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# **Methane Generation Rates from Tank 50 Simulant with Methylmercury Containing Saltstone Grout Solids**

**M.R. Duignan**

**C.L. Crawford**

**M.L. Restivo**

**M.R. Alexander**

**K.A. Hill**

**J.M. Pareizs**

February 2020

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## REVIEWS AND APPROVALS

### AUTHORS:

M.R. Duignan, SRNL-EM&ES-CPT-SS&E	Date
C.L. Crawford, SRNL-EM&ES-CPT-SS&E	Date
M.L. Restivo, SRNL-EM&ES-CPT-SS&E	Date
M.R. Alexander, SRNL-EM&ES-EM&ES O&S-RS	Date
K.A. Hill, SRNL-EM&ES-MS&E-AMR	Date
J.M. Pareizs, SRNL-EM&ES-CPT-CFD	Date

### TECHNICAL REVIEW:

C.A. Nash, SRNL-EM&ES-CPT-SS&E	Date
--------------------------------	------

### APPROVALS:

A.D. Cozzi, Manager SRNL-EM&ES-MS&E-AMR	Date
B.J. Wiedenman, Manager SRNL-EM&ES-CPT-SS&E	Date
F.M. Pennebaker, Program Manager SRNL-EM&ES-CPT	Date
S.D. Fink, Director SRNL-EM&ES-CPT	Date
R.C. Jolly, Jr., Manager SRR DWPF Saltstone Facility Engineering	Date

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## EXECUTIVE SUMMARY

This report documents the tests performed to address the requirements listed in the Technical Assistance Request [6.1], which resulted in a Test Plan [6.2] to obtain the required information. To that end the results are documented herein to determine the capacity, and reaction time, for methylmercury (MeHg) contained within Tank 50 salt solution simulant<sup>1</sup> (T50SS) to produce methane when mixed with saltstone dry feed ingredients, as individual components (cement, slag cement<sup>2</sup>, and fly ash)<sup>3</sup> or a combination of those components.

The testing was performed in two phases at 35°C, which principally differed by the duration of gas generation. The first phase was to demonstrate methane generation in T50SS from two different concentrations of MeHg after a nominal 24-hour period. The purpose was to demonstrate the methane concentration and methane generation rate (MGR) over that period to compare to the approximate 100 ppm observed during a past test [6.3] with radioactive Tank 50 waste and at two different concentrations of MeHg, i.e., 100 mg/L and 200 mg/L. Depending on the amount of methane obtained from the first phase another, second, phase repeated a select portion of the first phase to demonstrate methane generation over a different time period. Previous testing identified the formation of methane with radioactive waste and methane measurements were performed following 28 days [6.3], during which time the formation rate could have decreased. The purpose of Phase-2 testing was to better understand the timing for the methane reaction prior to designing and conducting safety significant tests. That is, if the first phase of testing obtained a concentration of methane much less than 100 ppm, using the same 200-mL sealed reactors<sup>4</sup>, the second phase would be a much longer test, e.g., 4 days, or if the concentration was much higher, then the second phase would be much shorter, e.g., 1 hour. The principal reason for this test design was to determine if methane is primarily generated shortly after saltstone is manufactured and during its transfer to the Saltstone Disposition Facility (SDF), or does it continue to generate for some time after the grout is settling in the SDF vault. Highlights of the results follow.

- Combining MeHg with material containing sulfide, e.g., Na<sub>2</sub>S or slag, generated methane gas while MeHg disappeared. This finding indicates that sulfide in the pH=14 salt solution is causing the destruction of MeHg resulting in methane gas.
- 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.
- No methane gas was generated when MeHg was mixed solely with individual grout premix solids of cement and fly ash.
- In general, the amount of methane produced correlated directly with MeHg concentration.
- In general, the MGR was higher during the first hour of forming saltstone than at 24 hours.
- The generation of both H<sub>2</sub> and N<sub>2</sub>O were also detected but at rates of approximately an order of magnitude less than methane.
- Methane was continually generated at the 1-hour mark and at the 24-hour mark after adding T50SS to grout pre-mix solids that contain slag. When the peak rate occurs and the period of methane production are unknown.

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<sup>1</sup> See Table 3 in the final report from previous testing [6.3], which is shown as Table 5 in this document. The actual makeup of the simulant can be found in SRNL Electronic Notebook [6.4].

<sup>2</sup> 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.

<sup>3</sup> 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.

<sup>4</sup> The reactors have an actual internal volume of approximately 195 mL, and once filled, have head-space volumes that ranged from 114 mL to 120 mL.

Suggestions for future work follow.

- Quantify the methane generation rate during the life cycle of methylmercury consumption from Tank 50 waste, i.e., methane generation rates need to be measured at different periods to complement the scoping results at 1 hour and 24 hours.
- Determine if the rate of methane generation differs for mixtures of saltstone as a slurry or as a solid.
- Evaluate the effects of pH on total mercury because measurements showed that total mercury remained soluble in the pH~14 salt solution.



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## LIST OF ABBREVIATIONS

AMR	Applied Materials Research (Group)
BFS	Blast Furnace Slag
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-AFS	Gas Chromatograph Atomic Fluorescence Spectrometer
HGR	Hydrogen Gas Rate
MGR	Methane Gas Rate
MeHg	Methylmercury
MS&E	Materials Science & Engineering (Section)
N	Number of Samples
N/A	Not Applicable
ND	Not Detected
ppm	Parts Per Million
RS	Research Support (Group)
SDF	Saltstone Disposal Facility
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SS&E	Separation Sciences & Engineering (Group)
TOC	Total Organic Carbon
XRD	X-Ray Diffraction

## 1.0 Introduction

Results are documented herein to determine the capacity for methylmercury (MeHg) contained within Tank 50 salt solution simulant<sup>5</sup> (T50SS) to produce methane when mixed with saltstone dry feed ingredients, i.e., individual components (cement, slag cement<sup>6</sup>, and fly ash)<sup>7</sup> or a combination of those components.

The testing was performed in two phases at 35°C, which principally differed by the duration of gas generation. The first phase was to demonstrate methane generation in T50SS from two different concentrations of MeHg after a 24-hour period. The purpose was to demonstrate the methane concentration and methane generation rate (MGR) over that period to compare to the approximate 100 ppm observed during a past test [6.3] with radioactive Tank 50 waste and at two different concentrations of MeHg, i.e., 100 mg/L and 200 mg/L. Depending on the amount of methane obtained from the first phase of testing another, second, phase repeated a select portion of the first phase to demonstrate methane generation over a different time period. That is, if the first phase obtained a concentration of methane much less than 100 ppm, using the same 200-mL sealed reactors<sup>8</sup>, the second phase would be a much longer test, e.g., 4 days, or if the concentration was much higher, then the second phase would be much shorter, e.g., 1 hour. The principal reason for this test design was to determine if methane is primarily generated shortly after saltstone is manufactured and during its transfer to the Saltstone Disposition Facility (SDF), or does it continue to generate for some time after the grout is settling in the SDF vault.

## 2.0 Experimental Setup

### 2.1 Test Matrix

Detailed results are documented herein to determine the capacity for methylmercury contained within Tank 50 waste to produce methane. Phase 1 testing evaluated the release of methane due to methylmercury in the salt solution at the end of a 1-day period. T50SS without MeHg was used as a control sample and T50SS spiked with 100 and 200 mg/L of methylmercury and then mixed with dry grout premix ingredients to create mixtures to measure methane, hydrogen, and other gas concentrations at near room temperature (35°C). This temperature was chosen to be close to room temperature but slightly above to avoid fluctuations due to normal hourly changes. Another control sample of T50SS + MeHg + Na<sub>2</sub>S was included to determine the theoretical reaction kinetics of mercury immobilization to demonstrate an upper limit of methane production. Table 1 and Table 2 list the Phase 1 test matrix using 9 sealed reactors simultaneously.

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<sup>5</sup> Shown as Table 4.

<sup>6</sup> 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.

<sup>7</sup> The following convention of mass ratios will be followed: Cement/slag/Fly Ash, e.g., 10/45/45 or 0/60/40.

<sup>8</sup> The actual internal volume is approximately 195 mL. Once filled the reactors' head-space volumes ranged from 114 to 120 mL.

**Table 1. Phase 1, Test Series 1: One-day test matrix for 100 mg/L methylmercury at 35°C**

Test Number	Reactor Number	Slag (1) g/L (2)	Fly Ash g/L (2)	Cement g/L (2)	N <sub>2</sub> S g/L	Sulfur M (3)	MeHg (4) mg/L	MeHg M (3)	Hg M (3)	S/Hg molar ratio (3)	Comments
1	HGV-7	0	0	0	0	0	0	0	0	0	Control for no mercury
2	HGV-8	0	0	0	12	1.54E-01	100	4.64E-04	4.64E-04	332	N <sub>2</sub> S will be used as a control to determine the theoretic reaction kinetics of mercury immobilization
3	HGV-9	466	466	104	0	1.45E-01	100	4.64E-04	4.64E-04	313	10/45/45 (2QCY2019): 0.85 water to grout premix mass ratio
4	HGV-10	621	414	0	0	1.94E-01	100	4.64E-04	4.64E-04	418	0/60/40 (2QCY2019): 0.85 water to grout premix mass ratio
5	HGV-11	268	0	0	0	8.36E-02	100	4.64E-04	4.64E-04	180	Slag from batch 2QCY2019
6	HGV-12	268	0	0	0	8.36E-02	100	4.64E-04	4.64E-04	180	Slag from batch 4QCY2016
7	HGV-13	0	268	0	0	0	100	4.64E-04	4.64E-04	0	Fly Ash from batch 2QCY2019
8	HGV-14	0	268	0	0	0	100	4.64E-04	4.64E-04	0	Fly Ash from batch 4QCY2016
9	HGV-15	0	0	52.8	0	0	100	4.64E-04	4.64E-04	0	Cement from batch 2QCY2019
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. For the individual premix component testing, the mass of each component in reactors, HGV-11, -12, -13, -14, and -15 matched the corresponding mass in the 10/45/45 mixture. To maintain the volume of the head space constant for all reactors the simulant volume was increased, resulting in lower concentrations than in the 10/45/45 mixture. (3) Reactor HGV-8 contained sodium sulfide. For Reactors HGV-9, -10, -11, and -12, the sulfur is contained in the slag, which was measured to be approximately 1 wt% [Appendix D]. Slag contains approximately 2 wt% of gypsum that contains sulfate, which is a non-reduced form of sulfur. However, the majority of the sulfur in slag is in reduced forms of sulfide and other sulfur species. For this work all of the sulfur in slag was assumed to be sulfide. MW: 200.59 (Hg), 215.62 (MeHg), 78.05 (Na <sub>2</sub> S), 32.07 (S) (4) MeHg = Methylmercury (CH <sub>3</sub> Hg <sup>+</sup> )											

Each reactor contained T50SS spiked with methylmercury, except the control reactor, and material listed below.

- Single solids, e.g. Cement, Slag, and Fly Ash
- Mixtures of 10%, 45%, 45%; and 0%, 60%, 40% by weight (in the order of Cement, Slag, Fly Ash, respectively)
- T50SS blank (A control without methylmercury – baseline methane (should be zero))
- Na<sub>2</sub>S (A control to determine the theoretical reaction kinetics of mercury immobilization)

The results from each mixture in Table 1 and Table 2 will be discussed, 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 different grout pre-mix batches indicated in those two tables are listed in Table 3. Batch 2QCY2019 is what is currently being used by SDF and Batch 4QCY2016 is from previous testing [6.3].

**Table 2. Phase 1, Test Series 2: One-day test matrix for 200 mg/L methylmercury at 35°C**

Test Number	Reactor Number	Slag (1) g/L (2)	Fly Ash g/L (2)	Cement g/L (2)	N <sub>2</sub> S g/L	Sulfur M (3)	MeHg (4) mg/L	MeHg M (3)	Hg M (3)	S/Hg molar ratio (3)	Comments
1	HGV-7	0	0	0	0	0	0	0	0	0	Control for no mercury
2	HGV-8	0	0	0	12	1.54E-01	200	9.28E-04	9.28E-04	166	N <sub>2</sub> S will be used as a control to determine the theoretic reaction
3	HGV-9	466	466	104	0	1.45E-01	200	9.28E-04	9.28E-04	157	10/45/45 (2QCY2019): 0.85 water to grout premix mass ratio
4	HGV-10	621	414	0	0	1.94E-01	200	9.28E-04	9.28E-04	209	0/60/40 (2QCY2019): 0.85 water to grout premix ratio
5	HGV-11	268	0	0	0	8.36E-02	200	9.28E-04	9.28E-04	90	Slag from batch 2QCY2019
6	HGV-12	268	0	0	0	8.36E-02	200	9.28E-04	9.28E-04	90	Slag from batch 4QCY2016
7	HGV-13	0	268	0	0	0	200	9.28E-04	9.28E-04	0	Fly Ash from batch 2QCY2019
8	HGV-14	0	268	0	0	0	200	9.28E-04	9.28E-04	0	Fly Ash from batch 4QCY2016
9	HGV-15	0	0	52.8	0	0	200	9.28E-04	9.28E-04	0	Cement from batch 2QCY2019

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. For the individual premix component testing, the mass of each component in reactors, HGV-11, -12, -13, -14, and -15 matched the corresponding mass in the 10/45/45 mixture. To maintain the volume of the head space constant for all reactors the simulant volume was increased, resulting in lower concentrations than in the 10/45/45 mixture.

(3) Reactor HGV-8 contained sodium sulfide. For Reactors HGV-9, -10, -11, and -12, the sulfur is contained in the slag, which was measured to be approximately 1 wt% [Appendix D]. Slag contains approximately 2 wt% of gypsum that contains sulfate, which is a non-reduced form of sulfur. However, the majority of the sulfur in slag is in reduced forms of sulfide and other sulfur species. For this work all of the sulfur in slag was assumed to be sulfide. MW: 200.59 (Hg), 215.62 (MeHg), 78.05 (Na<sub>2</sub>S), 32.07 (S)

(4) MeHg = Methylmercury (CH<sub>3</sub>Hg<sup>+</sup>)

**Table 3. Grout Pre-mix Batches**

Grout Pre-Mix	Manufacturer	Batch	Date Obtained	P.O. Number
Batch = AAA				
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
Batch = BBB				
Cement	Holcim	4QCY16	17-May-16	SRRA078919R-1
Slag	Lehigh	4QCY16	17-May-16	SRRA078187-1
Fly Ash	SEFA	4QCY16	17-May-16	SRRA075819-1

## 2.2 Tank 50 Simulant

The T50SS makeup, shown in Table 4, was similar to that made for past tests [6.3]. This T50SS was the base material to spike with methylmercury, and then with grout premix solids to demonstrate the potential to generate methane.

**Table 4. Simulant of Tank 50 waste**

<b>Tank 50 Waste (1) &amp; Simulant Used</b>			
Component	Mol. Wt.	Actual	Simulant
Name	g/mol	M (2)	M (2, 3)
Total Sodium	22.99	5.77 ±0.5%	5.21 ±4.2%
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	1.2368	1.218
(1) Waste sample of 2nd Quarter Calendar Year 2018			
(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.			

### 2.3 Methylmercury

To the T50SS was added enough MeHg, molecular weight of 215.62 g/mole, to have concentrations of 100 mg/L and 200 mg/L. The available source is MeHg used was 1 M methylmercury (II) hydroxide dissolved in H<sub>2</sub>O, with a molecular weight of 232.62 g/mole. The amounts needed per liter are shown in Table 5. Several spike batches of each concentration were made as needed, which were then mixed with the material to be tested in each reactor.

**Table 5. Concentrations of MeHg**

Supply of Methylmercury Hydroxide (1 M)		
MW =	232.62	g/gmole (CH <sub>3</sub> HgOH)
MW =	215.62	g/gmole (CH <sub>3</sub> Hg <sup>+</sup> )
Water % =	76.60	wt%
CH <sub>3</sub> HgOH =	23.30	wt%
Density =	1.20	g/mL
need		
100	ppm (mg/L) of CH <sub>3</sub> Hg <sup>+</sup>	
0.0004638	M of 1 M CH <sub>3</sub> HgOH in H <sub>2</sub> O	
0.4638	mL from the 1 M stock	
0.557	grams per liter of Tank 50 SS	
need		
200	ppm (mg/L) of CH <sub>3</sub> Hg <sup>+</sup>	
0.0009276	M of 1 M CH <sub>3</sub> HgOH in H <sub>2</sub> O	
0.9276	mL from the 1 M stock	
1.113	grams per liter of T50SS	



Due to concern over stability of mercury species, the method of handling and storing was important [6.5]. After gas sampling the reactors in a test series, the liquid samples to be analyzed for MeHg were pulled as soon as possible from each reactor, filtered in a 0.45-micron disposable vacuum filtration device, and then placed in 5-mL Teflon bottles with little, to no, head space. Those samples were then refrigerated to 4°C, or lower, while waiting to be transported for analyses. When in transit, or waiting to be analyzed, the samples were maintained cold.

