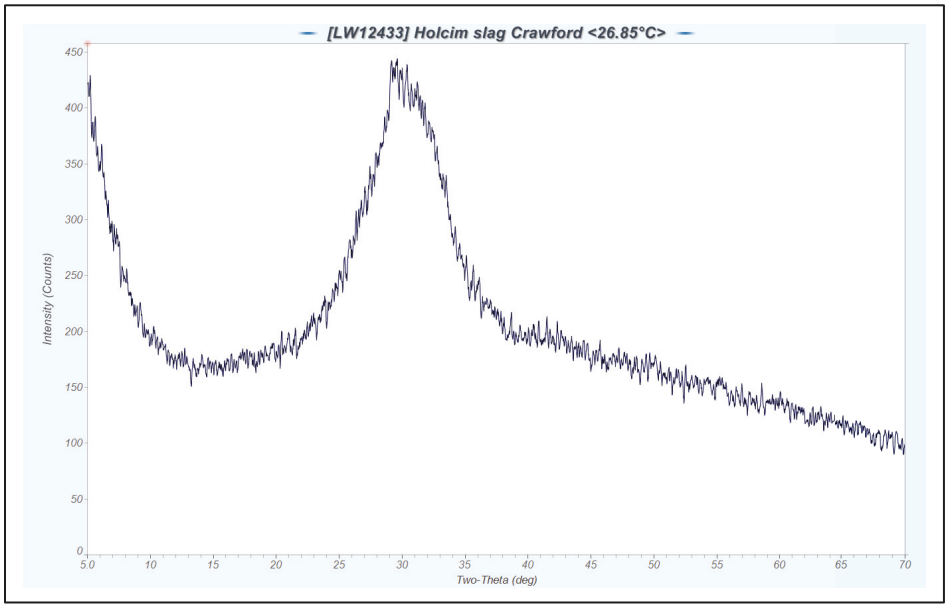

Figure 14. XRD Spectra for Holcim slag

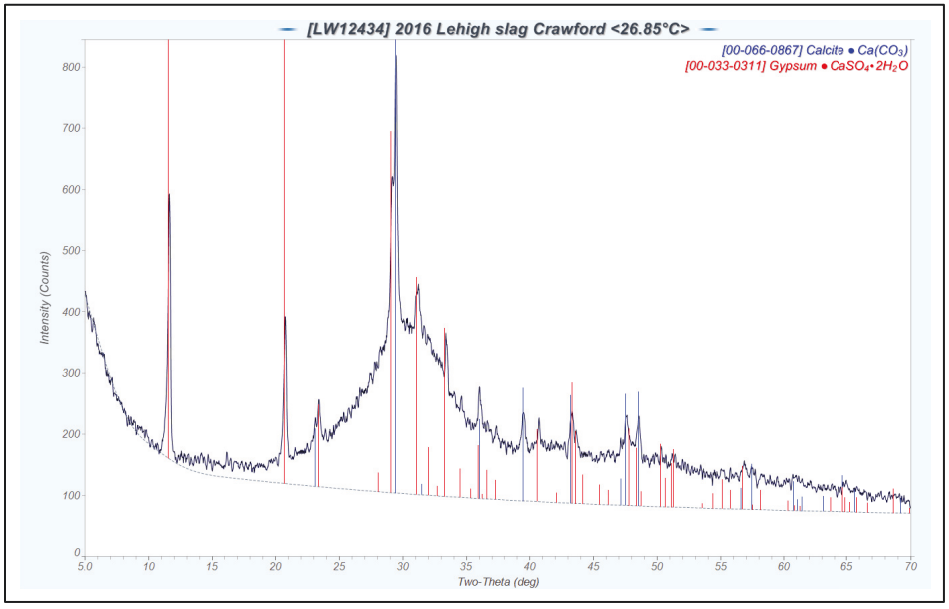

Figure 15. XRD Spectra for 2016 Lehigh slag

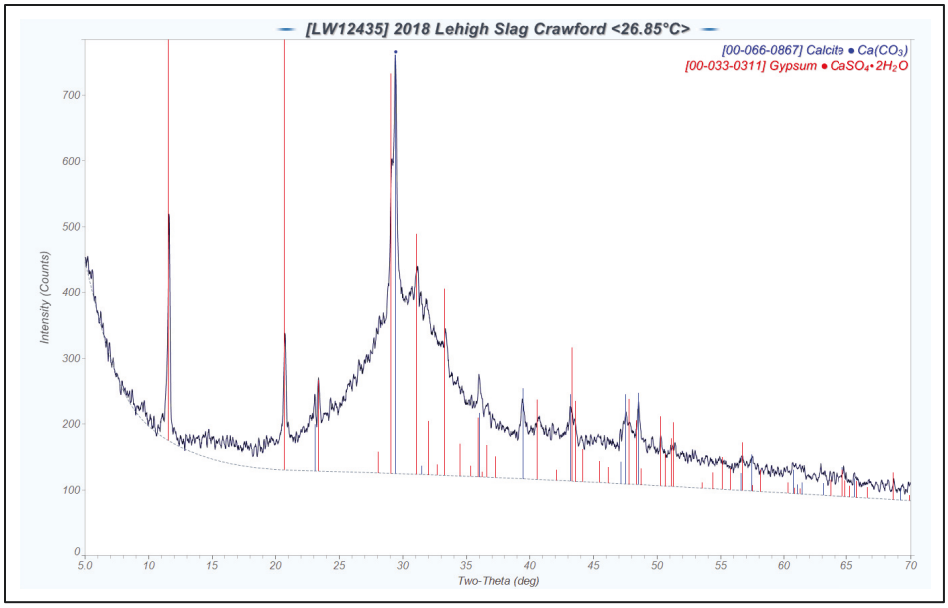

Figure 16. XRD Spectra for 2018 Lehigh slag

The same slags were dissolved and analyzed for elemental chemical content as shown in Table 11. The Ca and S amounts are higher for the gypsum/limestone containing slags. The Holcim slag contains 0.80 ± 0.003 wt% S and the 2016 and 2018 Lehigh slags contain 1.26 ± 0.03 wt% S and 1.01 ± 0.06 wt% S, respectively. For the work in this report a sulfur concentration in slag of 1 wt% was employed.

Table 11. Elemental sulphur and calcium composition in slag

Slag Source	Average Total S	Standard Deviation	Relative Standard Deviation
	wt%	wt%	%
Holcim	0.8	0.003	0.36
2016 Lehigh	1.26	0.027	2.14
2018 Lehigh	1.01	0.055	5.44

Slag Source	Average Total Ca	Standard Deviation	Relative Standard Deviation
	wt%	wt%	%
Holcim	23.45	0.188	0.80
2016 Lehigh	28.02	0.222	0.79
2018 Lehigh	26.69	0.501	1.88

Appendix B: Calibrations of M&TE for the Sealed Reactors and GC Calibration Gases

The table below lists the thermocouples and pressure transducer used on the 9 reactors and the results of the calibrations performed on these instruments.

Table 12. Measurement and test equipment list for sealed reactors

Channel Number	DAS (1) Number	M&TE Number ELN-	Instrument Name	Used Where	Manu-facturer	Model Number	Calibrated Range	Required Tolerance	Calibration Data	Pre-Test Uncertainty
1	T0	37084	T0		Omega	HKQSS-116U-12	0-200°C	± 2.2°C	6/8/2020	± 1.451 °C
2	T1	37094	T1		Omega	HKQSS-116U-12	0-200°C	± 2.2°C	6/8/2020	± 1.520 °C
3	T2	46374	T2		Omega	HKQSS-116U-12	0-200°C	± 2.2°C	6/12/2020	± 1.457 °C
4	T3	37097	T3		Omega	HKQSS-116U-12	0-200°C	± 2.2°C	6/10/2020	± 1.452 °C
16	V0	37215	P0 (V0)	HGV-7	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 0.75 PSIG	6/2/2020	± 0.524 psig
17	V1	37207	P1 (V1)	HGV-8	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 0.75 PSIG	10/2/2019	± 0.674 psig
18	V2	37211	P2 (V2)	HGV-9	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 1.125 PSIG	6/2/2020	± 0.991 psig
19	V3	37217	P3 (V3)	HGV-10	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 0.75 PSIG	6/16/2020	± 0.425 psig
20	V4	46339	P4 (V4)	HGV-11	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 0.75 PSIG	6/2/2020	± 0.477 psig
21	V5	37213	P5 (V5)	HGV-12	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 0.75 PSIG	6/16/2020	± 0.413 psig
22	V6	37205	P6 (V6)	HGV-13	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 0.75 PSIG	6/16/2020	± 0.520 psig
23	V7	46447	P7 (V7)	HGV-14 (2)	Setra	225G-150P-G-D4-11-06	0-150 PSIG	± 0.75 PSIG	6/16/2020	± 0.520 psig
Temperature Readout										
		47305	Readout		Omega	CSC32-E-C2	0-200 °C	± 2.2°C	8/10/2020	± 1.107°C
		47301	Thermocouple, Type E		Omega	HEQSS-18U-12U	0-200 °C	± 2.2°C	8/10/2020	± 1.107°C

(1) DAS = Data Acquisition System
(2) For Test Series 1 the reactor was HGV-15, but the M&TE equipment was transferred to HGV-14 for Test Series 2, 3, 4, and 5.

Table 13. Calibration Gas Standards Used with the Gas Chromatograph

Manufacturer	Exp. Date	Lot	CH_4	CO_2	H_2	Kr	N_2O	O_2	N_2	Air	Accuracy
MESA Specialty Gases & Equipment	07/27/23	0-206-6	5000 ppm	none	none	none	none	none	none	Balance	±2%
MESA Specialty Gases & Equipment	01/18/21	CC493837	1000 ppm	none	none	none	none	none	none	Balance	±2%
MESA Specialty Gases & Equipment	10/18/20	EB0027356	100 ppm	1.00%	50 ppm	0.50%	0.50%	none	none	Balance	±2%
SpecGas, Inc.	02/28/22	BC456858	50.1 ppm	1.02%	50.3 ppm	none	4.99%	1.00%	Balance	none	±2%

Appendix C: Statistical Analyses

This appendix contains the results from several investigations of methane generation data from sealed reactor tests. The measurement equations supporting the Methane Generation Rate (MGR) and Hydrogen Generation Rate (HGR) calculations are provided and these equations were used to estimate the uncertainties of these determinations. Uncertainties for 5 test series at multiple time intervals are included in the evaluation. Finally, the appendix ends with comparisons of the results from several investigations of gas generation rate data from these sealed reactor tests. Test Series 4 and 5 evaluate the effect of water-to-solids mass ratio (mass ratio) on the gas generation and the statistical significance was investigated using the software package JMP™ Pro Version 11.2.1 [6.15].

Methane Generation Rate

The software package GUM Workbench Version 2.4.1.411 [6.14] was utilized to evaluate MGR uncertainties. The GUM statistical package has undergone verification and validation per the software qualification procedure (Manual 1Q, Procedure 20-1, Revision 14) [6.16]. The equations utilized to evaluate the uncertainties of these MGR values in this software along with definitions of the terms of the equations are provided in Figure 17.

The (2-sigma) uncertainty of measurements of mass utilized in these measurements equations is 0.05 g. The standard deviations for T (average temperature at sampling) and P_i (initial reactor pressure at start of GC sampling) were taken as the maximum of the pretest uncertainties as reported in Appendix B (representing 2 sigma uncertainties) for the thermocouple and pressure instruments, respectively, provided earlier in the report. Using the largest uncertainty is expected to bound the uncertainties across all the reactors.

The GC term in the measurement equation represents the uncertainties of the various GC calibrations performed in support of this study. The instrument used for the measurements supporting these tests was calibrated with gas standards with a listed tolerance (assumed 2-sigma) of ±2% before and after sampling to develop a response factor for the gas samples between calibration runs. Multiple calibrations of the GC used to support these tests were conducted with a standard of concentration 50.1 ppm, 1000 ppm, or combination of both standards for methane and 50.3 ppm for hydrogen. Individual response factors were calculated for each standard sample and the mean was used as the response factor for these studies. Two examples of the data used to develop the calibrations and their associated uncertainties are provided in Exhibit A.1. An uncertainty for each calibration of the GC used for the testing was determined as a relative standard deviation based upon the square root of the sum of the squares of the relative standard deviations for the methane standards and the calculated response factor (RF=area/standard concentration). The same method was used to calculate uncertainties for the other gas calibrations used in this study.

Equation:

$$A=RH_v*((14.7+P_i)/14.7)*(298/(273+T));$$

$$S_v=S_m/\rho_s;$$
$$S_{vg}=(S_v/1000)/3.785;$$

$$HS_r=R_v-I_v-(M_v+((S_m-T_m)/\rho_g));$$
$$HS_{tot}=HS_r+HS_{tube}+HS_{port};$$
$$RH_v=(HS_{tot}/1000)*(0.13368/3.785);$$

$$MGR=(A*GC*CH_4/1000000)*(1/t)*(1/S_{vg});$$

Quantity	Unit	Definition
A	ft3	correction to 1 atm at 25 degrees C
RH_v	ft3	total headspace volume in mL that is converted to ft3
P_i	psig	initial reactor pressure at start of GC sampling
T	oC	average temperature at sampling
S_v	mL	volume of simulant
S_m	g	mass of simulant
ρ_s	g/mL	density of simulant
S_{vg}	mL	volume of simulant converted to gallons
HS_r	mL	headspace of reactor excluding tube volume
R_v	mL	reactor internal volume
I_v	mL	volume of Teflon insert
M_v	mL	mixture volume
T_m	g	target mass of simulant
ρ_g	g/mL	density of grout
HS_{tot}	mL	total headspace volume including GC-tube and purge system volume
HS_{tube}	mL	added headspace from GC attachement tubing
HS_{port}	mL	added headspace due to purge-tube removal
MGR	(ft3/hr)/gal	methane generation rate
GC	unitless	term to represent realtive uncertainty of GC calibration
CH_4	ppm	concentration of sampled methane
t	hours	time elapsed

Figure 17. GUM Workbench MGR model equations[8]

The experimental uncertainty of the gas concentration measurements was calculated within the GUM software and is based on the average and standard deviation of the individual measurements that contribute to the reported average which is used to calculate average MGR and other gas generation rates. The measurement equations of Figure 17 and Exhibit C.2were used to calculate MGR uncertainties for the reactor vessels for the tests. An example of the Gum Workbench output for the 2-hour test with HGV-9

[8] The same equations apply to the calculation of hydrogen gas by using the concentration of sampled hydrogen in the final equation to calculate the HGR.

from Test Series 3 is provided in Exhibit C.2. The partial derivatives used in the calculation of the MGR uncertainty are provided in Exhibit C.3.

At the end of this appendix, Table 14 provides a summary of the GUM inputs for MGR and HGR (hydrogen generation rate) and associated GUM uncertainties from the uncertainty budgets. Table 15 and Table 16 provide a summary of the GUM output for MGR and HGR and include 95% confidence intervals for the results of the gas generation rate calculation, respectively.

Exhibit C.1. Estimating the uncertainties of the GC calibrations for CH_4
Example using 50.1 ppm CH_4 gas standard

Injection Time=100							
SRMT	SampleName		Area				
Detectors			moduleA:tcd				
Time (GMT -240 mins)		RF	CH4	std con			
6/23/2020 13:10	BC456858	2.670459	133.79	50.1	**Test Series 1**	Hour 2-6	
6/23/2020 13:12	BC456858	2.825549	141.56	50.1	**Test Series 1**	Mean	2.668234
6/23/2020 13:14	BC456858	2.672255	133.88	50.1	**Test Series 1**	STD	0.309245
6/23/2020 13:16	BC456858	2.913772	145.98	50.1	**Test Series 1**	%RSD	11.58986
6/23/2020 13:19	BC456858	2.655689	133.05	50.1	**Test Series 1**		
6/23/2020 13:21	BC456858	3.032934	151.95	50.1	**Test Series 1**		
6/23/2020 13:23	BC456858	2.51996	126.25	50.1	**Test Series 1**		
6/23/2020 13:25	BC456858	2.488822	124.69	50.1	**Test Series 1**		
6/23/2020 13:27	BC456858	2.964671	148.53	50.1	**Test Series 1**		
6/23/2020 13:29	BC456858	2.666866	133.61	50.1	**Test Series 1**		
6/23/2020 16:13	BC456858	2.636727	132.1	50.1	**Test Series 1**		
6/23/2020 16:15	BC456858	2.581038	129.31	50.1	**Test Series 1**		
6/23/2020 16:17	BC456858	1.539521	77.13	50.1	**Test Series 1**		
6/23/2020 16:19	BC456858	2.797804	140.17	50.1	**Test Series 1**		
6/23/2020 16:21	BC456858	2.697206	135.13	50.1	**Test Series 1**		
6/23/2020 16:23	BC456858	2.997405	150.17	50.1	**Test Series 1**		
6/23/2020 16:25	BC456858	2.718762	136.21	50.1	**Test Series 1**		
6/23/2020 16:27	BC456858	2.581238	129.32	50.1	**Test Series 1**		
6/23/2020 16:30	BC456858	2.568263	128.67	50.1	**Test Series 1**		
6/23/2020 16:32	BC456858	2.835729	142.07	50.1	**Test Series 1**		

Exhibit C.2. Gum Workbench MGR uncertainty results for 2-hours, Test Series 3, Reactor HGR-9

Methane Generation Rate

Author: Stephanie Taylor

Model Equation:

$A=RH_v*((14.7+P_I)/14.7)*(298/(273+T));$

$S_v=S_m/\rho_s;$

$S_{vg}=(S_v/1000)/3.785;$

$HS_T=R_v-I_v-(M_v+((S_m-T_m)/\rho_g));$

$HS_{tot}=HS_T+HS_{tube}+HS_{port};$

$RH_v=(HS_{tot}/1000)*(0.13368/3.785);$

$MGR=(A*GC*CH_4/1000000)*(1/t)*(1/S_{vg});$

List of Quantities:

Quantity	Unit	Definition
A	ft3	correction to 1 atm at 25 degrees C
RH_v	ft3	total headspace volume in mL that is converted to ft3
P_I	psig	initial reactor pressure at start of GC sampling
T	oC	average temperature at sampling
S_v	mL	volume of simulant
S_m	g	mass of simulant
ρ_s	g/mL	density of simulant
S_{vg}	mL	volume of simulant converted to gallons
HS_T	mL	headspace of reactor excluding tube volume
R_v	mL	reactor internal volume
I_v	mL	volume of Teflon insert
M_v	mL	mixture volume
T_m	g	target mass of simulant
ρ_g	g/mL	density of grout
HS_{tot}	mL	total headspace volume including GC-tube and purge system volume
HS_{tube}	mL	added headspace from GC attachement tubing
HS_{port}	mL	added headspace due to purge-tube removal
MGR	(ft3/hr)/gal	methane generation rate
GC	unitless	term to represent realtive uncertainty of GC calibration
CH_4	ppm	concentration of sampled methane
t	hours	time elapsed

P_I:
Type B normal distribution
Value: 12.475 psig
Expanded Uncertainty: 0.991 psig
Coverage Factor: 2

Generated with GUM Workbench Pro Version 2.4.1.411

Based on instrument list tolerance provided.

Max instrument tolerance 1.125 PSIG. The highest pretest uncertainty was 0.991psig.

The expanded uncertainties for P_I and T were taken as the maximum of the Pre Test Uncertainty or tolerance values (representing 2 sigma uncertainties) for the thermocouple and pressure instruments. Using the largest temperature and pressure uncertainty is expected to bound the uncertainties in the sampling across all of the reactors.

T:
Type B normal distribution
Value: 28.73 oC
Expanded Uncertainty: 1.52 oC
Coverage Factor: 2

Based on instrument list tolerance provided.

All Omega Thermocouplers used have a 2.2 oC tolerance. The max pretest uncertainty was 1.520 oC.

The expanded uncertainties for P_I and T were taken as the maximum of the Pre Test Uncertainty or tolerance values (representing 2 sigma uncertainties) for the thermocouple and pressure instruments. Using the largest temperature and pressure uncertainty is expected to bound the uncertainties in the sampling across all of the reactors.

S_m:
Type B normal distribution
Value: 33.01 g
Expanded Uncertainty: 0.05 g
Coverage Factor: 2

The (2-sigma) uncertainty of measurements of mass utilized in these measurements equations is 0.05 g based on balance tolerance.

ρ_s:
Type B normal distribution
Value: 1.2208 g/mL
Expanded Uncertainty: 0.012 g/mL
Coverage Factor: 1

Based on the 3 simulant batches used for these tests.

R_v:
Type B normal distribution
Value: 194.44 mL
Expanded Uncertainty: 2 %
Coverage Factor: 2

From Previous Measurements - reference appendix on volumes

0.4% used for balance uncertainty and 1% used for density uncertainty and calculations made for each reactor in appendix.

I_v:
Type B normal distribution
Value: 21.459 mL
Expanded Uncertainty: 0.227 mL
Coverage Factor: 1

Value from previous measurements

scale calibration error divided by density of teflon (0.5g/2.2g/mL=0.227mL)

M_v:
Type B normal distribution
Value: 55.74 mL
Expanded Uncertainty: 1 %
Coverage Factor: 1

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Exhibit C.2. Gum Workbench MGR uncertainty results for 2-hours, Test Series 3, Reactor HGR-9
(continued)

Measured 55.74 for 0.85 or 56.39 for 0.59 mixutre

standard deviation for volume test for 0.85 premix is 1.11 g or 1.12 mL resulting in 1.00% RSD standard deviation for volume test for 0.59 premix is 0.67 g or mL resulting in 0.59% RSD

Largest relative uncertainty expected to bound the uncertainties across reactors.

T_m: Constant
Value: 33 g

ρ_g: Type B normal distribution
Value: 1.6364 g/mL
Expanded Uncertainty: 0.0377 g/mL
Coverage Factor: 1

Based on standard deviation of 7 grout batches (SRNL-STI-2019-00106, Table 13)

HS_{tube}: Type B normal distribution
Value: 2.576 mL
Expanded Uncertainty: 10 %
Coverage Factor: 1

Value based on CAD drawings. A 10% uncertainty is used to estimate error in manufactured component volume compared to CAD drawing.

HS_{port}: Type B normal distribution
Value: 2.121 mL
Expanded Uncertainty: 10 %
Coverage Factor: 1

Value is not applicable for Test Series 1 & 2 (Port was plugged with grout). Value is 2.121 based off of CAD drawings for Test Series 3, 4, & 5 and for "redo" tests after port was removed entirely with an estimated uncertainty 10% compared to CAD drawings.

GC: Type B normal distribution
Value: 1 unitless
Expanded Uncertainty: 2.74 %
Coverage Factor: 1

A 2% relative uncertainty associated with the calibration gas is incorporated into this calculation as well as the standard deviation of each calibration that was used for calculating the GC response factor.

CH_4: Type A summarized
Mean: 338.79 ppm
Experimental Standard Deviation: 3.55 ppm
Number of observations: 7

Measurements captured in the experiments

t: Type B rectangular distribution
Value: 2.37 hours
Halfwidth of Limits: 0.05 hours

Test Series 3, 2 hours

Interim Results:

Quantity	Value	Standard Uncertainty
A	$7.863 \cdot 10^{-3}$ ft3	$197 \cdot 10^{-6}$ ft3
RH_v	$4.3064 \cdot 10^{-3}$ ft3	$72.8 \cdot 10^{-6}$ ft3
S_v	27.040 mL	0.267 mL
S_{vg}	$7.1439 \cdot 10^{-3}$ mL	$70.4 \cdot 10^{-6}$ mL
HS_r	117.23 mL	2.04 mL
HS_{tot}	121.93 mL	2.06 mL

Exhibit C.2. Gum Workbench MGR uncertainty results for 2-hours, Test Series 3, Reactor HGR-9 *(continued)*

Methane Generation Rate

Uncertainty Budgets:

MGR: methane generation rate

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
A	$7.863 \cdot 10^{-3}$ ft3	$197 \cdot 10^{-6}$ ft3				
RH_v	$4.3064 \cdot 10^{-3}$ ft3	$72.8 \cdot 10^{-6}$ ft3				
P_I	12.475 psig	0.496 psig	normal	$5.8 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$ (ft3/hr)/gal	20.3 %
T	28.730 oC	0.760 oC	normal	$-520 \cdot 10^{-9}$	$-400 \cdot 10^{-9}$ (ft3/hr)/gal	0.4 %
S_v	27.040 mL	0.267 mL				
S_m	33.0100 g	0.0250 g	normal	$-5.6 \cdot 10^{-6}$	$-140 \cdot 10^{-9}$ (ft3/hr)/gal	0.0 %
ρ_s	1.2208 g/mL	0.0120 g/mL	normal	$130 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$ (ft3/hr)/gal	5.9 %
S_{vg}	$7.1439 \cdot 10^{-3}$ mL	$70.4 \cdot 10^{-6}$ mL				
HS_r	117.23 mL	2.04 mL				
R_v	194.44 mL	1.94 mL	normal	$1.3 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$ (ft3/hr)/gal	15.5 %
I_v	21.459 mL	0.227 mL	normal	$-1.3 \cdot 10^{-6}$	$-290 \cdot 10^{-9}$ (ft3/hr)/gal	0.2 %
M_v	55.740 mL	0.557 mL	normal	$-1.3 \cdot 10^{-6}$	$-720 \cdot 10^{-9}$ (ft3/hr)/gal	1.3 %
T_m	33.0 g					
ρ_g	1.6364 g/mL	0.0377 g/mL	normal	$4.8 \cdot 10^{-9}$	$180 \cdot 10^{-12}$ (ft3/hr)/gal	0.0 %
HS_{tot}	121.93 mL	2.06 mL				
HS_{tube}	2.576 mL	0.258 mL	normal	$1.3 \cdot 10^{-6}$	$330 \cdot 10^{-9}$ (ft3/hr)/gal	0.3 %
HS_{port}	2.121 mL	0.212 mL	normal	$1.3 \cdot 10^{-6}$	$270 \cdot 10^{-9}$ (ft3/hr)/gal	0.2 %
GC	1.0000 unitless	0.0274 unitless	normal	$160 \cdot 10^{-6}$	$4.3 \cdot 10^{-6}$ (ft3/hr)/gal	45.9 %
CH_4	338.79 ppm	1.34 ppm	normal	$460 \cdot 10^{-9}$	$620 \cdot 10^{-9}$ (ft3/hr)/gal	1.0 %
t	2.3700 hours	0.0289 hours	rectangular	$-66 \cdot 10^{-6}$	$-1.9 \cdot 10^{-6}$ (ft3/hr)/gal	9.1 %
MGR	$157.33 \cdot 10^{-6}$ (ft3/hr)/gal	$6.37 \cdot 10^{-6}$ (ft3/hr)/gal				

Date: 11/13/2020 | File: MGR.smu | Page 5 of 6

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Methane Generation Rate

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
MGR	$157 \cdot 10^{-6}$ (ft3/hr)/gal	8.1 % (relative)	2.00	95% (normal)

Date: 11/13/2020 | File: MGR.smu | Page 6 of 6

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Exhibit C.3. Gum Workbench MGR uncertainty partial derivatives

Partial Derivatives:

$\partial A/\partial P_i = 298.0/(273.0 + T)\cdot RH_v\cdot 1.0/14.7;$

$\partial A/\partial T = RH_v\cdot(14.7 + P_i)/14.7\cdot(-298.0)/sqr(273.0 + T);$

$\partial A/\partial S_m = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial S_m;$

$\partial A/\partial R_v = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial R_v;$

$\partial A/\partial l_v = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial l_v;$

$\partial A/\partial M_v = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial M_v;$

$\partial A/\partial T_m = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial T_m;$

$\partial A/\partial \rho_g = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial \rho_g;$

$\partial A/\partial HS_{tube} = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial HS_{tube};$

$\partial A/\partial HS_{port} = 298.0/(273.0 + T)\cdot(14.7 + P_i)/14.7\cdot\partial RH_v/\partial HS_{port};$

$\partial RH_v/\partial S_m = 0.13368/3.785\cdot\partial HS_{tot}/\partial S_m/1000.0;$

$\partial RH_v/\partial R_v = 0.13368/3.785\cdot\partial HS_{tot}/\partial R_v/1000.0;$

$\partial RH_v/\partial l_v = 0.13368/3.785\cdot\partial HS_{tot}/\partial l_v/1000.0;$

$\partial RH_v/\partial M_v = 0.13368/3.785\cdot\partial HS_{tot}/\partial M_v/1000.0;$

$\partial RH_v/\partial T_m = 0.13368/3.785\cdot\partial HS_{tot}/\partial T_m/1000.0;$

$\partial RH_v/\partial \rho_g = 0.13368/3.785\cdot\partial HS_{tot}/\partial \rho_g/1000.0;$

$\partial RH_v/\partial HS_{tube} = 0.13368/3.785\cdot\partial HS_{tot}/\partial HS_{tube}/1000.0;$

$\partial RH_v/\partial HS_{port} = 0.13368/3.785\cdot\partial HS_{tot}/\partial HS_{port}/1000.0;$

Partial Derivatives:

$\partial S_v/\partial S_m = 1.0/\rho_s;$

$\partial S_v/\partial \rho_s = (-S_m)/sqr(\rho_s);$

$\partial S_{vg}/\partial S_m = \partial S_v/\partial S_m/1000.0/3.785;$

$\partial S_{vg}/\partial \rho_s = \partial S_v/\partial \rho_s/1000.0/3.785;$

$\partial HS_r/\partial S_m = -1.0/\rho_g;$

$\partial HS_r/\partial R_v = 1.0;$

$\partial HS_r/\partial l_v = -1.0;$

$\partial HS_r/\partial M_v = -1.0;$

$\partial HS_r/\partial T_m = -(-1.0)/\rho_g;$

$\partial HS_r/\partial \rho_g = -(-(S_m - T_m))/sqr(\rho_g);$

$\partial HS_{tot}/\partial S_m = \partial HS_r/\partial S_m;$

$\partial HS_{tot}/\partial R_v = \partial HS_r/\partial R_v;$

$\partial HS_{tot}/\partial l_v = \partial HS_r/\partial l_v;$

$\partial HS_{tot}/\partial M_v = \partial HS_r/\partial M_v;$

$\partial HS_{tot}/\partial T_m = \partial HS_r/\partial T_m;$

$\partial HS_{tot}/\partial \rho_g = \partial HS_r/\partial \rho_g;$

$\partial HS_{tot}/\partial HS_{tube} = 1.0;$

$\partial HS_{tot}/\partial HS_{port} = 1.0;$

Exhibit C.3. Gum Workbench MGR uncertainty partial derivatives *(continued)*

Partial Derivatives:

$\partial MGR/\partial P_i = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial P_i/1000000.0;$

$\partial MGR/\partial T = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial T/1000000.0;$

$\partial MGR/\partial S_m = A \cdot GC \cdot CH_4/1000000.0 \cdot 1.0/t \cdot (-1.0 \cdot \partial S_{vg}/\partial S_m)/sqr(S_{vg}) + 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial$
$\backslash Sm/1000000.0;$

$\partial MGR/\partial \rho_s = A \cdot GC \cdot CH_4/1000000.0 \cdot 1.0/t \cdot (-1.0 \cdot \partial S_{vg}/\partial \rho_s)/sqr(S_{vg});$

$\partial MGR/\partial R_v = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial R_v/1000000.0;$

$\partial MGR/\partial l_v = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial l_v/1000000.0;$

$\partial MGR/\partial M_v = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial M_v/1000000.0;$

$\partial MGR/\partial T_m = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial T_m/1000000.0;$

$\partial MGR/\partial \rho_g = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial \rho_g/1000000.0;$

$\partial MGR/\partial HS_{tube} = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial HS_{tube}/1000000.0;$

$\partial MGR/\partial HS_{port} = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot GC \cdot \partial A/\partial HS_{port}/1000000.0;$

$\partial MGR/\partial GC = 1.0/S_{vg} \cdot 1.0/t \cdot CH_4 \cdot A/1000000.0;$

$\partial MGR/\partial CH_4 = 1.0/S_{vg} \cdot 1.0/t \cdot A \cdot GC/1000000.0;$

$\partial MGR/\partial t = 1.0/S_{vg} \cdot A \cdot GC \cdot CH_4/1000000.0 \cdot (-1.0)/sqr(t);$

Table 14. Summary of inputs and interim uncertainty determinations from GUM

TEST ID Code	Test Series Number	Target Duration hours	*Water to Mass*	MeHg Conc. mg/L	Reactor HGV-	Reactor Insert Used	Elapsed Time hours	Elapsed time uncertainty hours
TS1-2h-0.85	1	2	*0.85*	100	9	C	2.24	0.0289
TS1-4h-0.85	1	4	*0.85*	100	8	B	4.00	0.0289
TS1-6h-0.85	1	6	*0.85*	100	7	A	6.00	0.0289
TS1-18h-0.85	R 1	18	*0.85*	100	13	F	18.50	0.0289
TS1-30h-0.85	R 1	30	*0.85*	100	11	E	28.50	0.0289
TS1-48h-0.85	1	48	*0.85*	100	12	F	48.02	0.0289
TS1-72h-0.85	1	72	*0.85*	100	10	D	72.03	0.0289
TS1-96h-0.85	1	96	*0.85*	100	15	H	95.19	0.0289
TS2-2h-0.85	2	2	*0.85*	100	9	C	2.20	0.0289
TS2-4h-0.85	2	4	*0.85*	100	8	B	4.03	0.0289
TS2-6h-0.85	2	6	*0.85*	100	7	A	6.07	0.0289
TS2-18h-0.85	2	18	*0.85*	100	13	G	18.28	0.0289
TS2-30h-0.85	2	30	*0.85*	100	11	E	29.90	0.0289
TS2-48h-0.85	2	48	*0.85*	100	12	F	49.05	0.0289
TS2-72h-0.85	R 2	72	*0.85*	100	8	B	72.13	0.0289
TS2-96h-0.85	2	96	*0.85*	100	15	H	96.00	0.0289
TS3-2h-0.85	3	2	*0.85*	100	9	C	2.37	0.0289
TS3-4h-0.85	3	4	*0.85*	100	8	B	4.02	0.0289
TS3-6h-0.85	3	6	*0.85*	100	7	A	6.02	0.0289
TS3-18h-0.85	3	18	*0.85*	100	14	G	18.44	0.0289
TS3-30h-0.85	R 3	30	*0.85*	100	9	C	30.03	0.0289
TS3-48h-0.85	R 3	48	*0.85*	100	10	D	48.14	0.0289
TS3-72h-0.85	3	72	*0.85*	100	10	D	72.06	0.0289
TS3-96h-0.85	R 3	96	*0.85*	100	7	A	96.31	0.0289
TS4-2h-0.85	4	2	*0.85*	100	10	C	2.03	0.0289
TS4-6h-0.85	4	6	*0.85*	100	11	D	6.01	0.0289
TS4-18h-0.85	4	18	*0.85*	100	13	D	17.76	0.0289
TS4-30h-0.85	4	30	*0.85*	100	7	A	30.32	0.0289
TS4-2h-0.59	4	2	*0.59*	100	8	E	1.99	0.0289
TS4-6h-0.59	4	6	*0.59*	100	9	F	5.96	0.0289
TS4-18h-0.59	4	18	*0.59*	100	14	G	18.05	0.0289
TS4-30h-0.59	4	30	*0.59*	100	7	H	30.06	0.0289
TS5-2h-0.85	5	2	*0.85*	100	9	C	2.10	0.0289
TS5-6h-0.85	5	6	*0.85*	100	8	B	6.07	0.0289
TS5-18h-0.85	5	18	*0.85*	100	10	D	18.35	0.0289
TS5-30h-0.85	5	30	*0.85*	100	7	A	30.01	0.0289
TS5-2h-0.59	5	2	*0.59*	100	8	E	2.07	0.0289
TS5-6h-0.59	5	6	*0.59*	100	11	G	6.05	0.0289
TS5-18h-0.59	5	18	*0.59*	100	13	H	18.35	0.0289
TS5-30h-0.59	5	30	*0.59*	100	14	E	30.02	0.0289

R indicates a test redone after the original test series using a different GC calibration and simulant mixture than the other tests in the series.

