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Methylmercury Speciation and Retention Evaluation to Support Saltstone Waste Acceptance Criteria

L.N. Oji

C.A. Langton

February 2019

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REVIEWS AND APPROVALS

AUTHORS:

____

L.N. Oji, SRNL, CPT-ACP Date

____

C.A. Langton, SRNL, SRNL-WPT Date

TECHNICAL REVIEW (per E-7 Procedure 2.60)

____

W.R. Wilmarth, SRNL-ESD Operations Date

APPROVALS:

____

B.J. Wiedenman, Manager, SRNL-CPT-ACP Date

____

S.D. Fink, Director, SRL-CPT Date

____

C.C. Herman, Associate Lab Director, SRNL-ES Date

PREFACE OR ACKNOWLEDGEMENTS

This task was performed with funding provided by DOE HQTD1002, Task 2.3.6: Develop organo-mercury based WAC for grout materials. Cementitious reagents were supplied by Savannah River Remediation, LLC Saltstone Facility.

EXECUTIVE SUMMARY

Mercury is a contaminant of concern in Savannah River Site (SRS) high level waste (HLW). For five decades elemental mercury was used in the catalytic dissolution of aluminum cladding from the enriched-alloy uranium recovery process. Over 60,000 kg of mercury are now distributed in the SRS HLW tanks. The mercury speciation in the liquid waste streams resulting from conditioning HLW sludge for vitrification and in the decontaminated low activity sodium salt solution removed from the tanks was initially thought to be primarily ionic with a minor amount of elemental mercury. Recent sampling detected organic mercury, primarily methylmercury, $HgCH_3^+$ ($MeHg^+$), and a trace amount of ethylmercury (EtHg) in these streams in addition to the ionic and elemental forms.

The objective of this work was to identify the fate of the organic mercury in saltstone, a waste form containing portland cement, slag cement, and Class F fly ash. This information is needed to evaluate total mercury and organic mercury limits for the saltstone Waste Acceptance Criteria to assure regulatory compliance with mixed waste disposal requirements and to evaluate opportunities to enhance the waste form performance.

X-ray diffraction and scanning electron microscopy/energy dispersive x-ray analysis results indicate that the $MeHg^+$ reacts with sulfide in the cementitious reagents to form nanoparticles of β-HgS, metacinnabar. The slag component of the cementitious reagents is the source of the sulfide which is released during hydration. HgS nanoparticles suggests great affinity between Hg and S and rapid reaction kinetics.

The solubility product of metacinnabar is very low, $pK_{sp} = 53$. Consequently, β-HgS is not expected to be solubilized by TCLP extraction fluid or saltstone pore solution or leachate, and complete reaction of the $MeHg^+$ with S^{2-} was expected. However, data obtained in this study indicate that leachates contained trace amounts of organic Hg. Incomplete reaction of organic Hg in saltstone may be the result of: (1) unknown side reactions, (2) depletion of sulfide ions in the waste form, (3) inaccessibility of sulfide due to reaction rims around the slag particles resulting in slow equilibrium kinetics, and / or (4) formation of other Hg phases which are more soluble.

Determination of the reaction pathway and fate of the methyl group is currently in progress. One of many possible reactions is shown in Equation 1. The fate of the methyl group was not determined in this study. However, methane, CH_4, was detected in a concurrent study to evaluate thermolytic hydrogen generation rate of saltstone containing Tank 50 salt solution containing organic mercury (e.g., MeHgOH).

Equation 1: $CH_3Hg(OH) + S^{2-} = HgS + CH_4 + \frac{1}{2} O_2$
Where sulfide ion, S^{2-}, is provided by hydration of the slag.

The task requested to be performed is summarized in the Work Authorization / Task Change Request (TCR) HQTD1002, Task 2.3.6: Develop organo-mercury based WAC for grout materials. This report addresses the first phase in the study.

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LIST OF ABBREVIATIONS

AD	(SRNL) Analytical Development
AFS	Atomic Fluorescence Spectroscopy
CM	Cementitious Materials
CVAA	Cold Vapor Atomic Adsorption
DOE-EM	United States Department of Energy – Environmental Management
DOE-EM-TD	USDOE-EM Technology Development
DSS	Decontaminated Salt Solution
EDX	Energy Dispersive X-ray Spectroscopy
ELN	Electronic Laboratory Notebook
EPA-SW	Environmental Protection Agency - Solid Waste
HQTD	Head Quarter Technology Development
LDR	Land Disposal Restrictions
LIMS	Laboratory Information Management System
LLW	Low level waste
MCU	Modular Caustic Side Solvent Extraction Unit
MeHg	Methylmercury
mmHg	Monomethyl mercury also known and MeHg
RCRA	Resource Conservation and Recovery Act
SDF	Saltstone Disposal Facility
SEM	Scanning Electron Microscope
SME	Sludge Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SPF	Saltstone Production Facility
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TCLP	Toxicity Characteristic Leaching Procedure
TRC	Technical Change Request
WAC	Waste Acceptance Criteria
WSRC	Westinghouse Savannah River Company
XRD	X-ray Diffraction

1.0 Introduction

The Saltstone Production Facility (SPF) receives and treats decontaminated mixed low-level waste (LLW) salt solution from Tank 50. The treatment consists of mixing the salt solution with cementitious materials, portland cement, slag, and fly ash, to produce a grout waste form which is pumped from the SPF to the Saltstone Disposal Facility (SDF) where it solidifies. The treatment results in solidifying corrosive salt solution with a pH > 12.5 and chemically stabilizing Cr and Hg, which are the Resource Conservation and Recovery Act (RCRA) regulated hazardous constituents in the solution. The mobility of radioactive contaminants in the waste is also reduced by microencapsulation and chemical stabilization.

To qualify for land disposal, saltstone must pass the RCRA Toxicity Characteristic Leaching Procedure requirements for RCRA metals. The current total mercury limit, 325 mg/L [1], was established experimentally based on experiments that involved ionic mercury, Hg^{2+} [2, 3]. Recently, organic mercury was detected in the Tank 50 decontaminated salt solution which is the feed to the SPF [4, 5]. Consequently, testing is underway to determine how organic mercury as methylmercury, $HgCH_3^+$, (referred to as $MeHg^+$) is stabilized in saltstone. This information will be used to determine whether it is necessary to update the total Hg limit or to add an organic Hg limit to the Tank 50 Waste Acceptance Criteria (WAC) to assure saltstone meets RCRA regulatory requirements [6].