## 2.4 Reactors Used as Controls

The mixtures in each of the reactor were to demonstrate unknown methane generation rates. To clearly understand the results two reactors were used as controls.

- One reactor contained T50SS with no methylmercury based on the T50SS makeup shown in Table 4. It should not produce any methane as was demonstrated in previous simulant tests that contained T50SS with glycolate [6.3].
- One reactor contained T50SS with methylmercury and spiked with enough sodium sulfide to have more moles of sulfide than mercury. This reaction was to demonstrate the fastest reaction of all the reactors based on the assumption that the sources of sulfur in the grout premix solids would either need to dissolve or that a mass transfer restriction would exist in transporting the mercury species to the solid interface.

Na<sub>2</sub>S 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 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 and 0.001 M shown in Table 1 and Table 2, respectively.

## 2.5 Mercury Needed

Tank 50 waste is the salt solution source, but it is the mercury contained in that waste which is of concern. Table 6 shows what exists and what was the mercury target.

**Table 6. 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	0.00041129
MeHg in Tank 50 Waste (1)	37.6	mg/L	CH <sub>3</sub> Hg <sup>+</sup>	215.62	0.00017438
MeHg to use	100	mg/L	Hg	200.59	0.00049853
MeHg to use	200	mg/L	Hg	200.59	0.00099706
(1) The values were taken from [6.6]. 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 the last 5 years.					

Being conservative, the amount of mercury used was larger than what exists in the Tank 50 waste. It was also important to know the amount of sulfide expected in the grout premix materials, specifically slag. Table 7 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. For this T50SS test the assumption was that  $\text{Hg} + \text{S} \Rightarrow \text{HgS}$  is the sole reaction which is expected to differ from radioactive waste where sulfide can react with other compounds like chromium.

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. Several of the grout premix solids were tested individually to demonstrate the potential of generating methane, but two reactors contained the combination of grout premix materials as they are, or will be, used to prepare grout in Saltstone. These two tests were included to demonstrate how the production of methane is affected by the variances in grout composition. An initial part of the testing was to determine a water-to-grout mass ratio that would not completely solidify. To avoid this problem several dilute mixtures were made until the grout mixture would remain liquid with mixing. 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 mixture > 0.80 water-to-grout premix mass ratios the grout remained in a liquid state for at least 24 hours, which is the duration of the first set of tests.

**Table 7. Sulfur in Slag (1)**

S in Slag (2) wt%	Slag g slag/L	Sulfur g/L	Sulfur (3) M	S/Hg (4) ratio	S/Hg (5) ratio
1	200	2	0.062373	125	63
1	100	1	0.031187	63	31
1	50	0.5	0.015593	31	16
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 (3) MW = 32.065 (4) Ratio if 100% of sulfide is active, based on 0.0005 M Hg (5) Ratio if 50 % of sulfide is active, based on 0.0005 M Hg					

Table 8 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 numbers of the small batches tested were increased so that they displayed on a 1-Liter basis to be consistent. Because of the 200 mL size of the sealed reactors, the actual amounts used in each sealed reactor were much smaller and differ slightly for each reactor. These results also allow one to determine the solids that were used for all the tests with individual components as the masses were kept the same as for 10/45/45 mixture. For example, the mass of slag for an individual test used the mass of slag in the 10/45/45 test.

**Table 8. Grout Premix**

Material	Premix (1) 10/45/45		Premix (1) 0/60/40		Unit
T50SS Density	1.218		1.218		g/mL
T50SS Volume	1000		1000		mL
T50SS Mass	1218		1218		g
T50SS Solids	27.5		27.5		wt%
T50SS Solids	335.0		335.0		g
T50SS Water	883.1		883.1		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	2253.3		2253.3		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.					

## 2.6 Measurement Uncertainties

Besides the analytical measurements made on liquid samples, e.g., MeHg and total mercury, the principal measurements were gas concentrations, temperature, pressure, reactor head space volume, masses added, and time. This task was performed as scoping work; therefore, no explicit effort was made to calibrate experimental equipment or perform uncertainty analyses. However, all the experimental equipment was calibrated for previous work [6.3] for which measurement uncertainties were determined. The following uncertainties are assumed to apply.

### 2.6.1 *Gas Concentrations*

The gas chromatographs available have accuracies to measure CH<sub>4</sub> and H<sub>2</sub> to better than 10 ppm. However, results showed concentrations well above 100 ppm. Shortly before each sealed reactor test a calibration methane gas was used to determine the measurement uncertainties of methane 10 %RSD, for a confidence level of 95%. While considered accurate, the measurement uncertainties for N<sub>2</sub>O and CO<sub>2</sub> were not evaluated.

### 2.6.2 MGR and HGR Calculations

The uncertainty of the calculations of MGR and HGR, which depend on temperature, pressure, mass and volumes measured, were in a past test [6.3] determined to be  $\pm 10$  %RSD, for a confidence level of 95%; therefore, the same uncertainty is assumed to apply to this work.

### 2.6.3 Analytical Measurements

The standard measurement uncertainty for analytical measurements is  $\pm 20$  %RSD, at a confidence level of 95%.

## 2.7 Gas and Liquid Measurements

Besides methane, the gas headspace in each reactor was measured for hydrogen, carbon dioxide, and nitrous oxide. After the gas was sampled the slurry in each reactor was removed and filtered through a 0.45-micron disposable vacuum filtration device to obtain two liquid samples. One sample was dedicated to measure total mercury and MeHg, which was collected in a Teflon sample vial with prompt refrigeration. Total mercury was measured using a Direct Mercury Analyzer (DMA) instrument and MeHg was analyzed via a Gas Chromatograph Atomic Fluorescence Spectrometer (GC-AFS) instrument. The second sample was stored and may be used for other measurements to be determined.

## 2.8 Subsequent Test

The results of the methane evolution from the 1-day tests demonstrated methane concentrations well above the concentrations measured from past grout testing [6.1] of  $\sim 100$  ppm, which was seen from radioactive Tank 50 waste after 28 days. Based on the results in Phase 1, Test Series 1 & 2, a second phase was done to repeat Test Series 1 of Phase 1, but for a 1-hour period to determine if most of the methane is released during that first hour.

## 2.9 Sealed Reactor Equipment

The primary equipment for this testing includes nine (9) sealed stainless-steel reactors having nickel flange seals. The materials of construction were found to not interfere with previous hydrogen generation rate measurements down to  $10^{-9}$  (ft<sup>3</sup>/h) / gal [6.7] in testing with T50SS, samples, and various additives. 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 not 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 do 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 while sealing remained contained and mix with the nitrogen and generated gases. As for taking samples, the test material was only to be in contact with a Teflon cup, which was inserted into the sealed reactors to hold the T50SS and other test materials.

Figure 1 shows a schematic of a sealed reactor and Figure 2 shows the reactors in place after receiving the appropriate test mixture and sealed. HGV-7 is shown being pressurized with nitrogen. After all 9 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.

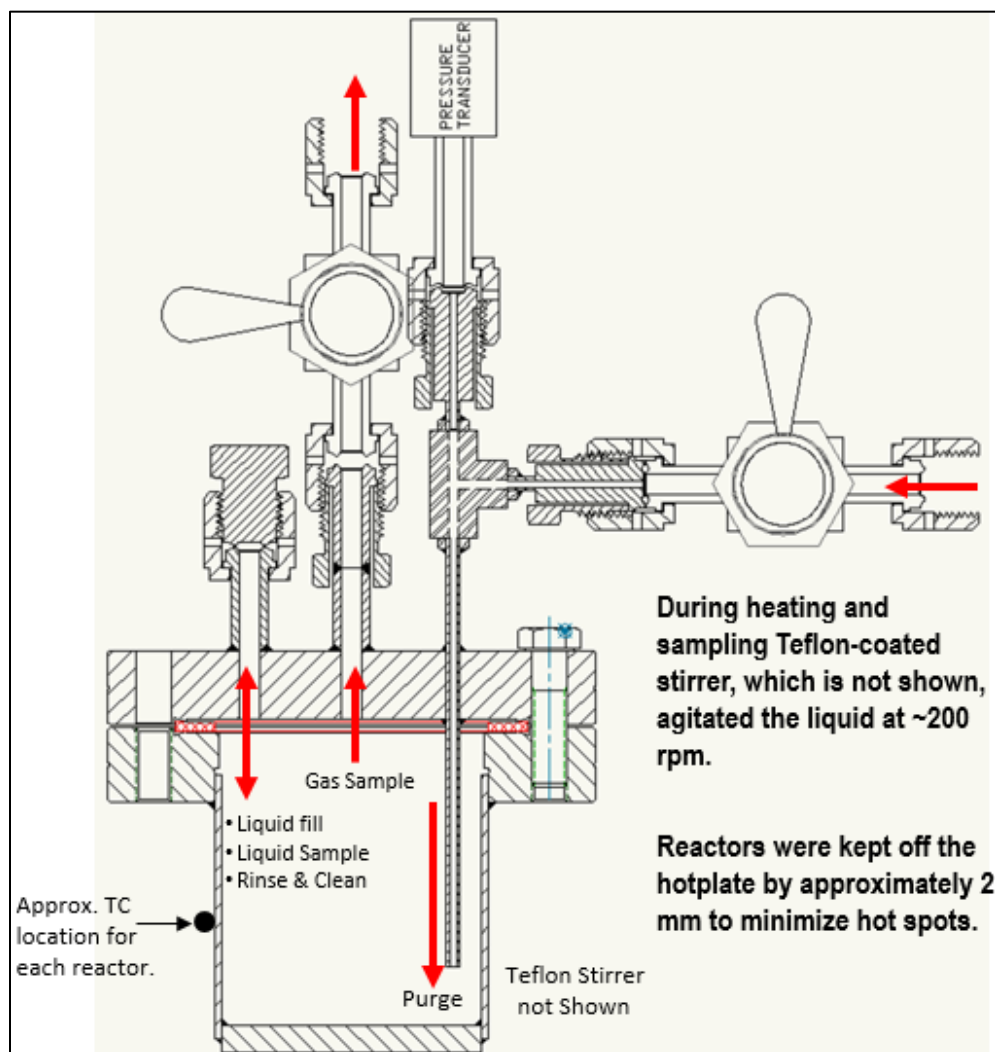
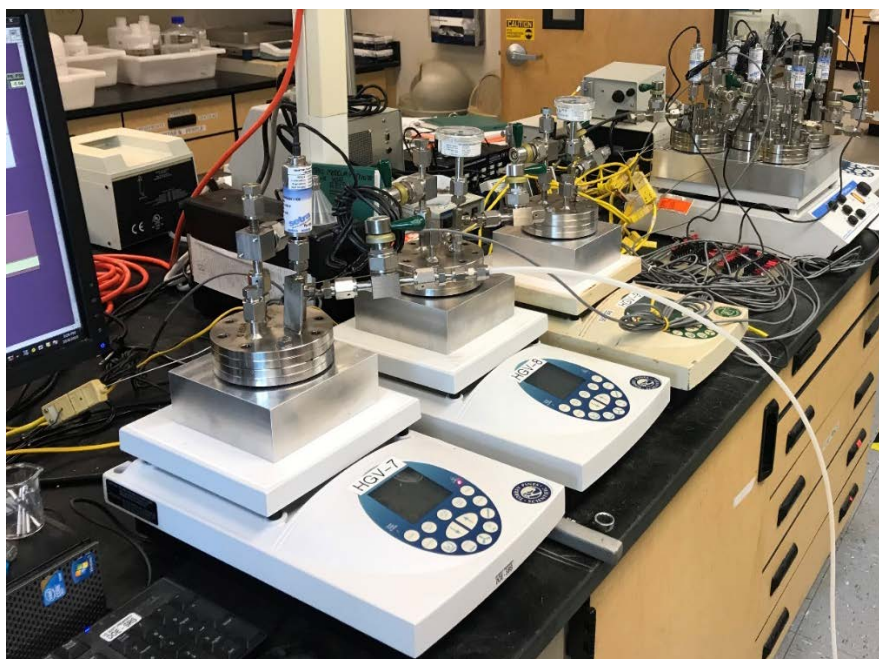


Figure 1. Sealed Reactor without Teflon Cup Insert



**Figure 2. Test setup with nine sealed reactors on mixing/heating plates**

The exact internal volume of each reactor is listed in Table 9 along with the volume of the mixture included and the resulting head space remaining.

**Table 9. Sealed reactor fill volumes and headspaces**

<b>Sealed Reactor Head Volume</b>					
<b>HGV</b>	<b>Reactor Vol.</b>	<b>Teflon</b>	<b>Insert Vol.</b>	<b>Mixture</b>	<b>Headspace</b>
<b>No.</b>	<b>mL (1)</b>	<b>Insert (2)</b>	<b>mL (3)</b>	<b>mL (4)</b>	<b>mL</b>
<b>7</b>	192.01	A	22.219	55.63	<b>114.16</b>
<b>8</b>	194.96	B	21.131	55.63	<b>118.20</b>
<b>9</b>	194.44	C	21.459	55.63	<b>117.35</b>
<b>10</b>	194.37	D	21.486	55.63	<b>117.25</b>
<b>11</b>	193.29	E	21.839	55.63	<b>115.82</b>
<b>12</b>	193.09	F	21.664	55.63	<b>115.79</b>
<b>13</b>	196.64	G	21.262	55.63	<b>119.75</b>
<b>14</b>	195.02	H	21.654	55.63	<b>117.74</b>
<b>15</b>	193.94	I	21.861	55.63	<b>116.45</b>

(1) Measured at 22.4°C.

(2) The alphabetical order entered of the inserts was arbitrary.

(3) Based on a measurement of mass and a standard room temperature density of 2.200 g/mL.

(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 55.63 mL. This volume includes the 2.715 mL volume of the stir bar.

## 2.10 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.
2. Fill Teflon inserts for the sealed reactors with dry mixtures of grout solids. The exceptions are the baseline reactors, i.e., HGV-7 that only contains control T50SS, and HGV-8 that contains T50SS with both MeHg and Na<sub>2</sub>S.
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, or 200 mg/L, of methylmercury. A small portion is not spiked to fill the baseline sealed reactor, HGV-7.
5. Fill reactor HGV-7 with the required amount of baseline T50SS and completely seal reactor. As this, and each of the other reactors, are slowly filled, the mixing agitator is turned on to approximately 200 rpm to mix the contents and prevent them from solidifying.
6. Repeat Step 5 for reactors HGV-9 through -15 using spiked T50SS.
7. The last reactor HGV-8 is handled slightly differently because Na<sub>2</sub>S is strongly hygroscopic and its exposure to the atmosphere needs to be minimized. The needed amount of chemical is removed from refrigeration and placed in the Teflon insert, then the reactor is partially sealed and T50SS is immediately introduced, after which the reactor is fully sealed.
8. After all reactors are sealed and mixing, they are pressurized with pure nitrogen to approximately 10 psig<sup>9</sup>, after which all valves are tightly closed, and valve stems are sealed.
9. All reactors are insulated and held at 35°C for 24 hours. (The duration will be discussed later, but it begins as soon as T50SS is added to a reactor and sealed and ends at the start of the first GC measurement.)
10. On the following day, the gas is sampled in each reactor, principally for methane, but also for hydrogen, carbon dioxide, and nitrous oxide.
11. After gas sampling all reactors, then each reactor is vented in the fume hood and then opened to sample the liquor from each reactor to measure MeHg and total mercury. (The liquor is filtered through a 0.45-micron filter, stored in Teflon bottles, and refrigerated while waiting to be analyzed.)

Phase 2 was very similar to Phase 1 except that the test period was reduced to 1 hour; therefore, there were slight differences to accommodate the coordination of all needed steps in the much shorter time period.

## 2.11 Quality Assurance

The customer requirements for this study identified the work as a scoping activity. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

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<sup>9</sup> An exact pressure value was not needed. It only had to be under the GC limit of 20 psig and it had to be known in order to calculate gas generation rates.

### 3.0 Results and Discussion

All the experimental data are shown and discussed in detail for each of the three test series in the appendices, including measurements of H<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub>. In this section, the gas of principal interest, methane, its production and generation-rate, are discussed along with the MeHg and total Hg remaining in the mixtures after each test series. The results are summarized in Table 10.

