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Evaluation of Mercury in Liquid Waste Processing Facilities

Comprehensive Action Plan for the Long-Term Management and Removal of Mercury in the Savannah River Site Liquid Waste System

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I. SUMMARY

Mercury (Hg) in the Savannah River Site (SRS) Liquid Waste System (LWS) originated from decades of canyon processing where it was used as a catalyst for dissolving the aluminum cladding of reactor fuel. Approximately 60 metric tons of mercury is currently present throughout the LWS. Mercury has long been a consideration in the LWS, from both hazard and processing perspectives. Mercury removal from the LWS is necessary to meet the long-term closure objectives.

In February 2015, the Department of Energy (DOE) requested Savannah River Remediation (SRR) *"It is DOE's expectation that SRR take an integrated, system-wide approach to evaluating the movement, monitoring, and collection of mercury through the entire Liquid Waste System/Facilities and utilize external expertise as needed. It is expected that the results from this integrated approach be used in the development of the final controls for resolving the recently declared Potential Inadequacy in the Safety Analysis (PISA) PI-20 15-0001. Periodic updates on the progress/results should be provided at the Senior Integrated Project Team meetings."*[1]

As a part of this effort, a Mercury Program Team (MPT) was established and the key objective of the MPT was to evaluate mercury in the LWS and develop a comprehensive action plan for long term management and removal of mercury including:

- Mercury inventory and speciation in the LWS,
- Holdup and chemical processing behavior during transfers, evaporation, and other unit operations,
- Impact identification, including worker safety and equipment degradation,
- Mercury removal and disposal options, and
- Resolution of PISA PI-2015-0001[2] (Mercury Accumulation in 242-25H Evaporator) and PI-2015-0007[3] (Higher than Expected Concentration of Methyl Mercury in Tank 50).

Mercury evaluation activities were conducted in two phases. 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. 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 LWS. In total 95 samples were strategically taken throughout the LWS to understand mercury behavior during processing operations. Sixty five samples were processed by Savannah River National Laboratory (SRNL) and sent to Eurofins for speciation. Eurofins is one of two commercial laboratories capable of mercury speciation of radioactive samples. Mercury speciation is a time consuming activity due to the need for extensive sample preparation, shipment limitations (maximum of 4 samples at a time), and the analysis of radioactive samples by this specialized off-site laboratory. At the completion of Phase I activities, an independent Mercury Expert Panel was chartered to review the Phase I activities and provide feedback on the proposed Phase II activities. These activities, including the feedback from Mercury Expert Panel, were documented in the Phase I report[4].

Phase II activities analyzed results from Phase I sampling and analysis activities and were captured in three major flowsheet evaluations: 1) Mercury Behavior during Salt Processing[5], 2) Mercury Behavior in Defense Waste Processing Facility (DWPF)[6], and 3) Mercury Behavior in the Tank Farm Flowsheet[7]. In addition, two System Engineering Evaluations (SEE's) were performed using key SRR and SRNL resources to identify the most feasible means to re-establish mercury removal capability in DWPF[8] and, as a backup plan, determine the most feasible means to remove mercury in other locations throughout the LWS[9]. A project team was formed within DWPF to implement the recommendations from the DWPF

SEE to re-establish mercury removal capability. The results of the LWS SEE primarily identified possible technology options and served as input into the DOE-EM Technology Plan to Address the EM Mercury Challenge[10].

Some key findings from these studies include the following:

- DWPF which was established as a purge point for mercury is not functioning as designed, in part due to the collection of "dirty mercury" in the Mercury Water Wash Tank (MWWT — the designed collection location). This study recommends to re-establish mercury removal capability at the DWPF and, as a backup plan, determine the most feasible means to remove mercury in other locations throughout the LWS.
- Sampling and measurement activities indicate that a significant amount of elemental mercury resides in the Slurry Mix Evaporator Condensate Tank (SMECT).
- Mercury speciation analysis at key processing locations in the LWS indicates a significant presence of organomercury compounds especially methylmercury (MeHg). Methylmercury is present in DWPF recycle and appears to be concentrating around the 2H evaporator which is dedicated to DWPF recycle processing.
- Mercury speciation analysis shows that methylmercury is preferentially released from the saltstone product during Toxicity Characteristic Leaching Procedure (TCLP) testing. Therefore, to keep the saltstone product below the hazardous waste landfill disposal limit of 0.2 mg/L, management of DWPF recycle, containing MeHg, and used for salt dissolution and salt batch preparation activities in the LWS is important.

