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Mercury Phase II Study – Mercury Behavior in Salt Processing Flowsheet

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Executive Summary

Mercury (Hg) in the Savannah River Site Liquid Waste System (LWS) originated from decades of canyon processing where it was used as a catalyst for dissolving the aluminum cladding of reactor fuel. Approximately 60 metric tons of mercury is currently present throughout the LWS. Mercury has long been a consideration in the LWS, from both hazard and processing perspectives. In February 2015, a Mercury Program Team was established at the request of the Department of Energy to develop a comprehensive action plan for long term management and removal of mercury. Evaluation was focused in two Phases. Phase I activities assessed the Liquid Waste inventory and chemical processing behavior using a system by system review methodology and determined the speciation of the different mercury forms (Hg+, Hg++, elemental Hg, organomercury, and soluble versus insoluble mercury) within the LWS. Phase II activities are building on the Phase I activities and results of the LWS flowsheet evaluations will be summarized in the following three reports:

- Mercury Behavior in the Salt Processing Flowsheet (i.e. this report);
- Mercury Behavior in the Defense Waste Processing Facility (DWPF) Flowsheet; and
- Mercury behavior in the Tank Farm Flowsheet (Evaporator Operations).

The evaluation of the mercury behavior in the salt processing flowsheet indicates:

- In the assembled Salt Batches 7, 8 and 9 in Tank 21, the total mercury is mostly soluble with methylmercury (MHg) contributing over 50% of the total mercury. Based on the analyses of samples from 2H Evaporator feed and drop tanks (Tanks 38/43), the source of MHg in Salt Batches 7, 8 and 9 can be attributed to the 2H evaporator concentrate used in assembling the salt batches. The 2H Evaporator is used to evaporate DWPF recycle water.
- Comparison of data between Tank 21/49, Salt Solution Feed Tank (SSFT), Decontaminated Salt Solution Hold Tank (DSSHT), and Tank 50 samples suggests that the total mercury as well as speciated forms in the assembled salt batches in Tanks 21/49 pass through the Actinide Removal Process (ARP) / Modular Caustic Side Solvent Extraction Unit (MCU) process to Tank 50 with no significant change in the mercury chemistry.
- In Tank 50, Decontaminated Salt Solution (DSS) from ARP/MCU is the major contributor to the total mercury including MHg.
- The Waste Acceptance Criteria (WAC) limits/targets for Tank 50 were revised to include limit/target for elemental Hg, MHg and dimethylmercury (DMHg), as a result of exceeding Hg release of 0.025 mg/L in the Toxicity Characteristic Leaching Procedure (TCLP) Universal Treatment Standard on the 4th Quarter 2014 Tank 50 saltstone sample, discovery of MHg in Tank 50 and the resultant Potential Inadequacy of the Safety Basis (PISA) (PI-2015-

0007) resolution. However, in all samples the total Hg leachate concentrations were low and well below the Land Disposal toxicity limit for Hg of 0.2 mg/L.

- Transfers into Tank 50 now must comply with the revised Saltstone WAC limit for total mercury, elemental Hg and MHg of 325, 18.2 and 350 mg/L, respectively, and WAC target of 1 mg/L for DMHg. Tank 50 contents are in compliance with the revised WAC limits and targets.
- Speciation analyses of TCLP leached solutions of the grout samples prepared from Tank 21, as well as Tank 50 samples, show the majority of the mercury released in the solution is MHg.

Based on the evaluation, the following recommendations are provided to address mercury in the salt processing flowsheet in the LWS.

- Currently measured total Hg leachate concentrations are low and well below the Land Disposal toxicity limit of 0.2 mg/L and are slightly below the TCLP Universal Treatment Standard of 0.025 mg/L. However, this could become a potential concern in the saltstone product should the concentration of organomercury in the LWS increase over time.
    - A firm technical understanding of the binding mechanisms for organomercury within the waste form is warranted.
- Pursue the following recommendations of the System Engineering Evaluations (SEE) Team
    - Develop, mature, and deploy technology for the conversion of the MHg in Tank 50 to ionic and elemental mercury using ultraviolet (UV) light; and
    - Develop methods/mechanisms to enhance retention of mercury in saltstone.

The mercury team has submitted the recommendations from the SEE to Department of Energy Office of Environmental Management (DOE-EM) as candidates for technology development needs in order to demonstrate proof of concept for development of alternate means to remove mercury from the LWS. Savannah River National Laboratory (SRNL) is funded through EM-21 for the first of these two recommendations.

1. Introduction

The Savannah River Site (SRS) Liquid Waste System (LWS) stores radioactive waste in 43 underground tanks. The radionuclides in the waste are removed through a series of separation processes, and the low-level fraction is immobilized in a grout waste form (saltstone) while the high level fraction is disposed in a glass waste form. Mercury (Hg) in the LWS originated from decades of canyon processing where it was used as a catalyst to dissolve aluminum clad reactor fuel. Approximately 60 metric tons of mercury is currently present throughout the LWS. Mercury has long been a consideration in the LWS, from both hazard and processing perspectives. Figure 1 shows the flow for mercury through the LWS. Mercury is designed to be removed from the LWS at the following points in the process:

- From the sludge in Defense Waste Processing Facility (DWPF) where mercury is steam-stripped as a part of the feed preparation processes;
- From the Tank Farm evaporator condensates;
- From liquid streams at the Effluent Treatment Plant (ETP) prior to discharge; and
- Immobilized in the low-level, grout waste form at the Salt Disposal Facility (SDF).