Table 14. Summary of inputs and interim uncertainty determinations from GUM *(continued)*

TEST ID Code	Average CH4 ppm	Std Dev CH4 ppm	Average CH4 uncertainty ppm	Term used to reprersent GC calibration uncertainty unitless	GC Calibration Standard Uncertainty unitless	Combined CH4 Uncertainty @95% %
TS1-2h-0.85	1416	30	11.3	1.00	0.118	12%
TS1-4h-0.85	1814	5	1.89	1.00	0.118	12%
TS1-6h-0.85	1779	9	3.4	1.00	0.118	12%
TS1-18h-0.85	1054	5	1.89	1.00	0.021	2%
TS1-30h-0.85	1126	4	1.51	1.00	0.021	2%
TS1-48h-0.85	2617	14	5.29	1.00	0.113	11%
TS1-72h-0.85	2597	18	6.8	1.00	0.113	11%
TS1-96h-0.85	2520	11	4.16	1.00	0.065	6%
TS2-2h-0.85	83	13	4.91	1.00	0.038	7%
TS2-4h-0.85	430	6	2.27	1.00	0.038	4%
TS2-6h-0.85	416	6	2.27	1.00	0.038	4%
TS2-18h-0.85	650	4	1.51	1.00	0.033	3%
TS2-30h-0.85	781	3	1.13	1.00	0.033	3%
TS2-48h-0.85	974	8	3.02	1.00	0.026	3%
TS2-72h-0.85	1054	3	1.13	1.00	0.021	2%
TS2-96h-0.85	1065	4	1.51	1.00	0.022	2%
TS3-2h-0.85	339	4	1.51	1.00	0.027	3%
TS3-4h-0.85	645	6	2.27	1.00	0.027	3%
TS3-6h-0.85	729	4	1.51	1.00	0.027	3%
TS3-18h-0.85	923	2	0.756	1.00	0.036	4%
TS3-30h-0.85	892	8	2.97	1.00	0.022	2%
TS3-48h-0.85	780	0	0	1.00	0.021	2%
TS3-72h-0.85	963	3	1.2	1.00	0.024	2%
TS3-96h-0.85	963	8	3.09	1.00	0.021	2%
TS4-2h-0.85	8	3	1.05	1.00	0.024	13%
TS4-6h-0.85	141	2	0.89	1.00	0.024	2%
TS4-18h-0.85	277	4	1.63	1.00	0.024	2%
TS4-30h-0.85	293	3	1.03	1.00	0.024	2%
TS4-2h-0.59	83	8	2.96	1.00	0.021	4%
TS4-6h-0.59	212	4	1.5	1.00	0.021	2%
TS4-18h-0.59	367	3	1.05	1.00	0.024	2%
TS4-30h-0.59	204	4	1.46	1.00	0.024	3%
TS5-2h-0.85	62	1	0.425	1.00	0.021	2%
TS5-6h-0.85	220	6	2.25	1.00	0.021	2%
TS5-18h-0.85	294	3	1.12	1.00	0.022	2%
TS5-30h-0.85	378	2	0.875	1.00	0.022	2%
TS5-2h-0.59	18	3	1.32	1.00	0.024	8%
TS5-6h-0.59	87	3	1.1	1.00	0.024	3%
TS5-18h-0.59	169	4	1.52	1.00	0.020	2%
TS5-30h-0.59	287	4	1.34	1.00	0.020	2%

Table 14. Summary of inputs and interim uncertainty determinations from GUM *(continued)*

TEST ID Code	Average H2 ppm	Std Dev H2 ppm	Average H2 uncertainty ppm	Term used to represent GC calibration uncertainty unitless	GC Calibration Standard Uncertainty unitless	Combined H2 Uncertainty @95% %
TS1-2h-0.85	9.2	0.33	0.13	1.00	0.039	8%
TS1-4h-0.85	12.2	2.38	0.90	1.00	0.039	17%
TS1-6h-0.85	23.8	2.63	0.99	1.00	0.039	11%
TS1-18h-0.85	37.1	0.52	0.20	1.00	0.052	10%
TS1-30h-0.85	20.7	4.37	1.65	1.00	0.052	19%
TS1-48h-0.85	15.5	0.17	0.06	1.00	0.055	11%
TS1-72h-0.85	14.4	0.31	0.12	1.00	0.055	11%
TS1-96h-0.85	20.9	1.39	0.53	1.00	0.029	8%
TS2-2h-0.85	17.2	1.35	0.51	1.00	0.029	8%
TS2-4h-0.85	56.5	1.58	0.60	1.00	0.029	6%
TS2-6h-0.85	58.6	1.89	0.71	1.00	0.029	6%
TS2-18h-0.85	102.6	0.75	0.28	1.00	0.023	5%
TS2-30h-0.85	115.5	0.41	0.16	1.00	0.023	5%
TS2-48h-0.85	116.7	0.88	0.33	1.00	0.027	6%
TS2-72h-0.85	146.1	0.65	0.25	1.00	0.031	6%
TS2-96h-0.85	158.5	0.26	0.10	1.00	0.023	5%
TS3-2h-0.85	14.0	0.53	0.20	1.00	0.029	7%
TS3-4h-0.85	20.4	0.46	0.17	1.00	0.029	6%
TS3-6h-0.85	61.6	1.08	0.41	1.00	0.029	6%
TS3-18h-0.85	134.8	1.17	0.44	1.00	0.022	4%
TS3-30h-0.85	149.6	1.70	0.64	1.00	0.132	26%
TS3-48h-0.85	148.3	0.00	0.00	1.00	0.031	6%
TS3-72h-0.85	174.9	1.76	0.67	1.00	0.023	5%
TS3-96h-0.85	511.6	10.60	4.01	1.00	0.052	11%
TS4-2h-0.85	11.4	0.53	0.20	1.00	0.024	6%
TS4-6h-0.85	26.1	0.72	0.27	1.00	0.024	5%
TS4-18h-0.85	40.9	0.20	0.08	1.00	0.023	5%
TS4-30h-0.85	52.1	0.26	0.10	1.00	0.023	5%
TS4-2h-0.59	9.7	0.50	0.19	1.00	0.033	8%
TS4-6h-0.59	28.2	0.36	0.14	1.00	0.033	7%
TS4-18h-0.59	52.1	0.52	0.20	1.00	0.024	5%
TS4-30h-0.59	33.4	0.30	0.11	1.00	0.024	5%
TS5-2h-0.85	6.1	0.34	0.13	1.00	0.026	7%
TS5-6h-0.85	19.4	0.94	0.36	1.00	0.026	6%
TS5-18h-0.85	87.6	0.39	0.15	1.00	0.034	7%
TS5-30h-0.85	79.4	0.48	0.18	1.00	0.034	7%
TS5-2h-0.59	0.9	2.37	0.87	1.00	0.028	194%
TS5-6h-0.59	20.2	0.88	0.33	1.00	0.028	7%
TS5-18h-0.59	39.8	0.44	0.17	1.00	0.028	6%
TS5-30h-0.59	61.9	0.28	0.11	1.00	0.028	6%

Table 14. Summary of inputs and interim uncertainty determinations from GUM *(continued)*

TEST ID Code	Reactor Head+Tube mL	Reactor Head+Tube uncertainty	Density Mixture g/mL	Density Mixture uncertainty	Target Waste g	Mixture Volume mL	Mixture Volume uncertainty	Insert Volume mL	Insert Volume uncertainty
TS1-2h-0.85	119.78	2.05	1.2145	0.0377	64.45	55.74	0.56	21.459	0.227
TS1-4h-0.85	120.73	2.06	1.2145	0.0377	64.45	55.74	0.56	21.131	0.227
TS1-6h-0.85	116.62	2.03	1.2145	0.0377	64.45	55.74	0.56	22.219	0.227
TS1-18h-0.85	149.69	2.23	1.2206	0.0377	64.45	55.74	0.56	21.66	0.227
TS1-30h-0.85	146.15	2.2	1.2206	0.0377	64.45	55.74	0.56	21.839	0.227
TS1-48h-0.85	117.97	2.04	1.2145	0.0377	64.45	55.74	0.56	21.664	0.227
TS1-72h-0.85	119.69	2.05	1.2145	0.0377	64.45	55.74	0.56	21.486	0.227
TS1-96h-0.85	119.12	2.05	1.2145	0.0377	64.45	55.74	0.56	21.654	0.227
TS2-2h-0.85	119.78	2.05	1.6364	0.0377	33.00	55.74	0.56	21.459	0.227
TS2-4h-0.85	120.70	2.06	1.6364	0.0377	33.00	55.74	0.56	21.131	0.227
TS2-6h-0.85	116.65	2.03	1.6364	0.0377	33.00	55.74	0.56	22.219	0.227
TS2-18h-0.85	122.17	2.07	1.6364	0.0377	33.00	55.74	0.56	21.262	0.227
TS2-30h-0.85	118.23	2.04	1.6364	0.0377	33.00	55.74	0.56	21.839	0.227
TS2-48h-0.85	118.21	2.04	1.6364	0.0377	33.00	55.74	0.56	21.664	0.227
TS2-72h-0.85	122.77	2.07	1.6364	0.0377	33.00	55.74	0.56	21.131	0.227
TS2-96h-0.85	119.09	2.05	1.6364	0.0377	33.00	55.74	0.56	21.654	0.227
TS3-2h-0.85	121.92	2.06	1.6364	0.0377	33.00	55.74	0.56	21.459	0.227
TS3-4h-0.85	122.73	2.07	1.6364	0.0377	33.00	55.74	0.56	21.131	0.227
TS3-6h-0.85	118.76	2.04	1.6364	0.0377	33.00	55.74	0.56	22.219	0.227
TS3-18h-0.85	122.70	2.07	1.6364	0.0377	33.00	55.74	0.56	21.262	0.227
TS3-30h-0.85	121.94	2.06	1.6364	0.0377	33.00	55.74	0.56	21.459	0.227
TS3-48h-0.85	121.79	2.06	1.6364	0.0377	33.00	55.74	0.56	21.486	0.227
TS3-72h-0.85	121.82	2.06	1.6364	0.0377	33.00	55.74	0.56	21.486	0.227
TS3-96h-0.85	118.71	2.04	1.6364	0.0377	33.00	55.74	0.56	22.219	0.227
TS4-2h-0.85	121.85	2.06	1.6364	0.0377	33.00	55.74	0.56	21.459	0.227
TS4-6h-0.85	120.72	2.05	1.6364	0.0377	33.00	55.74	0.56	21.486	0.227
TS4-18h-0.85	124.06	2.08	1.6364	0.0377	33.00	55.74	0.56	21.486	0.227
TS4-30h-0.85	118.74	2.04	1.6364	0.0377	33.00	55.74	0.56	22.219	0.227
TS4-2h-0.59	121.42	2.07	1.6364	0.0377	33.00	56.39	0.56	21.839	0.227
TS4-6h-0.59	121.06	2.06	1.6364	0.0377	33.00	56.39	0.56	21.664	0.227
TS4-18h-0.59	122.04	2.07	1.6364	0.0377	33.00	56.39	0.56	21.262	0.227
TS4-30h-0.59	118.65	2.04	1.6364	0.0377	33.00	56.39	0.56	21.654	0.227
TS5-2h-0.85	121.95	2.06	1.6364	0.0377	33.00	55.74	0.56	21.459	0.227
TS5-6h-0.85	122.77	2.07	1.6364	0.0377	33.00	55.74	0.56	21.131	0.227
TS5-18h-0.85	121.81	2.06	1.6364	0.0377	33.00	55.74	0.56	21.486	0.227
TS5-30h-0.85	118.76	2.04	1.6364	0.0377	33.00	55.74	0.56	22.219	0.227
TS5-2h-0.59	121.56	2.07	1.6364	0.0377	33.00	56.39	0.56	21.664	0.227
TS5-6h-0.59	120.33	2.05	1.6364	0.0377	33.00	56.39	0.56	21.262	0.227
TS5-18h-0.59	123.26	2.09	1.6364	0.0377	33.00	56.39	0.56	21.654	0.227
TS5-30h-0.59	121.47	2.07	1.6364	0.0377	33.00	56.39	0.56	21.839	0.227

Table 14. Summary of inputs and interim uncertainty determinations from GUM *(continued)*

TEST ID Code	Reactor Volume mL	Reactor Volume uncertainty	Reactor Head ml	Reactor Head uncertainty	*Reactor Liquid gal*	*Reactor Liquid uncertainty*	Density Simulant g/mL	Density Simulant uncertainty
TS1-2h-0.85	194.44	1.94	117.21	2.04	*0.01403*	*1.39E-04*	1.2145	0.012
TS1-4h-0.85	194.96	1.95	118.16	2.04	*0.01400*	*1.38E-04*	1.2145	0.012
TS1-6h-0.85	192.01	1.92	114.04	2.01	*0.01402*	*1.39E-04*	1.2145	0.012
TS1-18h-0.85	196.64	1.97	145.00	2.21	*0.00715*	*7.05E-05*	1.2206	0.012
TS1-30h-0.85	193.29	1.93	141.45	2.18	*0.00715*	*7.05E-05*	1.2206	0.012
TS1-48h-0.85	193.09	1.93	115.39	2.02	*0.01410*	*1.39E-04*	1.2145	0.012
TS1-72h-0.85	194.37	1.94	117.11	2.03	*0.01403*	*1.39E-04*	1.2145	0.012
TS1-96h-0.85	193.94	1.94	116.55	2.03	*0.01402*	*1.39E-04*	1.2145	0.012
TS2-2h-0.85	194.44	1.94	117.20	2.04	*0.00715*	*7.05E-05*	1.2208	0.012
TS2-4h-0.85	194.96	1.95	118.12	2.04	*0.00713*	*7.03E-05*	1.2208	0.012
TS2-6h-0.85	192.01	1.92	114.08	2.01	*0.00713*	*7.03E-05*	1.2208	0.012
TS2-18h-0.85	196.64	1.97	119.60	2.06	*0.00716*	*7.06E-05*	1.2208	0.012
TS2-30h-0.85	193.29	1.93	115.66	2.02	*0.00716*	*7.06E-05*	1.2208	0.012
TS2-48h-0.85	193.09	1.93	115.63	2.02	*0.00716*	*7.06E-05*	1.2208	0.012
TS2-72h-0.85	194.96	1.95	118.08	2.04	*0.00715*	*7.05E-05*	1.2206	0.012
TS2-96h-0.85	193.94	1.94	116.51	2.03	*0.00715*	*7.05E-05*	1.2208	0.012
TS3-2h-0.85	194.44	1.94	117.23	2.04	*0.00714*	*7.04E-05*	1.2208	0.012
TS3-4h-0.85	194.96	1.95	118.04	2.04	*0.00716*	*7.06E-05*	1.2208	0.012
TS3-6h-0.85	192.01	1.92	114.07	2.01	*0.00714*	*7.04E-05*	1.2208	0.012
TS3-18h-0.85	195.02	1.95	118.01	2.04	*0.00714*	*7.04E-05*	1.2208	0.012
TS3-30h-0.85	194.44	1.94	117.25	2.04	*0.00714*	*7.04E-05*	1.2206	0.012
TS3-48h-0.85	194.37	1.94	117.11	2.03	*0.00716*	*7.06E-05*	1.2206	0.012
TS3-72h-0.85	194.37	1.94	117.13	2.03	*0.00715*	*7.05E-05*	1.2208	0.012
TS3-96h-0.85	192.01	1.92	114.03	2.01	*0.00715*	*7.05E-05*	1.2206	0.012
TS4-2h-0.85	194.37	1.94	117.16	2.03	*0.00715*	*7.05E-05*	1.2206	0.012
TS4-6h-0.85	193.29	1.93	116.03	2.02	*0.00715*	*7.05E-05*	1.2206	0.012
TS4-18h-0.85	196.64	1.97	119.38	2.06	*0.00716*	*7.06E-05*	1.2206	0.012
TS4-30h-0.85	192.01	1.92	114.05	2.01	*0.00714*	*7.04E-05*	1.2206	0.012
TS4-2h-0.59	194.96	1.95	116.73	2.04	*0.00714*	*7.04E-05*	1.2206	0.012
TS4-6h-0.59	194.44	1.94	116.37	2.04	*0.00715*	*7.05E-05*	1.2206	0.012
TS4-18h-0.59	195.02	1.95	117.36	2.04	*0.00715*	*7.05E-05*	1.2206	0.012
TS4-30h-0.59	192.01	1.92	113.96	2.01	*0.00715*	*7.05E-05*	1.2206	0.012
TS5-2h-0.85	194.44	1.94	117.27	2.04	*0.00713*	*7.04E-05*	1.2206	0.012
TS5-6h-0.85	194.96	1.95	118.08	2.04	*0.00715*	*7.05E-05*	1.2206	0.012
TS5-18h-0.85	194.37	1.94	117.13	2.03	*0.00715*	*7.05E-05*	1.2206	0.012
TS5-30h-0.85	192.01	1.92	114.07	2.01	*0.00714*	*7.04E-05*	1.2206	0.012
TS5-2h-0.59	194.96	1.95	116.88	2.04	*0.00715*	*7.05E-05*	1.2206	0.012
TS5-6h-0.59	193.29	1.93	115.64	2.03	*0.00714*	*7.04E-05*	1.2206	0.012
TS5-18h-0.59	196.64	1.97	118.58	2.06	*0.00715*	*7.05E-05*	1.2206	0.012
TS5-30h-0.59	195.02	1.95	116.78	2.04	*0.00715*	*7.05E-05*	1.2206	0.012

Table 14. Summary of inputs and interim uncertainty determinations from GUM *(continued)*

TEST ID Code	Participating Simulant g	Participating Simulant uncertainty	*Actual Waste mL*	*Actual Waste uncertainty*	Avg. Temp at Measure C	Avg. Temp at Measure uncertainty
TS1-2h-0.85	64.49	0.025	*53.10*	*0.525*	30.3	0.76
TS1-4h-0.85	64.366	0.025	*53.00*	*0.524*	30.9	0.76
TS1-6h-0.85	64.46	0.025	*53.08*	*0.525*	32.7	0.76
TS1-18h-0.85	33.01	0.025	*27.04*	*0.267*	30.3	0.76
TS1-30h-0.85	33.03	0.025	*27.06*	*0.267*	28.7	0.76
TS1-48h-0.85	64.81	0.025	*53.36*	*0.528*	28.0	0.76
TS1-72h-0.85	64.49	0.025	*53.10*	*0.525*	31.4	0.76
TS1-96h-0.85	64.45	0.025	*53.07*	*0.525*	31.9	0.76
TS2-2h-0.85	33.06	0.025	*27.08*	*0.267*	29.9	0.76
TS2-4h-0.85	32.95	0.025	*26.99*	*0.266*	33.2	0.76
TS2-6h-0.85	32.96	0.025	*27.00*	*0.266*	34.4	0.76
TS2-18h-0.85	33.07	0.025	*27.09*	*0.267*	32.4	0.76
TS2-30h-0.85	33.09	0.025	*27.11*	*0.267*	32.1	0.76
TS2-48h-0.85	33.09	0.025	*27.11*	*0.267*	31.3	0.76
TS2-72h-0.85	33.02	0.025	*27.05*	*0.267*	28.6	0.76
TS2-96h-0.85	33.06	0.025	*27.08*	*0.267*	26.3	0.76
TS3-2h-0.85	33.01	0.025	*27.04*	*0.267*	28.7	0.76
TS3-4h-0.85	33.08	0.025	*27.10*	*0.267*	32.7	0.76
TS3-6h-0.85	32.97	0.025	*27.01*	*0.266*	33.9	0.76
TS3-18h-0.85	33.01	0.025	*27.04*	*0.267*	30.6	0.76
TS3-30h-0.85	32.98	0.025	*27.02*	*0.266*	26.9	0.76
TS3-48h-0.85	33.06	0.025	*27.09*	*0.267*	31.0	0.76
TS3-72h-0.85	33.02	0.025	*27.05*	*0.267*	29.3	0.76
TS3-96h-0.85	33.04	0.025	*27.07*	*0.267*	28.9	0.76
TS4-2h-0.85	33.01	0.025	*27.04*	*0.267*	28.1	0.76
TS4-6h-0.85	33.05	0.025	*27.08*	*0.267*	29.4	0.76
TS4-18h-0.85	33.06	0.025	*27.09*	*0.267*	31.0	0.76
TS4-30h-0.85	33	0.025	*27.04*	*0.267*	29.0	0.76
TS4-2h-0.59	33	0.025	*27.04*	*0.267*	28.8	0.76
TS4-6h-0.59	33.02	0.025	*27.05*	*0.267*	29.8	0.76
TS4-18h-0.59	33.02	0.025	*27.05*	*0.267*	31.4	0.76
TS4-30h-0.59	33.01	0.025	*27.04*	*0.267*	30.7	0.76
TS5-2h-0.85	32.96	0.025	*27.00*	*0.266*	27.9	0.76
TS5-6h-0.85	33.01	0.025	*27.04*	*0.267*	29.9	0.76
TS5-18h-0.85	33.03	0.025	*27.06*	*0.267*	30.9	0.76
TS5-30h-0.85	32.97	0.025	*27.01*	*0.266*	29.9	0.76
TS5-2h-0.59	33.05	0.025	*27.08*	*0.267*	29.6	0.76
TS5-6h-0.59	33	0.025	*27.04*	*0.267*	28.6	0.76
TS5-18h-0.59	33.03	0.025	*27.06*	*0.267*	31.4	0.76
TS5-30h-0.59	33.02	0.025	*27.05*	*0.267*	28.6	0.76

Table 14. Summary of inputs and interim uncertainty determinations from GUM *(continued)*

TEST ID Code	Initial Corrected Pressure psig	Initial Corrected Pressure uncertainty	Reactor Head ft3	Reactor Head ft3 uncertainty	For 1 atm & 25°C ft3	For 1 atm & 25°C ft 3 uncertainty
TS1-2h-0.85	13.585	0.496	4.23E-03	7.25E-05	8.00E-03	1.97E-04
TS1-4h-0.85	12.305	0.496	4.26E-03	7.26E-05	7.68E-03	1.93E-04
TS1-6h-0.85	13.375	0.496	4.12E-03	7.17E-05	7.67E-03	1.91E-04
TS1-18h-0.85	15.335	0.496	5.29E-03	7.88E-05	1.06E-02	2.37E-04
TS1-30h-0.85	12.055	0.496	5.16E-03	7.77E-05	9.28E-03	2.23E-04
TS1-48h-0.85	12.495	0.496	4.17E-03	7.20E-06	7.63E-03	1.93E-04
TS1-72h-0.85	11.085	0.496	4.23E-03	7.24E-05	7.26E-03	1.88E-04
TS1-96h-0.85	12.175	0.496	4.21E-03	7.23E-05	7.52E-03	1.90E-04
TS2-2h-0.85	13.615	0.496	4.23E-03	7.25E-05	8.02E-03	1.97E-04
TS2-4h-0.85	13.855	0.496	4.26E-03	7.26E-05	8.06E-03	1.97E-04
TS2-6h-0.85	13.895	0.496	4.12E-03	7.17E-05	7.77E-03	1.92E-04
TS2-18h-0.85	13.885	0.496	4.31E-03	7.32E-05	8.19E-03	2.00E-04
TS2-30h-0.85	12.515	0.496	4.18E-03	7.21E-05	7.55E-03	1.90E-04
TS2-48h-0.85	13.945	0.496	4.17E-03	7.20E-05	7.97E-03	1.96E-04
TS2-72h-0.85	12.485	0.496	4.34E-03	7.30E-05	7.92E-03	1.98E-04
TS2-96h-0.85	13.045	0.496	4.21E-03	7.23E-05	7.90E-03	2.12E-04
TS3-2h-0.85	12.475	0.496	4.31E-03	7.28E-05	7.86E-03	1.97E-04
TS3-4h-0.85	14.115	0.496	4.33E-03	7.30E-05	8.28E-03	2.00E-04
TS3-6h-0.85	14.555	0.496	4.19E-03	7.20E-05	8.11E-03	1.97E-04
TS3-18h-0.85	12.635	0.496	4.33E-03	7.30E-05	7.91E-03	1.97E-04
TS3-30h-0.85	13.035	0.496	4.31E-03	7.28E-05	8.08E-03	2.15E-04
TS3-48h-0.85	12.435	0.496	4.30E-03	7.28E-05	7.78E-03	2.10E-04
TS3-72h-0.85	12.335	0.496	4.30E-03	7.28E-05	7.80E-03	2.11E-04
TS3-96h-0.85	11.365	0.496	4.19E-03	7.20E-05	7.34E-03	2.04E-04
TS4-2h-0.85	14.545	0.496	4.30E-03	7.28E-05	8.47E-03	2.19E-04
TS4-6h-0.85	13.765	0.496	4.26E-03	7.25E-05	8.14E-03	2.14E-04
TS4-18h-0.85	16.625	0.496	4.38E-03	7.36E-05	9.15E-03	2.27E-04
TS4-30h-0.85	13.705	0.496	4.19E-03	7.20E-05	8.00E-03	2.12E-04
TS4-2h-0.59	8.105	0.496	4.29E-03	7.31E-05	6.57E-03	1.98E-04
TS4-6h-0.59	13.355	0.496	4.28E-03	7.29E-05	8.03E-03	2.13E-04
TS4-18h-0.59	13.675	0.496	4.31E-03	7.31E-05	8.15E-03	2.15E-04
TS4-30h-0.59	13.565	0.496	4.19E-03	7.21E-05	7.91E-03	2.10E-04
TS5-2h-0.85	14.295	0.496	4.31E-03	7.28E-05	8.41E-03	2.19E-04
TS5-6h-0.85	13.135	0.496	4.34E-03	7.30E-05	8.08E-03	2.15E-04
TS5-18h-0.85	13.055	0.496	4.30E-03	7.28E-05	7.97E-03	2.12E-04
TS5-30h-0.85	12.845	0.496	4.19E-03	7.20E-05	7.73E-03	2.08E-04
TS5-2h-0.59	13.275	0.496	4.29E-03	7.31E-05	8.05E-03	2.14E-04
TS5-6h-0.59	14.505	0.496	4.25E-03	7.25E-05	8.34E-03	2.17E-04
TS5-18h-0.59	13.675	0.496	4.35E-03	7.36E-05	8.23E-03	2.16E-04
TS5-30h-0.59	12.885	0.496	4.29E-03	7.31E-05	7.96E-03	2.13E-04

Table 15. MGR and uncertainty determinations from GUM

TEST ID Code	**Average MGR (GUM) (ft3/hr) / gal**	**Average MGR standard uncertainty***	**MGR Uncertainty @95%**	MGR Lower Limit* @95%	MGR Upper Limit* @95%
TS1-2h-0.85	**3.60E-04**	**4.38E-05**	**24%**	2.73E-04	4.48E-04
TS1-4h-0.85	**2.49E-04**	**3.01E-05**	**24%**	1.89E-04	3.09E-04
TS1-6h-0.85	**1.62E-04**	**1.96E-05**	**24%**	1.23E-04	2.01E-04
TS1-18h-0.85	**8.46E-05**	**2.74E-06**	**7%**	7.92E-05	9.01E-05
TS1-30h-0.85	**5.13E-05**	**1.71E-06**	**7%**	4.79E-05	5.47E-05
TS1-48h-0.85	**2.95E-05**	**3.43E-06**	**23%**	2.26E-05	3.64E-05
TS1-72h-0.85	**1.87E-05**	**2.17E-06**	**23%**	1.43E-05	2.30E-05
TS1-96h-0.85	**1.42E-05**	**1.00E-06**	**14%**	1.22E-05	1.62E-05
TS2-2h-0.85	**4.23E-05**	**3.23E-06**	**15%**	3.58E-05	4.87E-05
TS2-4h-0.85	**1.21E-04**	**5.68E-06**	**9%**	1.09E-04	1.32E-04
TS2-6h-0.85	**7.47E-05**	**3.50E-06**	**9%**	6.77E-05	8.17E-05
TS2-18h-0.85	**4.07E-05**	**1.72E-06**	**9%**	3.73E-05	4.42E-05
TS2-30h-0.85	**2.75E-05**	**1.18E-06**	**9%**	2.52E-05	2.99E-05
TS2-48h-0.85	**2.21E-05**	**8.23E-07**	**7%**	2.04E-05	2.37E-05
TS2-72h-0.85	**1.62E-05**	**5.52E-07**	**7%**	1.51E-05	1.73E-05
TS2-96h-0.85	**1.23E-05**	**4.25E-07**	**7%**	1.14E-05	1.31E-05
TS3-2h-0.85	**1.57E-04**	**6.33E-06**	**8%**	1.45E-04	1.70E-04
TS3-4h-0.85	**1.86E-04**	**7.13E-06**	**8%**	1.71E-04	2.00E-04
TS3-6h-0.85	**1.38E-04**	**5.22E-06**	**8%**	1.27E-04	1.48E-04
TS3-18h-0.85	**5.54E-05**	**2.49E-06**	**9%**	5.04E-05	6.04E-05
TS3-30h-0.85	**3.36E-05**	**1.12E-06**	**7%**	3.14E-05	3.58E-05
TS3-48h-0.85	**1.76E-05**	**6.24E-07**	**7%**	1.64E-05	1.89E-05
TS3-72h-0.85	**1.46E-05**	**5.44E-07**	**8%**	1.35E-05	1.57E-05
TS3-96h-0.85	**1.03E-05**	**3.72E-07**	**7%**	9.52E-06	1.10E-05
TS4-2h-0.85	**4.81E-06**	**6.42E-07**	**27%**	3.52E-06	6.09E-06
TS4-6h-0.85	**2.67E-05**	**9.74E-07**	**8%**	2.47E-05	2.86E-05
TS4-18h-0.85	**2.00E-05**	**7.32E-07**	**7%**	1.85E-05	2.14E-05
TS4-30h-0.85	**1.08E-05**	**4.05E-07**	**8%**	1.00E-05	1.16E-05
TS4-2h-0.59	**3.82E-05**	**2.07E-06**	**11%**	3.41E-05	4.23E-05
TS4-6h-0.59	**3.99E-05**	**1.44E-06**	**7%**	3.70E-05	4.28E-05
TS4-18h-0.59	**2.32E-05**	**8.60E-07**	**7%**	2.14E-05	2.49E-05
TS4-30h-0.59	**7.51E-06**	**2.84E-07**	**8%**	6.94E-06	8.08E-06
TS5-2h-0.85	**3.50E-05**	**1.33E-06**	**8%**	3.23E-05	3.76E-05
TS5-6h-0.85	**4.09E-05**	**1.52E-06**	**7%**	3.79E-05	4.39E-05
TS5-18h-0.85	**1.79E-05**	**6.48E-07**	**7%**	1.66E-05	1.92E-05
TS5-30h-0.85	**1.36E-05**	**4.95E-07**	**7%**	1.27E-05	1.46E-05
TS5-2h-0.59	**9.80E-06**	**8.15E-07**	**17%**	8.17E-06	1.14E-05
TS5-6h-0.59	**1.68E-05**	**6.56E-07**	**8%**	1.55E-05	1.81E-05
TS5-18h-0.59	**1.06E-05**	**3.80E-07**	**7%**	9.82E-06	1.13E-05
TS5-30h-0.59	**1.06E-05**	**3.77E-07**	**7%**	9.87E-06	1.14E-05

