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Innovative Mercury Treatment Technology Options for the Liquid Waste System at the Savannah River Site: Scoping Studies

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Cover Photograph: SRNL Intern, Charlyne Smith from Choppin University (Baltimore, MD), operating a full size sparge apparatus as part of developing mercury analysis and speciation protocols

DISCLAIMER

Dedication: This report is dedicated to Bill Wilmarth who was the SRNL lead for mercury research for many years before he recently passed. Bill encouraged a breadth and diversity of ideas in his collaborating teams with the goal of providing creative-actionable-disciplined research. Under Bill's guidance, SRNL advanced the technical basis for managing the mercury challenges facing the SRS Liquid Waste System and generated high level of support to DOE and to Savannah River Remediation.

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Savannah River National Laboratory ™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

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EXECUTIVE SUMMARY

The Savannah River Site (SRS) Liquid Waste System (LWS) contains liquids, salts and sludges that are currently being processed into final wasteforms for disposition, specifically, waste glass for sludges, solids and liquids containing high levels of radioactivity, and saltstone grout for low activity decontaminated liquid solutions. The LWS also contains approximately 60,000 kg of mercury present in the following physical and chemical forms, specifically:

 a) ionic inorganic mercury, organomercury (e.g., methylmercury), and other minor components found in LWS fluids
 b) mercury solids such as oxides, hydroxides, amalgams sulfides and sorbed mercury,
 c) accumulations of dense liquid elemental mercury, and
 d) vapor phase elemental and organomercury mercury found in tank headspace gas and in evaporators.

An effective and proactive management strategy of the mercury present in the LWS is needed to support processing of LWS wastes into glass and saltstone. Sustainable processing of the LAWS to completion requires mercury removal from the LWS at a rate of approximately 2,900 kg/yr. This removal can be accomplished through existing mercury treatment systems or newly implemented LWS "purge points".

The chemical speciation of mercury has emerged as the key factor that controls mercury behavior in the LWS. For example, past studies demonstrated that mercury speciation is adversely impacting the performance of existing removal systems so that significant levels of mercury are recycled from the Defense Waste Processing Facility (DWPF) back to the tank farm. Consequently, mercury concentrations have slowly increased in the LWS tank fluids over time. The presence of organo-mercury has also been identified as the cause of increased mercury leaching from saltstone.

In response to these challenges, the Department of Energy (DOE) Office of Environmental Management (EM-TD) Technology Development Program has supported a series of scoping studies predicated on manipulating or controlling mercury speciation and mercury behaviors within the constraints of LWS waste chemistry and safety conditions. The intent of these studies was to rapidly triage potential technology options and develop a technically based go / no go recommendation for further work. This composite report presents the results of three scoping studies: 1) advanced photooxidation processes, 2) chemical reduction, and 3) mercury getters.

The first study is focused on photooxidation as a potential approach for breakdown of methylmercury into ionic and elemental mercury forms that would reduce leachability to improve saltstone performance. Photooxidation was selected for testing because it can be deployed with minimal impacts on solution chemistry and with minimal flowsheet changes to maximize safety. Key findings include:

- UV light (e.g., <300nm wavelength) is strongly attenuated in LWS liquids, specifically, the light intensity decreased by a factor of approximately 10,000 over a one-centimeter distance. This suggests that virtually any LWS photooxidation process will be difficult to implement in practice.

- Photooxidation resulted in the conversion of methylmercury to inorganic and elemental mercury in simple solutions. However, photo-conversion of methylmercury was not observed in concentrated tank waste simulant. The underperformance in the concentrated simulant results from the attenuation of UV light combined with the complex "redox-buffer" aqueous matrix.

- The development of effective photo oxidation processes for LWS will be a challenge and this scoping study does not support advancing approach (no go). We recommend future efforts related

to oxidation processed in the LWS should be focused on persulfate (or permanganate) or other oxidants that can be deployed in a complex alkaline matrix, specifically using chemistries that are generally compatible and synergistic with existing tank farm conditions.

Chemical reduction was proposed as a method for potential conversion of inorganic ionic mercury (e.g., Hg^+ and Hg^{2+} and complexes) into elemental mercury in the wastes that feed into LWS evaporators, thus enhancing the effectiveness of the existing elemental mercury removal ("distillation") processes. Key findings include:

- Reduction of inorganic ionic mercury to elemental mercury was confirmed and occurred rapidly during laboratory testing, suggesting reduction is feasible in Tank 43 simulant.

- Stannous chloride was effective at doses above 10X to 100X. Formic acid was effective at doses above 1X but may be subject to side reactions with the methylmercury present in the evaporator feedstock which would result in collateral impacts such as generation of dimethylmercury. Oxalic acid underperformed the other tested reductants in Tank 43 simulant and was not effective at any dose.

- The data suggest that developing effective process for the LWS is feasible and the scoping study would support advancing this to further testing (go). Recommended future tests are focused on higher temperatures, performance in the presence of methylmercury, and an expanded portfolio of test reductants.

As an alternative to the chemical technologies evaluated in the first two speciation strategies, the third approach is focused on identification of potential "getters" to facilitate the targeted immobilization of organomercury in saltstone. The purpose of the saltstone wasteform is to stabilize contaminants, including Hg in the grout material and to resists subsequent leaching. However, recent data indicate that there is a potential trend toward increased Hg levels in saltstone leachates; the observed trends have been attributed to the predominance of methylmercury in the saltstone feedstock and its relatively higher leachability. Key findings of this study include:

- Several materials may improve the retention of methylmercury. Many of these incorporate a thiol or a reduced sulfur active component. Examples of promising materials include various forms of silica thiol, sulfur impregnated activated carbon (such as MERSORB), functionalized mercury chelating resins (such as AmberSep GT74), chitosan waste materials (such as granulated exoskeletons from seafood processing), SRS Tire Derived Fuel ash, and tire crumb waste materials. A major challenge for these materials may be the cost of implementation; current commercial costs may be prohibitive.

- None of the materials in the scoping table have been previously tested in grout; testing is underway in methylmercury spiked grout at SRNL.

- The data suggest that identifying a potential getter for the LWS may be feasible and this activity is recommended for further testing (go). Getters, particularly if they are effective for methylmercury, remain as a strategy that will provide defense in depth and increase system robustness and confidence. While use of getters is not crucial to continued operations at this time, developing knowledge and testing of alternative getters is a relatively low-cost endeavor that would support prudent-rapid response actions if mercury concentrations increase in Tank 50 (saltstone feedstock) or if future leaching tests approach SRS action levels.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
CCP	Corrosion Control Program
CH_3Hg^+	Methylmercury
DI	Deionized
diMeHg	Dimethylmercury
DOE	Department of Energy
DSS	Decontaminated Salt Solution
DWPF	Defense Waste Processing Facility
ECP	Enrichment Control Program
EM	Environmental Management
EPA	Environmental Protection Agency
Hg	Mercury
LLW	Low level waste
LWS	Liquid Waste System
MeHg	Methylmercury
nm	Nanometers
RCRA	Resource Conservation and Recovery Act
SAMMS	Self-Assembled Monolayers on Mesoporous Supports
SDF	Saltstone Disposal Facility
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRR	Savannah River Remediation
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TCLP	Toxicity Characteristic Leaching Procedure
TDF	Tire Derived Fuel
UV	Ultraviolet
WAC	Waste Acceptance Criteria

1.0 Introduction

There is an extensive history of mercury (Hg) use at the Savannah River Site (SRS). For decades, inorganic mercury has been used as a catalyst to aid in the dissolution of aluminum clad fuel and target assemblies associated with separation processes that support the US nuclear stockpile. This has led to the presence of approximately 60,000 kg of mercury in the Liquid Waste System (LWS) onsite (DOE-EM, 2016). The mercury is isolated within process vessels and storage tanks of the LWS (Figure 1-1), with minimal releases to the surrounding environment. The typical concentration of total mercury in the system is on the order of 100 mg/L. These levels are approximately six orders of magnitude higher than the concentrations that have been studied in most environmental systems. Management of these hazardous compounds in the LWS continues to be a priority for SRS.
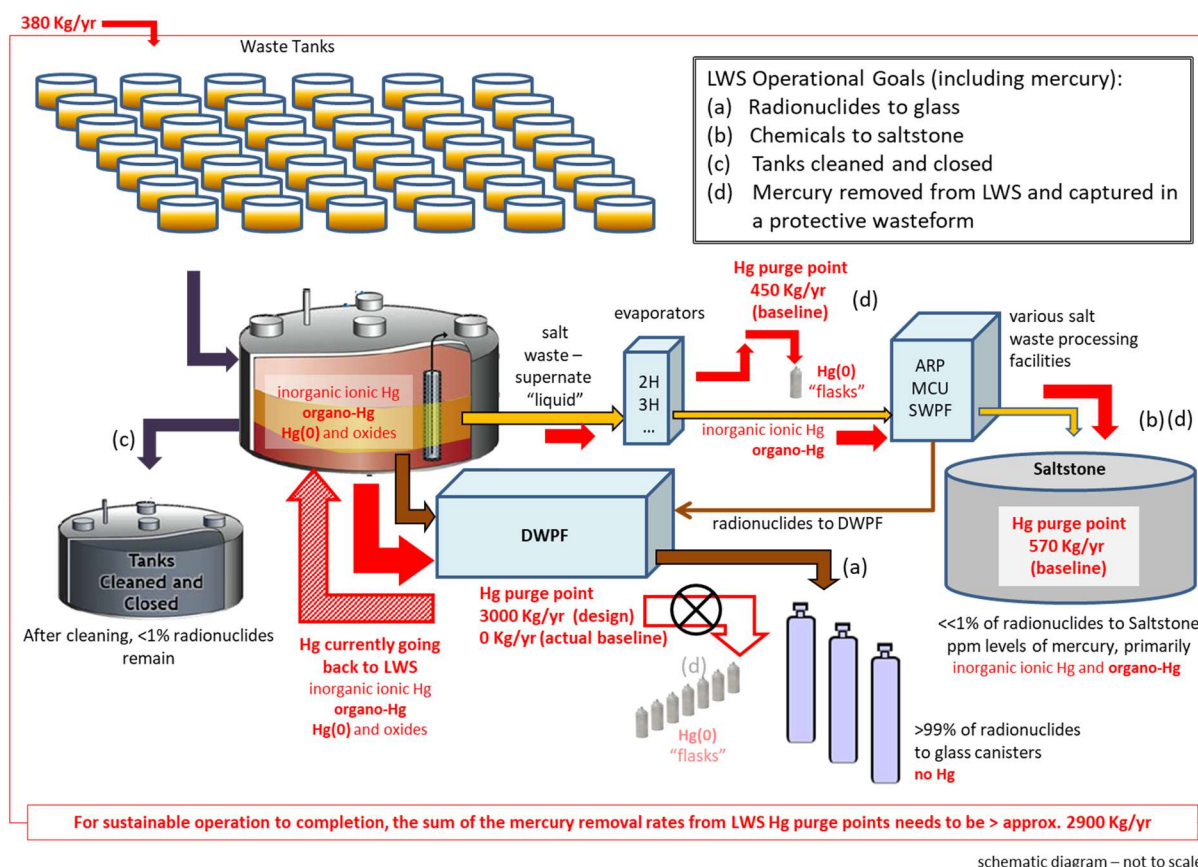
Figure 1-1. Fate of Mercury in the SRS Liquid Waste System

Liquid waste at SRS is a concentrated sodium nitrate solution containing radioactive and non-radioactive elements and ions along with residual inorganic and organic constituents. Liquid waste phases include an alkaline, high ionic strength liquid that is maintained at a high pH (salt solution) to control corrosion, a solid phase containing precipitated salts and other solids species (sludge), and a vapor phase associated with the headspace of process vessels. Mercury reactions in the complex, alkaline environment have resulted in the presence of solid, liquid (elemental), vapor, and dissolved mercury species (Boggess et al., 2019). Chemical speciation in tank waste controls mercury behavior in LWS operations – specific issues include the presence of mercury in the evaporators and mercury removal systems and leachate from

saltstone, as well as safety issues including potential worker exposure to vapors and the potential for flammability. Additional technical challenges include the complex and poorly understood chemistry responsible for mercury transformations, in addition to the inadequate performance of standard mercury treatment technologies.