The primary mercury removal point in the LWS is designed to be DWPF.

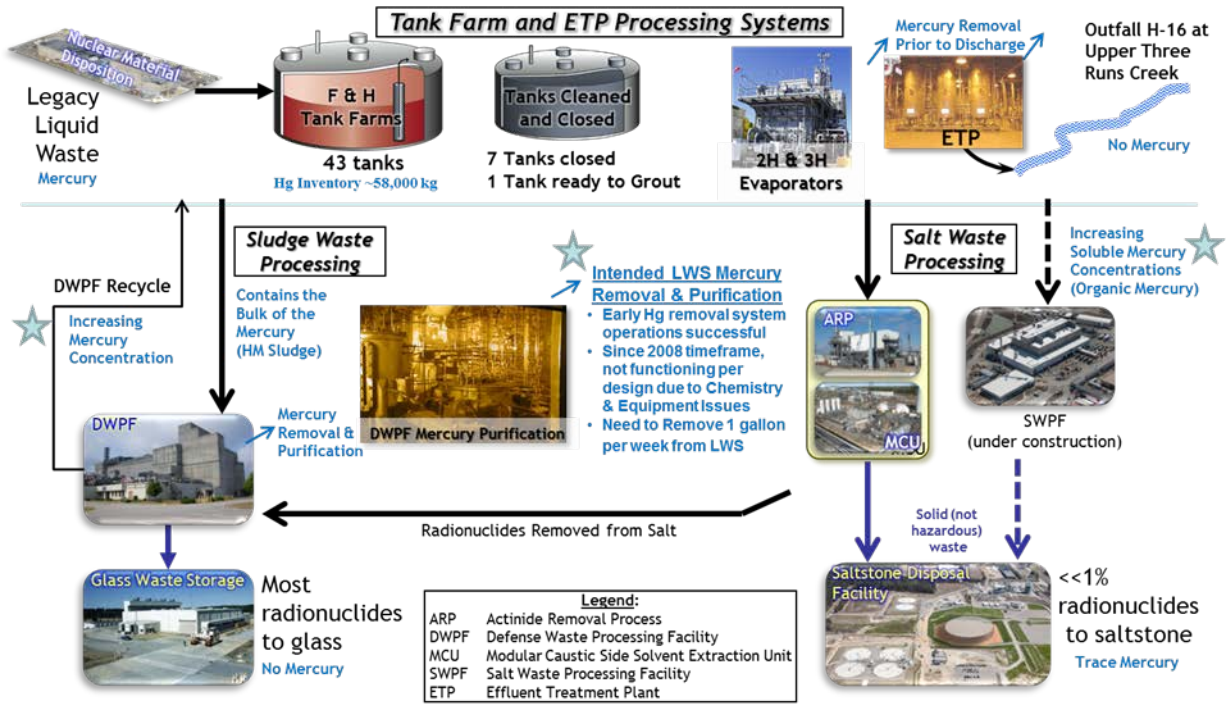

Figure 1. Mercury in Liquid Waste Facilities

In February 2015, a Mercury Program Team was established at the request of the Department of Energy to develop a comprehensive action plan for long term management and removal of mercury. Scope of the team in included:

- Mercury inventory and speciation in the LWS;
- Mercury holdup and chemical processing behavior;
- Impact identification, including worker safety and equipment degradation; and
- Mercury removal and disposal options.

A significant amount of effort was expended during the Phase I [1] activities to assess Liquid Waste inventory and chemical processing behavior using a system by system review methodology to determine the speciation of mercury (Hg(I), Hg(II), elemental Hg, organomercury, and soluble versus insoluble mercury) within the LWS. In particular, the discovery of a higher than expected methylmercury (MHg) species in the Tank 50 feed to saltstone resulted in additional mercury speciation activities being performed on the various process streams that were constituent feed streams into Tank 50. Additional mercury speciation activities were also initiated around specific process flowsheet operations [i.e., DWPF Chemical Processing Cell (CPC) sludge preparation unit operations, Actinide Removal Process (ARP) / Modular Caustic Side Solvent Extraction Unit (MCU) processing, salt batch feed preparation, 2H and 3H evaporator operations] in order to understand mercury processing behavior and also identify potential sources of MHg formation.

Phase II activities are building on the Phase I activities, including additional sampling and characterization activities, a re-assessment of overall system knowledge, ranking and prioritizing critical gaps/information in mercury behavior across the flowsheet, assessing impacts of mercury removal and disposal options, and documenting an action plan for overall mercury management in the LWS. The Phase II results of the LWS flowsheet evaluations will be summarized in the following three reports:

- Mercury Behavior in the Salt Processing Flowsheet (i.e. this report);
- Mercury Behavior in the DWPF Flowsheet; and
- Mercury behavior in the Tank Farm Flowsheet (Evaporator Operations).

