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Mercury Speciation and Stabilization in Saltstone 19103

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ABSRTACT

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 stored 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. Results to date indicate that the $MeHg^+$ reacts with sulfide in the cementitious reagents, slag in particular, to for nanoparticles of β-HgS, meta cinnabar which is very insoluble and has a solubility product in water, pK_{sp}, at 25° C of 53.

INTRODUCTION

The Saltstone Production Facility (SPF) receives and treats decontaminated mixed low-level waste (LLW) salt solution from Tank 50-H. The treatment consists of mixing the salt solution with cementitious matierals; portland cement, slag, and fly ash, to form 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/or chemical stabilization.

To qualify for land disposal, saltstone must pass the RCRA Toxicity Characteristic Leaching Procedure requirements for Cr and Hg. The current total mercury limit, 325 mg/L [1], was established experimentally base 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, $HgCH_3^+$, is stabilized in saltstone. This information will be used to determine whether it is necessary to update the total Hg limit and/or add an organic Hg limit to the Tank 50 Waste Acceptance Criteria (WAC) to assure saltstone meets RCRA regulatory requirements.

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 $HgCH_3^+$ ($MeHg^+$), identifying the fate of the Hg^{2+} ion, i.e., phases responsible for stabilizing mercury in saltstone.

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. There is a possibility that methylation reactions are occurring in the H-Area waste receipt tank.

In addition, based on analyses of the aqueous condensates in the Slurry Mix Evaporator Condensate Tank (SMECT), organic antifoaming agents used in sludge processing (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 Tank 22 and then sent to the 2H evaporator system where it is concentrated. This high Hg and relatively high $MeHg^+$ salt solution/slurry in Tank 22 are used in salt batch preparation, e.g., to wash sludge batches. Decants from this washing were 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 has resulted in spreading $MeHg^+$ throughout the salt waste streams. Because very little $MeHg^+$ is removed by Modular Caustic Side Solvent Extraction Unit (MCU) and little is expected to be removed in the SWPF, $MeHg^+$ will remain in the decontaminated salt solution that is transferred to Tank 50 which is the feed tank to the saltsotne process.

The source and speciation of Hg in the H-Tank Farm is 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 $HgCH_3^+$ in Tank 50 ranged between 30 and 60 mg/L Hg compared to total Hg concentrations, 70 to 105 mg/L [4]. See Figure 1.

Mercury stabilization is one function of the saltstone waste form. The concentration of $Hg_{(total)}$ in the 1st quarter 2018 Toxicity Characteristic Leaching Procedure (TCLP) test is considerably higher than previously reported results but still well below (about 10X below) the limit of 0.2 mg/L total Hg [9]. See Figure 2.

Based on previous work, the mechanism for Hg^{2+} stabilization was assumed to be chemical reduction and precipitation as HgS. However, stabilization mechanisms for mixtures of ionic Hg and $HgCH_3^+$ may involve a combination of chemical sequestration and physical microencapsulation.

EXPERIMENTAL PROCEDURE

Simulated Saltstone Preparation

Cement, slag and fly ash were obtained from the Saltstone Facility 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 1. The resulting premix were 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.

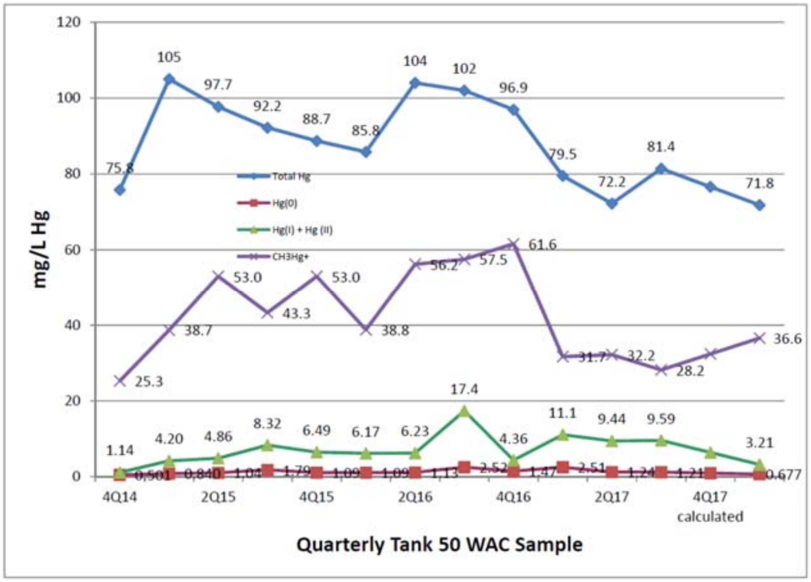


Figure 1. Summary of Hg species in Tank 50 quarterly analyses between 4Q 2014 and 1Q 2018 [4].