Over the past two years, efforts have increased to better understand the chemistry of mercury and mercury speciation within the LWS process. This work has indicated that mercury is present in the elemental state, solid phases as mercury oxides/hydroxides/sulfides/amalgams, and soluble phases such as ionic mercury complexes, and organo-mercury (e.g., methylated) species. Elemental mercury and organo-mercury are present in both the both the vapor and aqueous phases within the LWS. Importantly, sampling results indicate that organo-mercury species are a significant fraction of the soluble mercury species in the SRS radioactive liquid waste. The data show that mercury speciation is adversely impacting the mercury removal systems in the Defense Waste Processing Facility (DWPF) where the high-level radioactive sludge is vitrified into glass for final disposal, this results in a significant recycle of mercury back to the tank farm (Figure 1-1). As a result, mercury concentrations have been slowly increasing in the LWS tank liquids. The presence of organo-mercury has also been implicated in an observed increased mercury leaching from saltstone – saltstone is a solid concrete matrix that serves as the final waste form for the decontaminated salt supernate solutions from the waste tanks. Thus, the presence of organic mercury reduces the effectiveness of mercury removal systems built into the LWS and increases the leachability of mercury from the final disposal waste form. Strategies for the management of organic mercury are being developed to prevent long-term impacts to the disposal of the liquid waste (Bannochie et al., 2016).

2.0 Objectives

An overarching objective of ongoing SRS LWS mercury activities is to achieve removal of mercury from the LWS at a rate that would reduce overall mercury mass in the system over time (Figure 1-1). This would result in continued sustainable operation as the entire radioactive waste inventory is processed into final stabilized forms, primarily high-level waste glass canisters and a cementitious "saltstone". A promising strategy to help meet this objective is the deployment of technology(ies) to beneficially alter/manipulate mercury speciation within the LWS to control mercury behavior. This report documents the scoping evaluation results for three different mercury speciation control strategies: 1) advanced photooxidation processes, 2) chemical reduction, and 3) getters. Each of these topics is discussed in this document.

Photooxidation: Advanced photooxidation processes have the potential to break down methylmercury (MeHg) into ionic and elemental mercury forms. In this "speciation-control" example, conversion of organomercury to inorganic ionic mercury or elemental mercury improves the performance of the existing mercury removal system and saltstone by reducing the presence of MeHg. If more mercury can be sent to saltstone, this represents a potential "purge point" for mercury from the LWS that uses an existing high-quality environmentally protective wasteform. For complex high-level radioactive waste solution, such an oxidation, would ideally target organomercury preferentially and use technologies that minimize undesired reactions with the other waste constituents (e.g., to maintain the safety basis and minimize the potential for adverse collateral impacts).

Reduction: The second mercury speciation control strategy is a chemical reduction process to convert inorganic ionic mercury (e.g., Hg^+ and Hg^{2+} and complexes) into elemental mercury in the wastes feeding into LWS evaporators, thus enhancing the effectiveness of the existing elemental mercury removal ("distillation") processes. Note that chemical reduction, used alone, would impact inorganic ionic mercury, not organomercury, since the initial step in converting organomercury to any inorganic form, including

elemental mercury, is an oxidation reaction. Similar to above, chemical reduction should be scoped in a manner that minimizes undesired reactions and that focuses on maintaining the safety basis and limits the potential for adverse collateral impacts.

Mercury Getters: The third mercury speciation strategy is identification of potential "getters" for saltstone. Both photooxidation and reduction strategies rely on actively manipulating mercury speciation in the wastes by converting mercury to a more desirable form. In lieu of these chemical conversion strategies, several potential getters were identified that might potentially reduce the leachability of organomercury from saltstone. Addition of such getters to the saltstone mixture would help to increase retention of MeHg and reduce undesired leaching. This provides an alternative mitigation method to the primary two applications.

3.0 Photooxidation to Convert Methylmercury into Inorganic Ionic Mercury

3.1 Background

The formation of MeHg and other organomercury species in the SRS LWS and the Defense Waste Processing Facility (DWPF) reduce the effectiveness of the LWS mercury removal and control systems. The presence of organomercury species also increases the leachability of mercury from saltstone.

In a recent Systems Engineering Evaluation (SRR, 2015b), photooxidation was identified as promising technology for CH_3Hg^+ (MeHg) conversion/destruction. Photoreactions have the potential to break down MeHg into ionic and elemental mercury forms with minimal collateral chemical modification.

The technical literature related to MeHg and ionic mercury photoreactions, indicating sunlight as the primary pathway for MeHg loss/destruction is robust (Black et al., 2012; Lehnherr and St Louis, 2009; Celo, et al., 2006; Hammerschmidt and Fitzgerald, 2006 & 2010; Chen and Lin, 2003; Krabbenhoft, et al., 2002; Costa and Liss, 2000; Sellers et al., 1996 and 1997; Suda and Hirayama, 1993; Ahmed and Stoeppler, 1986; Inoko, 1981). The literature also documents that sunlight photoreactions in seawater reduce some ionic mercury to elemental mercury (e.g., Celo, 2006); so, there is a potential that a photoreactor could convert both ionic and MeHg to elemental mercury without additional chemical oxidants or reductants. The mechanism and products for the direct photodegradation pathway(s) are shown in summary form below (Inoko, 1981):

Direct photo-oxidation reaction:
$$CH_3HgCl \xrightarrow{hv} [CH_3HgCl]^* \rightarrow \bullet CH_3 + \bullet HgCl$$

A series of follow on reactions generate products such as:
CH_4 or C_2H_6 from $\bullet CH_3$
Hg_2Cl_2, $HgCl_2$ or $Hg(0)$ from $\bullet HgCl$

A photoreactor system should have the potential to convert MeHg to inorganic species at various locations within the LWS. However, the historical focus of the scientific literature emphasizes low concentrations and circumneutral pH in a dilute water matrix; thus, the data cannot be directly applied to the complex chemistry of concentrated alkaline liquid wastes. Focused studies to quantify MeHg transformation mechanisms and kinetics for realistic alkaline waste conditions using UVC wavelengths are needed to supplement the available literature. The data would help establish the conceptual basis for a photoreactor and provide information to support future LWS planning decisions.

3.2 Objective

The objective of this applied research was to study advanced oxidation processes and elucidate mechanisms and rates for the conversion of MeHg to inorganic mercury species to improve the performance of existing mercury removal systems, and to decrease the leachability of mercury incorporated into saltstone. All phases of the research emphasized conditions that are directly applicable to the complex chemistry of alkaline liquid waste solutions/simulants.

This work initially focused on the chemical conditions of Tank 50, the low-activity waste feed to the saltstone process. Converting organomercury to inorganic species in this solution would reduce mercury leachability from the resulting saltstone grout. The data can ultimately be used to summarize the potential benefits, costs and risks of each technology to support a "go"- "no go" evaluation by DOE/SRR for follow-on pilot-scale development and demonstration. The technology development activities for Tank 50 simulant could also be considered for application to other locations in the LWS system.

3.3 Experimental procedures

3.3.1 Materials

A radiometer that measures UVC and specific UV wavelengths of interest (254 nm and 185 nm) was procured and assembled in the SRNL machine shop. All equipment for these experiments was set up in a dedicated MeHg study laboratory in the Aiken County Technology Laboratory (ACTL). Ancillary supplies (reagents, glassware, etc.) were provided from existing stock or from SRNL contracted suppliers.

3.3.2 Methods

As a scoping step, the mechanisms and rates for the conversion of MeHg to inorganic mercury species by advanced oxidation processes were evaluated/quantified. The work was performed in several phases (Figure 3-1): 1) preparation of MeHg simulants/solutions, 2) determination of the optical properties of the simulants/solutions, 3) development of a cost effective, rapid mercury speciation methods, and 4) photoreactor tests.
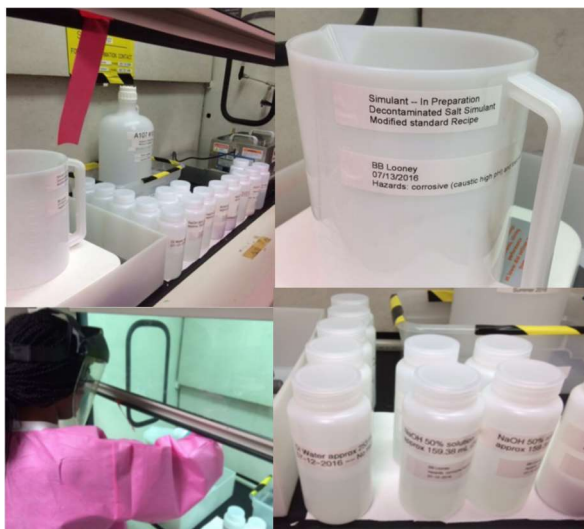

Figure 3-1. Photoreaction Testing

3.3.3 Simulant preparation

The objective of this work task was to prepare simulant recipe that is generally representative of Savannah River Site (SRS) Tank Waste Decontaminated Salt Solution (DSS). This simulant was used to evaluate various options for modifying and/or controlling mercury speciation and provide data for developing future waste treatment strategies. In particular, the research focused on various oxidation and reduction reactions to convert MeHg, a predominant mercury species in the Tank Farm, into inorganic ionic and elemental mercury forms that are amenable to removal with existing Tank Farm mercury treatment systems.

Figure 3-2. Simulant Preparation.

A standard SRS simulant recipe for DSS (see Peterson, 2000; Zamecnik et al., 2005) was selected with the following notes/modifications. Cesium was eliminated from the standard SRS recipe (Peterson, 2000) – to better represent DSS per Zamecnik et al. (2005). Inorganic mercury was eliminated from the standard recipe – MeHg was spiked into small subsamples of the primary and secondary simulants immediately prior to each set of experiments. Stannous [tin(II)] chloride due to its reactivity with inorganic ionic mercury was eliminated from the standard recipe for the primary simulant. A secondary simulant solution with the tin(II) chloride added back was also be prepared to assess the potential significance of Sn-Hg reactions. The simulant was unfiltered for the experiments. Table 3-1 details components in each of the two simulants prepared. The solutions were spiked with the desired quantities of inorganic and/or MeHg prior to the experiments.

3.3.4 Optical properties

Optical properties of the simulant were assessed to allow for modeling of the light intensity as a function of depth. Simulants were measured in 1 cm path length quartz cuvettes. Light absorbed was measured with a scanning spectrophotometer (Thermo Scientific Genesys 10S UV-VIS); each sample was scanned for light absorbance in 1 nm wavelength increments over a range of wavelengths spanning 190 to 1100 nm. The tabulated raw absorbance data over 1 cm were converted to standardized first order attenuation factors (in uints of m^{-1}) to aid in projecting the potential for penetration of different wavelengths of light through tank waste solutions.