**Table 10. Methane Results at 35°C**

Test Name (1)	Test Duration (2)	Spike Concentration of MeHg	Results of Listed Grout Pre-mix and Batches				
			Control Na <sub>2</sub> S	10/45/45 (2QCY19)	0/60/40 (2QCY19)	0/100/0 (2QCY19)	0/100/0 (4QCY16)
			Gas Concentration				
	h	mg/L	ppm	ppm	ppm	ppm	ppm
Ph1-TS1	27.3	102.5	2574	990	442	1265	1047
Ph1-TS2	26.8	199.3	5391	2106	517	1426	2224
Ph2-TS1	1.0	101.8	945 (3)	0	142	232	258
			CH <sub>4</sub> Generaton Rate				
	h	mg/L	(ft <sup>3</sup> /h) / gal	(ft <sup>3</sup> /h) / gal	(ft <sup>3</sup> /h) / gal	(ft <sup>3</sup> /h) / gal	(ft <sup>3</sup> /h) / gal
Ph1-TS1	27.3	102.5	5.25E-05	3.66E-05	1.97E-05	2.63E-05	2.20E-05
Ph1-TS2	26.8	199.3	1.13E-04	7.98E-05	1.97E-05	3.01E-05	4.73E-05
Ph2-TS1	1.0	101.8	5.30E-04	0	1.53E-04	1.29E-04	1.51E-04
			Moles CH <sub>4</sub> Generated Versus Moles MM Available				
	h	mg/L	%	%	%	%	%
Ph1-TS1	27.3	102.5	87	65	35	47	39
Ph1-TS2	26.8	199.3	92	69	20	27	42
Ph2-TS1	1.0	101.8	17 (3)	0	5	4	5
			MeHg Remaining in Mixtures				
	h	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Ph1-TS1	27.3	102.5	1.0	0.6	N/A (4)	< 0.1	< 0.1
Ph1-TS2	26.8	199.3	2.1	1.5	N/A (5)	0.9	1.2
Ph2-TS1	1.0	101.8	0.29 (3)	73.0	38.6	24.6	21.5
			Total Mercury Remaining in Mixtures				
	h	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Ph1-TS1	27.3	102.5	102	113	N/A (4)	104	101
Ph1-TS2	26.8	199.3	231	228	209	197	208
Ph2-TS1	1.0	101.8	103	102	104	103	104

- (1) Ph = Phase, TS = Test Series
- (2) Each reactor had a slightly different duration. The times listed are an average of all reactors in a test series.
- (3) The Na<sub>2</sub>S + MeHg remained a liquid; therefore, there were no solids to filter. For this 1-hour test the measure of methane gas (945 ppm) is consider representative of what was generated, but the concentration of MeHg in the liquid mixture (0.29 mg/L), while accurate, is not considered representative. The liquid sample was pulled at the time the gas was measured, but then it was refrigerated and transported for analysis, which takes several days. During the period the sample awaited analyzation the reaction between MeHg and sulfide should continue, resulting in almost total destruction of MeHg.
- (4) N/A = Not Available. This mixture solidified thus had no liquid to analyze.
- (5) Not enough liquid available to measure MeHg.



Furthermore, since some of the mixtures that did not contain sulfide, i.e., cement only (100/0/0), fly-ash only (0/0/100), and the control reactor of T50SS without MeHg, did not produce methane, they are not included in Table 10. Also note that the gas generation durations for the “24-hour” tests are averages of all the reactors in a test series, but the exact duration for each reactor was used when calculating MGR.

### 3.1 Effect of Concentration: 100 mg/L versus 200 mg/L of MeHg at 35°C

The first test phase had a gas generation duration of 24 hours with the concentrations of MeHg for Test Series 1 at 100 mg/L and at 200 mg/L for Test Series 2. The rows entitled Ph1-TS1 and Ph1-TS2 in Table 10 show those data. Note, from the measured volume of T50SS used and measured mass of MeHg used to spike the salt solution, the calculated MeHg concentrations for these two test series were 102.5 mg/L and 199.3 mg/L, respectively.

From the baseline mixtures of T50SS spiked with MeHg and with 12 mg/L of Na<sub>2</sub>S, but that had no grout pre-mix solids, the largest amount of methane production was expected. The production and the methane generation rate (MGR) was indeed the largest, and by doubling the MeHg concentration the production of methane doubled. For the two reactors containing the Na<sub>2</sub>S, the measured methane increased from 2574 ppm to 5391 ppm that had been spiked with 100 mg/L and 200 mg/L, respectively. For all the other reactors, i.e., those which did not contain Na<sub>2</sub>S but did contain grout pre-mix solids, the methane production was less, but still significant. Furthermore, from all of the reactors containing grout premix solids that contained the larger concentration of 200 mg/L of MeHg, the methane production was larger than for all the reactors with 100 mg/L of MeHg. As for the reactors with Na<sub>2</sub>S, a doubling of the MeHg concentration led to an increase to both the methane production and generation rates. However, only three reactors, of five, showed that the methane production doubled. Lastly, when comparing the two different batches of slag, i.e., 0/100/0 (2QCY19) to 0/100/0 (4QCY16), the results are different; however, it is not known if this difference is important.

Another way to look at the data is to compare the moles of methane generated to the moles of MeHg that were available to generate methane. The soluble Na<sub>2</sub>S resulted in almost total conversion to methane. That is, the methane moles produced amounted to 87% of the moles of MeHg available at 100 mg/L and 92% at 200 mg/L. It is not known that if the test duration were longer if the percentages would have continued to increase, but most of the conversion of MeHg to methane was significant. All of the mixtures containing concentrations of grout pre-mix solids, which contained slag, produced fewer moles of methane for the available moles of MeHg, but the number moles produced was significant and ranged from 20% to 65% of the theoretical total. Interestingly, the grout mixture of the 10/45/45 produced 2 to 3 times more methane than from the 0/60/40 mixture, even though the latter mixture contained approximately 33% more slag by mass than the former. The presence of cement in the former mixture may play a role in allowing the production of methane.

Also shown in Table 10 are the results of mercury in the reactor mixtures of T50SS. Measurable total mercury was basically not affected by solids in any of the mixtures spiked with either 100 mg/L or 200 mg/L of MeHg. After 24 hours, for all the reactors spiked with 100 mg/L the average measurement was 106.7 mg/L total Hg, with a single standard deviation fluctuation of 4.4 mg/L. Similar results were obtained at the end of the 1 hour test, which also used 100 mg/L. The average measurement was 103.0 mg/L total Hg, with a single standard deviation fluctuation of 0.8 mg/L. After 24 hours for all the reactors spiked with 200 mg/L the average measurement was 212.0 mg/L total Hg, with a single standard deviation fluctuation of 12.2 mg/L. It appears the mercury in some form remained soluble in the caustic mixtures. One study [6.9] indicates that mercury with sulfide remains soluble in a high-pH environment. The 11<sup>th</sup> columns of Table 1 and Table 2 show there were more moles of sulfide available than either Hg or MeHg.

Contrary to total Hg, the amount of MeHg was affected. For mixtures containing slag, that is, those that produced methane, most of the MeHg was consumed after 24 hours. In the mixtures spiked with 100 mg/L

of MeHg only 0.6 mg/L of MeHg or less remained. In mixtures spiked with 200 mg/L of MeHg only 1.5 mg/L of MeHg or less remained. Not shown in Table 10, but discussed in the appendices, for mixtures that did not contain slag, that is, those that did not produce methane, most of the MeHg was not consumed. In the mixtures spiked with 100 mg/L of MeHg, an average of 86.8 mg/L of MeHg remained, with a single standard deviation of 5.3 mg/L. In mixtures spiked with 200 mg/L of MeHg, an average of 165.0 mg/L of MeHg remained, with a single standard deviation of 7.1 mg/L. Finally, for the 1 hour test it appears the shorter gas generation period did not allow most of the MeHg to be destroyed. Of the original 100 mg/L of MeHg the remaining concentrations ranged from 21.5 mg/L to 73.0 mg/L. The MeHg in the Na<sub>2</sub>S was totally destroyed, so it appears mechanisms to leach sulfide in the salt solution to produce methane needs more than 60 minutes to complete the process.

### 3.2 Effect of Time: Comparing 1 hour to 24 hours of gas generation at 35°C

Based on the large amount of methane generated during the 24-hour tests, i.e., Phase 1, Test Series 1 and Test Series 2, a second phase test, i.e., Phase 2, Test Series 1, was performed for a much shorter period of 1 hour. Furthermore, Phase 2 was chosen to be performed at the lower of the two MeHg concentrations used for the Phase 1 tests, i.e., 100 mg/L, which is closer to the actual Tank 50 waste concentration of approximately 30 mg/L of MeHg [6.10]. For a concentration of 100-mg/L of MeHg, the rows entitled Ph1-TS1 and Ph2-TS1 in Table 10 contain the results at 1 hour and 24 hours. The effect of time is illustrated in Figure 3, Figure 4, and Figure 5. Note, from the measured volume of T50SS used and measured mass of MeHg used to spike the salt solution, the calculated MeHg concentrations for these two test series were 102.5 mg/L and 101.8 mg/L, respectively.

An unknown factor was if most, or all, of the generated methane that was measured after 24 hours would generate during the first hour. Figure 3 clearly shows that only a small fraction of the methane generated at 24 hours is generated after 60 minutes, but as will be seen in Figure 5, the generation rate of methane at 1 hour is significantly larger than at 24 hours.

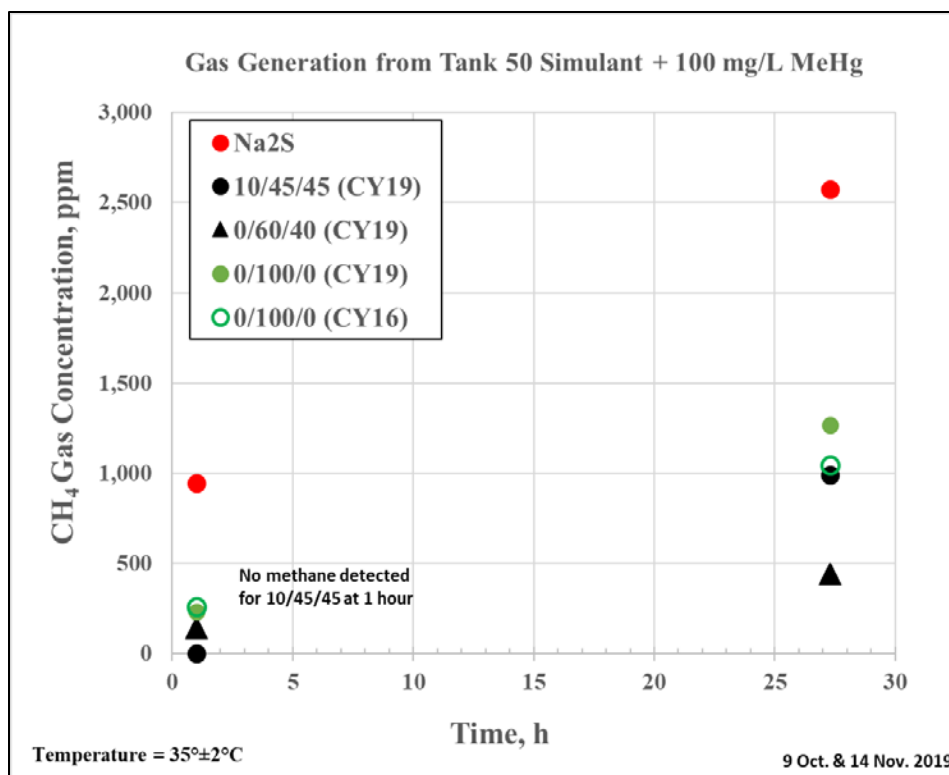


Figure 3. Methane concentrations from T50SS with 100 mg/L MeHg

Based on the available moles of MeHg in each of the reactors, Figure 4 depicts the percentage of moles of methane generated was considerably lower at the 1-hour mark. Even for the mixture with Na<sub>2</sub>S that had no grout premix solids, which was expected to be the fastest reaction of MeHg with sulfide, the almost 90% conversion evidenced at 24 hours was less than 20% at 1 hour. Unfortunately, with only two time periods, the lifecycle of methane generation is unknown. Also seen, is that the 0/60/40 grout premix combination only generated enough methane to equal 5% of the available moles of MeHg. The 10/45/45 mixture did not show any methane, so it appears that the reaction between MeHg and sulfide in the grout solids in the salt solution needs at least 1 hour to form methane. A more extensive test to evaluate methane generation in time is needed to better understand methane's lifecycle.

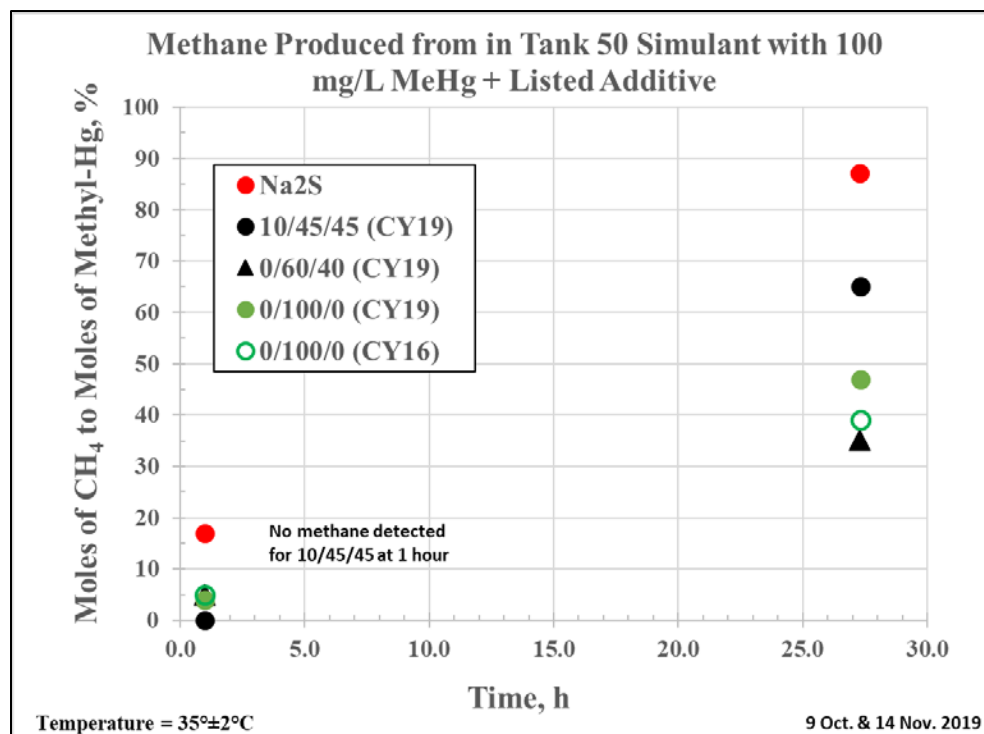


Figure 4. Mass percentage of methane produced relative to MeHg available

Figure 5 shows the methane generation rate measured at the two times. While Figure 3 showed that a smaller amount of methane was generated after 1 hour than after 24 hours, the rate of generation after 24 hour dropped by almost an order of magnitude. In fact, from a past test [6.3] using radioactive Tank 50 waste, mixed the grout premix solids, the MGR after 28 days just above  $1 \times 10^{-7}$  (ft<sup>3</sup>/h) / gallon of salt solution, which is less than two orders of magnitude from the 24-hour MGR. However, the radioactive waste was not spiked with 100 mg/L of MeHg because it naturally contained a MeHg concentration of ~31 mg/L for the 2QCY18 waste [6.10] used in that test.