*Units are in $(ft^3/hr)/gal$

Table 16. HGR and uncertainty determinations from GUM

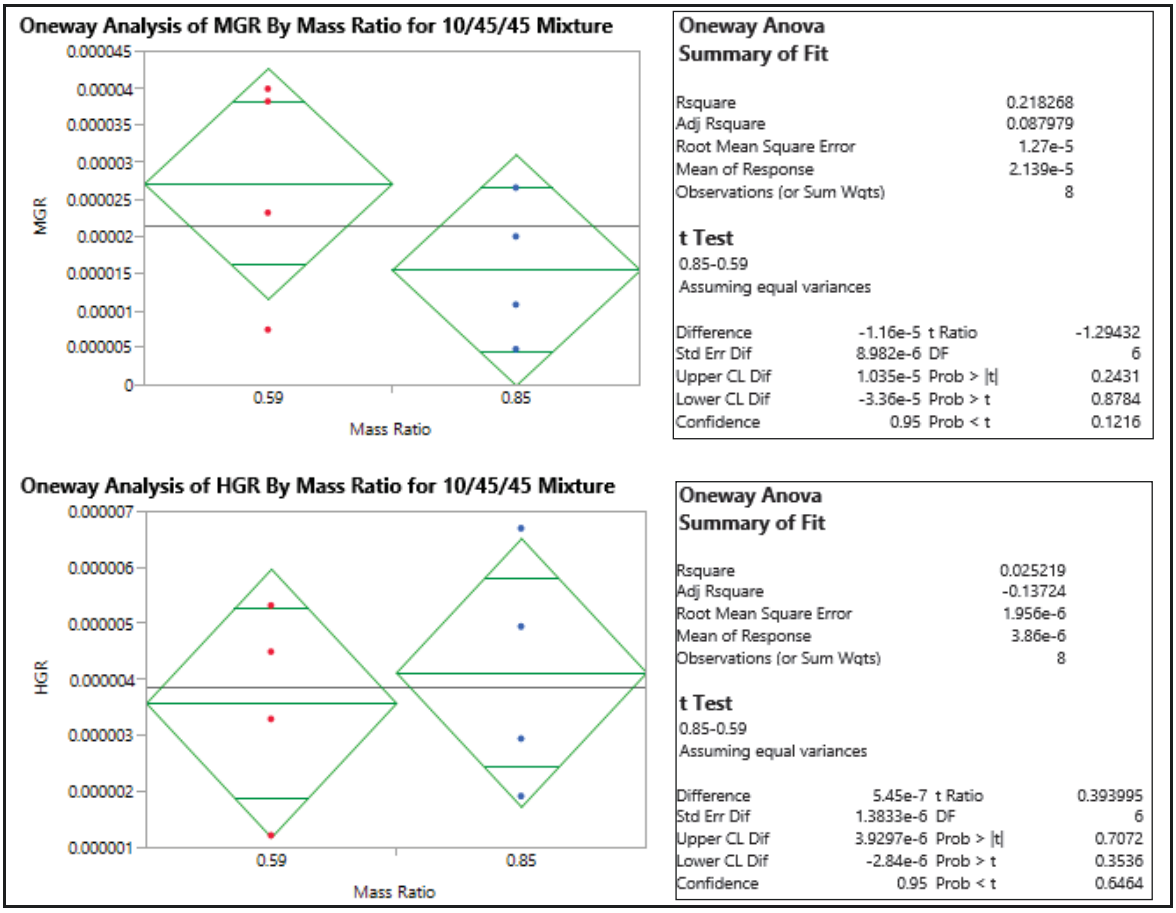
TEST ID Code	**Average HGR (ft3/hr) / gal**	**Average HGR standard uncertainty***	**HGR Uncertainty @95%**	HGR Lower Limit* @95%	HGR Upper Limit* @95%
TS1-2h-0.85	**2.35E-06**	**1.18E-07**	**10%**	2.11E-06	2.59E-06
TS1-4h-0.85	**1.68E-06**	**1.47E-07**	**18%**	1.39E-06	1.97E-06
TS1-6h-0.85	**2.17E-06**	**1.37E-07**	**13%**	1.90E-06	2.45E-06
TS1-18h-0.85	**2.98E-06**	**1.72E-07**	**12%**	2.63E-06	3.32E-06
TS1-30h-0.85	**9.42E-07**	**9.31E-08**	**20%**	7.56E-07	1.13E-06
TS1-48h-0.85	**1.75E-07**	**1.08E-08**	**12%**	1.53E-07	1.96E-07
TS1-72h-0.85	**1.03E-07**	**6.44E-09**	**12%**	9.03E-08	1.16E-07
TS1-96h-0.85	**1.18E-07**	**5.54E-09**	**9%**	1.06E-07	1.29E-07
TS2-2h-0.85	**8.77E-06**	**4.47E-07**	**10%**	7.87E-06	9.66E-06
TS2-4h-0.85	**1.59E-05**	**6.53E-07**	**8%**	1.45E-05	1.72E-05
TS2-6h-0.85	**1.05E-05**	**4.36E-07**	**8%**	9.64E-06	1.14E-05
TS2-18h-0.85	**6.42E-06**	**2.27E-07**	**7%**	5.97E-06	6.88E-06
TS2-30h-0.85	**4.07E-06**	**1.46E-07**	**7%**	3.78E-06	4.37E-06
TS2-48h-0.85	**2.65E-06**	**1.01E-07**	**8%**	2.44E-06	2.85E-06
TS2-72h-0.85	**2.25E-06**	**9.20E-08**	**8%**	2.06E-06	2.43E-06
TS2-96h-0.85	**1.82E-06**	**6.40E-08**	**7%**	1.70E-06	1.95E-06
TS3-2h-0.85	**6.48E-06**	**2.86E-07**	**9%**	5.91E-06	7.06E-06
TS3-4h-0.85	**5.86E-06**	**2.40E-07**	**8%**	5.38E-06	6.34E-06
TS3-6h-0.85	**1.16E-05**	**4.67E-07**	**8%**	1.07E-05	1.26E-05
TS3-18h-0.85	**8.10E-06**	**2.80E-07**	**7%**	7.54E-06	8.66E-06
TS3-30h-0.85	**5.58E-06**	**7.51E-07**	**27%**	4.08E-06	7.09E-06
TS3-48h-0.85	**3.35E-06**	**1.37E-07**	**8%**	3.08E-06	3.63E-06
TS3-72h-0.85	**2.65E-06**	**9.48E-08**	**7%**	2.46E-06	2.84E-06
TS3-96h-0.85	**5.45E-06**	**3.24E-07**	**12%**	4.80E-06	6.10E-06
TS4-2h-0.85	**6.68E-06**	**2.81E-07**	**8%**	6.12E-06	7.24E-06
TS4-6h-0.85	**4.93E-06**	**1.85E-07**	**8%**	4.56E-06	5.30E-06
TS4-18h-0.85	**2.95E-06**	**1.00E-07**	**7%**	2.75E-06	3.15E-06
TS4-30h-0.85	**1.92E-06**	**6.71E-08**	**7%**	1.79E-06	2.06E-06
TS4-2h-0.59	**4.48E-06**	**2.26E-07**	**10%**	4.03E-06	4.93E-06
TS4-6h-0.59	**5.32E-06**	**2.28E-07**	**9%**	4.87E-06	5.78E-06
TS4-18h-0.59	**3.29E-06**	**1.18E-07**	**7%**	3.06E-06	3.53E-06
TS4-30h-0.59	**1.23E-06**	**4.42E-08**	**7%**	1.14E-06	1.32E-06
TS5-2h-0.85	**3.45E-06**	**1.54E-07**	**7%**	3.15E-06	3.76E-06
TS5-6h-0.85	**3.62E-06**	**1.51E-07**	**8%**	3.31E-06	3.92E-06
TS5-18h-0.85	**5.32E-06**	**2.30E-07**	**9%**	4.86E-06	5.78E-06
TS5-30h-0.85	**2.87E-06**	**1.24E-07**	**9%**	2.62E-06	3.12E-06
TS5-2h-0.59	**4.84E-07**	**4.73E-07**	**200%**	0.00E+00	1.43E-06
TS5-6h-0.59	**3.91E-06**	**1.64E-07**	**8%**	3.58E-06	4.23E-06
TS5-18h-0.59	**2.51E-06**	**9.74E-08**	**8%**	2.32E-06	2.71E-06
TS5-30h-0.59	**2.30E-06**	**8.94E-08**	**8%**	2.12E-06	2.48E-06

*Units are in $(ft^3/hr)/gal$

Comparison of results for water-to-solids mass ratio (mass ratio) on generation rates

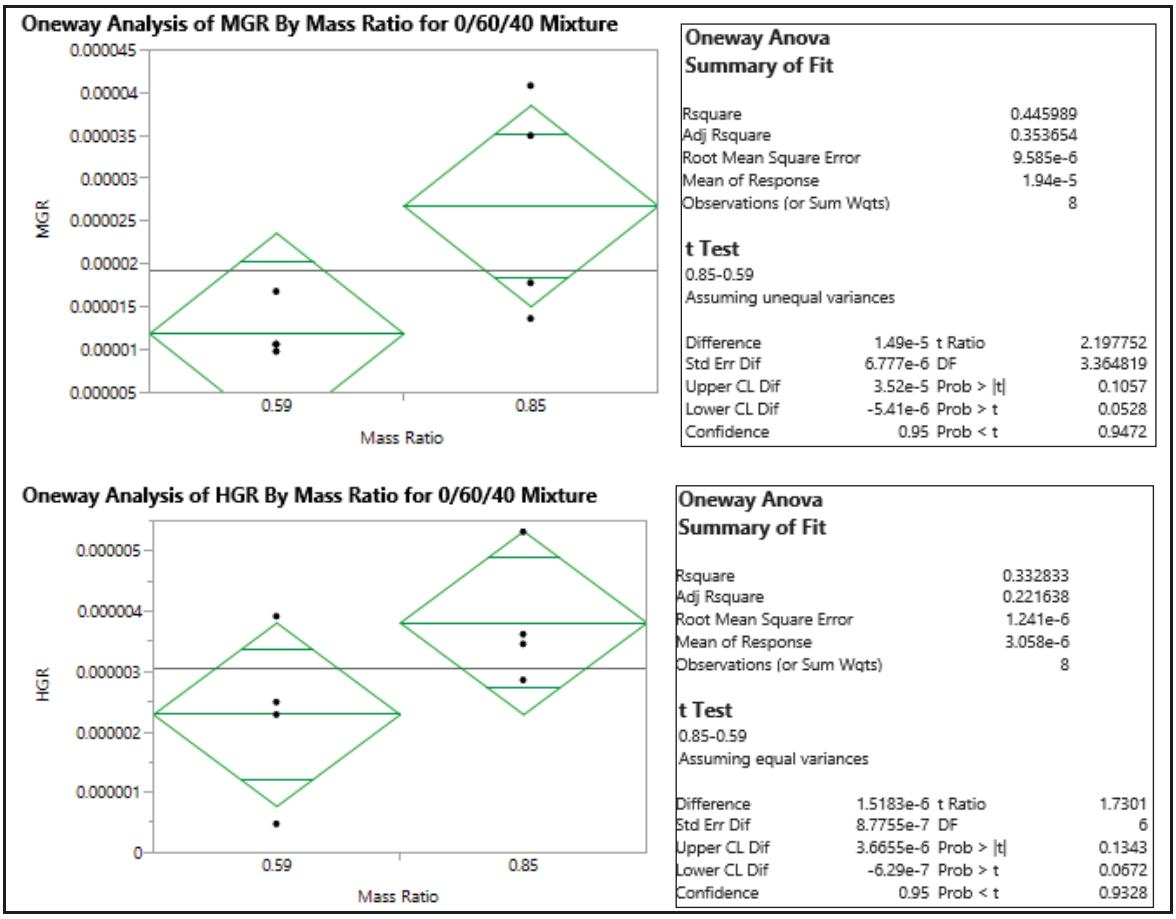
A comparison of the results for the Test Series 4, MGR and HGR values from 0.59 mass ratio and 0.85 mass ratio for 10/45/45 mixture, and Test Series 5, MGR and HGR values from 0.59 mass ratio and 0.85 mass ratio for 0/60/40 mixture, is of interest. Exhibit C.4 and Exhibit C.5 provide a statistical comparison of the averages of these results.

Exhibit C.4. MGR and HGR Results for 0.59 vs 0.85 mass ratio for 10/45/45 Mixture



This exhibit demonstrates that there is no indication of a statistically significant (at the 5% significance level, since the p value is 0.2431 for MGR and 0.7072 for HGR) difference in the average MGRs and HGRs for the tests of the two different mass ratios as part of this study for the 10/45/45 mixture.

Exhibit C.5. MGR and HGR results for 0.59 vs 0.85 mass ratio for 0/60/40 mixture



This exhibit demonstrates that there is no indication of a statistically significant (at the 5% significance level, since the p value is 0.1057 for MGR and 0.1343 for HGR) difference in the average MGRs and HGRs for the tests of the two different mass ratios as part of this study for the 0/60/40 mixture. Because variances cannot be assumed to be equal between the 2 different mass ratios for the MGR analysis, Welch's test (p-value 0.1057) further supports that there is no statistical difference between the MGR averages for the 0/60/40 mixture.

Appendix D: Solubility of Gases in Salt Solutions

To illustrate the solubility in Tank 50 simulant of several of gases under study, especially methane; Table 17 shows an example. The table contains information of a single reactor HGV-9 that contained the 10/45/45 grout premix mixture from the 27-hour test done during scoping tests [6.4]) and all of the Henry's Law constants came from a Hanford report [6.8] for salt solution similar to T50SS[9]. The solubility should be the same for all the reactors, but one is chosen so that the dimensions can be used to make the calculation. The temperature at measurement is between 25°C and 30°C. The lower temperature is used here to give the more conservative results, that is, the largest quantity of dissolved gases. The results show that besides nitrous oxide all the other gases are fractions of a percent. For the principal gas of concern, methane, almost none, < 0.1%, dissolves in the simulant.

Table 17. Dissolved gases in Tank 50 salt solution simulant

Item	Unit	O_2	CH_4	H_2	N_2	N_2O
Measured gas	PPM (1)	117602	990	132	875530	94
Sealed Reactor	Number	HGV-9	HGV-9	HGV-9	HGV-9	HGV-9
Mixture	Contents (batch 2QCY19)	10/45/45 grout	10/45/45 grout	10/45/45 grout	10/45/45 grout	10/45/45 grout
Pressure at measurement	psig	11	11	11	11	11
Volume of simulant	liters	0.02719	0.02719	0.02719	0.02719	0.02719
Density of simulant (2)	kg/liter	1.219	1.219	1.219	1.219	1.219
Mass of simulant	kg	0.0331	0.0331	0.0331	0.0331	0.0331
Dissolved solids in simulant (3)	wt%	26.9	26.9	26.9	26.9	26.9
Density of water at 25°C	kg/liter	0.997	0.997	0.997	0.997	0.997
Volume of water in simulant	liters	0.02430	0.02430	0.02430	0.02430	0.02430
Volume of Head space	mL	117.4	117.4	117.4	117.4	117.4
Temperature gas at measurement	°C	25	25	25	25	25
Henry's constant for gas (4)	mol, gas/(kg-water*atm)	9.97E-04	9.87E-05	3.85E-04	3.17E-04	1.18E-02
Absolute gas pressure	atm	1.748	1.748	1.748	1.748	1.748
Partial Pressure	atm	0.20560	0.00173	0.00023	1.53069	0.00016
Moles of dissolvable gas in water	mol, gas/kg-water	2.050E-04	1.708E-07	8.885E-08	4.852E-04	1.939E-06
Moles dissolved gas	mol, CH_4	6.794E-06	5.662E-09	2.945E-09	1.608E-05	6.427E-08
Volume of gas, 0°C, 273K	mL gas	1.522E-01	1.268E-04	6.596E-05	3.603E-01	1.440E-03
Volume of gas at test temperature	mL gas	1.661E-01	1.384E-04	7.201E-05	3.932E-01	1.572E-03
Volume head-space gas at pressure	mL	205.2	205.2	205.2	205.2	205.2
Dissolved gas per head-space volume	PPM	810	0.67	0.35	1917	7.66
Dissolved gas vs. head-space gas	**%**	**0.69**	**0.07**	**0.27**	**0.22**	**8.15**

(1) PPM values are from measurements except O_2 & N_2, which were based on Ideal-Gas concentrations when reactors were sealed & pressurized before gases are generated from test mixture.
(2) This is the average density from the three batches of simulant made for testing.
(3) From PSAL measurement. This total solids value is for the example data in this table; however, several simulant batches were made from all the test series total solids concentration were very consistent as 26.9 wt% ±0.7 wt% (2 sigma)
(4) Constants from "Solubilities of Gases in Simulated Tank 241-SY-101 Wastes," PNL-10785, Norton and Pederson, September 1995. (Values for H_2, N_2O, and N_2 were taken from Table 4.8 in that reference. Values for CH_4 and O_2 are from Table 4.7 of the reference but were increased to the more conservative values in Table 4.8 by interpolating using H_2 values for CH_4 and N_2 values for O_2 bteween Table 7 and 8.)

Henry's Constant (4) mol/(kg-water*atm)	Source at 25°C	Henry's Constant (4) mol/(kg-water*atm)	Source at 25°C
5.77E-06	For Methane, Table 4.7	1.40E-05	For Oxygen, Table 4.7
2.25E-05	For Hydrogen, Table 4.7	4.45E-06	For Nitrogen, Table 4.7
3.85E-04	For Hydrogen, Table 4.8	3.17E-04	For Nitrogen, Table 4.8
9.87E-05	Interpolating Methane for Table 4.8	9.97E-04	Interpolating Oxygen for Table 4.8

[9] The Hanford salt solution simulant (pH=14, density 1.18 g/mL) from the PNL source [6.8] was very similar to the T50SS SRS simulant (pH=14, density 1.21 g/mL). It was made up with the same 6 components of Na^+, OH^-, AlO_2^-, NO_3^-, NO_2^-, and CO_3^{2-}; therefore, HT50SS ~ HSS is assumed.

Appendix E: Sealed Reactor Volumes

Reactor Volumes for the Head Space and the Liquid and Solids Additions

To have an accurate measure of the gas volume after each test it is necessary to accurately know each reactor head space. That head space if a function of the:

A. Internal reactor volume
B. Volume of Teflon insert to hold test mixtures
C. Mixture Volumes
D. Volume of spaces added in the process of measuring gas concentrations
E. Piping used to connect a reactor to the GC instrument
F. Added space when purge tubes were removed after Test Series 2

Head Space = A-B-C+D+E+F

The overall information was given in Table 9. However, the following discussion shows the origin of those head-space volumes.

Internal Reactor Volume

Prior to testing, the internal volume of each reactor was measured, Figure 1. The calibration periods differ because the first set of reactors, i.e., HGV-2 to HGV-8 were calibrated for a previous test [6.5], which most were dedicated to radioactive work. A new set of reactors were constructed and calibrated at the later date listed in the table. The method to measure the internal volume for the two batches of reactors was slightly different but similar. A reactor was filled with water and the mass entered was measured and shown in Table 18 using the M&TE equipment shown in Table 19.

Table 18. Internal volumes determined of sealed reactor used for this study

	Reactor	Calibration	Temp.	Temp.	Water	Water	Water	Water	Density	Volume	Volume	Total
	Number	Date	Reactor	Water	Before	Left after	Left after	in Reactor	Water	of Each	of Valve	Control
					Filling	in Body	in Stem	Proper	of Cal	Reactor	Body	Volume
	HGV-		°C	°C	g	g (1)	g	g	g/mL	mL	mL (1)	mL
1st Cal	7	19-Sep-17	21.8	23.62	200.13	10.00	9.18	190.96	0.99758	191.42	0.59	192.01
	8	19-Sep-17	21.9	23.7	200.06	6.95	6.17	193.89	0.99756	194.36	0.59	194.96
2nd Cal	9	3-Dec-18	23.13	21.79	210.02		16.03	193.98	0.99764	194.44		
	10	4-Dec-18	22.79	21.64	210.02		16.10	193.92	0.99770	194.37		
	11	5-Dec-18	22.8	21.14	210.02		17.17	192.85	0.99776	193.29		
	12	6-Dec-18	22.88	21.84	210.03		17.40	192.64	0.99767	193.09		
	13	7-Dec-18	22.68	22.04	210.04		13.85	196.18	0.99767	196.64		
	14	8-Dec-18	22.61	21.43	210.01		15.43	194.58	0.99774	195.02		
	15	9-Dec-18	22.78	21.63	210.02		16.52	193.50	0.99770	193.94		
(1) Filling operation differed slightly from the first to the second volume calibration.												

Table 19. Measuring and Test Equipment Used to Calibrate Reactors

Measurement	M&TE TR No.	Make	Model	Model No	Range	Tolerance
Temperature	30325	Digi-Sense	ThermoLogR	None	-40 to 125°C	±0.2°C
Mass	40150	Mettler Toledo	FACT	AB304-S	0 to 320 g	±0.4% Reading

Teflon Insert Volumes
From the internal volumes of each reactor it was necessary to subtract items in the reactor that occupy space, like the test mixture itself and the Teflon insert that contained the mixture. After the Teflon inserts were fabricated from Teflon containers, they were marked with letters and then weighed to obtain the mass. Knowing the density of Teflon, i.e., 2.2 g/L then the volumes could be obtained, which are shown in Table 20. Once again, the M&TE used is shown in Table 19.

Table 20. Measuring and test equipment used to calibrate reactors

Insert Number	Insert Identifier	Mass g	Volume mL (1)
1	A	48.88	22.22
2	B	46.49	21.13
3	C	47.21	21.46
4	D	47.27	21.49
5	E	48.05	21.84
6	F	47.66	21.66
7	G	46.78	21.26
8	H	47.64	21.65
9	I	48.09	21.86
10	J	46.29	21.04
(1) Based on Teflon [Polytetrafluoroethylene (PTFE)] with density = 2.200 g/mL.			

Mixture Volumes
To obtain the volumes occupied by test mixtures a three-step process was used:

1. Make four grout mixtures with solids premixes of 10/45/45, which means: 10% cement, 45% slag, and 45% fly ash by mass, and 0/60/40 for each water-to-solids mass ratios of 0.85 and 0.59. Then fill the Teflon insert, with the Teflon coated stirrer, to about ½ full to leave a head space of ~100 mL as determined from previous work [6.5]. A mark was made on the wall of the Teflon insert. Both 0.85 mixtures had the same mass of 28 g; only the percentages of each constituent were changed. This process was first done for the 0.85 mass ratio. Later, when the work scope was increased to include the 0.59 mass ratio the process was repeated, but a new mark on the Teflon insert was needed because the volume was slightly larger. To minimize errors the amount of simulant to use for the 0.59 mass ratio was kept the same as for the 0.85 mass ratio, which meant for the lower mass ratio, i.e., more grout solids, the overall grout volume was slightly larger. Table 21 shows the mass of the mixture constituents to be used in each test.

2. Fill the Teflon insert, used to measure the 0.85 mass-ratio mixtures, to the mark made in Step 1 with just T50SS simulant to obtain the volume needed for Test Series 1, which did not use grout solids. Test Series 1 was only performed once so no measurement was necessary with the Teflon insert used to measure masses for the 0.59 mass-ratio mixtures.

Table 21. Mass of mixtures to fill volume in Teflon insert

Material (1)	Total Mass of Dry Premix for 0.85 mixture grams (2)	Total Mass of Dry Premix for 0.59 mixture grams (2)	Salt Solution grams (3)
Control (Salt Solution Only)	0.0	0.0	65.12
Premix 10% / 45% / 45%	28.0 (2.8 g + 12.6 g + 12.6 g)	40.4 (4.04 g + 18.19 g + 18.19 g)	33.00
Premix 0% / 60% / 40%	28.0 (0 g + 16.8 g + 11.2 g)	40.4 (0 g + 24.26 g + 16.17 g)	33.00

(1) "Premix" means grout premix solids, which are in the order of Cement/Slag/Fly Ash in percentage by mass.
(2) The 0.85 and 0.59 is the water-to-solids grout premix mass ratio used.
(3) This is the simulant needed to fill each reactor to have the same volume in each reactor when added to the test solids.

The balance used for the measurements in Table 21 was MS&E No. 36119, calibration expiration of 08/02/2021, which is daily checked with weight set MS&E No. 33583, calibration expiration 07.27/2021.

3. Once the Teflon inserts were marked the volumes could be determined. Water was used to accurately measure the volume in the Teflon insert. Without the Teflon stirrer, water was filled to marks made in Step 1. The process was repeated many times to obtain good averages, Table 22.

Table 22. Determining volumes occupied by the mixtures using water

Reactor Teflon Water Insert Volume Calibration (1)			
0.85 Water-to-Grout Premix Solids Dilutions			
Volume Test	Test Date	Mass g (2)	Volume mL
1	6-Sep-19	56.29	56.40
2	6-Sep-19	54.75	54.86
3	6-Sep-19	55.64	55.75
4	11-Sep-19	56.16	56.28
5	11-Sep-19	55.40	55.51
6	11-Sep-19	55.56	55.67
	Average	**55.63**	**55.74**

(1) Fixed volume in Teflon reactor insert was measured by the mass of water to a fixed line and then converted to a volume.
(2) 2 x Standard Deviation = 1.11 g or mL
(3) Density used = 0.998 g/mL at 22°C

Reactor Teflon Water Insert Volume Calibration (1)			
0.59 Water-to-Grout Premix Solids Dilutions			
Volume Test	Test Date	Mass g (2)	Volume mL
1	9-Jun-20	56.01	56.12
2	9-Jun-20	56.89	57.00
3	9-Jun-20	55.96	56.07
4	9-Jun-20	56.19	56.30
5	9-Jun-20	56.29	56.40
6	9-Jun-20	56.35	56.46
	Average	**56.28**	**56.39**

(1) Fixed volume in Teflon reactor insert was measured by the mass of water to a fixed line and then converted to a volume.
(2) 2 x Standard Deviation = 0.67 g or mL
(3) Density used = 0.998 g/mL at 22°C

The balance used for the measurements in was MS&E No. 36119, calibration expiration of 08/02/2021, which is daily checked with weight set MS&E No. 33583, calibration expiration 07.27/2021.

Added Volumes to Reactor Head Space: Piping connecting GC to a reactor

To connect the GC to the reactor tube, tube fittings are needed,"" and they create extra volume into which the gas migrates before measurements can be made; therefore, it needs to be included to the head space. Table 23 is a consolidation of the hand calculations shown in Figure 18 to be clearly understood. The piping includes a ~5-foot long, 1/16-inch tube and three fittings that combined to increase the head space by 2.58 mL. The length was measured with a rule graded to the 16th (0.0625 in.) of an inch and the inside diameter was gauged by a drill diameter, which is accurate to 1/10000 of an inch. The internal volumes of the fittings came from computer aided drawings. Linear dimensions are expected to be accurate to 1/1000 inch based on standard machined-parts.

Table 23. Volumes of piping and fittings between the GC and a sealed reactor

Tube	ID =	0.0265 inch	Length =	58.75 inch	Volume =	0.032	in^3
	Connection Fittings*						
1/4 Swag Union (SS-400-6)		ID=0.25 in	Length =	2.2 inch	Volume =	0.108	in^3
1/16" x 1/4" reducer		ID=0.18 in	Length =	0.64 inch	Volume =	0.016	in^3
VCR 1/4" Gland		ID=0.05 in	Length =	0.26 inch	Volume =	0.001	in^3
					Total Volume =	0.157	in^3
* Volumes were taken off CAD Drawings.						2.576	mL

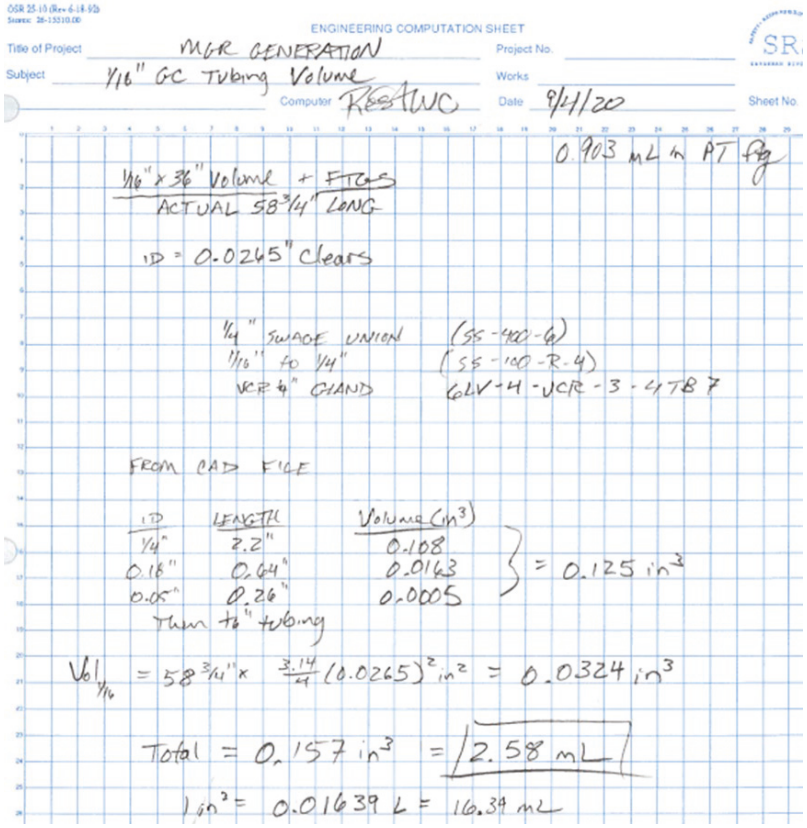


Figure 18. Hand-calculation of volumes of piping and fittings between the GC and a sealed reactor

Added Volumes to Reactor Head Space: After purge tube was removed

During Test Series 2, the purge tubes in most of the eight reactors in use became plugged with grout and cleaning and removing the grout, to prepare the reactors for Test Series 3, became problematic. Therefore, before Test Series 3 was performed, the purge tubes were removed. This was done by cutting the tubes in each reactor leaving a ½-inch stub in the head space so that the open tube end is above the mixture surface to prevent grout to enter while allowing the pressure transducer to measure the head-space pressure. Table 24 is a consolidation of the hand calculations shown in Figure 19 to be clearly understood. The purge-pressure measurement system consists of a series of small volumes, listed as A through F, which are summed to obtain a purge-system volume that must be added to the head volume because it increases the reactor internal volume shown in Table 18.

Table 24. Volume of purge system

Dimensions from CAD Drawing										
Section	Name									
A	Remaining purge tube:	ID =	0.055	in	Length =	2.16	in	Volume =	0.005	in^3
B	T-fitting:	ID =	0.09	in	Length =	1.435	in	Volume =	0.009	in^3
C	Male VCR fittings:	ID =	0.06	in	Length =	1.295	in	Volume =	0.004	in^3
C	Male VCR fittings:	ID =	0.06	in	Length =	1.295	in	Volume =	0.004	in^3
D	Pressure Transducer:	Measured by filling with water and weighing = 0.903 mL						Volume =	0.055	in^3
E	Female VCR fittings:	ID =	0.18	in	Length =	1.22	in	Volume =	0.031	in^3
F	'urge-Tube Section Removed:	OD =	0.125	in	Length =	1.769	in	Volume =	0.022	in^3
								Total Volume to add to Head Space =	0.129	in^3
									2.121	mL

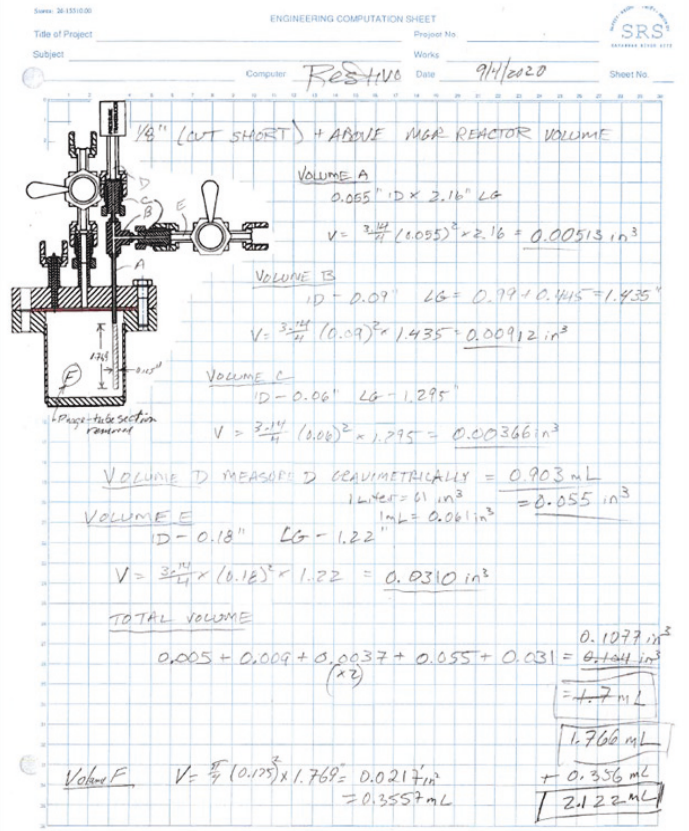


Figure 19. Hand calculation of volume of purge system

Appendix F: Test Series 1 Results

Control - Using Na_2S to Demonstrate Largest and Fastest Methane Generation over a Period of 96 hours with a Tank 50 Simulant with a Concentration of 100 mg/L MeHg

Temperature and Pressure

Figure 20 shows the temperature and pressure histories during the test period. The target temperature was 35°C ± 5°C and the pressure was between 12 and 14 psig, to not exceed the GC limit of 20 psig, to protect the equipment. Any pressure was acceptable as long as it did not exceed the GC limit and it was known in order calculate MGR. Each reactor had its own dedicated thermocouple (TC) and pressure transducer. Each TC was located on the outside of the reactor body, approximately midway between the reactor bottom and the top of the mixture within the reactor, similar to what is shown in Figure 1. The bottom of the main reactor body was surrounded by an aluminum block, as shown in Figure 2, that helped to hold the reactor in place and make the temperature more uniform. What is not shown is the insulation surrounding each reactor during the test. From previous testing, discussed in Appendix D of reference [6.5], the internal mixture temperature will be higher than the external temperature by less than 0.5°C at a target temperature of 35°C from the external temperature when using the aluminum block. For the temperature data, two trends are seen: a fluctuation around the target of 35°C of less than 4°C, once steady state is reached, and larger fluctuations from the 48-h test. The thermocouple on Reactor HGV-12, for the 48-h test, was on a heat plate that was hard to control. It had to be adjusted manually a couple of times when its temperature because too low or high. However, in general it met the criterion of 35°C ±5°C.

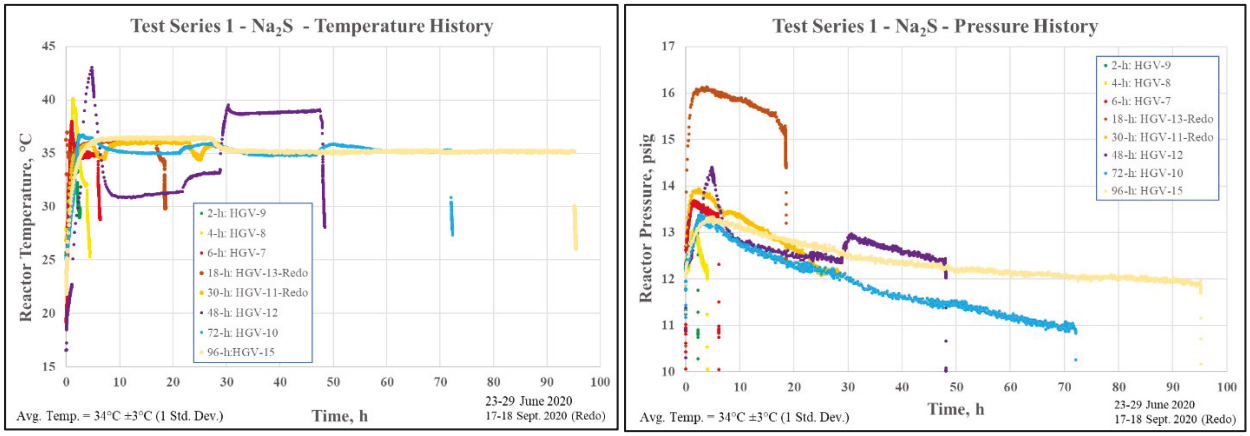


Figure 20. Test Series 1 temperature & pressure profiles

All the pressures started at the target, except the 18-hour test, but it was still on the 20-psig ceiling; therefore, it was acceptable. However, a surprising result occurred with the pressures over time. For all the reactors during each test duration the pressure dropped. Before beginning the next test series, it was important to understand this reduction of pressure because it was initially thought that the reactors were leaking and consequently meaning the test results were compromised. These results only became obvious when the test was complete, and the temperature and pressure data were analyzed. The pressure changes were small, ~2 psig, and the initial pressures between 13 and 14 psig are not crucial; however, knowing the pressures and that the reactors remain leak free are very important. All the reactors seals were checked and nothing unusual was found. It was determined, see Appendix M, that the reduction in pressure was the excess sulfide reacting with the oxygen in the head space; therefore, the conclusion was that the reactors remained leak-tight.

Gas Concentrations

Figure 21 shows the gas concentration measured in the headspace of each reactor, which are listed in Table 25. The GC measured hydrogen, nitrous oxide, carbon dioxide, but principally for methane. Figure 21 shows that small amounts of H_2, N_2O, and CO_2 were detected, which will be discussed later in this appendix, in comparison to the larger amounts of CH_4. A few aspects of the information in Figure 21 need explanation. There are two datum points from previous scoping work [6.4] done under similar conditions at 1 hour and 27 hours and they appear to match the overall trend in time for methane generation obtained in this current test. Two datum points of the current test, i.e., at 18 and 30 hours, were compromised in that when their reactors were opened, some of the simulant was found under the Teflon cup that held the reactor mixture. Those data are not shown. However, those two points were redone at a later date, which are listed on Figure 21, and those results are circled on the figure. Those results are good, but they clearly show the effect of scale. They show the correct trend, in that the 30-h ppm is slightly higher than the 18-h ppm, but they are both much lower that the entire set of data. The reason is that the amount of simulant used was approximately one half of what it should have been. These two tests were included in a series of 6 repeat tests and the other four tests were for other test series, i.e., Test Series 2 and 3, which were for grout mixtures. The grout mixtures used approximately half the simulant that was used for the Na_2S tests. The lower amount was accidentally used, but that does not invalidate the tests because the amount of sulfide was still in excess of what was needed, recall Table 1. However, this meant that reactor head space was larger than for the other reactors, which means the space contains more nitrogen and residual air; therefore, the ppm of methane would be much lower. As will be seen when the methane generation rate (MGR) is discussed, those two datum points fit well with all the other data. This error shows how important it is when talking about gas generation in the small-scale reactors, i.e., 200 mL, to focus on rate and not the absolute mass generated.