In addition during Phase II, the following System Engineering Evaluations (SEE) were completed:

- Re-establish mercury removal capability within DWPF;[2] and
- Determine the best alternative mercury removal location within the LWS.[3]

This report provides an evaluation of mercury behavior in the salt processing flowsheet. This flowsheet starts with the preparation of a salt batch in Tank 21, salt processing through the ARP and MCU facilities to produce decontaminated salt solution (DSS) sent to Tank 50 for processing by the Saltstone Production Facility (SDF) into a saltstone waste form for disposal at the Saltstone Disposal Facility (SDF). Samples were collected at strategic locations in the flowsheet to understand mercury behavior around specific processing operations. Samples were analyzed for total Hg, total soluble Hg, particulate Hg, elemental Hg, ionic Hg, MHg, ethyl Hg, and dimethylmercury (DMHg).

2. Mercury Behavior (Salt Batch Preparation)

Salt solution from the waste tanks, as specified in the System Plan [4], is gathered and qualified in Tank 21. Figure 2 shows makeup of Salt Batch 9 in Tank 21.

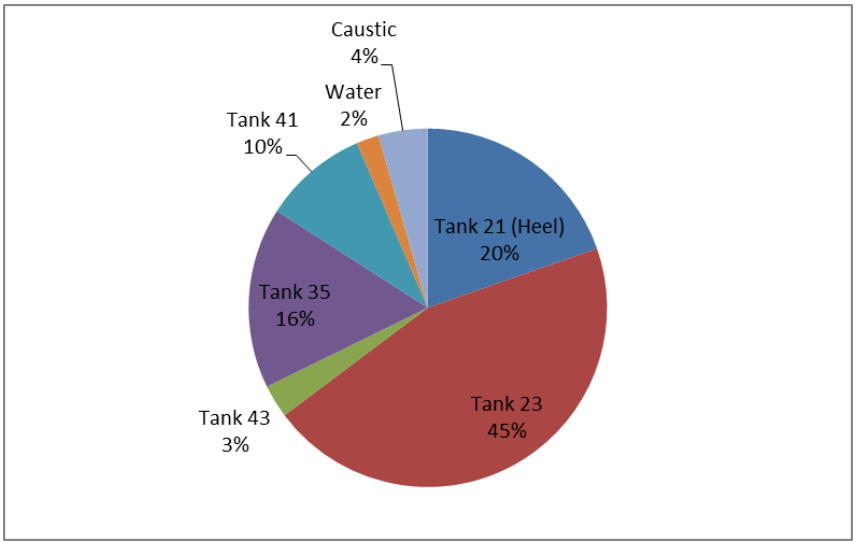

Figure 2. Makeup of Salt Batch 9 in Tank 21 (total volume of batch was 1,236 kgal).

The qualified salt batch from Tank 21 is transferred to Tank 49 and mixed with the heel from the previous batch to feed the ARP/MCU processes.

Figure 3 shows mercury concentration (total Hg and MHg) in Tanks 21 and 49 for the Salt Batch 8 and 7B, respectively. Table 1 provides mercury speciation data on Salt Batch 7B and 8 contained in Tanks 49 and 21, respectively.[5, 6, 7] The mercury concentrations for total, dissolved Hg and MHg are in reasonable agreement for these two separate salt batches. The ionic mercury concentration for Tank 21 and 49 measured 5.9 and 15 mg Hg/L, respectively. Methylmercury concentrations approached 60 mg/L and account for over fifty percent of the soluble

mercury in the salt feed for Salt Batch 7/8. The remaining mercury species are believed to be organomercury based on the measured total mercury and could represent a measurement low bias in the MHg analysis.

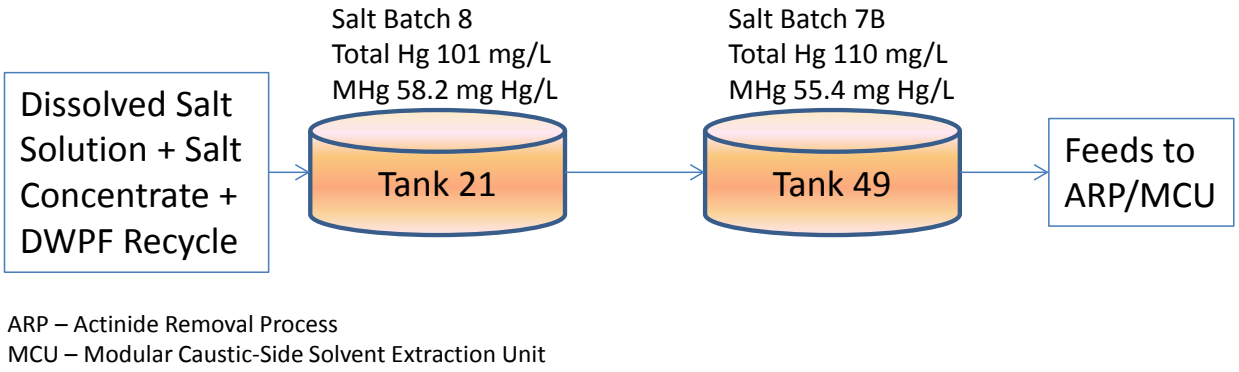

Figure 3. Mercury Concentration (Total Hg and MHg) in Salt Batches 7B and 8.