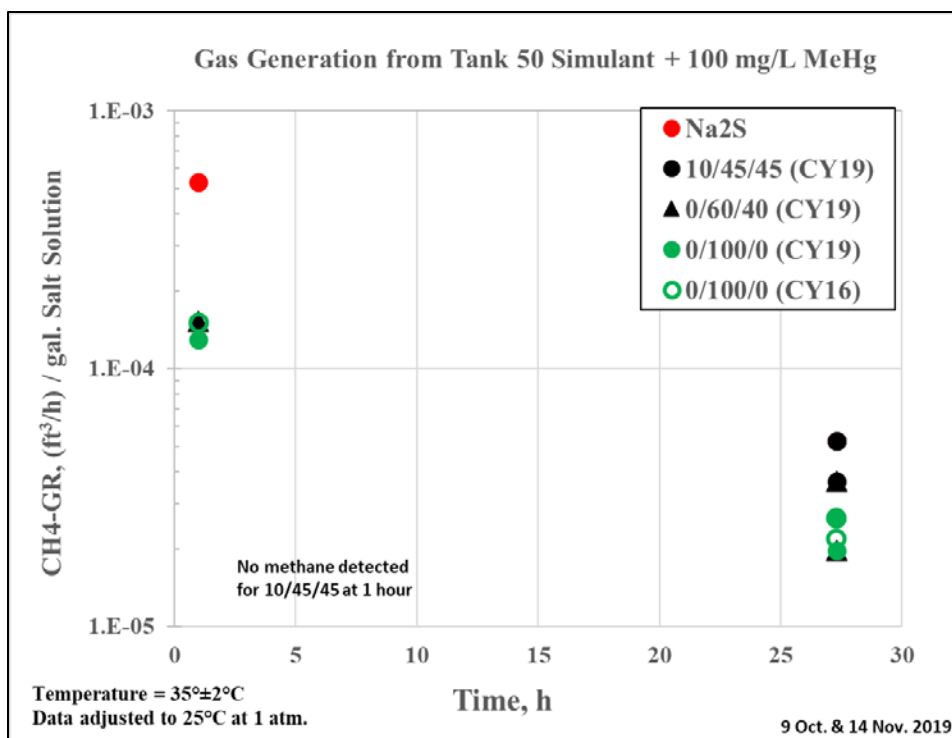
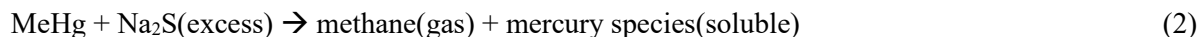


Figure 5. MGR from T50SS with 100 mg/L MeHg

### 3.3 First Order Chemical Reaction Kinetics

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



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

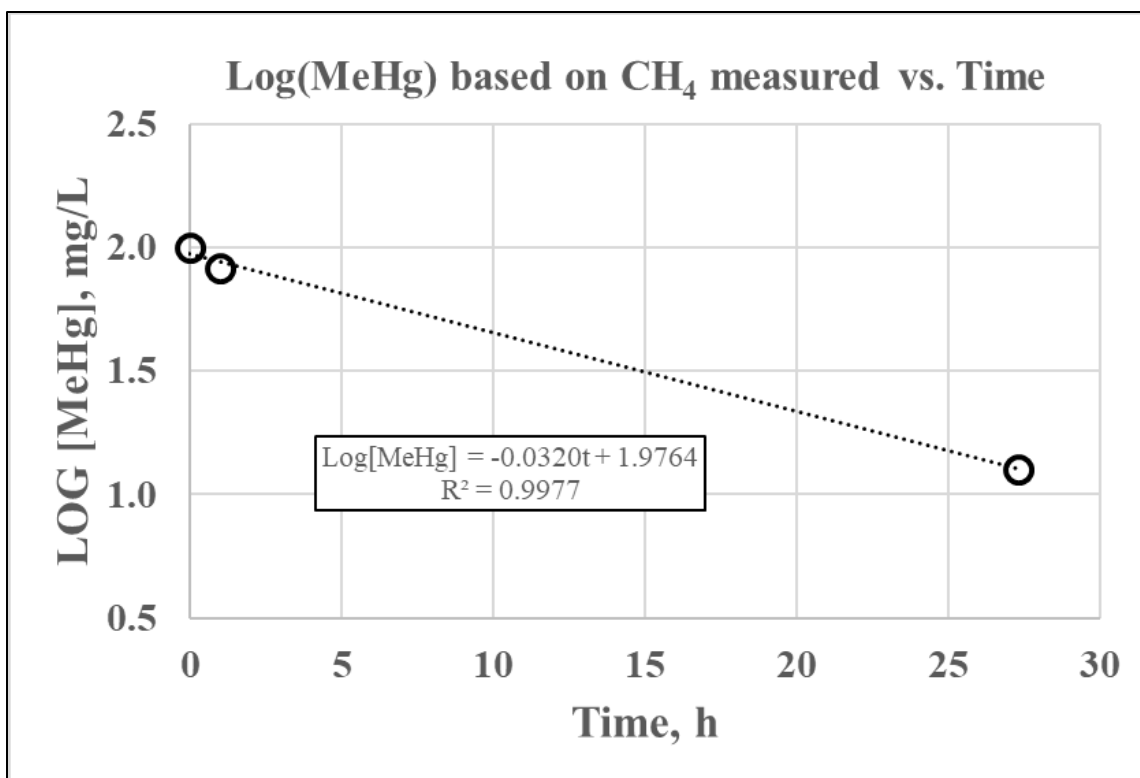
$$\text{Rate} = k[\text{MeHg}][\text{Na}_2\text{S}] \quad (3)$$

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)

$$\text{Rate} = k'[\text{MeHg}], \text{ with } k' = k[\text{Na}_2\text{S}] \quad (4)$$

The 100-mg/L data shown in Table 10 (Moles  $\text{CH}_4$  Generated from Versus Moles MeHg Available, with attention to  $\text{Na}_2\text{S}$ ) can be used to calculate the concentrations of MeHg. For the 1-hour test the concentration of MeHg is estimated to be 83.3 mg/L (based on the 16.7% of  $\text{CH}_4$  moles from available moles of MeHg) and the 27.3-hr test the concentration of MeHg to be 12.7 mg/L (based on the 87.3% of  $\text{CH}_4$  moles from available moles of MeHg), respectively. MeHg concentration is plotted vs. time in Figure 6. The results are shown to be linear for this first-order reaction using the starting concentration of MeHg and the two test concentrations of MeHg when graphed in log space. From the trend line a value of  $k'$  can be obtained from the Equation (5) [6.8]

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



**Figure 6. First Order Chemical Reaction for Na<sub>2</sub>S with MeHg**

The value of  $k'$  is calculated to be  $0.0320 \times 2.3 = 0.0736 \text{ hr}^{-1}$ . 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 constant 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, using the Phase 1, Test Series 2 data with MeHg = 200 mg/L, one can calculate that ~ 185 mg/L of MeHg would remain after 1 hour and ~ 27 mg/L of MeHg would remain after 26.8 hours. There was no 1-hour test for Phase 1, Test Series 2 but for the 26.8-hour test the methane measurement indicated that 91.5% of the available MeHg moles were converted to methane; therefore, the MeHg remaining can be estimated at  $200 \text{ mg/L} \times (1 - 91.5/100) = 17 \text{ mg/L}$ . The predicted value of 27 mg/L of MeHg at 26.8 hours over estimates the value based the methane measurement from a first-order reaction, but considering the limited data set and the measurement uncertainty, the comparison is reasonable. Further testing would be needed to improve the prediction.

It is important to note that, as mentioned note in Note 3 of Table 10, analyzing liquid samples at times longer than when a sample was pulled allowed the sulfide-MeHg reactions to continue, which showed the amount of MeHg destruction to be considerably larger than when methane gas was measured. Therefore, the MeHg destruction values calculated here are probably closer to the values that should have been measured if measured at the same time the methane. However, this calculation is only for first-order reactions. MeHg destruction values could also be calculated for all the mixtures with grout pre-mix solids, but the sulfur contained in the slag solids first need to leach into the T50SS and the sulfur will be in both reduced, i.e.,  $\text{S}^{4-}$ ,  $\text{S}^{3-}$ ,  $\text{S}^{2-}$ , and non-reduced, i.e.,  $\text{SO}_4$ , forms, so the reactions are more complex. As such, it would be useful to repeat the experiments at several time intervals to better understand the methane production from MeHg destruction.

#### 4.0 Conclusions

- Combining MeHg with material containing sulfide, e.g., Na<sub>2</sub>S or slag, generated methane gas while MeHg disappeared. This indicates that sulfide in the pH=14 salt solution is causing the destruction of MeHg resulting in methane gas.
- 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.
- No methane gas was generated when MeHg was mixed solely with individual grout premix solids of cement and fly ash.
- In general, methane produced correlated directly with MeHg concentration.
- In general, the MGR was higher during the first hour of forming saltstone than at 24 hours.
- The generation of both H<sub>2</sub> and N<sub>2</sub>O were also detected but at rates of approximately an order of magnitude less than methane.
- Methane was continually generated at the 1-hour mark and at the 24-hour mark after adding T50SS to grout pre-mix solids that contain slag. When the peak rate occurs, and the period of methane production are unknown.

#### 5.0 Recommendation for Future Work

- Quantify the methane generation rate during the life cycle of methylmercury consumption from Tank 50 waste, i.e., methane generation rates need to be measured at different periods to complement the scoping results at 1 hour and 24 hours.
- Determine if the rate of methane generation differs for mixtures of saltstone as a slurry or as a solid.
- Evaluate the effects of pH on total mercury because measurements showed that total mercury remained soluble in the pH~14 salt solution.

#### 6.0 References

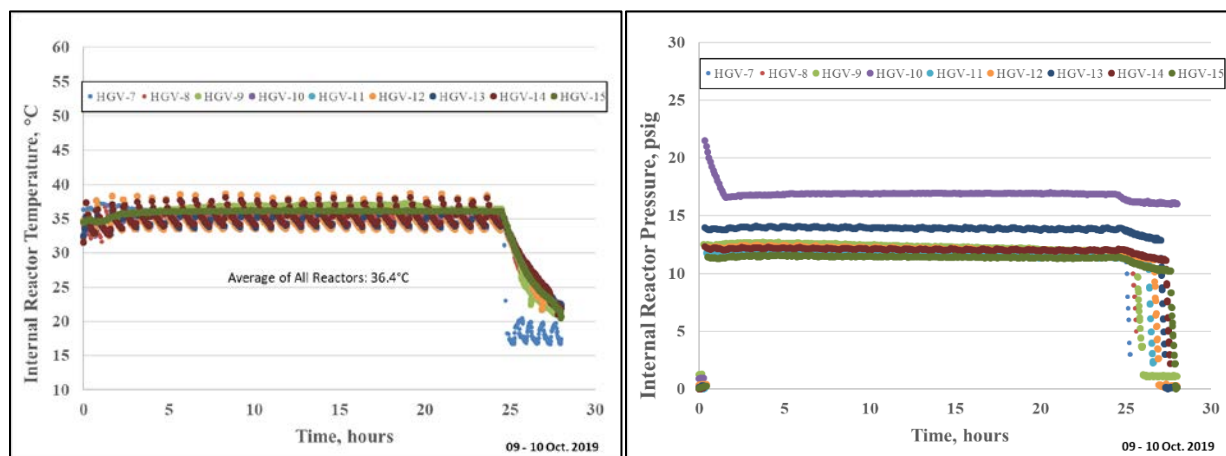
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## Appendix A. Phase 1, Test Series 1: 24-hour test with a concentration of 102.5 mg/L MeHg

### Temperature and Pressure

Figure 7 shows the temperature and pressure histories during the test period. 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 main body of the bottom 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. From previous testing, [in Appendix D of reference 6.3], the internal temperature mixture will be higher than the external temperature by approximately 0.5°C at a target temperature of 35°C from the external temperature when using the aluminum block. Each temperature trace is corrected for the appropriate difference. For the temperature data, two trends are seen: a fluctuation around the target of 35°C of about 2°C and a more constant temperature readout near the target temperature. The temperature fluctuations came from the large heater plate seen in Figure 2 because it does not have its own temperature control and therefore needed a separate controller which turned the heating on each time the temperature dropped below 1°C of the target and turned it off at 1°C above the target. There were 5 reactors on the large heating plate, i.e., HGV-10, HGV-11, HGV-12, HGV-13, and HGV-14. The other 4 reactors, i.e., HGV-7, HGV-8, HGV-9, and HGV-15 were on individual heating plates that had their own temperature controllers; therefore, these reactors were more stable. The assigning of a reactor to a heating plate was arbitrary.



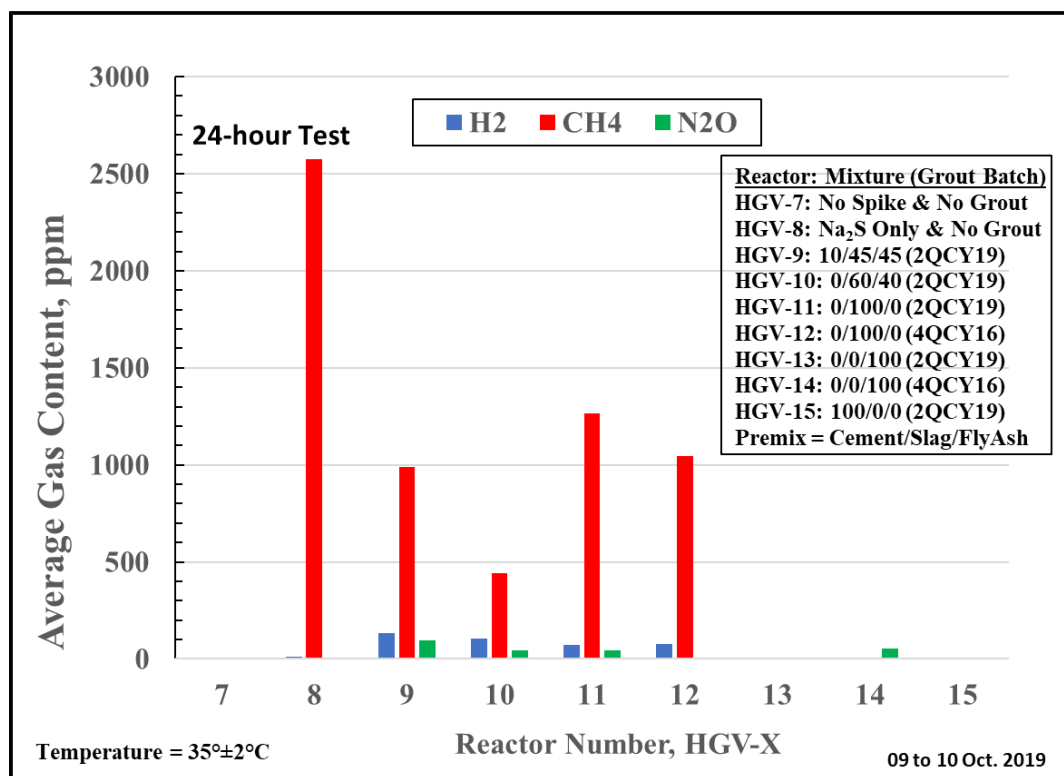
**Figure 7. Phase 1, Test Series 1 temperature & pressure profiles**

Less fluctuation is evident for the pressure because of the longer time necessary for pressure to respond to temperature changes, but slightly more fluctuations can be seen from the five reactors on the large heating plate. After a test, the test pressure was needed to calculate gas generation rates, but during a test the exact pressure values were not important; they were targeted to be close to 10 psig. A variation among the nine reactors did exist and that is a function of pressure first established when sealing each reactor and, of course, the pressure generated when heating to 35°C. The only outlier was from HGV-10, which started above 20 psig and then dropped after a few hours. Subsequently, when the reactor was opened after testing some of the grout mixture was found in the pressure transducer port, which was probably caused by a pressure surge from opening the nitrogen valve too fast when pressurizing. That reactor was checked for leaks as the pressure dropped to about 17 psig. No leaks were found; therefore, that drop in pressure was probably the result of the pressure equalizing in the pressure transducer port between the transducer and the reactor head space. For all the reactors, the exact pressure was not important during the experiment, but what was important was that the pressures held constant during the test period to indicate that no generated gases escaped. The reactors remained leak-tight.



### Gas Concentrations

Figure 8 shows the gas concentration measured in the headspace of each reactor, which are listed in Table 9. The GC measured for hydrogen, nitrous oxide, carbon dioxide, but principally for methane. Figure 8 shows that no CO<sub>2</sub> was detected (primarily because it dissolves in the caustic solution) and small amounts of H<sub>2</sub> and N<sub>2</sub>O were detected in comparison to the larger amounts of CH<sub>4</sub>.



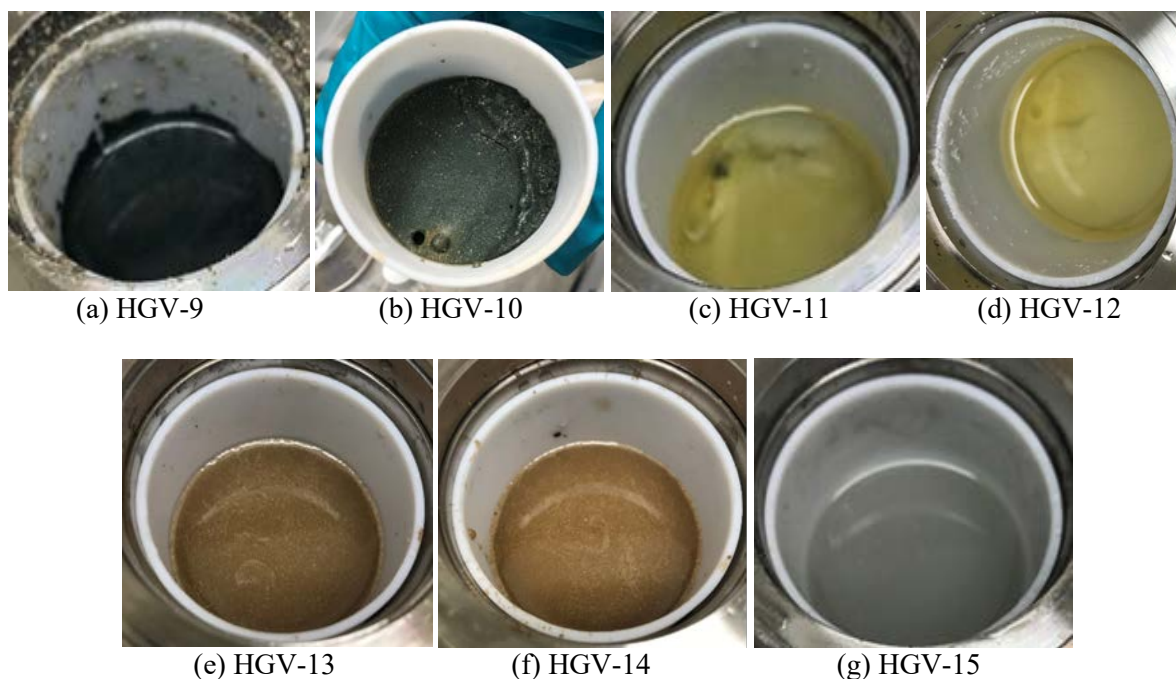
**Figure 8. Phase 1, Test Series 1 gas concentrations: 24-hour test**

As expected, the 1<sup>st</sup> reactor, HGV-7, which was a control for methane, showed none of these gases. HGV-7 only contained T50SS with no MeHg spike and no grout premix solids. The 2<sup>nd</sup> reactor, HGV-8, was similar to the first reactor in that it contained no grout pre-mix solids, but the T50SS was spiked with 100 mg/L of MeHg and 12 mg/L of Na<sub>2</sub>S. It was a control for methane generation containing both soluble sulfide and MeHg, and it was expected to produce CH<sub>4</sub> the fastest and the largest amount. The moles of CH<sub>4</sub> produced were close to 90% of the moles of MeHg available, which was considerably larger than all the other mixtures. The 3<sup>rd</sup> and 4<sup>th</sup> reactors, see Figure 9(a) and Figure 9(b), contained the standard mixtures of grout pre-mix solids and resulted in significant methane production as did the 5<sup>th</sup> and 6<sup>th</sup> reactors, Figure 9(c) and Figure 9(d). It is clear that the active ingredient in those four reactors was the sulfide in the slag because the 7<sup>th</sup>, 8<sup>th</sup>, and 9<sup>th</sup> reactors, see Figure 9(e), Figure 9(f), and Figure 9(g), contained no sulfide and therefore generated no methane. That is, those three reactors contained either cement or fly ash, but no slag.

