

Evaluation of Mercury in Liquid Waste Processing Facilities

Phase I Report

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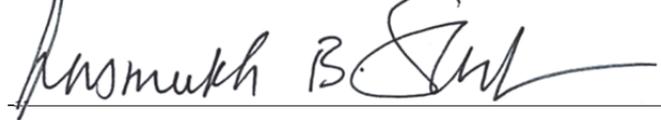
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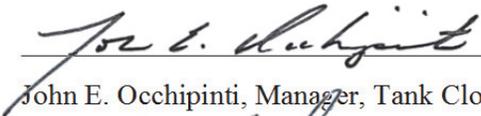
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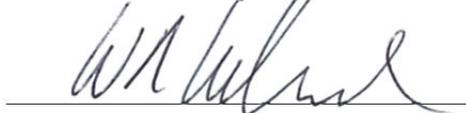
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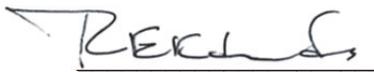
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Executive Summary

This report provides a summary of Phase I activities conducted to support an Integrated Evaluation of Mercury in Liquid Waste System (LWS) Processing Facilities. Phase I activities included a review and assessment of the liquid waste inventory and chemical processing behavior of mercury using a system by system review methodology approach. Gaps in understanding mercury behavior as well as action items from the structured reviews are being tracked. 64% of the gaps and actions have been resolved.

A significant amount of effort was expended during the Phase I activities to assess and determine the speciation of the different Mercury forms (Hg^+ , Hg^{++} , elemental Hg, organomercury, and soluble versus insoluble mercury) within the liquid waste system. In particular, the discovery of a higher than expected monomethyl mercury (MMHg) compound in the Tank 50 feed to saltstone resulted in additional mercury speciation activities to be performed on the various process streams that are constituent feed streams into Tank 50. Additional mercury speciation activities were also initiated around specific process flowsheet operations (i.e., DWPF (Defense Waste Processing Facility) Chemical Processing Cell (CPC) sludge preparation unit operations, 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 MMHg. About 50% of these speciation activities are complete at this time. A number of sources of MMHg have been ruled out based on this sampling and analysis effort, however, completion of this effort will be required to determine the source.

Due to the presence of MMHg in Tank 50, transfer from Waste Collection Hold Tank (WCHT) to Tank 50 and MCU processing was put on “Hold” after MCU and DWPF outages. Based on the speciation and Toxicity Characteristic Leaching Procedure (TCLP) results, the following decisions were made to initiate operations of the LWS.

- Complete Salt Batch 7 processing at MCU
- Transfer Salt Batch 8 from Tank 21 to Tank 49.
- Process Tank 21 Salt Batch 8 material through ARP/MCU and send the decontaminated salt solution (DSS) to Tank 50.
- Release the WCHT transfer to Tank 50.

Sampling and analysis activities were also conducted within DWPF during CPC processing of Slurry Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) Batch 735. This was a first step to better understand mercury behavior during CPC processing operations and to understand chemistry issues with both mercury recovery in the Mercury Wash Water Tank (MWWT) and the high fraction of mercury being returned to the tank farm in DWPF recycle. Data indicate ~43% of the mercury was being returned to the tank farm during Batch 735 processing versus prior estimates of over 80%.

A review of past mercury related events and corresponding corrective actions taken within DWPF indicates that Mercury collection and recovery was successful during sludge-only operations between 1996 and 2008, however, with the start of salt processing in conjunction with HM sludge feeds, a shift in mercury behavior occurred. The shift in behavior resulted in less mercury collection in the Mercury Water Wash Tank (MWWT) than previously experienced and the mercury that was recovered was “dirty” mercury (i.e. sludge/mercury mix) which could not be successfully processed in the DWPF Mercury Purification Process (MPP). Comprehensive SRNL testing was performed; however, an exact cause for

the change in mercury behavior was not identified. Recent analysis following successful sampling of the Slurry Mix Evaporator Condensate Tank (SMECT), Slurry Receipt and Adjustment Tank (SRAT) and MWWT sumps indicate that the mercury in the MWWT is still “dirty” (i.e. sludge containing) Mercury, but the mercury being recovered in the SMECT is relatively clean mercury, analogous to the mercury being collected and recovered from the MWWT during sludge-only operations. The SMECT mercury pump, however, has not functioned properly thus preventing mercury recover from this vessel. Following pump removal, the 2013 video inspection of the SMECT mercury pump revealed that the high pressure water lines for the pump had been severed; the cause has not been determined. With the change in mercury chemistry behavior, the failure of the SMECT mercury pump, and the plugging of the MPP with dirty mercury, all efforts to collect and recover mercury have been unsuccessful since the start of salt processing thru DWPF.

Two major reviews were completed in Phase-1. The first review was the Mercury Flowsheet Extent of Condition Review which focused on identifying potential impacts/issues as a result of increased levels of organic and inorganic mercury in the liquid waste system. The second review was an Expert Panel Review consisting of external industrial and national laboratories personnel convened to provide an assessment on our approach to understand the mercury behavior in the LWS and propose near-term and long-term solutions. Recommendations from the review teams are being tracked to resolution.

Phase II activities will take an integrated approach to re-assess the overall system knowledge, to rank and prioritize critical gaps/information, assess impacts of removal and disposal options, and document an action plan needed to resolve overall mercury management. The following activities are also recommended during Phase II:

- Perform a System Engineering Evaluation (SEE) to “Re-establish Mercury Removal Capability with DWPF”: DWPF experienced both chemistry and equipment issues during coupled operations with Actinide Removal Process (ARP)/MCU product streams. Mercury preferentially went to the Slurry Mix Evaporator Condensate Tank (SMECT) versus the MWWT as intended; the mercury which did go to the MWWT was “dirty mercury” and could not be processed successfully in the Mercury Purification Process; and the SMECT to MWWT mercury pump failed to successfully operate. Recent mercury samples from DWPF vessel sumps designed to collect mercury indicated that the mercury in the SMECT is relatively clean elemental mercury. A SEE is recommended to brainstorm and assess potential options to re-establish mercury removal capability taking advantage of the relatively clean collection of mercury in the SMECT.
- Perform SEE to “Determine the Best Alternative Mercury Removal Location within the LWS”: It is possible that removal of mercury in DWPF may not be sufficient to meet system removal requirements (75% removed in DWPF) and also prevent significant recycling of mercury to the tank farm. A SEE is recommended to determine the best possible alternative means to remove mercury from the liquid waste system.
- Assess and recommend synergistic actions to improve mercury recovery associated with implementation of alternative reductant in DWPF.
- Assess prior recommended actions and action effectiveness from the past reviews related to mercury recovery.

The Phase II action plan will include the results from the SEEs and the assessment actions above.

1 Introduction

Mercury originated from decades of canyon processing (used to aid reactor fuel dissolution) and is present throughout the Liquid Waste System (LWS) (~60 metric tons). Mercury has long been a consideration in the LWS, both from a hazard and a processing perspective. There have been no exposures, no releases, and all waste treatment complies with requirements. Mercury is removed at evaporators, stripped and removed at Defense Waste Processing Facility (DWPF), and removed at Effluent Treatment Plant (ETP) (Figure 1 and 2). Figure 2 shows an estimate of mercury inventory in the liquid waste facilities.

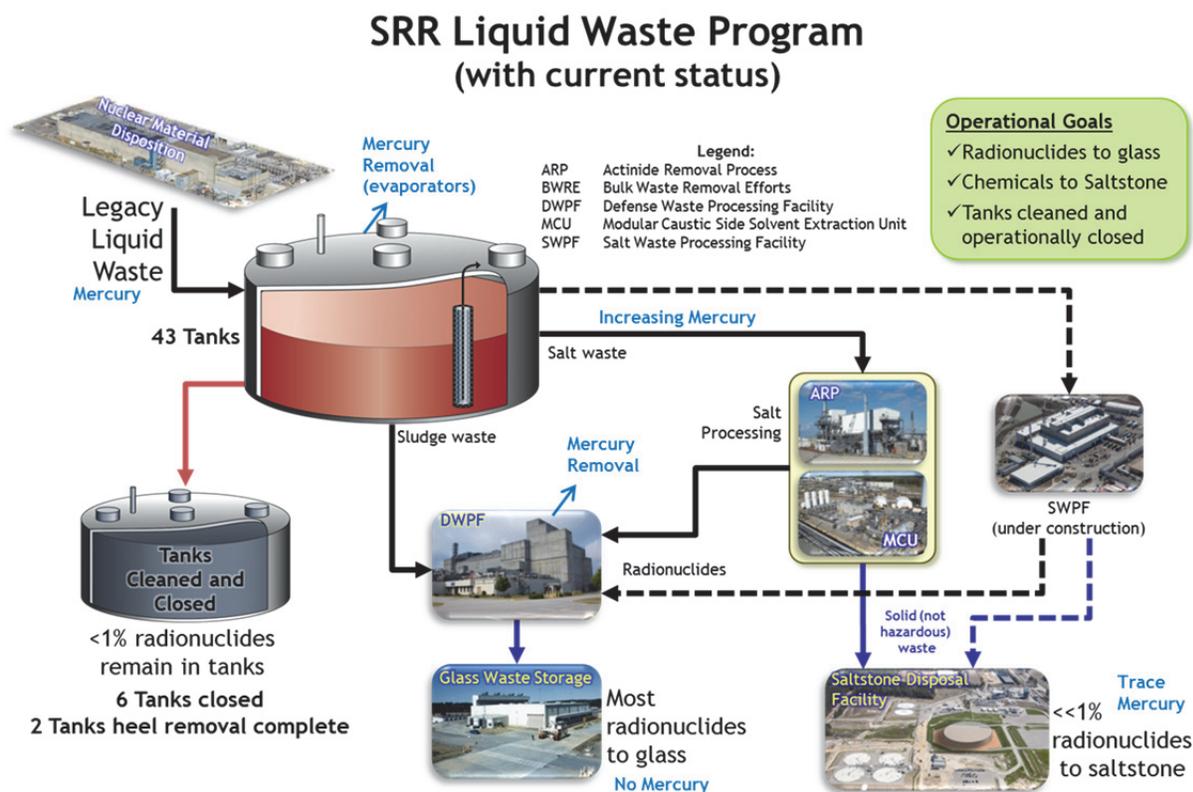


Figure 1 — Mercury in Liquid Waste Facilities.

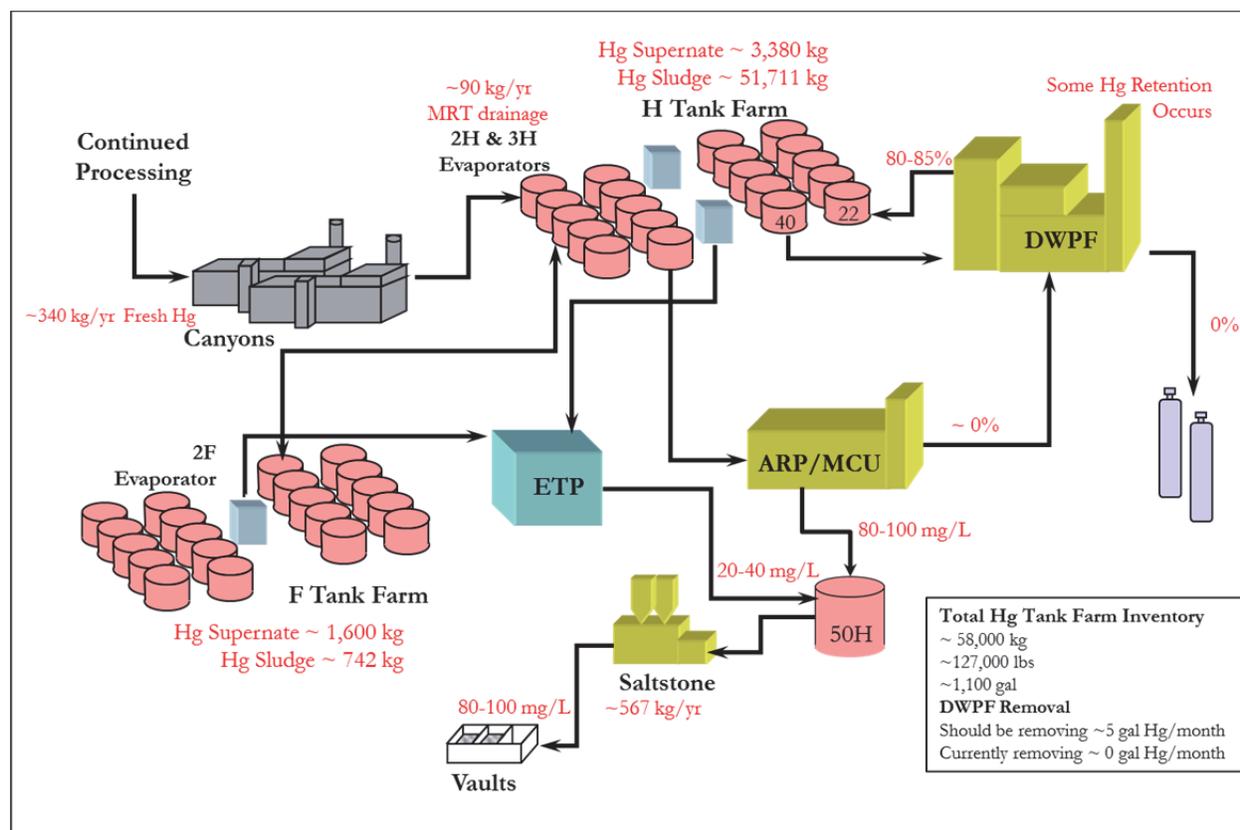


Figure 2 — Estimated Mercury Inventory in Liquid Waste Facilities

Figure 3 shows the amount of mercury in the sludge batches fed to DWPF. Mercury concentration in the processed sludge batches range from 100 mg/kg to 3,600 mg/kg. The majority of the mercury present in the Tank Farm is mostly insoluble and processed with sludge through the DWPF. The concentration of mercury has increased substantially with time and, with the increased processing of H-Area waste (H-Area Tank Farm contains ~90% of the mercury) is expected to increase in future sludge batches since the majority of the sludge remaining is H-Area sludge and an appreciable amount of mercury is currently being returned to the tank farm in DWPF recycle. Salt batches, which are expected to contain low levels of mercury (mostly soluble mercury), have seen substantial increase in concentration as shown in Table 8. Salt Batch 1 had a soluble mercury concentration of 9.75 mg/L while Salt Batches 4 through 7b ranged between 40 mg/L and 88 mg/L.

Folk, in a letter to MacVean [1], indicated that DOE is expecting SRR to take an integrated, system-wide approach to evaluate mercury through the entire LWS. The response from MacVean to Folk [2] stated that SRR is initiating a liquid waste integrated, system wide approach to evaluating mercury behavior. A Mercury Program Team was formed to evaluate mercury in the LWS and develop a comprehensive action plan for long term management and removal of mercury. Following the formation of the Mercury Program Team, two issues related to mercury [Toxicity Characteristic Leaching Procedure (TCLP) and monomethyl mercury (MMHg) PISA] imposed constraints on operations of LWS facilities. A TCLP saltstone Team was formed to address TCLP issue and the Nuclear Safety Group led the effort to address the MMHg issue. Furthermore, a Saltstone/ARP/MCU Restart Issue Resolution Integration War Room

was convened to provide a broader integrated focus on the resolution of issues pertaining to the restart of the LWS facilities. To support the War Room activities, some of the key action items from the Mercury Program Team were rolled up to the War Room schedule. The Mercury Program Team closely interfaced with the Nuclear Safety Group and the TCLP Saltstone Team. The three teams worked together to address the behavior of mercury in the LWS and safely restart the facilities. This report summarizes activities of the Mercury Program Team.

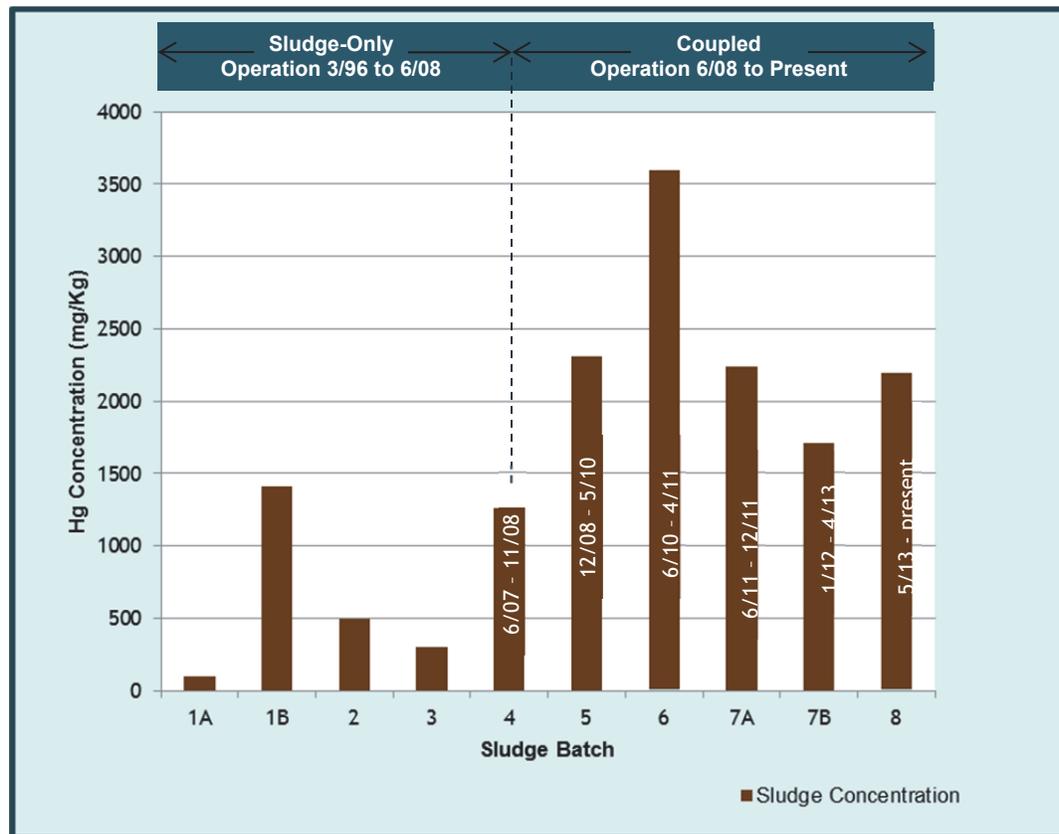


Figure 3 — Mercury Concentration in Sludge Batches.

2 Objective

The objective of the Mercury Program Team is to conduct an integrated, system-wide evaluation of mercury behavior in the LWS including

- Mercury inventory and speciation in the liquid waste system
- Holdup and chemical processing behavior of mercury
- Impact Identification, including worker safety and equipment degradation
- Mercury removal and disposal options

This evaluation is being conducted in two phases

- Phase I: Review liquid waste inventory and chemical processing behavior using a system by system review methodology

- Assess current knowledge
- Identify gaps & information needs
- Identify and execute selected near-term action recommendations
- Phase II: Integrated assessment
 - Re-Assess overall system knowledge
 - Identify critical gaps & information needs – rank and prioritize gaps/actions
 - Assess impacts and removal/disposal options

This report provides a summary of the Phase I.

3 Review Methodology

The following Phase I review methodology was adopted to address the objectives discussed in Section 2.

- Establish a dedicated Mercury Program Team
- Develop & track schedule in SRR Plan of the Week (POW)
- Provide briefings to SRR/ DOE Senior Integrated Project Team (IPT)/ Facility Management Teams
- Conduct Phase I reviews of selected LW systems/processes
 - Liquid waste inventory and speciation
 - Chemical processing behavior
- Track near-term gap analysis actions from systematic reviews
- Track review follow-up action items to closure
- Establish key interfaces for Saltstone TCLP Mercury Team
- Establish Mercury Expert Panel

4 Mercury Program Team

Figure 4 shows the core members of the Mercury Program Team. Other resources, as needed, were requested to support the team.