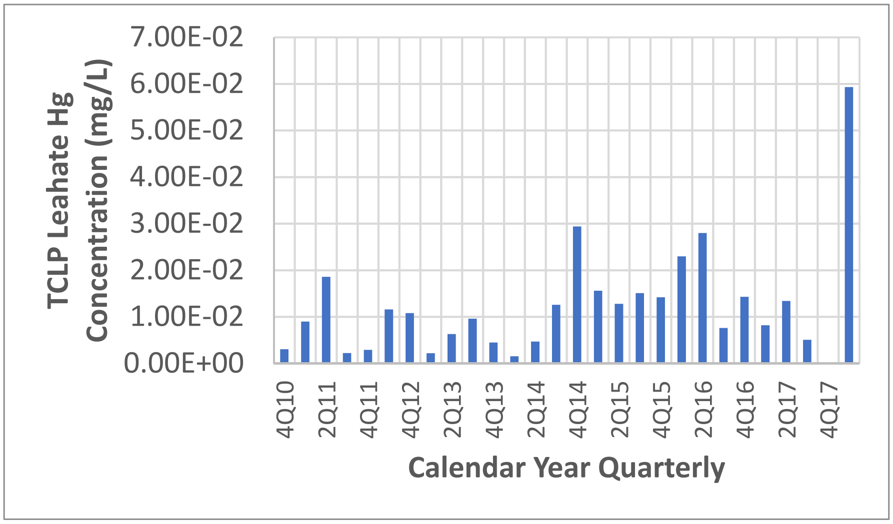


Figure 2. The TCLP results for saltstone samples prepared with quarterly Tank 50 samples [9]. The TCLP limit for Hg is 0.2 mg/L.

Table 3. Cementitious ingredients used to prepare simulated saltstone.

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	100
Total premix sample weight	1000

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

Table 4. 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 solution was purchased and used to spike four simulated solutions at the following concentrations: 0, 150, 250, and 500 mg/L. The mass of the mmHg stock solution needed for each spiked solution was calculated based on the density of the stock solution, 1.2 g/ml. See Tables 3 and 4.

Table 5. Preparation of methylmercury spiked simulated salt solutions.

MeHg(OH) Spiked Simulated Solutions (mg/L)	Target Mass of 1.0 M MeHg(OH) 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 6. SRNL analytical measurements for MeHg in spiked salt solutions.

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

*Multiply cation concentration by 1.07 to calculate MeHg(OH) in spiked solutions.

Saltstone was prepared from premixed cementitious reagents and spiked salt solutions in 1300 g batches. The weight ratios of premixed cementitious reagents to salt solution were 55 and 45 wt.%, respectively. The water to cementitious materials (CM) 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.

Simulated salt solutions were spiked with 0, 150, 250, and 500 mg/L MeHgOH and used to prepare saltstone samples which were cured for 28days. The samples were prepared for the TCLP test by crushing them to 3 different particles sizes all of which passed through a 9.5 mm sieve. 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 5. Testing three different particles sizes is a variation of the TCLP protocol which specifies that samples be size reduced such that they pass through a 9.5 mm (0.375 inch) standard sieve.

Table 7. 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 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, i.e. 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. A 5-gram sample of collected from a crushed monolith was sent to SRNL AD for testing for each size fraction and each MeHgOH spike.

Duplicate samples were run for each size fraction and each MeHgOH waste loading. The TCLP extraction was performed in a poly bottle and 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.

$MeHg^+$ Liquid – Solid Partitioning

Saltstone containing no MeHgOH was 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 saltstone and soluble organic mercury as a function of time. This partitioning test was performed in glass containers which were completely filled with salt solution. The samples were tumbled in a TCLP rotator for the times listed. Due to the SRNL Safety Pause, no samples were collected between 14 and 92 days. At the end of each exposure time, the salt solution was filtered through 0.45 and 0.2 µm filters and analyzed for $MeHg^+$ by SRNL AD personnel using atomic fluorescence spectroscopy (AFS).

The filtered solids were also characterized using SEM and 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 MeH compound plated out on the sides of the container. This time for the control test was 26 days.