### Operational Notes

This Phase 1, Test Series 1 was the first of three sets of tests. While several shakedown operations were performed to perfect the test operation, performing the first test was a learning experience. When the reactors were opened, after sampling the gas space, there was evidence of some splattering of the grout solids, especially seen in Figure 9(a). When the reactors were pressurized with nitrogen it appears the valve, to allow the nitrogen to enter, was opened too fast. The small volume of the mixture probably made it difficult to control the introduction of the pressurizing nitrogen. Furthermore, as can be seen in Figure 1,

the gas purge tube was close to the bottom of the Teflon insert and thus submerged under the agitating mixture. For subsequent tests the valve was changed to pressurize slower.



**Figure 9. Phase 1, Test Series 1 mixtures immediately after opening the sealed reactors: (a) 10/45/45 (CY19 batch), (b) grout pre-mix 0/60/40 (CY19 batch), (c) grout pre-mix 0/100/0 (CY19 batch), (d) 0/100/0 (CY16 batch), (e) 0/0/100 (CY19 batch), (f) 0/0/100 (CY16 batch), and (g) 100/0/0 (CY19 batch)**

(Note, HG-7 and -8, are not shown but the fully liquid mixtures were similar to those shown in Figure 13(a) and (b), respectively, for Phase 1, Test Series 2.)

The introduction of nitrogen was performed better for the remaining reactors, as can be seen in the Figure 9(b through g). Also evident from mixtures shown in Figure 9(b through d, but especially b) is that some solidification of the mixtures occurred over the 24-hour test. As previously explained, five reactors were placed on the large heating/stirring plate, i.e., HG-10, HG-11, HG-12, HG-13, and HG-14. Unfortunately, only after the second test series of Phase 1 was it realized that as the temperature controller turned the power off and on to the large heating plate to maintain the temperature at 35°C it also turned the power off and on to the magnetic stirring bars. This means that for slightly greater than 50% of the time during the 24 hours the stirrer bars were not spinning, which allowed the mixtures to solidify. The grout pre-mix of 0/60/40, Figure 9(b), definitely solidified and it appears the reactors with only slag, i.e., Figure 9(c and d) settled and formed some solids. The two reactors with only fly ash, i.e., Figure 9(e and f), did not solidify and remained a slurry. For the other four reactors on the individual heating/stirring locations, the Teflon stirrers never stopped mixing thus the mixtures remained loose slurries, Figure 9(a and g). Not shown are HG-7 and HG-8 that only contained liquids, so there was no issue of solids forming. Despite forming of solids, the reactors generated methane, but it is not known if the process of solidifying over the 24 hours impacted the methane generation.

#### Gas Generation Rates

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 10 and Table 11 show the gas generation rates for CH<sub>4</sub>, H<sub>2</sub>, and N<sub>2</sub>O. The principal gas of interest, methane, did show generation rates, MGR, which were calculated with Eq. (1):

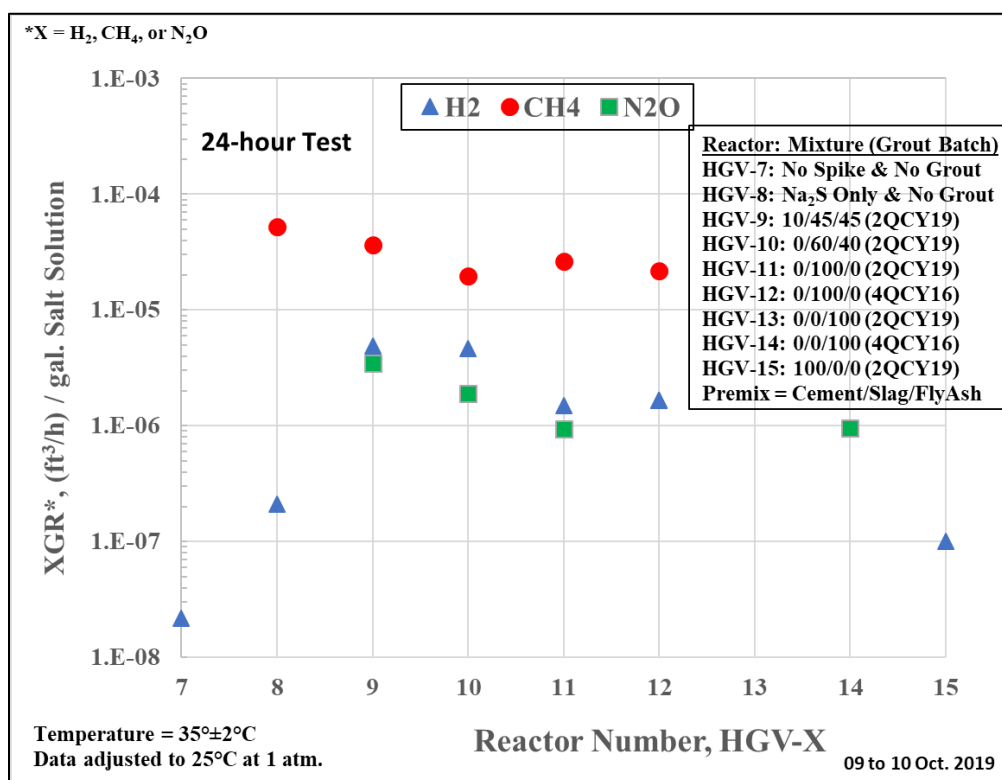
**MGR =**

$$[(\text{Head Space Vol., ft}^3) \cdot A \cdot \text{CH}_4 \text{ Measured, ppm} / 1000000] / (\text{Test Time, hours}) / \text{Vol. Liquid, gal (1)}$$

where  $A = \text{Adjustment factor to } 25^\circ\text{C and } 1 \text{ atm} = [P_{\text{initial sample}} / P_{\text{standard}}] [T_{\text{standard}} / T_{\text{sampling}}] =$

$$[(\text{Initial Sample Head Pressure, psig} + 14.7 \text{ psia}) / 14.7 \text{ psia}] [298 \text{ K} / (T^\circ\text{C at sampling} + 273 \text{ K})]$$

with  $P_{\text{standard}} = 1 \text{ atm} = 14.7 \text{ psia}$  and  $T_{\text{standard}} = 25^\circ\text{C}$



**Figure 10. Phase 1, Test Series 1 gas generation rates**

From the reactor with Na<sub>2</sub>S, the largest MGR was expected and obtained at  $5.3 \times 10^{-5} \text{ (ft}^3/\text{h) / gallon of salt solution}$ . For all the reactors containing slag, the MGR was between  $2.0$  and  $4.0 \times 10^{-5} \text{ (ft}^3/\text{h) / gallon of salt solution}$ . As already stated, the reactors without slag resulted in no generation of methane. Along with methane, small amounts of hydrogen were detected, Figure 8, but the calculated generation rates are approximately an order of magnitude less than methane. This result also holds for the small amounts of nitrous oxide detected.

**Table 11. Phase 1, Test Series 1 gas generation rates**

Sealed Reactor Name	Tank 50 Simulant Mixture	Grout Premix Batch	Gas Generation Rate		
			CH <sub>4</sub> (ft <sup>3</sup> /h) / gal	H <sub>2</sub> (ft <sup>3</sup> /h) / gal	N <sub>2</sub> O (ft <sup>3</sup> /h) / gal
HGV-7	No Spike	N/A	ND	2.2E-08	ND
HGV-8	Na <sub>2</sub> S	N/A	5.2E-05	2.1E-07	ND
HGV-9	10/45/45	2QFY19	3.7E-05	4.9E-06	3.5E-06
HGV-10	0/60/40	2QFY19	2.0E-05	4.6E-06	1.9E-06
HGV-11	0/100/0	2QFY19	2.6E-05	1.5E-06	9.4E-07
HGV-12	0/100/0	4QFY16	2.2E-05	1.6E-06	ND
HGV-13	0/0/100	2QFY19	ND	ND	ND
HGV-14	0/0/100	4QFY16	ND	ND	9.6E-07
HGV-15	100/0/0	2QCY19	ND	1.0E-07	ND
ND = Not Detected      N/A = Not Applicable					

#### Mercury Results

The results in Table 12 clearly show that when methane was detected, see Figure 8, most, or all, of the MeHg was consumed, i.e., HGV-8, HGV-9, HGV-11, and HGV-12. All of these reactors contained sulfide either directly or within the slag solids.

**Table 12. Phase 1, Test Series 1 gas generation rates**

Reactor or Simulant State	Tank 50 Simulant Type of Spike	Total Mercury (mg/L)	MeHg (mg/L)
Pre-test	No Spike	< 0.001	< 0.1
Pre-test	102.5 mg/L MeHg	105	89
HGV-7	No Spike	< 0.001	< 0.1
HGV-8	Na <sub>2</sub> S	102	1
HGV-9	MeHg + 10/45/45 (1)	113	0.6
HGV-10	MeHg + 0/60/40	N/A (2)	N/A
HGV-11	MeHg + 0/100/0	104	< 0.1
HGV-12	MeHg + 0/100/0	101	< 0.1
HGV-13	MeHg + 0/0/100	109	84.3
HGV-14	MeHg + 0/0/100	109	92.8
HGV-15	MeHg + 100/0/0	109	83.2
Post-test	102.5 mg/L MeHg	104	102
(1) MeHg = 102.5 mg/L methyl mercury and grout premix sequence is cement/BFS/fly ash.			
(2) HGV-10 solidified thus had no liquid to analyze.			

When methane was not detected, most of the MeHg remained, i.e., HGV-13, HGV-14, and HGV-15. All of these reactors did not contain slag, so probably did not contain any sulfide. What was surprising was that the total mercury was not affected from the presence of grout premix solids. Within measurement uncertainty of approximately 20 %RSD at a 95% confidence level, the measurements of total mercury from all the spike samples with 100 mg/L of MeHg indicate that the mercury remained soluble in the liquid. Furthermore, no noticeable solids precipitated when filtering slurry mixtures, e.g., cinnabar, HgS. From one source [6.9] it appears that as the pH of a mixture increases the solubility of mercury sulfide increases. All of the included tests purposely had a much larger amount of sulfide than the Hg or MeHg, so much of the sulfide was available to combine with mercury and this may be the reason the measured total mercury concentration was similar to the amount of mercury spiked into the simulant.

## Appendix B. Phase 1, Test Series 2: 24-hour test with a concentration of 199.3 mg/L MeHg

### Temperature and Pressure

Figure 11 shows the temperature and pressure histories during the test period. For an explanation on TC placements and temperature fluctuations, see the discussion in the Temperature and Pressure paragraph of Appendix A. For Phase 1, Test Series 2 there were 4 reactors on the large heating plate, i.e., HGV-10, HGV-11, HGV-12, and HGV-13. The other 4 reactors, i.e., HGV-7, HGV-8, HGV-9, and HGV-15 were on individual heating plates that had their own temperature controllers and therefore better controlled. The assigning of a reactor to a heating plate was arbitrary. Note that HGV-14 was not used in this test series because it was damaged during the test setup, so only 8 reactors were employed.

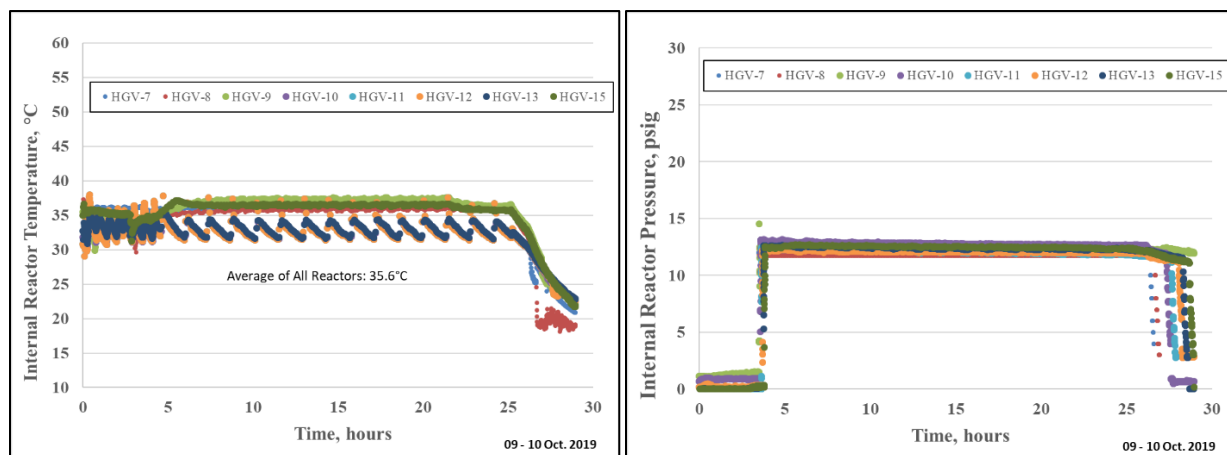
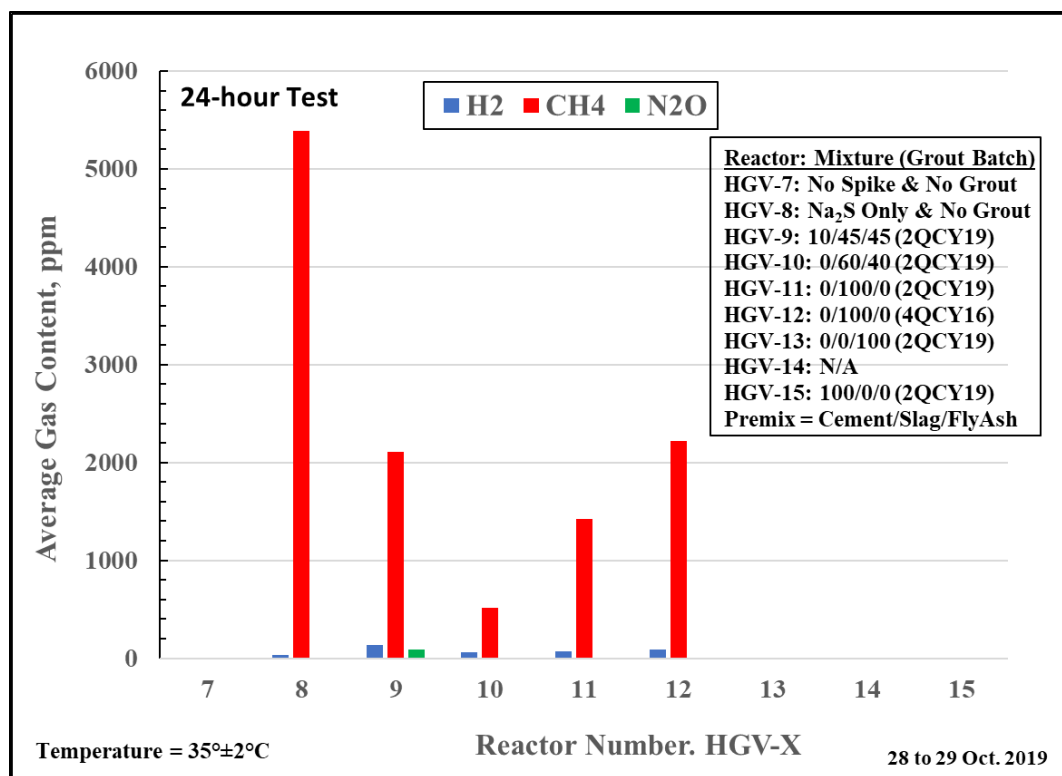


Figure 11. Phase 1, Test Series 2 temperature & pressure profiles

### Gas Concentrations

Figure 12 shows the gas concentration measured after Phase 1, Test Series 2 using 200 mg/L in the T50SS. The data show the amount of gas contained in the headspace, which are listed Table 9. The GC measured for hydrogen, nitrous oxide, carbon dioxide, but principally for methane.