The experimental objective of this task is to establish an experimental basis for the mercury limit (total and organic) in the Saltstone WAC. These objectives were addressed by measuring the retention of $HgCH_3^+$ ($MeHg^+$) and identifying the fate of the Hg^{2+} ion (i.e., phases responsible for stabilizing mercury in saltstone).

The task requested to be performed is summarized in the Work Authorization / Task Change Request (TCR) HQTD1002, Task 2.3.6: Develop organo-mercury based WAC for grout materials [9]. This report addresses the first phase in the study.

1.1 Background

The source of mercury in the SRS liquid waste tanks was mercuric nitrate used as a catalyst to dissolve aluminum during reactor assembly processing. As the waste was processed through the waste evaporators, mercury partitioned into the sludge solids due to the limited solubility in the concentrated high sodium alkaline waste stream. Formation of organomercury was originally thought to be limited to the evaporator system where organic antifoam agents were used. Cessation of antifoam additions to the evaporators removed this production source [14]. There is a possibility that methylation reactions are occurring in the H-Canyon waste receipt tank, Tank 39 [15].

In addition, based on analyses of the aqueous condensates in the Slurry Mix Evaporator Condensate Tank (SMECT), organic antifoaming agents used in sludge processing which are added to the Sludge Receipt and Adjustment Tank (SRAT) and Sludge Mix Evaporator (SME) appear to also have resulted in methylation of mercury in these condensates [7, 8]. This condensate is dispositioned to the Recycle Tank (RCT) and then sent to the 2H evaporator system where it is concentrated. This high Hg concentration and relatively high $MeHg^+$ salt solution/slurry in the RCT is used in salt batch preparation (e.g., to wash sludge batches). Decants from this washing are returned to the 3H Evaporator system. The evaporator concentrate solution, which is concentrated in Hg species, is incorporated in subsequent salt solution transfers during salt batch assembly. This practice has resulted in spreading $MeHg^+$ throughout the salt waste streams. Because very little $MeHg^+$ is removed by Modular Caustic Side Solvent Extraction Unit (MCU) [16], and little is expected to be removed in the Salt Waste Processing Facility (SWPF), $MeHg^+$ will remain in the decontaminated salt solution that is transferred to Tank 50 which is the feed tank to the SPF process.

The source and speciation of Hg in the H-Tank Farm are described in more detail elsewhere [7, 8]. Currently $MeHg^+$ makes up more than half of the total Hg in the Tank 50 waste solution. Between 2014 and 2017, the concentrations of $MeHg^+$ in Tank 50 ranged between 30 and 60 mg/L Hg compared to total Hg concentrations, which ranged from 70 to 105 mg/L [4]. See Figure 1-1.

The function of the cementitious materials used to make saltstone is to treat DSS to meet Land Disposal Restrictions (LDR) and thereby provide an acceptable path for disposal. The concentration of $Hg_{(total)}$ in the 1st quarter 2018 Toxicity Characteristic Leaching Procedure (TCLP) test is considerably higher than previously reported results. See Figure 2. Although still well below (about 10X below) the limit of 0.2 mg/L total Hg [9], this research was initiated to understand organic mercury speciation in saltstone.

The mechanism for Hg^{2+} stabilization was assumed to be reaction with S^{2-} resulting in precipitation as HgS [2, 3]. However, stabilization mechanisms for mixtures of ionic Hg and $HgCH_3^+$ may involve a combination of chemical sequestration and physical microencapsulation.

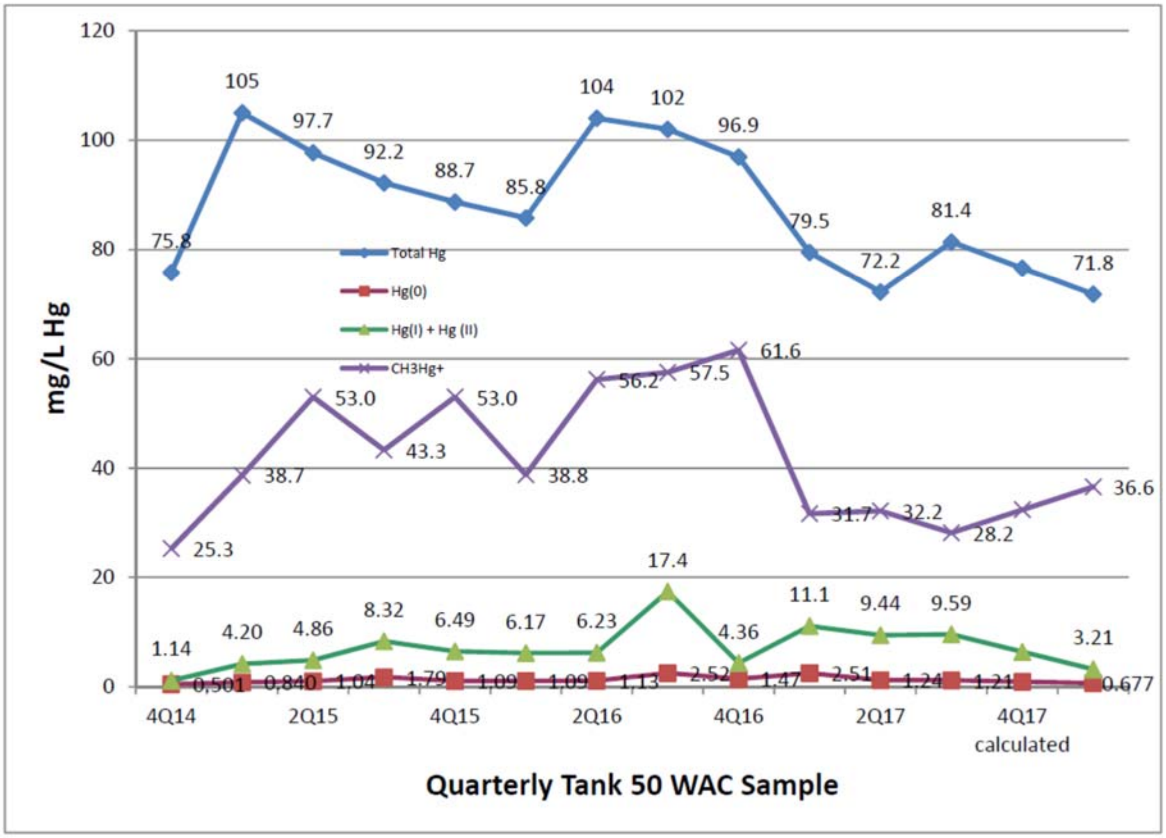

Figure 1-1. Summary of Hg species in Tank 50 quarterly analyses between 4Q 2014 and 1Q 2018 [6].

