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Methylmercury Speciation and Retention Evaluation to Support Tank 50 and Saltstone Waste Acceptance Criteria: Parts 2 and 3

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PREFACE OR ACKNOWLEDGEMENTS

The authors acknowledge A. Fellinger and D. McCabe for tracking progress on this work scope and reviewing this report, respectively. The authors also acknowledge C.L. Crawford, K. Hill and M. Alexander for collaborating on this task and for performing complementary experiments on TCLP testing of $MeHg^+$ spiked simulated Saltstone samples (size fraction -3/8 inch to + 5/16 inch) to confirm batch test findings. The combined testing supports the current Tank 50 WAC for Hg and $MeHg^+$. The authors also thank J. Manna for performing a statistical analysis on the slag sequestration results and to D. McCabe for his excellent review of this report.

EXECUTIVE SUMMARY

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

The waste in Tank 50 is fed to the Saltstone facility, where it is mixed with grout-forming additives and poured into vaults to produce an immobilized waste form. The Tank 50 Hg and $MeHg^+$ concentration limits are based on Saltstone passing the total mercury limit (maximum of 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, 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 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.

This report contains results from Parts 2 and 3 of HQTD 1002, Task 2.3.6. In Part 2, three slags, cement and fly ash that had been used in the Saltstone process between 2013 and 2019, were tested for their ability to stabilize $MeHg^+$ in 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 a 24-hour exposure test. The results indicated that the older slag from 2013 was slower to react than the 2016 and 2019 slags when the concentration of $MeHg^+$ is low (75 mg/L), but higher concentration of $MeHg^+$ in the salt solution drove the reaction to remove $MeHg^+$ from solution. 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 storage for as long as seven years. At higher $MeHg^+$ concentrations in the solution, the chemical gradient across this interfacial region is higher which can result in higher ion transport across the layer. These results should not be interpreted as implying that the Saltstone produced when using the 2013 slag when it was fresh would be non-compliant.

Commercial mercury getters were also tested in Part 2. 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 $MeHg^+$. One gram of Mersorb® sequestered 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 in the Part 1 study.

Part 3 of this report was focused on identifying a "getter" for pretreating salt solution with $MeHg^+$ concentrations that approached or exceeded the WAC limit to assure the resulting Saltstone would pass the TCLP test and not display the characteristic of Hg toxicity. Part 3 evaluated sequestration of $MeHg^+$ by Mersorb® and other potential "getters" as a function of short exposure times in batch tests using 149 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. The goal was to demonstrate sequestration of $MeHg^+$ within the time required to pump Saltstone grout from the SSRT into an SDU. The other new getters tested consisted of four porous silicate substrates that were impregnated with sulfur. The substrates selected were Diatomaceous Earth (food grade), Harborlite-700, 200 mesh Foam Glass, and Ground Foam Glass. Porous silicate substrates impregnated with sulfur were hypothesized to react as pozzolans and have potential to microencapsulate precipitated HgS particles.

Testing also examined if using Crystalline Silicotitanate to treat tank waste for Cs^+ removal would impact $MeHg^+$ in the liquid, since it is also a monovalent cation.

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 %. 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 % of the $MeHg^+$ from solution. Sulfur impregnated foamed glass did not react with $MeHg^+$ and exhibited no $MeHg^+$ removal.

The results presented in this report were used to design TCLP tests requested by Savannah River Remediation (SRR) WRPS in which simulated salt solution was spiked with chromate and methyl mercury. The samples used for TCLP testing were crushed and sieved to a discrete size fraction (3/8 to 5/16 inch). The objective of this TCLP testing was as a direct comparison to the TCLP testing performed for the Tank 50 WAC. That work was performed by Crawford, et al. [12]. These simulant scoping tests indicate that the current Tank 50 WAC limits for total Hg (325 mg/L) and methyl mercury (350 mg/L) are adequate for protecting the TCLP Hg limit of 0.2 mg/L with the simulant formulation and conditions tested. Whether this can be extended to other formulations or conditions has not been tested.

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LIST OF ABBREVIATIONS

AD	(SRNL) Analytical Development
AFS	Atomic Fluorescence Spectroscopy
CM	Cementitious Materials
CST	Crystalline Silicotitanate
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
ELN	Electronic Laboratory Notebook
GAC	Granular Activated Carbon
LDR	Land Disposal Restrictions
LIMS	Laboratory Information Management System
LLW	Low level waste
MCU	Modular Caustic Side Solvent Extraction Unit
MeHg	Methylmercury
($MeHg^+$)	Methylmercury cation
1Q, 2Q	First Quarter or fiscal year, second quarter of fiscal year
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
SRR	Savannah River Remediation
SRS	Savannah River Site
SSRT	Salt Solution Receipt Tank
SWPF	Salt Waste Processing Facility
TCLP	Toxicity Characteristic Leaching Procedure
TCR	Technical Change Request
TTQAP	Technical Task and Quality Assurance Plan
WAC	Waste Acceptance Criteria

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 species, 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. The function of the cementitious materials used to make Saltstone is to treat DSS to meet the Environmental Protection Agency Land Disposal Restrictions (LDR) which address Hg leachability and thereby provide an acceptable path for disposal.