3.3.5 Mercury speciation analysis

Mercury species were determined by selective reduction (reagent manipulation) and modified sparging protocols based on EPA Methods 1631 and 245.7 (EPA, 2002; EPA, 2005). The task was used as a cost-effective selective reduction speciation analysis schema to quantify mercury species. This set of tasks was completed to support analysis of large numbers of samples.

Figure 3-3 summarizes the proposed selective reduction analytical schema. The strategy relies on selectively converting the various forms of mercury in an aqueous sample into elemental mercury (Hg(0)), and then immediately sparging the Hg(0) from the solution into a detector for analysis. The planned schema included an initial sparge step with no reagent addition to determine the presence of elemental mercury directly. However, the levels of mercury in the experiment were approximately 100x the solubility of Hg(0) making this step unreliable since the excess mercury would tend to volatilize during the experiment (or

coalesce into a separate phase in a quiescent sample). Thus, the initial purge step was eliminated as shown. In the final method, the loss of mercury from the overall mass balance was tracked and attributed to formation of elemental mercury or other recalcitrant forms (e.g., oxide solids).

The oxidant (BrCl) and reductant (stannous chloride) were prepared according to EPA Method 1631. For samples where oxidant was used, the oxidation of MeHg by BrCl was performed at room temperature for 24 to 48 hours prior to the addition of stannous chloride, sparging, and detection. For concentrated simulant brines, reagent quantities for both oxidants and reductants required adjustment from standard EPA methods due to the presence of high concentrations of transition metals and nitrate/nitrite - simulants act as redox buffer solutions. To effectively oxidize MeHg in the complex simulant solutions, and to effectively reduce the inorganic mercury to elemental mercury for sparging, we added 3x the reagent quantities typically used in EPA method 1631. During the scoping work, the schema was applied to known concentrations of organic mercury and inorganic ionic mercury in deionized water and in simulant. In all cases, the detection and quantification of sparged mercury was performed using a Lumix Zeeman Effect Spectrometer.

Standards were prepared with concentrations of 0, 40, 60, and 100 ppm in deionized water (inorganic ionic mercury), as well as 100 ppm in water and stimulants (MeHg). The inorganic mercury spiking solution contained 1000 ppm (as Hg) in 2% nitric acid (High Purity Standards) and the MeHg spiking solution contained 1000 mg/L (as CH_3HgCl, or 798 mg/L (as Hg)) in deionized water (Alfa-Aesar). Three aliquots were measured for each sample: (1) ionic Hg, and (2) total Hg. MeHg and other/elemental mercury were calculated as depicted in Figure 3-3. Blanks and unreacted standard solutions were run with each set of samples. The masses of all mercury species were tracked in terms of g (as Hg) and all mercury species concentrations were tracked in units of mg/L (as Hg) and moles/L.

3.3.6 Photoreaction tests

Photoreaction tests were used to determine reaction rates of mercury transformation using UVC light having wavelengths between 100 and 280 nm. Using a lab scale UVC photoreactor, kinetic studies were performed for MeHg conversion/destruction. Deionized water and SRS LWS simulant were spiked with MeHg and then exposed to known amounts of UVC light (sec-W/m^2) including a control (with no UVC exposure). When MeHg conversion was observed, kinetic equations were developed, and kinetic parameters estimated. Multiwell plates or quartz tube microreactors fabricated in the SRNL glass shop were used for the photoreactions (Figure 3-4). The microreactors were exposed to UVC light for varying times and varying total light energy. The combination of light intensity (W/m^2) and time (sec) were used as the primary metric of cumulative UVC dose/exposure for each reactor (sec-W/m^2 = J/m^2). The sample exposure times ranged from 0 to 21,600 seconds. The light intensity in the chamber ranged from 0.005 to 0.008 W/m^2.

3.3.6.1 UVC Photoreactor

The tests utilized low cost, commercially available UVC light sources (Atlantic Ultraviolet RRD12‑2S SANIRAY direct fixture) equipped with standard germicidal lamps emitting primarily 254 nm wavelength. The light exposures were performed in a box fabricated by the SRNL machine shop. The exposure box was fitted with tubing barbs to allow air circulation to maintain ambient temperatures and was lined with expanded polytetrafluoroethylene (ePTFE, which reflects 99+% of the light in the UVC range). The intensity of the light (mW/cm^2) in the box was measured using a radiometer (International Light Technology, ILT5000A equipped with calibrated SED240/NS254/W Germicidal Detector system).

Table 3-1. Chemicals Used in DSS Recipes

| Compound	Mass (g) or volume (mL)	Component	Target (M)
Primary simulant			
DI H_2O	1771	---	---
NaOH (50% wt)	637.5	OH^-	2.06
$Al(NO_3) \cdot 39H_2O$	262.5	AlO_2^-	0.28
$NaNO_3$	249.5	NO_3^-	2.03
KNO_3	3.8	K^+	0.015
$Na_2CO_3 \cdot H_2O$	46.5	CO_3^{2-}	0.15
Na_2SO_4	49.5	SO_4^{2-}	0.14
NaCl	3.5	Cl^-	0.024
NaF	2.95	F^-	0.028
$Na_2HPO_4 \cdot 7H_2O$	4.7	PO_4^{3-}	0.007
$Na_2C_2O_4$	6.7	$C_2O_4^{2-}$	0.02
$Na_2SiO_3 \cdot 9H_2O$	21.3	SiO_3^{2-}	0.03
$Na_2MoO_4 \cdot 2H_2O$	0.043	MoO_4^{2-}	0.00007
$CuSO_4 \cdot 5H_2O$	0.0135	Cu	2.20E-05
Na_2CrO_4	0.585	Cr	1.40E-03
$Zn(NO_3)2 \cdot 6H_2O$	0.092	Zn	1.20E-04
$Pb(NO_3)_2$	0.0075	Pb	1.10E-05
$Fe(NO_3)_3 \cdot 9H_2O$	0.0255	Fe	2.60E-05
NH_4NO_3	0.2005	NH_3	0.001
$NaNO_2$	86.5	NO_2^-	0.5
Secondary simulant			
"primary simulant"	1000 mL	---	---
$SnCl_2 \cdot 2H_2O$	0.0045	Sn	2.00E-05
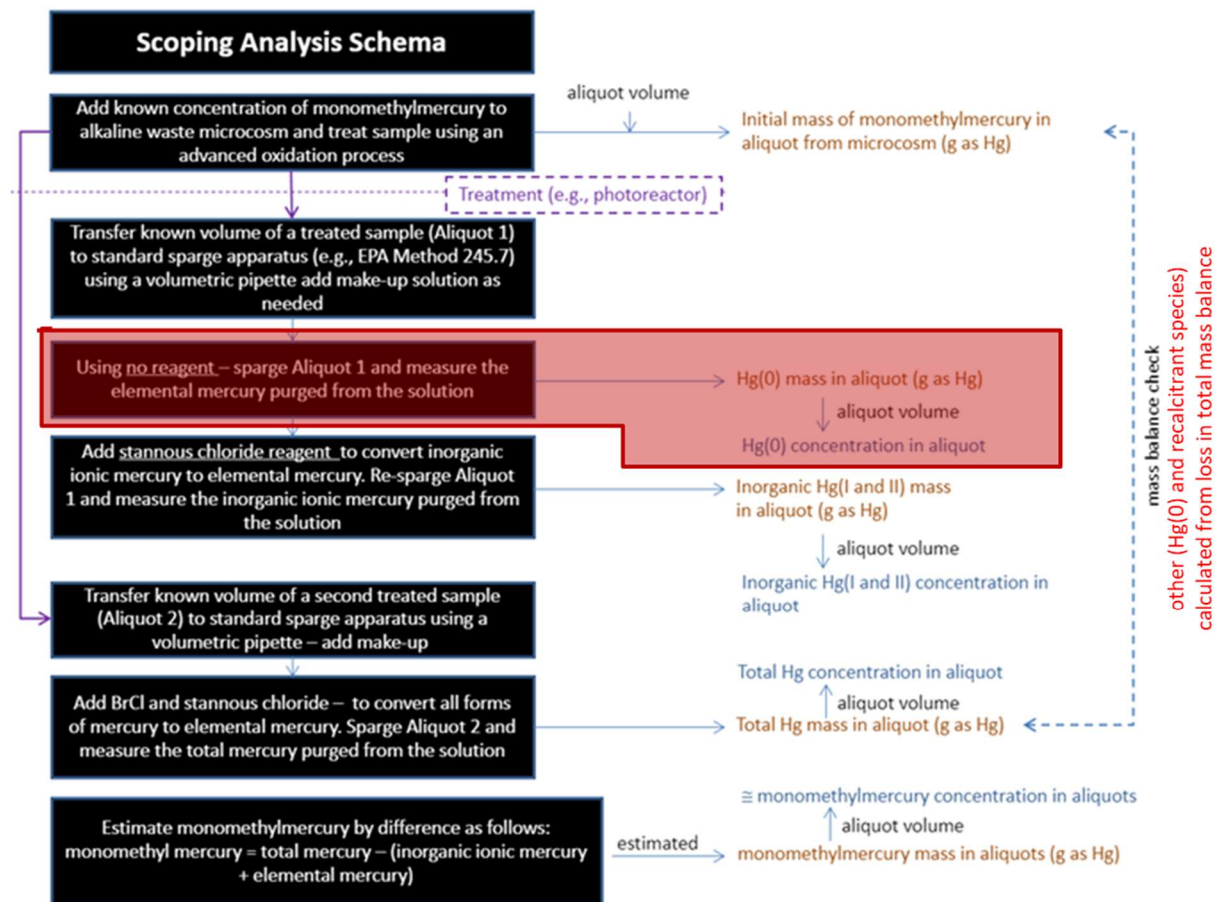
Figure 3-3. Selective Reduction Analysis Schema
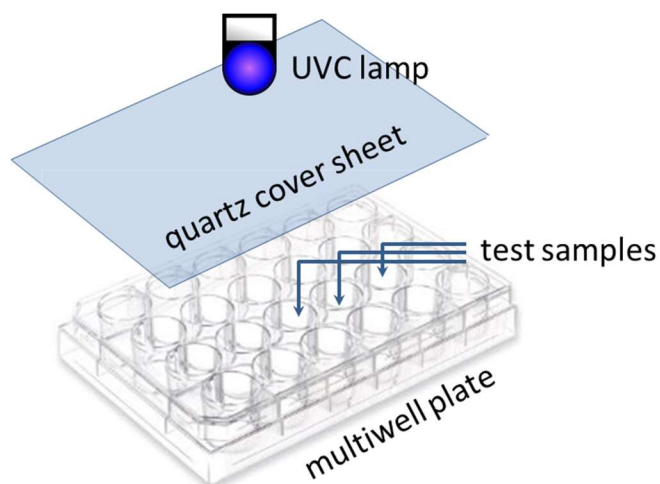
Figure 3-4. Microreactor Setup Using Multiwell Plates

3.4 <u>Results and Discussion</u>

3.4.1 Simulant preparation

Two base simulants were safely prepared for testing. Neither of these contained mercury. For experiments with MeHg, the simulants were spiked just before the start of testing. The nomenclature for the various simulants was:

- decontaminated salt simulant (DSS) –
- no cesium (NC) –
- mercury information: no mercury (NM) or 100 mg/L of either inorganic Hg (100inM) or MeHg (100MeM) --
- tin information: no tin (NT) or standard tin (ST)

As an example, sample DSS-NC-100MeM-NT would represent a decontaminated salt simulant with no cesium added, containing 100 mg/L of MeHg and no added stannous chloride in the base simulant mix.