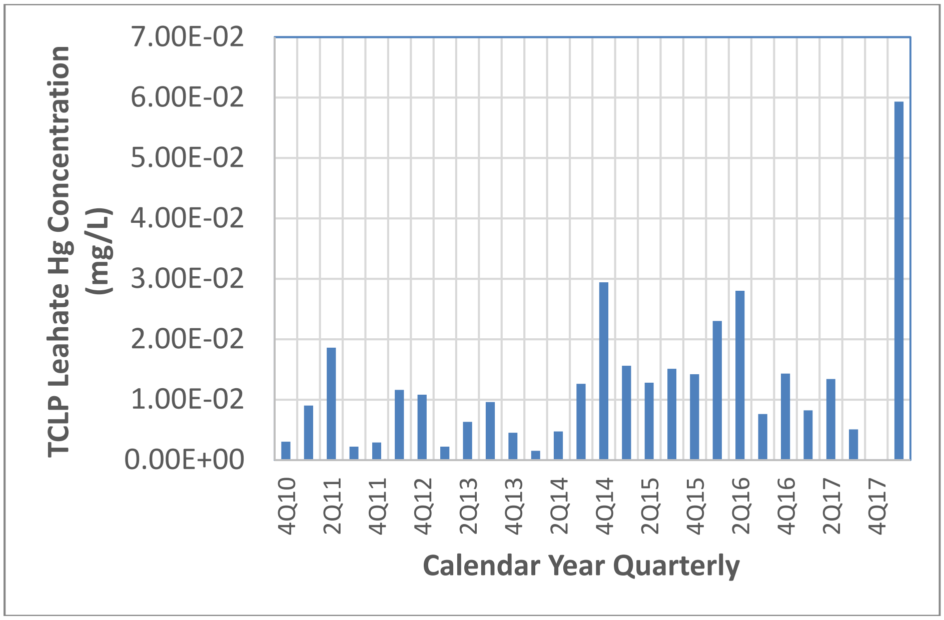

Figure 1-2. The TCLP results for saltstone samples prepared with quarterly Tank 50 samples [9]. The TCLP limit for Hg is 0.2 mg/L.

2.0 Experimental Procedure

2.1 Simulated Saltstone Preparation

2.1.1 Preparation of Saltstone Dry Reagents

Cement, slag and fly ash were obtained from the SPF and used to prepare 1500 g batches of premix in the following mass proportions 10:45:45. All ingredients were obtained from the Saltstone Facility in 2016 and are listed in Table 2-1. The resulting premix was mechanically mixed in a clear poly-bag for several minutes. Tank 50 simulant solution was prepared in 2L batches using the reagent chemicals and proportions shown in Table 2-1. The ingredients are listed in the order of addition used to prepare the simulant.

Table 2-1. Ingredients and proportions used to prepare saltstone in this study.

Component (from Z-Area 5-17-2016)	Weight of component (g)
Leigh Slag from Z-area	450
SEFA Flyash Class F*	450
Holcim Portland Type I/II Cement From Z-Area (5-17-2016)	100
Total premix sample weight	1000

* Fly ash was thermally fabricated via the STAR® process a thermal beneficiation process.

2.1.2 Simulated Solution Preparation

Tank 50 simulant solution was prepared in 2L batches using the reagent chemicals and proportions shown in Table 2-2. The ingredients are listed in the order of addition used to prepare the simulant salt solution which is based on the 3Q13 Tank 50 WAC analysis [17]. This simulant has been used as a standard composition for SRNL laboratory testing since that time.

Table 2-2. Ingredients and proportions in a 2L batches of simulated Tank 50 salt solution.

Reagent	Mass of component for 2 L batch (g)
DI Water	100.0
KNO_3	1.806
Na_2SO_4	14.916
DI Water	100.0
50 % NaOH solution	399.60
$Al(NO_3)_3 \cdot 9H_2O$	111.003
DI water	100.0
$Na_2PO_4 \cdot 12H_2O$	3.316
Na_2CO_3	42.011
DI water	100.0
$NaNO_3$	290.3
$NaNO_2$	62.968
DI Water	1140.4
Dissolved solids (mass %)	27.42
Water (mass %)	72.58
Specific gravity (measured)	1.2332

Methylmercury hydroxide 1.0 M aqueous solution procured from Alfa Aesar, Lot: N05C061, was used to spike four simulated solutions at the following concentrations: 0, 150, 250, and 500 mg/L. The mass of the MeHgOH stock solution needed for each spiked solution was calculated based on the density of the stock solution, 1.2 g/mL. See Tables 2-3 and 2-4.

Table 2-3. Preparation of methylmercury spiked simulated salt solutions.

MeHgOH Spiked Simulated Solutions (mg/L)	Target Mass of 1.0 M MeHgOH Solution for 1.0 L Spiked Salt Solution (g)	Actual Mass of $MeHg^+$ 1M Solution added to 1.0 L Spiked Salt Solution (g)
0	0	0
150	0.7738	0.7760
250	1.2896	1.2904
500	2.5792	2.5791

Table 2-4. SRNL analytical measurements for $MeHg^+$ in spiked salt solutions.

Spiked MeHgOH Salt Solution ID (mg/L)	$MeHg^+$ concentration SRNL AD analysis (mg/L)	Calculated MeHgOH concentration* (mg/L)
0	0	0
150	147	158.6
250	240	250.9
500	476	513.5

*Measurements were made using atomic fluorescence spectroscopy (AFS). The reported measurement uncertainty was ± 20 % for this method and applies to all AFS measurements reported in this study. The observed uncertainty in standard solutions used in this study was ± 5 %.

**Multiply cation concentration by a factor of 1.07 to calculate MeHgOH in spiked solutions.

2.1.3 Preparation of Simulated Saltstone

Saltstone was prepared from premixed cementitious reagents and spiked salt solutions. The batch size was 1300 g. The weight ratios of premixed cementitious reagents to salt solution were 55 and 45 wt.%, respectively. The water to cementitious materials (CM) mass ratio was 0.60. The premix was added to the salt solution and stirred for 5 minutes while maintaining a vortex in the slurry. The slurries were cast into 51 x 102 mm (2 x 4 inch) molds and 100 mL containers with lids and cured for a minimum of 28 days in sealed bags.