Similar to Phase I, at the end of Phase II activities prior to issuing the comprehensive action plan, the MPT chartered an independent team of mercury chemistry experts, in an advisory capacity, to review the work to date and to provide additional recommendations specifically related to findings, conclusions, and actions going forward. The recommendations from the Mercury Expert Advisory team (Attachment A) following Phase II are included in the comprehensive action plan for long term management and removal of mercury.

The comprehensive action plan (Table 1) was developed based on the above evaluations. Additionally, mercury related activities to reduce mercury vapors in the Effluent Treatment Facility[11], the current tank farm vapor monitoring for fugitive and episodic releases[12,13] and known LWS equipment issues believed to be caused by mercury are included in the comprehensive action plan for completeness.

A significant number of the key Comprehensive Action Plan actions have already been completed related to mercury in addition to the remaining activities listed in the plan. These include:

- Industrial Hygiene and Worker Protection (Monitoring and Personal Protective Equipment)
  - Worker communications completed
  - Methylmercury permeability testing of latex gloves and other materials completed
  - Precautions, such as 'sniffers', are taken to detect mercury should it be present prior to performing work
- Tank Farm Safety Analysis
  - Compensatory actions for PISA PI-2015-0001[2] implemented, pending minor evaporator modifications which includes installation of sight glass
- Saltstone Safety Analysis
  - Safety Analysis changed to address mercury levels (PISA PI-2015-0007[3]) that affect worker/facility safety
- Saltstone Performance

  - TCLP particle size variability
  - Hazardous waste landfill disposal limit clarified
- Performance Assessment Impact (Tank Closure Grout and Saltstone)
  - Assessment completed and "No Impacts" documented

Recommendations for remaining actions of the Comprehensive Action Plan are categorized under three broad categories:

A. Plant Operations
B. Technology Development
C. Sampling & Monitoring

The execution of these action items support long term management and removal of mercury in the LWS. SRR actions are tracked in relevant facility POW's (some critical action items may be tracked in SRR-POW) and/or in the STAR system. SRR and SRNL are tracking technology development initiatives and progress in concert with the DOE EM Technology Plan to address the Mercury Challenge. The MPT will meet periodically to review the status of the action items. The Comprehensive Action Plan (Table 1) will be updated, if significant changes were to occur or if new information arises with potential impacts on mercury behavior in the LWS.

Table 1. Comprehensive Action Plan for the Long-Term Management and Removal of Mercury in the SRS LWS

Category	Facility	Status	Actions	Performing Organization
Plant Operations	TF/ETP	Complete	Evaluate Industrial Hygiene (IH) and Worker Protection	LWS
	Saltstone	Complete	Clarified with South Carolina Department of Health and Environmental Control (SCDHEC) that SRR needs to meet mercury hazardous waste landfill disposal limit of 0.2 mg/L	LWS
	DWPF	Initiated	Raise pH in SMECT to keep mercury in elemental form	DWPF
	DWPF	Initiated	Establish mercury pumping capability from SMECT and/or Mercury Water Wash Tank (MWWT) to Mercury Purification Process Cell (MPPC)	DWPF
	DWPF	Future Outage scope	Improve performance of mercury removal [e.g., flush/clean Slurry Receipt and Adjustment Tank (SRAT) condensers, scrubber baskets, lower purge rates with implementation of nitric-glycolic flowsheet]	DWPF
	DWPF	Future Outage scope	Evaluate need for reestablishing MPPC (Note: Decision following establishment of mercury pumping capability from SMECT to MPPC) and determine acceptable disposal path for mercury	DWPF
	TF	Initiated	2H/3H Evaporators changes for mercury. Install sight glass to determine level of mercury.	Tank Farm
	TF/ETP	Initiated	Complete path forward action items outlined for the reduction of mercury vapors in the ETP operation areas[11] (X-EPF-H-00016)	ETP
	TF/ETP	Planned	Confirm that episodic and fugitive emissions are not occurring at waste tanks[12] / Tracked in STAR[13]	Tank Farm (Vapor Monitoring)
	TF	Planned	Conduct material compatibility review and evaluate potential for mercury particulate carryover and to form mercury deposits on ventilation system components during acid cleaning of waste tanks	TF
Technology Development	TF	Initiated	Removal of ionic mercury via reductant with a chemical additive to the evaporator (2H) system to enhance current mercury removal	SRNL