Table 1. Mercury Speciation Data for Salt Batch (SB) 7B and 8 (mg Hg/L) [RSD]

Tank	Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg	Ionic Hg	MHg	DMHg	Ethyl Hg
21 (SB8)	101 [2.6]	120 [5.4]	ND	<6.2	5.9 [11]	58.2 [2.6]	0.0156 [5.6]	<22
21 Decon[a] (SB8)	86.7 [3.6]	85 [2.0]	1.7	2.2 [69]	5.7 [19]	41.1 [5.8]	<0.00012	<4.4
49 (SB7B)	110 [2.8]	109 [1.3]	-	6.8 [112]	15 [2.3]	55.4 [5.7]	0.511*	<17

- Only one measurement

As part of the make–up for Salt Batch 7 and 8, salt concentrate from Tank 38 and/or Tank 43 was also added to Tank 21. Tanks 38 and 43 are drop and feed tanks for the 2H Evaporator, respectively, and are primarily used for concentrating DWPF Recycles from Tank 22. Mercury speciation analyses for Tanks 38 and 43 samples were not available when these batches were assembled; however, Tanks 38 and 43 were analyzed at two different elevations for mercury speciation before Salt Batch 9 was assembled. [8, 9] Tank 38 surface sample had 496 mg Hg/L of total Hg and 200 mg Hg/L of MHg while the subsurface sample (at the jet suction)

[a] Due to high Cs concentration, the sample was contacted with solvent at SRNL to extract Cs prior to shipping the sample to Eurofins for Hg speciation analysis.

had 476 mg Hg/L of total Hg and 160 mg Hg/L of MHg. Tank 43 surface sample had 286 mg Hg/L of total Hg and 135 mg Hg/L of MHg while the subsurface sample (at the jet suction) had 234 mg Hg/L of total Hg and 134 mg Hg/L of MHg. Considering no significant change in chemistry in Tanks 38 and 43 from Salt Batch 7 to 9 processing, it can be inferred that the major contribution of MHg in Salt Batch 7 and 8, ought to be from evaporator concentrate produced by evaporation of DWPF recycle. Additional details and analyses will be provided in the "Mercury Phase II Study - Mercury Behavior across the High-Level Waste Evaporator System" report. [10]

In the assembled Salt Batches 7, 8 and 9 in Tank 21, the total mercury is mostly soluble with methylmercury (MHg) contributing over 50% of the total mercury. Based on the analyses of samples from 2H Evaporator feed and drop tanks (Tanks 38/43), the source of MHg in Salt Batches 7, 8 and 9 can be attributed to the 2H evaporator concentrate used in assembling the salt batches.

3. Mercury Behavior (ARP / MCU Operations)

The ARP is housed within two separate facilities, with the Monosodium Titanate (MST) addition performed in 241-96H and the filtration of MST solids in 512-S. Batches of qualified salt waste are contacted with 0.2 g MST per liter of salt waste solution. For each cycle, the solids from a series of batches are combined in the Late Wash Precipitate Tank (LWPT). The solution is circulated through a cross-flow filter to remove and concentrate the insoluble solids and Sr/actinide loaded MST. Filtrate emerges on the shell-side of the crossflow filter, is passed through a secondary filter, and collects in the Late Wash Hold Tank (LWHT). The filtrate from the process is sent to the MCU for Cs removal. The concentrated solids in the LWPT are then washed to a sodium molarity of nearly 0.5 M and filtered to remove soluble sodium salts. The washed MST/sludge slurry is sent to DWPF for vitrification. Spent wash water from the solids washing operation is transferred to Tank 50 to feed SPF.

At MCU, salt waste solution received from LWHT is stored in the Salt Solution Receipt Tank. MCU utilizes the caustic side solvent extraction (CSSX) process to remove Cs from the salt waste solution. This process uses an organic solvent, containing a Cs-specific sequestering agent, to remove Cs ions from the salt waste solution. Stream of salt waste solution from the Salt Solution Feed Tank (SSFT) is fed through banks of centrifugal contactors where it is mixed with a stream of an organic solvent and diluent (Isopar L). Cesium is transferred from the salt waste solution to the solvent. The Cs is then stripped from the solvent in another bank of

contactors, and the strip effluent is stored in the Strip Effluent Hold Tank (SEHT). The Decontaminated Salt Solution (DSS) resulting from solvent extraction is then transferred to the Decontaminated Salt Solution Hold Tank (DSSHT). The solvent is continuously recycled during the process and is stored in the Solvent Hold Tank (SHT).