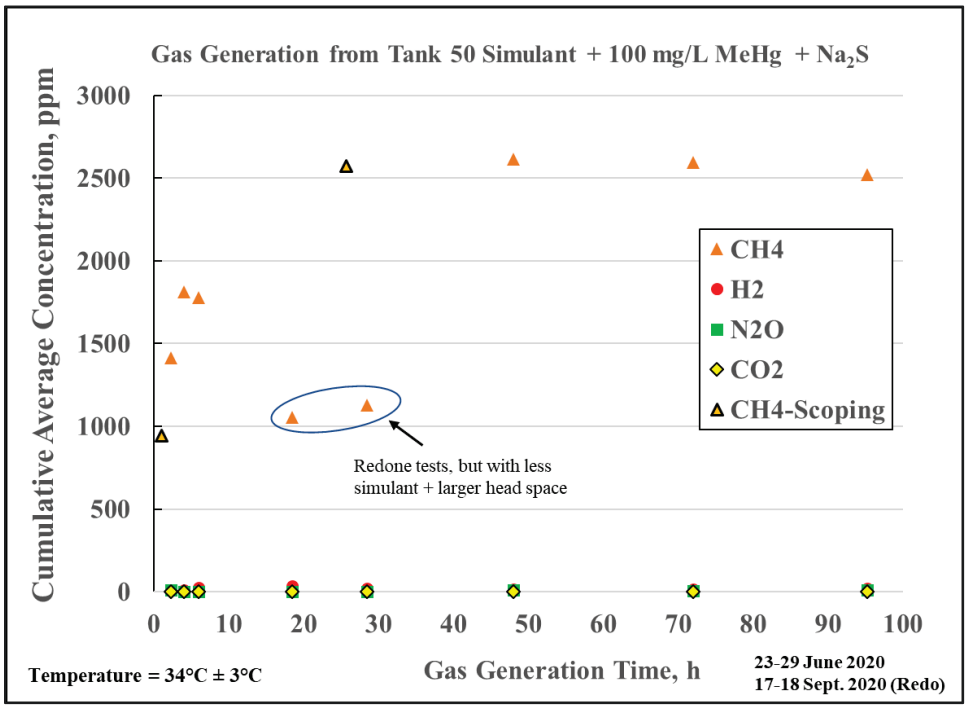


Figure 21. Test Series 1 gas concentrations

It is clear from Figure 21 that methane generation began very fast, even within the first hour, and it appears after 1 day the generation had reached an asymptote of ~2500 ppm. This was confirmed in the MeHg destruction test, from the results shown in Figure 22, which indicates at least 95% of the MeHg is destroyed. Knowing the available total moles of MeHg, ~1.3 x 10^{-5} moles, from the measured concentration of 99.9

mg/L of MeHg, then that can be compared to moles of methane generated. The closed circles in Figure 22 show that methane reached an asymptote after approximately 18 hours. Subsequently, the MeHg in the solution was measured with time, the closed triangles. The results indicate the one-to-one relationship between methane generation with the loss of MeHg, within the MeHg and the methane gas concentration measurement uncertainties of ±20% and 24%, respectively, at the 95% confidence level. In fact, the match is even better because the error bars shown are ±10%. As methane was formed through MeHg destruction, it too, confirms the process happened fast and reached a similar asymptote, within measurement uncertainty. The actual values for the fraction of methane moles produced and fraction of MeHg destroyed are listed in Table 10.

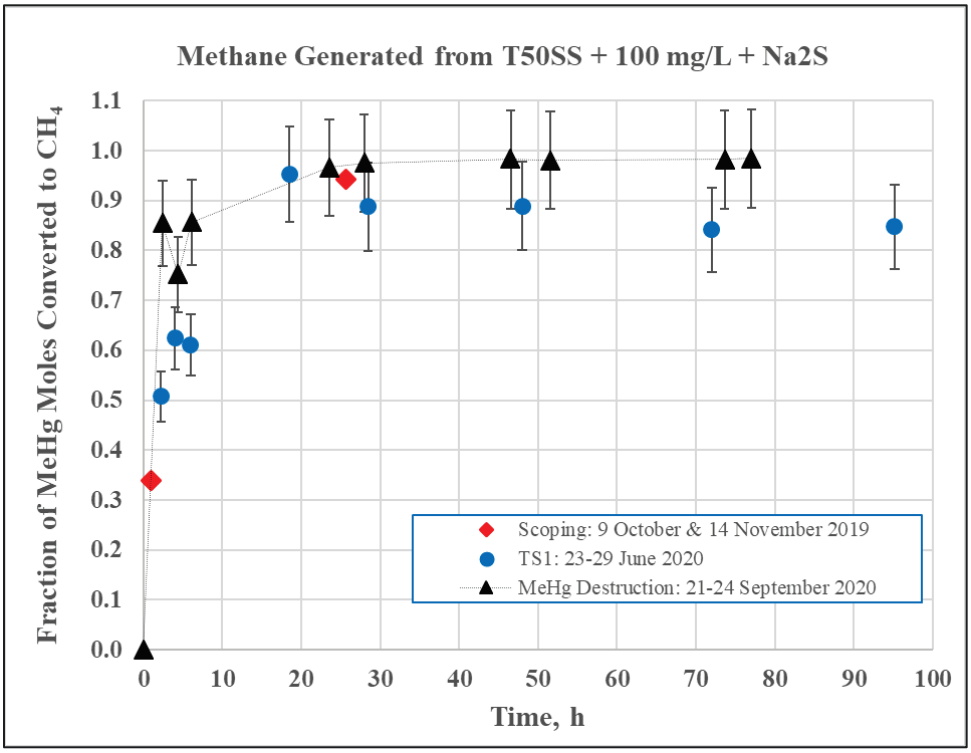


Figure 22. Test Series 1 fraction of MeHg converted to methane versus faction MeHg destroyed

Methane Generation Rate

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 23 and Table 25 show the gas generation rates for CH_4. The methane generation rate (MGR) was calculated with Eq. (1), which is the same method used for all other gases that will be discussed:

MGR =

[[(Head Space Vol[10], ft^3) • **A** • CH_4 Measured, ppm / 1000000] / (Duration, h)] / Vol. Liquid[11], gal **(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)]

[10] Head Space Volume also includes the volume of plumbing that leads to the GC because it adds to the gas space once connected.
[11] Liquid volume is only of the Tank 50 salt solution simulant because no grout is used in Test Series 1.

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

This equation is shown for the principal gas, methane, but has the same form for all the gases discussed, i.e., hydrogen, nitrous oxide, and carbon dioxide.

The principal gas measured is methane and Figure 23 clearly shows MGR drops rapidly over the first 24 hours and tapers off during the next 3 days. The cumulative MGR follows the power-law relation shown in the figure with a correlation coefficient of 0.99. The largest MGR occurred after the first hour of 5.3 x 10-4 (ft^3/h) / gallon of salt solution and drops to more than an order of magnitude after 4 days. The error bars shown are ±24% RSD at the 95% confidence level.

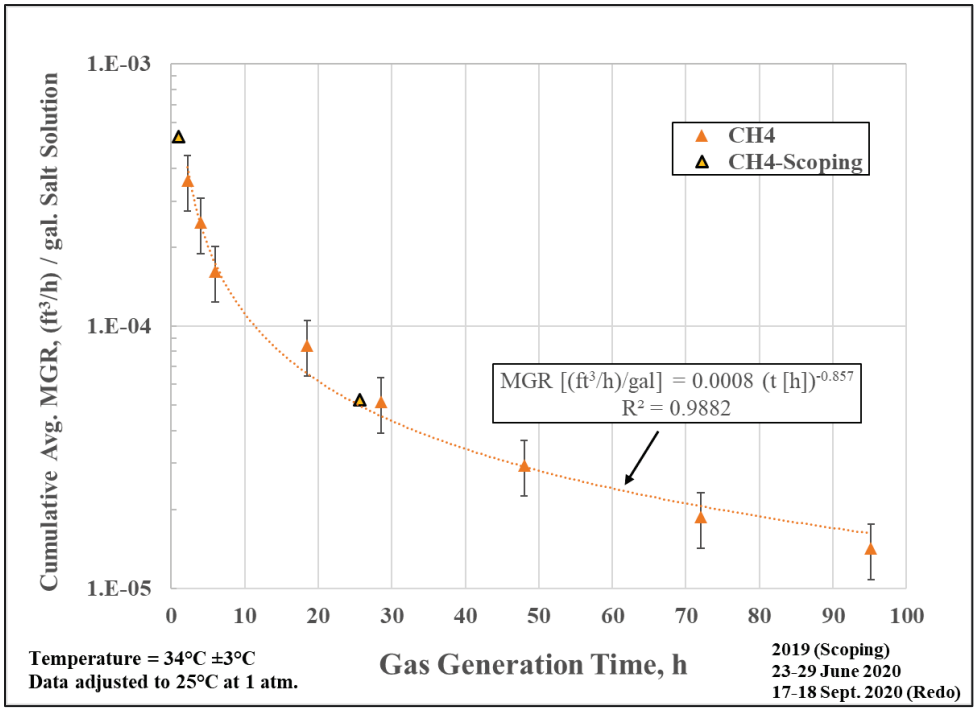


Figure 23. Test Series 1 methane gas generation rates

For sealed reactors, only the accumulated amount of gas can be measured for a fixed time period, but to obtain a more instantaneous measure of MGR the accumulated mass of methane from each period was subtracted from the preceding test period. Figure 24 shows the MGR for 9-time intervals of from the first hour to the last 24 hours.

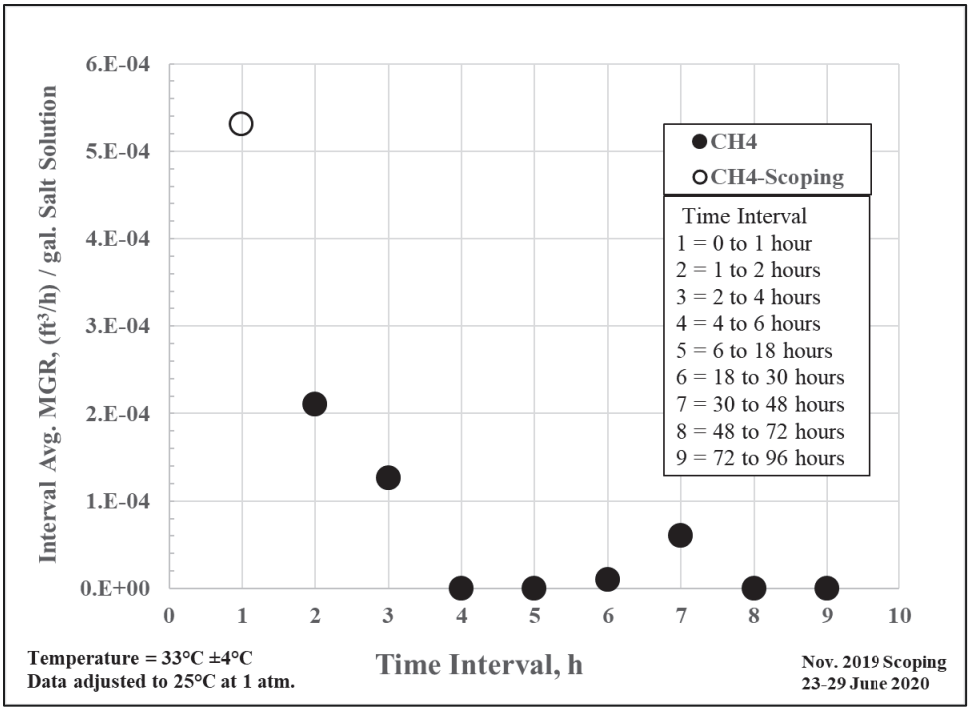


Figure 24. Test Series 1 methane gas generation rates between test intervals

Somewhere during the 2-hour interval from 4 to 6 hours, MGR drops to an insignificant level. This implies that the drop in MGR after approximately 6 hours shown in Figure 23 occurs mostly because of the increase in time rather than any significant drop in the rate in the production of methane. However, this does not mean that methane is not produced after 6 hours but only that its measurement is not significant.

Other Measured Gases

Concentrations of hydrogen, nitrous oxide, and carbon dioxide were also measured, but they were far below that of methane. Using Equation (1) to determine the generation rates for each gas, those rates were an order, or several orders, of magnitude less, as shown in Figure 25. The rates span over 5 orders of magnitude; however, as shown in Table 25 the concentration of N_2O and C_2O are less than 10 ppm and, while detectable, are below a quantifiable level. For concentration below 1 ppm the values in the table are listed as 0 ppm. Hydrogen does have concentrations above 10 ppm, above which is considered quantifiable. However, H_2, N_2O, and C_2O play a minor role in gas generation when compared to methane. The source of H_2, with HGR of 1.2×10^{-7} (ft^3 / h) / gal measured at 4 days, see Table 25, is most likely due to tramp TOC in the simulant. For previous grout testing, the T50SS simulant was made from the same reagents and that simulant was measured to have 80 mg/L of TOC[12].

[12] See Table 3 of reference [6.5]

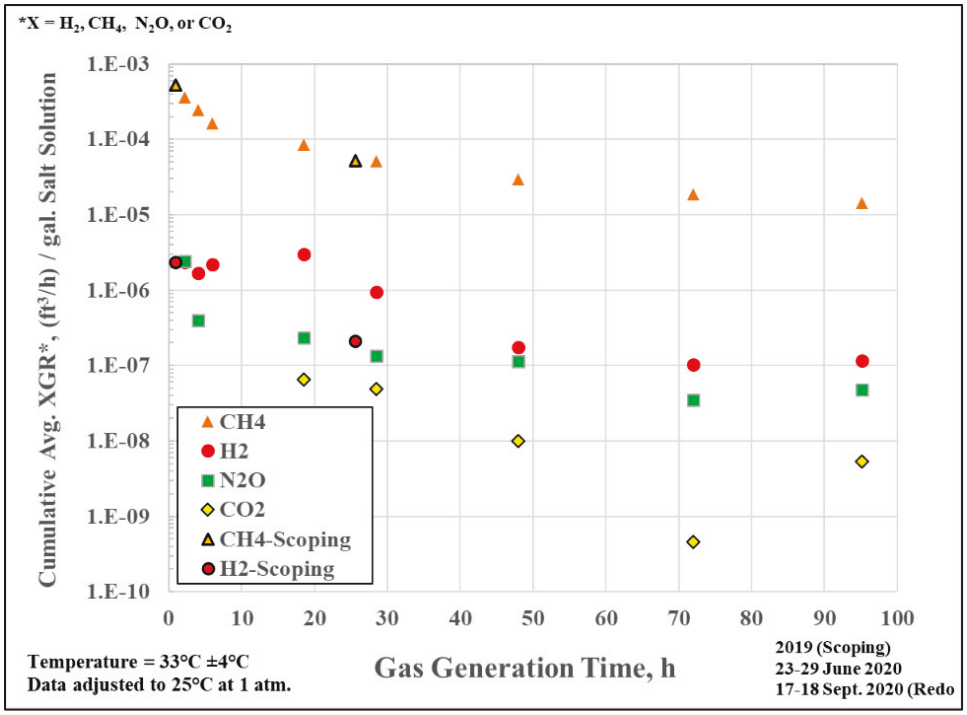


Figure 25. Test Series 1 methane gas generation rates for all gases measured

Table 25. Test Series 1 gas concentrations and gas generation rates

Reactor HGV-	Duration h (1)	Temp. °C (2)	CH_4 ppm	CH_4 (ft^3/hr) / gal	H_2 ppm	H_2 (ft^3/hr) / gal	N_2O ppm	N_2O (ft^3/hr) / gal	CO_2 ppm	CO_2 (ft^3/hr) / gal
8	1.0	35	945	5.30E-04	4	2.33E-06	0	0.00E+00	(1)	(1)
9	2.2	32	1416	3.61E-04	9	2.35E-06	9	2.42E-06	0	0.00E+00
8	4.0	34	1814	2.49E-04	12	1.68E-06	3	4.01E-07	0	0.00E+00
7	6.0	34	1779	1.62E-04	24	2.17E-06	0	0.00E+00	0	0.00E+00
13	18.5	34	1054	8.46E-05	37	2.98E-06	3	2.32E-07	1	6.52E-08
8	25.7	30	2574	5.25E-05	10	2.12E-07	0	0.00E+00	(1)	(1)
11	28.5	35	1126	5.13E-05	21	9.43E-07	3	1.33E-07	1	4.85E-08
12	48.0	32	2617	2.95E-05	15	1.75E-07	10	1.12E-07	1	1.00E-08
10	72.0	35	2597	1.87E-05	14	1.03E-07	5	3.45E-08	0	4.52E-10
15	95.2	35	2520	1.42E-05	21	1.17E-07	8	4.73E-08	1	5.35E-09

(1) 18-h and 30-h tests are results from repeat tests. Intial test had misplaced simulant. 1-h and 25.7-h tests (the grey rows) are from previous scoping work (SRNL-STI-2019-00106) during which CO_2 was not measured.
(2) Overall temperature average = 33°C ±4°C.

Mercury Results

To confirm the concentration of MeHg in the spiked T50SS simulant, samples were taken immediately after spiking and before filling any of the reactors. Then when the last reactor was filled several days later, the spike simulant was sampled again. This was to show all reactors used approximately the same starting concentration of MeHg before the simulant was further spiked with a source of sulfide that would allow methane to generate as the MeHg was being destroyed. Table 26 shows both the total Hg and the MeHg concentrations, along with the MeHg spiked concentration from when the simulant was spiked with MeHgOH source material. Within the analytical measurement uncertainty ±20% at the 95% confidence level, all the measured values indicate the target concentration 100 mg/L of MeHg was obtained. The measured values of MeHg are low, but they may have been slightly low because the measurements were made 3 months after the simulant was spiked.

Table 26. Test Series 1 MeHg and total Hg results of spiked simulant

Test Series Number	Reactor Fill Period	Date Simulant Sampled	T50SS (1) Density g/mL	Composed MeHg Spike mg/L	Date Sample Analyzed	Analyzed Total Hg mg/L (2)	Date Sample Analyzed	Analyzed MeHg mg/L (3)	Comments
1	First	23-Jun-20	1.2210	99.9	9-Jul-20	100	22-Sep-20	84	Sampled before filling reactors (4)
1	Last	25-Jun-20	1.2210	99.9	9-Jul-20	94	22-Sep-20	83	Sampled after last reactor was filled (4)

(1) T50SS = Tank 50 Salt Solution simulant
(2) Analyzed by Direct Mercury Analyzer using Atomic Absorption Spectroscopy. Two sigma uncertainty is ±20%.
(3) Analyzed by Gas Chromatography Cold-Vapor Atomic Flourescence Spectrophotometry. Two sigma uncertainty is ±20%.
(4) These samples were taken before being spiked with sulfide-containing solids of Na_2S.

Appendix G: Test Series 2 Results

T50SS Simulant, Concentration of 100 mg/L MeHg in a Grout Mixture of 10/45/45 Grout Premix Solids, Water-To-Solids Mass Ratio of 0.85, Over 96 hours

Temperature and Pressure

Figure 26 shows the temperature and pressure histories during the test period. The target temperature was 34°C ± 4°C and the pressure was between 12 and 15 psig. See the preceding Test Series 1 for details on the temperature and pressure operation.

The reduction in pressures shown in Figure 20 for the preceding test series is more pronounced than for this first series involving grout. While grout solids do contain sulfide, its release from grout is more complex [6.22] and slower than for Na_2S. That is, the reaction between sulfide with the residual oxygen in the head space is probably less, as discussed in Appendix M. Still, there is some pressure reduction, but it is not due to reactor leaks, but due to the sulfide-oxygen reaction.

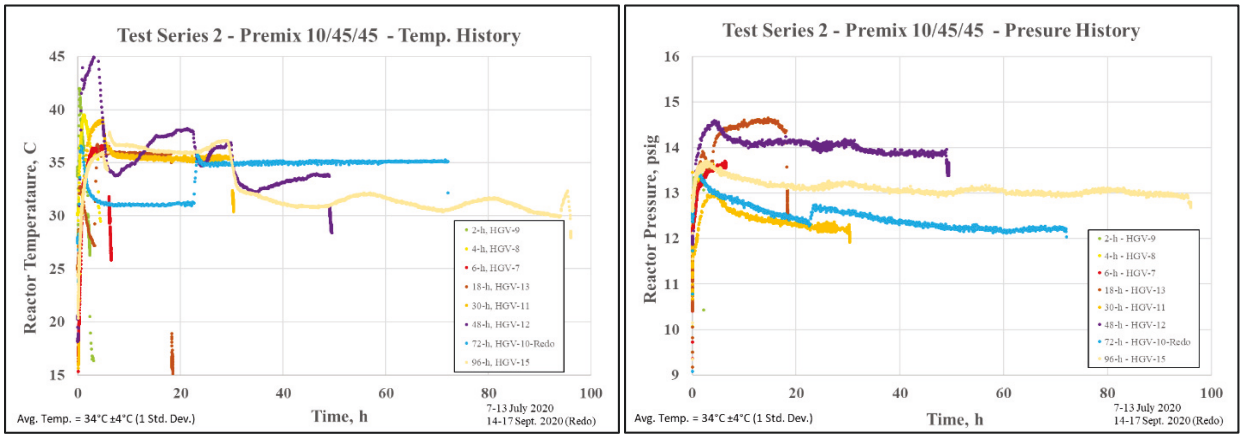


Figure 26. Test Series 2 temperature & pressure profiles

Gas Concentrations

Figure 27 shows the methane gas concentration measured in the headspace of each reactor. Besides methane, the GC was used to measure hydrogen, nitrous oxide, and carbon dioxide, which are not shown in the figure because they are an order of magnitude less, but they will be discussed later. The data are listed in Table 27. Note the single point indicated as a redo test at 72 hours. The initial test had some of the simulant misplaced, which compromised the results, so it was repeated later as shown on the figure. Furthermore, shown on Figure 27 are two points obtained from previous scoping work [6.4] done under similar conditions at 1 hour and 27 hours. The measurement at 27 hours is above current set of points for an unknown reason, but the scoping tests had only one result for the 10/45/45 mixture, so it may be an outlier. The scoping results at 1 hour shows no methane was detected, which was not surprising since it may take longer than 1 hour for the grout to begin to leach reduced sulfide.

A significant difference between the results from Test Series 1, using Na_2S, and Test Series 2, using grout is the speed at which the methane production reached its asymptote. For the former, it was reached in less than 1 day, while for the latter, it took approximately 3 days. The absolute amount of methane was double for the Na_2S mixture since the amount of sulfide in the grout is less[13], as well as it must leach out of the grout solids before being able to react with MeHg.

[13] Table 1 shows the ratio of sulfur to mercury for each of the mixtures. For soluble Na_2S, the sulfur is soluble as sulfide in the solution. For the grout, the sulfur is also in the form of sulfate, which does not react with MeHg. Furthermore, the reduced sulfides only become available as the grout solids begin to the break down.

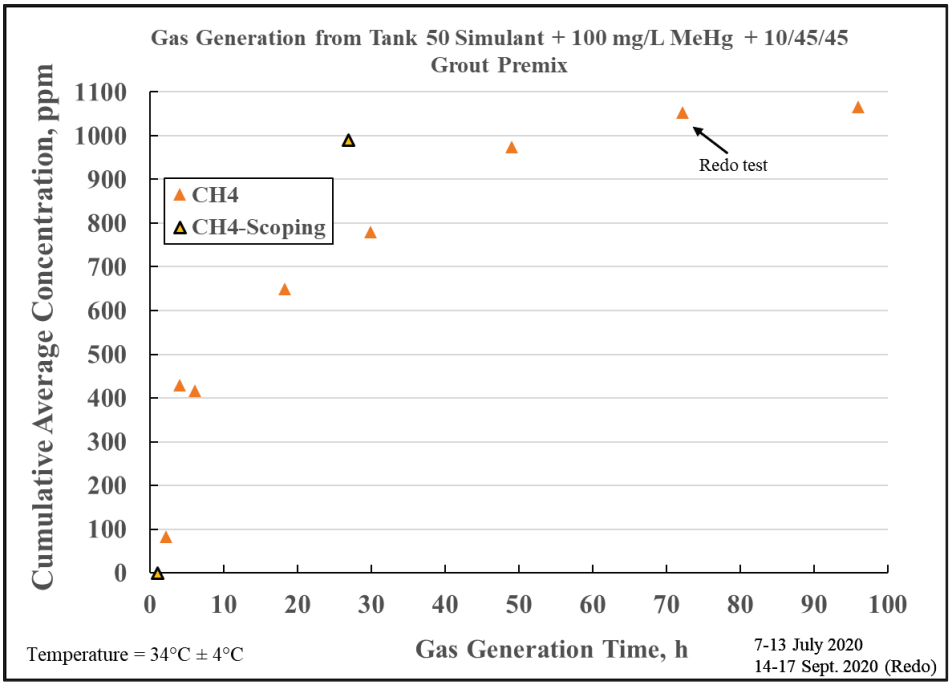


Figure 27. Test Series 2 gas concentrations

Figure 27 shows that methane generation began after about 2 hours, but it took more than 3 days to reach an asymptote of ~1050 ppm. While the results from the MeHg destruction test are less definitive than seen for Test Series 1, Figure 22, Figure 28 indicates that after 27 hours MeHg was still being destroyed. The MeHg and the methane gas concentration measurement uncertainties are ±20% and 15%, respectively, at the 95% confidence level.

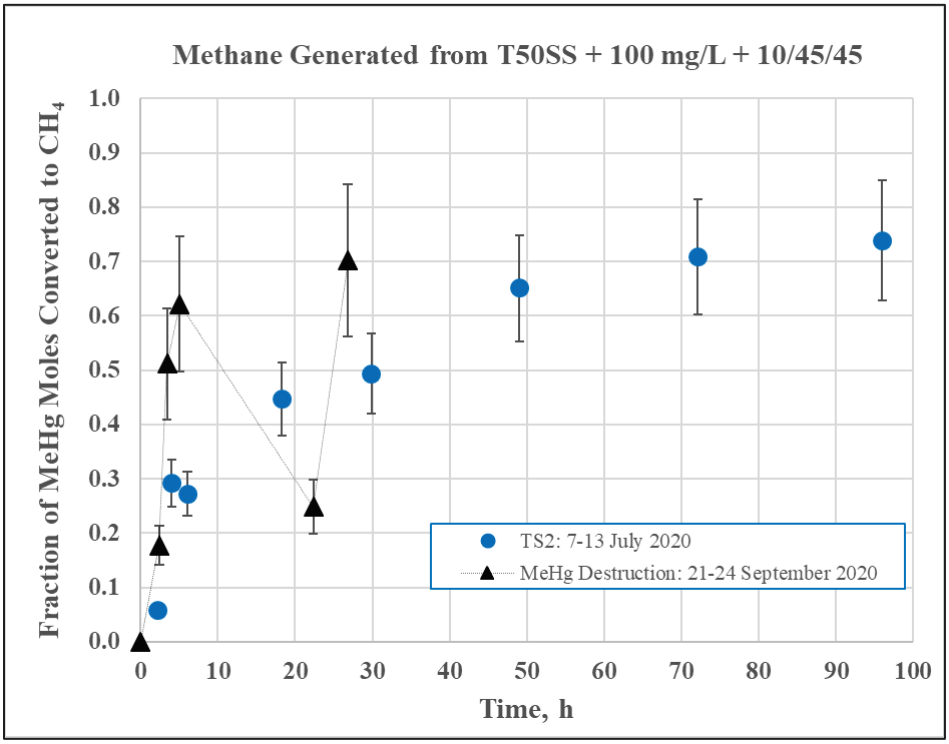


Figure 28. Test Series 2 fraction of MeHg converted to methane versus faction MeHg destroyed

The MeHg Destruction test for the 10/45/45 grout mixture was designed to end at 77 hours, but after 24 hours, the grout slurry, while still being mixed, had a consistency which made it much more difficult to draw liquid samples to analyze. This is probably the reason the result at 24 hours is much lower than the other points, i.e., a poor sample, but the result at 27 hours indicates that at ~70% of the MeHg destroyed the process was slowing. The test was stopped at this point because obtaining further samples was not possible. The results from measuring methane indicate the mole fraction of methane gas appears to peak at 4 days with around 75% of the moles of methane produced from the number of moles that could have been produced if all the MeHg were converted. The asymptote of methane production within measurement uncertainty is the same as for asymptote of MeHg destruction. The actual values for the fraction of methane moles produced and fraction of MeHg destroyed are listed in Table 10.

The destruction of MeHg appears to happen faster than the production of methane with 60% destroyed within the first 6 hours where it appears the methane generated takes about 2 days to reach this percent. However, the data do not show a clear picture. After 6 hours the MeHg destruction drops to about 25% after 1 day before it increases again. It could be a sampling problem with the grout mixture not being uniform, even though it was being mixed, indicating the concentration may vary in different regions of the mixture. In any case, literature [6.22] on the blast furnace slag (BFS) in grout suggests that the release of sulfide from grout, which is needed to produce methane, is complex. That study indicates that the two sulfurs from thiosulfate, $S_2SO_3^{2-}$, have different oxidation states, with the outer as 2^- and the inner as 6^+, so on average the oxidation state of sulfur in $S_2O_3^{2-}$ is equal to 4^+. The six tables in that reference [6.22] shows varying degree of oxidation, and Figures 4 [6.22] shows how the oxidation changes with depth of particles; they also show how the BFS can oxidize from the outer surface towards the inner center with storage time of months. Table 5 [6.22] shows that for slag particles smaller than 3 mm, which were stored in a desiccator, only had 26% oxidation (so maybe the remaining 74% is reduced S^{2-} as CaS.).

Operational Notes

After the gas was sampled from each reactor, they were opened to view the state of the grout. The 10/45/45 grout mixture were purposely made slightly dilute with a water-to-solids mass ratio of grout premix of 0.85, which is less that the standard mass ratio of 0.59. This was done to help keep the mixture as a moving slurry while being continuously mixed. Figure 29 shows two of the reactors with the grout still being mixed as a slurry. Figure 29(a) was taken immediately after the 2-h test and Figure 29(b) taken after the 18-h test. For the longer period test pulsations in the grout could still be observed but without movement they would not be evident from still photographs.

(a) HGV-8 (b) HGV-13

Figure 29. Two reactors from Test Series 2 with 10/45/45 grout mixtures, (a) after 4-h test with grout still moving as a slurry and (b) after the 18-hour test with grout still as a slurry

Methane Generation Rate

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 30 and Table 25 show the gas generation rates for CH_4 from Test Series 2. The methane generation rate (MGR) was calculated with Eq. (1), which is the same method used for all other gases that will be discussed:

MGR =

[[(Head Space Vol[14], ft^3) • **A** • CH_4 Measured, ppm / 1000000] / (Duration, h)] / Vol. Liquid[15], gal **(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

This equation is shown for the principal gas, methane, but has the same form for all the gases discussed, i.e., hydrogen, nitrous oxide, and carbon dioxide.

The principal gas measured is methane and Figure 30 shows MGR increases rapidly during the first 4 hours and peaks at 1.2 x 10-4 (ft^3/h) / gallon of salt solution as sulfide is leached from grout solids and then drops rapidly for about 24 hours. It then tapers off during the next 3 days. The error bars shown are ±15% RSD at the 95% confidence level. The trend follows the power-law relation shown on the figure with a correlation coefficient of 0.99, but at a slower rate than was shown in Test Series 1, Figure 23. This is probably do to the fact that reduced sulfide is still be leached from the grout to produce more methane. Note that both the scoping point and the 2-hour point were not included in that trend line. Not shown is the scoping datum point at 1 hour because no methane was detected, see Figure 27 and Table 27, which includes all the Test Series 2 data. As previous explained, some time is necessary for the grout solids to release reduced sulfide to produce methane.

[14] See footnote 10.

[15] Liquid volume is only of the Tank 50 salt solution simulant contained in the grout mixture.

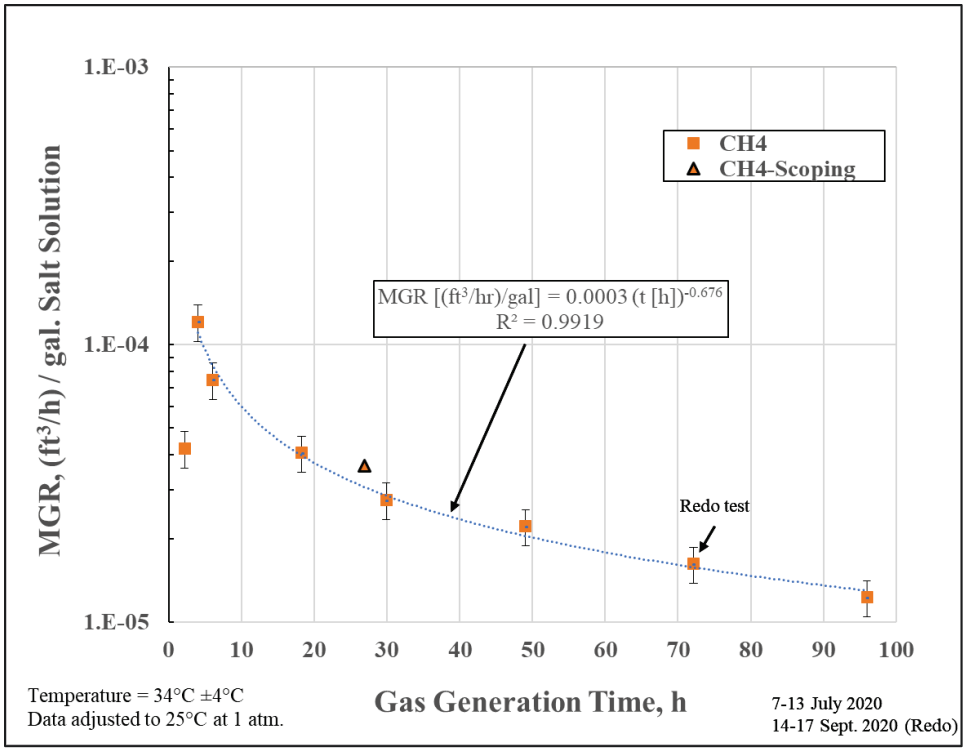


Figure 30. Test Series 2 methane gas generation rates

It is important to remember that for sealed reactors only the cumulative amount of gas is measured for a fixed time period, but in an attempt to obtain a more instantaneous measure of MGR the accumulated mass of methane from each period was subtracted from the preceding test period. Figure 31 shows the MGR for the time intervals between the 9-time periods from 1 to 96 hours, which ranged from 0 to 1 hour to 3 to 4 days. The error bars shown are ±21% RSD at the 95% confidence level. For the 3rd interval from 2 to 4 hours it appears that MGR reached a maximum. The 4th interval from 4 to 6 hours the methane accumulation was less at 6 hours than 4 hours, see Figure 27 or Figure 28, so MGR was negative, and is shown as zero. This could be due to several reasons, like measurement uncertainty, the peak occurs at 4 hours, or due to the fact that the release of reduced sulfide from grout is complex, and the batch of grout in the 6-hour sealed reactor acted slightly different from the mixture in the 4-hour reactor. However, as the intervals continue MGR continues to slow down from the 6- to 18-hour interval onwards. It appears that somewhere after 4 hours, and before 6 hours, MGR reached its peak.