3.4.2 Optical properties

A representative nonradioactive DSS simulant was successfully prepared containing 21 compounds and used for optical and photoreaction tests. The UVC light absorption in spiked and unspiked simulant was measured. A significant broad light absorption was observed over the entire UV & lower wavelengths of the visible range (Figure 3-5). At key UV wavelengths (e.g., <300 nm) light was not able to significantly penetrate the simulant solutions. At these wavelengths, light intensity was reduced by approximately 10,000x over a 1 cm depth (light intensity was reduced about 35% over a 1 mm depth). The observed high measured attenuation factor will inform and influence the required design for any potential LWS photoreactor. The absorbance was also measure for DI water (baseline) and for a 100 mg/L MeHg and inorganic mercury standard solution in DI water. The MeHg solution (in DI water) showed minimal light absorbance at wavelengths greater than 250 nm. The inorganic Hg solution showed minimal light absorbance above 300 nm with some light attenuated around 300nm by nitrate in the solution (nitric acid is used as a preservative in the purchased standard that was used to spike the samples).

The data showed that UV wavelength light has minimal ability to penetrate a significant depth/distance into the liquids present in the LWS. Thus, the use of UV treatment processes is unlikely to be effective. These

data provide additional context to supplement the interpretation of previous SRS LWS research in which documented a significant underperformance in an oxalic acid destruction that relied on a UV photoreactor and hydrogen peroxide (Areva, 2010; Martino et al., 2012). Minimal oxalic acid conversion was documented in tank waste conditions compared to reasonable conversion in simpler lab matrices. The earlier testing was performed in solutions that contained solids and sludges and the quartz tubes were blocked by visible deposits after short operational periods. The underperformance was attributed to sludge deposits blocking the light, but our measurements in Figure 3-5 suggest that light attenuation in the liquid solution might also contribute to their observations.
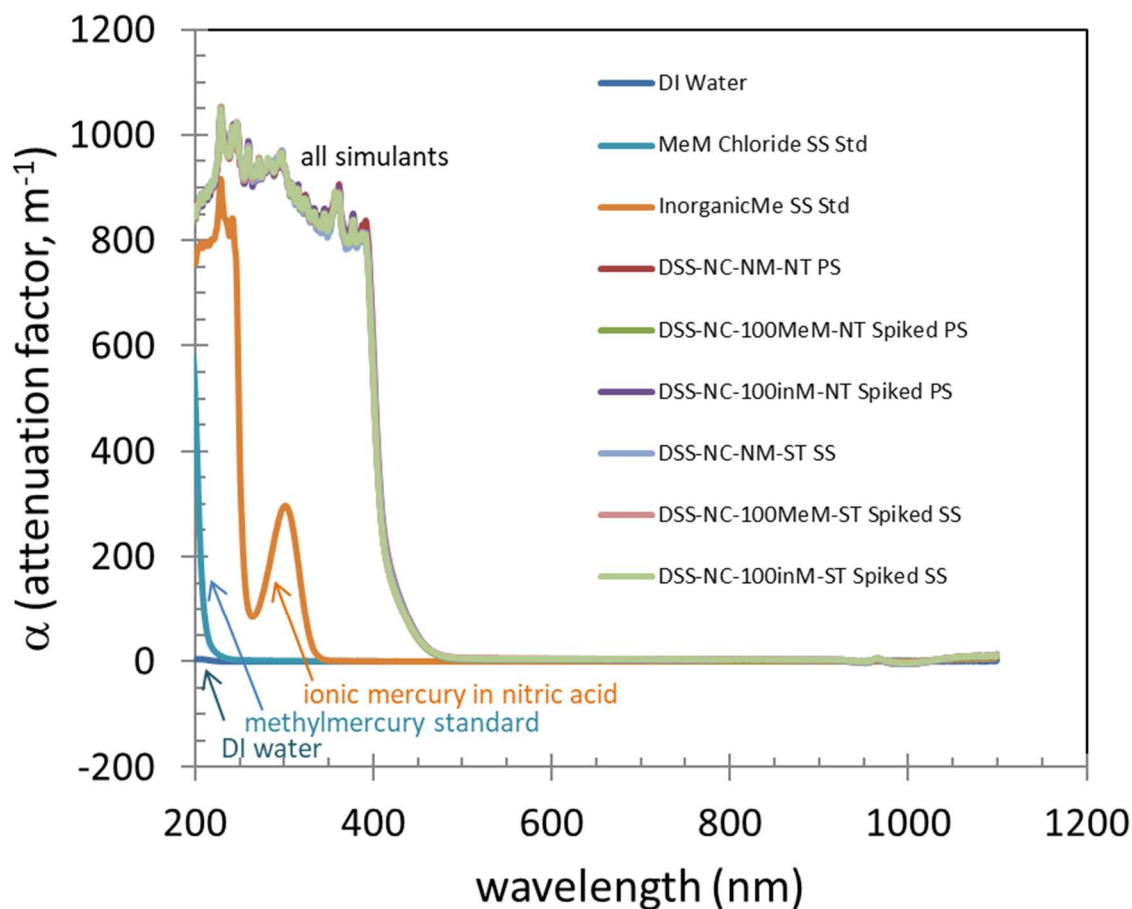
Figure 3-5: Optical Properties

3.4.3 Mercury speciation analysis

The simplified selective reduction analytical scheme was validated using solutions and DI water standards and spiked simulants of known concentration and known speciation. The resulting data (Figure 3-6: Mercury Speciation Analysis), demonstrate the equivalency of inorganic ionic mercury response and the MeHg response for the samples in which oxidant (BrCl) was added. This result provided independent quality assurance on the reagent standards and demonstrated the effectiveness of the BrCl in converting MeHg to inorganic mercury prior to addition of stannous chloride and sparging. Importantly, MeHg showed minimal detector response in the case of selective reduction samples where no bromate was added (open symbols). Further, the MeHg data showed good performance in both deionized water and in concentrated

simulant. The observed behaviors: a) quantitative and equivalent responses, b) good mass balance, and c) robust performance in the range of matrix solutions -- all support the viability of the selective reduction schema to support the lab testing of advanced oxidation processes.
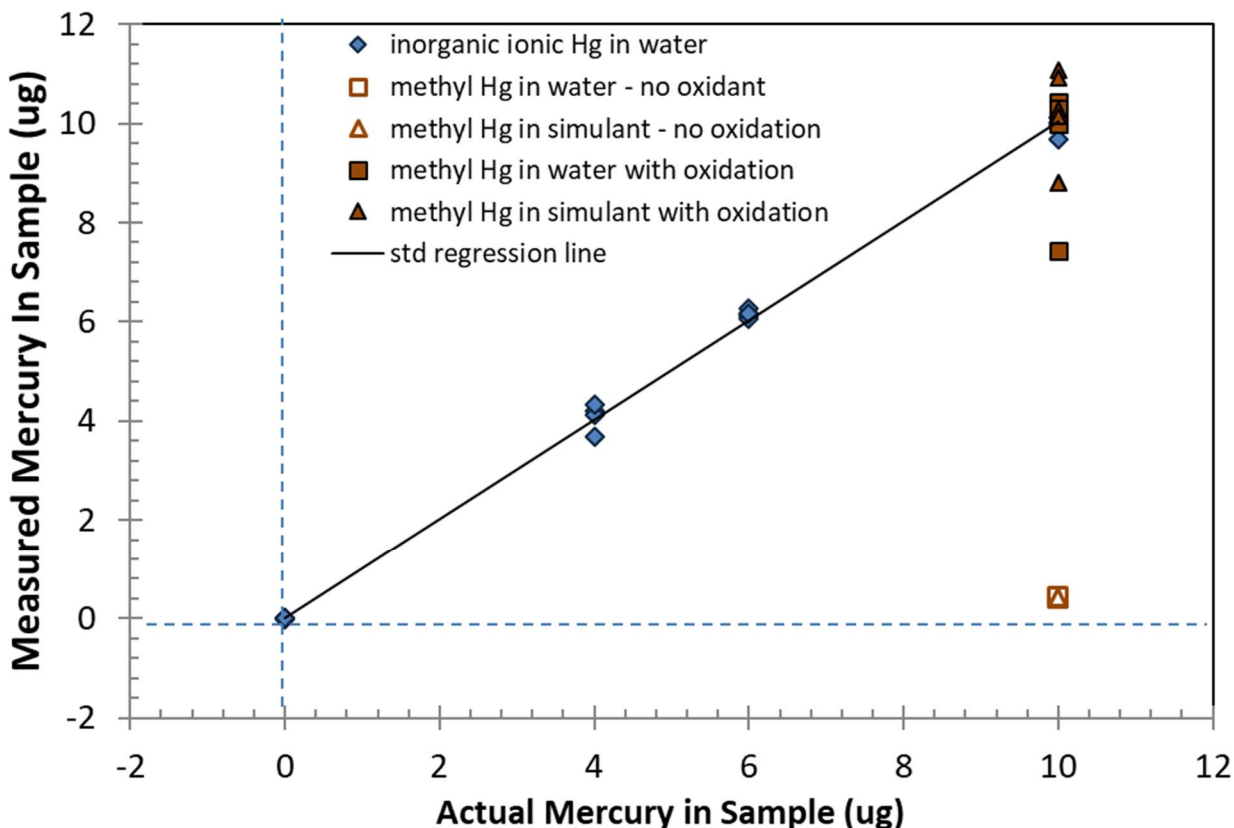
Figure 3-6: Mercury Speciation Analysis

3.4.4 Photoreaction tests

When exposed to UVC light, there was significant transformation of MeHg in inorganic mercury in aqueous standard solutions in deionized water (Figure 3-7). There was no measurable MeHg transformation in simulant solutions (all samples and exposures). This difference in performance appears to result from a combination of light attenuation and competing reactions when applied to more complex media. The following discussion develops a scoping interpretation for the data from the spikes in deionized water.