Category	Facility	Status	Actions	Performing Organization
	TF	Initiated	Removal of organic mercury via photoreaction (Tank 50)	SRNL
	TF	Initiated	Develop methods to determine speciation of mercury in sludge	SRNL
	TF	Not Funded	Hg absorbents/Ion exchange for organomercury	SRNL
	TF	Not Funded	Mercury getters as additions to grout formulations	SRNL
	DWPF	Not Funded	Develop alternative anti-foam (DWPF is initiating R&D program to develop alternate anti-foam) or alternate means to prevent foaming in DWPF Chemical Process Cell (CPC) vessels[14]. (X-TTR-S-00046)	DWPF/SRNL
	SS	Not Funded	Determine maximum concentration of MeHg that can be present in the saltstone grout without failing TCLP criteria of 0.2 mg/L.	SS/SRNL
Sampling and Monitoring	DWPF	Continue	Monitor mercury in the SRAT sludge batches after concentration	DWPF
	TF	Continue	Monitor mercury collection from Evaporator System	Tank Farm
	SS	Continue	Monitor mercury speciation of Tank 50 quarterly samples	Saltstone
	SS	Continue	Monitor mercury release from TCLP Tank 50 quarterly samples	Saltstone
	TF	Continue	Monitor mercury in salt batch qualification samples	Tank Farm
	SHT	Continue	Monitor mercury in monthly MCU solvent sample	Tank Farm
	All	Initiated	Develop in-house capability to measure organomercury.	SRNL
	All	Initiated	Run certified laboratory-to-laboratory comparison for select waste tank samples for mercury speciation variability	SRR/SRNL
	TF/ETP	Planned	Perform specific and nearly continuous monitoring of mercury vapor on waste tank tops	Tank Farm (Vapor Monitoring)

Category	Facility	Status	Actions	Performing Organization
	LWS	Planned	Develop a conceptual and/or mass balance model for mercury in the LWS	SRR
	LWS	Planned	Add organic carbon analyses for potential alkylating agents to the suite of mercury analyses	Tank Farm
	TF	Continue	Update waste transfer time-line as new sludge and salt batches are prepared	System Planning

II. DISCUSSION

Phase I & II Studies

The key objective of the study was to evaluate mercury in the LWS and develop a comprehensive action plan for long term management and removal of mercury. Mercury evaluation activities were conducted in two phases. During the Phase I and II review, several knowledge gaps were identified. These gaps were assigned to the key subject matter experts and were carried forward as action items. These action items are summarized in Tables 2 (Phase I) and 3 (Phase II). Some action items required collection of additional data while others required clarification. However, majority of them were addressed or open items were incorporated in the Table 1 as a part of comprehensive action plan for the long-term management and removal of mercury.

Phase I activities assessed the liquid waste inventory and chemical processing behavior using a system-by-system review methodology and determined the speciation of the different mercury forms (Hg+, Hg++, elemental Hg, organomercury, and soluble versus insoluble mercury) within the LWS. During Phase I, gaps in the current understanding of the mercury behavior in the LWS were identified, documented and tracked. During the Phase I[4], 64% of the identified gaps were closed and documented. Current status of identified gaps during Phase I are summarized in Table 2.

During the Phase I study, the following two Expert Panels were convened to review the initial assessment of the mercury in the LWS:

- Mercury Flowsheet Extent-of-Condition Review
- Mercury Expert Panel

Mercury Expert Advisory Panel Reviews after Phase I:

Major recommendations of the Expert Panel are summarized below:

- Panel recommended 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 Recycle Condensate Tank (RCT) and Tank 22.
- Panel recommended 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 recommended 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
- Panel believed 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. Panel recommended 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.

A complete summary of Recommendations/Findings of the Expert Panels are summarized in Phase – I report[4].