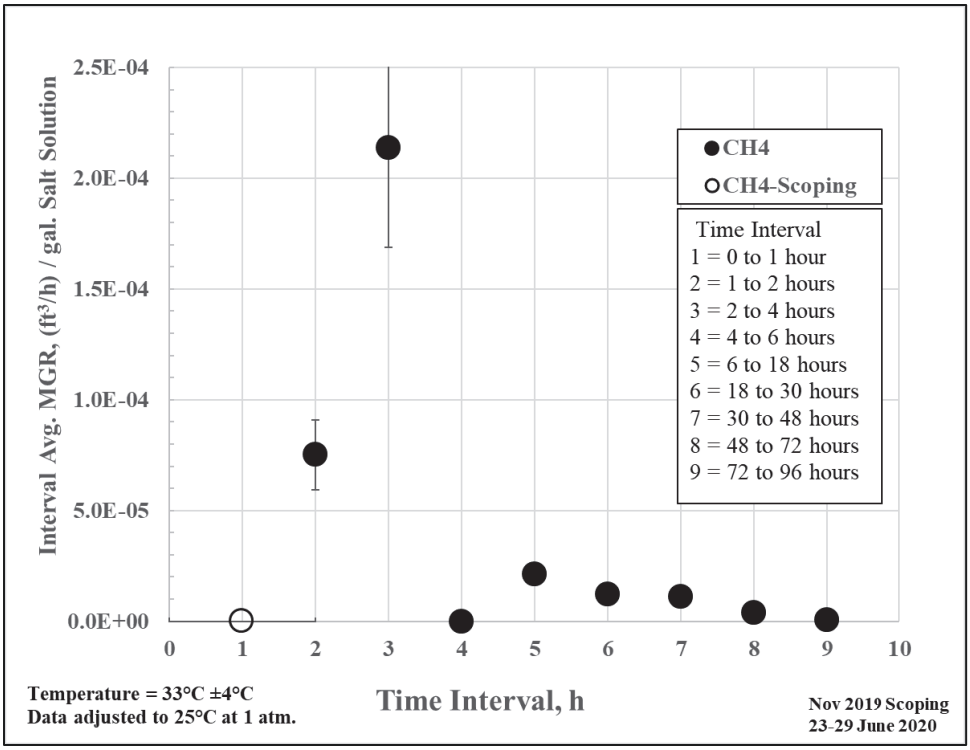


Figure 31. Test Series 2 methane gas generation rates between test intervals

Other Measured Gases

Concentrations of hydrogen, nitrous oxide, and carbon dioxide were also measured, but they were far below that of methane. The results are spread of 5 decades of MGR. Using Equation (1) to determine the generation rates for each gas those rates were several times, to several orders of magnitude, less than methane, as shown in Figure 25. With respect to both H_2 and N_2O Table 27 show the concentrations reached several hundred ppm, so while less than methane, are quantifiable. However, C_2O was barely detectable at less than 12 ppm. For concentrations below 1 ppm, the values in the table are listed as 0 ppm. All three gases only play a minor role in gas generation.

As to the source of H_2, it is most likely the TOC in the test mixture. As explained for the Na_2S mixture of Test Series 1, the T50SS simulant could have 80 mg/L of tramp TOC. Furthermore, for Test Series 2 the grout mixture contains cementitious solids, which were measured to contain a total of between 113 mg/L and 175 mg/L of TOC[16]. This larger concentration of TOC most likely resulted in an HGR of 1.8×10^{6} (ft^3 / h) / gal at 4 days, see Table 27, which is higher than for the Na_2S mixture by an order of magnitude, see Table 25.

[16] In Reference [6.5] see Table 3 for the TOC in simulant and Table 4 for the TOC in the cementitious components.

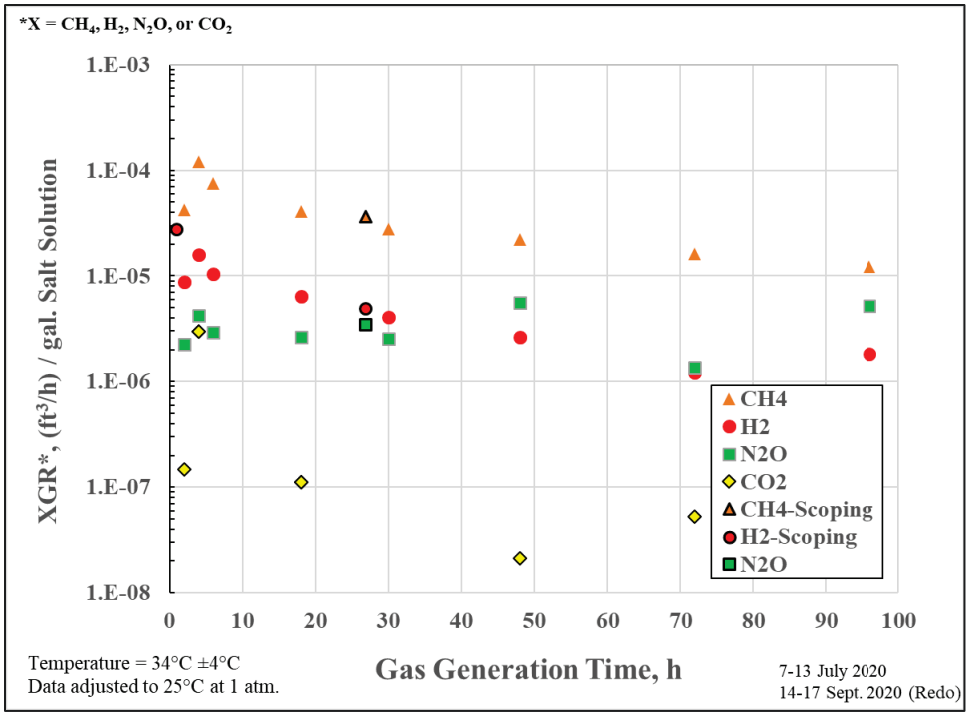


Figure 32. Test Series 2 methane gas generation rates for all gases measured

Table 27. Test Series 2 gas concentration and gas generation rates

Reactor HGV-	Duration h (1)	Temp. °C (2)	CH_4 ppm	CH_4 (ft^3/hr) / gal	H_2 ppm	H_2 (ft^3/hr) / gal	N_2O ppm	N_2O (ft^3/hr) / gal	CO_2 ppm	CO_2 (ft^3/hr) / gal
9	1.0	34	0	0	26	2.75E-05	0	0	(1)	(1)
9	2.2	34	83	4.22E-05	17	8.76E-06	4	2.24E-06	0.29	1.48E-07
8	4.0	37	430	1.21E-04	57	1.59E-05	15	4.20E-06	11	2.99E-06
7	6.1	30	416	7.47E-05	59	1.05E-05	16	2.91E-06	0	0
13	18.3	32	650	4.07E-05	103	6.42E-06	42	2.65E-06	2	1.11E-07
9	26.9	37	990	3.66E-05	132	4.90E-06	94	3.46E-06	(1)	(1)
11	29.9	35	781	2.75E-05	116	4.07E-06	72	2.53E-06	0	0
12	49.0	36	974	2.21E-05	117	2.65E-06	248	5.62E-06	1	2.13E-08
8	72.0	34	1054	1.62E-05	146	1.21E-06	163	1.35E-06	6	5.28E-08
15	96.0	33	1065	1.23E-05	159	1.82E-06	454	5.22E-06	0.07	8.27E-10

(1) 72-h test is the result from a repeat test. Intial test had misplaced simulant. The 1-h and 26.9-h tests (the grey rows) are from previous scoping work (SRNL-STI-2019-00106) during which CO_2 was not measured.
(2) Overall temperature average = 34°C ±4°C (excluding temperatures of the scoping data at 1 hour and 27 hours).

Mercury Results

To confirm that the initial concentration of MeHg in the spiked T50SS simulant, samples were taken immediately after spiking and before filling any of the reactors. Then when the last reactor was filled, several days later, the spiked simulant was sampled again. All these results are before the simulant was further spiked with a source of sulfide, which would allow methane to generate as the MeHg was being destroyed. Table 28 shows both the measured total Hg and the MeHg concentrations along with the MeHg spiked concentration based on the measured MeHgOH source material. Within measurement uncertainty, all the measured values indicate the target concentration 100 mg/L of MeHg was obtained. The measured

values of MeHg are very close to the composed spiked concentrations and within the analytical measurement uncertainty ±20% of reading.

Table 28. Test Series 2 MeHg and total Hg results of spiked simulant

Test Series Number	Reactor Fill Period	Date Simulant Sampled	T50SS (1) Density g/mL	Composed MeHg Spike mg/L	Date Sample Analyzed	Analyzed Total Hg mg/L (2)	Date Sample Analyzed	Analyzed MeHg mg/L (3)	Comments
2	First	7-Jul-20	1.2208	104.5	9-Jul-20	100	19-Oct-20	107	Sampled before filling reactors (4)
2	Last	9-Jul-20	1.2208	104.5	9-Jul-20	99	19-Oct-20	103	Sampled after last reactor was filled (4)

(1) T50SS = Tank 50 Salt Solution simulant
(2) Analyzed by Direct Mercury Analyzer using Atomic Absorption Spectroscopy. Two sigma uncertainty is ±20%.
(3) Analyzed by Gas Chromatography Cold-Vapor Atomic Flourescence Spectrophotometry. Two sigma uncertainty is ±20%.
(4) These samples were taken before being spiked with sulfide-containing premix grout solids.

Appendix H: Test Series 3 Results

T50SS Simulant, Concentration of 100 mg/L MeHg in a Grout Mixture of 0/60/40 Grout Premix Solids, Water-To-Solids Mass Ratio of 0.85, Over 96 hours

Temperature and Pressure

Figure 33 shows the temperature and pressure histories during the test period. The target temperature was 35°C ± 5°C and the overall average of all 8 reactor was 34°C ± 2°C and the pressure was between 11 and 15 psig. See Test Series 1, Appendix F, for details on the temperature and pressure operation.

The reduction in pressures shown in Figure 20 for Test Series 1 is similar to this second series involving grout with the 0/60/40 mixture of premix grout solids, which had no cement. However, it is slightly more than the pressure reduction for Test Series 2, which had a grout mixture of 10/45/45 of premix solids. The big difference is the lack of cement, and the results to be discussed show a faster methane generation during the first few hours. This may be the reason why the pressures dropped more than the mixture with cement. No leaks were found from the reactors to explain the 2 to 3 psi drop in pressures. Also note that the temperatures for HGV-9 and HGV-10 for the 30-hour and the 48-hour redo tests, respectively, leveled out at just above 33°C so they were adjusted slightly at 24 hours to move closer to the target of 35°C. This is the reason why a slight jump in temperature and pressure can be seen.

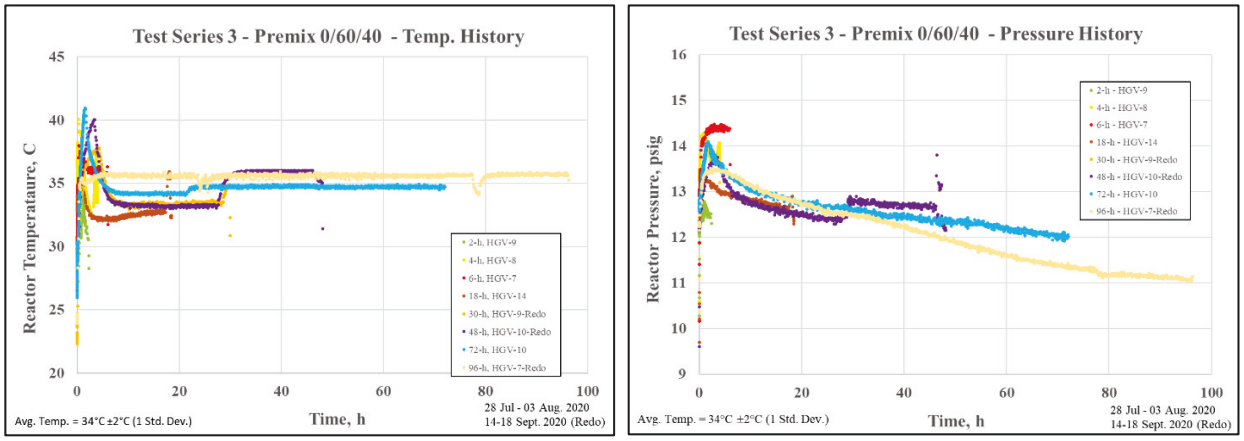


Figure 33. Test Series 3 temperature & pressure profiles

Gas Concentrations

Figure 34 shows the methane gas concentration measured in the headspace of each reactor. Besides methane, the GC was used to measure hydrogen, nitrous oxide, and carbon dioxide, which are not shown in the figure because they are an order of magnitude less, but they will be discussed later. The data are listed in Table 29. Note the three points are indicated as a redo tests at 30, 72, and hours. The initial tests had some of the simulant misplaced, which compromised the results, so they were repeated later as shown on the figure. A fourth point at 48 hours is lower than the others. On sampling that test the fitting to the GC was not tight so after the first reading was obtained the head gas was depleted. The single datum point was slightly lower but the MGR obtained from this point still gave an accurate result, which will be discussed later. Also shown on Figure 34 are two datum points obtained from previous scoping work [6.4] done under similar conditions at 1 hour and 27 hours. The measurement is below current set of points for an unknown reason, but the scoping tests had only one result for the 0/60/40 mixture, so it may be an outlier. The scoping result at 1 hour at 142 ppm is in line with the current data set and implies that sulfide may have leached from this grout mixture faster than from the 10/45/45 mixture which had no detectable methane after the first hour. The presence of cement may have an effect of slowing the leaching process, that is, it is possible that Ca^{2+} from the cement slows down the release of S^{2-}.

This faster speed is evident in the entire data set as the methane concentration reaches an asymptote after approximately 2 days instead of the 3 days for the 10/45/45 grout premix solids mixture. Once the asymptote is reached both mixtures had approximately the same result of 1000 ppm.

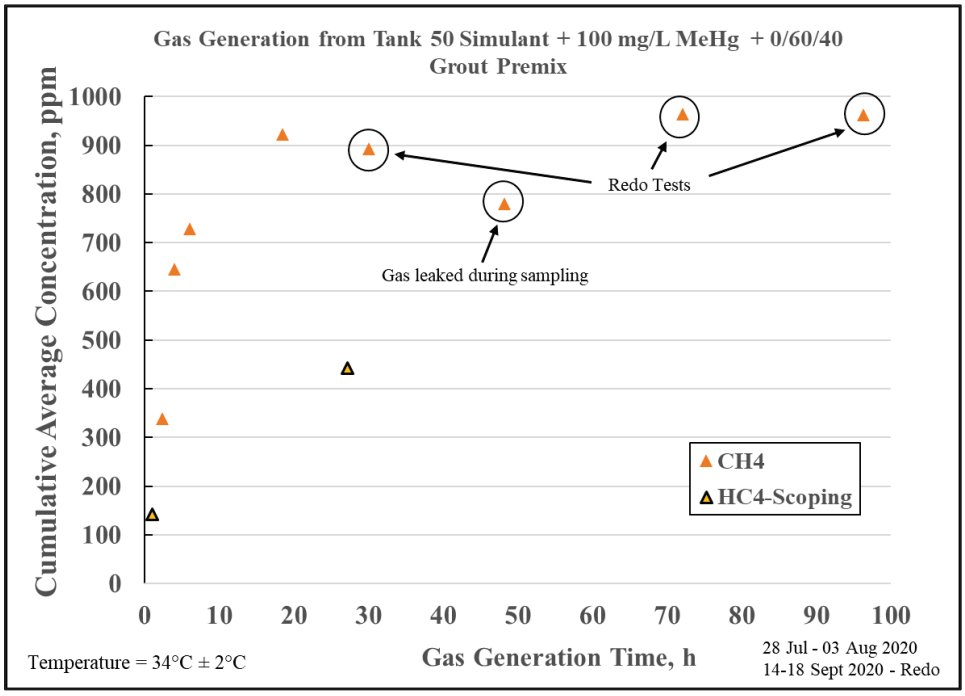


Figure 34. Test Series 3 gas concentrations

After the gas generation tests, another set of tests were performed to demonstrate the destruction of MeHg while methane is generated. As for the previous test series, similar test mixture was made to measure MeHg concentration with time. Test Series 3 used the cement-less mixture of 0/60/40 of grout premix solids. Like the Test Series 2, the results are less definitive than seen for Test Series 1, Figure 22. Figure 35 indicates that after 27 hours MeHg was still being destroyed. The MeHg and the methane gas concentration measurement uncertainties were ±20% and ±9%, respectively, at the 95% confidence level. Similarly, as for the 10/45/45 test, the MeHg Destruction test for the 0/60/40 grout mixture was designed to end at 77 hours, but after 24 hours the grout slurry, while still being mixed, had a consistency which made it much more difficult to draw liquid samples to analyze. However, the result at 27 hours indicates that at just over 70% of the MeHg destroyed, the process may have been slowing, based on the generation of methane gas reaching its asymptote, which is basically the same results as for Test Series 2. Once again, the test was stopped at this point because obtaining further samples were not possible. The results from measuring methane indicate the mole fraction of methane gas appears to peak at 1 day with around 60% of the moles of methane produced from the number of moles that could have been produced if all the MeHg were converted. The asymptote of methane production matches the peak MeHg destruction, within measurement uncertainty. What stands out from both Figure 28, or the 10/45/45 mixture, and Figure 35, the 0/60/40 mixture, is the MeHg destruction begins very fast, but then it drops to approximately 30% after 24 hours, after which it picks up again. As discussed for Test Series 2, the drop in MeHg destruction could have been caused by several reasons, like poor mixing (it was only mixed enough to keep the grout as a slurry), or the difficulty in obtaining as sample from the thick grout mixture, or from the complex reactions in the releasing sulfide from mixture. The values for the fraction of methane moles produced and fraction of MeHg destroyed are listed in Table 10.

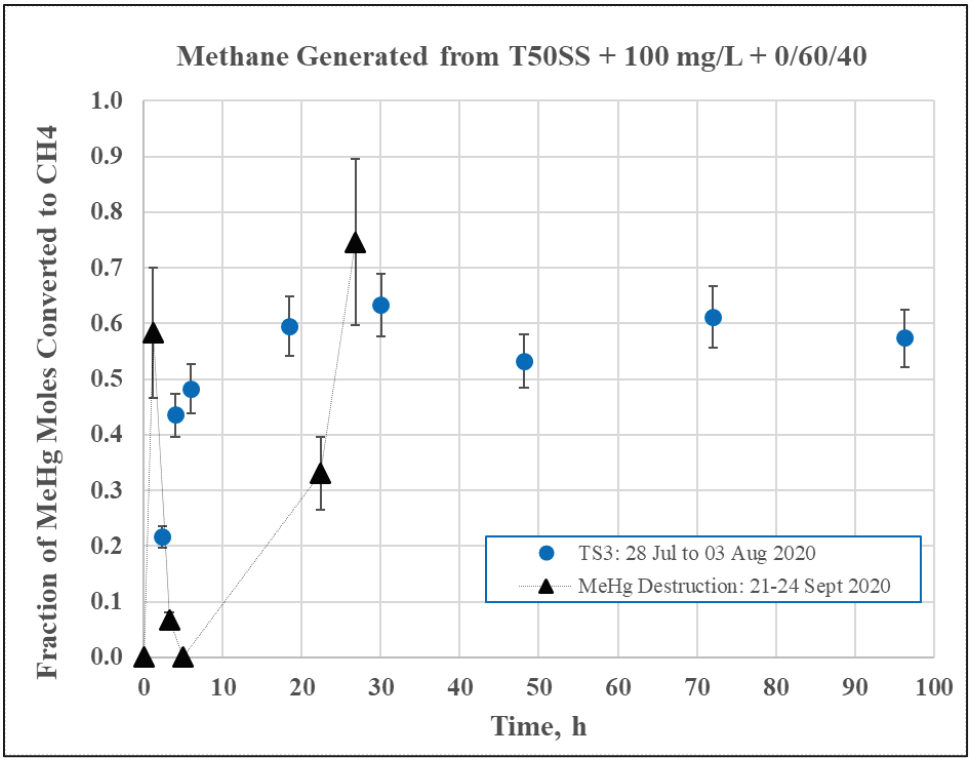
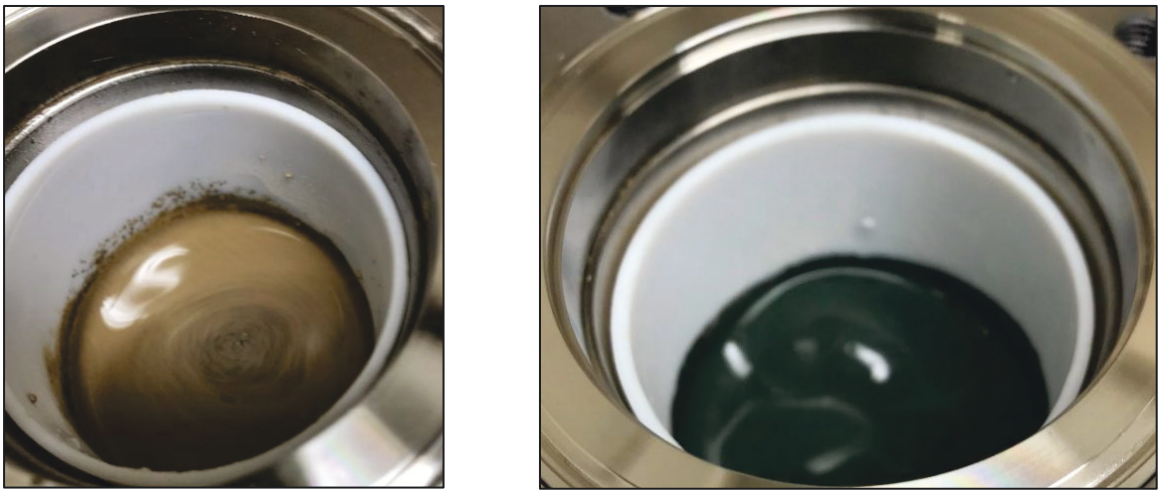


Figure 35. Test Series 3 fraction of MeHg converted to methane versus faction MeHg destroyed

Operational Notes

After the gas was sampled from each reactor, the reactors were opened to view the state of the grout. The 0/60/40 grout mixture were purposely made slightly dilute with a water-to-solids mass ratio of grout premix of 0.85, which is less that the standard mass ratio of 0.59. This was done to help keep the mixture as a moving slurry while being continuously mixed. Figure 36 shows two of the reactors with the grout still being mixed as a slurry. Figure 29(a) was taken immediately after the 2-h test and Figure 36(b) taken after the 18-h test. For the longer periods, pulsations in the grout could still be observed but they would be difficult to detect from still photographs.



(a) HGV-9 (b) HGV-14

Figure 36. Two reactors from Test Series 3 with 0/60/40 grout mixtures, (a) after 2-h test with grout still moving as a slurry and (b) after the 18-hour test with grout still as a slurry

Methane Generation Rate

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 37 and Table 29 show the gas generation rates for CH_4 from Test Series 3. The methane generation rate (MGR) was calculated with Eq. (1), which is the same method used for all other gases that will be discussed:

MGR =

[[(Head Space Vol[17], ft^3) • **A** • CH_4 Measured, ppm / 1000000] / (Duration, h)] / Vol. Liquid[18], gal **(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

This equation is shown for the principal gas, methane, but has the same form for all the gases discussed, i.e., hydrogen, nitrous oxide, and carbon dioxide.

The principal gas measured is methane and Figure 37 shows MGR increases rapidly during the first 4 hours and peaks at 1.9 x 10-4 (ft^3/h) / gallon of salt solution as sulfide is leached from grout solids and then drops rapidly for about 24 hours. MGR then tapers off during the next 3 days

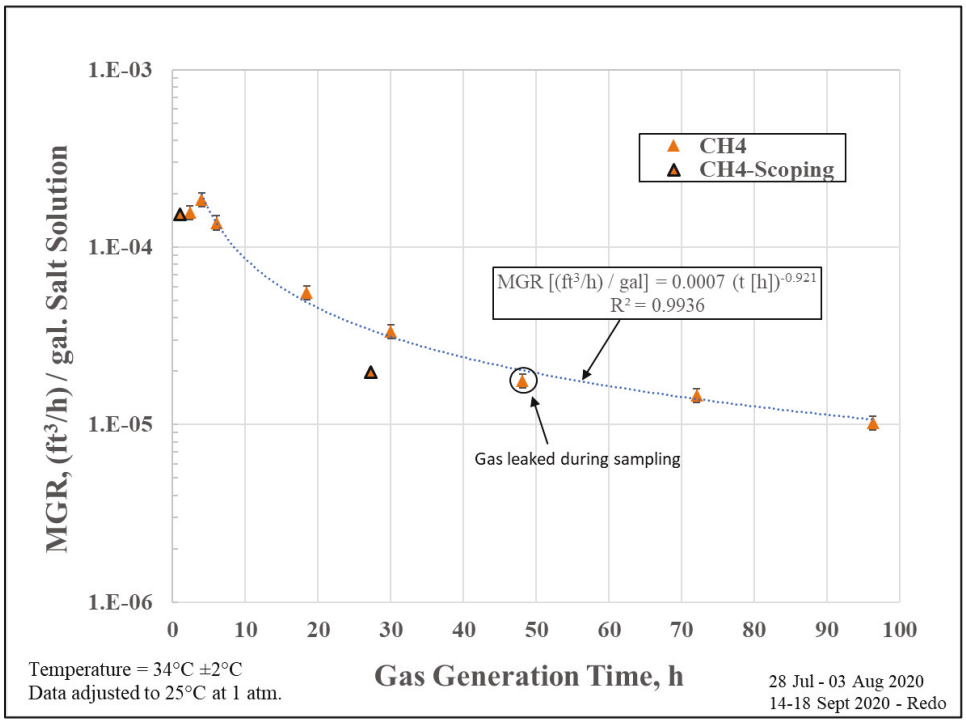


Figure 37. Test Series 3 methane gas generation rates

[17] See footnote 10.

[18] Liquid volume is only of the Tank 50 salt solution simulant contained in the grout mixture.

The error bars shown are ±9% RSD at the 95% confidence level. The trend follows the power-law relation shown on the figure with a correlation coefficient of 0.99, but at a much slower rate than was shown in Test Series 1, Figure 23. This is probably do to the fact that reduced sulfide is still being leached from the grout to produce more methane. Note that both the scoping point and the 2-hour point were not included in that trend line. Unlike the for the 10/45/45 mixture, the 0/60/40 methane was detected after the first hour. Not shown is the scoping datum point at 1 hour because no methane was detected, see Table 29, which includes all the data. The mass of the grout solids for Test Series 3 contained 60% slag, which contains the sulfide, while Test Series 2 the mass of slag was 45%. However, both grout mixtures had an excess in sulfur versus mercury, Table 1; therefore, the presence of cement for the 10/45/45 maybe have caused the sulfide to be released as a slower rate.

As for the two previous test series an attempt was made to obtain a more instantaneous measure of MGR the accumulated mass of methane from each period was subtracted from the preceding test period. Figure 38 shows the MGR for the time intervals between the 9-time periods from 1 to 96 hours, which ranged from 0 to 1 hour to 3 to 4 days. As for Test Series 2, the 3rd interval from 2 to 4 hours it appears that MGR reached a maximum. The 4th interval from 4 to 6 hours the methane accumulation dropped significantly. MGR continues to slow down the 4 hours and drops to zero after 6 hours. It appears that the peak generation rate occurs near the 4-hour period.

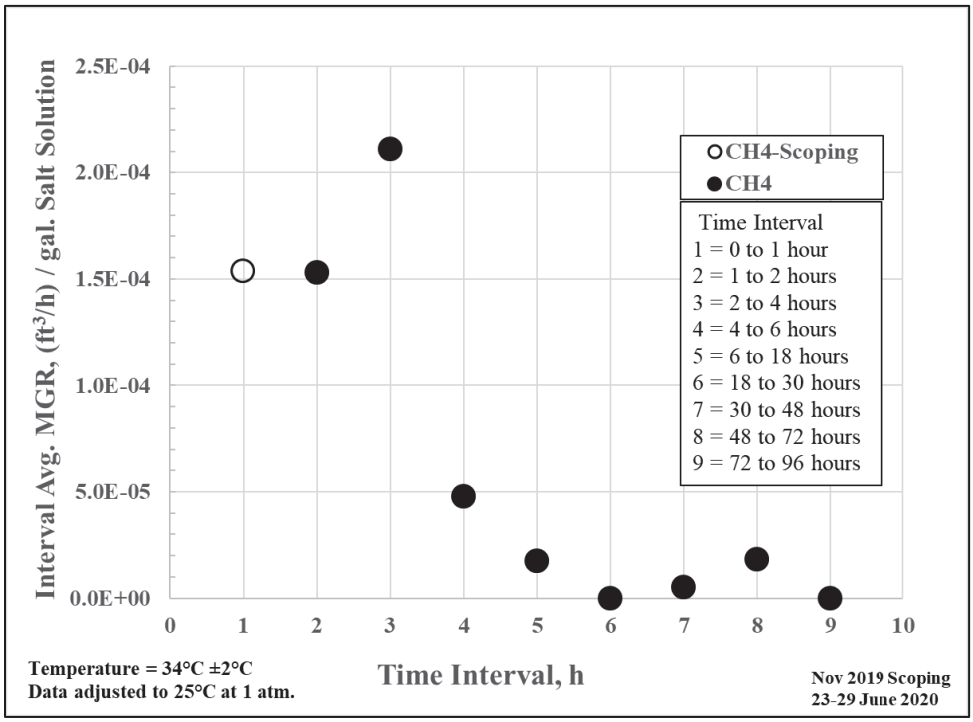


Figure 38. Test Series 3 methane gas generation rates between test intervals

Other Measured Gases

Concentrations of hydrogen, nitrous oxide, and carbon dioxide were also measured, but they were far below that of methane. The results are spread of 5 decades of MGR. Using Equation (1) to determine the generation rates for each gas those rates were one order, to several orders, of magnitude, less than methane, as shown in Figure 38. With respect to H_2, Table 29, the concentrations reached several hundred ppm, so while less than methane, but quantifiable. N_2O, was less that measured from the 10/45/45 grout mixture, but after about 3 days became quantifiable. At the low-test temperature of 35°C. C_2O remains barely

detectable. at less than 6 ppm. For concentrations below 1 ppm, the values in the table are listed as 0 ppm. All three gases only play a minor role in gas generation versus methane.

As explained for the Test Series 2 results, the source of H_2, it is most likely the TOC in the test mixture, which is a combination of T50SS simulant and cementitious solids. However, for Test Series 3, with the 0/60/40 grout mixture, the HGR was 5.5 x 10^{-6} (ft^3 / h) / gal at 4 days, see Table 29, which is a factor of 3 larger than for Test Series 2, see Table 27, with the 10/45/45 grout mixture. The slag is the largest source of TOC[19] of the three cementitious components and for Test Series 3 the slag component was 15 wt% larger.

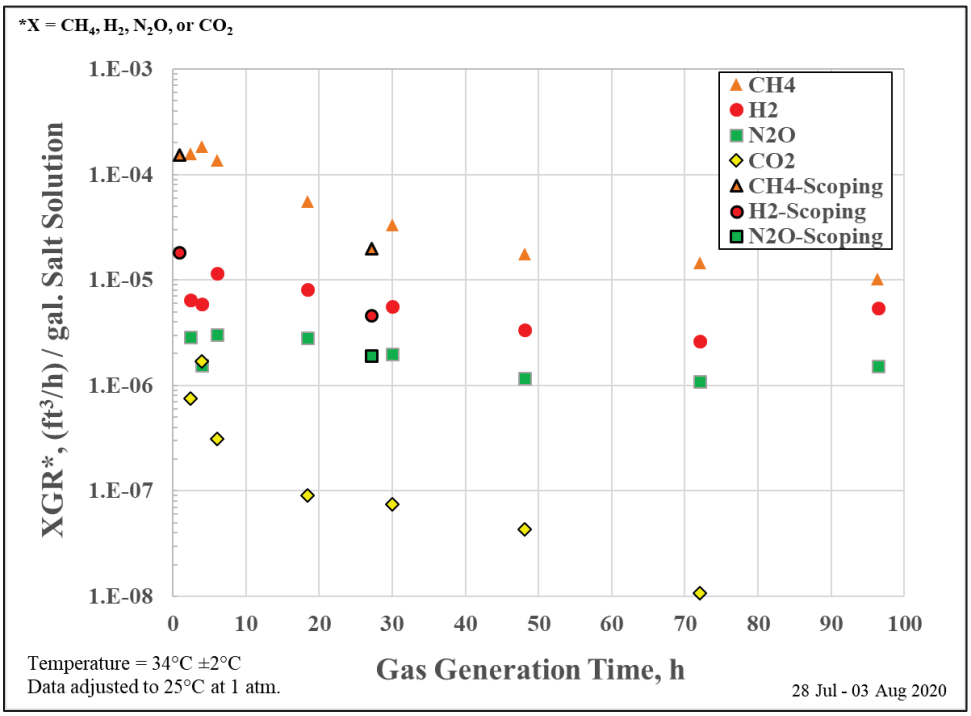


Figure 39. Test Series 3 methane gas generation rates for all gases measured

Table 29. Test Series 3 gas concentrations and gas generation rates

Reactor HGV-	Duration h (1)	Temp. °C (2)	CH4 ppm	CH4 (ft3/hr) / gal	H2 ppm	H2 (ft3/hr) / gal	N2O ppm	N2O (ft3/hr) / gal	CO2 ppm	CO2 (ft3/hr) / gal
10	0.98	31.3	142	1.53E-04	17	1.81E-05	0	0	(1)	(1)
9	2.37	28.7	339	1.57E-04	14	6.48E-06	6	2.89E-06	2	7.53E-07
8	4.02	32.7	645	1.86E-04	20	5.87E-06	5	1.55E-06	6	1.70E-06
7	6.02	33.9	729	1.38E-04	62	1.16E-05	16	3.04E-06	2	3.11E-07
14	18.44	30.6	923	5.54E-05	135	8.09E-06	47	2.84E-06	2	9.12E-08
10	27.20	28.3	442	1.97E-05	103	4.62E-06	42	1.89E-06	(1)	(1)
9	30.03	26.9	892	3.36E-05	150	5.64E-06	53	1.99E-06	2	7.45E-08
10	48.14	31.0	780	1.76E-05	148	3.35E-06	52	1.17E-06	2	4.32E-08
10	72.06	29.3	963	1.46E-05	175	2.65E-06	72	1.08E-06	1	1.07E-08
7	96.31	28.9	963	1.03E-05	512	5.45E-06	143	1.52E-06	0	5.17E-09

(1) 30-h, 48-h, and 96-h tests are the results from repeat tests. Intial tests had misplaced simulant. 1-h and 27.2-h tests (the grey rows) are from previous scoping work (SRNL-STI-2019-00106) during which CO_2 was not measured.
(2) Overall temperature average = 34°C ±2°C.

[19] See Table 4 in Reference [6.5].

Mercury Results

To confirm that the initial concentration of MeHg in the spiked T50SS simulant, samples were taken immediately after spiking and before filling any of the reactors. Then, when the last reactor was filled, several days later, the spiked simulant was sampled again. All these results are before the simulant was further spiked with a source of sulfide, which would allow methane to generate as the MeHg was being destroyed. Table 30 shows both the measured total Hg and the MeHg concentrations along with the MeHg spiked concentration based on the measured MeHgOH source material. Within measurement uncertainty, all the measured values indicate the target concentration 100 mg/L of MeHg was obtained. The measured values of MeHg are well within the analytical measurement uncertainty ±20% at the 95% confidence level.

Table 30. Test Series 3 MeHg and total Hg results of spiked simulant

Test Series Number	Reactor Fill Period	Date Simulant Sampled	T50SS (1) Density g/mL	Composed MeHg Spike mg/L	Date Sample Analyzed	Analyzed Total Hg mg/L (2)	Date Sample Analyzed	Analyzed MeHg mg/L (3)	Comments
3	First	28-Jul-20	1.2208	107.8	8-Sep-20	96	19-Oct-20	99	Sampled before filling reactors (4)
3	Last	30-Jul-20	1.2208	107.8	8-Sep-20	101	19-Oct-20	106	Sampled after last reactor was filled (4)

(1) T50SS = Tank 50 Salt Solution simulant
(2) Analyzed by Direct Mercury Analyzer using Atomic Absorption Spectroscopy. Two sigma uncertainty is ±20%.
(3) Analyzed by Gas Chromatography Cold-Vapor Atomic Flourescence Spectrophotometry. Two sigma uncertainty is ±20%.
(4) These samples were taken before being spiked with sulfide-containing premix grout.

