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Methylmercury Speciation and Retention in Saltstone 21361

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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 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 of mercury.

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. Experimental data are 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 form nanoparticles of β-HgS, meta cinnabar, which is very insoluble and has a solubility product in water, pK_{sp}, at 25° C of 53. In addition, getters on activated carbon substrates and diatomaceous earth show potential for pretreatment of Tank 50 salt solution and as solid additives to the saltstone reagent blend in the event that additional Hg stabilization is required.

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 materials; portland cement, slag, and fly ash, to form a grout slurry which is pumped from the SPF to the Saltstone Disposal Facility (SDF) . 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 and soluble salts in the waste is also reduced by chemical stabilization and microencapsulation.

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, $HgCH_3^+$, is stabilized in Saltstone. This information will be used to determine whether it is necessary to update the total Hg limit and/or to add an organic Hg limit to the Tank 50 Waste Acceptance Criteria (WAC) to assure Saltstone meets RCRA regulatory requirements.

BACKGROUND

Saltstone currently meets Land Disposal Restrictions (LDR) and thereby supports an acceptable path for disposal. The functions of the cementitious materials in Saltstone are to solidify the aqueous liquid, chemically stabilize hazardous RCRA metals, i.e., chromate and mercury species (CrO_4^{2-}, Hg, Hg^{2+}, $HgCH_3^+$) and pertechnetate (TcO_4^-) and physically encapsulate soluble salts.

Mercury in the SRS liquid waste tanks was introduced to the upstream processes as mercuric nitrate which was 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 fraction. Formation of organomercury was originally thought to be the result of reaction with organic antifoam agents and limited to the evaporator system where these chemicals were used. Cessation of antifoam additions to the evaporators removed this production source of organic chemicals. There is an additional possibility that methylation reactions are occurring in the H-Area waste receipt tank. Details concerning the speciation of Hg in the H-Tank Farm are described in more detail elsewhere [6, 7, 8]. Currently methylmercury ($MeHg^+$) 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, which ranged from 70 to 105 mg/L [4]. Although still well below the Toxicity Characteristic Leaching Procedure (TCLP) limit of 0.2 mg/L total Hg [9], recent results have increased slightly due to an increase in $MeHg^+$ in the Saltstone feed from Tank 50.

Consequently, DOE-EM funded testing to (1) understand the stabilization mechanism of organic mercury sequestration in Saltstone, (2) provide a technical basis for total Hg and $MeHg^+$ concentration limits in the Tank 50 WAC, and (3) provide technology that could be deployed to stabilize higher concentrations of $MeHg^+$ in Saltstone in case the concentrations in Tank 50 salt solution increase.

EXPERIMENTAL PROCEDURE

Simulated Saltstone Preparation

Tank 50 simulant solution was prepared in 2 L batches using the reagent chemicals and proportions shown in Table 1. The ingredients are listed in the order of addition used to prepare the simulant solution. Methylmercury hydroxide 1.0 M solution was used to spike four simulated solutions. The target MeHgOH concentrations were: 0, 75, 150, and 300 mg/L. The $MeHg^+$ concentration of these solutions was determined analytically by Atomic Fluorescence Spectroscopy (AFS) and are also shown in Table 2. 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.

Sample Preparation for Testing Reagent Cementitious Materials in MeHgOH Spiked Salt Solution

The first set of experiments was designed to evaluate the effectiveness of individual Saltstone cementitious ingredients and potential getters for sequestering $MeHg^+$. Getters are additives that selectively sequester ions, in this case mercury species. The materials are listed in Table 3. Slag cement, portland cement, Class F fly ash, Ameresco co-generation tire ash, and three Mersorb® sulfur impregnated granulated activated carbon (GAC) samples were added to MeHgOH spiked salt solution and tumbled for 24 hours. Sorption of $MeHg^+$ by crystalline silicotitanate (CST), a material used to remove cesium (Cs^+) from some salt solutions, was also evaluated. The ingredients and proportions for each sample are listed in Table 4.

Samples consisting of the solid phase and simulated salt solution were placed in a rotary tumbler for the 24 hours. After each contact time, solid/liquid separation was performed using a 30 mL syringe fitted with a disposable 0.2 micron-filter. Each filtrate was analyzed for $MeHg^{+}$. Tumbling and filtering were performed in the same way for all the tests performed for this report except for the time dependent exposures. All tests were performed at ambient temperature (~ 26 °C).

Table 1. 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
KNO3	1.806
Na2SO4	14.916
DI Water	100.0
50 % NaOH solution	399.60
Al(NO3)3·9H2O	111.003
DI water	100.0
Na2PO4·12H2O	3.316
Na2CO3	42.011
DI water	100.0
NaNO3	290.3
NaNO2	62.968
DI Water	1140.4
Properties	
Dissolved solids (mass %)	27.42
Water (mass %)	72.58
Specific gravity (measured, g/mL)	1.238

Table 0-2. SRNL analytical measurements for $MeHg^{+}$ in spiked salt solutions.

Spiked MeHgOH Salt Solution ID (mg/L)	$MeHg^{+}$ concentration SRNL AD analysis (mg/L)	Calculated Hg concentration* (mg/L)
0	0	0
75	80.1	74.6
150	149.4	139
300	296.7	276

* Multiply the SRNL AD analytical value for $MeHg^{+}$ by 0.93 to calculate Hg concentrations.

Table 3. Solid materials evaluated for reaction with MeHgOH.