Phase II activities built on Phase I activities and results of the LWS flowsheet evaluations, and were summarized in the following three reports and two System Engineering Evaluations (SEE):

- Mercury Behavior in the Salt Processing Flowsheet[5];
- Mercury Behavior in the Defense Waste Processing Facility (DWPF) Flowsheet[6] ; and
- Mercury behavior in the Tank Farm Flowsheet (Evaporator Operations)[7];
- System Engineering Evaluation – Defense Waste processing Facility Mercury Removal Study[8]; and
- System Engineering Evaluation – Liquid Waste System Mercury Removal Study[9].

Table 3 provides the status of the issues and recommendations provided by the two Expert Panel reviews, three Phase II reports and two SEE reports. Majority of the issues/recommendations were closed during Phase II evaluations as shown in Table 3. Open items in the Table 3 were captured in the comprehensive action plan. The comprehensive action plan (Table 1) provides actions for long term management and removal of mercury through the LWS.

Mercury Expert Advisory Panel Reviews

After completion of the Phase II scope, Mercury Expert Advisory Panel was reconvened to review SRR assessment of the mercury in the LWS and the proposed comprehensive action plan (Table 1) for long term management and removal of mercury through the LWS.

Mercury Expert Advisory Panel report on the SRR assessment of the mercury in the LWS is provided as Attachment A. Panel recommendations are in agreement with the proposed comprehensive action plan provided in Table 1. Panel provided the following additional recommendations that were addressed in the comprehensive action plan.

- Reduction or elimination of new mercury discharges from H-canyon to the tank farm because it would benefit the mercury problem in the Tank Farm. *[SRR has not included this recommendation as the part of the comprehensive long-term action plan because SRR has no control over H-Canyon Operations.]*
- Develop a conceptual model for mercury in the LWS that is followed with a simple mass balance model based upon measured and observed process conditions. *[SRR has included this recommendation as a part of the comprehensive long-term action plan under Sampling & Monitoring.]*
- Add organic analyses for potential alkylating agents to the suite of mercury analyses. *[SRR analyzes total organic carbon for periodically for several vessels and has included this*

recommendation as a part of the comprehensive long-term action plan under Sampling & Monitoring.]

III. COMPREHENSIVE ACTION PLAN

A comprehensive action plan for the long-term management and removal of mercury is shown in Table 1. Recommendations for actions are categorized under the following three broad categories:

A. Plant Operations,
B. Technology Development, and
C. Sampling & Monitoring.

A. Plant Operations

This category includes actions that are necessary to manage/control and remove mercury from the Liquid Waste operating facilities.

DWPF

DWPF is the intended removal point in the overall LWS flowsheet for removal of mercury. Plant operations actions, based on the system engineering evaluation, to enable DWPF to re-establish this removal capability are included.

At DWPF, SMECT level indicator as well as mercury mass balance performed during SRAT and SME cycles indicates that significant amount of elemental mercury potentially resides in the SMECT and is not removed via MWWT. There are two key actions that are currently being executed. First action includes raising the pH of the SMECT condensate by progressively reducing the amount of nitric acid added to maintain the pH at the upper end of the allowable range. This will reduce dissolution of elemental Hg, hence limiting recycling of mercury to the tank farm. Second, establish mercury pumping capability from SMECT and/or MWWT to MPPC to purge the mercury from the LWS. Design modification of the existing mercury removal pump and associated jumpers along with other required modifications necessary to purge mercury from SMECT and transfer the contents to MPPC is continuing. Some of the key activities planned include:

Near-term Effort:

- Establish accurate mercury level measurement in the SMECT
- Develop a backup mercury level measurement method for the SMECT and other CPC tanks
- Clean and flush the MWWT (mercury and sludge mixture) to the SMECT
- Clean and/or replace the clogged reflux jumper from the MWWT to the SRAT
- Perform testing of material clogging the MPPC piping to determine how to flush the piping if it becomes necessary
- Establish a pumping path directly between the SMECT mercury sump and the MPPC
- Install MWWT piping bypass spool piece to replace MWWT mercury pump
- Install a new jumper from the SMECT to the MWWT bypass spool piece
- Install existing jumper from the MWWT bypass spool piece to the MPPC connection in the CPC