In order to understand the interaction between various MCU process steps, samples were taken from the MCU process vessels. Since MCU operates in batch mode, the samples represent a "snapshot" of the facility during operation.[5, 11, 12] Figure 4 shows the flow of salt waste solution from Tank 49 through the ARP/MCU process and provides a snapshot of mercury concentration (total Hg and MHg) in the MCU process vessels. Table 2 provides mercury speciation data on MCU process vessel samples.

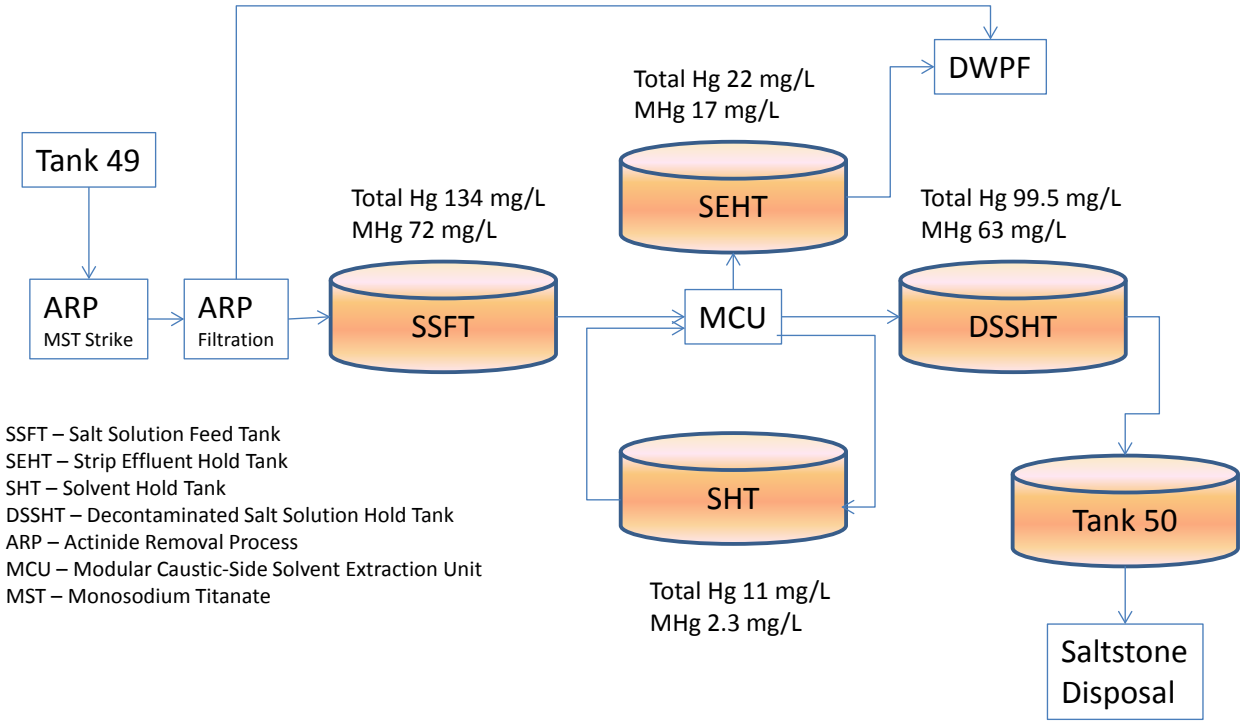

Figure 4. Mercury Concentration (Total Hg and MHg) in ARP/MCU Process Vessels during Salt Batch 7B and 8 Processing.

Comparison of the mercury concentration in the SSFT and the DSSHT (i.e. the salt feed to MCU versus the DSS stream) exhibits similar concentrations for each of the mercury species and a similar species distribution, but, in general, the concentrations in the DSSHT are slightly higher than the SSFT. However, they are within the analytical uncertainty of the measurements. These results tend to indicate that there is no major impact from the ARP/MCU process on the mercury waste chemistry, i.e. the mercury passes through the process into the DSS. It

should be noted that the volumes of strip effluent and solvent streams are small compared to Tank 49 solution processed through the ARP/MCU system.

However, the measurements from the SHT and SEHT indicate the chemistry is more complicated. The SEHT shows total mercury and dissolved mercury at concentrations of 22 mg Hg/L, with ionic species measuring 3.6 mg Hg/L and MHg measuring 16.6 mg Hg/L. The only way for mercury to make it to the SEHT is to be extracted into the solvent and be stripped into the effluent stream. In an effort to better understand the impact of MCU on the distribution of mercury compounds, SRNL performed a series of organic-aqueous phase contacts with two extraction stages, one scrub and one strip stage, using actual Tank 21H samples, and freshly prepared solvent. The mercury content of the cesium-decontaminated Tank 21H sample is listed in Table 1 as the "21 Decon" result. A comparison of the data from this before and after extract shows a reduction in total, dissolved, and methylmercury indicating some interaction is possible between one of the solvent components and the mercury in the waste. Peters reports distribution values for the scrub of ~0.8 and the strip of ~2 as measured without temperature correction [13]. A distribution value <1 indicates a preferential distribution into the aqueous phase, while a value >1 indicates preferential distribution into the organic phase.