Material	Source
Lehigh Slag 2Q2019	Z-Area
Lehigh Slag 2Q2016	Z-Area
Holcim Slag 2013	Z-Area
Fly ash 2Q2019	Z-Area
Cement 2Q2019	Z-Area
Cogen Fly ash	Ameresco Cogeneration Plant, Jackson SC
IONSIV® IE-911 CST	Honeywell UOP, Des Plaines, IL
MERSORB®	NUCON International, Columbus OH
MERSORB®-CR	
MERSORB®-SI	

Table 4. Ingredient proportions in each sample.

Sample ID*	$MeHg^+$ and (Hg) Concentration in Simulated Salt Solution (from Table 2-2)	Solid Component (g)	MeHgOH spiked simulated salt solution	
			Mass (g)	Volume (ml)
Lehigh slag 2Q19, 0.0 total Hg-1	0	1.0031	51.3319	41.46
Lehigh slag 2Q19, 0.0 total Hg-2		1.0084	51.439	41.55
Lehigh slag 2Q19, 75 total Hg-1	80.1 (74.6)	1.0021	51.3319	41.46
Lehigh slag 2Q19, 75 total Hg-2		1.005	51.439	41.55
Lehigh slag 2Q19, 150 total Hg-1	149.4 (139)	1.0025	51.3767	41.50
Lehigh slag 2Q19, 150 total Hg-2		1.0028	51.2425	41.39
Lehigh slag 2Q19, 300 total Hg-1	296.7 (276)	1.0034	51.831	41.87
Lehigh slag 2Q19, 300 total Hg-2		1.0018	51.549	41.64
Lehigh slag 2Q16 0.0 total Hg-1	0	1.0011	51.9182	41.94
Lehigh slag 2Q16 0.0 total Hg-2		1.0018	51.0385	41.23
Lehigh slag 2Q16 75 total Hg-1	80.1 (74.6)	1.0004	51.6532	41.72
Lehigh slag 2Q16 75 total Hg-2		1.0003	51.2582	41.40
Lehigh slag 2Q16 150 total Hg-1	149.4 (139)	1.0007	51.7027	41.76
Lehigh slag 2Q16 150 total Hg-2		1.0002	51.6508	41.72
Lehigh slag 2Q16 300 total Hg-1	296.7 (276)	1.0004	51.882	41.91
Lehigh slag 2Q16 300 total Hg-2		0.9998	51.726	41.78
Holcim slag 2013 0 total Hg-1	0	1.0006	51.1049	41.28
Holcim slag 2013 0 total Hg-2		1.0005	51.3059	41.44
Holcim slag 2013 75 total Hg-1	80.1 (74.6)	1.0016	51.2346	41.38
Holcim slag 2013 75 total Hg-2		1.0006	51.6079	41.69
Holcim slag 2013 150 total Hg-1	149.4 (139)	1	51.3316	41.46
Holcim slag 2013 150 total Hg-2		1.0018	51.3059	41.44
Holcim slag 2013 300 total Hg-1	296.7 (276)	1.0018	51.356	41.48
Holcim slag 2013 300 total Hg-2		1.0018	51.7	41.76
Cement 2Q19 0.0 total Hg-1	0	1.0025	51.008	41.20
Cement 2Q19 0.0 total Hg-2		1.0015	51.8373	41.87
Cement 2Q19 75 total Hg-1	80.1 (74.6)	1.0019	51.0216	41.21
Cement 2Q19 75 total Hg-2		1.0022	51.6719	41.74
Cement 2Q19 150 total Hg-1	149.4 (139)	1.0021	51.7379	41.79
Cement 2Q19 150 total Hg-2		1.002	51.4069	41.52
Cement 2Q19 300 total Hg-1	296.7 (276)	1.0016	52.18	42.15
Cement 2Q19 300 total Hg-2		1.0016	51.633	41.71
Fly ash 2Q19 0.0 total Hg-1	0	1.0003	50.5858	40.86
Fly ash 2Q19 0.0 total Hg-2		1.0017	51.1077	41.28
Fly ash 2Q19 75 total Hg-1	80.1 (74.6)	0.9999	51.586	41.67
Fly ash 2Q19 75 total Hg-2		1.0007	51.7328	41.79
Fly ash 2Q19 150 total Hg-1	149.4 (139)	1.0015	51.0261	41.22
Fly ash 2Q19 150 total Hg-2		1.0007	51.2705	41.41
Fly ash 2Q19 300 total Hg-1	296.7 (276)	1.0013	51.698	41.76
Fly ash 2Q19 300 total Hg-2		1.0004	51.208	41.36

*For removal effectiveness calculations, the mass of each of the solid cementitious materials and "getters" was 1.000g.

Table 4 (continued). Ingredient proportions in each sample.

Sample ID*	$MeHg^+$ and (Hg) Concentration in Simulated Salt Solution (from Table 2-2)	Solid Component (g)	MeHgOH spiked simulated salt solution	
			Mass (g)	Volume (ml)
Cogen Fly ash 0.0 total Hg-1	0	0.8405	50.7035	40.96
Cogen Fly ash 0.0 total Hg-2		1.0027	51.4468	41.56
Cogen Fly ash 75 total Hg-1	80.1 (74.6)	1.0009	50.9182	41.13
Cogen Fly ash 75 total Hg-2		1.0032	51.4999	41.60
Cogen Fly ash 150 total Hg-1	149.4 (139)	1.0014	51.2971	41.44
Cogen Fly ash 150 total Hg-2		1.0037	51.5806	41.66
Cogen Fly ash 300 total Hg-1	296.7 (276)	1.0025	51.594	41.68
Cogen Fly ash 300 total Hg-2		1.0031	51.036	41.22
IE-911 CST 0.0 total Hg-1	0	0.9955	51.6584	41.73
IE-911 CST 0.0 total Hg-2		1.0007	51.8545	41.89
IE-911 CST 75 total Hg-1	80.1 (74.6)	1.0005	51.3537	41.48
IE-911 CST 75 total Hg-2		1.0003	52.2994	42.25
IE-911 CST 150 total Hg-1	149.4 (139)	1.0032	51.16	41.32
IE-911 CST 150 total Hg-2		1.0027	51.3925	41.51
IE-911 CST 300 total Hg-1	296.7 (276)	1.0028	51.321	41.45
IE-911 CST 300 total Hg-2		1.0033	50.836	41.06
Mersorb CR-150- tot. Hg-1	149.4 (139)	1.0015	51.599	41.68
Mersorb CR-150- tot. Hg-2		1.0009	50.718	40.97
Mersorb-150- tot. Hg-1		1.0014	50.664	40.92
Mersorb -150- tot. Hg-2		1.0016	50.801	41.03
Mersorb-SI-150- tot. Hg-1		1.0004	50.1	40.47
Mersorb -SI-150- tot. Hg-2		1.0008	50.192	40.54