- Install existing water / acid wash jumper to the MWWT bypass spool piece to preserve the MWWT cleaning / flushing capability
- Test the permanently installed piping between the CPC and the purification cell to ensure that it is clean. Flush the piping if it isn't clean
- Replace the MPPC lights in anticipation of future cell work
- Pump single pump content (1.7 gallons) from the SMECT to the Mercury Acid Wash Tank (MAWT) in the MPPC
- Take a sample from the MAWT, remove it from the purification cell, and have it tested for compliance with disposal WAC requirements

Mid-Term Effort:

- Based on the test results from the sample, determine what functionality is required from the MPPC
- Develop a plan to clean the MPPC and a design to make it as functional as required
- Determine shipping requirements for off-site processing and disposal
- Install a revised SRAT camera to help minimize carryover events from the SRAT to the MWWT / SMECT.
- Implement required refurbishment / modification of the purification cell.
- Begin pumping and shipping mercury in quantity.

Tank Farm / ETP Actions

At Tank Farm (TF), SRR has initiated a program[12] to confirm that episodic and fugitive emissions are not occurring at waste tanks; this effort is a result of the Hanford Tank Farm Vapors issue and ensures similar issues do not exist at SRS. Currently, IH mercury controls for SRR are based on the conservative assumption that all measured mercury vapors are dimethyl mercury which is used to set the SRR administrative control limit (ACL) of 0.008mg/m^3. Exposures above the ACL require supplied air respiratory protection. In contrast, the 8-hr threshold limit value for dimethyl mercury is 0.01mg/m^3 (the level to which it is believed a worker can be exposed day after day for a working lifetime without adverse health effects). Key mercury vapor related activities tracked in STAR[13] include:

- Develop a plan to perform nearly continuous monitoring of mercury vapor concentrations on waste tank tops to help confirm that SRS is not experiencing episodic or fugitive emissions that could put personnel at risk from tank vapors. Monitoring plan issued March 2016. Issue report August 2017.
- Develop and conduct a training briefing to ensure that personnel understand the mercury vapor hazard, especially for waste tanks with high concentrations of mercury vapors. Issue training package September 2016.
- Develop and conduct training for Cognizant System Engineers for ventilation Systems to ensure that they understand the liquid vapor management program and how their systems impact the program and help protect personnel from chemical vapor hazards. Issue training package September 2016

- Enhance existing procedure for responding to potential chemical vapor exposures. Target September 2016.
- Enhance participation of Industrial Hygiene in the Consolidated Hazards Analysis (CHA) process. Completed June 2017.
- Evaluate process used for pre-job and post-job radiological reviews. Determine if this process can be implemented for pre-job and post-job IH reviews. Competed January 2016.
- Establish and implement a methodology for communicating exposure information to other members of similar exposure group. Target December 2016.
- Update SEG rosters and implement a system to provide for regular updates to SEG rosters. Target October 2016.
- Review Employee Notification Reports for changes to make reports simpler and clearer. Complete June 2016.

ETP treats low level contaminated effluent from Tank Farm, Tritium, & Canyons and transfers to Upper Three Runs Creek and ultimately to Savannah River. Effluent is known to contain mercury with the Tank Farm Evaporators Overheads being the major source. In September 2015, IH personnel observed mercury vapors in some locations of the process room exceeded the SRR action limit of 0.008 mg/m^3. A path forward was developed to aid in mitigating the higher levels of mercury vapor. SRR is continuing to address actions outlined in the path forward[11] to reduce mercury vapor in the ETP facility. IH surveys indicated three potential problem areas – Process Building Sumps, Organic Removal Area, and Evaporator Feed Tanks. Majority of the 23 action items outlined in the path forward are expected to be completed by End of FY 2016. IH has increased monitoring of mercury vapors during operations and maintenance activities. IH Escort is required for entry into process areas and if there is sustained mercury reading above 0.008 mg/m^3 a supplied breathing air respiratory protection is required.

To minimize mercury vapor exposure to personnel and/or address mercury equipment related issues, additional good practices adopted by the SRR include:

- SRR conducts air dispersion modeling to determine proper stack heights to minimize mercury vapor exposure to the personnel during in-tank waste processing,
- SRR is incorporating Evaporator design changes (installation of sight-glass) to monitor mercury collection level,
- SRR evaluates, as needed, deposits in process systems that may be mercury related compounds[15,16] , and
- SRR routinely performs assessment of components. Frequency of preventive maintenance and /or replacement is described in the System Health Plans.