To qualify for land disposal, Saltstone must pass the RCRA Toxicity Characteristic Leaching Procedure requirements for RCRA metals. The current total mercury (Hg) limit for Tank 50 solution is 325 mg/L [1] and 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 and/or to add an organic Hg limit to the Tank 50 Waste Acceptance Criteria (WAC) to assure Saltstone meets RCRA regulatory requirements.

This work was authorized by the DOE Office of Environmental Management as HQTD 1002 Task 2.3.6 which had the objective of providing a technical basis for the organic mercury waste acceptance criterion (WAC) for Tank 50 salt solution [6]. To date, the highest total Hg and $MeHg^+$ concentrations in the Tank 50 solution were 105 and 62 mg/L, respectively.

Part 1 of this study identified the $MeHg^+$ sequestration mechanism to be precipitation of nanoparticles of HgS. The source of the sulfide was identified as slag, one of the ingredients in Saltstone [7]. This report addresses the second and third phases in the study. The main objective of this task was to establish an experimental basis for the mercury limit (total and organic) in the Saltstone WAC. This objective was partially addressed in the Part 1 Study in which data on the retention of $MeHg^+$ in Saltstone is presented. $MeHg^+$ was found to react with sulfide in the slag to form HgS and CH_4. However, after curing the saltstone for 28 days, a fraction of 1 percent of the $MeHg^+$ was not stabilized and could be extracted as $MeHg^+$ by leaching pulverized samples. This finding could jeopardize regulatory compliance of the waste form if future $MeHg^+$ concentrations in Tank 50 increase beyond expected levels. Consequently, additional testing was performed and is presented in this report. Part 2 and Part 3 experiments were performed to evaluate:

(1) Effectiveness of each of the cementitious materials in Saltstone, Portland cement, slag cement, and Class F Fly ash, on sequestration of $MeHg^+$. This was accomplished by tumbling each of these materials for 1 day in $MeHg^+$ spiked salt solution, i.e., batch test.

(2) Variability in slag stabilization of $MeHg^+$. This was done by testing slag from 2013, 2016 and 2019. Cement and fly ash received in Z-Area in the second quarter of 2019 was also tested.

(3) Other commercially available materials used or considered for sequestering soluble redox sensitive ions and cations. Tests evaluated materials for sequestering $MeHg^+$ by chemical reaction or by sorption. Short term batch tests were used in this evaluation.

(4) The short-term effectiveness of the best $MeHg^+$ sequestering material identified in prior testing, Mersorb® (sulfur species impregnated granular active carbon). The objective of these short-term (5 to 60 minute) exposures was to evaluate potential application of this material as a salt solution pretreatment in the Saltstone Processing Facility (SPF) if future problems arise.

(5) Potential $MeHg^+$ sequestering materials prepared at SRNL. Testing evaluated whether a combination of chemical stabilization resulting from reaction with sulfur impregnated porous silicate substrates performed as well as Mersorb®. Silica substrates are pozzolanic and are similar in composition to Class F fly ash where as Mersorb® products are carbon substrates.

(6) Potential of Crystalline Silicotitanate to absorb $MeHg^+$. Since this material is used in treatment of some tank wastes at SRS, it is important to know if the $MeHg^+$ concentration will be altered in that process.

1.1 Background

The source of mercury in the Savannah River Site (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 its 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 also a possibility that methylation reactions are occurring in the H-Canyon waste receipt tank, Tank 39.

In addition, the Defense Waste Processing Facility (DWPF) is a source of organomercury species in Tank 50. Based on analyses of the aqueous condensates in the Slurry Mix Evaporator Condensate Tank (SMECT) within DWPF, 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 [8, 9]. This condensate is dispositioned to the Recycle Tank (RCT) in the DWPF and then sent to the 2H evaporator system in the Tank Farm where it is concentrated. This high Hg concentration and relatively high $MeHg^+$ salt solution/slurry from 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 into subsequent salt solution transfers during salt batch preparation. This practice has resulted in spreading $MeHg^+$ throughout the salt waste streams in the Tank Farms. Because very little $MeHg^+$ is removed by Modular Caustic Side Solvent Extraction Unit (MCU) , 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 [8, 9]. 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 about 30 and 60 mg/L Hg compared to total Hg concentrations, which ranged from 70 to 105 mg/L [4]. The concentration of $Hg_{(total)}$ in the 1st quarter 2018 Toxicity Characteristic Leaching Procedure (TCLP) test is considerably higher than previously reported results. Although still well below (about 10X below) the limit of 0.2 mg/L total Hg [10], this research was initiated to understand organic mercury speciation and behavior during reaction with the Saltstone cementitious reagents with the salt solution.