Monolith Batch Leaching Test

Monolith batch leaching was performed using a modified EPA SW-1315 protocol. Leachates were collected at only 4 leach intervals (1, 7, 14 and 91 days) due to the 2018 SRNL-wide Safety pause. Duplicate saltstone samples were prepared with solutions containing 0, 150, 250, and 500 mg/L

MeHgOH. The saltstone slurry was cast into 2 x 4 inches (51.8 x 101.6 mm) plastic molds and capped. After curing for 60 days (earliest time samples could by demolded due to the safety pause), the monoliths were measured, and the leaching test was initiated. The surface area of each monolith was claculated and used to determine the volume of leachate for each sample. Deionized water was used as the leachate. See Table 6.

Table 8. Monolith dimensions used to calculate specimen surface areas and leachahte volumes.

Sample ID*	Average Height (cm)	Radius ± 0.02 (cm)	Surface Area (cm^2)	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 correspondes to revised designation MeHgOH).

RESULTS

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). However, results were unexpectedly low compared to the values expected for the three MeHg(OH) spiked solutions. Because the mercury was added to the salt solutions as MeHgOH, total Hg leached was assumed to be equivalent to organic mercury leached and subsequent 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 7.

Table 7. 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	158.59	136.75	117
250 MeHgOH	240	258.92	223.26	120
500 MeHgOH	476	513.53	442.81	283

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 MeHg(OH) and ingredients in salt solution or saltstone were not anticipated and therefore not evaluated.

TCLP Results

Extracts from the TCLP test were filtered and analyzed for $MeHg^+$ using the SRNL AFS method. This analytical method was selected because it provided analyses that best matched the concentrations in the initial spiked salt solutions. Analytical results were converted to total Hg values for comparison with the EPA limit. Results are presented in Table 8 and are plotted in Figure 3.

Table 8. 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	EPA TCLP Limit
150 mg/L MeHgOH-1	0.221	0.150	0.157	0.2
150 mg/L MeHgOH-2	0.231	0.145	0.172	0.2
250 mg/L MeHgOH-1	0.510	0.295	0.190	0.2
250 mg/L MeHgOH-2	0.552	0.309	0.219	0.2
500 mg/L MeHgOH-1	1.228	0.589	0.416	0.2
500 mg/L MeHgOH-2	1.226	0.633	0.444	0.2

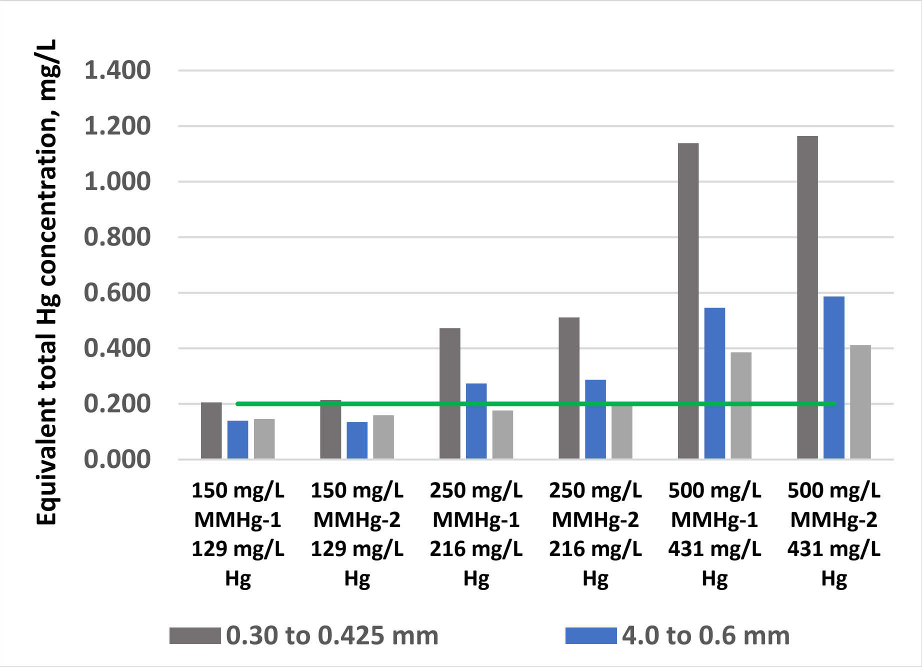


Figure 3. Total Hg in TCLP leachates calculated from $MeHg^+$ analyses.