Mercury attack on aluminum components is well established. During oxalic acid cleaning of the sludge heel in Tanks 5F/ 6F, corrosion products primarily consisting of aluminum hydroxide along with a small quantity of mercury were observed in the ventilation stack. The major source of corrosion products was from the reaction between aluminum duct/stack extension and NOx vapors during oxalic acid cleaning process and to a limited extent from mercury attack on aluminum[17]. To minimize such occurrences, SRR developed guidelines based on a material compatibility evaluation[18] for the waste tank ventilation materials. During Tank 12H oxalic acid cleaning, degradation in flow was observed on the inlet side of the re-heater. Sample analysis[19] indicated that the deposits on the re-heater were predominately mercury

and tin. Lack of any aluminum corrosion products was due to the absence of aluminum in the Tank 12H ventilation ductwork construction. The tin coating on the re-heater stainless steel fins was most likely attacked by mercury. The formation of tin oxide along with the mercury solids potentially contributed to the plugging of re-heater. X-ESR-H-00590[20] provides options to help mitigate mercury during any future oxalic acid cleaning campaigns. An action item is added to the Comprehensive Action Plan for future oxalic acid cleaning of waste tanks. For Tank 37 the sample analysis of the re-heater indicated significant destruction of aluminum fins by mercury. The failure was attributed to the Type II pitting of the inner copper tube of the re-heater. This was not a result of acid cleaning of waste tank.

LWS System Planning and Processing Actions

Mercury speciation analysis at key processing locations in the LWS has indicated significant presence of organomercury compounds especially MeHg in the recycling stream within the LWS. Formation of MeHg probably occurs during the SRAT cycle where mercury is steam stripped. However, due to the presence of antifoam agents which decomposes into methyl ions results in the formation of MeHg. Small quantities of MeHg could also form in during SME boildown as well as evaporator operations depending on the presence of organic carbon. In addition, speciation analysis shows that majority of the mercury released from the saltstone during TCLP test is MeHg. Therefore, to keep the saltstone below the hazard waste limit of 0.2 mg/L, management of MeHg in the LWS is critical. Currently during salt batch preparation, the amount of recycle is managed to avoid significant quantities of MeHg in any given salt batch.

SRR is also evaluating possibilities to reduce conservatism in the elemental mercury limit for saltstone feed as well as the DMHg limit that require sample analysis. Lastly, a longer term solution for DWPF recycle may be required versus using it for beneficial reuse to dissolve salt; this needs to be pursued if means to prevent organic mercury formation cannot be found.

B. Technology Development

The Technology Development activities discussed below are risk mitigation activities in case the mercury removal from the DWPF is not successful. These technologies may provide mercury removal at alternate purge points in the LWS. Mercury speciation analysis at key processing locations in the LWS has indicated significant presence of organomercury compounds especially MeHg. These studies confirmed that mercury is recycling within the LWS. During the Phase I and II studies, SRR identified several purge points that can be used for removing mercury from the system. However, SEE indicated that to effectively make use of these as mercury purge locations require technology development. Five key technologies listed in Table 1under Technology Development were proposed to the DOE-EM for funding. DOE-EM has funded the following three programs at SRNL.

- First program is examining potential chemistries/technical approaches e.g. UV-C photoreactor on Tank 50 that would convert the organomercury species to mercuric ions and down select to one to two probable technologies and perform an initial round of testing with the goal of selecting one technology for development and demonstration.
- Sampling results indicate that 2H Evaporator feed/drop tanks have substantial amount of ionic mercury. This program is examining potential chemistries/technical approaches that would convert the ionic mercury species to elemental mercury and down select to one to two probable

chemical additives such as $SnCl_2$ or H_2O_2, and perform an initial round of testing with the goal of selecting one additive for development and demonstration.

- Mercury is believed to be in the form of mercury oxide in sludge. There is evidence for oxide in sludge but there is no definitive data that all of the mercury is in the form of mercury oxide. Other species could be present such as elemental mercury, mercuric sulfide, etc. These different forms may have different behavior across the DWPF flowsheet. This program would subject sludge to a number of contacts with differing inorganic solvents which would preferentially extract specific mercury species. The task would quantify up to ten different potential mercury species.