Appendix I: Test Series 4 Results

T50SS Simulant, Concentration of 100 mg/L MeHg in a Grout Mixture of 10/45/45 Grout Premix Solids, Water-To-Solids Mass Ratio of 0.59 and 0.85 for Solidified Grout over 30 hours

The two main differences between Test Series 2, with a grout mixture of 10/45/45 of premix grout solids and this test series, with the same grout mixture, are: 1) that four reactors contained the standard water-to-solids mass ratio of 0.59, and 2) the grout was allowed to solidify. That is, Test Series 4 was performed to determine if there is significant difference of methane generation due to the more dilute mixture than the 0.85 mass ratio that was maintained as a slurry in Test Series 2. Test Series 4 used 8 reactors and the other four reactors contained the same grout mixture and mass ratio of 0.85 as for Test Series 2, but the grout in those reactors was also allowed to solidify so the results between the 0.59 and 0.85 mass ratios of solidified grout could be compared. Another difference was that this test series was limited to 30 hours instead of 4 days because the comparison was not principally to demonstrate long-term reactions but to compare how the two mixtures compared during the initial stages of grout developed after being formed.

Temperature and Pressure

Figure 40 shows the temperature and pressure histories during the test period. The target temperature was 35°C ±5°C and the overall average of all 8 reactor was 33°C ± 4°C and the pressure was between 12 and 18 psig. See the preceding appendix for details on the temperature and pressure operation. See Test Series 1, Appendix F, for details on the temperature and pressure operation.

The reduction in pressures shown in Figure 20 for Test Series 1, without grout, is still more pronounced for this second series involving grout. While grout solids do contain sulfide, release from grout is more complex and slower that for Na_2S. However, it appears that the pressure reduction for this 0/60/40 grout mixture is less than what was measured for the 10/45/45 grout mixture. There still is some pressure reduction, probably due to the reaction between sulfide with the residual oxygen, as discussed in Appendix M, but the lack of cement in the grout solids may be affecting the reaction. No reactor leaks were found.

On the pressure history one reactor shows a pressure at 8 psig. At the very start, when this reactor, HGV-8, was pressurized with N_2, and sealed, the pressure began to drop. The fill port was tightened further, and the pressure stabilized. The reactor was not unsealed to re-pressurize to minimize contamination and since the occurrence only lasted within the first 15 minutes, no significant methane generation was expected; therefore, the reactor was allowed to continue heating to 35°C. As will be seen, the results indicate the reactor was not significantly affected.

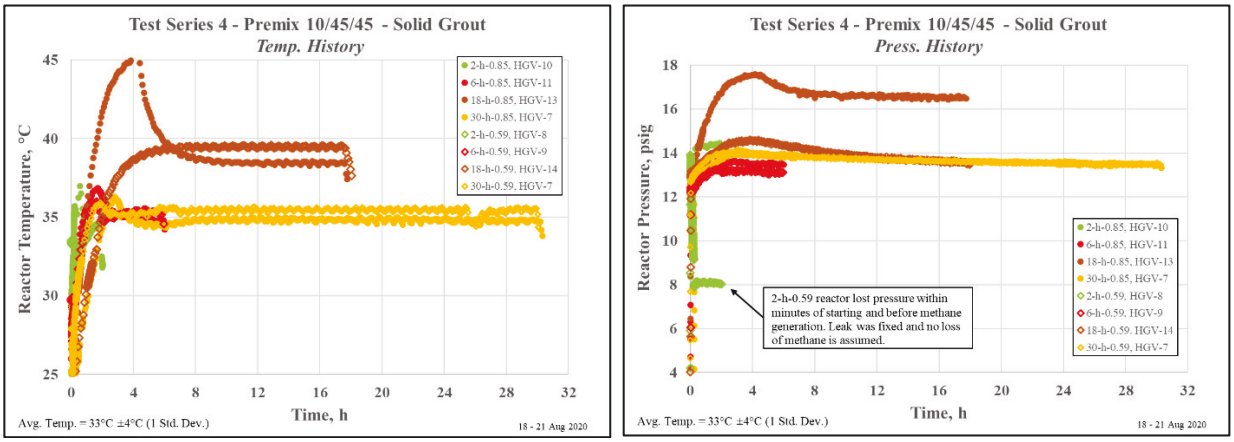


Figure 40. Test Series 4 temperature & pressure profiles

Gas Concentrations

Figure 41 shows the methane gas concentration measured in the headspace of each reactor. Besides methane, the GC was used to measure hydrogen, nitrous oxide, and carbon dioxide, which are not shown in the figure because they are an order of magnitude less, but they will be discussed later. The data values are listed in Table 31. The principal feature in the figure is the difference between the open triangles, of the 0.59 mass ratio mixture, and the closed triangles, of the 0.85 mass ratio mixture. The grout in all the reactors was mixed for 30 minutes and then the agitation was terminated to allow it to solidify.

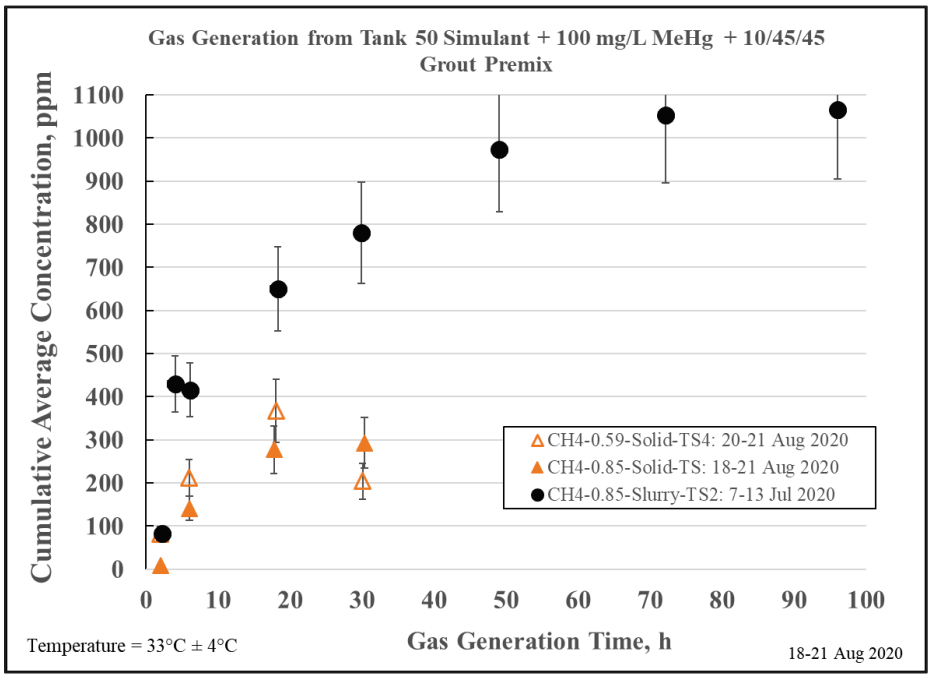


Figure 41. Test Series 4 gas concentrations

On those data points, ±20% error bars are shown, which is standard instrument uncertainty. However, the calibration standards used were accurate to less than 5%, so the results are probably more accurate than shown, but it appears that if there was a difference in the methane generation between the two different mass ratios of the mixtures, it was small. Note that at the 30-hour trend of the results from the two mixtures changes. This may be from measurement uncertainty or due to the more dilute mixture releasing more methane. However, there does seem to be a large difference between the methane generation from grout as a slurry and solidified grout. The data shown as the filled circles are from Test Series 2, which had the same grout mixture, of 10/45/45, but was continually agitated. The continual movement probably helps the leaching process to release reduced sulfide faster. The results imply that grout in movement releases more methane. It seems reasonable to assume that the solidified grouts will reach an asymptotic value, as the slurried grout, but methane produced from the slurried grout is significantly larger.

Another way to look at the data is to compare the number of methane moles released to the total number of available moles of MeHg, assuming there is an excess of reduced sulfide. Figure 42 depicts the mole fraction of methane gas, which appears to peak at 18 hours at around 20 to 25% of the moles of methane produced from the total that could be released. However, implied from the Test Series 2 results, which are the closed circles, the process of releasing methane probably continues to its maximum conversion after approximately 2 days, but by then the grout will be solidified and amount released will be significantly below the value of 70% shown for slurried grout. The values for the fraction of moles produced are listed in Table 10

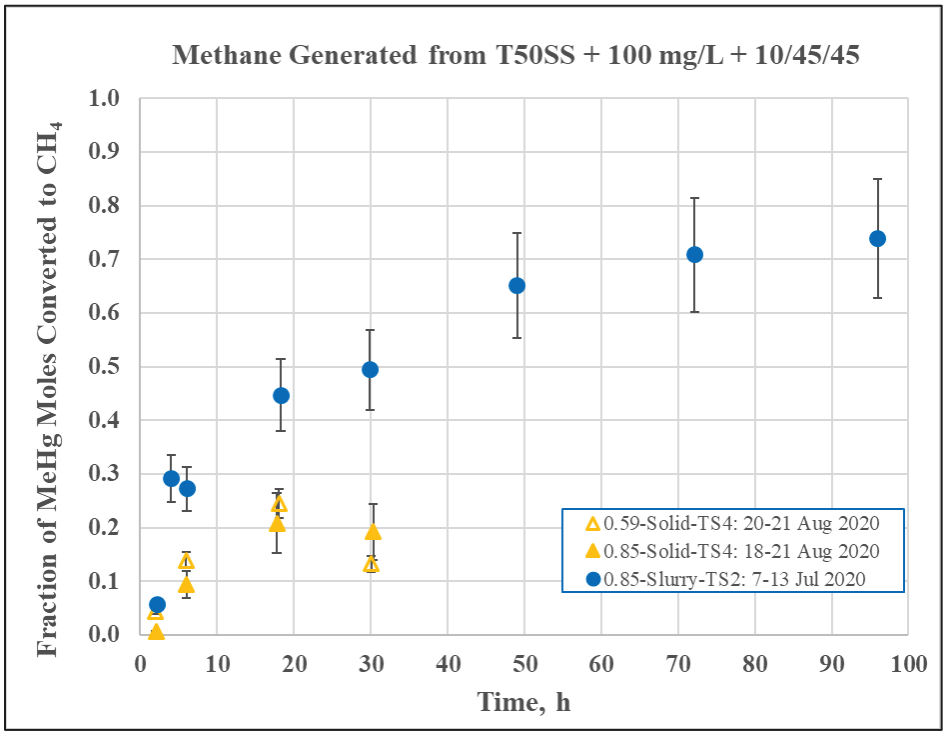


Figure 42. Test Series 4 fraction of MeHg converted to methane versus faction MeHg destroyed

Operational Notes

After the gas was sampled from each reactor, they were opened to view the state of the grout. For this test series the 10/45/45 grout mixture was made with two different water-to-solids mass ratios, the standard ratio of 0.59 and the slightly dilute ratio of 0.85. Both mixtures were agitated for ~30 minutes in the sealed reactors and then stopped to allow the grout to solidify. Figure 43 shows both mixtures at different test times. Figure 43(a) is from the 2-hour test of the 0.59 mixture and it appears to be lighter in color than grout from the 6-h test of the 0.85 mixture shown in Figure 43(b). Both grouts were stiff to the touch, but the 0.59 mixture may have oxidized more after opening the reactor.

(a) HGV-8 (b) HGV-11

Figure 43. Two reactors from Test Series 4 with 10/45/45 grout, (a) after 2-h test of the 0.59 mixture and (b) after 6-h test of the 0.85 mixture. Both were solidified.

Methane Generation Rate

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 44 and Table 31 show the gas generation rates for CH_4 from Test Series 4. The methane generation rate (MGR) was calculated with Eq. (1), which is the same method used for all other gases that will be discussed later:

MGR =

[[(Head Space Vol[20], ft^3) • A • CH_4 Measured, ppm / 1000000] / (Duration, h)] / Vol. Liquid[21], gal (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

This equation is shown for the principal gas, methane, but has the same form for all the gases discussed, i.e., methane, hydrogen, nitrous oxide, and carbon dioxide.

The principal gas measured is methane and Figure 44 shows MGR increases rapidly during the first 6 hours and peaks at 2.7 x 10-5 and 4.0 x 10-5 (ft^3/h) / gallon of salt solution as sulfide is leached from grout solids, for the 0.85 and 0.59 mass ratio, respectively. The MGR then drops rapidly for the next 24 hours. The error bars shown are ±15%, ±11%, and ±27% RSD at the 95% confidence level for the data sets of Test Series 2, Test Series 4 (0.59 mass ratio), and Test Series 4 (0.85 mass ratio), respectively. The two data sets for the solidified grout at mass ratios of 0.59 and 0.85 are statistically the same. For the grout that was maintained as a slurry, Test Series 2, the MGR significantly larger at all time periods, most likely because sulfide could be released more easily to form methane.

[20] See footnote 10.
[21] Liquid volume is only of the Tank 50 salt solution simulant contained in the grout mixture.

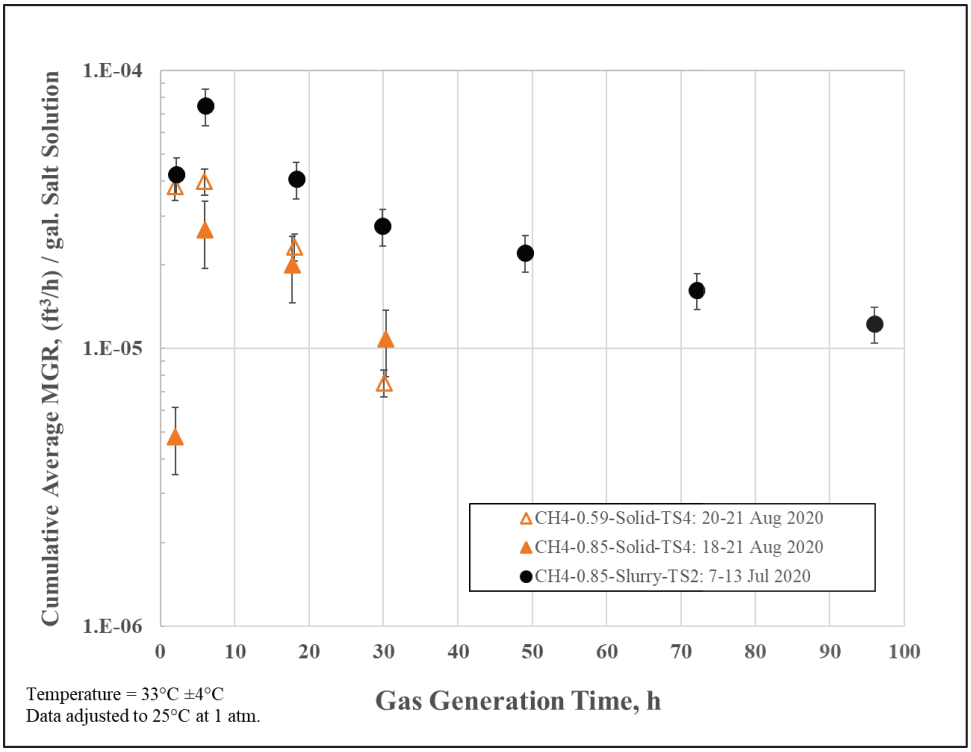


Figure 44. Test Series 4 methane gas generation rates

Other Measured Gases

Concentrations of hydrogen, nitrous oxide, and carbon dioxide were also measured, but they were far below that of methane. The results are spread over 4 decades of generation rate. Using Equation (1) to determine the generation rates for each gas those rates were an order, or several orders, of magnitude less than methane, as shown in Figure 45. However, as shown in Table 31, the concentrations are less than 55 ppm for H_2 and N_2O, which are quantifiable, but the concentration is less than 10 ppm CO_2, which while detectable is not quantifiable. For concentrations below 1 ppm, the value in the table is listed as 0 ppm. All three gases only play a minor role in gas generation.

As explained in the results for Test Series 2 and Test Series 3, the source of H_2 is most likely the TOC in the T50SS simulant and the cementitious solids. Furthermore, the HGR is lower for Test Series 4 with solidified grout, than those preceding two test series with continually mixed grout, which is similar to the lower MGR for methane. The solid grout either retains more gas or impedes the chemical reactions to create more gas.

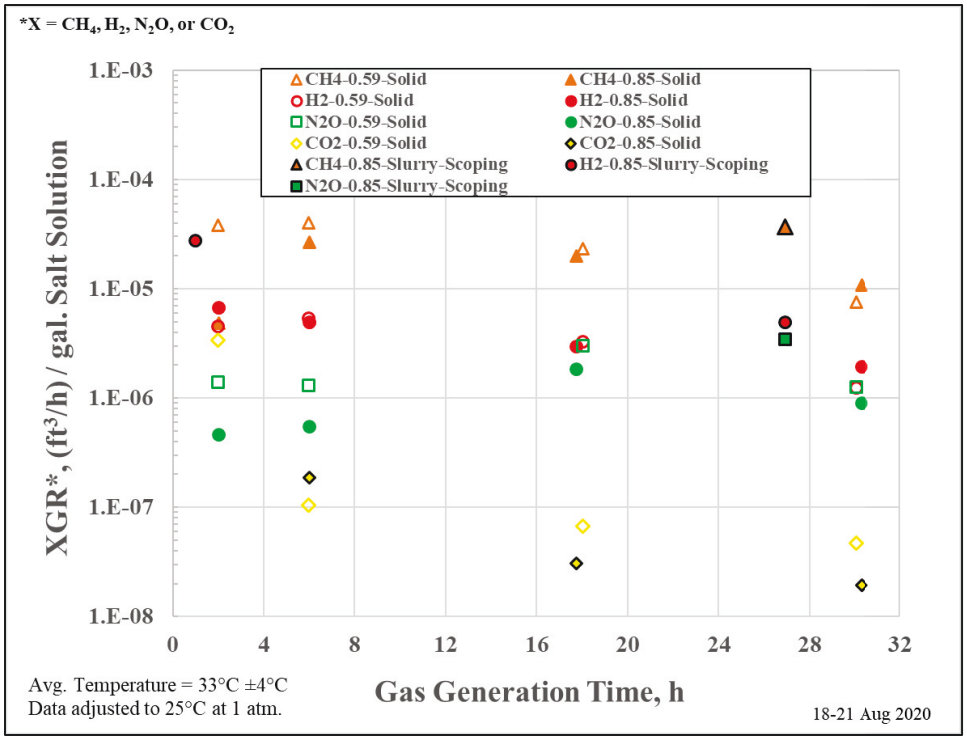


Figure 45. Test Series 4 methane gas generation rates between test intervals

Table 31. Test Series 4 gas production and generation rates

Reactor HGV-	Mass Ratio (1)	Duration h	Temp. °C (2)	CH_4 ppm	CH_4 (ft^3/hr) / gal	H_2 ppm	H_2 (ft^3/hr) / gal	N_2O ppm	N_2O (ft^3/hr) / gal	CO_2 ppm	CO_2 (ft^3/hr) / gal
10	0.85	2.0	29	8	4.82E-06	11	6.70E-06	1	4.61E-07	< D (3)	< D (3)
11	0.85	6.0	35	141	2.66E-05	26	4.94E-06	3	5.44E-07	1	1.86E-07
13	0.85	17.8	33	277	2.00E-05	41	2.96E-06	25	1.84E-06	0	3.07E-08
7	0.85	30.3	34	293	1.08E-05	52	1.93E-06	24	8.89E-07	1	1.94E-08
8	0.59	2.0	32	83	3.82E-05	10	4.49E-06	3	1.40E-06	7	3.40E-06
9	0.59	6.0	33	212	3.99E-05	28	5.33E-06	7	1.31E-06	1	1.05E-07
14	0.59	18.0	33	367	2.32E-05	52	3.30E-06	48	3.01E-06	1	6.71E-08
7	0.59	30.1	34	204	7.51E-06	33	1.23E-06	34	1.26E-06	1	4.68E-08

(1) The mass ratio is the water-to-solids grout premix of the dilute mixture of 0.85 to the standard mixture of 0.59. However, both mixtures were only mixed for 30 minutes and then allowed to solidify.
(2) Temperature averages for the 0.85 mass ratio tests and 0.59 mass ratio tests were 33°C ±4°C and 33°C ±3°C, respectively.
(3) < D = Below the detection limit.

Mercury Results

To confirm that the initial concentration of MeHg in the spiked T50SS simulant, samples were taken immediately after spiking and before filling any of the reactors. Then when the last reactor was filled, several days later, the spiked simulant was sampled again. All these results are before the simulant was further spiked with a source of sulfide, which would allow methane to generate as the MeHg was being destroyed. Table 32 shows both the measured total Hg and the MeHg concentrations along with the MeHg spiked concentration based on the measured MeHgOH source material. Within the analytical measurement uncertainty ±20% at the 95% confidence level, all the measured values indicate the target concentration 100 mg/L of MeHg was obtained.

Table 32. Test Series 4 MeHg and total Hg results of spiked simulant

Test Series Number	Reactor Fill Period	Date Simulant Sampled	T50SS (1) Density g/mL	Composed MeHg Spike mg/L	Date Sample Analyzed	Analyzed Total Hg mg/L (2)	Date Sample Analyzed	Analyzed MeHg mg/L (3)	Comments
4	First	18-Aug-20	1.2206	107.2	8-Sep-20	121	19-Oct-20	132	Sampled before filling reactors (4)
4	Last	20-Aug-20	1.2206	107.2	8-Sep-20	119	19-Oct-20	136	Sampled after last reactor was filled (4)

(1) T50SS = Tank 50 Salt Solution simulant
(2) Analyzed by Direct Mercury Analyzer using Atomic Absorption Spectroscopy. Two sigma uncertainty is ±20%.
(3) Analyzed by Gas Chromatography Cold-Vapor Atomic Flourescence Spectrophotometry. Two sigma uncertainty is ±20%.
(4) These samples were taken before being spiked with sulfide-containing premix grout.

Appendix J: Test Series 5 Results

T50SS Simulant, Concentration of 100 mg/L MeHg in a Grout Mixture of 0/60/40 Grout Premix Solids, Water-To-Solids Mass Ratio of 0.59 and 0.85 for Solidified Grout over 30 hours

The two main differences between Test Series 3, with a grout mixture of 0/60/40 of premix grout solids and this test series, with the same grout mixture, are: 1) that four reactors contained the standard water-to-solids mass ratio of 0.59, and 2) the grout was allowed to solidify. That is, Test Series 5 was performed to determine if there is significant difference of methane generation due to the more dilute mixture than the 0.85 mass ratio that was maintained as a slurry in Test Series 3. Test Series 5 used 8 reactors and the other four reactors contained the same grout mixture and mass ratio of 0.85 as for Test Series 3, but the grout in those reactors was also allowed to solidify so the results between the 0.59 and 0.85 mass ratios of solidified grout could be compared. Another difference was that this test series was limited to 30 hours instead of 4 days because the comparison was not principally to demonstrate long-term reactions but to compare how the two mixtures compared during the initial stages of grout developed after being formed. Finally, a comparison between Test Series 4 and 5 shows methane generation differences of the two mixtures of premix solids of grout, i.e., 10/45/45 for Test Series 4 and the cement-less 0/60/40 for Test Series 5.

Temperature and Pressure

Figure 46 shows the temperature and pressure histories during the test period. The target temperature was 35°C ±5°C and the overall average of all 8 reactor was 32°C ± 3°C and the pressure was between 12 and 18 psig. See Test Series 1, Appendix F, for details on the temperature and pressure operation.

The reduction in pressures shown in Figure 20 for the Test Series 1, without grout, is more pronounced than for this test series with grout. While grout solids do contain sulfide release from grout is more complex and slower that for Na_2S. That is, the reaction between sulfide with the residual oxygen must still be occurring, as discussed in Appendix M, but due to the more complex release of sulfide from grout the effect is not as pronounced. Still, there is some pressure reduction that is not from reactor leaks, but to the sulfide-oxygen reaction.

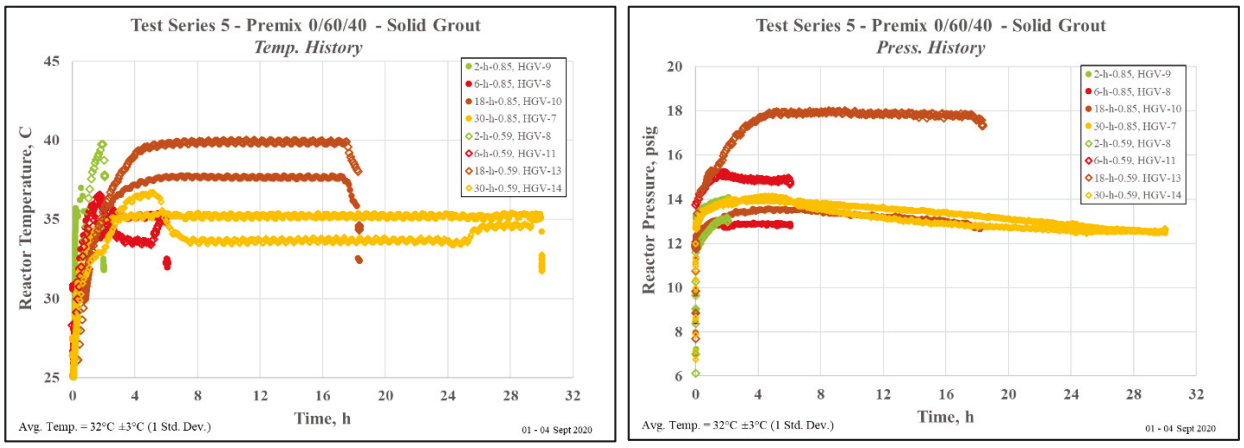


Figure 46. Test Series 5 temperature & pressure profiles

Gas Concentrations

Figure 47 shows the methane gas concentration measured in the headspace of each reactor. Besides methane, the GC was used to measure hydrogen, nitrous oxide, and carbon dioxide, which are not shown in the figure because they are an order of magnitude less, but they will be discussed later. The data values are listed in Table 33. The principal feature in the figure is the difference between the open triangles, of

the 0.59 mass ratio mixture, and the closed triangles, of the 0.85 mass ratio mixture. The grout in all the reactors was mixed for 30 minutes and then the agitation was terminated to allow it to solidify.

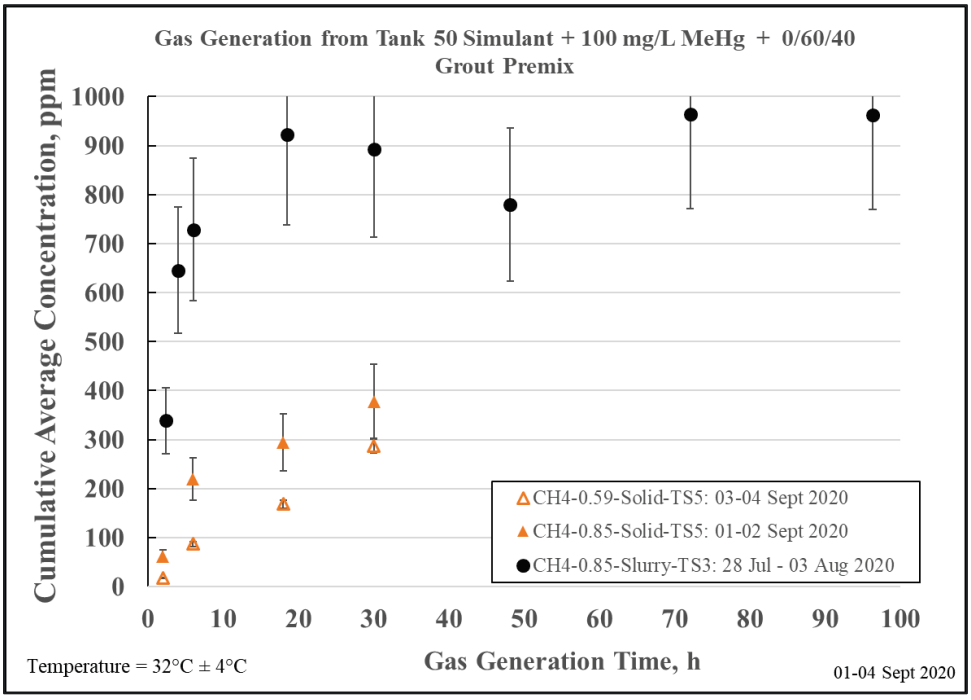


Figure 47. Test Series 5 gas concentrations

On those data points ±20% error bars are shown, which is standard instrument uncertainty. However, the calibration standards used were accurate to less than 5%, so the results are probably more accurate than shown. There appears to be a significant difference in the methane generation between the two different mass ratios of the solidified 0/60/40 grout mixture with the dilute mixture producing from 1.3 to 2 times more methane. This is just the opposite result elicited from Test Series 4 for the 10/45/45 mixture. It appears the cement may play a role in this difference, which is unknown.

The data shown as the filled circles are from Test Series 3, which had the same grout mixture, of 0/60/40, but was continually agitated. The continual movement probably helps the leaching process to release reduced sulfide faster. It seems reasonable to assume that the solidified grouts will reach an asymptotic value of methane, as does the slurried grout, but methane produced from the slurried grout is significantly larger.

Another way to look at the data is to compare the number of methane moles released to the total number of available moles of MeHg, assuming there is an excess of reduced sulfide, see Table 1. Figure 48 depicts the mole fraction of methane gas for the 0/60/40 grout mixture appears to peak at 30 hours at around 20% of the moles of methane produced from the total that could be released. This is similar to what happened for the 10/45/45 grout mixture, Figure 42. Implied from the Test Series 3 results, which are the closed circles, the process of releasing methane from the solidified grout most likely has reached its peak, which significantly below the value of 70% shown for slurried grout. The values for the fraction of moles produced are listed in Table 10.

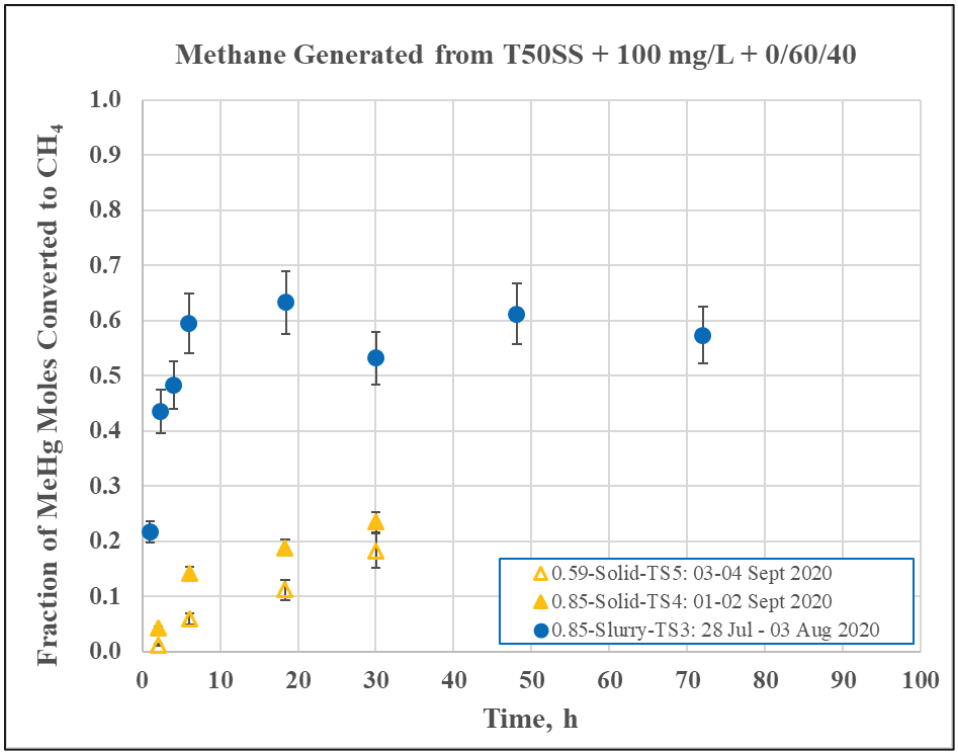


Figure 48. Test Series 5 fraction of MeHg converted to methane versus faction MeHg destroyed

Operational Notes

After the gas was sampled from each reactor, they were opened to view the state of the grout. For this test series the 0/60/40 grout mixture was made with two different water-to-solids mass ratios, the standard mass ratio of 0.59 and the slightly dilute mass ratio of 0.85. Both mixtures were agitated for ~30 minutes in the sealed reactors and then stopped to allow the grout to solidify. Figure 49 shows the 0.59 mixtures in each of the four reactors. Figure 49(a) is from the 2-hour test and it appears to still be liquid but is was firm to the touch. Figure 49(b) shows the grout after 6 hours, which was firmer and darker in color. Figure 49(c) shows the grout after 18 hours and its color is beginning to turn a light brown. Figure 49(d) shows the solidified grout after 30 hours, which turned completely a light brown.

(a) HGV-8 (b) HGV-11 (c) HGV-13 (d) HGV-14

Figure 49. Four reactors from Test Series 5 with 0/60/40 grout of the 0.59 mass ratio after: (a) 2-hours, (b) 6 hours, (c) 18 hours, and (d) 30 hours. All were solidified to a certain degree.

Figure 50 shows the 0.85 mixtures in all four reactors. Figure 50(a) and Figure 50(b) are from the 2-hour and the 6-hour tests, respectively. While they appear to still be liquid, they were firm to the touch. Figure

50(c) and Figure 50(d) show the grout after 18 and 30 hours, respectively, which are changing colors to light brown, very similar to the 0.59 mixture.

(a) HGV-9 (b) HGV-8 (c) HGV-9 (d) HGV-8

Figure 50. Two reactors from Test Series 5 with 0/60/40 grout of the 0.85 mass ratio after: (a) 2-hours, (b) 6 hours, (c) 18 hours, and (d) 30 hours. All were solidified to a certain degree.

Methane Generation Rate

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 51 and Table 33 show the gas generation rates for CH_4 from Test Series 5. The methane generation rate (MGR) was calculated with Eq. (1), which is the same method used for all other gases that will be discussed later:

MGR =

[[(Head Space Vol[22], ft^3) • **A** • CH_4 Measured, ppm / 1000000] / (Duration, h)] / Vol. Liquid[23], gal **(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

This equation is shown for the principal gas, methane, but has the same form for all the gases discussed, i.e., methane, hydrogen, nitrous oxide, and carbon dioxide.

The principal gas measured is methane and Figure 51 shows MGR increases rapidly during the first 6 hours and peaks at 4.1 x 10-5 and 1.7 x 10-5 (ft^3/h) / gallon of salt solution as sulfide is leached from grout solids, for the 0.85 and 0.59 mass ratio, respectively. The MGR then drops rapidly over the next 24 hours. The error bars shown are ±17%, ±8%, and ±9 RSD at the 95% confidence level for the data sets of Test Series 3, Test Series 5 (0.59 mass ratio), and Test Series 5 (0.85 mass ratio), respectively The two data sets for the solidified grout at mass ratios of 0.59 and 0.85 are statistically different with the MGR of the 0.85 mixture consistently being larger. This is the opposite result from the 10/45/45 mixture of Test Series 4. The lack of cement in the 0/60/40 may be playing a role. For the grout that was maintained as a slurry, Test Series 3, the MGR significantly larger at all time periods, most likely due to the fact that sulfide could be released more easily to form methane.