Mercury speciation was measured in the MeHg spiked deionized water solutions after light exposures at 0, 34, 48 and 116 joules/cm^2. The mercury speciation was determined using selective reduction schema and the following phases are graphed: MeHg, inorganic mercury, dissolved elemental mercury (this was set to the solubility of elemental mercury for all exposure points), and other Hg species that are described in more detail below. From 0 to 50 joules/cm^2 MeHg decreased to near zero and the inorganic mercury increased. Over time, the total mercury in the sample decreased. This decrease was attributed to loss of inorganic mercury as it is converted to either elemental mercury or recalcitrant forms of mercury that are not effectively analyzed (such as mercury oxides). In this conceptual model, elemental mercury at levels above solubility can be lost from micro reactor due to volatilization and/or formation of a separate phase that is not effectively sampled by pipette. By the final sampling point, all MeHg and almost all inorganic mercury

have been converted and removed from the bulk solution. A simple model describing the sequential transformation was generated using first order kinetic series equations (Figure 3-8). In these equations the independent variable is the total exposure in joules/cm^2. The equations and estimated kinetic parameters are depicted in Figure 3-8.
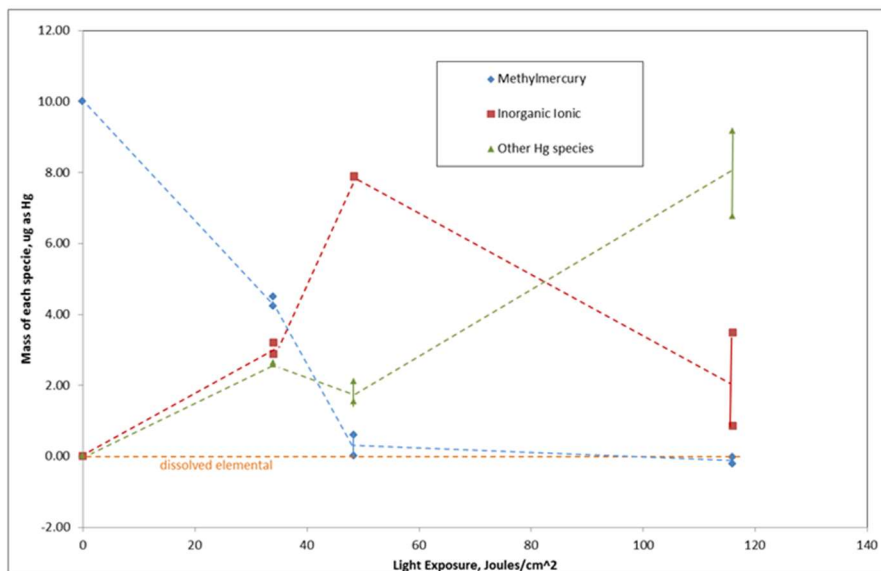
Figure 3-7. Photo-Transformation of MeHg Standard (raw data)
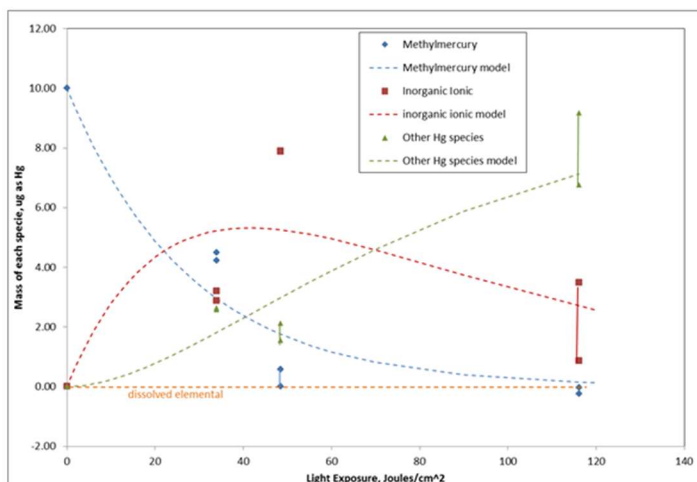
Kinetic Coefficients

$$k_{\Phi_1} - 0.0358 \, \text{cm}^2/\text{Joule}$$
$$k_{\Phi_2} - 0.0152 \, \text{cm}^2/\text{Joule}$$

$$\frac{d[MeHg]}{d[\Phi]} = -k_{\Phi_1}[MeHg]$$

$$\frac{d[Hg(II)]}{d[\Phi]} = k_{\Phi_1}[MeHg] - k_{\Phi_2}[Hg(II)]$$

$$\frac{d[Other \, Hg \, Sp]}{d[\Phi]} = k_{\Phi_2}[Hg(II)]$$

Figure 3-8: Hg Transformation Model

3.5 <u>Conclusions</u>

The results documented significant attenuation of the active wavelengths of light in the LWS DSS simulant solution. For UV wavelengths <300 nm, light intensity was reduced by approximately 10,000x over a 1 cm distance in all DSS simulants.

The results validated the potential for selective reduction as a mercury speciation strategy to support experiments under controlled conditions. The data confirmed that reductants such as stannous chloride, used alone, have no impact on MeHg in solution.

The results confirmed that advanced oxidation techniques, particularly photoreactions, are capable of converting MeHg into inorganic mercury species such as inorganic ionic mercury and elemental mercury (along with other more recalcitrant mercury species). However, the observed conversion occurred relatively slowly and only in simple spiked deionized water solutions. The data suggest a sequential conversion process that can be modeled using a series of sequential first order processes.

No observable photo-conversion of MeHg was observed in concentrated tank waste simulant. The underperformance of the photoreactions in simulant is the result of several factors. First, the significant attenuation of UV light in the simulant solutions. Second, the simulant is a complex aqueous matrix that contains transition metals and high levels of nitrate/nitrite – this results in buffering redox conditions.

While the photo-oxidation was ineffective in laboratory testing, the potential value of targeted advanced oxidation reactions remains promising for manipulating mercury speciation in the LWS. A lesson learned from this research is that such processes most be able to work in alkaline-redox-buffered LWS conditions and need to be conceptualized to minimize potential collateral impacts on LWS chemistry, flowsheet and safety (Looney et al., 2017). Recent literature suggests the potential for persulfate or persulfate as reagents for possible advanced oxidation processes (e.g., Liang and Lei, 2015). While both these oxidants have been used in alkaline conditions, the scientific literature on persulfate highlights synergy with alkaline conditions. Specifically, persulfate been shown to be activated in high pH alkaline conditions and in the presence of transition metals. Thus, a persulfate (or permanganate) flowsheet is generally synergistic with LWS solution conditions compared to oxidants that work best in acidic conditions. We recommend that future examination of advanced oxidation emphasize reagents that have significant potential for application at high pH in a complex transition-metal-rich LWS matrix.

3.6 Recommendations, Path Forward or Future Work

The data suggest that developing effective photo oxidation processes for LWS will be a challenge and the scoping study would not support advancing this to further testing (no-go). We recommend future efforts related to oxidation in the LWS focus on persulfate (or permanganate) or other oxidants that can be deployed in a complex alkaline matrix.

4.0 Chemical Reduction to Convert Inorganic Ionic Mercury into Elemental Mercury

4.1 Background

Evaporators, used to minimize waste volumes, are a major component in the treatment of liquid waste. These systems are used to evaporate water from liquid waste to reduce volume, making better use of available tank storage capacity. Evaporator operations during the past 60 years have reduced over 150 million gallons of liquid waste to about 36 million gallons at SRS. The evaporators boil the alkaline wastewater, causing the water to separate from the waste solution and result in a volume reduction of 70 to 75%. Two evaporator systems are currently operating at SRS - the 2H and 3H systems. Both evaporator systems have components that allows for the accumulation and removal of elemental mercury. A summary table of Hg behavior in the evaporators is included in Table 4-1 below.

In the elemental state, key parameters that impact mercury removal are the high specific gravity of the condensed liquid, the relatively low aqueous solubility and the modestly high vapor pressure. Elemental mercury above solubility will accumulate as a separate phase liquid. Once present as a separate phase, the high specific gravity (SG = 13.6) controls movement and allows for a simple gravitational separation. Consistent with these properties, the existing mercury removal components of the evaporator system rely on thermally enhanced partitioning of elemental mercury to the vapor phase, condensation in the overhead tank liquids, and gravitational separation to remove elemental mercury.

Mercury speciation data indicates that approximately 1% of the soluble mercury in the feedstock tanks is present in the elemental state (Figure 4-1) in a form that is removed in the existing system. Therefore, developing a mechanism to convert the other forms of mercury to elemental has the potential to increase the removal capacity of the existing system in the evaporator with minimal process impact. Further details describing the processes by which Hg(II) may be chemically reduced to Hg(0) for removal can be found in Table 4-2.

We performed a scoping calculation to validate the relationship between elemental mercury and mercury collection in SRS LWS evaporators (SRR, 2015). Using only the elemental component of the speciation concentration data from Tank 43 and operational parameters from 7-May-2015 (Q = 9.55 gpm) the theoretical mercury collection in the 2H evaporator system was calculated to be between 6 and 13 ml/day of elemental mercury. Between 4-May-2015 and 29-May-2015 approximately 400 ml of elemental mercury were recovered from the 2H evaporator, a rate of 8 ml/day. Extending the calculation to include all inorganic ionic mercury projects that the potential mercury removal rates could be increased by a factor of 15. On an annualized basis, this would increase the mercury removal from the LWS by 1000 to 1500 kg.
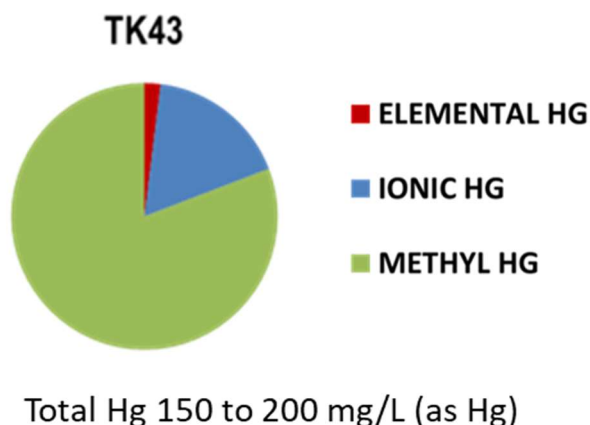
4.2 Objective

Reduction experiments are targeted to enhance removal of ionic mercury at the H-area evaporators using chemical addition of process approved reducing agent to enhance the reduction of ionic mercury to elemental mercury in a waste simulant. Reducing agents evaluated include stannous chloride, formic acid, and oxalic acid.

Table 4-1. Behavior of Hg in Evaporators (adapted from Jackson et al., 2017**)**

Species	Entering	Internal Processes	Exiting
Hg(0)	Dissolved in salt solution and microscopic globules.	Volatilization to vapor for separation and cooling to produce liquid.	Pure phase mercury accumulated for disposal.
Hg(I) and Hg (II)	Dissolved in the salt solution.	Partial reduction to Hg(0). Concentration due to solvent loss. Possible enrichment from dissolution of solids.	Concentrated dissolved species in solution that is sent to salt processing.
MeHg$^+$	Dissolved in the salt solution.	No identified reactions. Concentration due to solvent loss.	Concentrated dissolved species in solution that is sent to salt processing.
DMHg	Dissolved in the salt solution.	Volatilization to the vapor phase. Limited condensation based upon thermochemistry data.	Unknown. Vapor pressure will limit condensation. Possible accumulation or stack release.
Solid	Solid phase as particles entrained in salt solution.	Coagulation and settling, possible dissolution during heating.	Maintenance to remove. Residual deposits on coils.

Table 4-2. Chemically Reduce Hg(II) to Hg(0) for Removal. (adapted from Jackson et al., 2017**)**

Species	Entering	Internal Processes	Exiting
Hg(0)	Dissolved in salt solution and microscopic globules.	Volatilization to vapor for separation and cooling to produce liquid.	Pure phase mercury accumulated for disposal.
Hg(I) and Hg (II)	Dissolved in the salt solution.	Partial reduction to Hg(0). Concentration due to solvent loss. Possible enrichment from dissolution of solids.	Concentrated dissolved species in solution that is sent to salt processing.
MeHg$^+$	Dissolved in the salt solution.	No identified reactions. Concentration due to solvent loss.	Concentrated dissolved species in solution that is sent to salt processing.
DMHg	Dissolved in the salt solution.	Volatilization to the vapor phase. Limited Condensation based upon thermochemistry data.	Unknown. Vapor pressure will limit condensation. Possible accumulation or stack release.
Solid	Solid phase as particles entrained in salt solution.	Coagulation and settling, possible dissolution during heating.	Maintenance to remove. Residual deposits on coils.