2.1.4 TCLP Extractions

The simulated salt solutions were spiked with 0, 150, 250, and 500 mg/L MeHgOH and were used to prepare saltstone samples as described above. The samples were cured for 28 days. The samples were prepared for the TCLP test by crushing them to three different particles sizes all of which passed through a 9.5 mm sieve.[a] Particle size of each spiked saltstone sample was varied to evaluate the effect of surface area on the fraction of $MeHg^+$ extracted. The sieve sizes for the fractions collected for TCLP testing are listed in Table 2-5. The size fractions were intended to provide information on retention mechanisms and were not intended to represent the size fraction used for regulatory compliance. The size fraction with the largest particles also had the largest range of particle sizes as shown in Figure 2-1.

Table 2-5. Sieve fractions used in the TCLP testing.

Designation	Sieve Fraction
Coarse	< 9.525 mm (-3/8 inch sieve and includes all fines generated by crushing)
Medium	4.0 to 0.6 mm
Fine	0.3 to 0.425 mm

The TCLP extractions were performed by SRNL Analytical Development (AD) personnel using a modified protocol of the EPA SW-1311 procedure. The modifications consisted of: (1) a smaller mass of material and a proportionate mass of leachate (1:20 waste form to leachate) and (2) varying the particle sizes of the crushed / ground material all of which passed through a 9.5 mm sieve. Duplicate 5-gram samples collected

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[a] The TCLP test specifies that monolithic samples to be crushed and passed through a 9.5 mm (0.375 inch) standard sieve.

from the crushed monoliths were sent for testing for each size fraction and each MeHgOH spike concentration.

Duplicate samples were analyzed for each size fraction and each MeHgOH waste loading. The TCLP extraction was performed in Teflon bottles with 100 mL of Extraction Fluid 2. After tumbling for 18 hours the extraction fluid was filtered through a 0.7 µm glass frit filter. $MeHg^+$ was the only Hg species analyzed in the filtered extraction fluid.

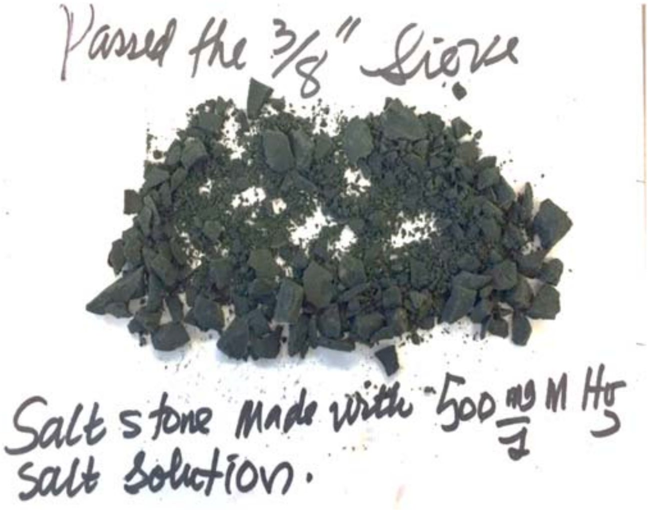


Figure 2-1. Photograph of material containing the largest size fraction (all crushed material passing through the 9.5 mm sieve.

2.1.5 $MeHg^+$ Liquid – Solid Partitioning

Saltstone containing no MeHgOH was cured for 28 days and then crushed to < 0.425 µm and 0.5 g was exposed to simulated salt solution spiked with 500 mg/L MeHgOH for 1, 7, 14, and 92 days to evaluate the partitioning between and reaction between saltstone and the soluble organic mercury as a function of time. This partitioning test was performed in glass containers which were completely filled with salt solution, approximately 40 ml of salt solution to eliminate head space. The saltstone mass to salt solution is about 80 times higher than that of saltstone. The samples were tumbled in a TCLP rotator for the times listed. At the end of each exposure time, the salt solution was filtered through 0.45 and 0.2 µm filters and analyzed for $MeHg^+$ using atomic fluorescence spectroscopy (AFS).

The filtered solids were also characterized using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). In addition, a control test was repeated with simulated salt solution spiked with 500 mg/L MeHgOH and no crushed solids to determine whether Hg or a Hg compound plated out on the sides of the container. This time for the control test was 26 days.

2.1.6 Monolith Batch Leaching Test

Monolith batch leaching was performed using a modified EPA SW-1315 protocol. Leachates were collected at 4 leach intervals (1, 7, 14 and 91 days). Duplicate saltstone samples were prepared with solutions containing 0, 150, 250, and 500 mg/L MeHgOH. The saltstone slurry was cast into 51.8 x 101.6 mm (2 x 4 inches) plastic molds and capped. After curing for 60 days, the monoliths were measured, and the leaching test was initiated. The surface area of each monolith was calculated and used to determine the volume of leachate for each sample. Deionized water was used as the leachate. See Table 2-6.

Table 2-6. Monolith dimensions used to calculate specimen surface areas and leachate volumes.

Sample ID*	Average Height (cm)	Radius ± 0.02 (cm)	Surface Area (cm^2)	Deionized Water Leachate Volume (mL)
0 mg/L mmHgOH-A	8.66 ± 0.01	2.55	179.65	176.95
0 mg/L mmHgOH-B	8.86 ± 0.02	2.56	182.06	183.49
150 mg/L mmHgOH-A	9.42 ± 0.02	2.56	192.30	193.26
150 mg/L mmHgOH-B	9.56 ± 0.02	2.56	194.70	196.40
250 mg/L mmHgOH-A	9.67 ± 0.01	2.51	191.20	191.99
250 mg/L mmHgOH-B	9.66 ± 0.07	2.54	196.25	195.00
500 mg/L mmHgOH-A	9.85 ± 0.12	2.55	201.28	198.71
500 mg/L mmHgOH-B	9.57 ± 0.26	2.57	198.88	196.24

*Original sample labels (mmHgOH) corresponde to revised designation MeHgOH.

2.2 Quality Assurance

The work outline and associated quality assurance requirements described in Technical Task and Quality Assurance Plan (TTQAP), SRNL-RP-2017-00721 have been met with this report.[13] 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. Results are recorded in ELN 258. SRNL AD data are documented in LIMS.

3.0 Results

3.1 Analysis of $MeHg^+$ Spiked Salt Solution

Simulated salt solutions spiked with methylmercury hydroxide were initially analyzed for total Hg by cold vapor atomic adsorption (CVAA). Permanganate was used to digest the sample. However, results were unexpectedly low compared to the values expected for the three MeHgOH spiked solutions. Subsequent leachate analyses were performed by atomic fluorescence spectroscopy method (AFS). Good agreement between spiked solution concentrations and measured $MeHg^+$ results were obtained were obtained for the AFS method. Results are presented in Table 3-1.