1.2 Quality Assurance

The work outline and associated quality assurance requirements described in Technical Task and Quality Assurance Plan (TTQAP), SRNL-RP-2019-00357, Revision 0 have been met with this report [10]. 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 00258-03. SRNL Analytical Development (AD) data are documented in LIMS and the laboratory Information Management System.

2.0 Experimental Procedure

2.1 Saltstone Cementitious Component Evaluation as a Function of $MeHg^+$ Concentration

2.1.1 Simulated Solution Preparation

Tank 50 simulant solution was prepared in 2 L 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 solution.

Table 2-1. 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
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
Properties	
Dissolved solids (mass %)	27.42
Water (mass %)	72.58
Specific gravity (measured, g/mL)	1.238

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 by SRNL AD and are shown in Table 2-2. 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. Good agreement between spiked solution concentrations and measured $MeHg^+$ results were obtained for the Atomic Fluorescence Spectroscopy (AFS) method.

Table 2-2. 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.

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

The first set of experiments was designed to evaluate the effectiveness of Saltstone premix 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 2-3. 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 2-4.

Table 2-3. 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	

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 which are described in section 3.2.3. All tests were performed at ambient temperature (~ 26 °C).

Table 2-4. 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

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

Table 2-4. Ingredient proportions in each sample (continued).

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)
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
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	51.160	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	50.100	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.

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

The objective of this study was to identify a commercially available solid "getter" that could be added to the Saltstone premix or to the Salt Solution Receipt Tank (SSRT) or other location to enhance $MeHg^+$ stabilization in the Saltstone waste form. Rapid reaction that resulted in removal of organic mercury from filtered simulated Tank 50 salt solution 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 2-5. In these experiments the sample size was ½ of that used in the first experiment, i.e., 0.5 g of Mersorb® to about 25.6g of simulated salt solution which resulted in the same relative proportions.

Table 2-5. 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

The specific gravity of the simulated salt solution = 1.233.

2.4 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 tested which have granular activated carbon substrates. Porous silicate substrates impregnated with sulfur could react as pozzolans in Saltstone and microencapsulate HgS formed by reaction of $MeHg^+$ with sulfur species. The porous silicate materials tested are listed in Table 2-6.

Table 2-6. 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

2.4.1 Preparation of elemental sulfur-based mercury getters.

Preparation of these sulfur impregnated getters involved the 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 melts and flows 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 this sulfur impregnated substrates in continuous inert nitrogen atmosphere is summarized as follows:

- Ramp furnace temperature to 100 ºC at a ramp rate of 10 ºC/minute,
- Maintain furnace temperature at 100 ºC for I hour,
- Ramp furnace temperature to 150 ºC at a ramp rate of 10 ºC/minute and maintain at this temperature for another hour,
- Ramp furnace temperature to 200 ºC at a ramp rate of 10 ºC/minute and hold at his temperature for 2 hours,
- After this 2-hours at 200 ºC, the furnace was turned off and the system cooled down to 30 ºC 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.

2.4.2 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 MeHgOH spiked simulated salt solution. The simulated salt solution had been spiked with 114 mg/L $MeHg^+$ per SRNL AD analysis. The analytical $MeHg^+$ value was used in the calculations to determine the mass of $MeHg^+$ that was removed from solution. The sample weights for the sulfur impregnated porous substrate getters and for the Silicathiol® are shown in Table 2-7 along with the contact times.

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 2-7. 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
Harborlite®-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

3.0 Results

3.1 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 were contacted with simulated Tank 50 solution containing three different MeHg^+ concentrations (80, 149, and 297 mg/L MeHg^+) are presented in Table 3-1. 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 3-1. Compared to the 2016 and 2019 slag samples, the oldest slag sample (2013), removed the least MeHg^+ per 1 gram of slag from solutions spiked with 75 mg/L MeHg^+ after a contact time of 24 hours. However, this relationship was reversed for solutions spiked with 297 mg/L MeHg^+. See Figure 3-2. One possible explanation for these results is that as the slag ages during laboratory storage, a "weathered" 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. The cure time for Saltstone is 28 days, not 24 hours used in this laboratory testing, which would have increased sequestration of Hg and all Saltstone regulatory samples passed the TCLP test and were not characteristically hazardous.