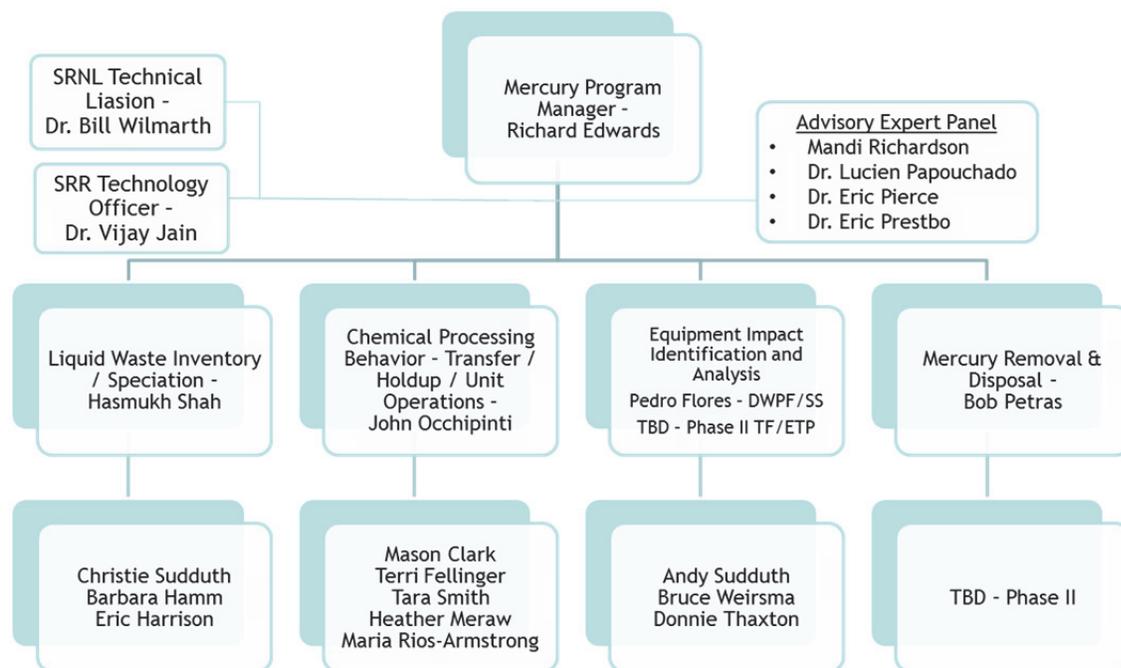


Figure 4 — Mercury Program Core Team Members

5 Summary of Phase I Systematic Liquid Waste System Review

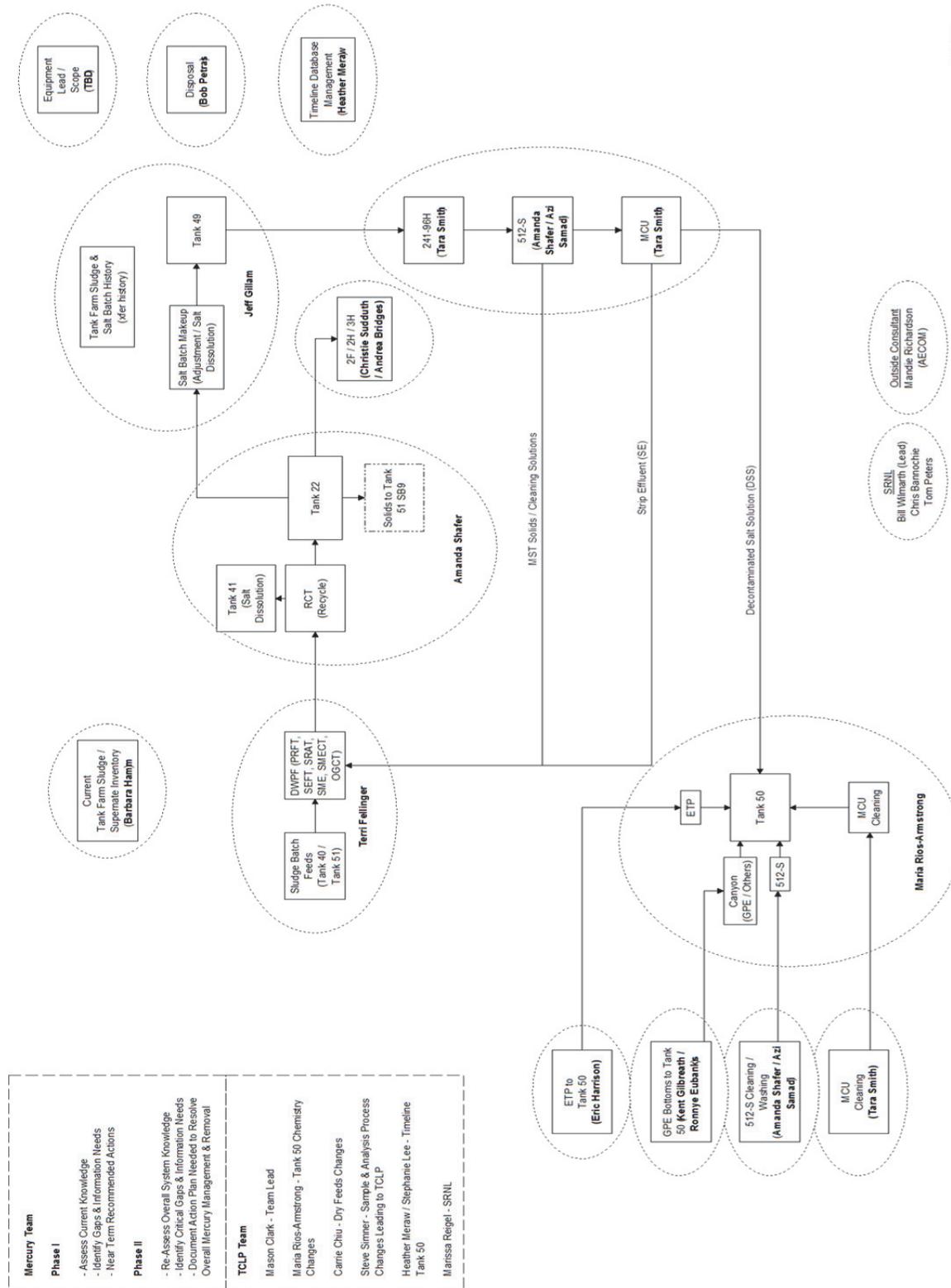
The Mercury Program Team reviewed the LWS flowsheet and determined the systems listed in Table 1 as key systems/ processes that influence the chemical behavior of mercury. Reviews of these key systems/processes shown as circles in (Figure 5) were conducted in a pre-determined format and were aimed at determining what was known about the behavior of mercury in the various process flowsheet operations which make-up the Liquid Waste and determine where significant gaps in knowledge or understanding in mercury behavior existed. Gaps and action items were captured for each of the systems presented. With the discovery of higher than expected levels of MMHg in the decontaminated feed to saltstone (Tank 50), a significant emphasis was placed on understanding the origins of MMHg within the liquid waste system. Detailed presentations for each system are summarized in [3].

Systematic reviews of the LWS resulted in 95 Gaps and identified actions. At the end of Phase I, 64% of these items were closed or resolved.

Table 1 — List of Systems Reviewed with the presenting author

	Name	Subject
1	Harrison	ETP
2	Gillam	Tank Farm Sludge and Salt Batch History
3	Shafer/Fellinger	Recycle Collection Tank (RCT)/ Tank 22/ Tank 41 Salt Dissolution
4	Shafer	Salt Batch make-up and Tank 49; Reuse of Recycle for Salt Batch make-up
5	Smith	241-96H, Modular Caustic Side Solvent Extraction Unit (MCU), MCU Cleaning

	Name	Subject
6	Samadi/Shafer	512-S/ 512-S Cleaning/ Washing
7	Gilbreath/Eubanks	Canyon to Tank 50 (General Purpose Evaporator (GPE) Bottoms/ Tank 39)
8	Rios-Armstrong	Tank 50 Chemistry (Includes ETP, Canyon, 512-S, and MCU Cleaning)
9	Fellinger	DWPF processing vessels; Sludge Batch Feeds Tank 40/ 51
10	Sudduth/Bridges	2H/ 3H/ 2F Evaporators
11	Hamm	Current Sludge/ Salt/ Supernate Inventory
12	Riegel	Mercury Analytical Methods used at SRS



3/16/2015

Figure 5 — Key Systems (Circled) Considered for Mercury Evaluation

5.1 Effluent Treatment Plant (ETP)

ETP in H-Area is a physical/ chemical wastewater treatment plant that removes chemical and radioactive contaminants from wastewater prior to releasing the treated water to the environment. Treatment unit operations include filtration, Hg and organic removal, reverse osmosis, and ion exchange to decontaminate water for release. The waste concentrate (evaporator bottoms) stream from the Effluent Treatment Facility (ETF) is transferred to Tank 50H and stored until disposed at the Saltstone Disposal Facility. Therefore, the ETF waste concentrate stream must meet the Saltstone limits after being mixed with the other Tank 50 influents.

Evaporation operations reduce the volume of the concentrate stream to be transferred to Tank 50/ Saltstone. The current ETF Waste Acceptance Criteria (WAC) for Hg is 35.2 mg/L and was determined based on the limiting effluent concentration at 325 mg/L (Total Hg) for the Saltstone WAC by the following equation.

$$WAC (ETF)^1 = \frac{WAC(Saltstone)}{CF \times \left[\left(\frac{0.95}{DF}\right) + 0.05\right]}$$

Where

CF = 130

DF = 45

Table 2 provides a summary of the ETP system and Table 3 provides the gaps in our current understanding of mercury in the system and the path forward to address the gaps.

Table 2 — Mercury in Effluent Treatment System

	Summary
System Inputs	<ul style="list-style-type: none"> • Tank Farm Evaporator Overheads • H-Canyon Acid Recovery and GPE Overheads • SRNL and Area Completion Projects² (ACP) and (sample wells) via truck • Tritium and C Lab
System Outputs	<ul style="list-style-type: none"> • Waste Concentrate to Tank 50 • Treated Water to Upper Three Runs Creek (UTC)
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • Operations begin in 1988 • R-basin and H-Canyon diversion in 2006 results in Hg spike • Partial transition from SIR-200 to GT-73 Hg removal resin

¹ A 95/5 split is an assumption from X-CLC-H-00044. A 5% of the feed into the system is filtrate concentrate and does not pass through Hg removal. The remaining 95% of the feed goes through the Organic Removal Hg columns and has a DF of 45.

² It is a stream that is in the 10's of gallons. Typically, very low levels across the board and results from the sampling ground water wells that are too high in some component to be discharged to grade.

	Summary
Routine Samples	<ul style="list-style-type: none"> • Each Waste Water Collection Tank prior to processing • Waste Concentrate Tank prior to transfer to Waste Collection Hold Tank (WCHT) • WCHT prior to transfer to Tank 50 • Treated Water prior to discharge to UTC
Mercury data	<ul style="list-style-type: none"> • WWCT (0 to 5 mg/ L typical) • WCT/ WCHT (5 to 50 mg/ L typical) • Treated Water (0/ less than detection limit typical)
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • None internal. Due to the path from WWCT (Waste Water Collection Tank) through filter concentration into evaporator bottoms, ETP's Hg concentration output to Tank 50 is dependent on influent concentrations. Hg upsets upstream translate to increased Hg concentration output to Tank 50.
Mercury Mass Balance	<ul style="list-style-type: none"> • TBD. Should be determined once additional data is collected • WWCT totals the influent Hg mass • Treated Water to UTC essentially zero • WCT (Waste Collection Tank)/ WCHT to Tank 50 and Hg removal resin to represent the balance out

Table 3 — Gaps and Recommendations for Mercury Estimates in ETF

	Gaps and Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> • Mass of Hg removed through ion exchange. Currently disposal of resin on TCLP basis. Total Hg mass in disposed resin was not previously determined. • Speciation of Hg in the solids fraction of the ETP waste concentrate
Recommendations (Prioritized list)	<ul style="list-style-type: none"> • Perform mercury mass balance • Analyze WCT/ WCHT for Hg concentration prior to transfer to Tank 50

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Mercury speciation of WCHT sample
 - Mercury speciation analyses of the WCHT sample complete. Discussion is provided in Section 8.

5.2 Tank Farm Sludge and Salt Batch History

A chronological depiction of Tank Farm waste transfers leading up to and including assembly of salt batches has been constructed. This is a tool to identify potential historical mercury pathways and a tool to support other aspects of the mercury process troubleshooting. Included are transfers between Tanks 21, 22, 23, 24, 38, and 41, and of DWPF recycle, and transfers for Sludge Batch processing.

Table 4 — Tank Farm Sludge and Salt Batch History

	Summary
System Inputs	<ul style="list-style-type: none"> • Transfer history from FY2000 through FY2014
System Outputs	<ul style="list-style-type: none"> • Chronological depiction of transfers impacting Salt Batch makeup.
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • As depicted
Routine Samples	<ul style="list-style-type: none"> • N/ A
Mercury data	<ul style="list-style-type: none"> • N/ A
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • N/ A
Mercury Mass Balance	<ul style="list-style-type: none"> • N/ A

Table 5 summarizes the gaps in the current understanding of the mercury mass balance with respect to historical Salt Batch makeup, and provides a path forward to address the gaps.

Table 5 — Gaps and Recommendations for Tank Farm Salt and Sludge

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> • None³. The quantity and state of mercury in existing tank inventories is the subject of other presentations.
Recommendations	<ul style="list-style-type: none"> • Determine the fraction of DWPF Recycle liquid, by Sludge Batch, in each Salt Batch – for comparison to total mercury or other parameters of the Salt Batches (Complete).

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Using historical transfer history, transfer volume, and tank levels, the volume of DWPF Recycle liquid (from each Sludge Batch) and also for Tank 38 liquid and Aluminum leachate ultimately dispositioned to each Salt Batch, has been determined. The data is shown in Figure 6.

³ There were gaps observed in the sludge mass processed between Sludge Batch 1 through 3 where the number of canisters poured was higher than the sludge mass projected by WCS. Therefore, in 2005 DWPF material estimate was created using dial-up factor. System Plans from 2006 through 2012 used the revised sludge mass. ‘Recommended values adjusted in 2012’ provides an updated estimate which include reductions due to the lower mass actually found in Tank 13H.

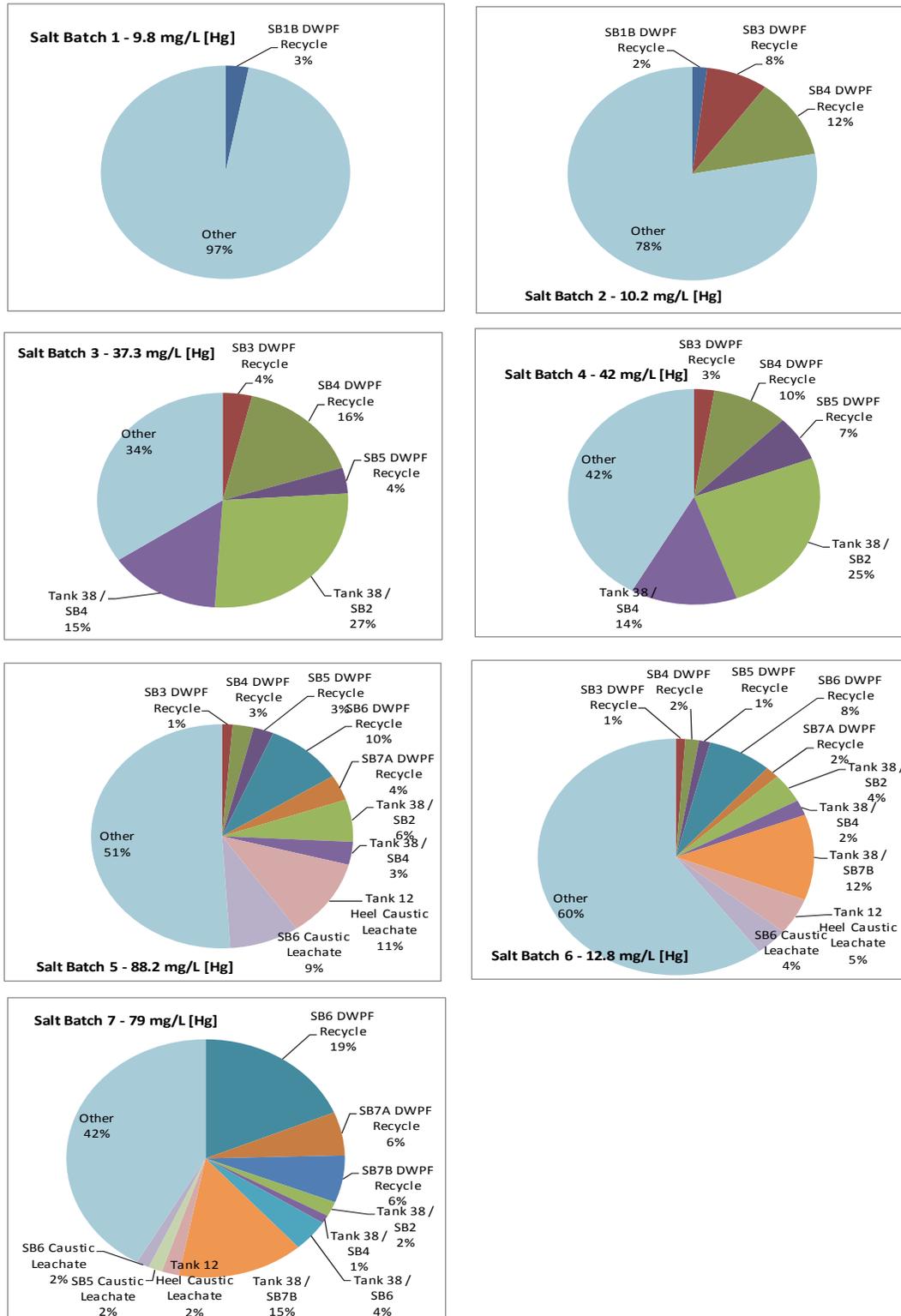


Figure 6 — Waste Streams added for Salt Batch Makeup and Mercury Level in Each Salt Batch

5.3 RCT/Tank 22/Tank 41 Salt Dissolution

Tank 22 stores DWPF recycle waste and is feed for the 2H Evaporator system. Historically DWPF recycle was also sent to Tank 21; Tank 21 feed was transferred into Tank 22 for 2H Evaporator feed. The DWPF recycle material contains some insoluble solids. In the 2014 Solids Removal Campaign, Tank 22 solids were sent to Tank 51 for sludge batch preparation. Tank 22 solids were also included in the salt batch recipes. Table 6 provides a summary of the DWPF waste recycle system.

Table 6 — DWPF Waste Recycle System Summary

	Summary
System Inputs	<ul style="list-style-type: none"> DWPF recycle
System Outputs	<ul style="list-style-type: none"> 2H Evaporator (Tanks 38 and 43) Salt Batches (Tank 21) Sludge Batches (Tank 51)
Process Timeline and History of Key Events	<ul style="list-style-type: none"> Bulk Waste Removal (BWR) was completed in 1986 to prepare for DWPF recycle August 1997 to present received DWPF recycle Solids layer rebaselined in 2013 for radionuclide Included in Salt Batches since 2009 Solids removal campaign 2014 to Tank 51
Routine Samples	<ul style="list-style-type: none"> Corrosion Control Program (No Mercury information obtained)
Mercury data	<ul style="list-style-type: none"> Samples from RCT were measured for total mercury and were performed on a tickler or by Engineering request. 66 samples since May 2003 Sludge Batch 9 preparation requires removal of ~14,000 kg with total solids (mercury equal to 1.48 wt.% or ~ 556 gallons). SRNL-STI-2014-00380
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> N/A
Mercury Mass Balance ⁴	<ul style="list-style-type: none"> March 23, 2015 Results If historical mercury concentration in RCT sample is used, 895.8 mg/ kg of RCT solution Total mercury, 3.24E+03 kg or 63 gallons (Tank 22) Amount Potential sent to 2H: 2.72E+04 kg or 531 gallons Hg with 8,017,846 gallons since FY 2010 Amount Potential sent to Salt Batches: 1,945 kg or 38 gallons Hg with 573,751 gallons of Tank 22 sent to salt batch makeup.