Table 3-1. Comparison of Hg analyses for MeHgOH spiked solutions.

Solution ID	SRNL AD AFS Measurement $MeHg^+$ (mg/L)	Calculated Equivalent MeHgOH (mg/L)	Calculated Equivalent Hg (mg/L)	SRNL AD CVAA Measurement Hg (mg/L)
0 MeHgOH	0	0	0	0
150 MeHgOH	147	158.6	136.8	117
250 MeHgOH	240	258.9	223.3	120
500 MeHgOH	476	513.5	442.8	283

*Multiply [$MeHg^+$] by 1.0788 calculate [MeHgOH]. Multiply [$MeHg^+$] by 0.9303 calculate [Hg].

Based on these results all subsequent analyses for samples spiked with only organic Hg were performed by the AFS method. At the time this study was performed, other forms of Hg as the result of chemical reactions between MeHgOH and ingredients in salt solution or saltstone were not anticipated and therefore not evaluated.

3.2 TCLP Results

Extracts from the TCLP test were filtered and analyzed for $MeHg^+$ using the SRNL AFS method. Analytical results were converted to total Hg values for comparison with the EPA limit. Results are presented in Table 3-2 and are plotted in Figure 3-1.

Table 3-2. TCLP Leachate results for saltstone made with simulated solution containing 150, 250, and 500 mg/L methyl mercury as methyl mercury hydroxide.

	Hg (mg/L) in TCLP Leachate			
Simulated Saltstone Sample ID	0.3 to 0.425 mm size fraction	0.6 to 4.0 mm Size fraction	< 0.375 inch < 9.525 mm	TCLP Limit
150 mg/L mmHgOH-1	0.221	0.150	0.157	0.2
150 mg/L mmHgOH-2	0.231	0.145	0.172	0.2
250 mg/L mmHgOH-1	0.510	0.295	0.190	0.2
250 mg/L mmHgOH-2	0.552	0.309	0.219	0.2
500 mg/L mmHgOH-1	1.228	0.589	0.416	0.2
500 mg/L mmHgOH-2	1.226	0.633	0.444	0.2

Red values are above the TCLP limit and samples are characteristically hazardous for Hg. Green values are less than the TCLP limit and samples do not display the characteristic of Hg toxicity.

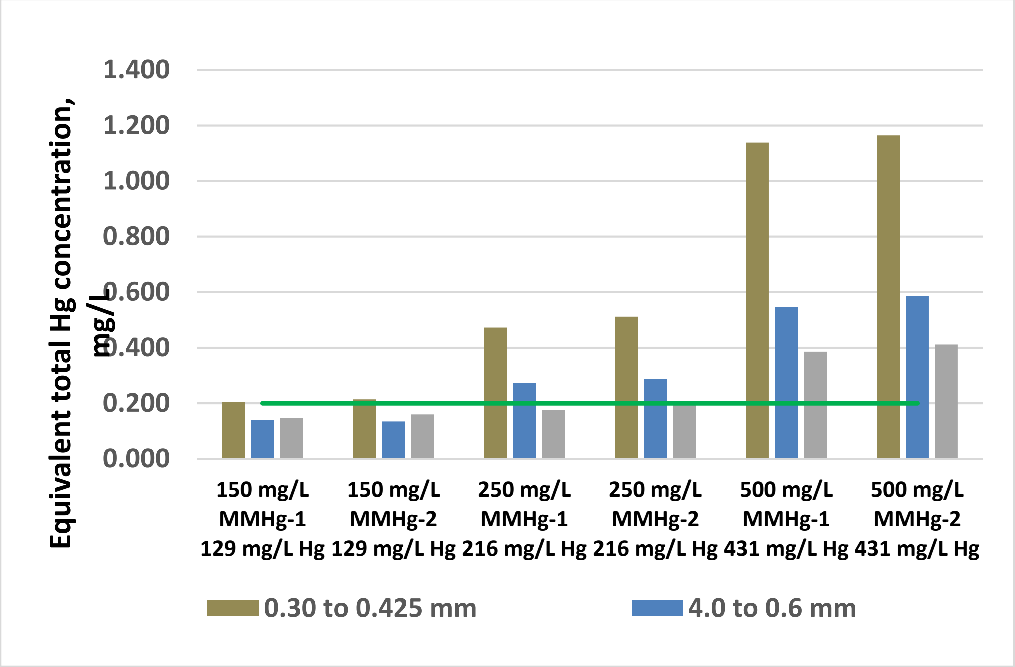


Figure 3-1. Total Hg in TCLP leachates calculated from $MeHg^+$ analyses.

3.3 MeHgOH Liquid – Solid Partitioning

$MeHg^+$ partitioning between spiked salt solutions and cured saltstone was evaluated as a function of exposure time and MeHgOH concentration in the solution. AFS results for $MeHg^+$ in the spiked solutions after contacting the crushed saltstone were converted to equivalent MeHgOH values and presented in Table 3-3. The MeHgOH mass percentages removed from solution are listed in Table 3-4 and plotted in Figure 3-2.

Table 3-3. Calculated MeHgOH concentrations in simulated salt solution after exposure to 0.5 g of crushed saltstone.

Spike Salt Solution ID	Total MeHgOH in Spiked Solution per AD analyses (mg)	MeHgOH removed from Solution per 0.5 g Crushed Saltstone* (mg)			
		1 day	7 days	14 days	92 days
150 MeHgOH	6.66	6.01	6.59	6.46	6.16
250 MeHgOH	10.87	7.06	10.16	10.57	10.32
500 MeHgOH	21.57	7.76	9.83	12.57	14.80

Table 3-4. Mass Percent MeHgOH removed from soltuion as a function of exposure time and initial concentration in solution.

Spike Salt Solution ID	% MeHgOH removed from Solution per 0.5 g Crushed Saltstone			
	1 day	7 days	14 days	92 days
150 MeHgOH	89.97	99.07	97.00	95.98
250 MeHgOH	64.44	84.55	98.85	95.98
500 MeHgOH	36.55	46.11	59.03	69.43

* Multiply $MeHg^+$ by 1.07 to calculate MeHgOH listed in Table 3-4.