A statistical analysis of the data from the slag testing was performed. At 75 mg/L Hg, the 2Q19 slag is statistically different from the 2Q16 and 2Q13, but the 2Q16 and 2Q13 are not different from each other. Conversely, at 150 and 300 mg/L Hg, the 2Q19 and 2Q16 slags are not different from each other, but the 2Q13 sample is statistically different. Overall, 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. This difference in the 2Q13 slag is attributed to the changes discussed above that during laboratory storage of the material under conditions that did not preclude reaction with air.

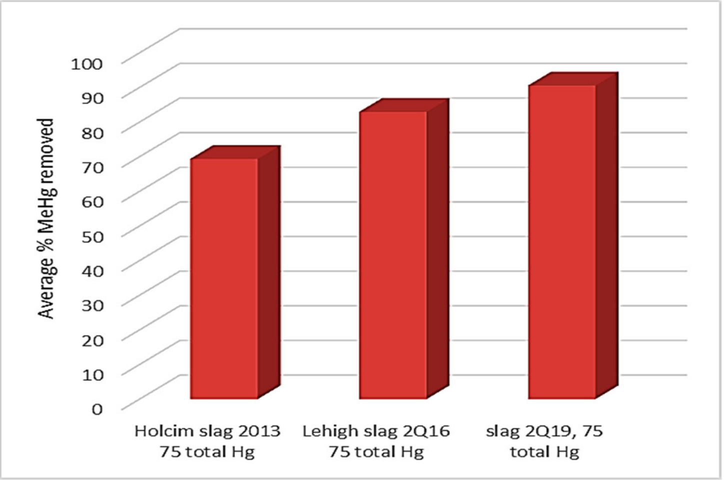

Figure 3-1. Comparison of the percent MeHg removed from simulated Tank 50 solutions spiked with 75 mg/L MeHg$^+$ after 24 h for the three slags used in the Saltstone facility and tested in this study.

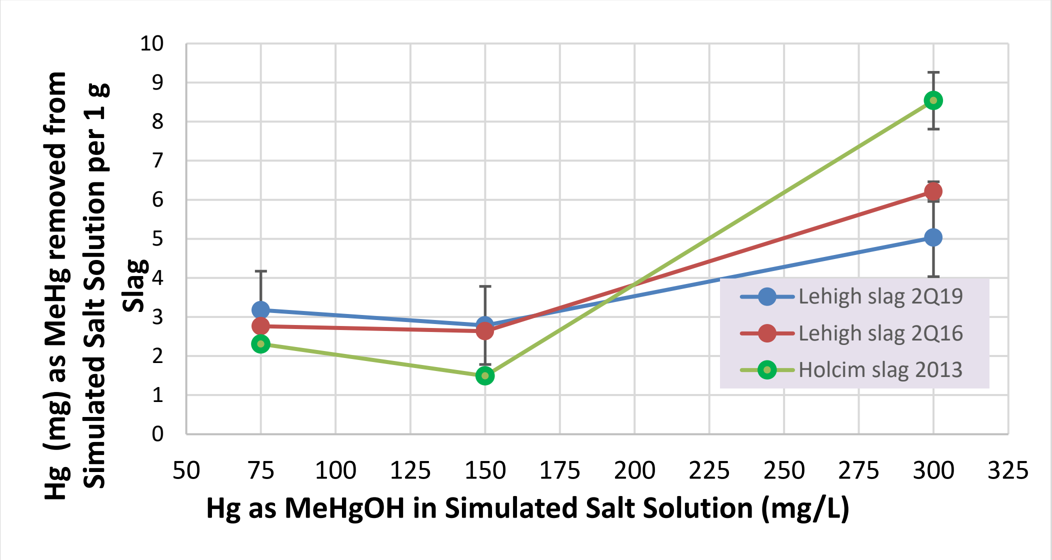

Figure 3-2. Comparison of Hg stabilization by three slags tested in this study as a function of MeHgOH in the simulated salt solution concentration. Comparison of Hg stabilization after 24 h for the three slags used in the Saltstone facility and tested in this study. (1 sigma error bars displayed.)