MeHg(OH) Liquid – Solid Partitioning

MeHg+ partaitionng 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 9 and plotted in Figure 4. The MeHgOH mass percentages removed from solution are listed in Table 10 and plotted in Figure 5.

Table 9. Calculated MeHgOH concentrations in simulated salt solution after exposure to 0.5 g of crushed saltstone.

Spike Salt Solution ID	Total Hg in Solution	Equivalent MeHg(OH) 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

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

Table 10. Mass Percent MeHgOH removed from soltuion as a function of exposure time and initial concentration in solution.

Spike Salt Solution ID	% MeHg(OH) 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

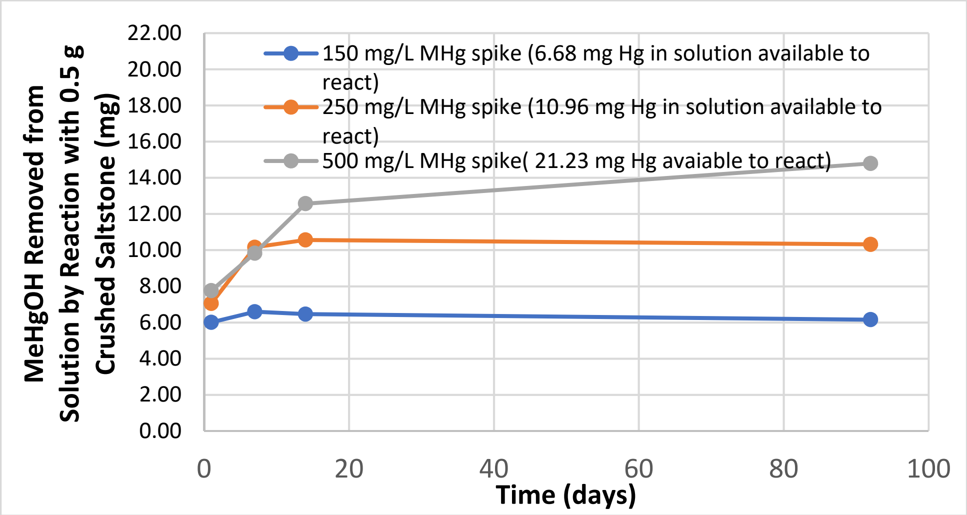


Figure 4. MeHgOH removed from salt solution by 0.5 g of crushed saltstone as a function of time and spike concentration.

Saltstone Monolith Leaching

Leachates were collected from saltstone moliths spiked with 150, 250 and 500 mg/L MeHgOH at 4 separate time intervals. Duplicate samples were tested. Results are tabulated in Table 11.

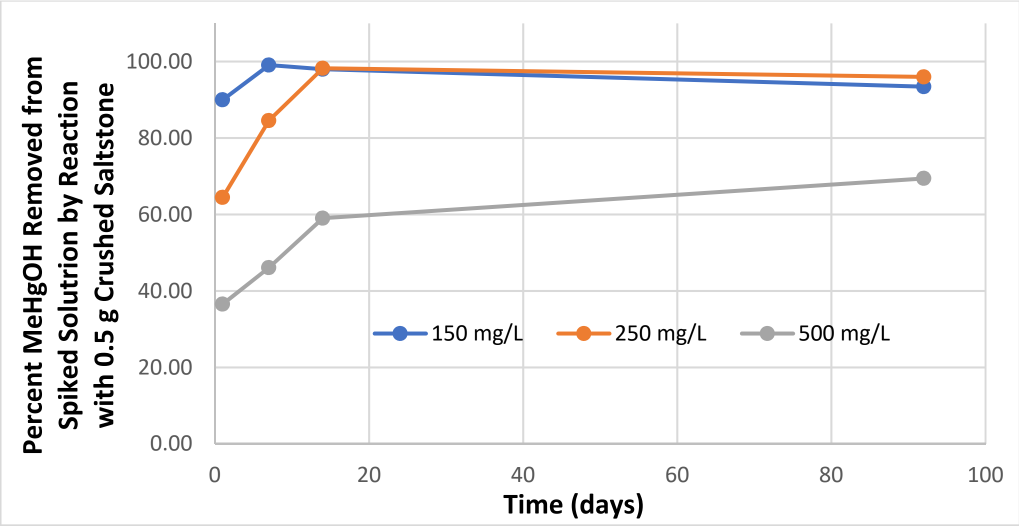


Figure 5. Percent MeHgOH removed from salt solution by 0.5 g of crushed saltstone as a function of time and spike concentration.