*For removal effectiveness calculations, the mass of each of the solid cementitious materials and "getters" was 1.000g.

Mersorb® – MeHgOH Spiked Salt Solution Short Exposure Time Getter Evaluation

The objective of these tests was to identify commercially available solid "getters" that could be used as a pretreatment added to the Salt Solution Receipt Tank (SSRT) or other location to enhance $MeHg^+$ stabilization in the final Saltstone waste form. Rapid reaction resulting in a solid, low solubility chemically, i.e., stabilized Hg phase and was the criterion for a positive result. Mersorb®, the best performing additive tested in the prior 24-hour exposures, was selected for rapid $MeHg^+$ sequestration for times between 5 and 60 minutes. Five minutes was the shortest exposure time that could be achieved in the existing experimental configuration.

A two-liter batch of fresh simulated salt solution was prepared and spiked with MeHgOH targeted at a concentration of 150 mg/L (140 mg/L $MeHg^+$). Analysis of the solution showed a concentration of 114 mg/L $MeHg^+$. The measured analytical value was used in all subsequent calculations. Sample proportions and exposure times along with the amount of $MeHg^+$ removed from the solutions are listed in Table 5. In these experiments the sample size was ½ of that used in the first experiment, i.e., 0.5 g of Mersorb® to about 25.6 g of simulated salt solution which resulted in the same relative proportions. The specific gravity of the simulated salt solution = 1.233.

Table 5. Ingredients and proportions in Mersorb® reaction time test samples.

Mersorb® Exposure Time (min)	[$MeHg^+$] in Simulated Salt Solution (result is from SRNL AD (mg/L)	Mass of Mersorb® (g)	Mass of Solution Spiked with MeHgOH (g)	Mass of $MeHg^+$ in Sample Solution Before Exposure (mg)	Mass of Hg in Sample Solution Before Exposure (mg)
5	114	0.5005	25.6594	2.363	2.198
10	114	0.5002	25.6721	2.364	2.199
20	114	0.5002	25.6663	2.363	2.199
60	114	0.5005	25.6796	2.365	2.200

Sulfur Impregnated Silica Substrate – MeHgOH Spiked Salt Solution Sample Preparation

A third set of experiments were performed to determine whether sulfur impregnated porous silicate substrates had advantages in sequestering $MeHg^+$ compared to the Mersorb® products which have granular activated carbon substrates. Porous silicate substrates impregnated with sulfur were postulated to react as pozzolans in Saltstone and microencapsulate HgS formed by reaction of $MeHg^+$ with sulfur species, thereby enhancing sequestration of the Hg. Porous silicate materials tested are listed in Table 6.

Table 6. Silicate Substrates impregnated with sulfur at SRNL and Silicathiol.

Material	Source
Diatomaceous Earth (food grade)	P. F. Harris Manufacturing Company, LLC P.O. Box1922, Cartersville, Ga 30120
Harborlite®-700	Imerys,1732 North First Street Suite 450, San Jose Ca 95112
Ground Foam glass (-200 mesh)	Good Planet Laboratory, Albuquerque, New Mexico
Crushed Foam glass	Good Planet Laboratory, Albuquerque, New Mexico
Silicathiol®	Biotage, 10430 Harris Oaks Blvd Suite C, Charlotte, NC 28269

Preparation of elemental sulfur-based mercury getters.

Preparation of the sulfur impregnated getters involved heating blends of these silicate materials with 20 wt. % of elemental sulfur in a nitrogen atmosphere. The batch size for each preparation was 10 grams. The maximum impregnation temperature was 200 ºC which is above the melting point for elemental sulfur in air (152 ºC) and below the boiling point of sulfur in air (444 ºC). The temperature was selected to ensure that elemental sulfur melted and flowed into the substrate pores. After confirming the necessary nitrogen flow rate into the furnace and placing the individual ceramic crucible housing the samples into the furnace the furnace door was closed. The temperature run sequence for the sulfur impregnated substrates in continuous inert nitrogen atmosphere is summarized as follows:

- Ramp furnace temperature to 100 °C at a ramp rate of 10 °C/minute,
- Maintain furnace temperature at 100 °C for 1 hour,
- Ramp furnace temperature to 150 °C at a ramp rate of 10 °C/minute and maintain at this temperature for another hour,
- Ramp furnace temperature to 200 °C at a ramp rate of 10 °C/minute and hold at his temperature for 2 hours,
- After this 2-hours at 200 °C, the furnace was turned off and the system cooled down to 30 °C with the nitrogen gas still flowing throughout the entire cooling period,
- After cooling down to near room temperature, the ceramic sample container with cover was transferred into a dedicated vacuum desiccator for storage.