Table 3-1. 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 (74.6)	3.325	0.284	3.041	91.45	90.56	3.03
Lehigh slag 2Q19, 75 total Hg-2		3.332	0.000	3.332	89.67		3.32
Lehigh slag 2Q19, 150 total Hg-1	149.4 (139)	6.201	3.503	2.698	43.51	45.10	2.69
Lehigh slag 2Q19, 150 total Hg-2		6.185	3.298	2.887	46.68		2.88
Lehigh slag 2Q19, 300 total Hg-1	296.7 (276)	12.422	7.762	4.660	37.52	40.75	4.64
Lehigh slag 2Q19, 300 total Hg-2		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 (74.6)	3.346	0.544	2.802	83.74	82.96	2.80
Lehigh slag 2Q16 75 total Hg-2		3.320	0.591	2.729	82.19		2.73
Lehigh slag 2Q16 150 total Hg-1	149.4 (139)	6.240	3.692	2.548	40.85	42.34	2.55
Lehigh slag 2Q16 150 total Hg-2		6.234	3.502	2.732	43.83		2.73
Lehigh slag 2Q16 300 total Hg-1	296.7 (276)	12.570	6.179	6.392	50.85	49.46	6.37
Lehigh slag 2Q16 300 total Hg-2		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 (74.6)	3.319	0.971	2.348	70.75	69.39	2.34
Holcim slag 2013 75 total Hg-2		3.343	1.069	2.274	68.03		2.27
Holcim slag 2013 150 total Hg-1	149.4 (139)	6.186	4.742	1.444	23.35	24.16	1.44
Holcim slag 2013 150 total Hg-2		6.183	4.639	1.544	24.97		1.54
Holcim slag 2013 300 total Hg-1	296.7 (276)	12.308	3.239	9.069	73.68	69.27	9.05
Holcim slag 2013 300 total Hg-2		12.390	4.354	8.037	64.86		8.02

3.2 $MeHg^+$ Stabilization by Portland Cement and Class F Fly Ash

Results in Table 3-2 indicate that 2Q19 Portland cement and 2Q19 Class F fly ash received from the SPF did not stabilize $MeHg^+$. This is as expected, since they are not sulfur containing species and are not relied upon to provide any Hg sequestration function.

3.3 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, 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 3-3.

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. See Table 3-3. Negative values shown in Table 3-3 are believed to be the result of analytical testing/variability and do not indicate that $MeHg^+$ was generated by the CST, fly ash, or cement.

3.4 $MeHg^+$ 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 along with ability to incorporate the getter in the Saltstone premix or add it to the Salt Solution Receipt Tank (SSRT). 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 Mersorbs 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 3-3. These data and the results for the three slags tested are plotted in Figure 3-3. 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 3-3, all of the Mersorb® materials performed better than slag in the 24-hour tests.

Table 3-2. 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 (%)	$MeHg^+$ (mg) 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

Table 3-3. 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 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$^+$ (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 (74.6)	3.298	3.085	0.214	6.48	7.04	0.21
Cogen Fly ash 75 total Hg-2		3.336	3.083	0.254	7.60		0.25
Cogen Fly ash 150 total Hg-1	149.4 (139)	6.191	6.427	-0.235	-3.80	2.43	-0.23
Cogen Fly ash 150 total Hg-2		6.226	5.687	0.539	8.65		0.54
Cogen Fly ash 300 total Hg-1	296.7 (276)	12.365	10.615	1.750	14.16	11.83	1.75
Cogen Fly ash 300 total Hg-2		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 (74.6)	3.327	3.173	0.153	4.61	0	0.15
IE-911 CST 75 total Hg-2		3.388	3.536	-0.148	-4.37		-0.15
IE-911 CST 150 total Hg-1	149.4 (139)	6.175	6.248	-0.073	-1.19	0	-0.07
IE-911 CST 150 total Hg-2		6.203	6.165	0.038	0.62		0.04
IE-911 CST 300 total Hg-1	296.7 (276)	12.300	13.058	-0.759	-6.17	0	-0.76
IE-911 CST 300 total Hg-2		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