Also note that the measured concentration of dimethylmercury (DMHg) is reduced by almost two orders of magnitude (from 0.12 mg Hg/L to <0.0012 mg Hg/L) between the SSFT and DSSHT solutions. Some of the DMHg partitions to the strip effluent hold tank. Since DMHg is fairly volatile, it would also make sense that some may have partitioned to the contactor air purge and been discharged through the vessel vent system.

4. Mercury Behavior (Tank 50)

Tank 50 is a feed tank to the SPF and receives waste from four sources: DSS from MCU, solids washing solution from ARP filtration, General Purpose Evaporator (GPE) Bottoms from H-Canyon, and ETP concentrate. A Tank 50 material balance is maintained within the Waste Characterization System (WCS) to show compliance to the Saltstone Waste Acceptance Criteria (WAC).

Table 2. Mercury Speciation Data for ARP/MCU Process Vessels (mg Hg/L) [RSD]

Tank	Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg	Ionic Hg	MHg	DMHg	Ethyl Hg
SSFT	134 [1.2]	118 [3.7]	15	0.77 [5.4]	11.7 [6.4]	72 [13]	<0.12	<3.5
SHT*	14 [6]	13.5 [0.4]	-	0.27 [35]	3.44 [27]	3.7 [1.1]	Indeterminate	-
SHT**	11.1 [7.5]	12.3 [12]	0.64	0.25 [32]	3.1 [0.7]	2.3 [11]	Indeterminate	<0.03
SEHT	22.1 [1.8]	20.9 [1.9]	0.62	0.58 [31]	3.56 [4.2]	16.6 [6.0]	< 0.13	<18
DSSHT	99.5 [5.1]	101 [1.6]	0	0.6 [8.1]	9.83 [6.0]	62.6 [2.8]	<0.0012	<7

*SRNL-L3100-2015-00068, Rev. 1
**SRNL-L3100-2015-00144, Rev. 1

The WAC limits/targets for Tank 50 were revised to include separate limits/targets for elemental Hg, MHg and DMHg, as a result of exceeding Hg release of 0.025 mg/L in the Toxicity Characteristic Leaching Procedure (TCLP) Universal Treatment Standard on the 4th Quarter 2014 Tank 50 saltstone samples[b], discovery of MHg in Tank 50 and the resultant PISA (PI-2015-0007). However, in all samples the total Hg leachate concentrations were low and well below the Land Disposal toxicity limit of 0.2 mg/L. Transfers into Tank 50 now must comply with the current Saltstone WAC limit for total mercury, elemental Hg and MHg of 325, 18.2 and 350 mg/L, respectively, and WAC target of 1 mg/L for DMHg. [14]

Figure 5 shows the flow of DSS from Tank 50 through the Salt Processing Facility (SPF) to the Saltstone Disposal Unit (SDU) in the Saltstone Disposal Facility (SDF) and provides mercury concentrations (total Hg and MHg) in the Tank 50 and in the Toxicity Characteristic Leaching Procedure (TCLP) leachates. TCLP details are discussed in the next section.

Table 3 provides mercury speciation data for Tank 50 quarterly samples.[6, 12, 15, 16, 17, 18] Total mercury in Tank 50, based on multiple quarterly samples from various dates (4th Quarter 2014 to 2nd Quarter 2016) ranged from 76 mg/L to 105 mg Hg/L. Speciation analyses indicate MHg concentration ranging from 25 to 53 mg Hg/L. These concentrations in Tank 50 for total Hg and MHg have a similar range compared to the Salt Batch 7B and 8 [total Hg (101 -110 mg Hg/L) and MHg (55.4 to 58.2 mg Hg/L)] concentrations shown in Table 1. This further confirms the fact

[b] Saltstone samples were prepared using Tank 50 solution

that the majority of the Hg species pass through the ARP/MCU, with minimal contributions from other sources.