Silicathiol® was used as received from the manufacturer and was not impregnated with sulfur.

Elemental sulfur-based mercury getters - MeHgOH Spiked Salt Solution Sample Preparation
The impregnated silicate substrates were removed from the vacuum desiccator and weighed into vials which were immediately filled with simulated salt solution spiked with MeHgOH which resulted in a concentration of 114 mg/L $MeHg^+$ per AFS analytical analysis. The analytical $MeHg^+$ value was used in the calculations to determine the mass of $MeHg^+$ that was removed from solution. The sample weights and contact times for the sulfur impregnated porous substrate getters and for the Silicathiol® are shown in Table 7.

After the introduction of the salt solution into the 50-mL glass vials, each of which contained between 0.500 and 0.505 g of the mercury "getter", the glass vials were capped and vigorously agitated manually for the 5 and 10 minutes-contacts times. For the longer contact times of 20 and 60 minutes, the vigorous agitation was performed manually for the first five minutes and then transferred to a rotatory tumbler for the rest of the time. Experiments were performed at ambient room temperature, about 26 °C.

Table 7. Ingredients and proportions for sulfur impregnated silicate substrate samples.

Substrate / "Getter"	Exposure Time (min)	$MeHg^+$ in simulated Salt Solution (mg/L)	Mass of Sulfur "Getter"(g)	Mass of MeHgOH spiked solution (g)
Silicathiol®	5	114	0.5001	25.6785
	10	114	0.5000	25.669
	20	114	0.5005	25.672
	60	114	0.5001	25.6798
Ground Foam glass (-200 mesh)	5	114	0.5007	25.6671
	10	114	0.5001	25.6735
	20	114	0.5005	25.6765
	60	114	0.5002	25.688
Crushed Foam glass	5	114	0.5008	25.6713
	10	114	0.5001	25.671
	20	114	0.5002	25.6728
	60	114	0.5005	25.67691
Harbolite®-700	5	114	0.5005	25.672
	10	114	0.5005	25.6897
	20	114	0.5002	25.689
	60	114	0.5005	25.6763
Diatomaceous Earth (food grade)	5	114	0.0051	25.6822
	10	114	0.5005	25.6751
	20	114	0.5007	25.6743
	60	114	0.5007	25.6807

RESULTS

$MeHg^+$ Stabilization by Slag

Results for the $MeHg^+$ stabilization by three different slags obtained from Z-Area to support 2013, 2Q16, and 2Q19 regulatory compliance testing contacted with simulated Tank 50 solution containing three different $MeHg^+$ concentrations (80, 149, and 297 mg/L $MeHg^+$) are presented in Table 8. The contact time for these tests was 24 hours. The archived slag samples had been stored in SRNL.

A comparison of the percent $MeHg^+$ stabilized (removed from solution spiked with 75 mg/L $MeHg^+$) by three different slags used in the Saltstone Facility is shown in Figure 1. The oldest slag sample (2013),

removed the least $MeHg^+$ from solutions spiked with 75 mg/L $MeHg^+$. However, this relationship was reversed for solutions spiked with 297 mg/L $MeHg^+$. See Figure 2. One possible explanation for these results is that as the slag ages during laboratory storage, a layer is formed on the surface of particles as the result of surface oxidation, carbonation, or hydration. This layer may be less soluble in caustic salt solution or may act as a diffusion barrier for mercury ions and sulfide. The barrier could have formed during the several years of storage in the laboratory and was probably not present in the original fresh material when it was used in Saltstone. A statistical analysis of these data indicated that the 2Q19 sample and 2Q13 sample are different from each other in all conditions tested, and the 2Q16 and 2Q13 samples are different except at the lowest mercury concentration [10]. All three slags met the mercury stabilization requirements at the time they were used in Saltstone and all Saltstone samples passed the TCLP test.

Table 8. Methylmercury removed from MeHg+ spiked simulated Tank 50 solutions by archived Z-Area slag samples after 24 hours contact time.

Sample ID	$MeHg^+$ & (Hg) in simulated salt solution (mg/L)	$MeHg^+$ in sample solution before exposure (mg)	$MeHg^+$ in sample solution after exposure (mg)	$MeHg^+$ removed from solution (mg)	$MeHg^+$ removed from solution (%)	Average $MeHg^+$ removed from solution (%)	$MeHg^+$ removed from solution/ g solid reactant in 24 hours (mg)
Lehigh slag 2Q19, 0.0 total Hg-1	0	0	0	0	0	0	0
Lehigh slag 2Q19, 0.0 total Hg-2		0	0	0	0		0
Lehigh slag 2Q19, 75 total Hg-1	80.1	3.325	0.284	3.041	91.45	90.56	3.03
Lehigh slag 2Q19, 75 total Hg-2	(74.6)	3.332	0.000	3.332	89.67		3.32
Lehigh slag 2Q19, 150 total Hg-1	149.4	6.201	3.503	2.698	43.51	45.10	2.69
Lehigh slag 2Q19, 150 total Hg-2	(139)	6.185	3.298	2.887	46.68		2.88
Lehigh slag 2Q19, 300 total Hg-1	296.7	12.422	7.762	4.660	37.52	40.75	4.64
Lehigh slag 2Q19, 300 total Hg-2	(276)	12.354	6.920	5.435	43.99		5.42
Lehigh slag 2Q16 0.0 total Hg-1	0	0	0	0	0	0	0
Lehigh slag 2Q16 0.0 total Hg-2		0	0	0	0		0
Lehigh slag 2Q16 75 total Hg-1	80.1	3.346	0.544	2.802	83.74	82.96	2.80
Lehigh slag 2Q16 75 total Hg-2	(74.6)	3.320	0.591	2.729	82.19		2.73
Lehigh slag 2Q16 150 total Hg-1	149.4	6.240	3.692	2.548	40.85	42.34	2.55
Lehigh slag 2Q16 150 total Hg-2	(139)	6.234	3.502	2.732	43.83		2.73
Lehigh slag 2Q16 300 total Hg-1	296.7	12.570	6.179	6.392	50.85	49.46	6.37
Lehigh slag 2Q16 300 total Hg-2	(276)	12.533	6.499	6.033	48.14		6.01
Holcim slag 2013 0 total Hg-1	0	0	0	0	0	0	0
Holcim slag 2013 0 total Hg-2		0	0	0	0		0
Holcim slag 2013 75 total Hg-1	80.1	3.319	0.971	2.348	70.75	69.39	2.34
Holcim slag 2013 75 total Hg-2	(74.6)	3.343	1.069	2.274	68.03		2.27
Holcim slag 2013 150 total Hg-1	149.4	6.186	4.742	1.444	23.46	24.27	1.44
Holcim slag 2013 150 total Hg-2	(139)	6.183	4.639	1.544	25.09		1.54
Holcim slag 2013 300 total Hg-1	296.7	12.308	3.239	9.069	73.68	69.27	9.05
Holcim slag 2013 300 total Hg-2	(276)	12.390	4.354	8.037	64.86		8.02