Figure 4-1. Typical Mercury Speciation in Feedstock Tank (43) to the 2H Evaporator

4.3 Experimental Procedures

4.3.1 Materials

A stannous chloride solution (10% (w/v) in 20% (v/v) HCl) manufactured by SRNS (SRS MSDS # 47112-1) was used as the reducing agent during testing. Formic acid and oxalic acid were also assessed. These compounds were chosen through a heuristic evaluation and ranking based upon potential impacts associated with the introduction of a new compounds to the liquid waste process.

4.3.2 Methods

This task was used to identify a suite of potential reducing agents that will convert ionic mercury to elemental mercury, as well as a viable chemical reducing agents for further simulant-based laboratory testing. This evaluation was performed using non-radioactive waste simulant solutions that contained a known concentration of ionic mercury. Performance of the various reducing agents were assessed on the removal effectiveness as compared to aqueous solutions containing only ionic mercury and an associated salt.

The proposed treatment method was tested at the laboratory scale using spiked inorganic ionic mercury (Hg^{2+} and complexes) in three different solution matrices: a) deionized water, b) sodium hydroxide solution (pH 14), and c) Tank 42 simulant. The selected reducing agents were evaluated by performing a series of dose-response tests (dose factors from 1X to 500X, Table 4-3) in which the dose of the reducing agent is varied based upon the stoichiometric ratio (in equivalents) required to reduce the inorganic mercury in the solution to elemental mercury. For example, a dose factor (ratio) of 1 would indicate that the quantity of reductant added is equal to the theoretical amount required to reduce the mercury. Factors below 1 indicate that that the amount of added reductant is theoretically insufficient to perform complete reduction. Factors greater than 1 indicate that excess reductant was added; in complex-redox-buffered solutions such as those found in the SRS LWS, excess reagents are typically required to account for side reactions. The purpose of the dose response testing is to provide scoping data on the relative effectiveness of the tested reducing agents and to aid in determining the minimum doses necessary to promote conversion to elemental mercury. For each reductant being evaluated, the series of experimental runs listed in Table 4-3 were performed.

Table 4-3. Dose Response Experimental Conditions for Each Reductant in each Matrix

| Run	Reductant Dose Factor = [Reductant]/[Total Hg]	Temperature	Replicates
#1	1	ambient	2 to 4
#2	10	ambient	2 to 4
#3	100	ambient	2 to 4
#4	1,000	ambient	2 to 4
#5	10,000	ambient	2 to 4
#6	100,000	ambient	2 to 4
#7	1,000,000	ambient	2 to 4

The simulant composition was based on data mining of recent information on the representative waste composition in representative feedstock tank(s) supplying fluids to LWS evaporators. Specifically, the Tank 43 primary simulant recipe was based on samples collected under the Enrichment Control Program (ECP) and Corrosion Control Program (CCP). The simulant composition uses average values based upon samples collected and analyzed between January 2014 and May 2015. The various compounds and quantities used to prepare the simulant result in the target solution composition. The various reagents were organized into groups of similar-compatible compounds that were premixed and added together for safety and efficiency. Table 4-4 documents the recipe for the Tank 43 simulant using in testing alternative reductants. The sodium hydroxide solution was prepared in deionized water by diluting a 50% stock solution. The stannous chloride solution was prepared according to EPA Method 1631.

Reductant dose-response performance was based on the quantity of elemental mercury sparged from the sample aliquot after dosing. Mercury was quantified based on instrument response using an Ohio-Lumex RA-915+ portable mercury vapor analyzer with a RP-91 water analysis attachment.

In summary, the sample being analyzed was put into the first impinger and then the reducing agent was added to convert the ionic mercury to volatile elemental mercury. The elemental mercury, which is formed during continuous air pumping through the bubblers, was transferred to the second impinger that traps any liquid droplet carryover and then to the selected analytical cell of the RA-915+ analyzer, where the mercury atoms are detected (Figure 4-2). The output of the analyzer is then recorded and integrated as a function of time. Quantification of results was obtained by reference to calibration curves developed from the analysis of standard solutions under identical operating parameters.

**Table 4-4. Simulant Recipe Used to Represent Tank 43**

Tank 43 Simulant Recipe (no Hg)						
Group	Compound	Formula	CAS	Target	Actual	Units
1	DI water	H_2O	[7732-18]	1500	1500	ml
1	50% sodium hydroxide	NaOH	[1310-73-2]	223.7	223.7	ml
2	Aluminum nitrate	$Al(NO_2)_3$	[7784-27-2]	5.474	5.464	grams
2	Sodium nitrate	$NaNO_3$	[7631-99-4]	121.510	121.539	grams
2	Potassium nitrate	KNO_3	[7757-79-1]	1.476	1.480	grams
2	Zinc nitrate (hexahydrate)	$Zn(NO_3)_26H_2O$	[10196-18-6]	0.041	0.046	grams
2	Iron nitrate (nonahydrate)	$Fe(NO_3)_39H_2O$	[7782-61-8]	0.121	0.125	grams
3	Sodium carbonate	Na_2CO_3	[497-19-8]	71.277	71.278	grams
3	Sodium sulfate	Na_2SO_4	[7757-82-6]	4.664	4.679	grams
3	Sodium chloride	NaCl	[7647-14-5]	0.000	0.000	grams
3	Sodium fluoride	NaF	[7681-49-4]	0.000	0.000	grams
3	Sodium bromide	NaBr	[7647-15-6]	0.000	0.000	grams
3	Disodium phosphate (heptahydrate)	$Na_2(HPO_4) \cdot 7H_2O$	[7782-85-6]	1.620	1.622	grams
3	Sodium tetraborate decahydrate	$Na_2B_4O_7 \cdot 10H_2O$	[1303-96-4]	0.590	0.000	grams
3	Sodium oxalate	$Na_2C_2O_4$	[62-76-0]	0.580	0.583	grams
3	Sodium silicate (nonahydrate)	$Na_2(SiO_3)_3 \cdot 9H_2O$	[10213-79-3]	4.208	4.209	grams
3	Sodium chromate	Na_2CrO_4	[7775-11-3]	0.258	0.259	grams
4	DI water	H_2O	[7732-18]	210	210	ml
4	Sodium nitrite	$NaNO_2$	[7632-00-0]	203.536	203.536	grams
5	DI water	H_2O	RAISE FINAL VOLUME TO		2.5	liters
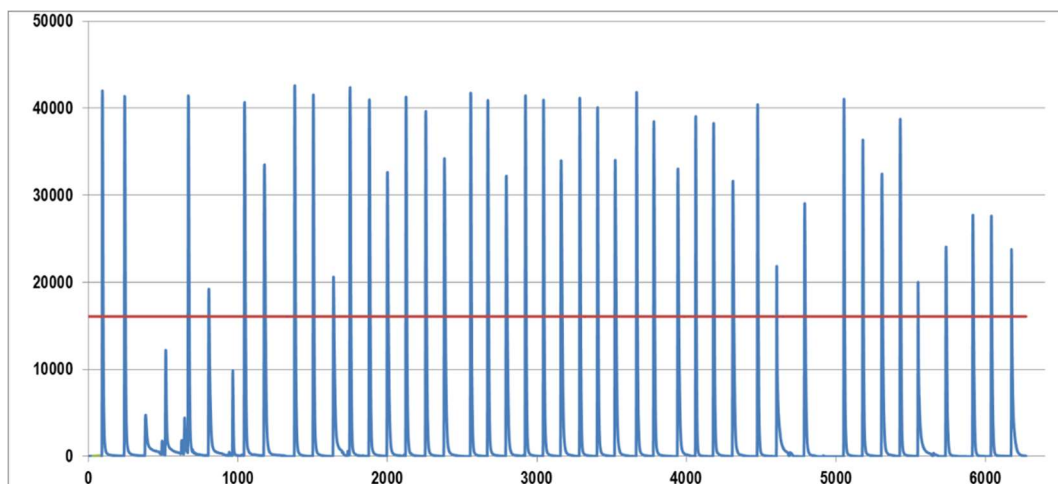
Figure 4-2. Instrument Response → Integrate Peaks → Mercury Reduction

4.4 Results and Discussion

The experimental data are organized into a standard graphical format for presentation. In Figure 4-3 through Figure 4-5, we present the results for the three tested reductants, stannous chloride, formic acid, and oxalic acid, respectively. In each figure, the dose increases from left to right. For each dose, the solution matrix is designated by color with the blue (left) bar representing the result for deionized water, the red (center) bar representing the result for sodium hydroxide (pH $\cong$ 14) solution, and the green (right) bar representing the result for the Tank 43 simulant. The grey shaded area near the top of the graph represents the range that indicates effective-complete conversion. Stannous chloride (Figure 4-3) was found to be an effective reductant at doses greater than approximately 1X for the simple deionized water and sodium hydroxide solutions. Higher doses, >10 X were required for effective conversion in the Tank 43 simulant.
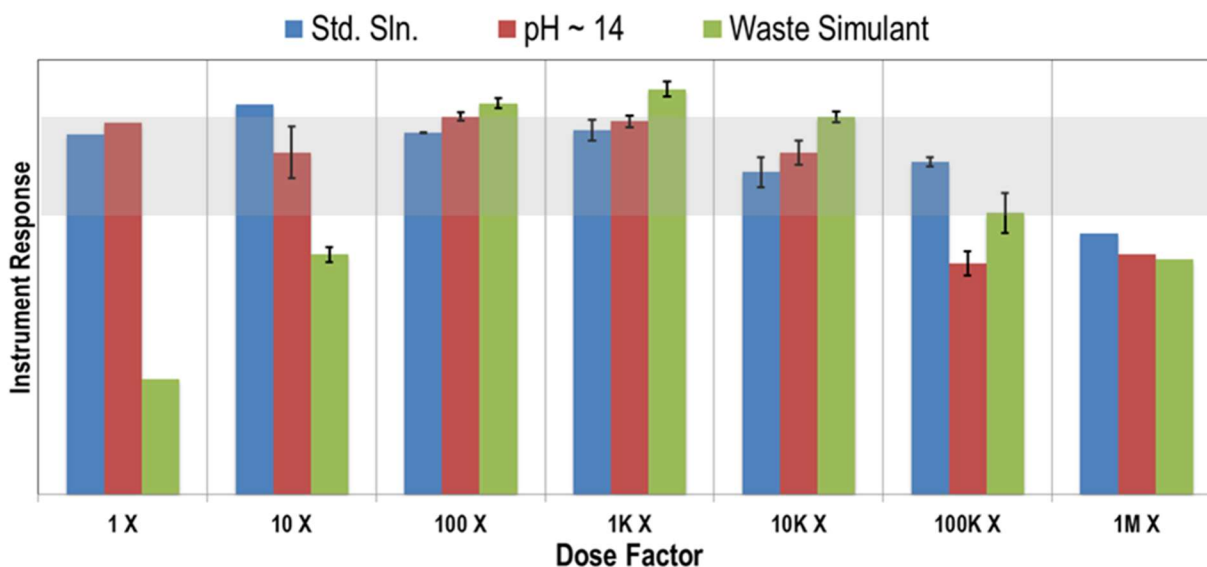
Figure 4-3. Stannous Chloride as Reductant in Reducing 1 mg/L Ionic Mercury