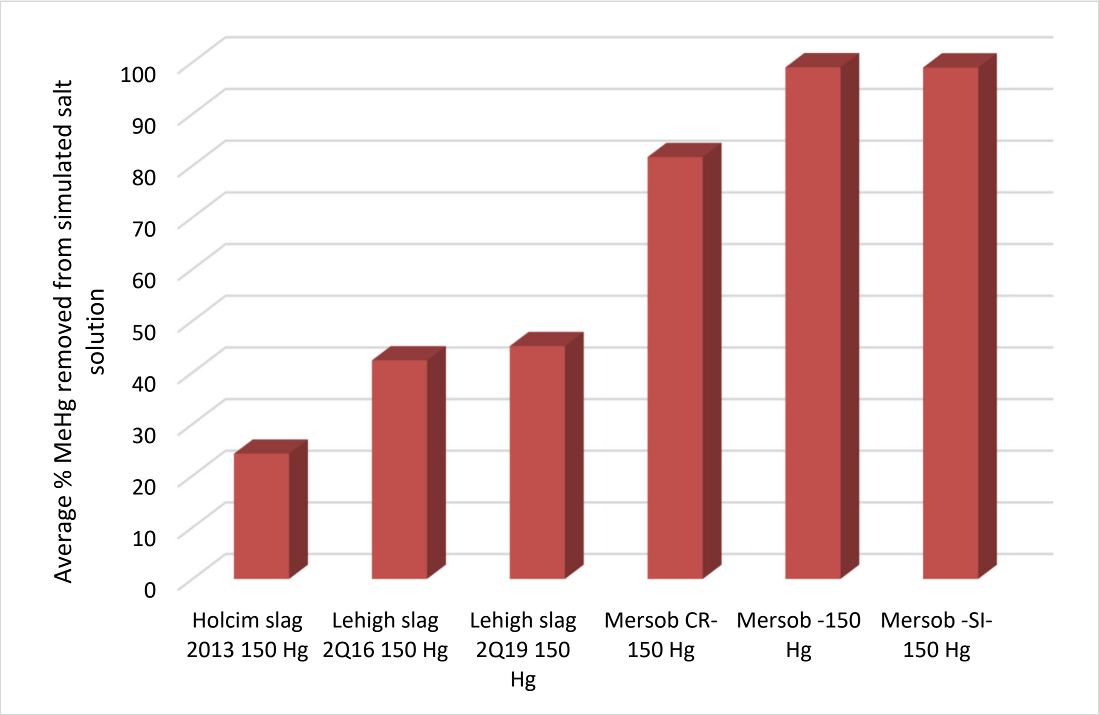

Figure 3-3. Comparison of $MeHg^+$ Stabilization in simulated salt solution spiked with 149 mg/L $MeHg^+$ (added as MeHgOH) after contact for 24 hours by the three slags used in the Saltstone Facility and three Mersorb® products supplied by NUCON International Inc.

3.5 $MeHg^+$ Stabilization by Potential Getters as a Function of Exposure Time

A comparison of the effectiveness of the three slag samples and Mersorb® in removing $MeHg^+$ from simulated salt solution after 24-hour exposure tests using solutions spiked with 149 mg/L $MeHg^+$ is provided in Table 3-4. 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 3-4. 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

3.5.1 Five to 60 Minute Exposure Times

Shorter exposure time results for Mersorb®, four sulfur impregnated silicate substrate materials, and Silicathiol® are provided in Table 3-5. At all exposure times evaluated, 5, 10, 20, 60 minutes, Mersorb® 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 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). Mercaptans have a distinctive odor and are methanethiol 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 was effective in reacting with soluble MeHg^{+} and removing it from solution, probably as 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 that initial sorption followed by desorption of MeHg^{+} by Silicathiol® rather than reaction to form HgS may be occurring at the shorter times, presumably due to 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 3-5. 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 (minutes)**	**10 (minutes)**	**20 (minutes)**	**60 (minutes)**			
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)	0.0	0.0	0.0	0.88	No measurable removal of MeHg^{+}	0.0	2.0
S Impregnated Ground Foam Glass	0.0	0.0	0.0	0.0	No removal of MeHg^{+}	0.0	NA

4.0 Conclusions

This work was authorized by the DOE Office of Environmental Management as HQTD 1002 Task 2.3.6 which had the objective of providing a technical basis for the organic mercury waste acceptance criterion (WAC) for Tank 50 salt solution. The current 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, 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 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.

In Part 1 of HQTD 1002, Task 2.3.6, $MeHg^+$ was shown to be redox sensitive and react with sulfide in slag, a cementitious ingredient in Saltstone. This reaction produces HgS as nanoparticles of β-cinnabar which has a very low solubility [11].

This report contains results from Parts 2 and 3 of HQTD 1002, Task 2.3.6. In Part 2, three slags, cement and fly ash used in the Saltstone process between 2013 and 2019, were tested for their ability to stabilize $MeHg^+$ in 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. The results indicated that the older slag from 2013 was slower to react that the 2016 and 2019 slags when the concentration of $MeHg^+$ is 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 can result in higher ion transport across the layer.

Commercial mercury getters were also tested in Part 2. 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 in the Part 1 study.