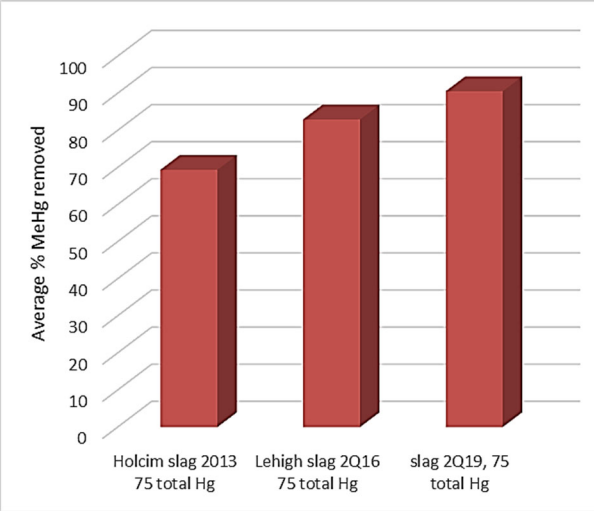

Figure 1. Comparison of Hg stabilization after 24 h for the three slags used in the Saltstone Facility.

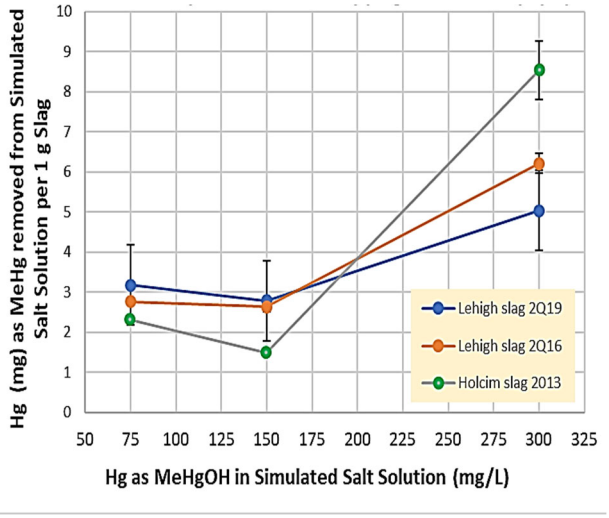

Figure 2. Comparison of mg Hg stabilizated per 1 g of slag after 24 h for three slags used in the Saltstone Facility. (1 sigma error bars displayed, average of 2 samples.)

$MeHg^+$ Stabilization by Portland Cement and Class F Fly Ash

Results in Table 9 indicate that 2Q19 Portland cement and 2Q19 Class F fly ash received from the SPF did not stabilize $MeHg^+$. This was as expected, since they are not sulfur/sulfide containing species and are not relied upon to provide any Hg sequestration function.

Table 9. Methylmercury removed from $MeHg^+$ spiked simulated Tank 50 solutions by archived Z-Area Portland cement and Class F Fly ash samples after 24 hours contact time.

Sample ID	$MeHg^+$ & (Hg) in simulated salt solution (mg/L)	$MeHg^+$ in sample solution before exposure (mg)	$MeHg^+$ in sample solution after exposure (mg)	$MeHg^+$ removed from solution (mg)	$MeHg^+$ removed from solution (%)	Average $MeHg^+$ removed from solution (%)	$MeHg^+$ removed from solution / g solid reactant in 24 hours (mg)
Cement 2Q19 0.0 total Hg-1	0	0.000	0.000	0.000	0.000	0	0.00
Cement 2Q19 0.0 total Hg-2		0.000	0.000	0.000	0.000		0.00
Cement 2Q19 75 total Hg-1	80.1 (74.6)	3.305	3.042	0.264	7.97	4.98	0.26
Cement 2Q19 75 total Hg-2		3.347	3.281	0.067	1.99		0.07
Cement 2Q19 150 total Hg-1	149.4 (139)	6.245	6.720	-0.475	-7.61	0	-0.47
Cement 2Q19 150 total Hg-2		6.205		6.205	--		6.19
Cement 2Q19 300 total Hg-1	296.7 (276)	12.505	13.277	-0.771	-6.17	0	-0.77
Cement 2Q19 300 total Hg-2		12.374	14.013	-1.639	-13.25		-1.64
Fly ash 2Q19 0.0 total Hg-1	0	0.00	0.000	0.000	0.00	0	0.00
Fly ash 2Q19 0.0 total Hg-2		0.00	0.000	0.000	0.00		0.00
Fly ash 2Q19 75 total Hg-1	80.1 (74.6)	3.342	3.338	0.004	0.12	0	0.00
Fly ash 2Q19 75 total Hg-2		3.351	3.485	-0.134	-4.00		-0.13
Fly ash 2Q19 150 total Hg-1	149.4 (139)	6.159	6.838	-0.679	-11.03	0	-0.68
Fly ash 2Q19 150 total Hg-2		6.188	6.311	-0.123	-1.99		-0.12
Fly ash 2Q19 300 total Hg-1	296.7 (276)	12.390	14.156	-1.766	-14.26	0	-1.76
Fly ash 2Q19 300 total Hg-2		12.273	13.526	-1.253	-10.21		-1.25