Formic acid (Figure 4-4) showed a relatively high degree of conversion for all doses in all solutions, However, the measured effectiveness appeared to drop off at very high doses in the Tank 43 simulant. Recent data generated in a separate study (Looney et al, 2020), indicated that formic acid in exiting LWS flowsheets may contribute to the formation of dimethylmercury (diMeHg) (through a disproportionation reaction with MeHg). If confirmed, that factor could impact the potential applicability of formate in the flowsheet as an evaporator reductant (since the predominant form of mercury in the feedstock to the evaporator is MeHg.
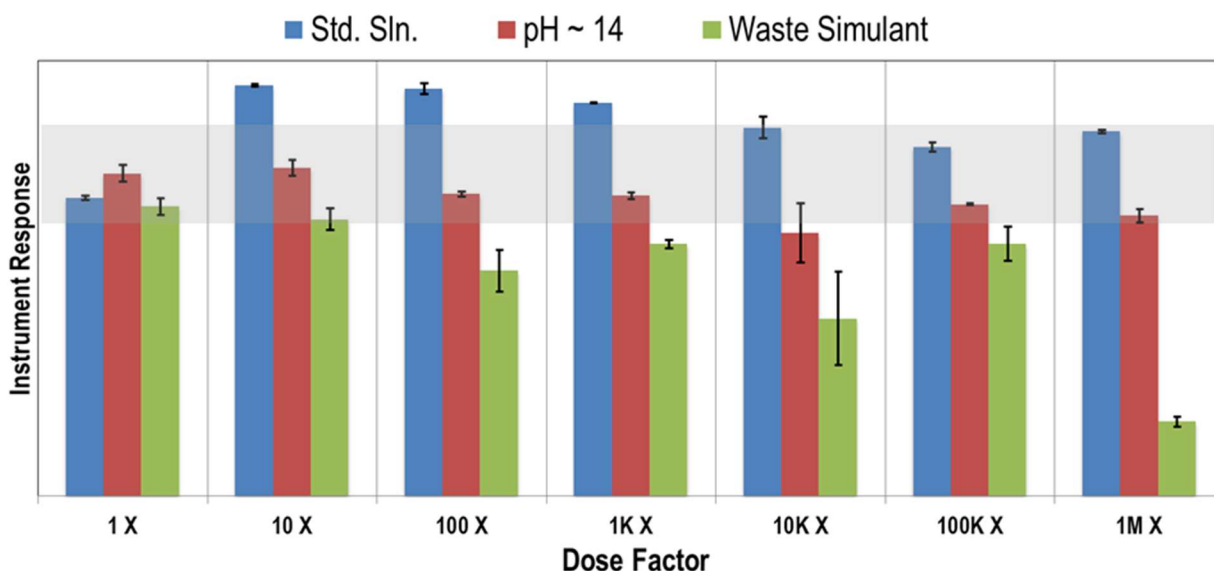
Figure 4-4. Formic Acid as Reductant in Reducing 1mg/L Ionic Mercury

Oxalic acid (Figure 4-5) was an effective reductant for doses >10X in the deionized water and sodium hydroxide solutions. Oxalic acid was ineffective as a reductant in Tank 43 simulant.
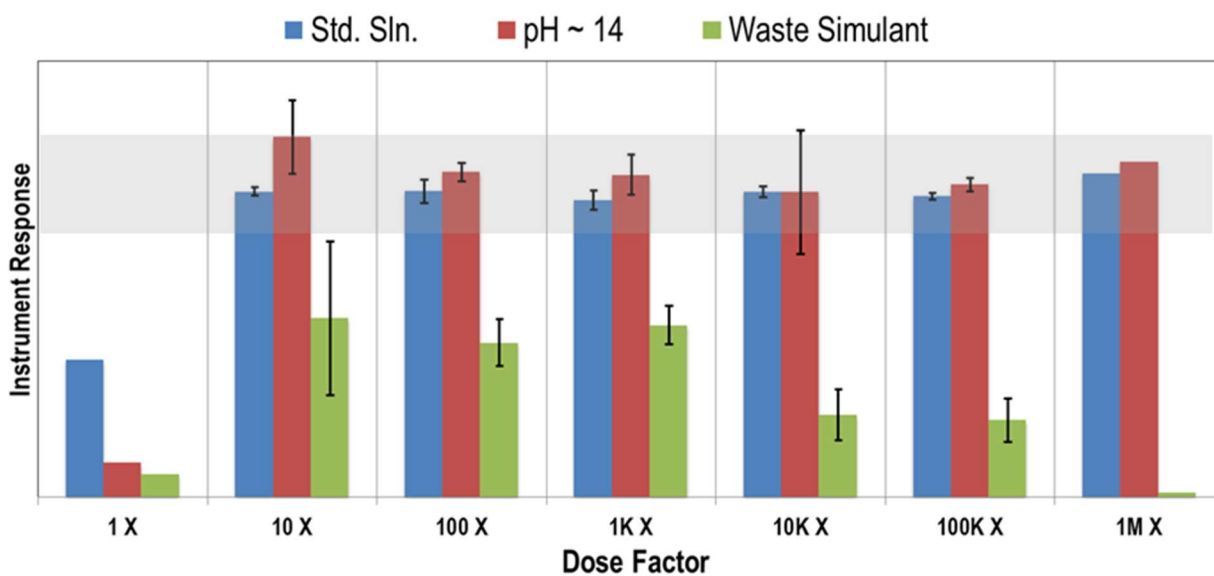

Figure 4-5. Oxalic Acid as Reducing 1 mg/L Ionic Mercury

4.5 Conclusions

The evaporators are now operating as a mercury treatment "purge point" for the LWS. However, the evaporators are only able to remove mercury that is in the elemental form. MeHg and inorganic ionic mercury are not removed in the current evaporator flowsheet scenario. As shown in Figure 4-1, MeHg is the predominant form of mercury in evaporator feedstock. Elemental mercury is a small component (approximately 1%) of the mercury inventory and inorganic ionic mercury is a significant fraction (approximately 19%) of the total. The central premise of the chemical reduction scoping tests is that the inorganic ionic mercury present in the evaporator feedstock is a promising target for conversion to elemental mercury that can then be removed by a proven and existing process. Converting some (or all) of the inorganic ionic mercury to elemental would significantly increase the quantity of mercury removed in the evaporator and contribute to the overall LWS mercury purge point removal goal of 2900 kg that is needed for sustainable LWS operation to completion.

The data demonstrated that reduction of inorganic ionic mercury to elemental mercury is relatively straightforward and rapid (occurring in just a few minutes in the laboratory apparatus) and that the reduction is feasible in Tank 43 simulant. The standard reductant used for mercury in most studies is stannous chloride. It was effective at doses above 10X to 100X. Formic acid was effective at doses above 1X but may be subject to side reactions with the MeHg present in the evaporator feedstock and associated collateral impacts such as generating diMeHg. Oxalic acid underperformed the other tested reductants in Tank 43 simulant and was not effective at any dose.

4.6 Recommendations, Path Forward or Future Work

The results of the testing were generally positive. The data suggest that developing effective process for the LWS is feasible and the scoping study would support advancing this to further testing (go). In moving this forward, a few key activities are recommended, notably testing at higher temperatures, testing in the presence of MeHg, and an expanded portfolio of test reductants to include other candidates such as borates (e.g., tetraethylborate, terapropylborate, cyanotrihydroborate, tetrahydroborate).

5.0 Getters

5.1 Background

The low-level waste (LLW) decontaminated supernate salt solutions in the LWS are solidified into a grout wasteform, saltstone. The saltstone is blended in the SRS Saltstone Production Facility (SPF) by combining fly ash, slag, and cement with LLW. This forms a grout slurry mixture that is then transferred to the Saltstone Disposal Facility (SDF) where it is dispositioned to vaults or tanks and allowed to solidify for long term management (Oji and Langton, 2018). The saltstone stabilizes the Hg in the grout material and resists leaching. For disposal, leaching from this material cannot exceed the Toxicity Characteristic Leach Procedure (TCLP) treatment standard of the Resource Conservation and Recovery Act (RCRA) (0.2 mg/L) (Oji and Langton, 2018). Recent readings have shown increased levels of mercury in saltstone leachates. This increased leaching has been attributed to mercury speciation. The predominant species in the feedstock to saltstone (Tank 50) is MeHg which has a higher leachability compared to inorganic or elemental mercury (Oji and Langton, 2018). Getters that specifically limit the leaching of MeHg represent a potential supplemental tool in an overall mercury management strategy and provide the potential for "defense-in-depth", increasing the robustness of the protection, Addition of mercury getters to grout formulations would enhance the retention of mercury, while also mitigating the need to completely convert the species within the waste.

5.2 Objectives

This task surveyed potential mercury getters for the organomercury species to enhance the retention of mercury in the grout matrix. A scoping evaluation of low cost, available getters was conducted, and a local potential additive was tested. Desired characteristics for a successful getter include:
ease of incorporation into the existing process, sufficient MeHg retention with high loading rates, and minimal adverse collateral impacts on wasteform properties of the grout. e.g., set time, compressive strength, etc.

5.3 Experimental Procedures

The primary objective of this work was a survey. One material, the residual ash from tire derived fuel (TDF) generated in the SRS biofuels energy facility was tested to determine its elemental content. X-Ray Fluorescence (XRF) was used to analyze the fly ash from TDF (Table 5-2) to better understand the properties and how they can be used to immobilize Hg species. A literature review of potential getters for Hg immobilization was also conducted (Table 5-3) to identify options for future research.

5.4 Results and Discussion

An analysis of potential options for Hg getters were derived from a literature review. Getters selected for assessment are included in Table 5-3. In summary, the ranking of potential applicability of getters for MeHg and inorganic Hg are ranked with 0 being the lowest and +++ being the highest. This is a culmination of the maturity, availability, cost, and loading of the getters based on a literature review. Maturity, or technology readiness level (TRL), ranks various technologies from TRL1 through TRL 9 where TRL 1 represents literature citation to TRL 9 which represents full scale testing in various environments. The associated DOE TRL levels and how they are determined are described in Table 5-1 (DOE G 413.3-4).

Table 5-1. DOE-EM TRL Testing Requirements

TRL Level	Scale of Testing	Fidelity	Environment [1,2]
9	Full	Identical	Operational (Full Range)
8	Full	Identical	Operational (Limited Range)
7	Full	Similar	Relevant
6	Engineering/ Pilot Scale	Similar	Relevant
5	Lab/Bench	Similar	Relevant
4	Lab	Pieces	Simulated
3	Lab	Pieces	Simulated
2		Paper	
1		Paper	

[1]Simulants should match relevant physical and chemical properties
[2] Testing with as wide a range of actual waste as practicable; and consistent with waste availability, safety, ALARA, cost, and project risk is highly desirable

The availability and cost simply document where these reagents can be purchased and cost per kilogram. Many are currently available or about to be available commercially, some are available on a research scale, or are available from waste products. Loading was scored based on the amount of mercury that can be sequestered per gram (highest scores were assigned to high capacity commercially available mercury sorbents that have proven effective for MeHg – with capacities of 300 to 600 mg/g as Hg).

Ideally, waste products would be used at SRS for large scale Hg immobilization to limit costs and provide a beneficial use for the waste. Example waste materials include TDF ash from the SRS biofuel facility, chitosan and chitosan derivatives from shells of crustaceans which could be available for a minimal cost, or other waste materials such as un-combusted tire crumb. If a getter strategy is implemented, a locally sourced material from a trusted source would streamline SRS saltstone production.

These combined factors contributed to the ranking (mark in bold font) of silica thiol, thiol SAMMS, sulfur impregnated carbon, and commercial functionalized mercury chelating resin (e.g. AmberSep GT74) as the most viable commercially available options for both MeHg and inorganic Hg. Several "green" options that use waste materials were also marked as potentially viable for future testing, these include chitosan waste materials (such as granulated exoskeletons from seafood processing), SRS TDF ash, and tire crumb waste materials.