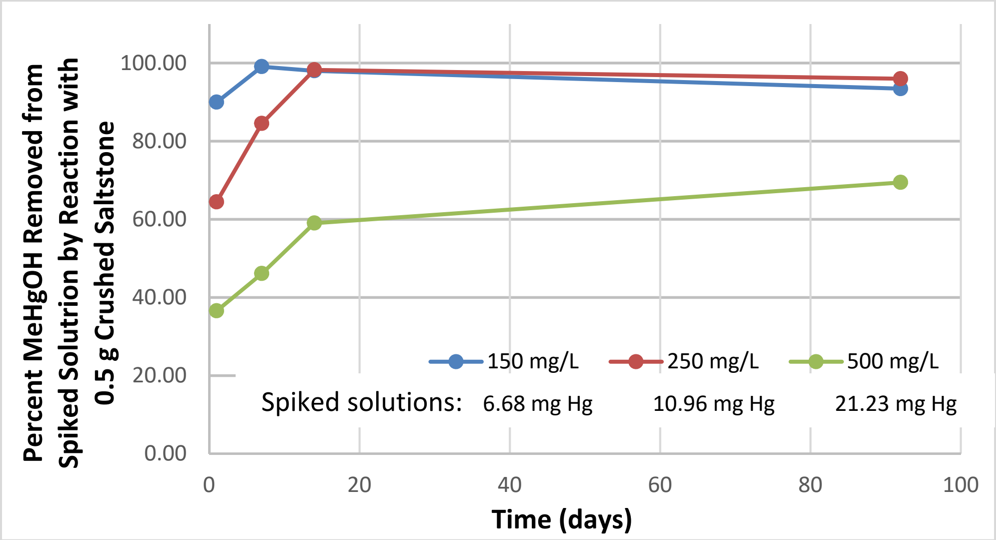


Figure 3-2. Percent MeHgOH removed from salt solution by 0.5 g of crushed saltstone as a function of time and spike concentration.

3.4 Saltstone Monolith Leaching

Leachates were collected from saltstone monoliths spiked with 150, 250 and 500 mg/L MeHgOH at four separate time intervals. Duplicate samples were tested. The leaching liquid (deionized water) was changed at each sampling interval. Results are tabulated in Table 3-5 and plotted as log values in Figure 3-3. The slope of the trendlines for the log values indicates that the diffusion is not the only mechanism controlling release of $MeHg^+$ from the simulated waste forms. These results indicate precipitation of an insoluble or a low solubility Hg phase in the saltstone matrix. If all the $MeHg^+$ was precipitated at the time the first leachates were collected and if the Hg remained insoluble for the length of the test (91 days), the trendlines would be horizontal.

Table 3-5. MeHgOH leachate concentrations results for EPA Method 1315 deionized water leachates (changed after each leach interval.

	Leaching time (days)	Calculated MeHgOH in Leachate (mg/L)	MeHgOH Leached per Sample Surface Area (mg/m^2)	∑MeHgOH released per Sample Surface (mg/m^2)
150 mg/L MeHgOH-A	1	16.94	1694.00	1694.00
	7	1.60	159.67	1853.67
	14	3.72	372.21	2225.88
	92	2.21	221.17	2447.05
150 mg/L MeHgOH -B	1	14.89	1489	1489
	7	1.35	134.86	1623.86
	14	2.64	264.32	1888.18
	92	2.06	206.06	2094.24
250 mg/L MeHgOH -A	1	89.65	8965.00	8965.00
	7	40.35	4034.97	12999.97
	14	4.96	496.28	13496.25
	92	3.61	361.42	13857.68
250 mg/L MeHgOH -B	1	94.29	9429.00	9429.00
	7	39.59	3959.45	13388.45
	14	4.10	409.97	13798.42
	92	3.79	378.68	14177.11
500 mg/L MeHgOH -A	1	325.82	32582.00	32582.00
	7	269.72	26971.75	59553.75
	14	210.38	21037.97	80591.72
	92	4.09	408.89	81000.61
500 mg/L MeHgOH -B	1	325.82	32582.00	32582.00
	7	187.71	18771.13	51353.13
	14	210.38	21037.97	72391.09
	92	4.44	444.49	72835.59

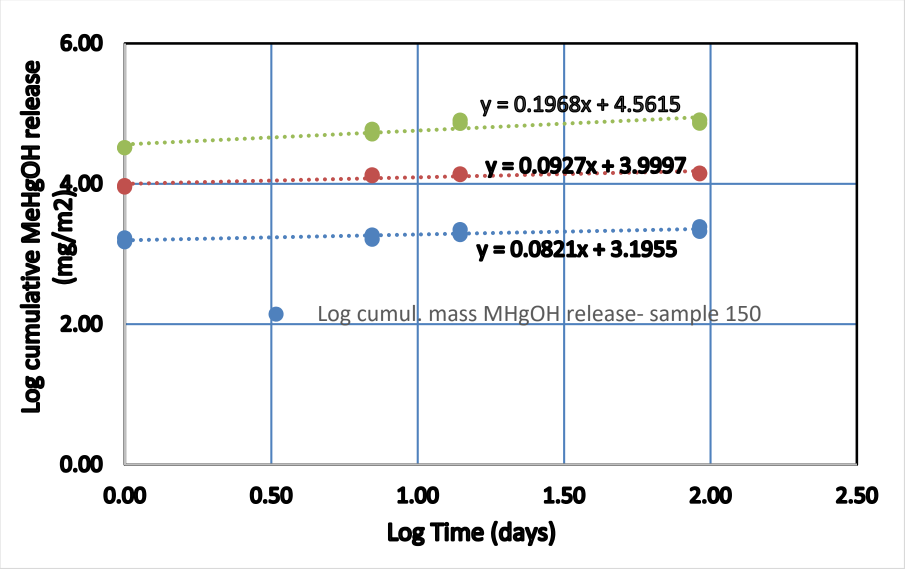


Figure 3-3. MeHgOH concentrations in leachates of modified EPA Method 1315.

4.0 Discussion

4.1 Hg analysis

Analysis of waste salt solutions, sludges, and leachates for total Hg and organic Hg species were performed by several different techniques coupled with different sample preparation/digestion methods. Multiple laboratories are currently engaged in analyzing SRS tank waste and TCLP leachates for total Hg and ionic, organic, and elemental Hg. See Table 4-1.

CVAA with $KMnO_4$ digestion and nitric acid dilution was shown in this study (stock solution analyses) to under report total mercury when methylmercury is a species in the sample matrix. If this method is used for total Hg when methylmercury is suspected to be present, control samples containing known concentrations of organic Hg and mixtures of ionic and organic Hg are warranted and aqua regia sample digestion is recommended [18].