Part 3 of this report was focused on identifying a "getter" for pretreating salt solution with $MeHg^+$ concentrations that approached or exceeded the WAC limit to assure the resulting Saltstone would pass the TCLP test and not display the characteristic of Hg toxicity. Part 3 evaluated sequestration of $MeHg^+$ by Mersorb® and other potential "getters" as a function of 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. The goal was to demonstrate sequestration of Hg within the time required to pump Saltstone grout from the SSRT into an SDU. The new getters tested consisted of four porous silicate substrates that were impregnated with sulfur. The substrates selected were Diatomaceous Earth (food grade), Harborlite-700, 200 mesh Foam Glass, and Ground Foam Glass. 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 forms in the food grade Diatomaceous Earth are better than elemental sulfur as precipitation / sequestering agents when bound to substrates.

The results presented in this report were used to design TCLP tests requested by WRPS in which simulated salt solution was spiked with chromate and methyl mercury. The TCLP samples were crushed and sieved to a discrete size fraction (3/8 to 5/16 inch). The objective of this TCLP testing was direct comparison to the Tank 50 WAC testing. That work was performed by Crawford, et al. [12]. These simulant scoping tests indicate that the current Tank 50 WAC limits for total Hg (325 mg/L) and methyl mercury (350 mg/L) are adequate for protecting the TCLP Hg limit of 0.2 mg/L with the simulant formulation and conditions tested. Whether this can be extended to other formulations or conditions has not been tested.

5.0 Path Forward

The following tasks were identified for providing additional understanding of $MeHg^+$ speciation in SRS Tank 50 salt solution and in Saltstone and for sequestration of $MeHg^+$:

1) Determine whether granulated activated carbon that makes up the Mersorb® substrate reacts with salt solution to form ammonia, NH_3 which was previously detected as a reaction produce between carbon in Class F fly ash and salt solution. This reaction was the reason that thermally beneficiated fly ash was specified as a Saltstone ingredient which does not contain the carbon and thus avoids ammonia formation.

2) Optimizing the quantity of Mersorb® and/or sulfur impregnated diatomaceous earth addition required to remove a unit mass of $MeHg^+$ from salt solution.

3) Evaluate soluble sulfides such as, calcium sulfide (CaS), bismuth sulfide (Bi_2S_3), and antimony sulfide (Sb_2S_3), as additives for precipitating $MeHg^+$ as beta cinnabar (HgS).

6.0 References

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Appendix A. Statistical Analysis for Slag Stabilization of $MeHg^+$

Analysis of Variance (ANOVA) Stabilization for Solution Spiked with 75 mg/L $MeHg^+$
One -way Analysis of Variance applied to several statistical tests to determine whether the population of results for $MeHg^+$ stabilization by 3 slags is random or statistically significant.

Anova: 75 Single Factor		**Comparison of means of duplicate samples spiked with 75 mg/L $MeHg^+$**				
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Lehigh 2Q19	2	6.35005	3.175025	0.039423		
Lehigh 2Q16	2	5.529061	2.764531	0.002643		
Holcim slag 2013	2	4.616886	2.308443	0.002564		
ANOVA						
Source of Variation	*Sum of the Squared Deviations SS*	*Degrees of Freedom df*	*Mean Square Value MS*	*F-Ratio*	*P-value*	*F Value*
Between Groups	0.751658	2	0.375829	25.2631	0.013269	9.552094
Within Groups	0.04463	3	0.014877			
Total	0.796288	5				

Conclusion: The level of statistical significance, p-value, is less than or equal to the significance level (≤ 0.05) and F-Ratio >> 1 so the null hypothesis was rejected and the conclusion is that the results are random, i.e., that not all of 75 ppm population means are equal. This analysis does not indicate which groups are different from each other. It simply indicates that not all of the group means are equal.

Tukey-Kramer Analysis of Stabilization for Solution Spiked with 75 mg/L $MeHg^+$
In order to determine which groups are different from each other, a post hoc test using the most commonly Tukey-Kramer test was performed, which compares the mean between each pairwise combination of groups.

	Absolute Mean Difference	**Q-Critical Value**	**Significant at 0.05 Alpha**
Lehigh 2Q19 vs Lehigh 2Q16	0.4104945	0.509711	No
Lehigh 2Q16 VS Holcim slag 2013	0.4560878	0.509711	No
Lehigh 2Q19 vs Holcim slag 2013	0.8665823	0.509711	Yes
Q (3 DF for 3 K at 0.05 alpha)	5.91		
n	2		
Q Critical Value	0.5097113		

Conclusion: Based on the Tukey-Kramer post hoc test, the following assessment was made with respect to stabilization of Hg by 3 different slags exposed to simulated salt solution spiked with 75 mg/L $MeHg^+$:

- The difference in means between Lehigh 2Q19 vs Lehigh 2Q16 are not statistically significant.
- The difference in means between Lehigh 2Q16 vs Holcim slag 2013 are not statistically significant.
- The difference in means between Lehigh 2Q19 vs Holcim slag 2013 is statistically significant.