$MeHg^+$ Stabilization by Cogen Fly Ash and IE911 Crystalline Silicotitanate

The Ameresco Cogen fly ash is a byproduct material from the Ameresco Cogeneration Facility in Jackson, SC. This facility burns biomass material and tires and provides power to the Savannah River Site. Because tires contain sulfur, the material was considered for testing. The Cogen Fly Ash removed up to about 1.5 mg $MeHg^+$ / g of ash, i.e., about 12 % of the $MeHg^+$ in the simulated Tank 50 solution spiked with 297 mg/L $MeHg^+$ in the 24-hour test. Results are tabulated in Table 10. Crystalline silicotitanate (CST) was tested because it is used to remove Cs^+ from the SRS salt solution and was reported to remove other +1 cations. CST did not remove $MeHg^+$ from simulated Tank 50 salt solution in these tests. Negative values shown in Table 10 are attributed to analytical testing/variability and do not indicate that $MeHg^+$ was generated by the CST, fly ash, or cement.

Table 10. Methylmercury removed from $MeHg^+$ spiked simulated Tank 50 solutions by archived Cogen Fly ash, IE-911 CST, and Mersorb® after 24 hours contact time.

Sample ID	$MeHg^+$ & (Hg) in simulated salt solution (mg/L)	$MeHg^+$ in solution before exposure (mg)	$MeHg^+$ in solution after exposure (mg)	$MeHg^+$ removed from solution (mg)	$MeHg^+$ removed from solution (%)	Average $MeHg^+$ removed from solution (%)	$MeHg^+$ (mg) removed from solution / g solid reactant in 24 hours (mg)
Cogen Fly ash 0.0 total Hg-1	0	0	0	0	0	0	0
Cogen Fly ash 0.0 total Hg-2		0	0	0	0		0
Cogen Fly ash 75 total Hg-1	80.1	3.298	3.085	0.214	6.48	7.04	0.21
Cogen Fly ash 75 total Hg-2	(74.6)	3.336	3.083	0.254	7.60		0.25
Cogen Fly ash 150 total Hg-1	149.4	6.191	6.427	-0.235	-3.80	2.43	-0.23
Cogen Fly ash 150 total Hg-2	(139)	6.226	5.687	0.539	8.65		0.54
Cogen Fly ash 300 total Hg-1	296.7	12.365	10.615	1.750	14.16	11.83	1.75
Cogen Fly ash 300 total Hg-2	(276)	12.231	11.069	1.163	9.50		1.16
IE9-11 CST 0.0 total Hg-1	0	0	0	0	--	0	0
IE-911 CST 0.0 total Hg-2		0	0	0	--		0
IE-911 CST 75 total Hg-1	80.1	3.327	3.173	0.153	4.61	0	0.15
IE-911 CST 75 total Hg-2	(74.6)	3.388	3.536	-0.148	-4.37		-0.15
IE-911 CST 150 total Hg-1	149.4	6.175	6.248	-0.073	-1.19	0	-0.07
IE-911 CST 150 total Hg-2	(139)	6.203	6.165	0.038	0.62		0.04
IE-911 CST 300 total Hg-1	296.7	12.300	13.058	-0.759	-6.17	0	-0.76
IE-911 CST 300 total Hg-2	(276)	12.183	13.428	-1.244	-10.21		-1.24
Mersorb® CR(150 total Hg)-1	149.4 (139)	6.228	1.146	5.082	81.61	81.67	5.07
Mersorb® CR(150 total Hg)-2		6.122	1.118	5.004	81.74		5.00
Mersorb® (150 total Hg) - 1		6.115	0.062	6.053	98.98	99.01	6.04
Mersorb® (150 total Hg) - 2		6.132	0.059	6.073	99.04		6.06
Mersorb® SI(150 total Hg) -1		6.047	0.062	5.985	98.97	98.98	5.98
Mersorb® SI (150 total Hg)-2		6.058	0.062	5.996	98.98		5.99

$MeHg^+$ Stabilization by Mersorb®

Commercially available "getters" that utilize sulfide chemistry to sequester cations were evaluated to determine whether enhancement of $MeHg^+$ stabilization may be an option for Saltstone in case $MeHg^+$ concenterations spike in Tank 50. Rapid reaction with $MeHg^+$ was identified as a criteria for pretreatment to the salt solution. Rapid reaction was not a criteria for adding these materials to the Saltstone premix. Three Mersorb products were recommended for use with salt solutions by the manufacturer, Mersorb®, Mersorb® SI and Mersorb® CR. These materials are used in the oil and gas industry and in other processes where metals including Hg^{2+} and organic mercury must be removed from off gas and liquid streams. The

Mersorb® materials tested are activated carbon particles (0.1 to 0.5mm) impregnated with sulfur compounds. $MeHg^+$ stabilization results for the three Mersorb® products tested by contacting them with simulated Tank 50 salt solution for 24 hours are presented in Table 10. These data and the results for the three slags tested are plotted in Figure 3. Mersorb® and Mersorb® Si stabilize 99 ± 0.03% of the $MeHg^+$ in simulated salt solution spiked with 149 mg/L $MeHg^+$ in 24 hours of contact time. As shown in Figure 3, all of the Mersorb® materials performed better than slag in the 24-hour tests.