Table 4-1. List of Hg analyses used for liquid and solid samples

Total Hg	Laboratory	Cautions
$KMnO_4$ digestion Cold Vapor atomic adsorption (CVAA)	SRNL AD SWRI	Incomplete digestion/oxidation (Potential for low totals) Large dilution
Aqua Regia digestion Cold Vapor atomic adsorption (CVAA)	SRNL	Good digestion Large dilution
Atomic Adsorption-Direct Hg Analyzer Milestone Model DMA80	SRNL	No digestion required. Dilution may be necessary. Low total concentrations required.
Hg Speciation	**Laboratory**	**Cautions**
Atomic Fluorescence Spectroscopy (AFS)	SRNL	Methylmercury reported as Hg Results agree with control concentrations
Up to 7 different speciation methods	EUROFINS	Large dilution

4.2 Reaction between MeHg$^+$ and Saltstone

Reactions between MeHg$^+$ in saltstone spiked with solution containing MeHgOH (Figure 4-1), and between MeHgOH spiked salt solution and saltstone premixed reagents (Figure 4-2) were evaluated by: 1) X-ray diffraction, 2) energy dispersive X-ray spectroscopy of high atomic weight particles in scanning electron microscope (SEM) images, and 3) leaching and liquid solid partitioning methods.

Mercury sulfide was identified by EDX spectra of bright (high atomic mass elements) nano particles (Figure 4-2). The atomic ratios of S and Hg for in these spectra were about 1:1 which corresponds to HgS. SEM and EDX results are provided in Figure 4-2. This phase was identified as metacinnabar, β-HgS in the XRD pattern for a crushed saltstone monolith sample exposed to simulated salt solution spiked with 500 mg/L MeHgOH. The XRD pattern is provided in Figures 4-3.

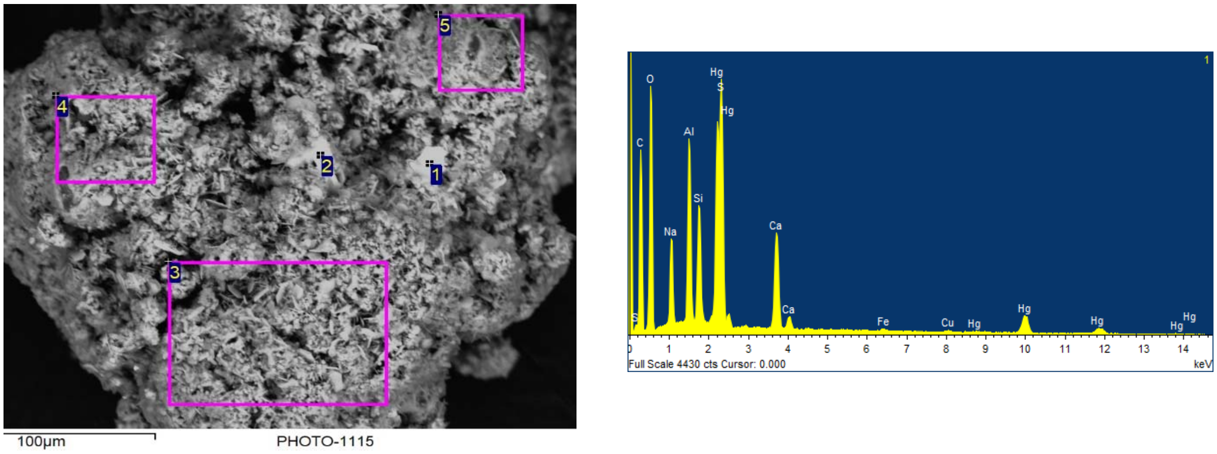
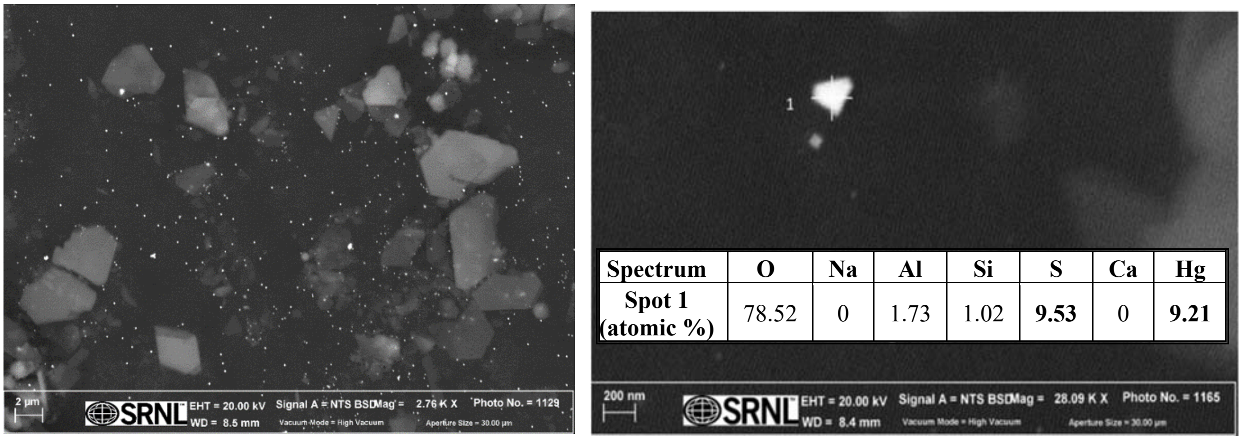


Figure 4-1. Left: sample of fractured surface of crushed saltstone spiked with salt solution containing 500 m,g/L MeHgOH. Right: Spectrum of bright spot (1) showing an area coated with HgS.



Spectrum	O	Na	Al	Si	S	Ca	Hg
Spot 1 (atomic %)	78.52	0	1.73	1.02	**9.53**	0	**9.21**

Figure 4-2. Left: Dispersed particles of crushed saltstone exposed to solution containing 500 mg/L MeHg$^+$ (Bright particles are HgS). Right: Large nanoparticle of HgS with chemical composition determined by EDX represented as atomic percent.