Table 11. MeHgOH results in Leach Method 1315 leachates.

	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	1.6	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

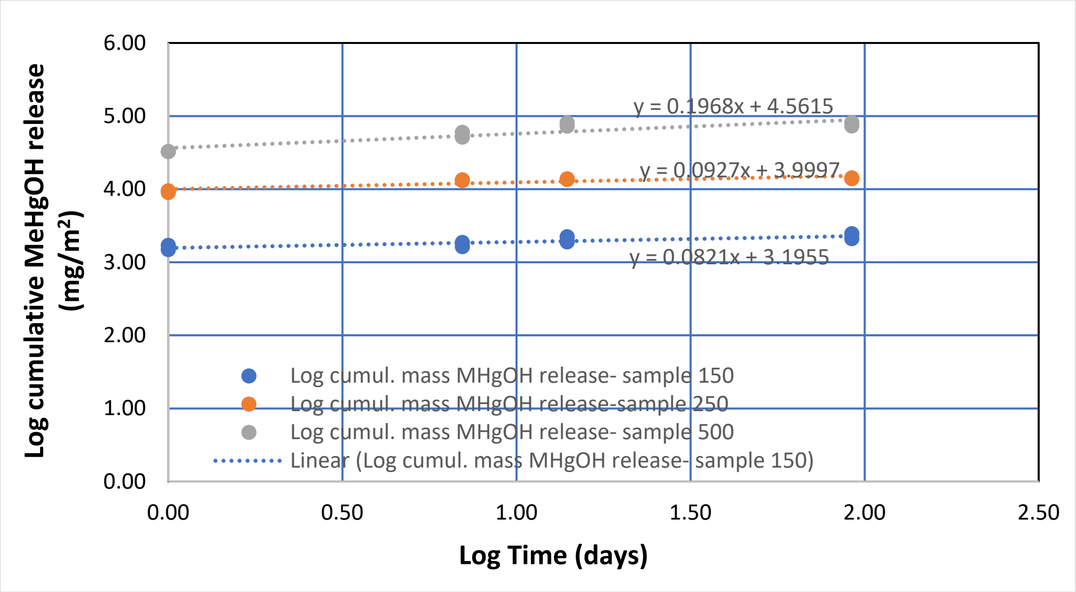


Figure 7. MeHgOH concentrations in leachates of modified EPA Method 1315.

DISCUSSION

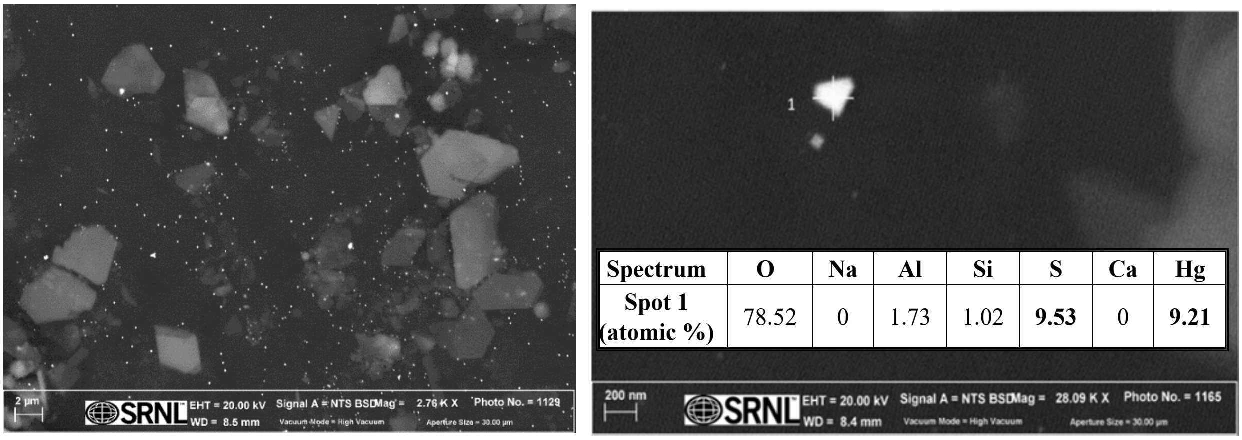
Analysis of waste salt solutions, sludges, and leachates for total Hg and organic Hg species have been performed by several different techniques coupled with different sample preparation/digestion methods. Multiple laboratories are currently engaged in analyzing SRS tank waste and TCLP leachates for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

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.