Stabilization for Solution Spiked with 150 mg/L $MeHg^+$

One -way Analysis of Variance applied to several statistical tests to determine whether the population of results for $MeHg^+$ stabilization by 3 slags is random or statistically significant.

Anova: 150 ppm Single Factor		**Comparison of means of duplicate samples spiked with150 mg/L $MeHg^+$**				
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Lehigh 2Q19	2	5.570211	2.785105	0.017609		
Lehigh 2Q16	2	5.277671	2.638836	0.017156		
Holcim slag 2013	2	2.985226	1.492613	0.004726		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2.003839	2	1.001919	76.11036	0.002687	9.552094
Within Groups	0.039492	3	0.013164			
Total	2.043331	5				

Conclusion: The level of statistical significance, p-value, is less than or equal to the significance level (≤ 0.05) and F-Ratio >> 1 so the null hypothesis was rejected and the conclusion is that the results are random, i.e., not all of 150 ppm population means are equal. This analysis does not indicate which groups are different from each other. It indicates that not all of the group means are equal.

Tukey-Kramer Analysis of Stabilization for Solution Spiked with 150 mg/L $MeHg^+$

In order to determine which groups are different from each other, a post hoc test using the most commonly Tukey-Kramer test must be conducted to compare the mean between each pairwise combination of groups.

	Absolute Mean Difference	**Q-Critical Value**	**Significant at 0.05 Alpha**
Lehigh 2Q19 vs Lehigh 2Q16	0.14627	0.479476	No
Lehigh 2Q16 VS Holcim slag 2013	1.146223	0.479476	Yes
Lehigh 2Q19 vs Holcim slag 2013	1.292492	0.479476	Yes
Q (3 DF for 3 K)	5.91		
n	2		
Q Critical Value	0.479476		

Conclusion: Based on the Tukey-Kramer post hoc test, the following assessment was made with respect to stabilization of Hg by 3 different slags exposed to simulated salt solution spiked with 150 mg/L $MeHg^+$:

- The difference in means between Lehigh 2Q19 vs Lehigh 2Q16 are not statistically significant.
- The difference in means between Lehigh 2Q16 vs Holcim slag 2013 is statistically significant.
- The difference in means between Lehigh 2Q19 vs Holcim slag 2013 is statistically significant.

Stabilization for Solution Spiked with 300 mg/L $MeHg^+$

One -way Analysis of Variance applied to several statistical tests to determine whether the population of results for $MeHg^+$ stabilization by 3 slags is random or statistically significant.

Anova: 300 ppm Single Factor		**Comparison of means of duplicate samples spiked with 300mg/L MeHg$^+$**				
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
Lehigh 2Q19	2	10.06944	5.034722	0.305		
Lehigh 2Q16	2	12.42365	6.211826	0.063097		
Holcim slag 2013	2	17.07526	8.537632	0.5306		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	12.71022	2	6.35511	21.21442	0.01697	9.552094
Within Groups	0.898697	3	0.299566			
Total	13.60892	5				

Conclusion: the p-value is less than or equal to the significance level (0.05), so we reject the null hypothesis and conclude that not all of 300 mg/L population means are equal. This analysis does not indicate which groups are different from each other. It simply indicates that not all of the group means are equal.

Tukey-Kramer Analysis of Stabilization for Solution Spiked with 150 mg/L MeHg$^+$
In order to determine which groups are different from each other, a post hoc test using the most commonly Tukey-Kramer test must be conducted to compare the mean between each pairwise combination of groups.

	Absolute Mean Difference	**Q-Critical Value**	**Significant at 0.05 Alpha**
Lehigh 2Q19 vs Lehigh 2Q16	1.177103399	2.287275444	No
Lehigh 2Q16 VS Holcim slag 2013	2.32580673	2.287275444	Yes
Lehigh 2Q19 vs Holcim slag 2013	3.50291013	2.287275444	Yes
Q (3 DF for 3 K)	5.91		
n	2		
Q Critical Value	2.287275444		

Conclusion: Based on the Tukey-Kramer post hoc test, the following assessment was made with respect to stabilization of Hg by 3 different slags exposed to simulated salt solution spiked with 300 mg/L MeHg$^+$:

- The difference in means between Lehigh 2Q19 vs Lehigh 2Q16 are not statistically significant.
- The difference in means between Lehigh 2Q16 vs Holcim slag 2013 is statistically significant.
- The difference in means between Lehigh 2Q19 vs Holcim slag 2013 is statistically significant.

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