Table 7 summarizes the gaps in the current understanding of the mercury mass balance and provides a path forward to address mercury behavior in the Tank 22. Data collection from Tank 22 combined with DWPF RCT samples will be utilized to continue to gain information regarding mercury in Tank 22.

⁴ The RCT mercury concentration is dependent on sludge batch and the stage of DWPF processing. The average value shown is the 66 samples that were analyzed from 2003 to 2015. DWPF was processing Sludge Batch 2 through Sludge Batch 8 during this time frame. The mercury concentration of each sludge batch varies. In addition, mercury is steam stripped at DWPF in the SRAT; therefore, RCT batches collected during SRAT processing are expected to have an increased mercury concentration. The potential values sent to the 2H Evaporator or salt batches are based on this average concentration of mercury over this period and the volumes transferred. Thus, the actual mercury concentrations should be determined in a sample for salt batch qualification or in the 2H Evaporator feed and drop tanks.

Table 7 — DWPF Waste Recycle Gaps and Recommendation

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> Mercury speciation in Tank 22
Recommendations (Prioritized list)	<ul style="list-style-type: none"> Perform Mercury Mass balance

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Tank 22 samples were sent to Eurofins⁵ for Hg Speciation [4]

Mercury speciation analyses of the Tank 22 sample complete. Discussion is provided in Section 8.

5.4 Salt Batch Makeup and Tank 49

Salt solution is gathered and qualified for the Integrated Salt Disposition Project (ISDP) processes— Actinide Removal Process (ARP)/ MCU. The sources have included dissolved salt and supernate from Tanks 8, 10, 12, 22, 23, 24, 25, 35, 38, and 41 with sodium hydroxide additions. For Salt Batches 1 and 2, the batches were compiled and qualified in Tank 49, the feed tank for ARP/ MCU. The subsequent batch were compiled in Tank 21 and qualified before transferring to Tank 49. Before transiting to Salt Batch 5, mixing capabilities were removed in Tank 49. The salt batch mercury concentration and process volume are in Table 8.

Table 8 — Mercury Concentration in Salt Batches

Salt Batch	Start Date for processing	Processing Volume based on Tank 49 level (gallons)	Total Mercury (mg/ L)	Total Mercury (kg)	Total Mercury (gallons)
1	4/ 21/ 2008	145,384	9.75	5.37	0.10
2	1/ 22/ 2009	697,998	10.2	26.95	0.52
3	5/ 28/ 2010	976,973	32.4	119.81	2.33
4a	7/ 23/ 2011	169,287	32.2	20.63	0.40
4b	9/ 20/ 2011	670,304	40.6	103.01	2.00
5	8/ 31/ 2012	394,173	88.2	131.59	2.56
6a	1/ 25/ 2013	142,260	*65.8	35.43	0.69
6b	3/ 2/ 2013	131,625	*59.4	29.59	0.58
6c	3/ 22/ 2013	88,838	*54.8	18.43	0.36
6d	4/ 17/ 2013	778,518	*51.5	151.76	2.95
7a	4/ 4/ 2014	15,198	*68.1	3.917	0.076
7b	7/ 4/ 2014	1,088,135	*68.7	282.95	18.06
Totals		5,298,696		929.42	18.06

*No mixing

⁵ Eurofins – Laboratory contracted by SRR to perform mercury speciation analyses.

Table 9 summarizes the gaps in the current understanding of the mercury mass balance and provides a path forward to address mercury behavior in the salt batches. Mercury speciation data will be collected in source tanks for future batches.

Table 9 — Gaps and Recommendations for Future Salt Batches

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> • Mercury speciation of future salt batches • LW 2H System tanks (38,43, OHT-1/2) samples have been pulled for Hg speciation • LW TK 39 (Canyon Receipt Tank) samples have been pulled for Hg Speciation • LW 3H System Tanks (30, 32, 37, OHT-1/2) and TK 39 are scheduled to be sampled in July -2015.
Recommendations (Prioritized list)	<ul style="list-style-type: none"> • Perform Mercury speciation and mass balance

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Salt Batch 8 sample sent to Eurofins for Hg Speciation [5]

Mercury speciation analyses of the Salt Batch 8 sample complete. Discussion is provided in Section 8.

5.5 ARP-MCU Process

As part of the liquid waste disposition project SRR utilizes MCU to extract Cs-137 from liquid salt waste via the solvent extraction process. MCU has operated using a BobCalixC6 extractant based solvent that has provided Cs-137 decontamination factors greater than 100 (with the target DF > 12). A Next Generation Solvent (MaxCalix extractant based solvent) utilizing MaxCalix extractant with tris (3,7-dimethyloctyl) guanidine hydrochloride (TiDG) as the suppressor was developed by SRR, Texas Tech University, Idaho National Laboratory, Argonne National Laboratory, Savannah River National Laboratory, and Oak Ridge National Laboratory to provide improved process performance characteristics and Cs-137 decontamination. In 2013, MCU switched from the CSSX flow sheet to the Next Generation flow sheet to improve extraction, stripping, contactor hydraulics, and coalescer efficiency. Flow sheet changes included chemical changes to the associated scrub and strip feeds, the addition of the Next Generation Solvent (NGS), and changes in the organic to aqueous ratios (O/A ratios).

Table 10 — Summary of MCU Process System

	Summary
System Inputs	<ul style="list-style-type: none"> • ARP output stream
System Outputs	<ul style="list-style-type: none"> • Strip Effluent Hold Tank (SEHT) to DWPF • Decontaminated Salt Solution (DSS) to Saltstone (Tank 50)

	Summary
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • Radioactive Operations started in April 2008 • April 2009 inadvertent transfer of 8 gal of salt to DWPF • April 2009 reduce ARP strike time to 12 hrs • Strip Effluent (SE) High Isopar events in February 2010, June 2010, July 2011, September 2012, November 2012 • July 2012 reduce MST concentration to 0.2 mg/L and reduce strike time to 8hrs • September 2013 add NGS chemicals • December 2013 start processing under NGS flowsheet • Solids upset April 2014, sent Salt directly to Tank 50
Routine Samples	<ul style="list-style-type: none"> • Every batch Decontaminated Salt Solution Hold Tank (DSSHT) (density, Cs-137, free hydroxide, uranium, aluminum, Isopar) • Every batch SEHT (density, pH, Cs-137, sodium, Isopar) • Monthly Solvent Hold Tank (SHT) (Solvent Constituents, pH, density, impurities) • Monthly DSSHT/ SEHT (radionuclides, Anions)
Mercury data	<ul style="list-style-type: none"> • 2012 solids in contactors • IH air monitoring • SHT Monthly 17.9 mg/ L • SEHT and DSSHT March Monthly's (~101 and ~82 mg/ L) • Waiting on Strip Tote samples (IH vapor sampling indicated Hg)
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • N/A
Mercury Mass Balance	<ul style="list-style-type: none"> • Salt Batch 7B samples are pulled from SFFT, SEHT, SHT and DSSHT for Hg speciation to understand entire Mass Balance of • Salt Batch 8 samples of (SSFT, SEHT, SHT, and DSSHT) are scheduled to be pulled upon completion of 100K gallons processing from Tank 49 • Mercury in Caustic Wash chemicals • Mercury is minimally extracted by the Solvent • Trace Organic could react with Hg given time and/or high temperature

Table 11 summarizes the gaps in the current understanding of the mercury mass balance and provides a path forward to address mercury behavior in the MCU process.

Table 11 — MCU Gaps and Recommendations

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> • Mercury uptake into the SHT • Impacts from Degradation products • Mercury in other chemicals
Recommendations (Prioritized list)	<ul style="list-style-type: none"> • Sample SSFT, SEHT, DSSHT and SHT for speciation and perform mass balance • Literature Review of process chemical interactions with mercury • Quantify SHT degradation

What has been done so far to resolve “gaps in understanding” and Recommendations:

- SHT sample sent to Eurofins for Hg speciation
- SSFT, SEHT, DSSHT and SHT samples for Hg speciation from Salt Batch 7B upon MCU restart to understand Hg behavior throughout the process

SSFT, SEHT, DSSHT, and SHT samples for Hg speciation have been pulled of Salt Batch 7B processing at MCU and prepared to be sent to Eurofins for analysis

5.6 512-S System

Actinide Removal Process (ARP) is located in 512-S. In this process, batches of salt solution containing Monosodium Titanate (MST) sorbent are received in the Late Wash Precipitate Tank (LWPT) and are concentrated by crossflow filtration, with the filtrate going to the Late Wash Hold Tank (LWHT) and the concentrated slurry remaining in the LWPT, where it is subsequently washed. After LWPT and LWHT contents are sent to downstream facilities, the filter is washed with oxalic acid which is pH adjusted and mixed with the LWPT heel and sent to DWPF. The ARP is housed within two separate facilities, with the MST addition performed in 241-96H and the filtration of MST solids in 512-S. Batches of salt waste are contacted with MST at a dose of 0.2 gm of MST per liter of waste. For each cycle, the solids from a series of batches are combined in the LWPT. The filtrate from the process is sent to the MCU for cesium removal. The solids are washed to a sodium molarity of nearly 0.5 M, after which they are concentrated and sent to DWPF via the Low Point Pump Pit (LPPP). During crossflow filtration, slurry is recirculated through the tube side of the filter from the LWPT. Filtrate emerges on the shells side of the crossflow filter, is forced through a secondary filter, and enters the LWHT. The surge tank is utilized during filter cleaning. During normal processing there are approximately 40 batches between cleanings. The number of batches between filter cleanings is limited by filter performance and 5 wt.% solids limitations in the LWPT. The 5 wt.% solids limit provides a dilution function that dissolves/re-suspends the oxalates so that there is no buildup. Table 12 provides a summary of 512-S system.

Table 12 — Summary of 512-S System

	Summary
System Inputs	<ul style="list-style-type: none"> • 96H
System Outputs	<ul style="list-style-type: none"> • LWHT to MCU • LWPT washed accumulated MST to DWPF
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • Rapid decline in filter performance starting in Salt Batch 5 and continuing through Salt Batch 6D

	Summary
	<ul style="list-style-type: none"> • August 2013 through February 2014, number of batches between cleaning was less than 20 with two cleaning cycles back to back • Different methods of cleaning including a long term oxalic soak and a caustic cleaning were also tried in December 2013 and January 2014 which did not improve the filter performance • In March 2014, 512-S filter flushes were completed prior to the cross-flow filter replacement • 512-S is back to processing at least ~40 batches per cycle since the replacement of the primary filter • Some improvements have been made in the operating strategy, which have helped improved throughput at 512-S
512-S Samples	<ul style="list-style-type: none"> • Series of LWPT and LWHT samples were taken in 2013 and 2014 to improve understanding of the process chemistry and physical properties of the material being filtered • Goal of sampling was to determine if solids (in addition to MST) were precipitating and causing the degraded performance of the filters • In 2013, samples were collected during the processing of Salt Batch 6D • In 2014, samples were collected after completion of cycle 1 of Salt Batch 7B
Mercury data	<ul style="list-style-type: none"> • Elemental analysis of the dried unwashed solids isolated from the 2013 LWPT samples showed Hg (on the order of E-03 to E-02 Wt. %) • Elemental analysis of the washed and dried solids isolated from the 2014 LWPT samples showed Hg (on the order of E-02 Wt. %) • The mercury analysis may reflect a low bias because the solids were dried at 120 °C for 12 hours prior to analysis, potentially volatilizing a portion of the mercury • Two spent secondary filters were analyzed (one (Filter 1) removed from service in August of 2014 after processing approximately 187,000 gallons of Salt Batch 7a and one (Filter 2) removed in April of 2014 after processing 487,000 gallons of Salt Batch 6d and first few batches of Salt Batch 7a • Filter 2 contained Hg compounds, possibly elemental, that was not observed on Filter 1
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • N/A
Mercury Mass Balance	<ul style="list-style-type: none"> • TBD once additional data is collected

Table 13 summarizes the gaps in the current understanding of the mercury mass balance and provides a path forward to address mercury behavior in the 512-S System.

Table 13 — 512S System Gaps and Recommendations

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> Analyze LWHT for soluble Hg and Hg Speciation. Also, have LWHT sample filtered and analyzed for Hg Analyze LWPT for soluble Hg and Hg Speciation. Identify if any sample left of LWPT-3(LWPT sample after filter cleaning) that can be analyzed for Hg Speciation Determine Wt% of Hg in LWPT-1, 2 and 3 (2013 samples) are on insoluble or Total solids basis.
Recommendations (Prioritized list)	<ul style="list-style-type: none"> Need to obtain the actual amount of mercury associated with the filtered and washed solids Slurry and filtrate could also be analyzed for mercury

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Completed wt.% determination of Hg in LWPT-1, 2 and 3 on Total solids basis

5.7 Canyon to Tank Farm Transfer

H and/ or F Canyon have been in operation since 1954. Both canyons have been using mercury to facilitate the nitric dissolution of aluminum clad and aluminum alloy feeds (among other uses) since 1959. This mercury has been used, recycled, and reused since this time. The H canyon has mainly sent waste into three tanks in HTF during this time period, Tanks 39, 50 and 51. There are three main sources of elemental mercury at SRS, (clean mercury) from Oak Ridge, TN which is stored in H-Canyon, recycled, (radioactive mercury) from F & H tank farm evaporators, and the most recent and potentially largest source, recycled mercury from the DWPF process. Table 14 provides a summary of H-Canyon to Tank Farm transfers.

Table 14 — H-Canyon to Tank Farm Transfers

	Summary
System Inputs	<ul style="list-style-type: none"> GPE stream to Tank 39 (until early 2005) GPE stream to Tank 50 (early 2005 to present) Highly Enriched Uranium (HEU) campaign (non-irradiated fuel) to Tank 50 from 2005 to 2011 “Normal” approved canyon waste streams to Tank 39 “Special” approved waste streams (SNM) to Tank 51 as part of various sludge batches
System Outputs	<ul style="list-style-type: none"> Tank 39 transfers to both F and H evaporators during this time frame Wash water transfers (sludge batch preparation) to F & H evaporator systems Sludge transfers to DWPF
Process Timeline and History of Key Events	<ul style="list-style-type: none"> Mercury Operations started in 1959 in Canyons H canyon transfers to Tank 39 since 2000, ~ 2.1 million gallons H canyon SNM transfers since 2000 into Tank 51 ~ 500 K gallons GPE transfers into Tank 50 since 2005, ~ 221 K gallons

	Summary
	<ul style="list-style-type: none"> H canyon HEU transfers into Tank 50 2005-2006 era ~ 820 K gallons
Routine Samples	<ul style="list-style-type: none"> None, only as requested
Mercury data	<ul style="list-style-type: none"> GPE ~ 0.365 mg/ L (only small amount of Hg sent to tank 39 and 50 from the GPE transfers) ~ 270 kg of Hg sent to Tank 39 since 2000 ~ 158 kg of Hg sent to Tank 50 since 2005 ~ 9 kg of Hg sent to Tank 51 as part of Sludge Batch 9 ~ 180 kg of Hg still in H Canyon as part of current processing waiting transfer into the HLW system (Tank 39 or 51)
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> N/A
Mercury Mass Balance	<ul style="list-style-type: none"> N/A

Table 15 summarizes the gaps in the current understanding of the mercury mass balance and provides a path forward to address mercury behavior in the Tank 39.

Table 15 — Gaps in Current Understanding and Recommendations for Mercury Behavior in Tank 39

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> Refine historical information as needed
Recommendations (Prioritized list)	<ul style="list-style-type: none"> Sample Tank 39 for Hg evaluation Investigate using less Hg in future canyon operations (SRNL has recently issued a flowsheet evaluation that increases the use of mercury) Work with H-Canyon to prioritize the recycling of recovered Hg from the HLW Evaporators or DWPF

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Sample of Tank 39 supernate for total mercury & speciation
- Evaluate sample for better understanding

5.8 Tank 50

Tank 50 currently receives waste from four sources: DSS from MCU, solids washing solution from 512-S, GPE stream 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). Transfers into Tank 50 must comply with the current Saltstone WAC limit for mercury of 325 mg/ L. Tank 50 transfers its contents to the Saltstone Production Facility (SPF). Table 16 provides a summary of Tank 50 Influent and chemistry.

Table 16 — Summary of Tank 50 Influent and Chemistry

	Summary
System Inputs	<ul style="list-style-type: none"> • Decontaminated Salt Solution (DSS) <ul style="list-style-type: none"> ○ Largest contributor by volume • H Canyon GPE • ETP • 512-S washing solution
System Outputs	<ul style="list-style-type: none"> • Saltstone Production Facility (SPF)
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • Tank 50 has been receiving transfers from <ul style="list-style-type: none"> ○ ETP since 2003 ○ H Canyon since 2005 <ul style="list-style-type: none"> ▪ GPE is the only stream currently allowed ○ MCU and 512-S since 2008 • WCHT transfers made into Tank 50 on 11/ 1/ 12, 2/ 11/ 14, 5/ 6/ 14, and 9/ 4/ 14 • Salt Batch (SB) transition dates (salt batch compiled in Tank 49) are as follows <ul style="list-style-type: none"> ○ SB1 – 4/ 25/ 08; SB2 – 1/ 22/ 09; SB3 – 5/ 28/ 10; SB4A – 7/ 23/ 11; SB4B – 9/ 20/ 11; SB5 – 8/ 31/ 12; SB6A – 1/ 25/ 13; SB6B – 3/ 2/ 13; SB6C – 3/ 22/ 13; SB6D – 4/ 17/ 13; SB7A – 4/ 4/ 14; SB7B – 7/ 3/ 14; SB8 – TBD • Tank 25 salt solution used for SB2-SB4; Tank 41 salt solution used for SB5-SB8; Tank 10 salt solution used for SB7; Tank 37 salt solution used for SB8 • 2H concentrate used in salt batches since SB3, recycle used in salt batches since SB2, Low Temperature Aluminum Dissolution (LTAD) leachate used in SB5, Sludge Batch 7A/ 7B decants went to Tank 4 which was used for SB6
Routine Samples	<ul style="list-style-type: none"> • Quarterly samples from Tank 50
Mercury data	<ul style="list-style-type: none"> • Tank 50 quarterly samples are analyzed for total mercury; sample is unfiltered and digested • Grout is made from quarterly Tank 50 samples; TCLP analysis is performed and mercury reported • Tank 50 mercury concentration and TCLP results show a trend up <ul style="list-style-type: none"> ○
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • 4th quarter 2014 TCLP value for mercury was higher than the assumed Land Disposal Restriction (LDR) treatment standard for mercury (0.025 mg/ L)⁶
Mercury Mass Balance	<ul style="list-style-type: none"> • Tank 50 material balance within the Waste Characterization System (WCS) <ul style="list-style-type: none"> ○ Transfers into and out of Tank 50 tracked ○ Rebaselined based on quarterly sample results ○ Mercury concentration assigned to each influent into Tank 50 ○ Material balance mercury concentration shows a trend up

⁶ Current assumption

Table 17 summarizes the gaps in the current understanding of the mercury mass balance and provides a path forward to address mercury behavior in Tank 50.