Reaction between $MeHg^+$ and Saltstone

Speciation of methylmercury hydroxide in saltstone was evaluated by: 1) X-ray diffraction (XRD), 2) energy dispersive spectroscopy (EDX) of high atomic weight particles in scanning electron microscope (SEM) images, and 3) Leaching and liquid solid partitioning methods.

Metacinnabar, was identified by EDX spectra of bright (high atomic mass elements) nano and micro particles in crushed saltstone samples. 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 Figures 8. This phase was identified as metacinnabar, β-HgS in the XRD pattern for saltstone exposed to simulated salt solution spiked with 500 mg/L MeHgOH. The XRD pattern is provided n Figures 9.



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

Figure 8. Left: Dispersed particles of crushed saltstone exposed to solution containing 500 mg/L MHg (Bright particles are HgS). Right: Large nanoparticle of HgS with chemical composition determined by EDX represented as atomic percent

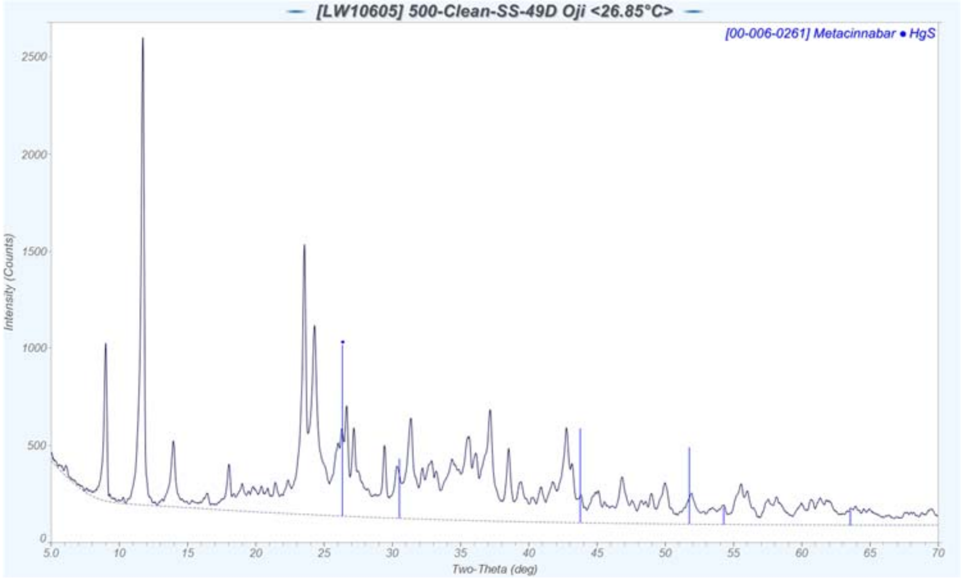


Figure 9. Metacinnabar, β-HgS, peaks identified in XRD pattern of crushed saltstone exposed to simulated salt solution containing 500 mg/L MeHgOH.

CONCLUSIONS

Based on identification of the solid mercury phase in crushed saltstone exposed to MeHg(OH) spiked salt solutions and in monolithic saltstone made with MeHg(OH) 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 cation is currently in progress. One of many possible reactions is shown in Equation1.

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 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 MeHg(OH);
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 high 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.

These results are not intended to be used for regulatory compliance 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 is occurs during setting and early curing of the matrix (1-7 days) and for samples made with 500 mg/L MeHg(OH) continues to occur over the 91-day test period. The amount of Hg removed increases as a function of spike concentration.

- Ninety percent of the Hg added to simulated salt solution as MeHgOH is removed from solution by cured saltstone when salt solution is mixed with crushed cured saltone, ad 99 % after 7 and 14 days contact time for the solutions spiked with 150 and 250 mg/L MeHgOH, respectively.
- Ninety six percent of the Hg had been removed from solution after 92 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 92 days.

The solubility product of metacinnabar and is very low, $pK_{sp} = 53$ [12]. Consequently, incomplete precipitation of organic Hg from saltstone pore solution is may be attributed to depletion in available sulfide and/or 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 in complete 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 is releases during hydration. HgS is very insoluble, Ksp = -53. 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 sulfide in the premix and/or limited availability of sulfide due to hydration rims on slag particles limiting hydration.

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