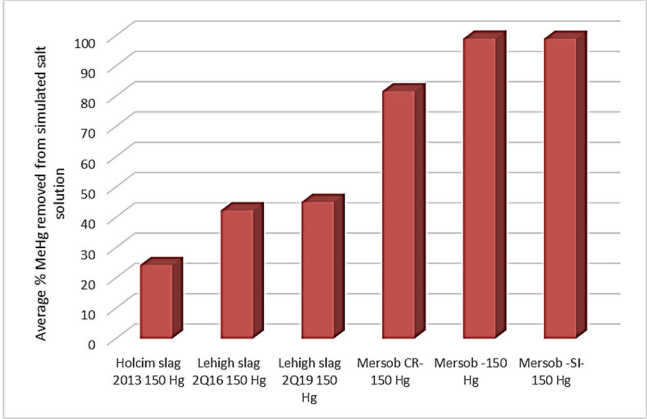

Figure 3. Mersorb® products. Comparison of $MeHg^+$ Stabilization in simulated salt solution spiked with 149 mg/L $MeHg^+$ (added as MeHgOH) after contact for 24 hours and three Mersorb® products.

A comparison of the effectiveness (mass $MeHg^+$ removed per unit mass of slag or getter) of the three slag samples and Mersorb® products in removing $MeHg^+$ from simulated salt solution after 24-hour exposure tests using solutions spiked with 149 mg/L $MeHg^+$ is provided in Table 11. Mersorb® removes more than twice the amount of $MeHg^+$ from solution compared to the three slags tested. Consequently, Mersorb® was selected for evaluation at shorter exposure times to determine whether it could be used to pretreat salt solution prior to mixing the solution with the cementitious reagents.

Table 11. Comparison of Mersorb® to Slag Stabilization of $MeHg^+$ in Simulated Salt Solutions.

Spiked Solution ID	**Sample ID 75**	**Sample ID 150**	**Sample ID 300**
Solution concentration based on analysis	**$MeHg^+$ 80 mg/L**	**$MeHg^+$ 149 mg/L**	**$MeHg^+$ 297 mg/L**
Material	**$MeHg^+$ removed from solution after contact with slag after 24 h (mg $MeHg^+$ / 1 g material) Average of duplicate samples**		
Lehigh Slag 2Q19	3.18	2.79	5.03
Lehigh Slag 2Q16	2.77	2.64	6.19
Holcim Slag 2013	2.31	1.49	8.54
Mersorb®	Not measured	6.06	Not measured

Five to 60 Minute Exposure Times

Shorter exposure time results for Mersorb®, four sulfur impregnated silicate substrate materials, and Silicathiol® are provided in Table 12. The short exposure times were intended to evaluate pretreatment feasibility in the Salt Solution Receipt Tank which feeds that Saltstone mixer. At all exposure times evaluated, 5, 10, 20, 60 minutes, Mersorb® was the most effective pretreatment reagent and stabilized between 99.75 and 99.99 % of the $MeHg^+$ in salt solution spiked with 114 mg/L $MeHg^+$. (A new batch of

$MeHg^+$ spiked salt solution was used in the short exposure tests. The new spiked solution had a lower $MeHg^+$ concentration than the spiked solution used in the 24-hour exposure tests, e.g., SRS Analytical Development analysis results were 114 rather than 149 mg/L).

Sulfur impregnated food grade (unwashed) diatomaceous earth was the next most effective pretreatment reagent and stabilized 93 % of the Hg added as $MeHg^+$ for the 5-minute exposure time and removed an average of 91.2 % of the $MeHg^+$ from solution for exposure times between 5 and 60 minutes. The food grade of diatomaceous earth is suspected of containing trace quantities of organic material which reacted with the impregnated sulfur to form mercaptan compounds (which are organosulfur compounds). Upon opening the reaction vials in a chemical hood, a hint of typical mercaptan odor was detected. The organosulfur formed in the sulfur impregnated unwashed diatomaceous material is postulated to have reacted with soluble $MeHg^+$ in the solution, probably forming HgS, although this was not confirmed.

Time dependent results for Silicathiol® showed high effectiveness for 5- and 10-minute exposure times but then a decrease in stabilization effectiveness after 20 and 60 minutes. These results suggest an initial sorption process followed by desorption of $MeHg^+$ by Silicathiol® rather than reaction to form HgS and possibly degradation of the silica substrate in the strong caustic solution.

Time dependent results for sulfur impregnated Harborlite®-700 which is a perlite substrate, indicated that reaction between the sulfur and $MeHg^+$ did not occur quickly but did increase over the exposure times and resulted in removal of about 25 % of the $MeHg^+$ from solution after 60 minutes. Results for sulfur impregnated crushed and pulverized foamed glass indicated that these materials did not remove $MeHg^+$ from solution as a function of exposure times up to 60 minutes.

Table 0-7. Time dependent $MeHg^+$ stabilization by sulfur impregnated substrates in contact with simulated salt solutions spiked labeled 114 mg/L $MeHg^+$.