[22] See footnote 10.

[23] Liquid volume is only of the Tank 50 salt solution simulant contained in the grout mixture.

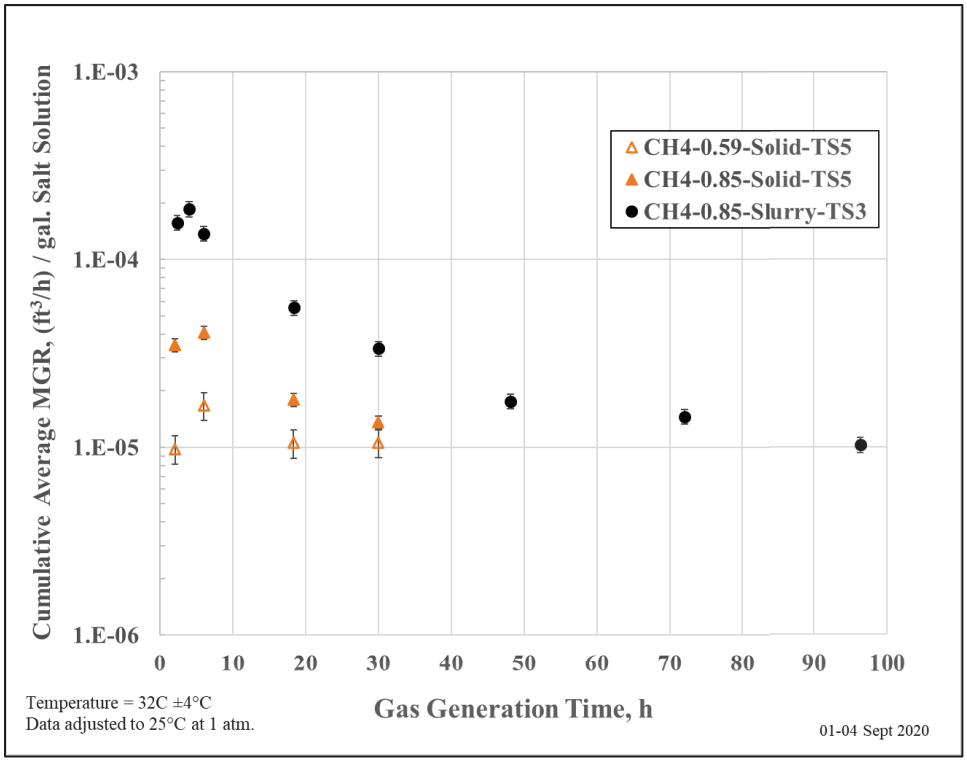


Figure 51. Test Series 5 methane gas generation rates

Other Measured Gases

Concentrations of hydrogen, nitrous oxide, and carbon dioxide were also measured, but they were a factor of at least 3 to an order of magnitude below that of methane. Table 33 shows that the concentrations were less than 90 ppm for H_2 and 55 ppm for N_2O, which are quantifiable, but it is less than 10 ppm for CO_2, which, while detectable, is not quantifiable. For concentrations below 1 ppm the value in the table is listed as 0 ppm. Figure 51 shows the results of using Equation (1) to calculate the gas generation rates for each gas and the results are spread of 4 decades of MGR. All three gases, i.e., H_2, N_2O, and CO_2 only play a minor role in gas generation at 35°C as compared to CH_4.

As explained in the results for Test Series 2 and Test Series 3, the source of H_2 is most likely the TOC in the T50SS simulant and the cementitious solids. Furthermore, the HGR is lower for Test Series 5 with solidified grout, than the two preceding test series with continually mixed grout, which is similar to the lower MGR for methane. The solid grout either retains more gas or impedes the chemical reactions to create more gas. However, the HGR for Test Series 5, with the 0/60/40 grout mixture, is about double that of Test Series 4, with the 10/45/45 grout mixture, possibly because of the higher concentration of slag, i.e., 60 wt% versus 45 wt%, see Table 33 and Table 31, respectively. Slag has the highest concentration of TOC of the three cementitious components[24].

[24] In Reference [6.5] see Table 4.

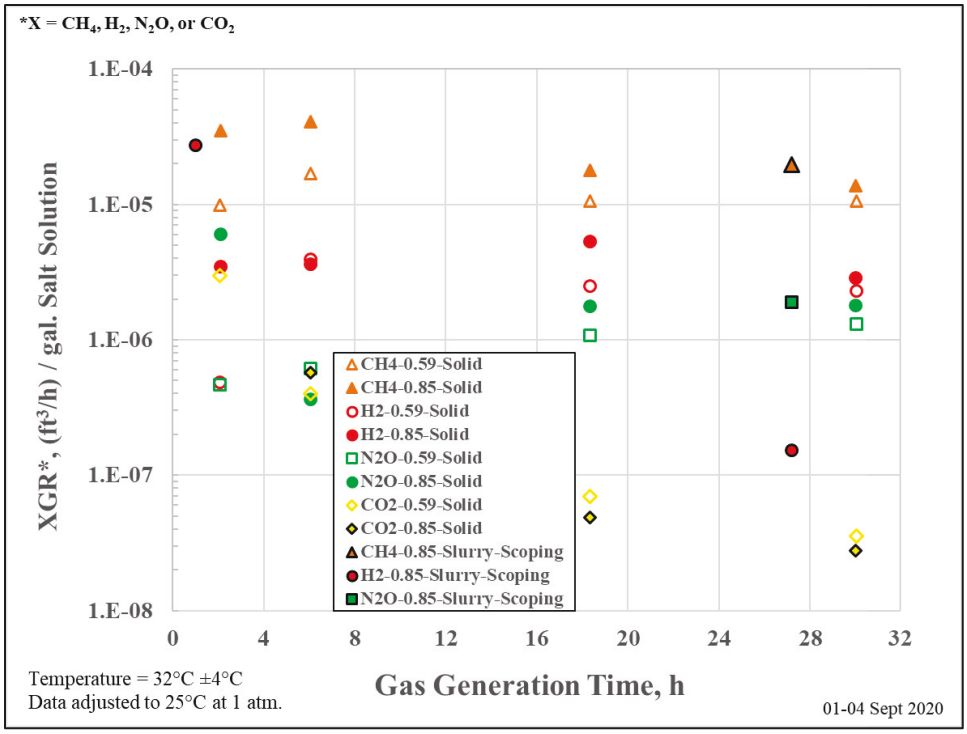


Figure 52. Test Series 5 methane gas generation rates between test intervals

Table 33. Test Series 5 gas production and generation rates

Reactor HGV-	Mass Ratio (1)	Duration h	Temp. °C (2)	CH_4 ppm	CH_4 (ft^3/hr) / gal	H_2 ppm	H_2 (ft^3/hr) / gal	N_2O ppm	N_2O (ft^3/hr) / gal	CO_2 ppm	CO_2 (ft^3/hr) / gal
9	0.85	2.1	28	62	3.50E-05	6	3.46E-06	11	5.98E-06	< D (3)	< D (3)
8	0.85	6.1	33	220	4.09E-05	19	3.62E-06	2	3.62E-07	3	5.75E-07
10	0.85	18.4	34	294	1.79E-05	88	5.32E-06	29	1.77E-06	1	4.85E-08
7	0.85	30.0	34	378	1.36E-05	79	2.87E-06	50	1.79E-06	1	2.78E-08
8	0.59	2.1	26	18	9.82E-06	1	4.87E-07	1	4.65E-07	5	2.99E-06
11	0.59	6.0	35	87	1.68E-05	20	3.91E-06	3	6.11E-07	2	3.97E-07
13	0.59	18.3	34	169	1.058E-05	40	2.50E-06	17	1.08E-06	1	7.00E-08
14	0.59	30.0	33	287	1.062E-05	62	2.30E-06	35	1.30E-06	1	3.55E-08

(1) The mass ratio is the water-to-solids grout premix of the dilute mixture of 0.85 to the standard mixture of 0.59. However, both mixtures were only mixed for 30 minutes and then allowed to solidify.
(2) Temperature averages for the 0.85 mass ratio tests and 0.59 mass ratio tests were 32°C ±2°C and 32°C ±4°C, respectively.
(3) < D = Below the detection limit.

Mercury Results

To confirm that the initial concentration of MeHg in the spiked T50SS simulant, samples were taken immediately after spiking and before filling any of the reactors. Then, when the last reactor was filled, several days later, the spiked simulant was sampled again. All these results are before the simulant was further spiked with a source of sulfide, which would allow methane to generate as the MeHg was being destroyed. Table 34 shows both the measured total Hg and the MeHg concentrations along with the MeHg spiked concentration based on the measured MeHgOH source material. Within the analytical measurement uncertainty ±20% at the 95% confidence level, all the measured values indicate the target concentration 100 mg/L of MeHg was obtained.

Table 34. Test Series 5 MeHg and total Hg results of spiked simulant

Test Series Number	Reactor Fill Period	Date Simulant Sampled	T50SS (1) Density g/mL	Composed MeHg Spike mg/L	Date Sample Analyzed	Analyzed Total Hg mg/L (2)	Date Sample Analyzed	Analyzed MeHg mg/L (3)	Comments
5	First	1-Sep-20	1.2206	109.5	8-Sep-20	106	19-Oct-20	108	Sampled before filling reactors (4)
5	Last	3-Sep-20	1.2206	109.5	8-Sep-20	111	19-Oct-20	110	Sampled after last reactor was filled (4)

(1) T50SS = Tank 50 Salt Solution simulant
(2) Analyzed by Direct Mercury Analyzer using Atomic Absorption Spectroscopy. Two sigma uncertainty is ±20%.
(3) Analyzed by Gas Chromatography Cold-Vapor Atomic Flourescence Spectrophotometry. Two sigma uncertainty is ±20%.
(4) These samples were taken before being spiked with sulfide-containing premix grout.

Appendix K: MeHg Destruction Test Results

Masses of Methane Released and Methyl Mercury Destroyed

Concurrent with measuring methane generation, another test was performed to directly measure the destruction of MeHg in the three main mixtures, i.e., Na_2S, grout with a 10/45/45 mixture of premix solids and grout with a 0/60/40 or premix solids. This was done because of the difficulty to measure both methane generation and MeHg destruction at the same time. From the previous scoping work [6.4], after the methane was measured, the reactors were opened to take liquid samples of them mixture which were then filtered and sent to be analyzed by a Gas Chromatograph – Cold-Vapor Atomic Fluorescence Spectrometer (GC-CVAFS). By the time the samples were drawn, filtered, shipped, and analyzed, the MeHg was destroyed because the reactions continued from the end of measuring methane to start of measuring MeHg. To address this problem a separate set of mixtures were made, using the same materials and methods that made the mixture for the sealed reactors. The salt solution simulant was made and brought to the GC-CVAFS location after which each test mixture made. After spiking each with MeHg the MeHg destruction test began immediately.

Each of the three mixtures were contained in Teflon bottles of the same size and shape as the Teflon inserts used in the sealed reactor. Furthermore, during the test the mixtures in the Teflon bottles were stirred in the same fashion, i.e., with approximately the same amount of mixing energy, as the mixtures in the reactors to be consistent. The principal difference between the two sets of tests was the temperature. While the sealed reactors were kept a 35°C ±5°C the mixture of the MeHg destruction test were allowed to remain a room temperature. To safely heat the mixtures to 35°C and keep them at that temperature overnight involved a lot of equipment, e.g., temperature controls, over-temperature monitors, etc., and the limited space available in the fume hood to do the measurements would cause major delays. It was decided to perform the test at room temperature principally because the target test temperature of 35°C is low, where effect due to thermolysis should be insignificant [6.5]; therefore, the difference between the target temperature and room temperature of ~ 25°C was expected to have an insignificant effect on the results. It turned out the room temperature ranged from 20°C to 26°C.

The test started as soon as each mixture was spiked with its source of sulfide, be it Na_2S or the slag in the grout mixtures. First each mixture was spiked with 100 mg/L of MeHg and after a minute of mixing, a sample was pulled confirm the MeHg concentration. Subsequently, each mixture was spiked with its source of sulfide, be it from Na_2S or from the slag in grout, which began the process of making sulfide available to destroy MeHg. The moment of spiking was taken as time zero ,and as the concentration of MeHg continually decreased samples were periodically pulled and analyzed, as soon as possible, generally within 5 to 10 minutes. The results for all three mixtures are listed in Table 35 for Na_2S, Table 36 for the 10/45/45 grout, and Table 37 for the 0/60/40 grout.

The tables show the target mixture duration and the measured duration when samples were pulled. These durations were chosen to not only closely match those used for the methane measurements in the sealed reactors but also fall conveniently within a worker's shift schedule. Also shown is the time it took to pull a sample to the time the GC-CVAFS began, which entailed dilution and mixing because of the high concentration of MeHg. Other data including the test temperature, the T50SS mass and density used, and the composition concentration of MeHg. Finally, the table show the MeHg concentration and its conversion to the mass measured so the value could be monitored with time relative to the starting mass, which is shown in the last column as the fraction of MeHg destroyed.

Table 35. MeHg Destruction Test – Na_2S mixture

MeHg Destruction Test Results: Test Series 1 = Na_2S
Mass Tank 50 Simulant used = 64.46 g T50SS Simulant Density = 1.2208 g/mL
Time Spiked with sulfide = 10:42 HH:MM
Composed MeHg Concentration = 108 mg/L (Target = 100 mg/L)

Target Test Duration hours	Date of Sample DD-MM-YY	Time Sample Taken HH:MM	Time Sample Analyzed HH:MM	Acual Duration Period h	Temperature of Sample °C	Measured MeHg Concentration mg/L	Mass of MeHg in Simulant g	Moles of MeHg in Simulant mol	MeHg Destroyed in Duration fraction
0	21-Sep-20	10:35	10:52	**0.0**	NA	112	5.914E-03	2.74E-05	**0.00**
2	21-Sep-20	13:08	14:00	**2.4**	24.2	16.3	8.607E-04	3.99E-06	**0.85**
4	21-Sep-20	15:05	15:43	**4.4**	24.3	27.8	1.468E-03	6.81E-06	**0.75**
6	21-Sep-20	16:50	17:23	**6.1**	25.2	16.1	8.501E-04	3.94E-06	**0.86**
24	22-Sep-20	10:15	0:30	**23.6**	23.9	3.77	1.991E-04	9.23E-07	**0.97**
29	22-Sep-20	14:40	15:43	**28.0**	24.5	2.71	1.431E-04	6.64E-07	**0.98**
48	23-Sep-20	9:15	9:30	**46.5**	23.5	1.99	1.051E-04	4.87E-07	**0.98**
53	23-Sep-20	14:15	14:28	**51.6**	24.0	2.19	1.156E-04	5.36E-07	**0.98**
72	24-Sep-20	12:20	12:30	**73.6**	24.3	2.02	1.067E-04	4.95E-07	**0.98**
77	24-Sep-20	15:44	15:59	**77.0**	25.4	1.71	9.029E-05	4.19E-07	**0.98**

Table 36. MeHg Destruction Test – 10/45/45 grout mixture

MeHg Destruction Test Results: Test Series 2 - 10/45/45 grout premix solids
Mass Tank 50 Simulant used = 33.07 g T50SS Simulant Density = 1.2208 g/mL
Time Spiked with sulfide = 11:56 HH:MM
Composed MeHg Concentration = 334 mg/L (Target = 100 mg/L. Larger amount due to pipette failure)

Target Test Duration hours	Date of Sample DD-MM-YY	Time Sample Taken HH:MM	Time Sample Analyzed HH:MM	Acual Duration Period h	Temperature of Sample °C	Measured MeHg Concentration mg/L	Mass of MeHg in Simulant g	Moles of MeHg in Simulant mol	MeHg Destroyed in Duration fraction
0	21-Sep-20	11:47	12:05	**0.0**	NA	383	1.038E-02	4.81E-05	**0.00**
2	21-Sep-20	14:20	14:55	**2.4**	20.4	315	8.533E-03	3.96E-05	**0.18**
4	21-Sep-20	15:22	15:56	**3.4**	20.3	187	5.066E-03	2.35E-05	**0.51**
6	21-Sep-20	16:59	17:36	**5.1**	20.5	145	3.928E-03	1.82E-05	**0.62**
24	22-Sep-20	10:17	0:43	**22.4**	19.8	288	7.802E-03	3.62E-05	**0.25**
29	22-Sep-20	14:45	15:58	**26.8**	20.5	114	3.088E-03	1.43E-05	**0.70**
48	23-Sep-20	After 29 hours the samples were to viscous to pull further samples.							

Table 37. MeHg Destruction Test – 0/60/40 grout mixture

MeHg Destruction Test Results: Test Series 3 - 0/60/40 grout premix solids
Mass Tank 50 Simulant used = 33.00 g T50SS Simulant Density = 1.2208 g/mL
Time Spiked with sulfide = 12:02 HH:MM
Composed MeHg Concentration = 108 mg/L

Target Test Duration hours	Date of Sample DD-MM-YY	Time Sample Taken HH:MM	Time Sample Analyzed HH:MM	Acual Duration Period h	Temperature of Sample °C	Measured MeHg Concentration mg/L	Mass of MeHg in Simulant g	Moles of MeHg in Simulant mol	MeHg Destroyed in Duration fraction
0	21-Sep-20	11:52	12:05	**0.0**	NA	80.4	2.173E-03	1.01E-05	**0.00**
2	21-Sep-20	13:14	14:13	**1.2**	23.2	33.5	9.054E-04	4.20E-06	**0.58**
4	21-Sep-20	15:17	16:09	**3.3**	24.3	75	2.027E-03	9.40E-06	**0.07**
6	21-Sep-20	17:02	17:49	**5.0**	25.8	98.3	2.657E-03	1.23E-05	**0.00**
24	22-Sep-20	10:25	0:56	**22.4**	23.5	53.8	1.454E-03	6.74E-06	**0.33**
29	22-Sep-20	14:50	16:09	**26.8**	23.6	20.4	5.514E-04	2.56E-06	**0.75**
48	23-Sep-20	After 29 hours the samples were to viscous to pull further samples.							

The intention was to measure the MeHg over the entire test period of 77 hours, slightly over 3 days, for all three mixtures, but that was not possible with the two grout mixtures. For the first mixture with Na_2S, this was easy to accomplish because it was a liquid, but for the mixtures with grout the sampling process was made more difficult as the grout became more viscous. As in the sealed reactors, the mixtures were continually stirred to remain a slurry, but, after about 29 hours, the grout was still a slurry but too viscous to pull samples. On the second data after 29 hours, the grout tests were terminated. However, 6 samples were obtained from each to have enough data to discuss the trends.

Preceding the MeHg destruction test the methane generation tests, Test Series 1-5 were performed. Each of the five test series used 8 sealed reactors to measure methane production with time. The methane data from those tests were used to determine the number of moles generated from each mixture compared to the total moles possible if 100% of the MeHg was converted to Methane to demonstrate the fraction converted.

Figure 53 shows a graphical presentation of the calculated results listed in Table 35 for the MeHg concentrations and in Table 38 for the methane concentrations. The error bars shown are only ±10% uncertainty, while the actual 95% confidence level uncertainty is closer to 20%. However, even at the smaller uncertainty all the data match and follow the same trend, including the two filled diamonds from a previous scoping tests [6.4]. The implication is that there is a one-to-one relationship between the destruction of MeHg and the production of CH_4, reaching an asymptote in less than 24 hours. The mixture had a pH~14 and an excess of S^{2-}, see Table 1.

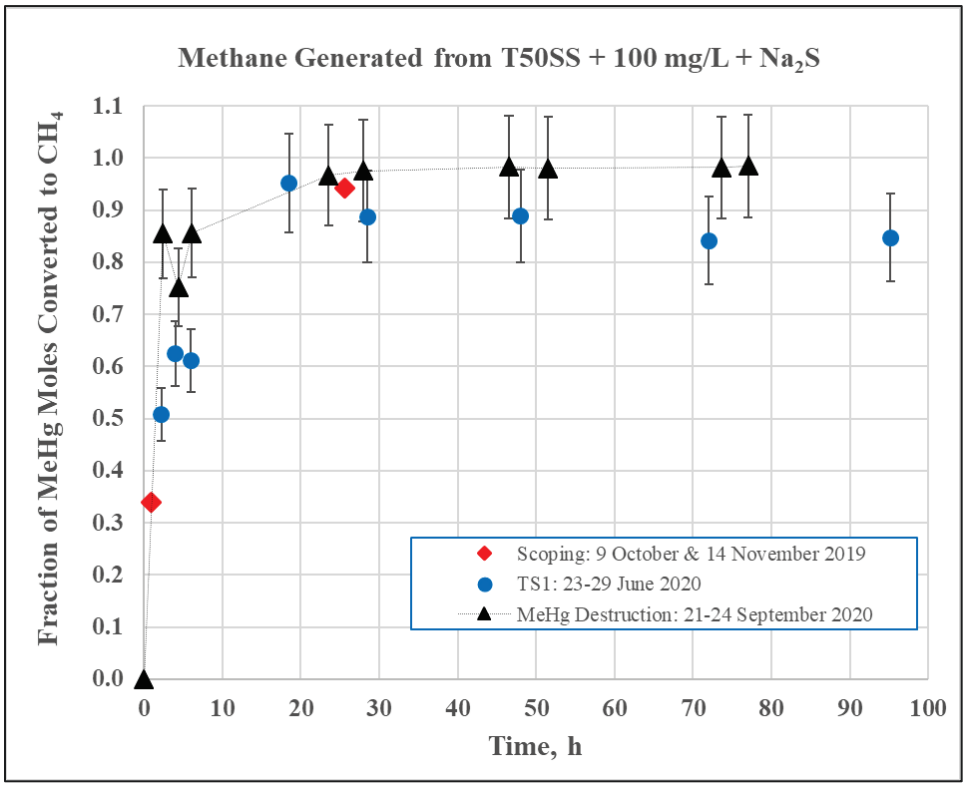


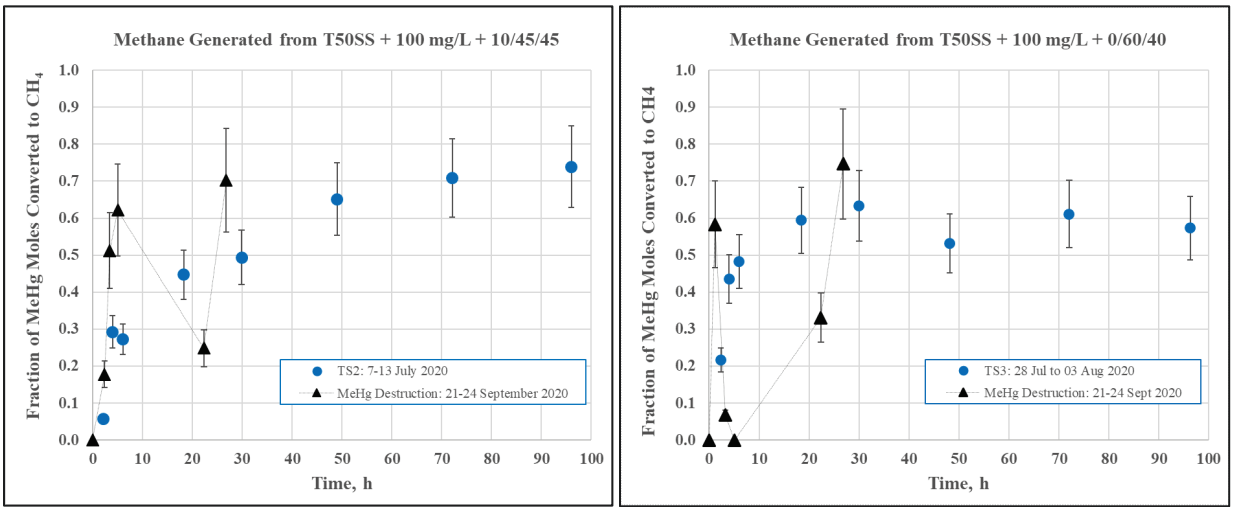
Figure 53. Test Series 1 fraction of methane produced and MeHg destroyed with time starting with 100 mg/L of MeHg from a mixture T50SS spiked with Na_2S

The next two test series, i.e., Test Series 2 and Test Series 3, used grout. Test Series 2 had the 10/45/45 grout premix and Test Series 3 had the 0/60/40 grout premix and for both the water-to-solids mass ratio was the dilute 0.85 to help maintain the mixtures as a slurry during the continual mixing. The results from

those tests are graphically shown in Figure 54(a) and Figure 54(b) with the calculations shown in Table 39 and Table 40, respectively. The error bars shown are ±20% for the MeHg concentrations uncertainty, which is from the analytical measurement and ±15% for the CH_4 measurement at the 95% confidence level. Actually, the CH_4 measurement accuracy is ±13% or better, see Table 14 in Appendix C.

It appears that the relationship of MeHg destruction to the release of CH_4 is more complex than for the Na_2S mixture of Test Series 1. As MeHg reacts with sulfide CH_4 is released, but there is also the process of sulfide being released from the grout, which is complex [6.22], so the one-to-one relationship of Test Series 1 is less evident. Once again, these mixtures had a pH~14 and an excess of S^{2-}, but the amount of excess is less known because of the way sulfide is released and that grout slag containing other forms of sulfur, e.g., sulfate, which does not react with MeHg.

Despite the complexities some conclusions can be made. The concentration of MeHg drops before methane is released and can be seen from the filled triangles increasing more rapidly than the filled circles of methane release. It may be a coincident, or an experimental error, but for both grout mixtures there was a drop in the loss of MeHg at 24 hours before returning to a destruction of MeHg of better than 70%. Both grout mixtures appear to reach a similar asymptote of approximately 65% of methane released of the available moles of MeHg. However, the distinct difference between the two grout mixtures is that the cement-less mixture of 0/60/40 grout premix reaches its asymptote much faster, within 18 hours, than the mixture of 10/45/45 grout premix, which too approximately 3 days to reach its maximum.



(a) Test Series 2 with 10/45/45 Grout Premix (b) Test Series 3 with 0/60/45 Grout Premix

Figure 54. Test Series 2 (a) and Test Series 3 (b) fraction of methane produced and MeHg destroyed with time starting with 100 mg/L of MeHg from grout as a slurry

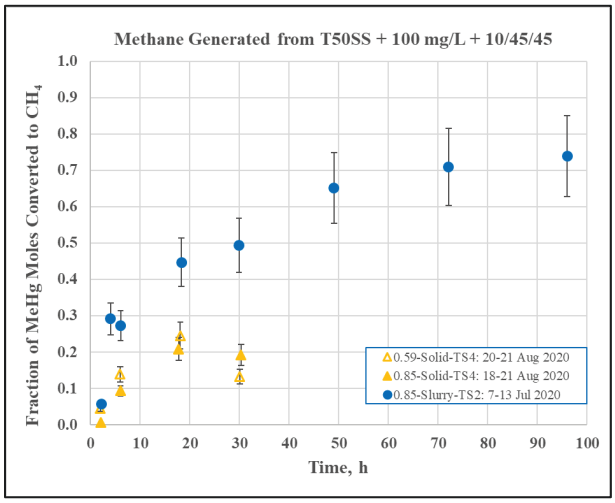
The last two test series, i.e., Test Series 4 and Test Series 5, also used grout but this time, the grout was allowed to solidify after each was well mixed. Each of the test series had four reactors with the 0.59 mass ratio and four reactors with the 0.85 mass ratio to see if the results would differ. Since each test series used all 8 reactors available the test durations were limited to 30 hours instead of the 96 hours for the preceding test series This shorter duration allowed each Test Series to be completed in a timely manner and the principal reason for these extra test was to see if solidified grout reacted differently that grout maintained as a slurry, which was expected to be evident in the first 24 hours, if a difference existed.

The 8 reactors of Test Series 4 contained the 10/45/45 grout premix and those of Test Series 5 had the 0/60/40 grout premix. Once the reactors were sealed the mixtures were stirred for 30 minutes after which

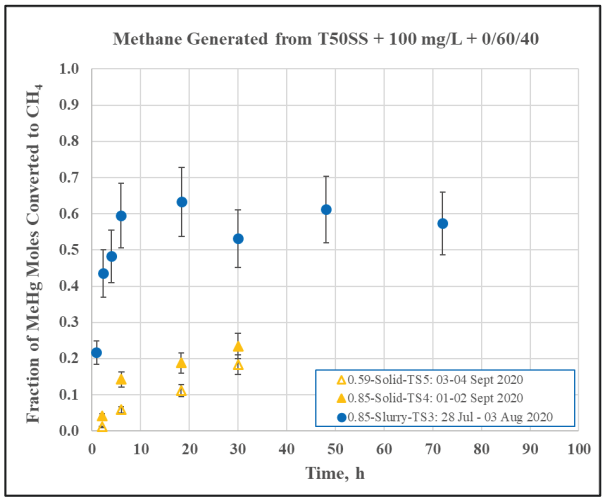
agitation was stopped to allow the grout to solidify. The results from those tests are graphically shown in Figure 55(a) and Figure 55(b) with the calculations shown in Table 41 and Table 42, respectively. The error bars shown are ±20% for the MeHg concentrations uncertainty, which is from the analytical measurement and ±15% for the CH_4 measurement at the 95% confidence level. Actually, the CH_4 measurement accuracy is ±13% or better, see Table 14 in Appendix C.

To facilitate the principal comparison between solidified and slurry grout the results of both test series with solidified grout are show along with the results from the test series with mixing grout, i.e., Test Series 2 in Figure 55(a) and Test Series 3 in Figure 55(b). The figures clearly show that the continually mixed grout, the filled circles, released more methane than for the solidified mixtures, the open and filled triangles. This is probably due to increased shear stress of the flowing mixtures upon the grout solids, which assist the solids to break down to release more of the sulfide and at a faster rate. The solidified grout only released approximately 25% of the mole of methane of the total moles of MeHg available as compared to the 60% to 70% for grout continually mixed.

Some other conclusions that can be made on the solidified grout tests are that the rate of increase of methane produced is approximately the same for the first 24 hours for both the 10/45/45 and the 0/60/40 grout mixtures, which is different than for the continually-mixed grout. And finally, differences from the solidified grout made with the 0.50 mass ratio or the 0.85 mass ratio appear insignificant. The results for 0.59 mass ratio are above those for the 0.85 mass ratio for the 10/45/45 mixture, but this trend is reversed for the 0/60/40 mixture. Statistically both sets of data are the same at the 95% confidence level as discussed on the last two pages of the statistical analysis in Appendix C.



(a) Test Series 4 with 10/45/45 Grout Premix



(b) Test Series 5 with 0/60/45 Grout Premix

Figure 55. Test Series 4 (a) and Test Series 4 (b) fraction of methane produced and MeHg destroyed with time starting with 100 mg/L of MeHg from grout as a solid

Composed Concentration of MeHg mg/L	Nomenclature Title	Explanation
99.9	TS1	Test Series 1: Tank 50 Simulant + 100 mg/L MeHg + Na2S
104.5	TS2	Test Series 2: Tank 50 Simulant + 100 mg/L MeHg + 10/45/45 grout premix solids, 0.85 water-to-solids mass ratio
107.8	TS3	Test Series 3: Tank 50 Simulant + 100 mg/L MeHg + 0/60/40 grout premix solids, 0.85 water-to-solids mass ratio
107.2	TS4	Test Series 4: Tank 50 Simulant + 100 mg/L MeHg + 10/45/45 grout premix solids, 0.85 & 0.59 water-to-solids mass ratios
109.5	TS5	Test Series 5: Tank 50 Simulant + 100 mg/L MeHg + 0/60/40 grout premix solids, 0.85 & 0.59 water-to-solids mass ratios
105.6	Redo	6 Test were redone that had simulant displaced under Teflon insert

Molecular Weight of CH_3Hg^+ =	215.616	g/mol	
Density of Simulant =	1.2145	g/mL	Test Series 1
Density of Simulant =	1.2208	g/mL	Test Series 2 & 3
Density of Simulant =	1.2206	g/mL	Test Series 4, 5, & Redo Tests
Density of Simulant =	1.2243	g/mL	Scoping: 1 h
Density of Simulant =	1.2207	g/mL	Scoping: 27 h
Density of CH4 at 25°C =	0.648	g/L	
Molecular Weight of CH4 =	16.04	g/mol	

= Yellow blocks are previous scoping data

= Green blocks are tests that were repeated to replace the ones that test simulant was found under Teflon insert.

= Blue blocks contain input data from experiments.