Similar to the results from Phase 1, Test Series 1 with 100 mg/L of MeHg, Figure 12 shows that no  $\text{CO}_2$  was detected (primarily because it dissolves in the caustic solution) and small amounts of  $\text{H}_2$  and  $\text{N}_2\text{O}$  were detected in comparison to the larger amounts of  $\text{CH}_4$ . As expected, the 1<sup>st</sup> reactor, HGV-7, was a control for methane, but it showed none of these gases. HGV-7 only contained T50SS with no MeHg spike and no grout premix solids. The 2<sup>nd</sup> reactor, HGV-8 was similar to the first reactor in that it contained no grout pre-mix solids, but the T50SS was spiked with 100 mg/L of MeHg and 12 mg/L of  $\text{Na}_2\text{S}$ . It was a control for methane generation with soluble sulfide and MeHg and it was expected to produce  $\text{CH}_4$  the fastest and the largest amount. In fact the methane concentration was almost exactly double from the Phase 1, Test Series 1 methane concentration, which had exactly one half the MeHg. The moles of  $\text{CH}_4$  was greater than 90% of the moles of MeHg available, which was considerable larger than all the other mixtures in this test series.



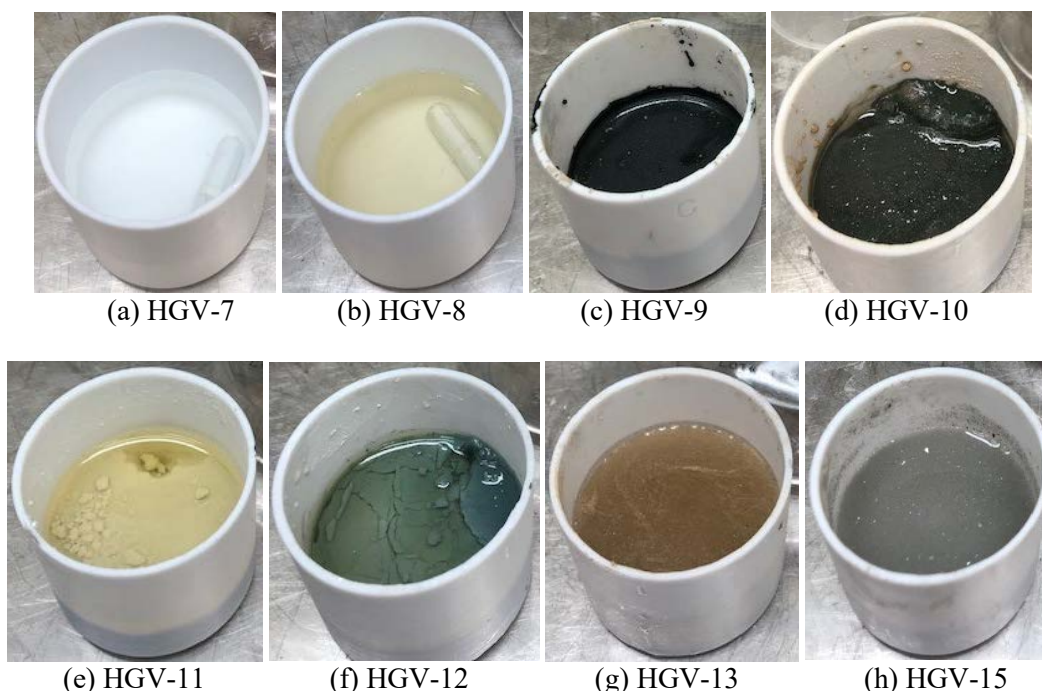
**Figure 12. Phase 1, Test Series 2 gas concentrations: 24-hour test**

The 3<sup>rd</sup> and 4<sup>th</sup> reactors, see Figure 13(c) and Figure 13 (d), contained the standard mixtures of grout pre-mix solids and resulted in significant methane production as did the 5<sup>th</sup> and 6<sup>th</sup> reactors, Figure 13 (e), and Figure 13 (f). It is clear that the active ingredient in those four reactors was the sulfide in the slag because the 7<sup>th</sup> and 8<sup>th</sup>, see Figure 13 (g) and Figure 13 (h), contained no slag implying no sulfide; therefore, no methane was evident. That is, those two reactors contained either cement or fly ash, but not slag.

As in Phase 1, Test Series 1, for Test Series 2 some splattering of the grout solids was still evident on the Teflon inserts in some of the reactors, see Figure 13; however, it was much less. That is, the gas valve was changed to allow a slower opening. Also evident from mixtures shown in Figure 13(d through f, but especially d) some solidification of the mixtures occurred over the 24-hour test.

As previously explained in the preceding test series, the mixtures in the reactors that were placed on the large heating/stirring plate, i.e., HGV-10, HGV-11, HGV-12, and HGV-13, showed signs of solidification. For the following 1-hour test the large heating/stirring plate was not used and for future tests its use will be limited to situations when stirring is not needed. The grout pre-mix of 0/60/40, Figure 13(d) definitely solidified and it appears the reactors with only slag, i.e., Figure 13(e and f) settled and formed some solids. The reactor with only fly ash, i.e., Figure 13(g), did not solidify and remained a slurry. For the other 4 reactors on the individual heating/stirring plates the Teflon stirrer bars never stopped and thus the mixtures remained fluid, Figure 13(a, b, c, and h). Also shown are HGV-7 and HGV-8, Figure 13(a and b) those reactors only contained liquids, so there was no issue of solids forming. Despite forming of solids, the reactors generated methane, but it is not known if the process of solidifying over the 24 hours impacted the methane generation. One interesting fact between the grout pre-mix 0/60/40 mixtures for both Phase 1, Test Series 1, Figure 9(b) and this Phase 1, Test Series 2, Figure 13(d), is that a raised ridge of material is evident. The reason is unknown.





**Figure 13. Phase 1, Test Series 2 mixtures immediately after opening the reactors: (a) no spikes, (b)  $\text{N}_2\text{S}$ , (c) grout pre-mix 10/45/45 (CY19 batch), (d) grout pre-mix 0/60/40 (CY19 batch), (e) grout pre-mix 0/100/0 (CY19 batch), (f) 0/100/0 (CY16 batch), (g) 0/0/100 (CY19 batch), (h) 100/0/0 (CY19 batch)**

(Notes: (1) HGV-14, was damaged and not included. (2) Mixtures shown in (e) and (f) were both mixtures of slag but from different batches, as in Phase 1, Test Series 1. The greenish color in (f) happens after exposed to air. Mixture (e) would eventually turn green, too.)

#### Gas Generation Rates

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 14 and Table 13 show the gas generation rates for  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{N}_2\text{O}$ . The principal gas of interest, methane, did show generation rates, MGR, which were calculated with Eq. (1) in Appendix A.

From the reactor with  $\text{Na}_2\text{S}$ , the largest MGR was expected and obtained at  $1.1 \times 10^{-4} \text{ (ft}^3\text{/h) / gallon of salt solution}$ . Furthermore, by doubling the concentration of MeHg from 100 mg/L to 200 mg/L this rate was almost exactly doubled from the Test Series 1 result of  $0.53 \times 10^{-4} \text{ (ft}^3\text{/h) / gallon of salt solution}$ . For all the reactors containing sulfide-containing slag, the MGR was between  $2.0$  and  $8.0 \times 10^{-5} \text{ (ft}^3\text{/h) / gallon of salt solution}$ . All of these Test Series 2 rates were larger than those from Test Series 1; however, only two, i.e., HGV-9 and HGV-12 had rates that doubled. The process of releasing sulfide from the grout solids to react with MeHg probably had an effect. Once again, for the reactors without sulfide-containing slag no methane was detected. Along with methane, small amounts of hydrogen were detected, Figure 12, but the calculated generation rates are more than an order of magnitude less than methane. This result also holds for the small amount of nitrous oxide detected.



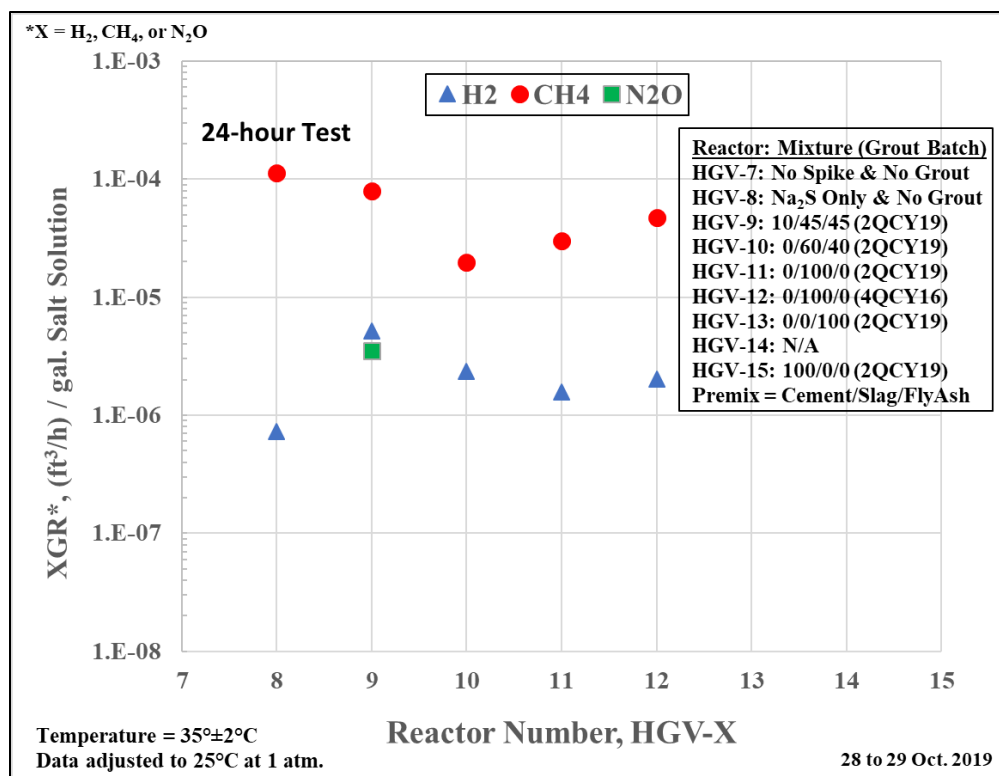


Figure 14. Phase 1, Test Series 2 gas concentrations

Table 13. Phase 1, Test Series 2 gas generation rates

Sealed Reactor Name	Tank 50 Simulant Mixture	Grout Premix Batch	Gas Generation Rate		
			CH <sub>4</sub> (ft <sup>3</sup> /h) / gal	H <sub>2</sub> (ft <sup>3</sup> /h) / gal	N <sub>2</sub> O (ft <sup>3</sup> /h) / gal
HGV-7	No Spike	N/A	ND	ND	ND
HGV-8	Na <sub>2</sub> S	N/A	1.1E-04	7.3E-07	ND
HGV-9	10/45/45	2QFY19	8.0E-05	5.2E-06	3.5E-06
HGV-10	0/60/40	2QFY19	2.0E-05	2.4E-06	ND
HGV-11	0/100/0	2QFY19	3.0E-05	1.6E-06	ND
HGV-12	0/100/0	4QFY16	4.7E-05	2.0E-06	ND
HGV-13	0/0/100	2QFY19	ND	ND	ND
HGV-14	0/0/100	4QFY16	(1)	(1)	(1)
HGV-15	100/0/0	2QCY19	ND	ND	ND
ND = Not Detected      N/A = Not Applicable					
(1) HGV-14 not used due to damage					

### Mercury Results

The results in Table 14 clearly show that when methane was detected, see Figure 12, MeHg was detectable but most, or all, of the MeHg was consumed, i.e., HGV-8, HGV-9, HGV-11, and HGV-12. Note that due to solidification of the mixture in HGV-10 there was not enough material to measure MeHg

**Table 14. Phase 1, Test Series 2 gas generation rates**

Reactor or Simulant State	Tank 50 Simulant Type of Spike	Total Mercury (mg/L)	MeHg (mg/L)
Pre-test	No Spike	< 0.001	< 0.2
Pre-test	199.3 mg/L MeHg	213	173
HGV-7	No Spike	< 0.001	< 0.2
HGV-8	Na <sub>2</sub> S	231	2.1
HGV-9	MeHg + 10/45/45 (1)	228	1.5
HGV-10	MeHg + 0/60/40	209	N/A (2)
HGV-11	MeHg + 0/100/0	197	0.9
HGV-12	MeHg + 0/100/0	208	1.2
HGV-13	MeHg + 0/0/100	210	170
HGV-14	MeHg + 0/0/100	N/A (3)	N/A
HGV-15	MeHg + 100/0/0	214	160
Post-test	199.3 mg/L MeHg	199	174
(1) MeHg = 199.3 mg/L methyl mercury and grout premix sequence is cement/BFS/fly ash.			
(2) Not enough liquid for MeHg analysis.			
(3) HGV-14 was damaged during Test Series 2 of Phase 1.			

When methane was not detected most of the MeHg remained, i.e., HGV-13 and HGV-15. These two mixtures did not contain slag implying that they did not contain any sulfide. As in the preceding test series, what was surprising was that the total mercury was not affected from the presence of grout premix solids. Within measurement uncertainty of approximately 20 %RSD at a 95% confidence level, the measurements of total mercury from all the spike samples with 100 mg/L of MeHg indicate that the mercury remained soluble in the liquid. As discussed in the first test series, no noticeable solids precipitated when filtering slurry mixtures, e.g., cinnabar, HgS. From one source [6.9] it appears that as the pH of a mixture increases the solubility of mercury sulfide increases. All of the included tests purposely had a much larger amount of sulfide than the Hg or MeHg, so much of the sulfide was available to combine with mercury and may be the reason the measured total mercury concentration was similar to the amount of mercury spiked into the simulant.

### Appendix C. Phase 2, Test Series 1: 1-hour test with a concentration of 101.8 mg/L MeHg

The second phase of testing depended on the results of the first phase. If the methane measured in the first phase was considerably less than that measured during radioactive waste testing [6.3] then this last phase would repeat the first phase but at a longer period than 24 hours. Conversely, if the methane measured was considerably more than the radioactive waste testing, then Phase 2 would be done a shorter gas generation time. From the radioactive Tank 50 waste the methane measured was on the order of 100 ppm in the 200-mL sealed reactors after 28 days of generation. As already discussed, after 24 hours the methane concentration from Phase 1, Test Series 1, with 100 mg/L of MeHg, was up to 1000 ppm, see Figure 8, from the reactors with slag. From Phase 1, Test Series 2, with 200 mg/L MeHg, methane was up to 2000 ppm, see Figure 12, from the reactors with slag. While radioactive waste only contains approximately 30 mg/L [6.10] of MeHg this scoping test with T50SS resulted in a much higher methane release over only 24 hours. Due to this result, the second phase of testing was performed at 1 hour to better understand the time frame that methane is generated. Of course, with a much shorter time it was important to have a very quick turnaround of creating a mixture to generate methane, pressurizing, and then sealing each reactor. Table 15 shows the gas generation times and on the average 1 hour was obtained. However, to calculate the gas generation rates, the exact times for each mixture was used.

The Phase 2 lineup of reactor mixtures was slightly different from Phase 1, in addition to the shorter gas-generation time to take advantage of the results from Phase 1. Because methane was not generated when slag-containing sulfide was not present; therefore, the mixtures of the non-slag containing reactors HGV-13 and HGV-15 were changed to be duplicates of important mixtures, i.e., HGV-9 with a grout premix of 10/45/45 and HGV-10 with a grout premix of 0/60/40.

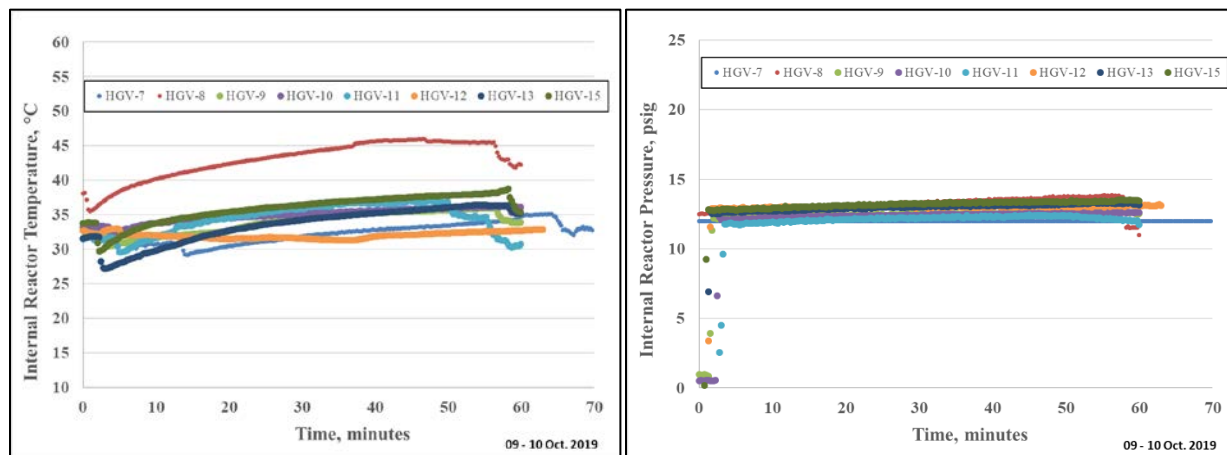
**Table 15. Phase 2, Test Series 1 gas generation times**

Reactor Name	Tank 50 Simulant Mixture	Grout Premix Batch	Start (1) Time hh:mm	End (2) Time hh:mm	EIapse Time hh:mm
HGV-7	No Spike	N/A	9:10	10:10	1:00
HGV-8 (3)	Na <sub>2</sub> S	N/A	14:01	15:00	0:59
HGV-9	10/45/45	2QFY19	9:30	10:30	1:00
HGV-10	0/60/40	2QFY19	9:51	10:50	0:59
HGV-11	0/100/0	2QFY19	11:25	12:25	1:00
HGV-12	0/100/0	4QFY16	11:35	12:38	1:03
HGV-13	10/45/45	2QFY19	12:00	13:00	1:00
HGV-15	0/60/40	2QCY19	13:40	14:40	1:00
Ave. =					1:00
Std Dev =					0:01
(1) Clock started after reactor was sealed.					
(2) Clock stopped at start of first gas sample.					
(3) HGV-8 was filled last due to the Na <sub>2</sub> S contents to minimize exposure to the air because of being hygroscopic.					