As a scoping test, ash from of SRS TDF ash was analyzed for its elemental composition. The data (ppm for each element) are shown in Table 5-2. The distribution of the elements can assist in determining if TDF ash could be a viable option for adding to saltstone for Hg immobilization. The ash is generated in a fluidized bed biofuel system that uses nominally 10% tire waste with 90% wood chips. The combustion zone is hot and contains oxygen. Note that the tire ash contains a significant quantity of sulfur – residual primarily from the original tire rubber, suggesting the potential for mercury sequestration. However, this sulfur is likely to be an oxidized inorganic form (not a thiol or reduced sulfide). Thus, determination of the viability of the TDF ash as a getter will require laboratory testing to determine potential loading and its impact on mercury leaching in spiked grout samples.

Table 5-2. XRF Analysis of Three Samples of Ash from TDF

Concentration of Elements in Tire Derived Fuel Ash (ppm)			
	PPHA-SBI-a	PPHA-SBI-b	PPHA-SBI-c
Si	167,703	167,984	167,096
Ca	138,388	138,666	139,000
K	39,618	39,882	39,816
S	30,270	30,150	30,310
Fe	25,458	25,318	25,388
Al	24,132	23,973	23,814
Mg	21,165	21,226	21,286
P	14,508	14,579	14,579
Mn	8,700	8,770	8,770
Ti	3,488	3,506	3,500
Na	2,990	2,745	2,797
Sr	947	947	947

Table 5-3. Literature Summary of Potential Getter Materials with Associated Hg Species and Benefits

Various functionalized inorganic substrates (mesoporous silica, clays, etc.)

Material	Description	General Class	MeHg	Inorganic Hg	Maturity (TRL)	Availability	Cost	Loading	Example References
Silica thiol	**Silica gel with bonded thiol functionality - commercially used for removing metals from pharmaceuticals on a commercial scale and for pretreatment of analytical samples (e.g. Prior to ion chromatography).**	Works by complexation of Hg species by sulfur and thiol functional groups - need to test effectiveness in alkaline (saltstone) conditions	+++	+++	8	Commercial product	Med-high ($0.50/ kg)	High (300 to 600 mg/g as hg)	DelaRosa, 2018; Štandeker et al, 2011; Walcarius et al., 2005, Yantasee et al., 2010
Thiol SAMMS	**Thiol functionalized porous ceramic -- SAMMS = Self-Assembled Monolayers on Mesoporous Supports that are created by attaching a monolayer of functional molecules to the ceramic matrix**	Works by complexation of Hg species by sulfur and thiol functional groups. Need to test effectiveness in alkaline (saltstone) conditions	+++	+++	6	Commercial product	Med-high ($1.00 per kg)	High (300 to 600 mg/g as hg)	Gilmore et al., 2013; PNNL, 2009

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TDF ash from SRS biofuel facility	**The Burma Road SRS biofuel energy generation facility uses approximately 10% tires in the fuel mix. Since tires contain sulfur and this ash is locally available in large quantities, scoping work was performed to assess the potential for this material to sequester mercury**	If ash contains sulfur may complex Hg species by sulfur and thiol functional groups - pilot testing of ash indicated relatively low levels of sulfur (likely volatilized in the fluidized bed incineration) and pilot contact of ash with inorganic and MeHg solutions indicated minimal sorption.	?(+)	?(+)	3	Bulk waste (available)	Low	Low	---
Functionalized sulfur impregnated organoclay	Granular high surface area clay (bentonite-like) filtration media developed for Hg sequestration such as "Organoclay MRM"	Made with waste material (green option) Works through high surface area, sorption of organic materials, complexation of Hg species by sulfur and mercapto/thiol functional groups - need to test effectiveness in alkaline (saltstone) conditions - note this is a clay that shrinks and swells based on moisture content so tests to assure that it would not result in saltstone cracking would be needed.	++	++	8	Commercial product	Med-high	High	Gilmore et al., 2013; CETCO, 2020

Various functionalized organic substrates (activated carbon, resins, plant materials, etc.)

Material	Description	General Class	MeHg	Inorganic Hg	Maturity (TRL)	Availability	Cost	Loading	Example References
Sulfur impregnated activated carbon (e.g., Mersorb)	**Activated carbon with added sulfur and thiol functionality**	Works through high surface areas, sorption of organic materials, complexation of hg species by sulfur and mercapto/thiol functional groups - need to test effectiveness in alkaline (saltstone) conditions and test compatibility with grout	+++	+++	8	Commercial product	Med-high ($1.00/kg)	High (300 to 600 mg/g as hg)	Gilmore et al., 2013; Kazemia et al., 2016; Mercury Absorbents 2020, Samuels et al. 2010
Commercial functionalized mercury chelating resin (such as AmberSep GT74)	**Industrial grade thiol functionalized polymer resin (AmberSep GT74 Resin is "a weakly acidic cation exchange resin with selectivity for mercury").**	Complexation of Hg species by sulfur and thiol functional groups - need to test effectiveness in alkaline (saltstone) conditions and test compatibility with grout	+++	+++	8	Commercial product	Med-high	High (300 to 600 mg/g as hg)	Gilmore et al., 2013; Dupont, 2020
Chitosan and chitosan derivatives	**A metal chelating biomaterial often using waste exoskeletons from seafood processing - can be formed into beads or granules**	"bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives. Made with waste material (green option)	? (++)	? (++)	5	Bulk waste (available)	Med	Unknown	Miretzky et al., 2009

Waste Tire Crumb	**Ground crumb from raw waste tires (not ash)**	Works through, complexation of Hg species by residual vulcanizing sulfur compounds – need to test effectiveness in alkaline (saltstone) conditions and test compatibility with grout. Made with waste material (green option)	? (++)	? (++)	5	Bulk waste (available)	Med	Unknown	Knocke et al., 1981. Gunasekara et al., 2000
Activated carbon	Activated carbon	Works through high surface areas, sorption of organic materials - many studies in environmental systems rely on secondary mechanisms such as sorbing natural organic matter from the environment as a component of the hg sorption	++	++	8	Commercial product	Med-high	Low-med	Gilmore et al., 2013; Gomez-Eyles et al., 2013
Biochar	Activated carbon - typically with lower surface area -- some biochars are made with waste material (green option)	Works through high surface areas, sorption of organic materials - many studies in environmental systems rely on secondary mechanisms such as sorbing natural organic matter from the environment as a component of the hg sorption	++	++	6	Near commercial product	Med-high	Low-med	Gomez-Eyles et al., 2013. Liu et al., 2018

Chelating resin with biogenic methionine	A "novel" metal chelating resin embedded with biogenically derived amino acid methionine.	"bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives	? (+)	+++	4	Research scale	Med-high	Med-high	Ali, 2018
Chelating resin with biogenic cyanoguanidine	A "novel" metal chelating resin embedded with biogenically derived cyanoguanidine	"bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives	? (+)	+++	4	Research scale	Med-high	Med-high	Ma et al, 2011
Chelating resin with biogenic aminothiadiazole	A "novel" metal chelating resin embedded with aminothiadiazole	"bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives	? (+)	+++	4	Research scale	Med-high	Med-high	Ziong et al, 2015
Nano-magnetic FexOy polymer (mercapto-functionalized)	Polymer containing mixed iron oxides with potential for magnetic separation after mercury removal.	Works by complexation of hg species by sulfur and thiol functional groups	? (+)	+++	4	Research scale	High	Med-high	Pan et al., 2012; Shan et al., 2015
Functionalized carbon nanotubes (tannin group)	A "novel" metal chelating material coated by natural tannin	"Bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives	? (++)	? (++)	3	Research scale	High	Unknown	Luzardo et al, 2017; Zhang et al., 2017

Material	Description	General Class							
Functionalized cellulose sorbent (thiol functional groups)	A "novel" metal chelating material of polymerized cellulose adsorbent modified to contain vicinal thiol groups	Works by complexation of Hg species by sulfur and thiol functional groups	? (++)	? (++)	3	Research scale	High	Unknown	Marchant, 1974
Tannin resins	Natural resin extracted from plants used directly for metal chelation	"Bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives.	? (++)	? (++)	4	Research scale	High	Unknown	Oliverez et al., 1999; Santana et al. 2002
Dried-Powdered Weeds	A metal chelating biomaterial using dried and powdered duckweed	"Bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives. Made with waste material (green option)	? (+)	? (+)	3	Research scale	High	Unknown	Xing et al., 2011
Peat Moss	A metal chelating biomaterial using dried and powdered peat moss	"Bio-sorbent" -- works through chelation on amino groups and/or ion exchange with protonated amines in chitosan or chitosan derivatives. Made with waste material (green option)	? (+)	? (+)	3	Research scale	High	Unknown	

Liquid Phase Getter

Material	Description	General Class	MeHg	Inorganic Hg	Maturity (TRL)	Availability	Cost	Loading	Example References

| Humic and fulvic acids | Liquid phase getter made of natural organic materials - typically produced by alkaline extraction from coal or another organic rich natural substrate. | Works through complexation of Hg species by sulfur and mercapto/thiol functional groups combined with reduce mobility out of grout wasteform | + | + | 4 | Commercial product | Med-high | Low-med | Hintelmann et al., 1997; Zhang et al., 2010; |

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5.5 <u>Conclusions</u>

The saltstone wasteform currently stabilizes contaminants, including Hg in the grout material and resists leaching. For disposal, leaching from this material cannot exceed the regulatory agreements based on a Toxicity Characteristic Leach Procedure (TCLP) treatment standard of the Resource Conservation and Recovery Act (RCRA) (0.2 mg/L) (Oji and Langton, 2018). While recent readings indicate a potential trend toward increased Hg levels in saltstone leachates, the current mix demonstrably reduces leaching of total Hg -- from a concentration of approximately 50 mg/L in the initial solution to 0.06 mg/L in leachate, thus meeting the TCLP limit. The observed leaching has been attributed to the predominance of MeHg and its relatively higher leachability compared to inorganic and elemental forms. Thus, getters, particularly if they are effective for MeHg, remain as a strategy to provide defense in depth and increase system robustness and confidence. Importantly, getters are not crucial to continued operations at this time. Nonetheless, developing knowledge and testing of getter alternatives is a relatively low-cost endeavor and may provide the ability for prudent and rapid response actions if mercury concentrations increase in Tank 50 (saltstone feedstock) in the future or if leaching tests approach SRS action levels.

The scoping evaluation of potential getters suggested materials that may have promise for improving MeHg retention. Many of these incorporate a thiol or a reduced sulfur active component. Examples of the materials that are most promising include various forms of silica thiol, sulfur impregnated activated carbon (such as MERSORB), functionalized mercury chelating resins (such as AmberSep GT74), chitosan waste materials (such as granulated exoskeletons from seafood processing), SRS TDF ash, and tire crumb waste materials. A major challenge for these materials may be cost at scale; current commercial costs (circa $1 per kg may be prohibitive). None of the materials in the scoping table have been tested in grout; however, several are currently being tested in MeHg spiked grout in SRNL.

5.6 <u>Recommendations, Path Forward or Future Work</u>

The results of the scoping effort were generally positive. The data suggest that identifying a potential getter for the LWS may be feasible and support advancing this to further testing (go). In moving this forward, a few key activities are recommended, notably testing of promising materials in spiked grout and examining leaching (MeHg retention) and impacts on the properties and durability of the cementation wasteform.

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