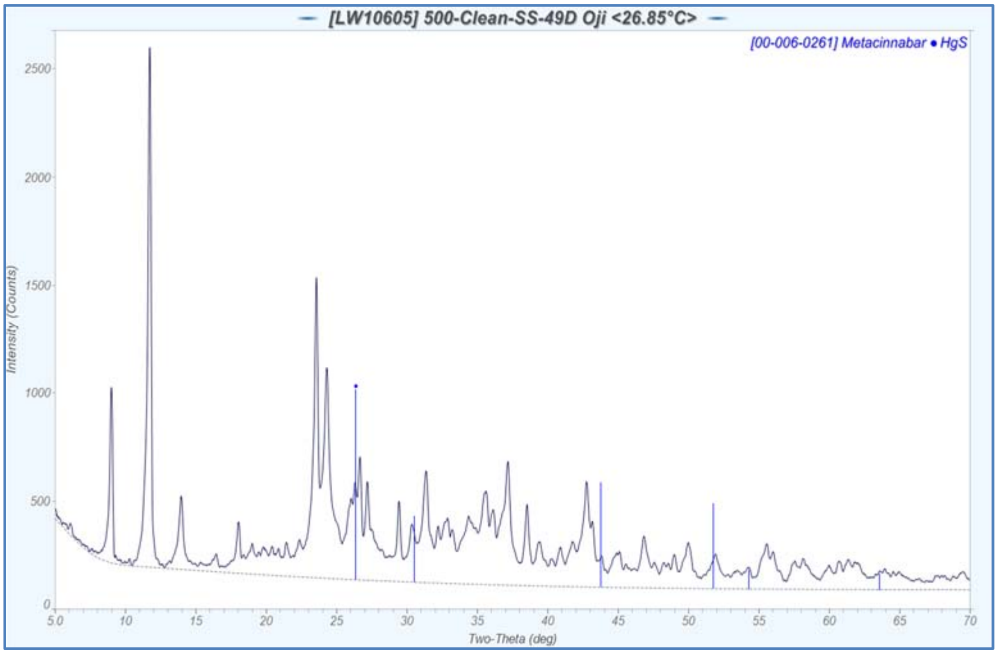


Figure 4-3. Metacinnabar, β-HgS, peaks identified in XRD pattern of crushed saltstone exposed to simulated salt solution containing 500 mg/L MeHgOH.

5.0 Conclusions

Based on identification of the solid mercury phase in crushed saltstone exposed to MeHgOH spiked salt solutions and in monolithic saltstone samples made with MeHgOH spiked salt solutions, precipitation of metacinnabar, β-HgS, was identified as the stabilization mechanism of organic mercury in saltstone. Determination of the reaction pathway and fate of the methyl group is currently in progress. One of many possible reactions is shown in Equation 1. The fate of the methyl group was not determined in this study. However, methane, CH_4, was detected in a concurrent study to evaluate thermolytic hydrogen generation rate of saltstone containing Tank 50 salt solution containing organic mercury (e.g., MeHgOH) [12].

Equation 1: $CH_3Hg(OH) + S^{2-} = HgS + CH_4 + \frac{1}{2} O_2$
where sulfide ion, S^{2-}, is provided by hydration of the slag

Results from the modified TCLP extraction experiment indicate:

(1) Most but not all the $MeHg^+$ was chemically stabilized (not leachable) after curing for 28 days for samples containing simulated salt solution with 150 mg/L MeHgOH;
(2) The concentration of Hg extracted in leachates increased as the concentration of $MeHg^+$ in the simulated salt solution used to prepare the saltstone sample increased. The higher the MeHgOH concentration, the more $MeHg^+$ extracted.
(3) The amount of Hg extracted from the simulated saltstone was a function of particle size which indicates that microencapsulation in addition to chemical stabilization is a mechanism for sequestering organic Hg. The finest particle size fraction (0.3 to 0.425 mm) had the highest concentration of $MeHg^+$ in the extract solution.
(4) $MeHg^+$ was the primary Hg species extracted in the leachates generated in this study. This finding is consistent with TCLP leachates analyses of saltstone samples made with Tank 50 solution [10].

These results are not intended for regulatory compliance use because the TCLP protocol was modified. Solid-liquid partitioning experiments were performed in parallel with the TCLP extraction tests. Results indicate removal of $MeHg^+$ from salt solution by contact with saltstone occurred during setting and early curing of the matrix (1 to 7 day). Samples made with 500 mg/L MeHgOH spiked salt solution continue to react with $MeHg^+$ to form more insoluble HgS over the 91-day test period. The amount of Hg removed increases as a function of spike concentration. Over 99 % after exposure for 7 and 14 days contact time for the solutions spiked with 150 and 250 mg/L MeHgOH, respectively. Ninety six percent of the Hg was removed from solution after 91 days of continuous contact for both of these MeHgOH concentrations. The amount of $MeHg^+$ removed from to salt solution spiked with 500 mg/L MeHgOH continued to increase from 37 to 69 percent over the entire exposure period of 91 days.

The solubility product of metacinnabar is very low, $pK_{sp} = 53$ [11]. Consequently, complete reaction of the $MeHg^+$ with S^{2-} was expected. However, results indicate that leachates contained trace amounts of organic Hg. Incomplete reaction of organic Hg in saltstone may be the result of unknown side reactions or due to depletion in available sulfide and slow kinetics. Hydration rims on slag particles may restrict continued slag hydration which releases sulfide and thereby reduce the amount of sulfide available for HgS precipitation. Evidence for kinetic effects being responsible for incomplete organic Hg reaction include the continued slow reduction in extractable Hg over 91 days for the sample containing the highest $MeHg^+$ concentration.

The slag component of the cementitious reagents is the source of the sulfide which releases during hydration. In addition, formation of HgS nanoparticles suggests great affinity between Hg and S and rapid reaction kinetics. β-HgS is not expected to be solubilized by TCLP extraction fluid or saltstone pore solution or leachate. Therefore, factors that limit complete precipitation of the $MeHg^+$ in saltstone samples prepared for the TCLP test may include: limited amount of sulfur/sulfide initially available to react with Hg species in the premix components and limited longer term availability of sulfide due to hydration rims on slag particles as hydration progresses.

6.0 References

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Distribution:

timothy.brown@srnl.doe.gov
alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
erich.hansen@srnl.doe.gov
connie.herman@srnl.doe.gov
daniel.mccabe@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
geoffrey.smoland@srnl.doe.gov
boyd.wiedenman@srnl.doe.gov
bill.wilmarth@srnl.doe.gov
patricia.suggs@srs.gov
Austin.Chandler@srs.gov
Kevin.Brotherton@srs.gov
Richard.Edwards@srs.gov
eric.freed@srs.gov
john.iaukea@srs.gov
Vijay.Jain@srs.gov
Victoria.Kmiec@srs.gov
aaron.staub@srs.gov

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