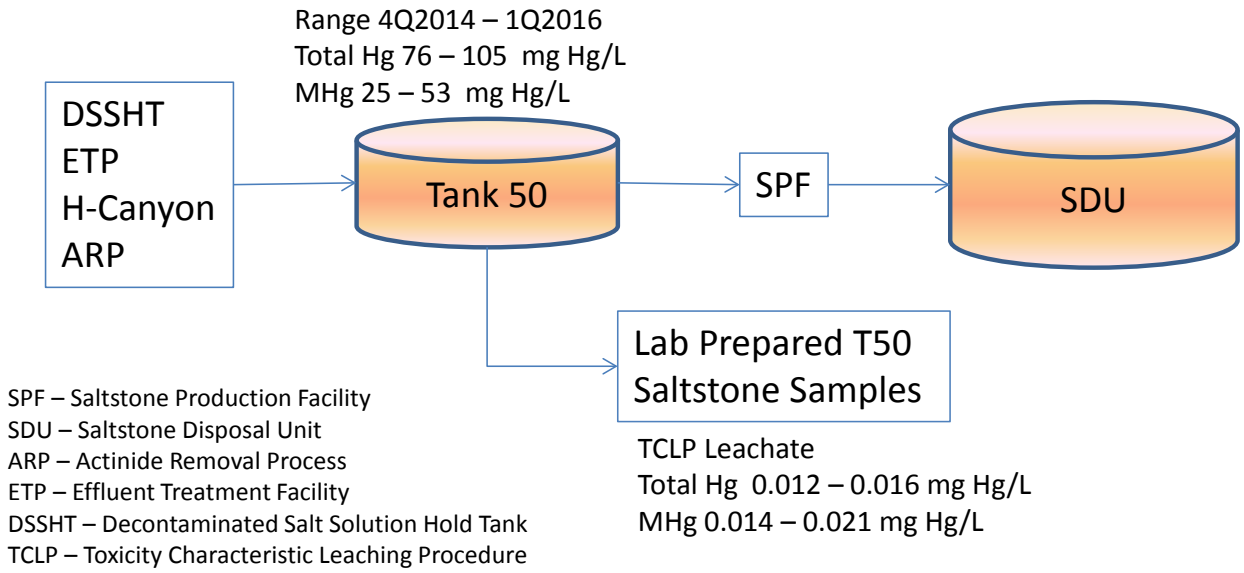

Figure 5. Mercury Concentration range (Total Hg and MHg) in Tank 50 and SDU

Table 3. Mercury Speciation Data for Tank 50 Quarterly Samples (mg Hg/L) [RSD]

Tank	Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg	Ionic Hg	MHg	DMHg	Ethyl Hg
50 4Q14	76 [0.7]	—	—	0.50 [12]	1.1 [1.4]	25 [5.2]	<0.0003	<4.4
50 1Q15	105 [3.3]	—	—	0.84 [19]	4.2 [5.2]	39 [7.1]	0.002 [11]	<4.4
50 2Q15	97.7 [5]	94.3 [8.9]	3.4	1.04 [16]	4.9 [24]	53 [2.9]	0.0235 [13]	<4.4
50 3Q15	92.2 [2.5]	81 [1.1]	9.5	1.8 [4.2]	8.3 [10]	43 [12]	0.012 [9.9]	<3.5
50 4Q15	89 [3.6]	78 [3]	9.2	1.1 [4.8]	6.5 [2.4]	53 [4.2]	0.088 [9.2]	<3.5
50 1Q16	86 [1.5]	73 [1.9]	12	1.1 [12]	6.2 [17]	39 [4.4]	0.21 [14]	<8.7
50 2Q16	104 [3.8]	90 [3.4]	13.5	1.13 [4.2]	6.2 [27]	56 [8]	0.026 [5.4]	<0.18

Both ETP concentrate stored in the Waste Collection Hold Tank (WCHT) and H-Canyon GPE Bottoms are input streams to Tank 50. Total mercury in the WCHT sample (filtered) was 0.08 mg Hg/L and no MHg was detected [21]. Total mercury in the GPE Bottoms (unfiltered) was 0.365 mg/L [19] (speciation analysis was not performed).

Based on the measured mercury concentration differences between the Tank 50 samples and WCHT/GPE Bottoms, the contribution of WCHT/GPE Bottoms to total mercury in Tank 50 is minimal and its influence on chemical nature of the mercury in Tank 50 can be considered insignificant. In Tank 50, the DSS from the ARP/MCU process continues to be a major contributor to the total Hg and MHg. Tank 50 contents are in compliance with the revised WAC limits and targets.

5. Mercury Behavior (Saltstone Processing and Disposal)

The Tank 50 salt solution is sent in batches (~30,000 gal) to the SPF where it is mixed with fly ash, blast furnace slag, and cement to form a cementitious waste form (saltstone) that is poured into engineered vaults (SDU) in the SDF.

In order to verify saltstone product performance, Tank 50 is sampled on a quarterly basis and the resulting saltstone formed is analyzed using the TCLP test. In this test, a crushed sample of the waste form is contacted with a reference solution and the leachates are measured for the contaminant of concern. Table 4 shows the mercury concentrations in the TCLP leachates from the 2Q2015 Tank 50 sample and the leachate from a Tank 21 sample of saltstone.[7, 17] Two samples of saltstone were prepared from each aqueous waste sample and crushed into two particle distributions (normal (N) at < 9.5 mm and large (L) between 5.6 and 9.5 mm).

Table 4. Mercury Speciation of TCLP Leachates (mg Hg/L) [RSD]

Tank[c]	Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg	Ionic Hg	MHg	DMHg	Ethyl Hg
50 (2Q-L)	0.014 [1.9]	0.012 [9.8]	0.0014	0.0002 [20]	0.00019 [3.7]	0.016 [8.3]	0.00034 [61]	<0.0058
50 (2Q-N)	0.016 [0.3]	0.014 [1.5]	0.00096	0.00055 [4.2]	0.00022 [21]	0.021 [33]	0.00085 [3.7]	<0.0058
21 (L)	0.012 [24]	0.011 [22]	0.00013	0.0001 [1.9]	0.000064 [1]	0.014 [29]	0.00013 [48]	<0.0058
21 (N)	0.012 [5.8]	0.012 [8.3]	0.0001	0.000094 [12]	0.00009 [24]	0.014 [3.9]	0.00013	<0.0057