#### Temperature and pressure

Figure 15 shows the temperature and pressure histories during the test period. For an explanation on TC placements and temperature fluctuations, see the discussion in the Temperature and Pressure paragraph of Appendix A. The time intervals of the temperature and pressure shown in Figure 15 differ from the 24-

hour tests in Phase 1 because the reactor seal time was only 1 hour and to better utilize the available equipment, only three heating/stirring plates were utilized; specifically, the heating plates originally dedicated for reactors HGV-7, HGV-8, and HGV-9, which were individual units with better temperature control.



**Figure 15. Phase 2, Test Series 1 temperature & pressure profiles**

Because the 1-hour period for each reactor was staggered to use the three heating plates, the times shown are in minutes with zero being the point a reactor was sealed. So for example, HGV-7 began at 09:00 and ended at about 10:00, while HGV-8 began at 14:00 and ended at about 15:00, so 09:00 and 14:00 are the zero point for each of those vessels. That is, the abscissa only shows the time during which a vessel was sealed and then when it was unsealed to begin gas sampling. In general, the temperatures were held close to the target of 35°C. For this 1-hour test, when the vessels were filled with the dry solid materials on the preceding day they were pre-heated to 35°C and held at that temperature overnight. If this step were not done then after filling each reactor on the test day with the T50SS, and then sealing the vessel, it probably would have taken longer than the 1-hour test to reach the 35°C target temperature. Even with the precaution, as can be seen from the temperature-history graph, there was slight decrease in the reactor temperature after filling with T50SS, on the order of 5°C. Then the reactors slowly returned to the target temperature as they sat on the heating plate after being sealed. The process worked well. As noted in the previous test, HGV-14 was not used in this test series because it was damaged during the test setup, so only 8 reactors were employed.

Also note that while temperature history of HGV-8 is included in the group of reactor temperature profiles, it sits about 10°C above the other temperatures. This was the last test of the day and the adjustment to trim it to 35°C was missed due to many other activities on that test day. The temperature measurement is accurate because the pressure increased during the hour of the test for HGV-8 was slightly larger than for the other reactors. The measured pressure for HGV-8 is included in the pressure history shown in Figure 15 and while its pressure increase appears to be similar to the other reactors it was slightly larger. For all reactors, except HGV-8, the average pressure increase over the hour period of the test was 0.6 psi, with a single standard deviation of 0.2 psi. For reactor HGV-8 the pressure increased was 1.3 psi, or double than for all the other reactors. If the gas in the headspace acted as an ideal gas the temperature increase of 10°C would lead to an increase in absolute pressure of approximately 3%, or about 0.9 psi; however, the gas was saturated with water, so the environment was not ideal leading to a slight larger increase.

### Gas Concentrations

Figure 16 shows the gas concentrations measured after Phase 2, Test Series 1 using T50SS spiked with 100 mg/L. The data show the amount of gas contained in the headspace of each reactor, which are listed in

Table 9. The GC measured for hydrogen, nitrous oxide, carbon dioxide, but principally for methane. Similar to the results the Phase 1, Test Series 1, Figure 16 shows that no CO<sub>2</sub> was detected (primarily because it dissolves in the caustic solution) and a small amount of H<sub>2</sub> was detected in comparison to the larger amounts of CH<sub>4</sub>. Furthermore, this time, no N<sub>2</sub>O was detected either, probably due to the much shorter gas generation time.

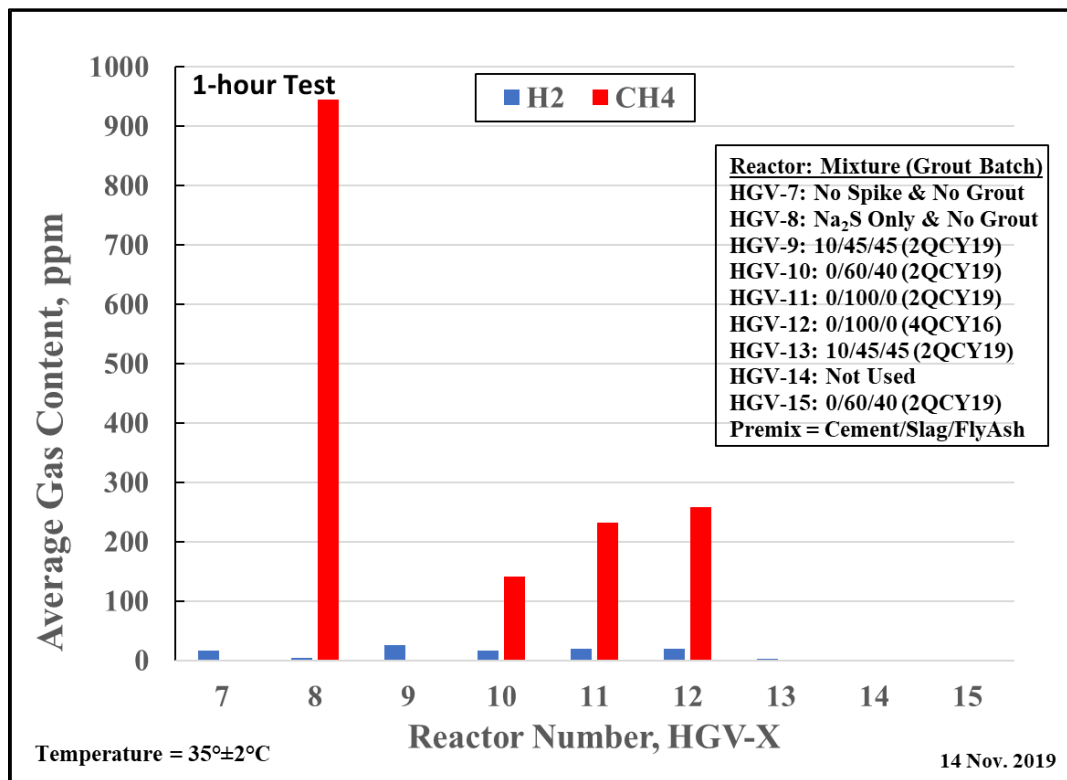
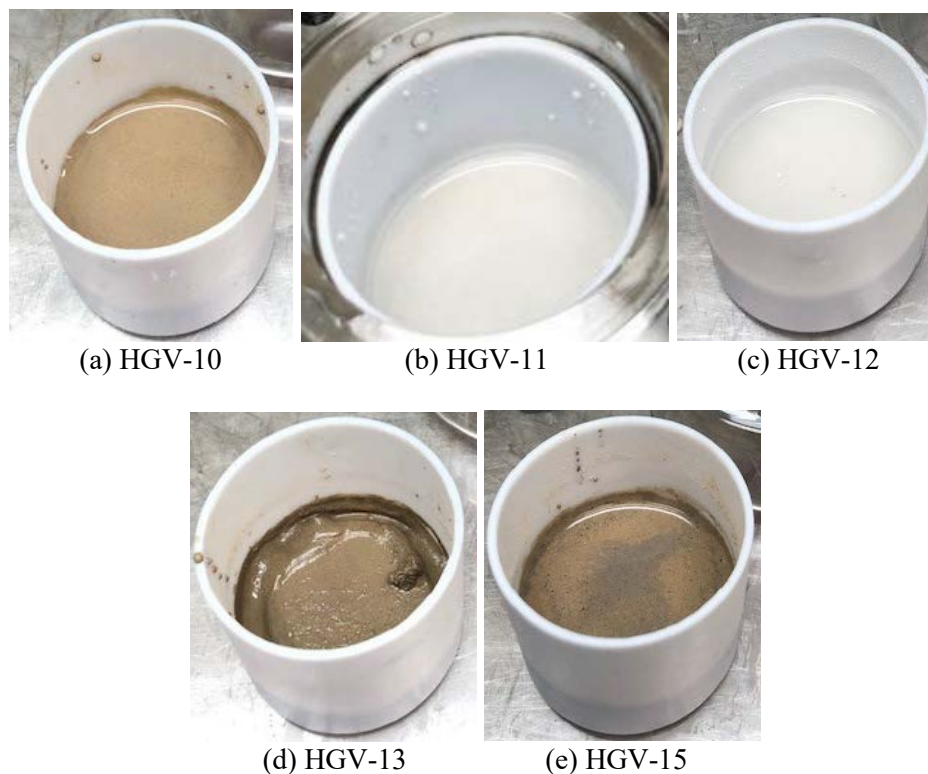


Figure 16. Phase 2, Test Series 1 gas concentrations: 1-hour test

As expected, the 1<sup>st</sup> reactor, HGV-7, was a control and showed none of these gases, except a trace amount of H<sub>2</sub>, possibly due to tramp Total Organic Carbon (TOC), which has been seen in past T50SS tests [6.3]. HGV-7 contained only T50SS with no MeHg spike and no grout premix solids. The 2<sup>nd</sup> reactor, HGV-8 was similar to the first reactor except that the T50SS was spiked with 100 mg/L of MeHg and 12 mg/L for Na<sub>2</sub>S, but contained no grout pre-mix solids. It was a control for methane generation with soluble sulfide and MeHg, so it was expected to produce CH<sub>4</sub> the fastest and the largest amount. HGV-8 in the Phase-2 1-hour test generated about half the methane concentration that was measured in HGV-8 of the Phase-1 24-hour test, which also had 100 mg/L MeHg. Even still, the CH<sub>4</sub> concentration in HGV-8 was much larger than all the other Phase-2 reactors. However, it appears that this 1-hour test was not long enough for the gas concentration to build up to the value obtained after 24 hours. This time, the concentration of moles of CH<sub>4</sub> generated was only about 17% of the moles of MeHg available as compared to the ~90% from Phase 1. From the 3<sup>rd</sup> reactor with a grout pre-mix of 10/45/45, no methane was detected. Figure 17 does not show any picture of this reactor's mixture because none was taken, and from the 4<sup>th</sup> reactors with a grout pre-mix of 0/60/40, seen as Figure 17(a), just slightly more than ~130 ppm of methane was detected, which means that only approximately 5% of available the moles of MeHg were generated into moles of CH<sub>4</sub>. As in previous tests, methane was detected from the 5<sup>th</sup> and 6<sup>th</sup> reactors, which contained the single grout pre-mix component of slag, seen as Figure 17(b) and Figure 17(c). The last two reactors, 7<sup>th</sup> and 8<sup>th</sup>, Figure 17(d) and Figure 17(e), were duplicate reactors with grout pre-mix of 10/45/45 and 0/60/40, respectively. The duplicate 10/45/45, i.e., HGV-13, gave the same result HGV-9 of no detectable methane, but from the duplicate 0/60/40, i.e., HGV-15, no methane was detected instead of the ~130 ppm detected in HGV-10.

This may indicate that 1 hour is near the time of initial methane production. Despite the challenges to fill, pressurize, seal each reactor, and then sample the head space for gas concentrations within 1 hour, the test ran smoothly. The photographs of Figure 17((a through e) show minimal splashing on the sides of the Teflon inserts.

All movements were well coordinated. However, subsequently, after gas sampling and removing the mixtures, HGV-13 was found to have a lower level of mixture in the Teflon insert and a bead of slurry down one side of the Teflon wall opposite of the purge tube location, see Figure 17(d). It turned out that approximately 9.8 g of the T50SS or about 8 mL, which was ~15% of volume of the mixture, was found on the outside of the Teflon insert. The location of the beads of slurry was directly under the location of the liquid introduction port. It appears that in filling the reactor some of the stream of T50SS being introduced split so that some entered the inside of the insert and some on the outside. The Teflon insert was designed to be a snug fit in the reactor so the gap between the Teflon wall and the inside wall of the reactor is small, but the insert must have been out of round just enough to present a slightly larger gap that caused some of the T50SS not to enter the insert. Of course, this resulted in a thicker mixture in the insert which made it much harder for the Teflon stirrer bar to mix the contents. The photograph shows the mixture was in the initial stages of solidifying. It was fortunate that HGV-13 was only a duplicate and this was a lessons learned to avoid a future occurrence.



**Figure 17. Phase 2, Test Series 1 mixtures immediately after opening the sealed reactors: (a) grout pre-mix 0/60/40 (CY19 batch), (b) grout pre-mix 0/100/0 (CY19 batch), (c) 0/100/0 (CY16 batch), (d) duplicate 10/45/45 (CY19 batch), (e) duplicate 0/60/40 (CY19 batch)**  
(Note, HGV-9, which was 10/45/45 (CY19 batch) is not shown because picture may not have been taken.)

### Gas Generation Rates

Based on the mass of salt solution, the volume of reactor headspace, and adjusted to 25°C at 1 atmosphere, Figure 18 and Table 16 show the gas generation rates for CH<sub>4</sub> and H<sub>2</sub>. For the 1-hour test N<sub>2</sub>O was not detected. The principal gas of interest, methane, did show generation rates, MGR, which were calculated with Eq. (1) shown in Appendix A.

For this test series the MeHg concentration, i.e., 100 mg/L, was the same as for Phase 1, Test Series 1. From the control with Na<sub>2</sub>S, the largest MGR was expected and obtained at  $5.3 \times 10^{-4}$  (ft<sup>3</sup>/h) / gallon of salt solution, which is an order of magnitude larger than from Phase 1, i.e.,  $0.52 \times 10^{-4}$  (ft<sup>3</sup>/h) / gallon of salt solution. For all the reactors containing slag the MGR was between  $1.3$  and  $1.5 \times 10^{-4}$  (ft<sup>3</sup>/h) / gallon of salt solution, which are also rates that are approximately an order of magnitude larger than obtained from the Phase 1, 24-hour test with 100 mg/L of MeHg. As in previous tests, a small amount of hydrogen was detected, seen in Figure 16, in each of the reactors, but the calculated generation rates are approximately an order of magnitude less than methane.