Figure 56. Information needed for calculations in the following 5 tables

Table 38. Fraction of methane released vs. mass of MeHg available - Na_2S mixture

TS1	Experimental Data					Moles of CH_3Hg^+			Moles of Methane						
Elapse Time	Average CH4	Std Deviation CH4	Reactor Avg. Temp at Measure	Reactor Initial. Press. at Measure	Participating Simulant	Participating Simulant	MeHg in Simulant	MeHg in Simulant	Cumulative Reactor Head	For 1 atm & 25°C	CH4 in Head	CH4 in Head	CH4 in Head	Moles MeHg Converted to CH4	Measure-ment Std. Dev.
hours	ppm	ppm	°C	psig	g	mL	g	mol	cm3	cm3	cm3	g	mol	fraction	fraction
1.0	944.7	48.4	35.3	12.90	64.61	52.77	0.0053	2.4451E-05	120.07	217.914571	0.20587	0.0001334	8.31682E-06	0.34	0.05
2.2	1416.0	30.4	30.3	12.55	64.49	53.10	0.0053	2.4603E-05	119.78	218.199345	0.30898	0.00020022	1.24824E-05	0.51	0.06
4.0	1814.0	4.8	30.9	11.27	64.37	53.00	0.0053	2.4555E-05	120.73	209.126523	0.37935	0.00024582	1.53256E-05	0.62	0.06
6.0	1779.3	9.5	32.7	12.34	64.46	53.08	0.0053	2.4591E-05	116.62	209.141159	0.37212	0.00024114	1.50334E-05	0.61	0.06
18.5	1054.0	5.0	30.3	15.05	33.01	27.18	0.0029	1.3312E-05	149.69	297.673881	0.31375	0.00020331	1.26751E-05	0.95	0.10
25.7	2573.6	17.3	29.9	11.00	64.49	52.83	0.0053	2.4501E-05	129.09	222.065741	0.57151	0.00037034	2.30885E-05	0.94	0.10
28.5	1126.0	4.0	28.7	11.77	33.03	27.20	0.0029	1.332E-05	146.15	259.928648	0.29268	0.00018966	1.1824E-05	0.89	0.09
48.0	2617.3	14.2	28.0	11.46	64.81	53.36	0.0053	2.4725E-05	117.97	207.838255	0.54397	0.00035249	2.19758E-05	0.89	0.09
72.0	2597.4	18.1	31.4	10.05	64.49	53.10	0.0053	2.4603E-05	119.69	197.258597	0.51236	0.00033201	2.0699E-05	0.84	0.09
95.2	2520.4	10.8	31.9	11.14	64.45	53.07	0.0053	2.4587E-05	119.12	204.656711	0.51582	0.00033425	2.08385E-05	0.85	0.09

Table 39. Fraction of methane released vs. mass of MeHg available – 10/45/45 grout mixture

TS2	Experimental Data					Moles of CH_3Hg^+			Moles of Methane						
Elapse Time	Average CH4	Std Deviation CH4	Reactor Avg. Temp at Measure	Reactor Initial. Press. at Measure	Participating Simulant	Participating Simulant	MeHg in Simulant	MeHg in Simulant	Cumulative Reactor Head	For 1 atm & 25°C	CH4 in Head	CH4 in Head	CH4 in Head	Moles MeHg Converted to CH4	Measure-ment Std. Dev.
hours	ppm	ppm	°C	psig	g	mL	g	mol	cm3	cm3	cm3	g	mol	fraction	fraction
1.0	0.0	0.0	31.3	12.57	33.26	27.17	0.0027	1.26E-05	118.25	214.839739	0	0	0	0.00	0.00
2.2	83.0	12.7	29.9	12.58	33.06	27.08	0.0028	1.3125E-05	122.77	224.134483	0.0186	1.2053E-05	7.51423E-07	0.06	0.01
4.0	429.9	6.5	33.2	12.82	32.95	26.99	0.0028	1.3081E-05	120.70	219.924684	0.09455	6.1265E-05	3.81954E-06	0.29	0.03
6.1	416.1	6.1	34.4	12.86	32.96	27.00	0.0028	1.3085E-05	116.65	211.984378	0.0882	5.7154E-05	3.56323E-06	0.27	0.03
18.3	650.0	3.9	32.4	12.85	33.07	27.09	0.0028	1.3129E-05	122.17	223.440065	0.14524	9.4113E-05	5.86742E-06	0.45	0.05
26.9	989.8	5.3	29.3	10.83	33.19	27.19	0.0027	1.261E-05	118.31	202.55721	0.2005	0.00012992	8.09999E-06	0.64	0.07
29.9	780.5	3.0	32.1	11.48	33.09	27.11	0.0028	1.3137E-05	118.23	205.68474	0.16054	0.00010403	6.48577E-06	0.49	0.05
49.0	974.4	8.3	31.3	12.91	33.09	27.11	0.0028	1.3137E-05	118.21	217.413341	0.21185	0.00013728	8.55839E-06	0.65	0.07
72.1	1065.4	4.3	28.6	11.45	33.02	27.05	0.0028	1.3109E-05	122.77	215.817197	0.22994	0.000149	9.28924E-06	0.71	0.07
96.0	1065.4	4.3	26.3	12.01	33.06	27.08	0.0027	1.2547E-05	119.09	215.408181	0.2295	0.00014872	9.27164E-06	0.74	0.08

Table 40. Fraction of methane released vs. mass of MeHg available – 0/60/40 grout mixture

TS3	Experimental Data					Moles of CH_3Hg^+			Moles of Methane						
Elapse Time	Average CH4	Std Deviation CH4	Reactor Avg. Temp at Measure	Reactor Initial. Press. at Measure	Participating Simulant	Participating Simulant	MeHg in Simulant	MeHg in Simulant	Cumulative Reactor Head	For 1 atm & 25°C	CH4 in Head	CH4 in Head	CH4 in Head	Moles MeHg Converted to CH4	Measure-ment Std. Dev.
hours	ppm	ppm	°C	psig	g	mL	g	mol	cm3	cm3	cm3	g	mol	fraction	fraction
1.0	141.6	11.3	31.5	12.68	33.16	27.09	0.0027	1.2563E-05	118.12	215.313116	0.03048	1.9752E-05	1.23145E-06	0.10	0.02
2.4	338.8	3.5	28.7	11.44	33.01	27.04	0.0029	1.3519E-05	121.93	214.143737	0.07255	4.7012E-05	2.93094E-06	0.22	0.02
4.0	645.4	6.2	32.7	13.08	33.08	27.10	0.0029	1.3547E-05	122.74	226.095195	0.14592	9.4556E-05	5.89503E-06	0.44	0.05
6.0	728.8	3.8	33.9	13.52	32.97	27.01	0.0029	1.3502E-05	118.77	221.387145	0.16134	0.00010455	6.51797E-06	0.48	0.05
18.4	923.1	2.3	30.6	11.60	33.01	27.04	0.0029	1.3519E-05	122.71	215.500777	0.19893	0.0001289	8.03644E-06	0.59	0.06
27.2	441.6	5.1	28.3	16.20	33.04	27.07	0.0027	1.2553E-05	118.22	245.795909	0.10854	7.0332E-05	4.38479E-06	0.35	0.04
30.03	892.0	7.8	26.9	12.00	32.98	27.02	0.0027	1.2531E-05	121.95	220.129572	0.19636	0.00012724	7.93268E-06	0.63	0.07
48.14	780.1	0.0	31.0	11.40	33.06	27.09	0.0027	1.2562E-05	121.80	211.996452	0.16538	0.00010717	6.68131E-06	0.53	0.05
72.1	963.4	3.2	29.3	11.30	33.02	27.05	0.0029	1.3523E-05	121.83	212.394356	0.20463	0.0001326	8.26687E-06	0.61	0.06
96.3	962.7	8.2	28.9	10.33	33.04	27.07	0.0029	1.3533E-05	118.72	199.569981	0.19213	0.0001245	7.7617E-06	0.57	0.06

Table 41. Fraction of methane released vs. mass of MeHg available – 10/45/45 grout mixture[25]

TS4	Experimental Data					Moles of CH_3Hg^+			Moles of Methane						
Elapse Time	Average CH4	Std Deviation CH4	Reactor Avg. Temp at Measure	Reactor Initial. Press. at Measure	Participating Simulant	Participating Simulant	MeHg in Simulant	MeHg in Simulant	Cumulative Reactor Head	For 1 atm & 25°C	CH4 in Head	CH4 in Head	CH4 in Head	Moles MeHg Converted to CH4	Measure-ment Std. Dev.
hours	ppm	ppm	°C	psig	g	mL	g	mol	cm3	cm3	cm3	g	mol	fraction	fraction
2.0	8.2	2.8	28.1	14.26	33.01	27.04	0.0029	1.3446E-05	121.86	237.570672	0.00196	1.2672E-06	7.90052E-08	0.01	0.00
6.0	140.8	2.4	29.4	12.73	33.05	27.08	0.0029	1.3462E-05	120.73	221.98249	0.03126	2.0257E-05	1.26288E-06	0.09	0.01
17.8	277.3	4.3	31.0	15.59	33.06	27.09	0.0029	1.3466E-05	124.07	250.614716	0.06949	4.5027E-05	2.80716E-06	0.21	0.02
30.3	293.1	2.7	29.0	12.67	33.00	27.04	0.0029	1.3442E-05	118.75	218.169023	0.06394	4.1431E-05	2.58299E-06	0.19	0.02
2.0	82.6	7.8	28.8	7.07	33.00	27.04	0.0029	1.3442E-05	121.43	177.556431	0.01467	9.5084E-06	5.9279E-07	0.04	0.01
6.0	211.6	4.0	29.8	12.32	33.02	27.05	0.0029	1.345E-05	121.07	219.032579	0.04636	3.004E-05	1.87282E-06	0.14	0.02
18.0	366.9	2.8	31.4	12.64	33.02	27.05	0.0029	1.345E-05	122.05	222.208004	0.08152	5.2827E-05	3.29348E-06	0.24	0.03
30.1	203.9	3.9	30.7	12.53	33.01	27.04	0.0029	1.3446E-05	118.66	215.662337	0.04398	2.85E-05	1.77682E-06	0.13	0.02

[25] Table 27 and Table 28 each compare the 0.85 (1st 30 hours) vs. 0.59 (2nd 30 hours) water-to-solids mass ratios of premix solids of solidified grout whereas Table 25 and Table 26 are only for 0.85 water-to-solids mass ratio for continually-mixed slurry.

Table 42. Fraction of methane released vs. mass of MeHg available – 0/60/40 grout mixture

TS5	Experimental Data					Moles of CH_3Hg^+			Moles of Methane						
Elapse Time	Average CH4	Std Deviation CH4	Reactor Avg. Temp at Measure	Reactor Initial. Press. at Measure	Participating Simulant	Participating Simulant	MeHg in Simulant	MeHg in Simulant	Cumulative Reactor Head	For 1 atm & 25°C	CH4 in Head	CH4 in Head	CH4 in Head	Moles MeHg Converted to CH4	Measure-ment Std. Dev.
hours	ppm	ppm	°C	psig	g	mL	g	mol	cm3	cm3	cm3	g	mol	fraction	fraction
2.1	62.3	1.1	27.9	13.26	32.96	27.00	0.0030	1.3713E-05	121.96	229.774532	0.01431	9.271E-06	5.77994E-07	0.04	0.00
6.1	219.6	5.9	29.9	12.10	33.01	27.04	0.0030	1.3734E-05	122.78	220.253662	0.04836	3.1337E-05	1.95369E-06	0.14	0.02
18.4	294.5	3.0	30.9	12.02	33.03	27.06	0.0030	1.3743E-05	121.82	217.167101	0.06395	4.1439E-05	2.58351E-06	0.19	0.02
30.0	377.8	2.3	29.9	11.81	32.97	27.01	0.0030	1.3718E-05	118.77	210.748351	0.07962	5.1595E-05	3.21666E-06	0.23	0.02
2.1	18.0	3.5	29.6	12.24	33.05	27.08	0.0030	1.3751E-05	121.57	219.433916	0.00396	2.5636E-06	1.59827E-07	0.01	0.00
6.0	86.9	2.9	28.6	13.47	33.00	27.04	0.0030	1.373E-05	120.34	227.870206	0.01979	1.2826E-05	7.99621E-07	0.06	0.01
18.3	168.6	4.0	31.4	12.64	33.03	27.06	0.0030	1.3743E-05	123.27	224.432562	0.03785	2.4526E-05	1.52904E-06	0.11	0.01
30.0	286.5	3.5	28.6	11.85	33.02	27.05	0.0030	1.3738E-05	121.48	216.801833	0.06212	4.0253E-05	2.50955E-06	0.18	0.02

Appendix L: Hg Speciation Analysis after MeHg Destruction

Hg Groups that Remain in Solution after MeHg Reacts with Sulfide in the Process of Generating CH_4

During previous scoping work [6.4], to demonstrate methane generation and rates in sealed reactors after 1 hour and 24 hours, the mixtures were filtered and sampled to analyze for the total Hg by a Direct Mercury Analyzer (DMA). For that test the mixtures of the pH~14 Tank 50 salt solution simulant were spiked with 0, 100, and 200 mg/L of soluble MeHg. They were tested as is or further spiked with sources of sulfide, i.e., Na_2S or grout solids, which contained sulfur in the slag solids that released reduced sulfides. The results showed that for the samples with sulfide, the MeHg was destroyed, but total soluble Hg was still present in these filtered, strongly alkaline mixtures. There is literature [6.10] that indicates in solutions with high pH containing sulfide there exist Hg groups that remain soluble. That work [6.4] recommended to study this result to try to understand what those groups are and in the Run Plan [6.3] it was stated that samples with depleted MeHg would be analyzed by Nuclear Magnetic Resonance Spectroscopy to further investigate the soluble groups of Hg. This appendix describes the results of the NMR analysis.

Sample Preparation

To perform this analysis one mixture of T50SS, spiked with 100 mg/L of MeHg, and then further spiked with 12.6 g/l of Na_2S, was chosen. This mixture would be the clearest example of destroyed MeHg that still contained the full soluble concentration of Hg. One of the mixtures with grout could have been used, but the release of sulfide from slag is complex [6.22], which could make understanding the results more difficult. Furthermore, attempting to analyze a grout mixture in which the solids are dissolving to release sulfide while the overall mixture is solidifying would challenge the NMR analysis to obtain good results. Two samples were made for the analysis:

1. (Control): 1 5-mL sample of T50SS simulant + 100 mg/L of MeHg and no sulfide, and
2. 20-mL sample of T50SS simulant + 100 mg/L of MeHg + 12.6 g/L of Na_2S.

A 12.6 g/L of concentration of Na_2S was used to match the previous [6.4] and current studies. Both samples were maintained refrigerated of $\leq$ 4ºC until the analyses could begin to maintain the MeHg stable as recommended [6.6]. Note that after spiking the T50SS simulant with Na_2S to destroy the MeHg no precipitation occurred it remained clear. Even after two months of storage under refrigeration the spiked sample remained clear of solids and clear. Once some of the sample was transferred to the NMR tube for analysis it became very slightly cloudy.

Total Hg Analyses

Prior to analyzing the sample for soluble Hg groups with NMR, they were analyzed for total Hg with a DMA. To make sure that both samples exhibited the needed concentrations of Hg they were both analyzed after spiking with 100 mg/L of MeHg, so they should have the same results. Then, after the second sample was spiked with Na_2S, and waiting for 3 days during which more than 95% of the MeHg is destroyed [6.4], both samples were analyzed again. The total Hg results were expected to be the same for both samples in each analysis campaign. Note that the analytical measurement uncertainty is ±20% at the 95% confidence level. Those results follow.

Initial DMA total Hg after spiking with 100 mg/L of MeHg:

1. Sample 1 (Control): 124 mg/L
2. Sample 2: 123 mg/L

DMA total Hg 3 days after spiking Sample 2 with 12.6 g/L of Na_2S:

1. Sample 1 (Control): 113 mg/L
2. Sample 2: 112 mg/L

Within measurement uncertainty both campaigns obtained the same total Hg concentration. At this point Sample 2 would have no, or relatively no, MeHg remaining due to the presence of excess sulfide. Clearly the total Hg remained the same. The samples were then ready to begin the NMR analyses.

NMR Analysis

Nuclear Magnetic Resonance Spectroscopy (NMRS) is a method to observe local magnetic fields around atomic nuclei. A sample is placed in a magnetic field and the NMR signal is produced by the excitation of the nuclei with radio waves, which are detected with sensitive radio receivers. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency so this gives access to details of the electronic structure of a molecule and its individual groups. The desire was to use NMRS to discover which soluble Hg species exist in a high pH solution after the MeHg is destroyed and methane gas is released after reacting with the excess of sulfide. To best analyze the samples for mercury speciation the NMR was set to two different frequencies so that the focus was either on mercury, which is referred to as ^{199}Hg-NMR, or on hydrogen, which is referred to as H-NMR. The former can determine types and number of mercury atoms in a molecule, while the latter is used to determine the types and number of hydrogen atoms in a molecule. The H-NMR is included because it is more sensitive by an order of magnitude in detection, down to the 1 to 2 ppm level, than the ^{199}Hg-NMR.

^{199}Hg-NMR

The ^{199}Hg-NMR analysis is shown in Figure 57 with the blue resonance pattern indicating that the control sample without the Na_2S spike maintained the full 100 mg/L of MeHg species, which from literature for caustic water samples suggest the MeHgOH species in the cation form of $(CH_3Hg)_3O^{1+}$[6.23].

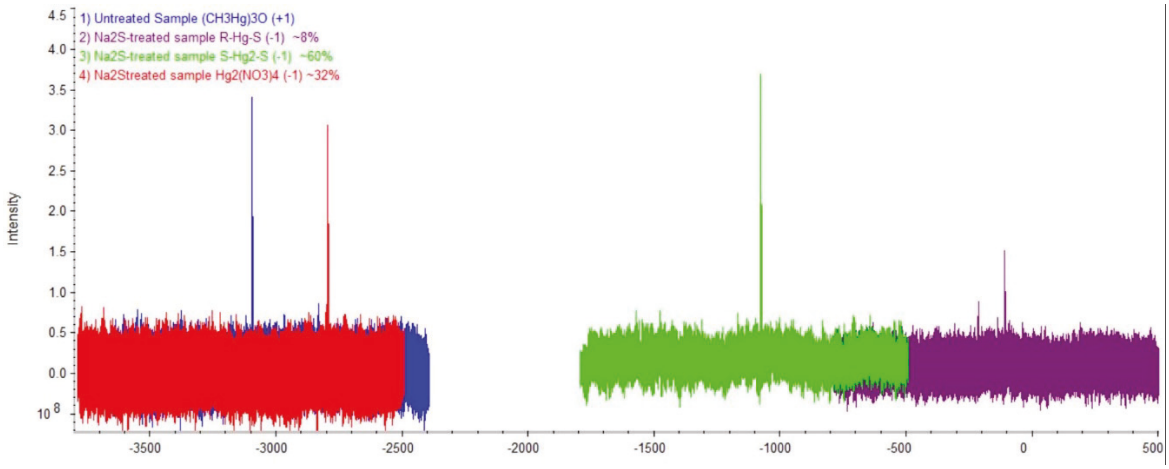


Figure 57. Combined ^{199}Hg-NMR analysis for two sample with and without Na_2S[26]

No other compounds containing Hg were identified in the control sample, i.e., with no Na_2S spike. For the sample spiked with Na_2S the MeHg was destroyed, i.e., there is no presence of the $(CH_3Hg)_3O^{1+}$peak at ~3100 ppm shift, which helped to generate methane, while the full concentration of 100 mg/L of Hg remained in soluble forms. Those forms were: 8% of $(R\text{-}Hg\text{-}S)^{1-}$, with 'R' possibly representing $-CH_2\text{-}OH$ or $-COO^-$ (carboxylate), 32% of $Hg(NO_3)_2$, and the bulk of the Hg, at 60% of $(S\text{-}Hg_2\text{-}S)^{2-}$. These

[26] In Figure 57 the blue resonance pattern is from the control sample and the other three are from the Na_2S-spiked sample. The abscissa is in the units of ppm of Hertz relative to the dimethylmercury. Dimethyl mercury is the standard compound used for setting the zero in the ^{199}Hg-NMR.

assignments were made using literature data from ^{199}Hg-NMR analyses [6.24]. Polysulfide forms of Hg (S_n-Hg-S_n) have been identified in the literature for caustic aqueous systems [6.25 and 6.26]. Furthermore, the sources of carboxylate could possibly be:

- Partial oxidation of carbon sourced from MeHg in the sample spiked with Na_2S.
- Organic contamination, but the control sample without the Na_2S spike showed very little evidence of contamination. However, the base simulant, which used the same reagents for a similar simulant in a previous study [6.5], was found to have tramp organic compounds at trace concentrations.

H-NMR

The H-NMR analysis is shown Figure 58 with the upper resonance pattern indicating that the control sample, i.e., without the Na_2S spike, shows presence of methylmercury as $(CH_3)HgOH$. Other species tentatively identified in the reacted sample on the bottom pattern show formate H-COO^- (which could be connected to Na^+ or Hg^+), methanol (CH_3OH), acetate CH_3-COO^- and dimethylmercury ($(CH_3)_2Hg$); however, the dimethylmercury intensity peak is very small.

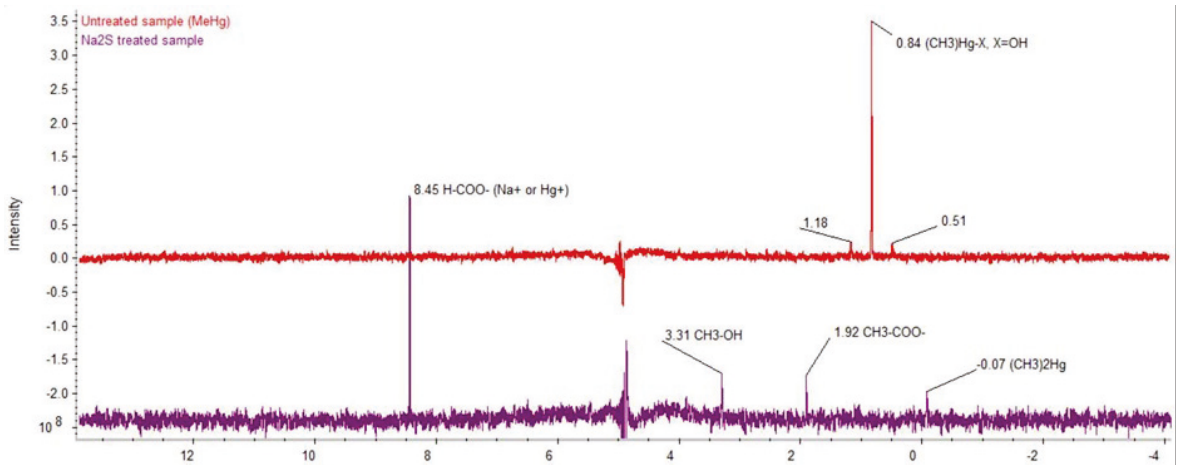


Figure 58. Combined H-NMR analysis for two samples with and without Na_2S[27]

Conclusion

NMR analysis was used to confirm the presence of primarily MeHg in the control sample and to tentatively identify, based on comparison to literature data, three soluble Hg-containing species (from ^{199}Hg-NMR) and three other organic species (from H-NMR) that result from the reaction of MeHg and soluble sulfide in the Na_2S spiked salt solution. These soluble Hg species could indeed account for the analyzed soluble total Hg found in post-reacted samples for this study and previous scoping tests [6.4].

Recommendations

All decomposition species identified in the NMR analyses are based on literature information. Further studies with spike additions of some, or all, of the decomposition species into a reacted system would be required to further confirm the presence of these compounds.

The NMR analysis and results presented here suggest that this technique could be applied to radioactive caustic tank waste samples from SRS Tank Farm to further investigate and understand the various Hg species present.

[27] In Figure 58 the top resonance pattern is from the control sample and the bottom is from the Na_2S-spiked sample. The abscissa is in units of ppm of Hertz relative to tetramethyl silane. Tetramethyl silane is the standard compound used for setting the zero in the H-NMR.

Appendix M: S_2 and O_2 reaction Effect on Pressure

A surprising result of the very first test series, Test Series 1, was that the pressure dropped continuously over the 96 hours of the test, Figure 59. This test series was the only one without grout and the reactors contained Tank 50 salt solution simulant + 100 mg/L of MeHg and spiked with 12.5 g/L of Na_2S. This means for this test series the sulfide was the most available to react, whereas for all other test series, which contained grout, the sulfide needed to be leached from the slag before being available. The immediate thought was the reactors were leaking, but these reactors had been thoroughly tested and were shown to be leak tight at pressures to 250 psig. In fact, a reactor was pressurized to more than 2000 psig [6.11] without failure. If there were a leak, it seems unlikely that all 8 reactors were leaking and at approximately the same rate. Another possibility for the pressure reductions could have been from some type of reaction that was affecting the pressure.

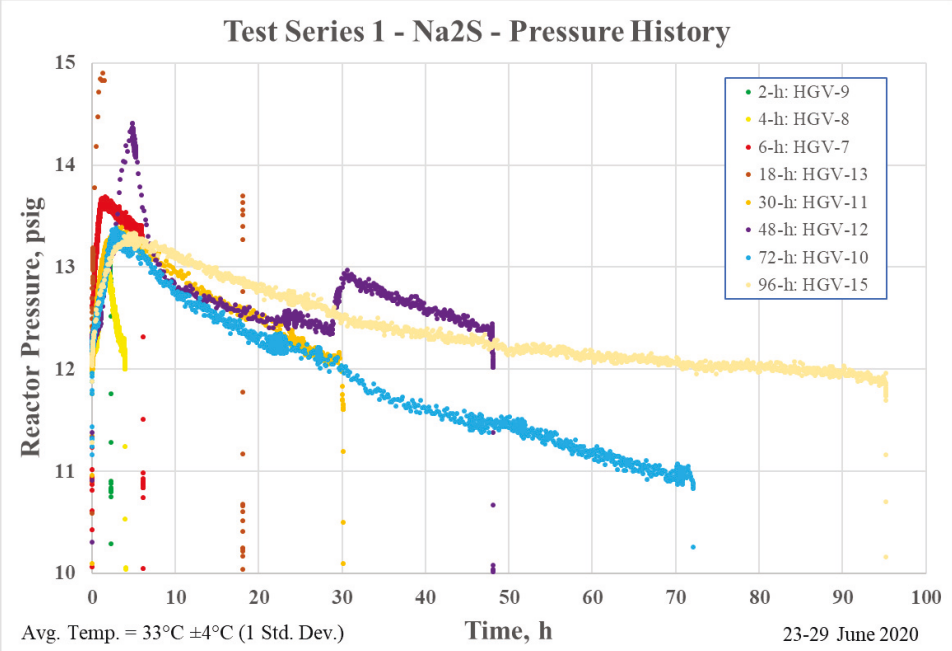


Figure 59. Pressure reduction during Test Series 1

The authors of reference [6.21] studied the kinetics of oxidation of aqueous sulfide by O_2 and showed that at pH ~ 9 and pH ~ 11 the rate of sulfide oxidation is the highest, but it is still high at pH > 11, and that this oxidation does affect pressure. If any test series would be affected, it would be Test Series 1 because it was included as a control to demonstrate the largest and fastest production of methane because the sulfide could be easily reduced to react with the MeHg. The sulfide was purposely made to be in excess to guarantee that the maximum amount of methane would be produced, so after, or during, methane production ample S^{2-} would have been available to react with the O_2 in the head space. The last step to seal reactors was pressurizing the head space with nitrogen so there would be sufficient pressure to draw gas samples after the test during. However, to prevent the loss of any initial methane generated the residual air in the head space was not purged but left and was diluted with the nitrogen.

To understand the makeup of the initial gas concentration in the head space immediately after the space was pressurized with N_2, and before gases, like methane, began to generate from the mixture an Ideal gas calculation is shown in Table 43. The estimate shows that the composition of the gas in the reactor head space should have been approximately 13% of O_2 and 86% of N_2.

Table 43. Gases in reactor head space after sealing and pressurizing with N_2 to 12 psig

Estimating the make-up of reactor head gases after sealing and pressurizing with N_2 to 12 psig but before gas generation							
Parameters						Mol. Wgt., g/gmole	
V_{HS} = Vol-Head Space =	120	mL				Air	28.965
T_{atm} =	25	C				N2	28.013
P_{atm} =	14.7	psia	101353	Pascal		O2	32.000
$P_1 = P_{atm}$ = Pressure Start =	0	psig				Ar	39.948
P_2 = Test Pressure =	12	psig	184090	Pascal		CO_2	44.010
Ideal Gas Universal Gas Constant = R_u =	8.314462	J/(mol-K)					
Dry Air ~ 78.1% N_2 , 20.9% O_2, 0.93% Ar, 0.04% CO_2, + trace (neglected for this analysis)							
Ideal-gas calculation of the number of moles of air in head space and that of the various components in air at standard conditions							
Air Moles of Head Space = (P_1 * V_1) / (R_U*T) =	0.004906077	moles AIR	By mass =	0.142103036	grams AIR		
Moles of N_2 = 0.781 x moles of air =	0.003830665	moles N_2	By mass =	0.107308407	grams N_2		
Moles of O_2 = 0.209 x moles of air =	0.001027332	moles O_2	By mass =	0.032874535	grams O_2		
Moles of Ar = 0.0093 x moles of air =	4.56265E-05	moles Ar	By mass =	0.001822688	grams Ar		
Moles of CO_2 = 0.0004 x moles of air =	1.96243E-06	moles CO_2	By mass =	8.63666E-05	grams CO_2		
Ideal-gas calculation of the number of moles of N_2 added to the air in head space after pressurizing to 12 psig							
Volume of Compressed Air = V_{HS} x P_1/ P_2 = V_{CA} =	66.07	mL	Gases are mixed, but this volume is as if gas is compressed by a cylinder				
Volume Occupied by Introduced N_2 = V_{HS} - V_{CA} = V_{N2}	53.93	mL	The compressed air allows this remaining volume for the N_2 to occupy.				
N_2 Moles Added to Head Space = (P_2 * V_{N2}) / (R_U*T) =	0.00401	moles N_2	By mass =	0.11219	grams of N_2 in added to head space		
Determining the ppm of each of the gas components before the other gases are generated from mixture during the test							
Total N_2 Moles in Head Space = In Air + Added =	0.00784	moles N_2	By mass =	0.21950	grams of N_2 in head space		
Total Moles in Head Space = Air + Added N_2 =	0.00891	moles	By mass =	0.25430	grams of gas in head space		
Molar precent of N_2 in head after pressurizing =	87.93%	879319	ppm by molarity	By mass =	86.3%	**863174**	ppm by mass
Molar precent of O_2 in head after pressurizing =	11.53%	115286	ppm by molarity	By mass =	12.9%	**129276**	ppm by mass
Molar precent of Ar in head after pressurizing =	0.51%	5120	ppm by molarity	By mass =	0.72%	**7168**	ppm by mass
Molar precent of CO_2 in head after pressurizing =	0.02%	220	ppm by molarity	By mass =	0.03%	**340**	ppm by mass
Total percentage (neglecting H20 and trace gases) =	99.99%			By mass =	100.00%		

In fact, the first GC measurements in all the test series was after 2 hours, which should be minimally affected for that short time period. Table 44 contains the average GC measurement of seven samples. The O_2 is slightly under, but then numbers are close the values they should have been immediately filling the reactor.

Table 44. GC measurement of oxygen and nitrogen in the reactor head space after 2 hours

Test	O_2, %	N_2, %
TS1	11.0	84.0

Figure 60 is a plot of the concentration measured of O_2 and N_2 from Test Series 1 that had sealed reactor durations at ~35°C from 2 to 96 hours. For convenience the O_2 results were multiplied by 10 so both O_2 and N_2 could be on the same scale. From the Ideal-gas value at 0 hours of 13% the O_2 drops to about 1% while the O_2 and N_2 increased slightly, but basically is unaffected.

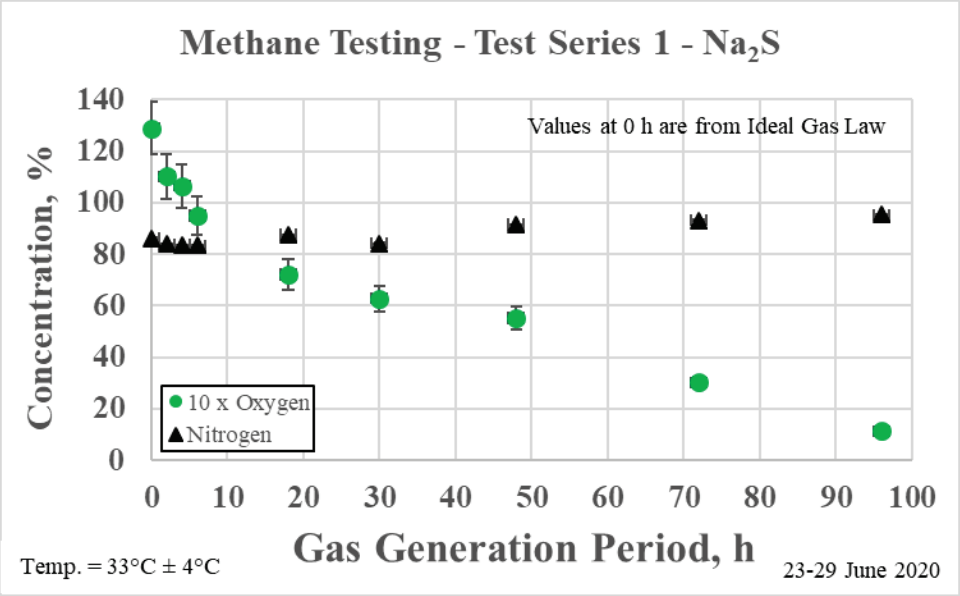


Figure 60. Change of O_2 and N_2 during Test Series 1

From the information just discussed, and once Test Series 2 was complete, it became clear that the reduction in pressures during Test Series 1 was primarily due to the oxidation of sulfide and not leaks. Figure 61 shows the pressure history of Test Series 2. That reactors in that series contained a 10/45/45 mixture of grout. While sulfide is also released with time, as it leaches from the grout slag solids, its release is more complex and slower. The pressures were much more stable for Test Series 2.

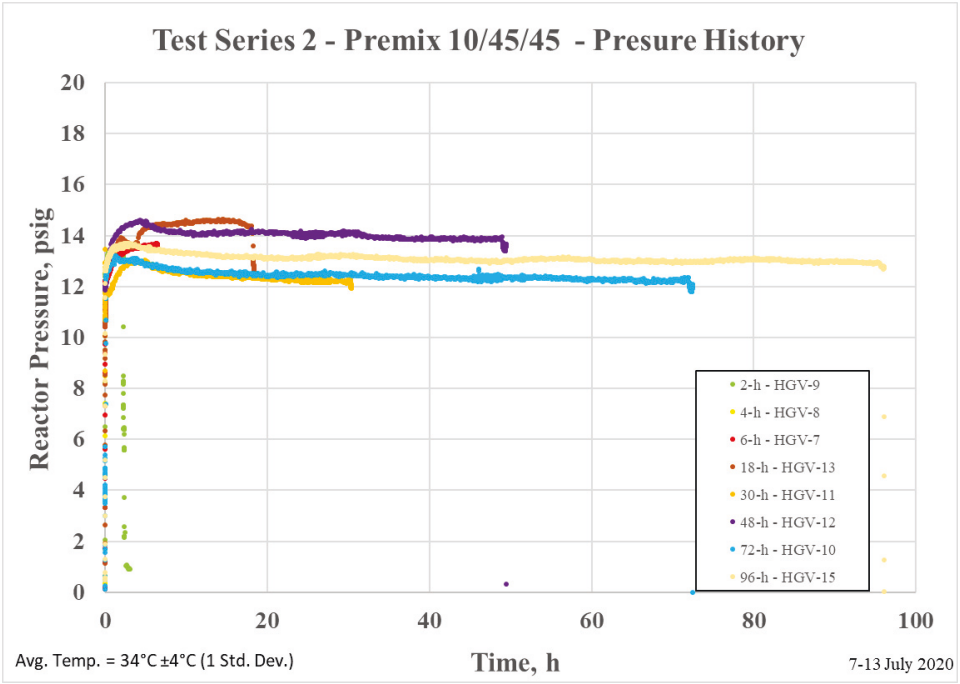


Figure 61. Change of O_2 and N_2 during Test Series 1

From Figure 62 a drop in O_2 is still seen, but the trend is not as straight forward as from Test Series 1. After 2 hours the O_2 drops to about 8% jumps to 9% then drops to about 5% and to above 7%, to finally end at close to 4%. The release of sulfide from grout is complex, which is probably why O_2 concentration

fluctuates. In any case, the effect on the head space pressure is much less pronounced and implies that the reactors were leak free.

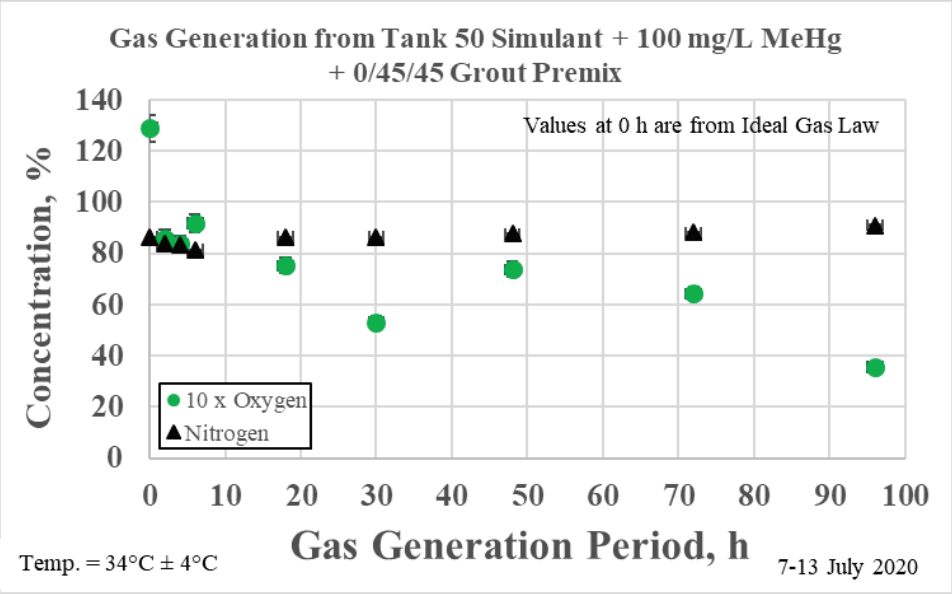


Figure 62. Change of O_2 and N_2 during Test Series 2

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