Table 17 — Tank 50 Gaps and Recommendations for Mercury Mass Balance

	Path Forward
Gaps in understanding or knowledge related to Mercury	<ul style="list-style-type: none"> • Species of mercury found in Tank 50 and influents to Tank 50 • Impacts of Next Generation Solvent (NGS) and oxalic acid cleaning at 512-S on mercury chemistry • Basis for mercury limit in SPF WAC is not adequate to protect Tank 50 from passing TCLP
Recommendations (Prioritized list)	<ul style="list-style-type: none"> • Evaluate results of mercury speciation analysis and SRNL variability studies and determine impact on SPF WAC <ul style="list-style-type: none"> ○ Revise WAC • Evaluate results of proposed Tank 21 TCLP test to determine potential impacts from processing SB8 • Obtain SB9 source tank samples to determine mercury concentration • Evaluate need to add TCLP testing to salt batch qualification

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Tank 50 4th Quarter 2014 and 1st and 2nd Quarter 2015 were sent to Eurofins for speciation analysis [6], [7]
- Tank 21 SB8 sample sent to Eurofins for speciation analysis [5]
- ETP WCHT sample sent to Eurofins for speciation analysis [4]
- Tank 21 SB8 sample used to make grout and TCLP analysis performed [8]
- Tank 21 SB8 sample was contacted with NGS solvent; sample from DSS generated from this test was sent to Eurofins for speciation analysis [7]
- Variability studies have been conducted
- Samples from SB9 source tanks obtained and sent to SRNL for analysis.

Mercury speciation analyses of the Salt Batch 8 sample are complete. Discussion is provided in Section 8.

5.9 DWPF Process Vessels and Sludge Batches

DWPF receives three radioactive waste streams from the Tank Farm for immobilization into a durable borosilicate glass. The three waste streams include a sludge slurry stream and two salt streams. Prior to 2008, DWPF only processed the sludge stream. The two salt streams feeds are products of the ARP and MCU. The ARP stream contains Monosodium Titanate (MST)-sludge solids and neutralized oxalic acid cleaning solution collected from the filtration steps performed at 512-S. The SE stream is the strip acid (dilute boric acid) containing Cs-137 from MCU. Based on the available volumes of the salt streams, DWPF has the option of either performing a sludge-only operation in which no salt streams are added or a coupled operation in which salt stream(s) are added. Options for coupled operation in DWPF include;

processing sludge and ARP together, or processing sludge and SE together, or processing sludge, ARP, and SE together. Depending on the mode of operation discussed above, the sludge is caustic boiled (~100°C) in the Sludge Receipt and Adjustment Tank (SRAT) during the addition of ARP. The product is cooled and sampled to determine the amount of acids to add to perform neutralization reactions, balance glass REDOX (Reduction and Oxidation), and reduce the mercury. The SRAT contents are then re-heated and acidified via the addition of 50 wt.% nitric acid followed by the addition of 90 wt.% formic acid at ~93°C. The SRAT contents are then heated to boiling to steam strip the reduced mercury to an endpoint of 0.45 wt.% (baseline – dried solids basis) in the SRAT product and, if available, the SE stream is added during this time. After processing is complete, the vessel is cooled and sampled, and then a portion of the sludge slurry is transferred to the Slurry Mix Evaporator (SME). The SME contents are heated to receive a dilute frit (glass forming oxides) stream generated from the canister decontamination process (each canister generates ~800 gallons of water), if available, followed by two to three frit slurry (1.5 wt.% formic acid solution) additions based on targeted waste loading (WL) (waste oxides per glass oxides). The product is concentrated by boiling (significant amount of stripping occurs during this process), cooled, and sampled for product control and compliance with Technical Safety Requirements (TSR). A portion of the SME product is then sent to the Melter Feed Tank (MFT). The MFT is the feed tank to the melter. No process additions are made to the MFT without a sample and hold for product quality and TSR compliance and the tank is maintained essentially at ~25°C. The qualified MFT product is then sent to the melter and vitrified at 1150°C. The molten glass from the melter is poured into stainless steel canisters that have a capacity of ~4000 pounds or 1800 Kilograms. As a result of the processing steps described above, several condensate streams (from SRAT, SME, and melter offgas) and by-product streams (laboratory waste, decontamination of equipment, filter dissolution, etc.) are produced. These condensate streams are sent to the RCT. Since some of the condensate streams are acidic, they are neutralized with caustic (include sodium nitrite) prior to being sent back to the Tank Farm via the Low Point Pump Pit Recycle Waste Tank (LPPP-RWT) for corrosion reasons.

In regards to mercury, DWPF was designed to reduce the mercury oxide contained in the sludge slurry to the elemental state via formic acid addition in the SRAT. The elemental mercury is then steam stripped from the sludge slurry during boiling steps of the SRAT. The vapor from the SRAT is passed through a condenser (cooled by process water) and the elemental mercury is then collected and subsequently removed from the LWS via the Mercury Water Wash Tank (MWWT) (110 gallon tank) through the Mercury Purification Cell (MPC).

The MPC primarily consists of two tanks and two scrubbers. Material from the Mercury Acid Wash (MAW) Tank (5 gallon capacity) is pumped through two scrubbers for cleaning with nitric acid and water before finally ending up in the Mercury Hold Tank (MHT). A pump is connected to the MHT to re-circulate mercury through the tank before ultimately filling up bottles for disposal from the facility.

Residual mercury, not removed via the steam stripping process, remains in the SRAT product which could:

- Fed to the melter (~1150°C), volatilized and collected in the Off Gas Condensate Tank (OGCT)
- Collect in the mercury sumps of the process vessels
- Deposit/ collect in the off gas systems downstream of the SRAT in the Chemical Process Cell (CPC) and Melt Cell (MC), and/ or

- Undergo chemical reactions due to the acidic conditions present in the condensate collection vessels (MWWT, Slurry Mix Evaporator Condensate Tank (SMECT), and OGCT) and sent back in recycle waste via the RCT to LPPP-RWT to the Tank Farm.

Table 18 provides a summary of mercury in the DWPF sludge batches.

A review of past mercury related events and corresponding corrective actions taken within DWPF, as shown in Figure 7, indicates that Mercury collection and recovery was successful during sludge-only operations between 1996 and 2008, however, with the start of salt processing in conjunction with HM sludge feeds, a shift in mercury behavior occurred. The shift in behavior resulted in less mercury collection in the MWWT than previously experienced and the mercury that was recovered was “dirty” mercury (i.e. sludge/mercury mix) which could not be successfully processed in the DWPF Mercury Purification Process (MPP). Comprehensive SRNL testing [9] was performed; however, an exact cause for the change in mercury behavior was not identified. Recent analysis following successful sampling of the SMECT, SRAT and MWWT sumps indicate that the mercury in the MWWT is still “dirty” (i.e. sludge containing) Mercury, but the mercury being recovered in the SMECT is relatively clean mercury, analogous to the mercury being collected and recovered from the MWWT during sludge-only operations. The SMECT mercury pump, however, has not functioned properly thus preventing mercury recover from this vessel. Following pump removal, the 2013 video inspection of the SMECT mercury pump revealed that the high pressure water lines for the pump had been severed; the cause has not been determined. With the change in mercury chemistry behavior, the failure of the SMECT mercury pump, and the plugging of the MPP with dirty mercury, all efforts to collect and recover mercury have been unsuccessful since the start of salt processing thru DWPF.

Table 18 — Mercury in DWPF Vessels and Sludge Batches

	Summary
System Inputs	<ul style="list-style-type: none"> • Qualified Sludge Slurry from Tank 40 • ARP stream (MST- Sludge solids/ neutralized oxalic acid) • MCU SE stream (dilute boric acid containing Cs-137)
System Outputs	<ul style="list-style-type: none"> • Stainless steel canisters containing radioactive glass • Neutralized condensate and by-product streams to the Tank Farm
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • Cold Run Demonstrations <ul style="list-style-type: none"> - Demonstrated functionality of Systems and Unit Operations including Hg Removal - Incoming sludge: 3.0 wt.% Hg total dried solids limit set for DWPF. - SRAT Product: 0.45wt% Hg total dried solids limit set for DWPF. • Radioactive Operations started in 3/6/1996 with Sludge Batch (SB) 1A. <ul style="list-style-type: none"> - Sludge Only Operations, feeding from Tank 51, Hg concentration 100 mg/ Kg - Sludge Batch 1A comprised of sludge from: Tanks 17, 18, 21, and 22. - Added dilute formic acid/ copper nitrate stream to substitute for PHA (old salt process), REDOX target used (F-N) - DWPF Batch # 20 thru #93 used DOW Corning 544 antifoam, produced 495cans@WL of ~28%, used frit 200 - R&D complete in 1997 to make flowsheet change to concentrated formic acid (90 wt.%) - Sludge Batch 1A ended 9/12/1998. • Sludge Batch 1B Start:10/11/1998, End: 11/ 11/ 2001 <ul style="list-style-type: none"> - Sludge Only Operations, feeding from Tank 51, Hg concentration 1410 mg/ Kg - Sludge Batch 1B comprised of sludge from: Heel of Sludge Batch 1A and Al dissolved Tank 42. - REDOX target used (F-3N) - DWPF Batch # 94 thru #208 used DOW Corning 544 antifoam, produced 726cans@WL of ~28%, used frit 200 - Hg recovered from the process and sent back to H-Canyon for re-use (~5.4 gallons) - Sludge was noted to be tacky adhering to surfaces in the DWPF Lab • Sludge Batch 2 Start:12/18/2001, End: 3/9/2004 <ul style="list-style-type: none"> - Sludge Only Operations, feeding from Tank 40, Hg concentration 496 mg/ Kg - Sludge Batch 2 comprised of sludge from: Tanks 8, 17, 18, 22 and heel of Tank 42. - REDOX target used (F-3N) - DWPF Batch # 209 thru #272 used IIT747 antifoam, produced 364 cans @ WL of ~28% to 32%, used frit 200 and 320 - Hg recovered from the process and sent back to Solid Waste (~6.2 gallons) - Processing issues with air entrainment and rheology - SME failure and melter replacement 10/18/2002 - "Mercury emissions from the Zone 1 exhaust stack are limited by an environmental permit to 0.0168 pph. Mercury monitoring downstream of the stack exhaust was originally required by DHEC, however they no longer require the monitoring because the limit is greater than the highest possible mercury content (assuming the mercury content is reduced to saturation at the respective condensers maximum air flow rates and exit temperatures). The monitors were abandoned in place in 2003." • Sludge Batch 3 Start:3/23/ 2004, End: 4/6/2007 <ul style="list-style-type: none"> - Sludge Only Operations, feeding from Tank 40, Hg concentration 300 mg/ Kg - Sludge Batch 3 comprised of sludge from: Heel of Sludge Batch 2, Tank 7 (Tank 18/ 19), Oxalate, and Coal thought to be high, but were not. F& H-Canyon receipts into

	Summary
	<p>SB3: Am/ Cm, Pu/ Gd, and Np</p> <ul style="list-style-type: none"> - Raised wash endpoints from 0.5 M Na in supernate to 1.0M in supernate - Implemented new REDOX correlation assigning coefficients to Nitrogen and Carbon sources. - DWPF Batch # 273 thru #402 used IIT747 antifoam, produced 726 cans @WL of 34%, used frit 418 and 202 • Sludge Batch 4 Start:5/30/2007, End: 11/26/2008 - Sludge Only and Coupled Operations, feeding from Tank 40, Hg concentration 1259 mg/ Kg - Sludge Batch 4 comprised of sludge from: large heel of Sludge Batch 3, and Tank 11 H-Canyon receipts into Sludge Batch: None - Coupled Operations started on 6/16/2008 with Salt Batch 1, Hg concentration is 9.75 mg/ L - DWPF Batch # 402B thru #467 used IIT747 antifoam, produced 314 cans @WL of 34%, used frit 418 and 510. - Al and Hg are higher in the sludge slurry. Mercury concentration forces longer cycle times and more frequent additions of antifoam - Catalytic hydrogen production in Shielded Cells Run high. Repeated run. • Sludge Batch 5 Start:12/1/2008, End: 6/3/2010 - Sludge Only and Coupled Operations, feeding from Tank 40, Hg concentration 2305 mg/ Kg - Sludge Batch 5 comprised of sludge from: heel of Sludge Batch 4, and Tank 11 Al dissolution, Tank 7. H-Canyon receipts into Sludge Batch 5: Pu/ Be/ Gd - Salt Batch 1, Hg concentration is 9.75 mg/ L. Salt Batch 2 started on 1/22/2009 Hg concentration is 10.2mg/ L. Salt Batch 3 started on 5/28/2010, Hg concentration is 34.2 mg/ L - DWPF Batch # 468 thru #530 used IIT747 antifoam, produced 323 cans @WL of 34%, used frit 418. - Longer cycle times due to Hg concentration and more frequent additions of antifoam - Catalytic hydrogen production observed in DWPF. pH of SRAT/ SME products very high. - Installed Isolok sampler on SRAT. Eliminated small sample stream going to the RCT. - Collected ~5 gallons of Hg in 2008. Sitting in a 5 gallon bucket in the purification cell. - Replaced the MWWT in January 2009. Prior to replacement, ~ 2 gallons of Hg was sent to the Hg purification cell and 4 gallons remain in the MWWT. - Mercury that was successfully removed from the tank (approximately 2 gallons) clogged up tanks in the purification cell. Likewise transfers made in July 2008 clogged up a tank in the purification cell. Also, noted floating material on the surface of tank. Appeared to be some sort of organic material, but not confirmed. - 2010 outage revealed mercury buildup in the SRAT condenser and SRAT scrubber - Hg probe in SMECT indicated 2", but prone to fluctuations. - SRAT Product limit raised to 0.60 wt.% Hg total dried solids • Sludge Batch 6 Start: 6/18/2010, End: 5/6/2011 - Sludge Only and Coupled Operations, feeding from Tank 40, Hg concentration 3592 mg/ Kg - Sludge Batch 6 comprised of sludge from: heel of Sludge Batch 5, and Tank 12 Al dissolution, Tank 4. H-Canyon receipts into Sludge Batch 6: Pu/ Gd - Salt Batch 3 started on 5/28/2010, Hg concentration is 34.2 mg/ L

	Summary
	<ul style="list-style-type: none"> - DWPF Batch # 531 thru #570 used IIT747 antifoam, produced 194 cans @WL of 36%, used frit 418. - Highest Hg concentration observed to date. Longer cycle times due to Hg concentration and more frequent additions of antifoam. pH of SRAT/ SME products very high. - SRAT Product limit raised to 0.80 wt.% Hg total dried solids - 8/2010 Reduced steam flow to SAS#1 from 370pph to 185pph. - Bubblers installed in the melter 9/2010. - PISA declared due to amount of antifoam going to the melter, due to long cycle time. Revised Calculation X-CLC-S-00164 to include carbon speciation. • Sludge Batch 7A Start:6/2/2011, End: 12/31/2011 - Sludge Only and Coupled Operations, feeding from Tank 40, Hg concentration 2241 mg/ Kg - Sludge Batch 7A comprised of sludge from: heel of Sludge Batch 6, and Tank 4, 7, 12. H-Canyon receipts into Sludge Batch 7A: Pu/ Gd - Salt Batch 3 started on 5/28/2010, Hg concentration is 34.2 mg/ L. Salt Batch 4A started on 7/23/2011, Hg concentration is 32.2mg/ L. Salt Batch 4B started on 9/20/2011, Hg concentration is 40.6 mg/ L. - DWPF Batch # 570B thru #608 used IIT747 antifoam, produced 198 cans @WL of 36%, used frit 418. - Study undertaken to understand antifoam performance, degradation products, and improved effectiveness. Report issued 9/2011 - 6 month batch - Coil fouling issues noted. • Sludge Batch 7B Start:1/09/2012, End: 5/07/2013 - Sludge Only and Coupled Operations, feeding from Tank 40, Hg concentration 1713 mg/ Kg - Sludge Batch 7B comprised of sludge from: heel of Sludge Batch 7A, and Tank 7, H-Canyon receipts into Sludge Batch 7B: none - Salt Batch 4 started on 7/23/2011, Hg concentration is 32.2mg/ L, Salt Batch 5 started on 8/31/2012, Hg concentration is 68.3 mg/ L, Salt Batch 6A started on 1/25/2013, Hg concentration is 65.8mg/ L, Salt Batch 6B started on 3/2/2013, Hg concentration is 59.4mg/ L, Salt Batch 6C started on 3/ 22/ 2013, Hg concentration is 54.8mg/ L, Salt Batch 6D started on 4/17/2013, Hg concentration is 51.5 mg/ L - DWPF Batch # 609 thru #670 used IIT747 antifoam, produced 310 cans @WL of 36%, used frit 418. - Carryover events noted in SME - PISA declared for sludge solids carryover in recycle on 11/8/2012. Compensatory action required pre-caustic adjustment of the RCT. - DWPF Review Team 2/2013. Noted issues with Hg recovery. • Sludge Batch 8 Start:5/7/2013, End: Still Processing - Sludge Only and Coupled Operations, feeding from Tank 40, Hg concentration 2192 mg/ Kg - Sludge Batch 8 comprised of sludge from: heel of Sludge Batch 7B, and Tank 7, Tank 12 (remaining), Tank 13. H-Canyon receipts into Sludge Batch 8: Pu LAP and DE-3013. - Salt Batch 6D started on 4/17/2013, Hg concentration is 51.5 mg/ L Salt Batch 7A started on 3/ 26/ 2014, Hg concentration is 68.1 mg/ L, Salt Batch 7B started on 5/27/2014 Hg concentration is 68.7 mg/ L

	Summary
	<ul style="list-style-type: none"> - DWPF Batch # 671 thru #735 to date used IIT747 antifoam, produced 314 cans to date @WL of 36%, used frit 803. - Sampling plan developed to sample SRAT sump, MWWT, and SMECT. - Hg samples retrieved from the SRAT sump, MWWT sump, and SMECT sump on 11/2013 and sent to SRNL for analysis. - Melter is currently unbubbled due to the PISA declared
Routine Samples	<p>Mercury sampling only:</p> <ul style="list-style-type: none"> • SRAT Receipt - Sampled for the first 10 batches of a new Sludge Batch. <i>Notes: Sampling typically suspended after WAPS sample obtained to confirm DWPF lab results. Then by engineering request only.</i> • SRAT Product – Upon engineering request. <i>Note: Recently suspended sampling efforts per batch for SB8.</i> • SMECT, SME, MFT, RCT, OGCT, BOGCT, DWTT – Upon engineering request. • PRFT and SEFT – no sampling. <i>Notes: Based on unit operations for the ARP stream, it was thought that majority of the Hg would stay with the salt solution. For SE; based on sampler configuration and limit of Isopar L in RCT, this tank is not sampled. Also, based on unit operations, it was thought that majority of the Hg would stay with the salt solution.</i>
Mercury data	<ul style="list-style-type: none"> • Mercury data has been collected in the past for SRAT receipt, SRAT product and periodically in the SME product where the mercury endpoint limit was increased in the SRAT (from 0.45 wt.% to 0.6 -0.8 wt.%). • Based on operational issues, samples were retrieved from the facility and sent to SRNL for analysis. Analysis by XRD has identified the following compounds: Calomel, $\text{Hg}_4(\text{OH})(\text{NO}_3)_3$, $\text{Hg}_{10}(\text{OH})_4(\text{NO}_3)_6$, and $\text{Hg}_3\text{CO}_3(\text{OH})\cdot 2\text{H}_2\text{O}$.
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • Low flows to the Gas Chromatographs (plugs of the HEME and HEPA filter). Causes downtime in the facility. • Plugs in the quencher and Steam Atomized Scrubbers for the Melter Off Gas System • Plugs in various Canyon ventilation jumpers • Carryover events from the SRAT and SME can deposit solids in the condensers and NH3 Scrubber and are a likely source for elemental Hg holdup. This leads to degraded performance of the equipment.
Mercury Mass Balance	<ul style="list-style-type: none"> • Based initial draft mercury mass balance on available DWPF data. It appears that 80% of the mercury received at DWPF is sent back to the Tank Farm. However the following assumption were made: <ul style="list-style-type: none"> - No mercury holdup in the ventilation systems. - Assumes 76 gallons of elemental mercury is present in the MWWT and SMECT based on Hg probes in the tanks. These are currently over ranged and there may be more mercury in the vessels than indicated. - Did not account for the mercury present in CPC Sump #1 - Only assumed elemental Hg release in the air emissions. This number may be low compared to the air emissions calculation (assumes other Hg species in addition to elemental mercury) for DWPF. The emissions are directly correlated to actual canisters produced. • Recent sample data pulled for Batch 735 from the SMECT, OGCT, and RCT indicate that approximately 57% is being retained in DWPF and 43% is being sent back to the Tank Farm. More data is needed to confirm this.