[c] Q=Calendar Quarter, L = Large Particle Fraction, N = Normal Particle Fraction

Speciation analyses of TCLP leachate solutions of the grout samples prepared from Tank 21 as well as from Tank 50 samples show that the majority of the released mercury is MHg. Methylmercury, therefore, is the primary contributor to the mercury release. The measured Total Hg leachate concentrations are low and well below the Land Disposal toxicity limit of 0.2 mg/L and are slightly below the TCLP Universal Treatment Standard of 0.025 mg/L. However, a firm technical understanding of the binding mechanisms for organomercury within the waste form is warranted since previous studies looked only at the binding of inorganic mercury [20]. This could be a potential concern in the saltstone product should the concentration of organomercury in the LWS increases over time.

6. System Engineering Evaluation

As part of an overall strategy to reduce the LWS mercury level, a SEE was conducted to identify and examine options to determine the best possible alternative means to remove mercury from the LWS (excluding DWPF) and provide a recommendation for implementation of a preferred option(s).[3] Twenty potential options to remove or mitigate mercury in the LWS were identified. The 20 options were subsequently reduced to 13 through a screening process. Based on the evaluation of the 13 options, three recommendations were made by the team:

- Deploy methods to remove elemental mercury mechanically from process tanks in the LWS
- Deploy technology to enhance removal of ionic mercury in the H-area evaporators by the addition of a reducing agent to convert ionic mercury to elemental mercury
- Pursue the conversion of the organic mercury cation (HgR+) in Tank 50 (feed to saltstone) to ionic and elemental mercury using ultraviolet (UV) light and maturing the technology for deployment. Parallel tests were recommended to enhance retention of mercury in saltstone. This recommendation is most relevant to the saltstone processing flowsheet.

The mercury team has submitted top recommendations from the SEE to the DOE-EM as candidates for technology development needs in order to demonstrate proof of concept for further development of alternate means to remove mercury from the LWS.

7. Conclusions

Mercury Program Team completed the evaluation of mercury behavior in the salt processing flowsheet. Key conclusions of the evaluation are summarized below:

- In the assembled Salt Batches 7, 8 and 9 in Tank 21, the total mercury is mostly soluble with MHg contributing over 50% of the total mercury. Based on the analyses of samples from the 2H Evaporator feed and drop tanks (Tanks 38/43), the source of MHg in Salt Batches 7, 8 and 9 can be attributed to the 2H evaporator concentrate used in assembling the salt batches.
- Comparison of data between Tank 21/49, SSFT, DSSHT, and Tank 50 samples suggests that the total mercury as well as speciated forms in the assembled salt batches pass through the ARP/MCU process to Tank 50 with no significant change in the mercury speciation. Some mercury does strip to the strip effluent and solvent hold tanks. However, the volume of strip effluent and solvent streams are small compared to Tank 49 solution processed through the ARP/MCU system.
- In Tank 50, DSS from ARP/MCU continues to be a major contributor to the total mercury including MHg. Contributions from the other sources to total mercury in Tank 50 is minimal.
- The WAC limits/targets for Tank 50 were revised to include limits/targets for elemental Hg, MHg and DMHg, as a result of exceeding Hg release of 0.025 mg/L in the TCLP Universal Treatment Standard on the 4th Quarter 2014 Tank 50 saltstone sample, discovery of MHg in Tank 50 and the resultant PISA (PI-2015-0007) resolution. However, in all samples the total Hg leachate concentrations were low and well below the Land Disposal toxicity limit of 0.2 mg/L.
- Transfers into Tank 50 now must comply with the revised Saltstone WAC limit for total mercury, elemental Hg and MHg of 325, 18.2 and 350 mg/L, respectively, and WAC target of 1 mg/L for DMHg. Tank 50 contents are in compliance with the revised WAC limits and targets.
- Mercury speciation analyses of TCLP leached solutions of the grout samples prepared from Tank 21, as well as Tank 50 samples, show the majority of the released mercury is MHg. Methylmercury, therefore, is the primary contributor to the mercury release.

8. Recommendations

- Currently measured total Hg leachate concentrations are low and well below the Land Disposal toxicity limit of 0.2 mg/L and are slightly below the TCLP Universal Treatment Standard of 0.025 mg/L. However, this could become a potential concern in the saltstone product should the concentration of organomercury in the LWS increase over time.
    - A firm technical understanding of the binding mechanisms for organomercury within the waste form is warranted.
- Pursue the following recommendations of the SEE Team:

- Develop, mature, and deploy technology for the conversion of the MHg in Tank 50 to ionic and elemental mercury using ultraviolet (UV) light; and
- Develop methods/mechanisms to enhance retention of mercury in saltstone.

The mercury team has submitted the recommendations from the SEE to the DOE-EM as candidates for technology development needs in order to demonstrate proof of concept for development of alternate means to remove mercury from the LWS. SRNL is funded through EM-21 for the first of these two recommendations.

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