	% $MeHg^+$ Removed as a function of contact time				Average % $MeHg^+$ Removed	Average mg $MeHg^+$ removed / g Getter	Coefficient of Variation
Material	**5 min**	**10 min**	**20 min**	**60 min**			
Mersorb®	99.90	99.91	99.91	99.75	99.87 ±0.08	5.09	0.00
S Impregnated diatomaceous Earth	93.11	91.56	92.00	87.98	91.16 ± 2.22	4.65	0.024
Silicathiol®	94.89	89.39	38.86	17.98	60.28 ± 37.83	3.07	0.63
S Impregnated Harborlite-700	0.0	11.40	7.02	25.26	10.92 ±10.65	0.74	0.98
S Impregnated Foam Glass (-200 mesh) & ground glass	0.0	0.0	0.0	0.88	No measurable removal of $MeHg^+$	0.0	2.0 (-200 mesh) NA (ground)

Conclusions

The objective of this study was to provide a technical basis for the organic mercury waste acceptance criterion (WAC) for Tank 50 salt solution. The current total mercury WAC for Tank 50 solution is 325 mg/L Hg regardless of the form of mercury which is about three times higher than the total Hg concentrations measured to date in Tank 50 solution. To date, the highest total Hg and $MeHg^+$ concentrations in the Tank 50 solution used to make these samples were 105 and 62 mg/L, respectively.

The Tank 50 Hg and $MeHg^+$ concentration limits are based on Saltstone passing the total mercury limit (0.2 mg/L) for leachate generated by the TCLP (EPA Method 1311). To date all Saltstone samples made with Tank 50 solution for regulatory compliance have passed the TCLP for Hg using crushed material in the accepted particle size range of 4.76 to 9.53 mm. However, the crushed material is irregular in shape and can have a wide range of surface areas. Consequently, testing was performed to (1) understand the stabilization mechanism of organic mercury sequestration in Saltstone, (2) provide a technical basis for total Hg and $MeHg^+$ concentration limits in Tank 50, and (3) provide technology that could be deployed to stabilize higher concentrations of $MeHg^+$ in Saltstone in case the concentrations in Tank 50 salt solution increase unexpectedly.

$MeHg^+$ was shown to be redox sensitive and react with sulfide in slag, a cementitious ingredient in Saltstone [11]. This reaction produces HgS as nanoparticles of β-cinnabar which has a very low solubility [11]. Three slags, cement and fly ash used in the Saltstone process between 2013 and 2019, were tested for their ability to stabilize $MeHg^+$ in an attempt to understand historic TCLP results. As expected, Portland cement and Class F fly ash do not react with $MeHg^+$. All three slags tested stabilized a portion of the $MeHg^+$ within 24-hour exposure test in spiked simulated waste solution. The results indicated that the older slag from 2013 was slower to react than the 2016 and 2019 slags when the concentration of $MeHg^+$ was low (75 mg/L) but higher concentration of $MeHg^+$ in the solution drove the reaction. This is consistent with a "weathered / altered layer" on the slag particles that forms as a function of time due to carbonation, oxidation, and hydration during laboratory storage of the slag samples. At higher $MeHg^+$ concentrations in the solution, the chemical gradient across this interfacial region is higher, which was postulated to result in higher ion transport across the layer. All slags tested resulted in Saltstone that passes the TCLP test for Hg at the time they were used in the process.

Commercial mercury getters were also tested. Mersorb®, a sulfur species impregnated granular activated carbon, performed better than the slags tested in a 24-hour exposure test using salt solution spiked with 149 mg/L $MeHg^+$ (samples were labeled 150-Hg). One gram of Mersorb® sequestered an average of 6.06 mg $MeHg^+$. This may be compared to the best performing slag (Lehigh Slag 2Q19) which removed only 2.80 mg $MeHg^+$ per gram from solution spiked with 149 mg/L $MeHg^+$ for an exposure time of 24 hours. HgS was identified as a reaction product for the Mersorb® material as it was for slag.

"Getters" were also evaluated for pretreating salt solution with $MeHg^+$ in case future concentrations of $MeHg^+$ approach or exceeded the WAC limit. Sequestration of $MeHg^+$ by Mersorb® and other potential "getters" were evaluated in short exposure times in batch tests using 114 mg/L $MeHg^+$ spiked solutions. One possible concept is to add these getters to the Salt Solution Receipt Tank (SSRT) in Z-Area immediately before mixing the salt solution with the cementitious materials. Four porous silicate substrates, Diatomaceous Earth (food grade), Harbolite-700, 200 mesh Foam Glass, and Ground Foam, were impregnated with sulfur were prepared along with Mersorb®. Sulfur-impregnated porous silicate substrates were hypothesized to react as pozzolans and microencapsulate precipitated HgS particles.

Mersorb® was the best getter tested and removed > 99.8 percent of the $MeHg^+$ from simulated Tank 50 salt solution spiked with 114 mg/L $MeHg^+$ in exposure tests between 5 and 60 minutes. Sulfur impregnated diatomaceous earth also performed well in these short exposure tests. The average percent $MeHg^+$ removed from solution for these test times was 91.16 %. Silicathiol® an experimental Hg sequestering reagent performed well in the 5- and 10-minute tests but lost effectiveness in the 20- and 60-minute tests. The Harborlite®-700 substrate was slow to react but after 60 minutes removed 25.26 % of the $MeHg^+$ from solution. Sulfur impregnated foamed glass did not react with $MeHg^+$ and exhibited no $MeHg^+$ removal. Based on these getter studies thiol forms of sulfur/disulfides which presumably form in

the food grade Diatomaceous Earth are better than elemental sulfur as precipitation / sequestering agents when bound to substrates.

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