As a part of the mercury overview performed for DWPF, the current status of the mercury sumps for the MWWT and SMECT indicate that these vessels contain significant quantities of mercury. The MWWT (110 gallon capacity) contains approximately 6 gallons and the SMECT (11,000 gallons capacity) contains approximately 70 gallons. The accumulation of mercury in these sumps is due to the inability to retrieve and send mercury to the mercury purification cell. The mercury purification cell has not been operated since 2009, due to difficulties and frequent plugs of the system. Based on the process chemistry, the mercury in the incoming streams continues to be reduced and steam stripped in the process. This is leading to accumulation in the MWWT and SMECT and higher concentrations of mercury being sent in the recycle stream back to the Tank Farm. This quantity of mercury has the potential to influence the chemistry of the condensate contained in the MWWT and SMECT and thus may impact the recycle stream sent back to the Tank Farm. Based on these observations, Table 19 provides the “gaps in knowledge and recommendations”.

Table 19 — Gaps and Recommendations for Mercury Data in DWPF

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> • Determine the impact of antifoam and solvent degradation products on Hg speciation for the DWPF recycle stream. • Determine why mercury is present in the SE stream from MCU • More data should be collected to confirm the Hg behavior of the SMECT, RCT, and OCGT results of Batch 735. SRAT and SME product data should also be obtained • Sample and analyze the solids plugging the vessels in the Mercury Purification Cell • Updating/ confirming the Hg chemistry/ assumptions made in the Basic Data Report
Recommendations (Prioritized list)	<ul style="list-style-type: none"> • Restore operation of the Mercury Purification Cell • Spare Hg pumps should be made available • Remove mercury from the MWWT/ SMECT to reduce the amount of mercury sent back in the recycle stream • Due to the potential introduction of Hg from the PRFT and SEFT, the SRAT product analysis should be resumed to ensure Hg endpoint is achieved • The PRFT sample analyzed by SRNL indicated mercury was present. Analysis should be performed for the PRFT to determine if Hg is present • Clean/ replace the scrubber baskets to reduce the high delta P observed for SME and RCT/ MFT scrubber • Flushing/ cleaning SRAT/ SME condensers

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Samples of the RCT and OGCT taken during Batch 735 are being sent to Eurofins Laboratory for mercury speciation. [10]
- Sampling plan has been developed for Batch 736 to include samples for performing a material balance around the SRAT and SME operations and speciation by Eurofins Laboratory. [11]

- Samples of the RCT and OGCT were taken during SRAT Batch 735 and were analyzed at DWPF Laboratory. Selected RCT and OGCT samples were also sent to Eurofins for mercury speciation analyses. For RCT and OGCT samples, Total Hg and soluble mercury analyzed by Eurofins were within 15 – 20 % of the DWPF Laboratory analyses, as shown in Table 20. Based on the SRAT Batch 735 analyses, the mercury mass balance is shown in Table 21.

Table 20 — Total and Soluble Mercury Analyses of SMECT, RCT, and OGCT Samples (Batch #735)

Sample Identification, DWPF Sample ID	Replicate #1 (PPM or mg/Kg)*	Replicate #2 (PPM or mg/Kg)*	Average (PPM or mg/Kg)*	Standard Deviation (PPM or mg/Kg)*
SMECT Samples – SRAT Only Condensate				
Prior to Start of SRAT Cycle – Baseline - 200020168	456	445	450	±8
Nitric Acid Addition - 200020175	645	757	701	±80
Formic Acid Addition - 200020179	916	836	876	±57
Concentration Mode - 200020181	975	1026	1000	±36
Strip Effluent Feed Tank (SEFT) Addition - 200020187	462	437	450	±18
End of SRAT cycle - 200020190	344	308	326	±25
SMECT Samples – SME Only Condensate				
After Second Decon Canister - 200020200	289	280	285	±6.7
After Last Decon Canister - 200020207	144	165	154	±15
After first frit drop - 200020209	145	156	151	±7.6
End of SME cycle - 200020211	138	125	131	±8.7
RCT Samples – Total Mercury				
Batch 4589- SMECT Condensate from the SRAT - 200020178	274	266	270	±5.5
Batch 4590- SMECT Condensate from the SRAT - 200020185	408.9	329.6	369	±56
Batch 4591- SMECT Condensate from the SME - 200020203	271	222	246	±35
Batch 4592- SMECT Condensate from the SME - 200020208	181	137	159	±31
Batch 4593- SMECT Condensate from the SME - 200020225	138	136	137	±1.0

Sample Identification, DWPF Sample ID	Replicate #1 (PPM or mg/Kg)*	Replicate #2 (PPM or mg/Kg)*	Average (PPM or mg/Kg)*	Standard Deviation (PPM or mg/Kg)*
RCT Samples – Soluble Mercury				
Batch 4589- SMECT Condensate from the SRAT - 200020178	33	35	34	±1.4
Batch 4590- SMECT Condensate from the SRAT - 200020185	94	94	94	±0
Batch 4591- SMECT Condensate from the SME – 200020203	74	54	64	±14
Batch 4592- SMECT Condensate from the SME - 200020208	58	60	59	±1.4
Batch 4593- SMECT Condensate from the SME - 200020225	28	7	17.5	±15
OGCT Samples – Total Mercury				
Melter Off Gas Condensate from Batch 735 - Aligns with RCT Batch 4594 - 200020236	188	187	188	±0.71
OGCT Samples – Soluble Mercury				
Melter Off Gas Condensate from Batch 735 - Aligns with RCT Batch 4594 - 200020236	103	104	104	±0.71

Table 21 — Distribution of Mercury in SRAT Batch 735

Percent Distribution of Hg in SRAT Batch 735	
% Hg Retention in DWPF	56.9%
% Total Hg sent back to Tank Farm based on RCT sample Analyses	43.1%
% Soluble Hg sent back to Tank Farm based on RCT analyses	22.7%

5.10 2H/ 3H/ 2F Evaporators

The evaporator system reduces the volume of high level waste so that more waste can be easily stored. Feed is pumped to the evaporator pot from the feed tank and heated. Relatively decontaminated water, overhead vapors, is boiled off. The overhead vapor passes through a condenser where it condenses into liquid called overheads. The overheads flow from the condenser to the Mercury Removal Tank (MRT) and elemental mercury settles to the bottom of the tank. The remaining overheads are routed to the two overhead tanks. At this point, the overheads are either pumped to the Effluent Treatment Project (ETP) or returned to the waste tanks for reprocessing.

The evaporator concentrates the wastes and is gravity drained from the evaporator into the drop tank. Condensable gases and steam that have bypassed the overheads system are diverted to a designated vent tank.

242-16H (2H) Evaporator

The 2H Evaporator directly supports the DWPF. Historically, Tank 22 is the DWPF Recycle Receipt Tank; waste from Tank 22 is then transferred to the Evaporator Feed and Vent Tank, Tank 43. Tank 38 is the Evaporator Concentrate Receipt Tank. Periodically, Tank 38 has undergone partial de-inventories as concentrated material is used to supplement salt batch compositions.

242-25(3H) Evaporator

The 3H Evaporator processes high level liquid waste from H-Canyon and F- and H-Tank Farms. In addition to this material, Sludge Batch decants also get processed. The Evaporator Feed Tank is Tank 32. There are two Evaporator Concentrate Receipt Tanks, Tanks 30 and 37. Presently, Tank 30 is the Concentrate Receipt Tank because Tank 37 has a high level of salt and is currently undergoing salt dissolution. Periodically, Tank 37 goes through partial de-inventories via salt dissolution campaigns. The dissolved salt solution from this particular campaign will be transferred to either Tanks 35 or 23 and later used as a component of the next salt batch recipe. The Evaporator Vent Tank is Tank 29.

242-16F (2F) Evaporator

This system is currently shutdown. When it was operational, Evaporator 2F processed high level liquid waste from F-Tank Farm. The Evaporator Feed Tank was Tank 26. The Evaporator Concentrate Receipt Tank was Tank 25. The Evaporator Vent Tank was Tank 44. Table 22 provides a summary of Evaporator Systems.

Table 22 — Summary of Mercury in Evaporator Systems

Evaporators	Summary		
	242-16H(2H)	242-25(3H)	242-16F(2F)
System Inputs	<ul style="list-style-type: none"> DWPF Recycle 	<ul style="list-style-type: none"> High level liquid waste from H-Canyon and F- and H- Tank Farms Sludge Batch decants 	<ul style="list-style-type: none"> When operating, high level waste from F-Tank Farm.
System Outputs	<ul style="list-style-type: none"> MRT to Overheads to ETP Salt dissolution campaigns and deliquoring 	<ul style="list-style-type: none"> MRT to Overheads to ETP Salt dissolution campaigns and deliquoring 	<ul style="list-style-type: none"> MRT to Overheads to ETP Salt dissolution campaigns and deliquoring

Evaporators	Summary		
	242-16H(2H)	242-25(3H)	242-16F(2F)
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • Began operating in 1982 • Antifoam was added during the startup of the evaporator • Dimethyl mercury (DMHg) was discovered in 2001 (similar quantities as 3H) • Antifoam stopped being used in the early 2000s 	<ul style="list-style-type: none"> • Began operating in 2000 • Antifoam was added during the startup of the evaporator • DMHg was discovered in 2001 (highest quantities of the 3 evaporators) • Antifoam stopped being used in the early 2000s • Discovery of Tank 37 backflush valve degradation in August 2014 • Entered PISA on January 7, 2015 because mercury removed from the MRT exceeded limit 	<ul style="list-style-type: none"> • Began operating in 1980 • Antifoam was added during the startup of the evaporator • DMHg was discovered in 2001 (least amount) • Antifoam stopped being used in the early 2000's • Shutdown in 2013
Routine Samples	<ul style="list-style-type: none"> • Tank 22 has CC⁷ (Corrosion Control) sample analysis performed every 180 days • Tanks 43 and 38 have CC sample analysis performed every 90 days and ECP⁸ (Enrichment Control Program) every 180 days 	<ul style="list-style-type: none"> • Tanks 32, 30 and 37 have CC sample analysis performed every 90 days and EFQ⁹ (Evaporator Feed Qualification) every 180 days • Tank 29 has CC analysis performed every 90 days 	<ul style="list-style-type: none"> • When operating, Tank 26 had CC sample analysis performed every 90 days and EFQ every 180 days. • When operating, Tank 25 had CC sample analysis performed every 180 days and EFQ every 180 days. • Tank 44 had CC analysis performed every 1460 days

⁷ Measurements don't include mercury. CC measures specific gravity, nitrite, nitrate, hydroxide and gross gamma

⁸ Measurements don't include mercury. ECP measures specific gravity, plutonium-238, plutonium-239, plutonium-241, uranium-233, uranium-234, uranium-235, uranium-236, uranium-238 and technetium-99.

⁹ Measurements don't include mercury. EFQ measures specific gravity, hydroxide, oxalate, carbonate, phosphate, sulfate, aluminum, sodium, silicon.

Evaporators	Summary		
	242-16H(2H)	242-25(3H)	242-16F(2F)
Mercury data	<ul style="list-style-type: none"> • 2014 digested and undigested mercury concentrations for Tanks 22, 43 and 38 	<ul style="list-style-type: none"> • There is no undigested or digested data available from the evaporator tanks. • 2014 digested mercury concentration from Tank 51 (which was a source of fresh feed to 3H in 2014) 	<ul style="list-style-type: none"> • There is no digested data available for the tanks in this evaporator system.
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • After the discovery of DMHg, studies were performed. The results revealed that components used in the antifoam showed a high propensity for creating DMHg. 	<ul style="list-style-type: none"> • After the discovery of DMHg, studies were performed. The results revealed that components used in the antifoam showed a high propensity for creating DMHg • Entered PISA on January 7, 2015 because mercury removed from the MRT exceeded limit • Potentially the Tank 37 backflush valve 	<ul style="list-style-type: none"> • After the discovery of DMHg, studies were performed. The results revealed that components used in the antifoam showed a high propensity for creating DMHg.
Mercury Mass Balance	<ul style="list-style-type: none"> • Using the 2014 digested mercury data, an approximate mass balance was calculated. • Material balance showed that increase in the mercury concentration is a natural product of the evaporation process. No unique change in feed caused the increase. 	<ul style="list-style-type: none"> • A mercury mass balance was not performed. There is no digested data available for the tanks in this evaporator system. • Tank 51 high mercury concentration (due to Tank 22 sludge removal campaign) is the suspected cause of increased MRT drainage 	<ul style="list-style-type: none"> • A mercury mass balance was not performed. There is no digested data available for the tanks in this evaporator system.

In all associated Evaporator Tanks, there are gaps of information that include no salt core and recent sludge sample data. There was more information available from the tanks connected to Evaporator 2H that allowed an approximate mercury mass balance to be completed. There is no digested and/ or speciation mercury data presently available for Evaporators 3H and 2F. An approximate mercury material mass balance calculation could not be done. In addition to that data, the MRT and overheads data had some gaps. For the MRT, Evaporator 3H was missing data from October 2010 through 2012; and from Evaporator 2H, MRT data was missing prior to 2001. Lastly, Evaporator 2F was missing volume fed to the overheads prior to FY08.

Mass balance using CY 2014 operations data for 16H Evaporator System indicates only 2% Hg removal. Approximately 2742 kg Hg was fed through 16H Evaporator, 2472 kg of Hg recycled back to the feed tank, 33 kg was collected in the MRT, and 22 Kg went to overhead tank. Figure 8 shows Hg concentration in mg/L as a function of time. Similarly mass balance for 25H Evaporator System using CY 2014 indicated approximately 2% Hg removal.

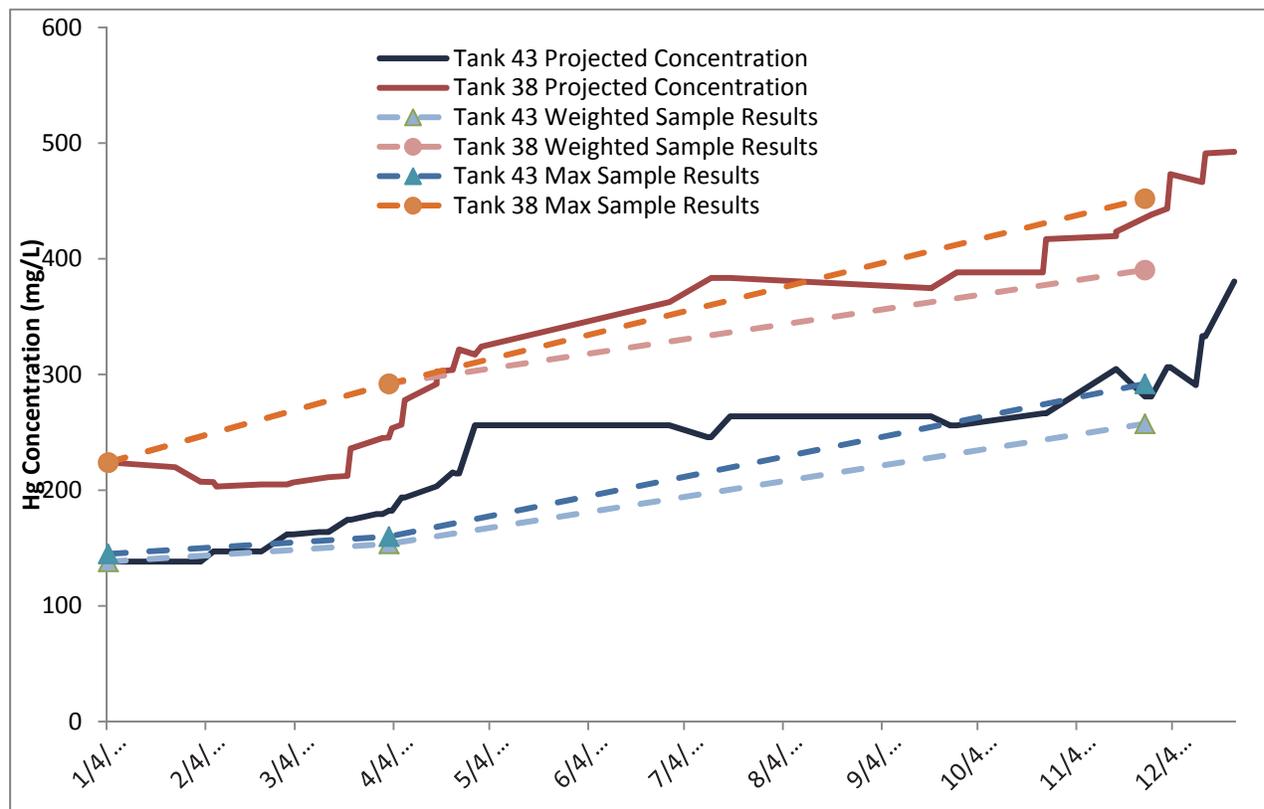


Figure 8 — Mercury Concentration in 16H Evaporator as a Function of Time

Table 23 provides gaps and recommendations for the evaporator systems.

Table 23 — Gaps and Recommendations for the Evaporator Systems

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> • Lack of salt core samples for all associated evaporator tanks with saltcake • Lack of recent sludge sample data for all associated evaporator tanks with sludge • Understanding how mercury speciation changes within the evaporator systems • Any mercury data for the 3H and 2F Evaporator Systems • Missing MRT data for Evaporators 3H and 2F • No overheads volume data prior to FY08

	Path Forward
Recommendations (Prioritized list)	<ul style="list-style-type: none"> • Perform speciation analysis on tanks that are a part of the 2H Evaporator System • Perform a speciation/ digested analysis on tanks that are a part of the 3H and 2F Evaporator System • Locate the missing MRT data for Evaporators 3H and 2F • Pull salt core samples for analysis for all associated evaporator tanks • Obtain recent sludge sample data for all associated evaporator tanks • Locate overhead data for Evaporator 2F prior to FY08

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Samples were pulled from Tanks 43 and 38 for CC/ECP (Corrosion Control/ Enrichment Control Program) analysis (surface and variable depth) and from each of the evaporator overheads tanks for this system for mercury speciation.
- Samples will be pulled from Tanks 32, 30 and 37 for CC/EFQ (Corrosion Control Program/Evaporator Feed Qualification Program) analysis. Analyses will include mercury speciation.

5.11 Current Sludge/ Salt/ Supernate Inventory

Table 24 provides a brief overview of the system planning process, a discussion of the mercury information used in the plan and a comparison to other sources, and estimates of future sludge batch mercury.

There are various estimates of the mercury in the tank, each of which has a different basis. In 2005, WCS had an estimate of about 68,351 kg of mercury added to the tank farm from the separations processes (canyons). This estimate was based on algorithms correlating the volume of fresh waste received from separations to a concentration of mercury for various waste types. This estimate was adjusted using various values of the 'dial-up' factors to a 2012 estimate of amounts received of about 90,000 kg in sludge.

In 2002, Joe Odum provided an estimate of 80,000 kg of mercury sent to the tank farm without explanation (ESH-FSS-2002-00102). These numbers probably were not corrected for mercury sent to DWPF in sludge batches or mercury returned to the tank farm (in both sludge and supernate) via DWPF recycle. Odum provided an estimate of future mercury from separations for FY03 thru FY06 of 20,000 kg. This estimate proved to be very high due to significant reductions in actual separations processing over those years.

The remaining amount of mercury in the sludge per WCS as of April 2015 was 53,365 kg in sludge. This number likely underestimates the amount of mercury returned to the tank farm (in sludge) from DWPF via recycle. Liquid Waste System Plan (Rev 20) calculations indicate about 59,000 kg of mercury to go for sludge batches 10 and onward. In addition to an allowance for future canyon processing, this number does contain some adjustments for Hg in DWPF recycle, but likely underestimates the actual amount returned. The amount of mercury that DWPF will have to process exceeds the inventory of mercury in the tank farm because some amount of the mercury sent to DWPF is returned and processed again.