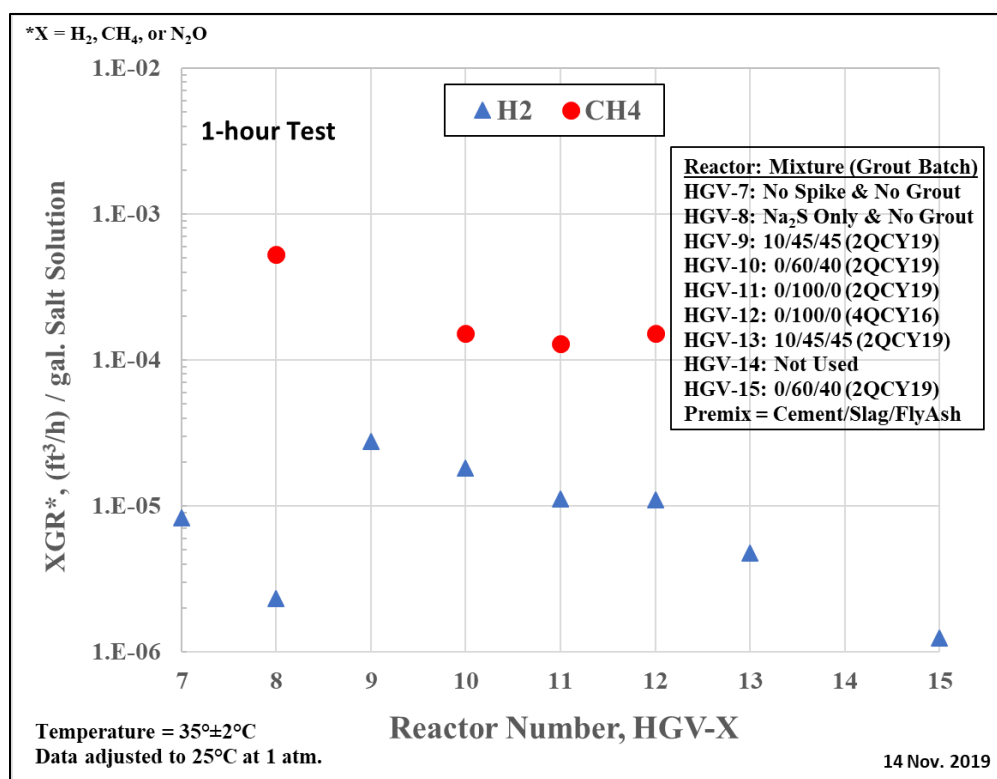


Figure 18. Phase 2, Test Series 1 gas concentrations

**Table 16. Phase 2, Test Series 1 gas generation rates**

Sealed Reactor Name	Tank 50 Simulant Mixture	Grout Premix Batch	Gas Generation Rate		
			CH <sub>4</sub> (ft <sup>3</sup> /h) / gal	H <sub>2</sub> (ft <sup>3</sup> /h) / gal	N <sub>2</sub> O (ft <sup>3</sup> /h) / gal
HGV-7	No Spike	N/A	ND	8.3E-06	ND
HGV-8	Na <sub>2</sub> S	N/A	5.3E-04	2.3E-06	ND
HGV-9	10/45/45	2QFY19	ND	2.7E-05	ND
HGV-10	0/60/40	2QFY19	1.5E-04	1.8E-05	ND
HGV-11	0/100/0	2QFY19	1.3E-04	1.1E-05	ND
HGV-12	0/100/0	4QFY16	1.5E-04	1.1E-05	ND
HGV-13	10/45/45	2QFY19	ND	4.7E-06	ND
HGV-15	0/60/40	2QCY19	ND	7.5E-05	ND
ND = Not Detected			N/A = Not Applicable		

### Mercury Results

For this 1-hour test, seven of the eight reactors contained both sulfide and MeHg; the control HGV-7 only contained T50SS. A finite amount of methane was expected from all seven reactors. However, Figure 16 shows that no methane was detected in three of the seven reactors. Furthermore, the unknown was whether 1 hour was insufficient time for the grout pre-mix solids to leach out the sulfide and all of the MeHg to be consumed, as happened for the 24-hour test, see Table 12. That is, in the Phase 1, Test Series 1, with 100 mg/L MeHg, after 24 hours for reactors HGV-8, HGV-9, HGV-11, and HGV-12, which all had both MeHg and sulfide, 99%, or better, of the MeHg was removed. Table 17 indicates that the 1-hour duration was insufficient to consume the same amount of MeHg as over a 24-hour period. There was MeHg remaining between 21% to 73% of the initial concentration of 100 mg/L. It appears that some finite time is needed for the sulfide bound in the grout premix solids to leach into the T50SS and react with the MeHg to produce methane. For the reactor containing Na<sub>2</sub>S, i.e., HGV-8, the lack of measured MeHg, i.e., < 2 mg/L, was initially confusing, if combining that combining MeHg with sulfide directly becomes methane. Approximately 950 ppm of methane was measured from HGV-8 but this only represents approximately 17% of the moles of MeHg available. From the 24-hour test over 2500 ppm of methane was measured, Figure 8, which represented about 90% of the moles of MeHg that were available. However, the MeHg result may not be representative of the MeHg concentration when the liquid sample was pulled because the soluble sulfide could continue to react with the MeHg in the liquid T50SS sample while it was waiting to be analyzed.

As for the Phase-1 tests, what was surprising was that the total mercury was not affected from the presence of grout premix solids. Within measurement uncertainty of approximately 20 %RSD at a 95% confidence level, the measurements of total mercury from all the spike samples with 100 mg/L of MeHg indicates that the mercury remained soluble in the liquid, except for HGV-13. As previous explained, and shown as Figure 17(d), some of the T50SS did not enter the Teflon insert; therefore, it may have been excluded from the liquid sample taken from the filtered mixtures. This is probably the reason the total mercury measurement was 70 mg/L instead of being closer to the spiked concentration of 100 mg/L. The large amount of retained total mercury may be due to the high pH of the T50SS. From one source [6.9] it appears that as the pH of a mixture increases the solubility of mercury sulfide increases. All of the included tests purposely had a much larger amount of sulfide than the Hg or MeHg, so much of the sulfide was available



to combine with mercury and may be the reason the measured total mercury concentration was similar to the amount of mercury spiked into the simulant.

**Table 17. Phase 2, Test Series 1 gas generation rates**

Reactor or Simulant State	Tank 50 Simulant Type of Spike	Total Mercury (mg/L)	MeHg (mg/L)
Pre-test	No Spike	< 0.005	< 2
Pre-test	101.8 mg/L MeHg	105	104
HGV-7	No Spike	< 0.005	< 2
HGV-8	Na <sub>2</sub> S	103	< 2
HGV-9	MeHg + 10/45/45 (1)	102	73
HGV-10	MeHg + 0/60/40	104	38.6
HGV-11	MeHg + 0/100/0	103	24.9
HGV-12	MeHg + 0/100/0	104	21.5
HGV-13	MeHg + 10/45/45	70	56.5
HGV-14	N/A (2)	N/A	N/A
HGV-15	MeHg + 0/60/40	97	30.5
Post-test	101.8 mg/L MeHg	99	105
(1) MeHg = 101.8 mg/L methyl mercury and grout premix sequence is cement/BFS/fly ash.			
(2) HGV-14 was damaged during previous testing.			

## Appendix D. Slag Analyses

SRNL was directed to perform analysis of various slags related to toxicity testing associated with the Saltstone Disposition Facility (SDF) [6.11]. Various slags were analyzed by X-ray Diffraction (XRD) and dissolution followed by chemical analysis. [6.12]. The XRD shown in Figure 19 of Holcim slag indicates an amorphous material with no peaks due to any crystalline phase present. However, crystal patterns associated with both gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and limestone ( $\text{CaCO}_3$ ) are shown in both the 2016 Lehigh slag, Figure 20, and the 2018 Lehigh slag, Figure 21. These crystalline materials are known to be additives with slag at nominally 2 wt% mass content.

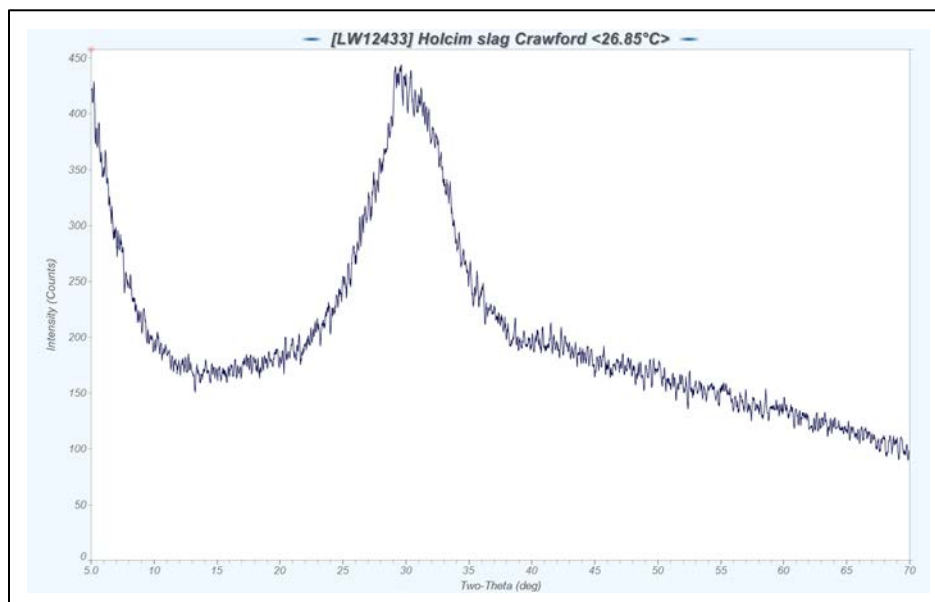


Figure 19. XRD Spectra for Holcim slag

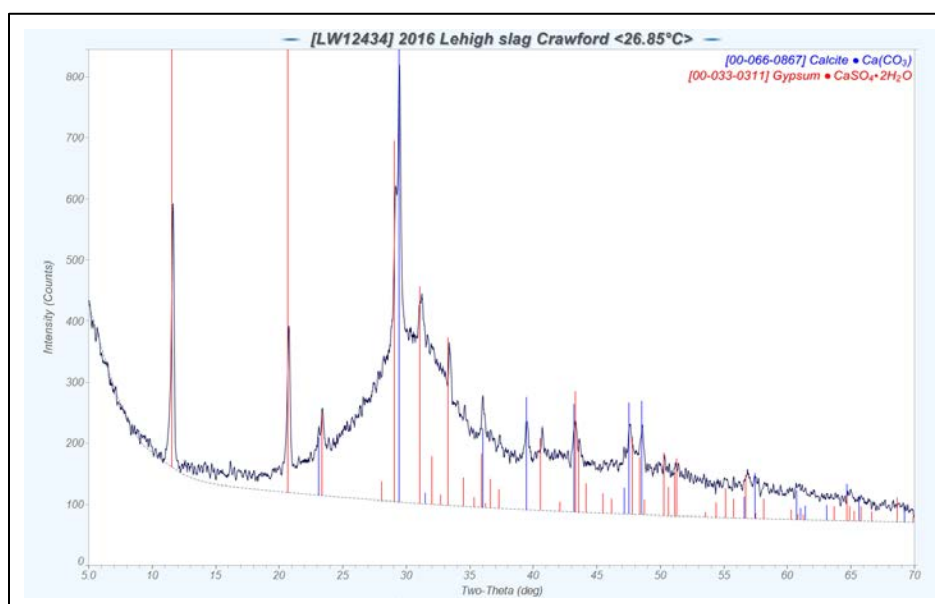
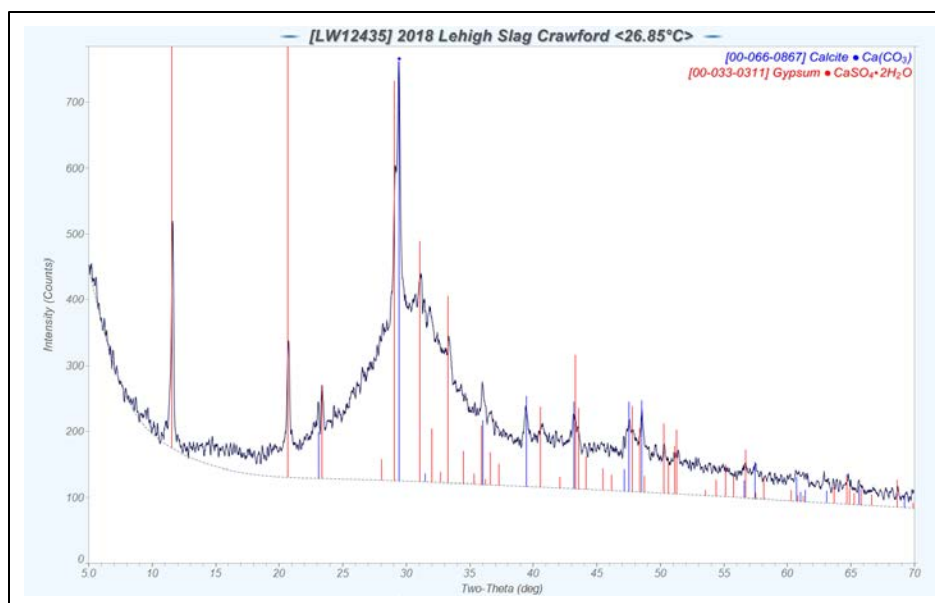


Figure 20. XRD Spectra for 2016 Lehigh slag



**Figure 21. XRD Spectra for 2018 Lehigh slag**

The same slags were dissolved and analyzed for elemental chemical content as shown in Table 18. The Ca and S amounts are higher for the gypsum/limestone containing slags. The Holcim slag contains  $0.80 \pm 0.003$  wt% S and the 2016 and 2018 Lehigh slags contain  $1.26 \pm 0.03$  wt% S and  $1.01 \pm 0.06$  wt% S, respectively. For the work in this report a sulfur concentration in slag of 1 wt% was employed.

**Table 18. Elemental Sulphur and Calcium Composition in Slag**

	Average Total S	Standard Deviation	%RSD
	wt%	wt%	
<b>Holcim Slag</b>	<b>0.80</b>	<b>0.003</b>	<b>0.36</b>
<b>2016 Lehigh Slag</b>	<b>1.26</b>	<b>0.027</b>	<b>2.14</b>
<b>2018 Lehigh Slag</b>	<b>1.01</b>	<b>0.055</b>	<b>5.44</b>

	Average Total Ca	Standard Deviation	%RSD
	wt%	wt%	
<b>Holcim Slag</b>	<b>23.45</b>	<b>0.188</b>	<b>0.80</b>
<b>2016 Lehigh Slag</b>	<b>28.02</b>	<b>0.222</b>	<b>0.79</b>
<b>2018 Lehigh Slag</b>	<b>26.69</b>	<b>0.501</b>	<b>1.88</b>

**Distribution:**

[matthew.alexander@srnl.doe.gov](mailto:matthew.alexander@srnl.doe.gov)  
[alex.cozzi@srnl.doe.gov](mailto:alex.cozzi@srnl.doe.gov)  
[charles.crawford@srnl.doe.gov](mailto:charles.crawford@srnl.doe.gov)  
[david.crowley@srnl.doe.gov](mailto:david.crowley@srnl.doe.gov)  
[jonathan.duffey@srnl.doe.gov](mailto:jonathan.duffey@srnl.doe.gov)  
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[charles.nash@srnl.doe.gov](mailto:charles.nash@srnl.doe.gov)  
[john.pareizs@srnl.doe.gov](mailto:john.pareizs@srnl.doe.gov)  
[frank.pennebaker@srnl.doe.gov](mailto:frank.pennebaker@srnl.doe.gov)  
[Amy.Ramsey@srnl.doe.gov](mailto:Amy.Ramsey@srnl.doe.gov)  
[William.Ramsey@SRNL.DOE.gov](mailto:William.Ramsey@SRNL.DOE.gov)  
[michael.restivo@srnl.doe.gov](mailto:michael.restivo@srnl.doe.gov)  
[michael.stone@srnl.doe.gov](mailto:michael.stone@srnl.doe.gov)  
[Boyd.Wiedenman@srnl.doe.gov](mailto:Boyd.Wiedenman@srnl.doe.gov)  
[Wesley.Woodham@srnl.doe.gov](mailto:Wesley.Woodham@srnl.doe.gov)

Records Administration (EDWS)

[Kevin.Brotherton@srs.gov](mailto:Kevin.Brotherton@srs.gov)  
[Austin.Chandler@srs.gov](mailto:Austin.Chandler@srs.gov)  
[bill.clark@srs.gov](mailto:bill.clark@srs.gov)  
[William.Condon@srs.gov](mailto:William.Condon@srs.gov)  
[jeffrey.crenshaw@srs.gov](mailto:jeffrey.crenshaw@srs.gov)  
[Richard.Edwards@srs.gov](mailto:Richard.Edwards@srs.gov)  
[Kenneth.Fernandez@srs.gov](mailto:Kenneth.Fernandez@srs.gov)  
[james.folk@srs.gov](mailto:james.folk@srs.gov)  
[eric.freed@srs.gov](mailto:eric.freed@srs.gov)  
[Curtis.Gardner@srs.gov](mailto:Curtis.Gardner@srs.gov)  
[Pauline.hang@srs.gov](mailto:Pauline.hang@srs.gov)  
[Thomas.Huff@srs.gov](mailto:Thomas.Huff@srs.gov)  
[john.iaukea@srs.gov](mailto:john.iaukea@srs.gov)  
[Vijay.Jain@srs.gov](mailto:Vijay.Jain@srs.gov)  
[Rudolph.jolly@srs.gov](mailto:Rudolph.jolly@srs.gov)  
[Jeremiah.Ledbetter@srs.gov](mailto:Jeremiah.Ledbetter@srs.gov)  
[Ryan.McNew@srs.gov](mailto:Ryan.McNew@srs.gov)  
[Anna.Murphy@srs.gov](mailto:Anna.Murphy@srs.gov)  
[tony.polk@srs.gov](mailto:tony.polk@srs.gov)  
[jeff.ray@srs.gov](mailto:jeff.ray@srs.gov)  
[Christine.Ridgeway@srs.gov](mailto:Christine.Ridgeway@srs.gov)  
[Anthony.Robinson@srs.gov](mailto:Anthony.Robinson@srs.gov)  
[kent.rosenberger@srs.gov](mailto:kent.rosenberger@srs.gov)  
[Azadeh.Samadi-Dezfouli@srs.gov](mailto:Azadeh.Samadi-Dezfouli@srs.gov)  
[mark-a.smith@srs.gov](mailto:mark-a.smith@srs.gov)  
[aaron.staub@srs.gov](mailto:aaron.staub@srs.gov)  
[patricia.suggs@srs.gov](mailto:patricia.suggs@srs.gov)  
[thomas.temple@srs.gov](mailto:thomas.temple@srs.gov)  
[steven.thomas@srs.gov](mailto:steven.thomas@srs.gov)  
[arthur.wiggins@srs.gov](mailto:arthur.wiggins@srs.gov)