DWPF has recently estimated receipt of about 30,000 kg of mercury to date [12]. Overall mercury mass balance will be reconciled as more data is collected and analyzed.

Table 24 — Summary of Mercury in the LW Planning Process

	Summary
System Inputs	<ul style="list-style-type: none"> • ‘Recommended Values Adjusted in 2012’ provides the inputs for mercury in the insoluble solids (sludge) is used in sludge batch planning.
System Outputs	<ul style="list-style-type: none"> • Mercuric Oxide (HgO) in future sludge batches (10 thru 22) in LWSP Revision 20, Case 1 (base case) ranges from 2 to 4 wt%. These estimates will likely be too low and will increase when new values for mercury returned to the tank farm from DWPF (in sludge) are created.
Process Timeline and History of Key Events	<ul style="list-style-type: none"> • DWPF material estimate created in 2005 using dial up factors with ‘recommended values’ used to project composition of sludge in tanks for sludge batch calculations. • ‘Recommended values adjusted in 2012’ provides an updated estimate which include reductions due to the lower mass actually found in Tank 13H.
Routine Samples	<ul style="list-style-type: none"> • N/ A
Mercury data	<p>WCS April 2015 (60,862 kg) Supernate 7,497 kg Hg Sludge 53,365 kg Hg Salt 0 kg Hg</p> <p>Approximate inventory per Joe Odum memo (ESS-FSS-2002-00102) was 80,000 kg Hg in 2002 with additions projected from 2003 through 2006 of 20,412 kg Hg</p> <p>Original DWPF Estimate 68,351 kg HgO 2005 Recommended Values 107, 428 kg HgO based on Sludge Characterization Model using Dial-up Factors (CBU-PIT-2006-00058, March 2006) 2012 Recommended Values 92,632 kg HgO. Revised estimate based on Tank 13 Bulk Waste Removal data.</p>
Process or Equipment problems related to Mercury	<ul style="list-style-type: none"> • N/ A
Mercury Mass Balance	<ul style="list-style-type: none"> • Update as additional data becomes available

Table 25 summarizes the gaps in the current information needed for system planning and recommendations for future work.

Table 25 — Gaps and Recommendations to LW Planning process

	Path Forward
Gaps in understanding or Knowledge related to Mercury	<ul style="list-style-type: none"> • Amount of mercury dispositioned as ‘sent to DWPF’ which has actually been returned to the tank farm and must be added to future batches. • Additional sampling of tank farm sludge for future batches will be performed during waste removal and sludge batch qualification.
Recommendations (Prioritized list)	<ul style="list-style-type: none"> • Continue sampling program to determine mercury in dissolved salt solution and evaporator concentrate. • Update DWPF material estimate by taking a sample of the heel in Tank 40 in addition to the sample of the heel combined with the

	Path Forward
	Tank 51 prepared sludge batch. <ul style="list-style-type: none"> • Develop an actual database (not an Excel spreadsheet) of tank data and include data qualifiers. • Develop a standardized protocol for entering removals and additions into Sludge 1.5.

What has been done so far to resolve “gaps in understanding” and Recommendations:

- Development of detailed salt and sludge batch makeup completed.
- Update mercury mass balance as additional data becomes available.

5.12 Mercury Analytical Methods used at SRS

There are four Analytical Laboratories at SRS Performing Hg Analyses:

- Cold Vapor Atomic Absorption (CVAA)
- Inductively Coupled Plasma (ICP) – Atomic Emission Spectroscopy (AES)
- ICP – Mass Spectroscopy (MS)
- Mercury Analysis of Sorbent Traps

Table 26 lists the mercury analyses methods currently by various laboratories at the SRS site.

Table 26 — List of Laboratories at SRS currently Analyzing Mercury Samples and Methods

Laboratory	CVAA	ICP-AES	ICP-MS	Sorbent Traps
SRNL Analytical	X	X	X	
DWPF Lab	X			
ETP Lab	X			
F/H Lab		X	X	X

CVAA is used to analyze the total mercury in the sample. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and the wavelength of light beam is characteristic for the metal being analyzed (i.e. Hg = 253.7 nm). This method is primarily used for metals in aqueous solutions at low concentrations (mg/ L to mg/ L). All analytical laboratories at SRS follow the EPA method for mercury CVAA analysis; however, at times the initial acid digestion will be an *aqua regia* rather than the concentrated sulfuric and nitric acid.

ICP-AES is the technique where the emission of light, from atoms and ions, is measured and related to the number of atoms present. The ICP source (plasma ~ 7000 K) provides the atomization and excitation energy to the sample. This method provides total mercury information only (all forms of mercury are converted to an atomic/ ionic mercury in the plasma). Also, this method is not extremely salt tolerant (must be < 1000 mg/ L Na as injected sample), which driving need to perform large dilutions on salty samples. Typically, this method is used for samples with larger Hg concentrations or low sodium content. Also, mercury carryover in the spray chamber is significant and often requires multiple blank runs to clean and certify cleanliness which lengthens run times.

ICP-MS is the method where ions are separated by their mass to charge ratio and the ICP source provides the excitation energy to the sample, ionizing the atoms. This method provides total mercury information only (all forms of mercury are converted to an atomic/ ionic mercury in the plasma conditions). Since mercury has six stable isotopes >1% relative abundance, it gives a very distinctive mass spectrum. This method is typically used for samples with lower Hg concentrations, but higher concentrations can be diluted to be within calibration ranges. Samples are diluted to keep mercury concentrations in the instrument low to minimize carryover in the spray chamber. For both ICP methods, the digestion method is typically specified by the customer.

Mercury Analysis of Sorbent Traps could be used by F/ H lab, but the equipment and method are in “idle” status (method has not been used recently). This method is for air samples only. The air samples are taken using Sorbent Traps and an air sampling pump. The Sorbent Traps contain different substrates that capture the different forms of mercury, and retain them as elemental mercury. Potassium Chloride (KCl) and Activated Carbon, retain oxidized and organic species, while Iodated Activated Carbon, retains elemental mercury. Substrates analyzed using a Thermal Desorption technique, coupled with Zeeman corrected Atomic Absorption (AA) Spectroscopy.

Potential sources of differences in results between the laboratories are:

Calibration range

- more sensitive methods are more prone to elevated analytical blanks
- carryover is persistent with mercury requiring vigilant attention
- Sample preparation
 - AA preparation method
- Dependent on total oxidation and successive total reduction for analyte recovery are sodium tolerant
- ICP sample preparation method
 - simple dilutions
 - sodium limited
 - particulates are not tolerated (they clog the nebulizer)
- Filtration will remove mercury containing solids
 - Filtration step specified by the customer

6 Open Items

Table 27 provides a list of open items/ questions raised during the Team Presentations and provides a current status of each open item.

Table 27 — List of Open Items Requiring Resolution

No	Action Item Description	Responsibility	Resolution Remarks
ETP			
1	Investigate and document Analytical Methods used at the ETP for Hg analysis	Peters/ Shah	Completed - Covered in presentation Hg Analytical Methods used at SRS
2	How many ETP transfers were made from WCHT to Tank 50 between Dec-14 and March-15	Harrison	None.

No	Action Item Description	Responsibility	Resolution Remarks
3	Evaluate need to pull the sample from WCHT for Hg Speciation and data comparison	Shah/ Harrison	WCHT sample was pulled on 3/16/15 and sent to SRNL. It will be shipped to Eurofins Lab in last week of March. Projected Hg speciation analysis in end of April.
3a	What to analyze for Organo Hg? ETP Timeline, History Mercury Column Change out, carbon beds	Wilmarth	Total Hg, Ionic Hg, Methyl Hg, elemental Hg
4	Investigate High Hg peak in 2006	Harrison	Two off normal influents, R-basin trucked transfers and an H-Canyon upset
5	What type of Hg, mercury columns remove?	Peters/ Harrison	In progress
6	Estimate mass of Hg from resin removed in the past	Petras/ Harrison	Data is not available
7	Do you measure Hg in Treated Water Storage Tanks?	Harrison	Practically none
8	Understand resin regeneration Solution Stream	Wilmarth	In progress
9	Document equipment problems related due to Hg-	Harrison	Completed - No Hg related equipment problems
10	Investigate and document WCT peak in Hg between 2011 and 2013	Harrison	Completed
11	Interpret CME (carbon mid data) data	Harrison	In Progress
12	Revise ETP Block diagram to show pH changes and Hg flow in the process	Harrison	In Progress
13	Why there is 86% mercury removal in the ETP process? Reexamine the data presented and investigate any process upsets	Harrison	In Progress
DWPF Sampling Needs			
1	Pull the SRAT sample during the caustic boiling step of the SRAT cycle while PRFT material is added.	Fellinger	Waiting for DWPF to start-up
2	Several samples would be pulled and set off to the side of for shipment to SRNL and then to Eurofins for Hg speciation ¹⁰ .	Fellinger/ Shah	Completed
3	Pull the SMECT samples during different steps of the SRAT Cycle (SRAT Batch # 735)	Mahannah / Buddy/ Fellinger	Completed
4	Pull the SMECT samples during different steps of the SME Cycle (SRAT Batch # 735)	Mahannah / Buddy/ Fellinger	Completed

¹⁰ The shipment of samples to SRNL and /or Eurofins Lab will be dependent on the results obtained from Tank 22

No	Action Item Description	Responsibility	Resolution Remarks
5	Pull the OGCT baseline and prior to transfer to RCT samples (SRAT Batch # 735)	Mahannah / Buddy/ Fellingner	Completed
6	Pull RCT baseline and prior to Tank Farm transfer samples (SRAT Batch # 735)	Mahannah / Buddy/ Fellingner	Completed
7	Document the DWPF Lab results of the analyzed samples of the vessels listed in action item# 3,4,5 and 6 (SRAT Batch # 735)	Fellingner	Completed (SRR-WSE-2015-00028, Analytical Results for the condensate samples for SRAT Batch 735)
8	Determine what samples needs to be sent to Eurofins and SRNL for Hg Speciation(SRAT Batch # 735)	Fellingner/ Shah	Completed (SRR-WSE-2015-00028)
Sludge and Salt Batch Make-up Transfer History			
1	Complete the time- line of hand written chart on Visio/ Power Point software	Chew/ Gillam	Completed
2	Come up with the plan to incorporate sub-component with the time line	Chew/ Meraw	Completed- Plan has been developed
3	Receive the data from all presenters to input into the plan	Chew/ Meraw	In Progress
4	Input the data as per the developed plan and link it to time line	Chew/ Meraw	In progress
5	Determine fraction of DWPF recycle in each Salt Batch	Gillam	Completed
Tank 22, Tank 41 and RCT			
1	Investigate the need to sample 2H ECP sample for Total Hg/ soluble?	Sherburne/ Bridges	Waiting for the Tank 38 and 43 speciation results
2	Investigate the need to sample 3H EFQ sample for Total/ Soluble Hg?	Sherburne/ Bridges	Waiting for the Tank 38 and 43 Speciation results to decide
3	Obtain Tank 41 sample for Total and Soluble Hg data (part of Salt Batch 9 make-up)	Rios-Armstrong/ Shah	Completed
4	Obtain Tank 13 sample for Total and Soluble Hg data (may be a recommendation from 2H/ 3H/ 2F Presentation)	Rios-Armstrong/ Shah	Completed
5	Obtain Tank 8 Sample for Total and Soluble Hg (part of Salt Batch 9 make-up). Find out any samples pulled in the past have Hg data	Rios-Armstrong/ Shah	Completed
6	Investigate the feasibility of sampling RCT for TOC? Formate?	Fellingner	RCT: Formate and TOC are analyzed for on every 10th batch (batches ending in 0s)
7	Obtain RCT soluble Mercury data and Track soluble and Total Hg in the RCT (Long Term)	Fellingner	Will be added in the Sample Schedule
8	Obtain Tank 22 sample for Soluble Hg Data	Shah/ Bannochie	Samples were pulled on 3/ 23 and received by SRNL

No	Action Item Description	Responsibility	Resolution Remarks
9	Obtain TK 22 sample for Hg Speciation	Shah/ Bannochie	Samples were pulled on 3/ 23 and received by SRNL
10	Include samples from source tanks for soluble and total Hg that is used for salt batch make up.	Rios-Armstrong/ Shah	Completed
Salt Batches Make-up and Tank 49			
1	Check TOC analytical data of Salt Batch # 3	Shafer	Based on blend Calculation
2	Check Phenol analytical data of Salt Batch # 3	Shafer	Based on blend Calculation
3	Compare Tank 50 TCLP Hg data vs Salt Batch Hg	Meraw/ Lee	Charts were emailed to all meeting attendees on 3/ 25/ 15
4	Document a narrative of Tank 50 TCLP Hg data vs Salt Batches Hg	Meraw/ Lee	Covered in Tank 50 Presentation
5	What % of DWPF recycle is in each sludge/ salt Batches? Show the data on pie chart batches Vs volumes	Gillam/ Shafer	Completed
241-96H, MCU, MCU Cleaning			
1	Look into using membrane grade Caustic for the wash (impurities with electrolysis i.e. HgCl process a main concern)	Smith	MCU can use membrane grade caustic. Procurement is set up such that changing to 0.025 M NaOH (after closing with SRNL/ORNL) wash will be membrane grade. Change is expected to occur within the next 6 months.
2	SRNL to investigate any possibility of Hg in Boric Acid manufacturing	Peters	Univar Vendor suggests no mercury in Boric Acid
3	MCU is lacking Hg Data- Analyze SEHT, DSSHT, and SHT data and evaluate path forward	Smith	Completed- Issued a memo (SRR-LWE-2015-00035) for the strategy to pull SSFT, SHT, SEHT and DSSHT samples for Salt Batch 7 @MCU
4	Quantify solvent degradation losses	Peters/ Smith	SRNL is working this actively for TiDG. All other compounds have not seen significant degradation losses.
5	Perform more thorough literary review of MCU process chemical interactions with various forms of Hg	Garrison/Peters	In Progress
H-Canyon to Tank 39 or 50 or 51			
1	Is antifoam added to GPE bottoms?	Gilbreath/ Eubanks	They have it in the past. Not used routinely
2	Evaluate a need to analyze SRE stream for Total Hg, soluble Hg, and Hg speciation.	Gilbreath/ Eubanks	Being Investigated
3	Evaluate a need to analyze GPE Bottoms for Hg speciation.	Gilbreath/ Eubanks	Total Hg was <0.36 mg/ L so it was decided not to analyze for Hg Speciation
4	Analyze Tank 39 supernate for soluble Hg and Hg speciation	Gilbreath/ Eubanks	Samples have been pulled- Analysis is in progress

No	Action Item Description	Responsibility	Resolution Remarks
5	Refine Historical Information as needed	Gilbreath/ Eubanks	In progress
6	Investigate why SRE batch 3, 4, 5 and 6 flowsheet now require more mercury	Gilbreath/ Eubanks	Completed (SRNL-STI-2014-00228 Modified SRE Dissolution Flowsheet)
7	Prepare a bar chart for Canyon Hg discharge over time	Gilbreath/ Eubanks	Completed
Tank 50			
1	Review Tom Britt's calculation that provided the basis to remove MMHg and DMHg Limits in Saltstone WAC	Britt/ Rios- Armstrong	In progress
2	When salt batch make up started using Tank 41?	Rios-Armstrong	Completed
3	When Tank 41 started receiving DWPF recycle?	Rios-Armstrong	Completed
4	Standardize Hg analytical methods and what to analyze for DWPF, RCT, Tank 22, Tank 50, WCHT, DSSHT etc. ...for total and soluble Hg	Mercury Program Team	Will be covered in Phase II Recommendation
5	Review Salt Batch 1 SRNL analytical data	Rios-Armstrong	In progress
6	Evaluate a need to determine Hg gradient in TK 50	Rios-Armstrong/ Clark	In Progress
7	Evaluate results of Hg speciation analysis and SRNL variability studies and determine impact on Saltstone WAC	Rios-Armstrong/ Clark	Completed
8	Evaluate results of Tank 21 TCLP test to determine potential impacts from processing Salt Batch 8	Shah/ Rios- Armstrong	Completed
9	Obtain Salt Batch 9 source tank samples to determine Hg concentration	Shah/Rios- Armstrong	Completed
	a. Tank 23 samples to be obtained after completion of Tank 37 salt dissolution transfers into Tank 23	Rios-Armstrong/ Shah	Completed
	b. Tank 8 sample to be obtained	Rios-Armstrong/ Shah	Completed
	c. Tank 41 sample to be obtained	Rios-Armstrong/ Shah	Completed
10	Evaluate need to add TCLP testing to salt batch qualification (Based on Salt Batch 8 results)	Mercury Program Team	Will be covered in Mercury Team Phase II Recommendation
512-S, 512-S Cleaning			
1	Analyze LWHT for soluble Hg and Hg Speciation. Also, have LWHT sample filtered and analyzed for Hg	Samadi	Being Investigated
2	Analyze LWPT for soluble Hg and Hg Speciation.	Samadi	Being Investigated

No	Action Item Description	Responsibility	Resolution Remarks
3	Identify if any sample left of LWPT-3(LWPT sample after filter cleaning) that can be analyzed for Hg Speciation	Samadi	Being Investigated
4	Determine Wt% of Hg in LWPT-1, 2 and 3 (2013 samples) are on insoluble or Total solids basis.	Samadi	Completed
5	Determine Hg in LWPT Samples pulled after completing Cycle 1 of salt batch 7B (2014)	Samadi	Being Investigated
DWPF and Sludge Batches (Tank 40)			
1	What happens to Hg when the SMECT liquid is brought into caustic precharged RCT Heel?	Fellinger	SRAT Batch 735 Samples have been sent to Eurofins for Hg Speciation Analysis
2	Should RCT be sampled for Hg (Total and Soluble) before the contents are transferred to Tank Farm?	Mercury Program Team/ Shah	In progress
3	Pull Hg data of RCT during the cold runs	Gillam	Completed
4	Redo the SMECT and RCT sampling during the SRAT and SME runs soon after the DWPF comes out of outage	Fellinger	Completed- SRR-WSE-2015-00028 Issued by Fellinger
5	Hg measurement for SRAT influent and Product	Iaukea/ Fellinger	In progress
6	RCT/ SMECT samples pulled for SRAT Batch 735 to be sent to SRNL for refrigeration	Fellinger/ Mahannah	Completed
7	Evaluate a need to send these samples to Eurofins for Hg speciation	Fellinger/ Shah	Completed- Samples sent to Eurofins
8	Where is the air sparger located in the SMECT? Do air/ nitrogen have any impact on Hg Chemistry?		In progress
9	What is the impact of antifoam and solvent degradation products on Hg speciation for DWPF recycle streams?	Fellinger/ Bricker	Being investigated
10	Why Hg is present in the two SEHT sample results?	Mercury Program Team/ Shah	Being Investigated- Salt Batch 7 samples are to be sent to Eurofins for Hg speciation
11	Analyze PRFT sample to determine Hg	Iaukea	In progress
12	Clean/ Replace the scrubber baskets to reduce the high delta P observed for SME and RCT/ MFT Scrubbers	Iaukea	In progress
13	Spare Hg pumps should be made available	Iaukea/ Strohmeier	In progress
14	Sample and analyze the solids plugging the vessels in the Hg purification cell	Iaukea/ Strohmeier	In progress
15	Restore operation of the Mercury Purification cell	Iaukea/ Strohmeier	In progress

No	Action Item Description	Responsibility	Resolution Remarks
2H, 3H, 2F Evaporators			
1	Tank 37 Back flush valve corrosion- Was it attributed to Hg? Any evidence from SRNL testing?	Bridges / Jacobs/ Rogerson	In progress
2	Investigate components degradation of 2H/ 3H systems due to Hg	Bridges / Jacobs/ Rogerson	2H Evaporator has no component degradation due to Hg. In Evaporator 3H, the corroded Tank 37 back flush valve may be due to Hg. However, there are no results to support this idea.
3	Pull the sodium aluminum silicate (NAS) data from the scale sample reports and determine Hg	Bridges / Jacobs/ Rogerson	In progress
4	Pull the process History on 1F/ 2H Systems	Bridges / Jacobs/ Rogerson	In progress
5	When did we stop using antifoam in the Evaporators?	Bridges / Jacobs/ Rogerson	No antifoam has been used since 2003.
6	Review SRNL report to determine whether Tank 38/ 43/ 51 samples for Hg were digested/ undigested and filtered?	Sudduth/ Bridges	Tank 38 and 43 samples were NOT filtered. Both a digested and undigested analysis was completed on at least one set of samples from each tank. When it became obvious that the digested method produced drastically different results, the undigested analysis was dropped for the remaining sample sets that were analyzed. Tank 51 analysis was completed on a sludge slurry sample; therefore appreciable amounts of solids were originally present. The digested mercury analysis was completed on a decanted supernate sample from this original sludge slurry sample. Tank 22 had a complete suite of analyses completed: Unfiltered and undigested; unfiltered and digested; filtered and undigested; and filtered and digested. Results showed there was no discernible difference between the filtered and unfiltered samples.
7	Investigate 2H overhead Hg number. What analytical method was used at ETP? Digested/ undigested/ Filtered	Sudduth/ Bridges	The overhead samples analyzed at ETP are not filtered. A digested CVAA analysis is performed. This method has been used since the 1990s
8	Steam flow relation to Hg collected in 2H and 3H	Sudduth/ Bridges John/ Paul	In progress

No	Action Item Description	Responsibility	Resolution Remarks
9	Look at 2H/ 3H Hg over heads volumes to ETP and compare to Hg collected from the MRT (may be combined with # 7)	Sudduth/ Bridges	See #7
10	Perform digested analyses on tanks that are a part of the evaporators systems (Tanks 39, 32, 37, 30, 29, 51, 26, 25 and 44)	Shah/ Mercury Team	Tank 39 is sampled. Other listed tanks are to be sampled
11	Draw correlations between the undigested results in WCS and digested results then update WCS accordingly	Shah/ Mercury Team	Will be covered in Mercury Team Phase II Recommendations
12	Investigate Higher mass of Hg in 2H overheads (can be combined with Action Item # 7 and 9)	Sudduth/ Bridges	See #7

7 Sampling Plan and Analyses

Based on the review of the systems, a sampling plan for the mercury speciation studies for the liquid waste system was developed as shown in Table 28. Samples were analyzed for Total Hg, Total soluble Hg, Particulate Hg, Elemental Hg, Ionic Hg, MMHg, Ethyl Hg, and DMHg. Sampling was prioritized based on the need date to make decision to restart operations as well as the expected influence of the process stream and/ or system had mercury behavior. **Table 28** provides a current status of the samples that were collected from LW facilities and sent for analyses.

8 Mercury Speciation Results

Table 29 provides a summary of sample analysis results obtained to date. This data is also presented in Figure 9. Mercury speciation analysis confirms the change in the chemical nature of the mercury present in the LWS. To date, LWS safety basis had assumed presence of mercury primarily in elemental or non-organic ionic form. However, the data shows presence of significant amount of MMHg in Tanks 21, 22 and 50. To date, the results show

- Total mercury in the ETP WCHT sample was 0.08 mg/L and no MMHg was detected.
- Total mercury in the GPE bottoms was 0.365 mg/L. Speciation analysis was not performed.
- Total mercury in Tank 50, based on multiple samples from various dates (4th Quarter 2014 to 2nd Quarter 2015) ranged from 78.7 mg/L to 126 mg/L. Speciation analyses indicates MMHg concentration ranging from 37.6 to 53.0 mg/L, DMHg concentration ranging from non-detectable (ND) to 0.235 mg/L, and ethyl mercury concentration 14.2 mg/L in sample collected on 4/7/2015. Both WCHT and GPE bottoms are input to Tank 50. Based on the measured mercury concentration differences between the Tank 50 sample and WCHT/GPE Bottoms, the contribution of WCHT as well as 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.
- Total mercury in Tank 21, which currently holds Salt Batch 8, was 101 mg/L. Speciation analyses indicates MMHg concentration of 58.2 mg/L, DMHg concentration of 0.015 mg/L, and ethyl mercury was ND. Even though Tank 50 analyses is based on Salt Batch 7 and undergoes 15 – 20

% dilution when processed through the ARP/MCU, the comparison of data between Tank 21 and Tank 50 samples suggests that the total mercury as well as speciated forms pass through the ARP/MCU process with no significant change in chemical nature of mercury. However, some mercury does strip to the Strip Effluent (82.2 mg/L) and Solvent (14.7 mg/L total Hg). It should be noted that the volumes of strip effluent and solvent are very small compared to Tank 21 solution processed through the ARP/MCU system. All WAC limits and targets remain in compliance except for MMHg concentration in the Saltstone WAC. Salt Batch 8 was determined to have MMHg concentration of 58.2 mg/L compared to the 2nd Quarter Tank 50 MMHg concentration of 53 mg/L [7]

- Speciation analyses of TCLP leached solutions of the grout samples prepared from Tank 21 as well as Tank 50 samples show majority of the released mercury has a chemical form of MMHg. MMHg, therefore, is the primary contributor to the mercury release measured for Universal Treatment Standard for Land Disposal Requirements (LDR).
- Total mercury in Tank 22, which is DWPF recycle receipt tank, was 119 mg/L. Speciation analyses indicates MMHg concentration of 31.2 mg/L, DMHg and ethyl mercury were ND.
- As shown in Figure 3 DWPF processes significant amounts of mercury in sludge batches. To understand the distribution of mercury in the DWPF vessels, several samples from SRAT Batch #735, as shown in Table 20, were collected from SMECT, RCT, and OGCT vessels. Details are provided in [11]. Based on the analyses of SRAT Batch 735 sampling, Table 21 indicates that 57% of the incoming mercury was retained in the DWPF and the remainder was recycled back to the Tank Farm (Tank 22).

Due to the presence of MMHg in Tank 50, transfer from Waste Collection Hold Tank (WCHT) to Tank 50 and MCU processing was put on “Hold”. Based on the speciation and Toxicity Characteristic Leaching Procedure (TCLP) results, the following decisions made to restart operations of the LWS.

- Complete Salt Batch 7 processing at MCU, transfer Salt Batch 8 from Tank 21 to Tank 49
 - Only four microbatches (nominally 14,860 gallons salt solution thus 16,500 decontaminated salt solution (DSS)) of Salt Batch 7 material were remaining to be processed when MCU processing was put on “hold”. Tank 50 1st and 2nd Quarter samples showed total mercury concentration less than 126 mg/L, and MMHg concentration remained approximately the same in both samples (53 mg/L). The 1st Quarter TCLP met the UTS LDR for mercury (0.025 mg/L) and the early 2nd Quarter TCLP has passed using the “large” particle size distribution after the 28 day cure time. Approximately 500,305 gallons of DSS was added to Tank 50 between the first and second quarter samples; even with these additions, the total mercury and methyl mercury concentration remained relatively constant. Based on these results, MCU was allowed to start processing of remaining Salt Batch 8 volume.
- Process Tank 21 Salt Batch 8 material through ARP/MCU and send the decontaminated salt solution (DSS) to Tank 50
 - TCLP was performed on a cesium removed (by simulated MCU processing) Tank 21 sample and the UTS LDR standard for mercury of less than 0.025 mg/L was met using large particle size (the standard procedure going forward) with 84% confidence level [SRNL-L3100-2015-0099]. Furthermore, the 2nd Quarter 2015 TCLP sample for Tank 50

also met the assumed UTS LDR for mercury [13]. Therefore, processing the Tank 21 Salt Batch 8 material through ARP/MCU and sending the decontaminated salt solution (DSS) to Tank 50 is presumed to meet the assumed UTS LDR for mercury.

- Release the WCHT transfer to Tank 50 “Hold”.
 - Based on speciation analysis activities of WCHT to verify that MMHg is less than 53 mg/L, WCHT stream was allowed to transfer to Tank 50 because MMHg was less than 20 mg/L.

Currently several samples as shown in Table 28 are at various stages of sample collection/analyses. As the sample analysis is complete, it is expected that a better understanding of the source of MMHg formation will emerge. Final results will be discussed in the Phase II report.

Table 28 — Samples Selected for Mercury Speciation Analyses

Priority Shipment	ELN Experiment	Samples	Matrix Type	Projected Sample Pull Date	Shipment Date	SRNL Results Receive Date	SRNL memo to SRR	SRNL Memo #	SRR TAR/TTR#	Remarks
1	L2320-00016-40	4Q14 TK 50 / TQ15 TK 50 / 14-Day 1Q15 TK 50 Salt stone SRNL TCLP Extractant Fluid	Aqueous		3/5/2015	4/1/2015		SRNL-L3100-2015-00054	X-TTR-Z-00005 and X-TTR-Z-00006	Complete
2	L2320-00016-41	Tank 21 / MCU SHT (Salt Batch 7B)	Aqueous/Organic		3/19/2015	4/20/2015		SRNL-L3100-2015-00068	X-TAR-H-00022	Completed
3	L2320-00016-43	Tank 22 / WCHT	Aqueous		3/19/2015	4/24/2015		SRNL-L3100-2015-00079	X-TAR-H-00023	Completed
4	L2320-00016-45	2Q TK 50 / Tank 21 (Decon)	Aqueous		4/16/2015	5/4/2015		SRNL-L3100-2015-00084	X-TTR-Z-00006 and X-TAR-Z-00006	Completed
5	L2320-00016-46	DWPF RCT1 / DWPF RCT 2 / DWPF OGCT	Aqueous	Around 3/18/15	5/14/2015	6/15/2015 (Revised date)	6/16-17/2015	SRNL-L3100-2015-00105	X-TAR-S-00002	Analysis in progress
6	L2320-00016-xx	2Q15 TK 50 / Tank 21 SaltstoneSRNL TCLP Extraction Fluids/ Tank 49	Aqueous	TK 49 sample was pulled on 5/7/15, 2Q15 TK 50 and TK 21 TCLP Extraction Fluids samples will be pulled upon completion of 28 days cure time	5/28/2015	6/15/2015 (Revised date)	6/16-17/2015	SRNL-L3100-2015-00106	X-TTR-Z-00006 and X-TTR-G-00002	Analysis in progress
7	L2320-00016-xx	Tank 38-1/TK 38-2/ OHT # 1	Aqueous	OHT # 1 (2H Evap) sample was pulled on 5/7/15 night, TK 38 samples=>> May-11	6/4/2015	6/19/2015	6/23/2015	SRNL-L3100-2015-00115	X-TTR-G-00002	some sample bottles were popped due to severe freezing at destination
8	L2320-00016-xx	Tank 43-1/TK 43-2/ OHT # 2	Aqueous	OHT # 2 (2H Evap) sample was pulled on 5/7/15 night, TK 43 samples=>> May-11	6/10/2015	6/25/2015	6/29/2015	SRNL-L3100-2015-00115	X-TTR-G-00002	Funding issue resolved, Contract was awarded to Eurofin on 6/30/2015.
9	L2320-00016-xx	3Q-TK50/MCU SSFT/MCU SHT (Salt Batch 7B)	Aqueous	3Q-TK 50 is scheduled to be pulled on 7/6 or 7/13. MCU Salt Batch 7B samples have been pulled and are at SRNL	7/20/2015*	8/16/2015*		SRNL-L3100-2015-xxxxx	X-TTR-G-00002	*Pending Resumption of Rad Shipments
10	L2320-00016-xx	MCU SEFT, MCU DSSHT, (Salt Batch 7B), 3H OHT-1	Aqueous/Organic	MCU SEFT and MCU DSSHT sample s have been pulled. 3H OHT sample is not yet pulled.	8/3/2015*	8/19/2015*		SRNL-L3100-2015-xxxxx	X-TTR-G-00002	*Pending Resumption of Rad Shipments; If OHT-1 is available
11	L2320-00016-xx	TK 30-1, TK 32-1, TK 37-1 (3H Evap System)	Aqueous	TK 30 and 32 samples have been pulled, TK 37 sample is not pulled yet.	8/10/2015*	8/26/2015*		SRNL-L3100-2015-xxxxx	X-TTR-G-00002	*Pending Resumption of Rad Shipments, if shipment 9 is delayed then this shipment will be delayed also.
12	L2320-00016-xx	TK 30-2, TK 32-2, TK 37-2 (3H Evap System)	Aqueous	TK 30 and 32 samples have been pulled, TK 37 sample is not pulled yet.	8/31/2015*	9/16/2015*		SRNL-L3100-2015-xxxxx	X-TTR-G-00002	*Pending Resumption of Rad Shipments, if shipment 9 is delayed then this shipment will be delayed also.
13	L2320-00016-xx	TK 39-1, TK 39-2, 3H OHT-2 (3H Evap System)	Aqueous	TK 30 and 32 samples have been pulled, TK 37 sample is not pulled yet.	9/14/2015*	9/30/2015*		SRNL-L3100-2015-xxxxx	X-TTR-G-00002	*Pending Resumption of Rad Shipments, if shipment 9 is delayed then this shipment will be delayed also.
14,15,16	L2320-00016-xx	DWPF SRAT Batch 736 Processing Samples (first batch after the outage)	Aqueous	On Agenda (depending on DWPF Start up)				SRNL-L3100-2015-xxxxx	X-TAR-S-00002	DWPF Lab pulls these samples per sampling plan provided by Terri F
17,18,19	L2320-00016-xx	MCU SSFT, MCU SEFT, MCU DSSHT, MCU SHT (Salt Batch 8)	Aqueous/Organic	On Agenda (depending on DWPF Start up)				SRNL-L3100-2015-xxxxx	X-TTR-G-00002	After we finished processing atleast 100K volume of Tank 49

Table 29 — Summary of Mercury Speciation Results¹¹

Sample (Analysed by Eurofins unless stated otherwise)	Concentration of various Hg species in Tank farm Tanks mg/L [%RSD] ¹					Species Fraction of Total Hg					Document Number
	Total Hg	Elemental Hg	Ionic Hg	Methyl Hg	Dimethyl Hg	Methyl Hg	Ethyl Hg	Dimethyl Hg	Fraction of Total Hg	Document Number	
4Q14 Tank 50	78.7 [2.1]	0.571 [11]	1.19 [0.39]	37.6 [25]	ND	50%			58%	SRNL-L3100-2015-00054, R-0	
1Q15 Tank 50	126[10]	0.912 [18]	5.04 [12]	53.5 [39]	0.00219 [12]	47%				SRNL-L3100-2015-00054, R-0	
14-day SRNL TCLP Extractant	0.151 [7.2]	0.000734[1.6]	0.0054 [16]	0.121 [16]	0.000139 [28]	84%				SRNL-L3100-2015-00054, R-0	
Concentration of various Hg species in Tank farm Tanks mg/L [%RSD]¹											
Sample	Total Hg	Total Soluble Hg	Particulate Hg	Elemental Hg	Ionic Hg	Methyl Hg	Ethyl Hg	Dimethyl Hg	Fraction of Total Hg	Document Number	
Tank 21	101[2.6]	120 [5.4]	ND	ND	5.88 [11]	58.2 [2.6]	ND	0.0156 [5.6]	58%	SRNL-L3100-2015-00084, R-0	
SHT	14.2 [6.0]	13.5 [0.44]	ND	0.272 [35]	3.44 [27]	3.72 [1.1]	ND	Indeterminate	53+%	SRNL-L3100-2015-00068, R-0	
Tank 22	119 [2.9]	111 [2.5]	8	77.0 [103]	56.5 [6.5]	31.2 [7.4]	ND	ND	80%	SRNL-L3100-2015-00079, R-0	
Tank 22 Reanalysis	-	-	-	20.0 [NA]	97%	SRNL-L3100-2015-00079, R-1	
WCHT	0.0816 [0.06]	0.0798 [0.80]	0.0018	0.0198 [77]	0.00494 [3.4]	ND	ND	ND	32%	SRNL-L3100-2015-00079, R-0	
WCHT Reanalysis	0.00280 [148]	12%	SRNL-L3100-2015-00079, R-1	
WCHT SRNL	0.0627 [3.9]	SRNL-L3100-2015-00079, R-1	
2Q15 Tank 50	97.7 [5.0]	94.3 [8.9]	3.4	1.04 [16]	4.86 [24]	53.0 [2.9]	14.2 [7.6]	0.0235 [13]	78%	SRNL-L3100-2015-00084, R-0	
Cs-Decon TK 21 (Salt Batch 8)	86.7 [3.6]	85.0 [2.0]	1.7	2.18 [69]	5.72 [19]	41.1 [5.8]	19.9 [7.5]	ND	81%	SRNL-L3100-2015-00084, R-0	
DWPF RCT-1	266 [11]	198 [18]	68	203 [29]	154 [7]	7.96 [2.8]	< 0.926	< 0.00140	105%	SRNL-L3100-2015-00105, R-0	
DWPF RCT-2	193 [2.9]	156 [5.6]	37	122 [36]	90.8 [9.6]	5.10 [3.2]	< 0.886	< 0.00134	85%	SRNL-L3100-2015-00105, R-0	
DWPF-OGCT	191 [2.7]	131 [4.3]	60	121 [43]	105 [6.5]	< 0.279	< 0.880	< 0.00136	95%	SRNL-L3100-2015-00105, R-0	
2Q TK 50 TCLP Extraction Fluid (Large Particles)	0.0135 [2.0]	0.0119 [9.9]	0.00162	0.000211 [20]	0.000196 [13]	0.0159 [7.6]	< 0.00575	0.000335 [61]	135%	SRNL-L3100-2015-00106, R-0	
TK 21 Cs Decon TCLP Extraction Fluid (Large Particles)	0.0122 [24]	0.0108 [22]	0.00141	0.0000988 [2.1]	0.0000629 [1.4]	0.0137 [30]	< 0.00571	0.000124 [47]	126%	SRNL-L3100-2015-00106, R-0	
TK 49 (Salt Batch 7B)	110 [4.1]	109 [0.2]	1	6.35 [110]	15.6 [3.8]	58.1 [6.5]	< 18.1	0.471	91%	SRNL-L3100-2015-00106, R-0	
TK 38-1 (Surface)	496 [2.6]	325 [2.5]	171	3.58 [46]	29.8 [7.1]	200 [6.2]	< 35.1	0.148 [52]	89%	SRNL-L3100-2015-00115, R-0	
TK 38-2 (Subsurface)	476 [14]	316 [1.3]	160	4.07 [90]	31.6 [4.7]	160 [6.8]	< 34.3	0.0525 [48]	82%	SRNL-L3100-2015-00115, R-0	
OHT-1	3.78 [6.5]	3.65 [7.5]	0.13	0.0587 [9.9]	0.505 [1.0]	2.45 [3.6]	< 0.115	0.000899 [942]	86%	SRNL-L3100-2015-00115, R-0	
TK 43-1 (Surface)	286 [2.7]	208 [0.75]	78	1.44 [18]	44.0 [5.6]	135 [12]	< 8.72	0.00468 [0.32]	93%	SRNL-L3100-2015-00115, R-0	
TK 43-2 (Subsurface)	234 [1.8]	186 [1.3]	48	3.46 [20]	30.5 [2.1]	134 [8.1]	< 8.45	0.613 [24]	96%	SRNL-L3100-2015-00115, R-0	
OHT-2	4.80 [6.8]	4.64 [1.6]	0.16	0.0636 [20]	0.224 [61]	5.58 [10]	< 0.570	0.00536 [8.0]	139%	SRNL-L3100-2015-00115, R-0	

¹¹ Refer to the source document before using the data presented in this table. There are additional limitations / clarifications related to the data that are provided in the source document.

9 Mercury Flowsheet Extent of Condition Review

The Mercury Flowsheet Extent of Condition Review was conducted on May 10 – 11, 2015.

9.1 Objective

The objectives of the Extent of Condition Review were

- Conduct a review of the overall liquid waste system (flowsheet/ processes/ facilities) to ensure that potential impacts/ issues of the recent information regarding measured concentrations of mercury (organic and inorganic) have been identified and adequately addressed.
- Primary focus of the review is potential DSA impacts of mercury, but the review should consider any other impacts considered appropriate.
 - Any identified impacts/ issues should be categorized as either: a) necessary for resumption of operations of a specific liquid waste process, or b) needed for long-term understanding or management of mercury in the liquid waste system.

9.2 Team Members

The team consisted of internal, external, and National Laboratory personnel to ensure a broad skill mix

- John Contardi (SRR) Team Lead
- John Occhipinti (SRR)
- John Schwenker (SRR)
- Connie Herman (SRNL)
- Mike Stone (SRNL)
- Bill Wilmarth (SRNL)
- Neil Davis (WRPS)
- Renee Spires (WRPS)

9.3 Approach

- The team utilized a systematic approach for each of the various LW processes/ operations
- Mercury War Room Communication Tool schematic was used to ensure the scope was adequately addressed
- In addition to the Mercury impacts the Team also reviewed the following topics
 - Use and impacts of organics in LW facilities
 - Potential for increasing concentrations of Liquid Waste constituents
 - Changing chemical speciation
- Where necessary facility representatives and subject matter experts met with the team
- Several issues identified by the Team are likely already being addressed as part of the War Room, TCLP, and Mercury Management Teams, but were nonetheless identified for completeness

9.4 Summary of Issues

9.4.1 Pre-Start Issues

Based on the team review, the following issues should be addressed prior to resumption of operations:

- Evaluate if the chemical consequences (Safety Basis analysis/ assumptions) are bounding for the current inventories related to DWPF (e.g. SMECT and MWWT)
 - In DWPF, evaluate whether the current plant operation/ configuration is consistent with the Safety Basis relative to the Mercury Removal system (i.e., is not operating the mercury removal system introducing any unanalyzed hazards)
- In the Tank Farms, determine if the current Hg concentrations are bounded by the Safety Basis (Complete)
- Ensure DMHg is addressed in the Saltstone flammability analysis (Pre-Start)
- Clearly define decision criteria including the acceptance criteria
- Clearly define the risk when using Tank 21 TCLP as basis for supporting salt batch transition (Pre-Start for SB8 transition)

9.4.2 Post-Start Issues

Based on the team review, the following issues may be addressed following resumption of operations:

- Develop a position for >500 mg/L soluble Hg in the Tank Farms
- Evaluate data relative to organics at DWPF
- Add prerequisites for Salt Batch 9 recipe change as needed based on revised WAC
- Evaluate Pu concentrations in DWPF recycle against the NCSE
- Determine if other metals (e.g. Chromium) are changing or could be impacting the LW flowsheet
- Determine if Hg solids are concentrating in Tank 50 due to Isopar mixing strategy and impacting the Hg concentration in the feed to saltstone or the sample concentration data
- Evaluate if Saltstone dry feeds are contributing to the TCLP variability

9.4.3 Recommendations

Team recommended the following to be considered as part of the on-going efforts

- Evaluate changing the Saltstone permit to not require the LDR limits at Saltstone
- Determine best locations for mercury to be purged from the LWS
- Develop/ justify how DMHg liquid samples are used to predict vapor space concentrations
- Recommendation to institute a statistical process control methodology for data that is collected. The methodology is intended to identify changes in the process early.

Recommendations from the review team are being tracked to resolution.

10 Expert Panel Review

The Expert Panel team consists of external Industry and National Laboratory personnel to assist the mercury program team in understanding the mercury behavior in the LWS. Team members include:

- Dr. Lou Papouchado, Retired SRS/ SRNL Chemistry Expertise
- Dr. Eric Pierce, ORNL Mercury Expert
- Mandi Richardson, AECOM Mercury Consultant
- Dr. Eric Prestbo, Tekran Corp. Chief Scientist, Mercury Behavior & Speciation Expert

The initial review team meeting was held on May 13 & 14. Sections below provide Expert Panel review scope (10.1) and a summary of their assessment (10.2).

10.1 Expert Panel Review Scope

10.1.1 Issue

Organomercury species have been found in the LWS. In early 2000's, organic mercury species were evaluated for the tank farm evaporator processes [14]. This evaluation was performed with an emphasis centered on DMHg and understanding potential Industrial Health (IH) concerns. In 2015 MMHg, at levels higher than expected, was found in the Tank 50 feed to the Saltstone facility [6]. This was discovered when mercury speciation was performed as part of understanding 4th quarter 2014 Tank 50 Grout TCLP results that were higher than expected. [15] A Saltstone PISA-2015-0007 "Higher than Expected Concentration of Methyl Mercury" April 10, 2015 was declared. Initial impacts assessed due to the higher levels of MMHg, included IH contingency actions, AB evaluation and additional sampling and speciation to determine the source of MMHg.

10.1.2 Problem Statement

MMHg was discovered at higher levels than expected in Liquid Waste supernate streams. The exact origin has not been established. DMHg, while known to be present at very low levels in the liquid waste system, was never formally evaluated as a potential contributor to flammability. As part of the Operational Decision Making (ODM) process for resumption of DWPF operations, the question of the potential flammability impacts from possible DMHg content in the MCU strip effluent were questioned since MCU strip Effluent was recently determined to contain unexpected quantities of mercury (up to ~80 mg/L per sample analysis). A comprehensive look at the overall liquid waste flowsheet, with a bias towards identifying additional potential issues due to organomercury compounds, has not been performed.

10.1.3 Scope of Review

1. Validate approach for gaining understanding of the overall mercury behavior, specifically the sampling schemes aimed to understand behavior around key chemical processing operations.
 - a. Provide targeted suggestions in areas (processing operations) requiring additional emphasis or understanding or areas that should have less emphasis.
 - b. Provide any recommendations for alternate methods for significant mercury removal (besides understanding and correcting issues associated with the DWPF Mercury removal system) from the liquid waste system.
 - c. Provide insight into any mechanisms, in addition to organomercury species, which might be causing increasing concentrations of soluble mercury in the system, potentially from DWPF recycle.
2. Validate chemistry properties of methylated organics being used to support chemical behavior understanding and underpin safety analysis, specifically:
 - a. Organomercury species identified as salts – underlying vapor pressure and flammability assumptions

- b. Organomercury species identified as volatile – underlying vapor pressure and flammability assumptions, including LFL and the use of DMHg as the bounding flammable compound.
 - c. Assumptions related to “missing organic mercury species” during sample speciation.
 - d. Use of kinetic rate expressions to provide bounding estimates for DMHg across the range of expected liquid waste flowsheet conditions.
3. Validate approach for understanding and providing margin with the Saltstone TCLP result for mercury against the RCRA UTS LDR requirement for mercury of 0.025 mg/L.
- a. Efforts to understanding key variables as they may impact TCLP results, such as, particle size, mercury speciation, cure time, vendor impacts, analytical impacts, and so forth.
 - b. Provide any recommendations for potential means to reduce mercury levels in Tank 50 (the salt feed immediately prior to saltstone) or to modify the saltstone waste form to bind an increased quantity of mercury.

10.2 Summary of Expert Panel Assessment

Summary of the Expert Panel initial assessment is provided in SRR-CES-2015-00010 and is reproduced in the following paragraphs.

10.2.1 Observations

- SRR team presentations were well done and properly organized and delivered a very clear and concise picture of the problems they were facing. Panel was effectively briefed on the problem.
- Presenters were very knowledgeable and were able to answer all our questions very professionally.
- It was obvious that a lot of effort has gone into addressing the mercury problem and they presented current and future plans clearly.
- Panel was encouraged that the SRR team had launched an initiative to develop an active sampling program to better understand the mercury mass balance across the system and the mercury speciation.

10.2.2 Assess approach for gaining an understanding of the overall mercury behavior, specifically the sampling schemes aimed to understand behavior around key chemical processing operations

Our preliminary evaluation is that the near-term approach used in gaining an understanding of the overall mercury behavior via sampling schemes appears to be sound. Panel recommends the development of a long-term sampling plan to further understand temporal and systems dynamics.

a. Provide targeted suggestions in areas (processing operations) requiring additional emphasis or understanding or areas that should have less emphasis.

- Panel’s initial view is that the DWPT recycle stream, the evaporators, and the feed to Saltstone need the most attention. Trying to sort out the tank farm complexity may not yield much benefit.

b. Provide any recommendations for alternate methods for significant mercury removal (besides understanding and correcting issues associated with the DWPF Mercury removal system) from the liquid waste system.

- Panel recommends focusing on improving mercury recovery from the evaporators by optimizing the physical and chemical conditions to capture elemental mercury (e.g. reducing agent). Laboratory based tests should be performed. As a longer term solution, we recommend introducing a solids removal (filter) and a mercury removal step (IX; e.g. GT-74) between the RCT and Tank 22.

c. Provide insight into any mechanisms, in addition to organomercury species, which might be causing increasing concentrations of soluble mercury in the system, potentially from DWPF recycle.

- At this stage, Panel believes that the presence of organics is the main driver behind the increased soluble mercury concentrations but looks forward to additional sample data. Mercury is being recycled back to the tank farm because the mercury recovery system in DWPF (Main Hg purge) is not working efficiently. Also, H area waste tanks are being processed and they are higher in mercury concentrations than F area waste.

10.2.3 Assess chemistry properties of methylated organics being used to support chemical behavior understanding and underpin safety analysis, specifically:

- a. Organomercury species identified as salts – underlying vapor pressure and flammability assumptions**
- Panel agrees with the SRR Team that MMHg salts (hydroxide and nitrate) in solution are not volatile and are non-flammable.
- b. Organomercury species identified as volatile – underlying vapor pressure and flammability assumptions, including LFL and the use of DMHg as the bounding flammable compound.**
- Using DMHg as the bounding compound is conservative. Also assuming it has the flammability of 2 methane molecules is also conservative.
 - Panel recommends using dimethyl sulfur or another dimethyl metal (tin) compound as a surrogate for flammability studies. The panel also recommends pouring fresh saltstone in the vault and measuring the DMHg coming off the surface as it cures and confirm that it is much lower than the conservative estimates. Pouring this saltstone is safe since there is no head space constraint at this point.
 - Panel also recommends utilizing alternative methods to calculate lower flammability limits to obtain more realistic estimates for dimethyl-mercury. For example, the use of other organo-metallic compounds (such as dimethyl-tin, dimethyl-zinc, etc.). This approach also requires linking LFL to molar heat of formation to estimate the heat of combustion
- c. Assumptions related to “missing organomercury species” during sample speciation.**
- Panel believes the mass balance of the sum of mercury species being lower than the total mercury is due to the cumulative losses and errors in sample preparation, dilution, and analysis. Panel highly recommends that setting up an in-house capability to measure organomercury is needed

which would require a significantly lower sample dilution. It may be possible to use head-space analysis to determine DMHg directly in native liquids.

d. Use of kinetic rate expressions to provide bounding estimates for DMHg across the range of expected liquid waste flowsheet conditions.

Panel agrees as long as they are applied to conditions matching the conditions used to measure the rates.

10.2.4 Assess approach for understanding and providing margin with the Saltstone TCLP result for mercury against the RCRA UTS LDR requirement for mercury of 0.025 mg/ L.

The panel agrees that SRR should negotiate with the state to raise the limit above the current limit driven by LDR.

- a. Efforts to understanding key variables as they may impact TCLP results, such as, particle size, mercury speciation, cure time, vendor impacts, analytical impacts, and so forth.
 - Panel agrees with this program and these efforts should continue. Panel supports further pursuing the particle size effect on TCLP. The panel recommends running certified laboratory to laboratory comparisons on mercury TCLP results for variability.
- b. Provide any recommendations for potential means to reduce mercury levels in Tank 50 (the salt feed immediately prior to Saltstone) or to modify the Saltstone waste form to bind an increased quantity of mercury.
 - Panel recommends using the pie charts for the different salt batch compositions and the estimated mercury levels coming from each fraction to see if there is a correlation between certain fractions with high mercury and the observed tank 50 results. This may lead to a better approach to preparing salt batches that can meet mercury limits.
 - A longer term approach is to provide a mercury removal step (e.g., GT-74) before tank 50, recirculating tank 50 or post tank 50, or to decompose the organomercury levels (e.g., UV light) going to Saltstone. Only a small DF is needed.

Recommendations from the review team are being tracked to resolution.

11 Summary and Path Forward

Phase I activities included a review and assessment of the liquid waste inventory and chemical processing behavior of mercury using a system by system review methodology approach. Gaps in understanding mercury behavior as well as action items from the structured reviews are being tracked. 64% of the gaps and actions were resolved.

A significant amount of effort was expended during the Phase I activities to assess and determine the speciation of the different Mercury forms (Hg^+ , Hg^{++} , elemental Hg, organomercury, and soluble versus insoluble mercury) within the liquid waste system. In particular, the discovery of a higher than expected MMHg compound in the Tank 50 feed to saltstone resulted in additional mercury speciation activities to be performed on the various process streams that are constituent feed streams into Tank 50. Additional mercury speciation activities were also initiated around specific process flowsheet

operations (i.e., DWPF Chemical Processing Cell sludge preparation unit operations, MCU processing, Salt Batch feed preparation, 2H and 3H evaporator operations) in order to understand mercury processing behavior and also identify potential sources of MMHg. About 50% of these speciation activities are complete at this time. A number of sources of MMHg have been ruled out based on this sampling and analysis effort, however, completion of this effort will be required to determine the source.

Due to the presence of MMHg in Tank 50, transfer from Waste Collection Hold Tank (WCHT) to Tank 50 and MCU processing was put on “Hold”. Based on the speciation and Toxicity Characteristic Leaching Procedure (TCLP) results, the following decisions made to initiate operations of the LWS.

- Complete Salt Batch 7 processing at MCU
- Transfer Salt Batch 8 from Tank 21 to Tank 49.
- Process Tank 21 Salt Batch 8 material through ARP/MCU and send the decontaminated salt solution (DSS) to Tank 50.
- Release the WCHT transfer to Tank 50.

Sampling and analysis activities were also conducted within DWPF during CPC processing of SRAT and SME Batch 735. This was a first step to better understand mercury behavior during CPC processing operations and to understand chemistry issues with both mercury recovery in the MWWT and the high fraction of mercury being returned to the tank farm in DWPF recycle. Data indicate ~43% of the mercury was being returned to the tank farm during Batch 735 processing versus prior estimates of over 80%.

Two major reviews were completed in Phase-1. The first review was the Mercury Flowsheet Extent of Condition Review which focused on identifying potential impacts/issues as a result of increased levels of organic and inorganic mercury in the liquid waste system. In the second review an Expert Panel consisting of external industrial and national laboratories personnel provided an assessment on our approach to understand the mercury behavior in the LWS. Suggestions from the both of these review teams are tracked.

Phase II activities will take an integrated approach to re-assess the overall system knowledge, to rank and prioritize critical gaps/information, assess impacts of removal and disposal options, and document an action plan needed to resolve overall mercury management. The following actions are also recommended during Phase II activities:

- Perform a System Engineering Evaluation (SEE) to “Re-establish Mercury Removal Capability within DWPF”

DWPF experienced both chemistry and equipment issues during coupled operations with ARP/MCU product streams. Mercury preferentially went to the SMECT versus the MWWT as intended; the mercury which did go to the MWWT was “dirty mercury” and could not be processed successfully in the Mercury Purification Process; and the SMECT to MWWT mercury pump failed to successfully operate. Recent mercury samples from DWPF vessel sumps designed to collect mercury indicated that the mercury in the SMECT is relatively clean elemental mercury. A SEE is recommended to brainstorm and assess potential options to re-establish mercury removal capability taking advantage of the relatively clean collection of mercury in the SMECT.

- Perform a SEE to “Determine the Best Alternative Mercury Removal Location within the LWS”.

It is possible that removal of mercury in DWPF may not be sufficient to meet system removal requirements (75% removed in DWPF) and also prevent significant recycling of mercury to the tank farm. A SEE is recommended to determine the best possible alternative means to remove mercury from the liquid waste system.

- Assess and recommend synergistic actions to improve mercury recovery associated with implementation of alternative reductant in DWPF.
- Assess prior recommended actions and action effectiveness ([16], [17], and [18]) related to mercury recovery.

The Phase II action plan will include the results from the SEEs and the assessment actions above as shown in Figure 10.

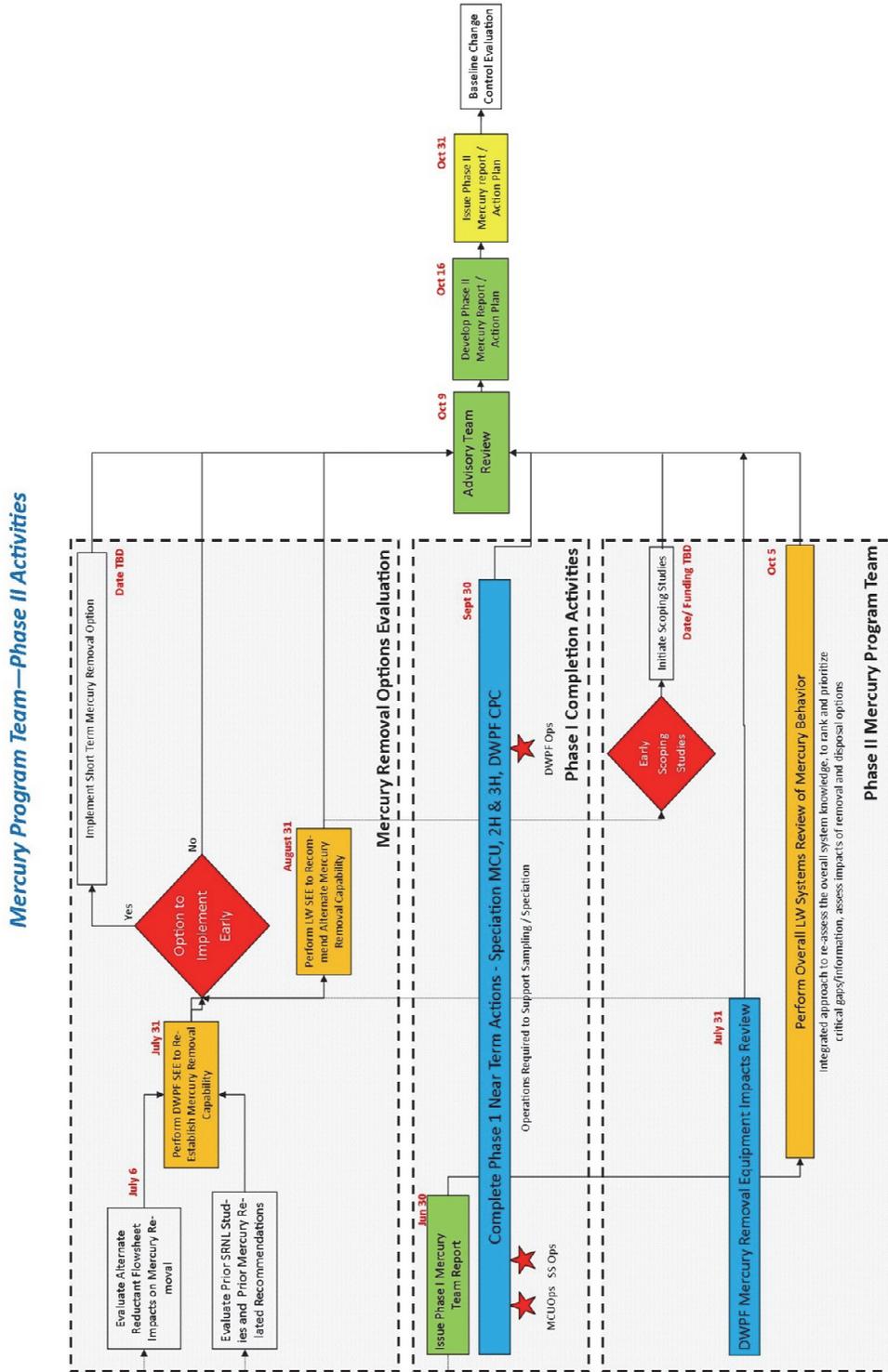


Figure 10 — Key Phase II Activities

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