There were two other programs, though important technologies for SRR were not funded at this time. These include:

- Wilmarth[21] showed that GT-73 was stable in the alkaline tank wastes and was effective at removing mercury in the form of mercuric ion from a simulated waste matrix and showed lower removal distribution coefficient when tested in low mercury containing actual waste sample. This task would evaluate application of GT-73 or similar resins to remove organomercury species and develop the basic data needed to design a deployable mercury removal system.
- Mercury getters for the organomercury species will be examined to enhance the retention of mercury in the grout matrix. Potential additives would be tested to ensure the retention of mercury but also to ensure there are impacts to the other important properties of the grout, e.g., set time, compressive strength, etc. Once potential candidates are identified and shown to be successful at improving the retention of mercury during TCLP testing, testing with actual waste would be conducted.

In addition, a task was added to the Table 1 to determine maximum concentration of MeHg that can be present in the saltstone grout without failing TCLP criteria of 0.2 mg/L for hazardous waste landfill disposal limit.

Technology development also includes a program to develop alternatives to the existing DWPF anti-foam to both minimize formation of flammable degradation products and mitigate the creation of organic mercury compounds. SRR has included this recommendation as a part of the comprehensive action plan for completeness. Scope is being executed outside the mercury program.

In addition, the following three basic science topics were proposed to the DOE-EM for FY17 funding.

- Elucidate mechanism and kinetics of the transformation of ionic mercury into organomercury compounds in complex waste solutions
- Elucidate vapor phase reaction chemistry of mercury
- Elucidate mechanism and kinetics of the conversion of organomercury into inorganic mercury in complex waste solutions

C. Sampling and Monitoring

This category focuses on monitoring mercury concentrations in the LWS. Sampling needs are included. Sampling and Monitoring is an integral part of the long-term management and removal of mercury in the LWS to ensure that the nature (form and amount) of mercury and/or collection points is not changing as new sludge and salt batches are processed through the LWS or significant flowsheet changes are introduced such as glycolic acid flowsheet.

Sampling & monitoring also includes an action item to support development of conceptual and/or mass balance based models that can be used for predicting trends in the overall LWS, and to assess the effectiveness of the proposed new and improved mercury purge points. Model could be used to assess locations of largest mass of undesirable mercury species and provide path for future data collection efforts.

Also included in this category is another important action item to develop in-house capability to measure organomercury in the samples. SRNL has procured the equipment for measuring organomercury and plans to conduct cold-testing in FY17.

Key locations identified as potential monitoring points for mercury include

- DWPF – Mercury in SRAT vessel after concentration
- Evaporator System – Mercury collection from evaporator system
- Tank Farm – Mercury speciation in salt batch qualification sample
- Saltstone – Mercury in Tank 50 sample and Tank 50 saltstone TCLP leachate
- MCU – Mercury in solvent sample

Others sampling locations may be added, if needed.

IV. RISK

Project risks were reviewed to determine if any new risks or changes to existing risks and risk handling strategies were required based on the LWS mercury behavior evaluation discussed in this report. Currently the SRR Risk & Opportunity Management Plan[22] (ROMP) has the following four risks associated with mercury:

- Risk 435– High Mercury in Sludge Impacts Processing at DWPF
- Risk 461 – Additional requirements imposed on Tank Farm operation due to Hanford vapor issues
- Risk 463 – Increased Level of Mercury in Saltstone Grout
- Risk 466 – Increased Levels of Mercury in HLW System Creates Industrial Hazards

As part of the ongoing Risk Management Program, the Risk Register is updated to reflect the current status of the risk handling strategies associated with the above risks. In this process the risks were reviewed and updated to align with the Comprehensive Action Plan. In addition a new risk “Risk 485 – Increased Levels of Organomercury on LW Operations” was added to the Risk Register. Revised and new risk handling strategies are tracked in the Site Tracking and Analysis System (STAR).

Table 2. Status of Identified Gaps in Current Understanding of Mercury Behavior in the LWS (Phase I)

	Issue/Recommendation	Facility	Resolution Remarks	Status
1	Investigate and document Analytical Methods used at the ETP for Hg analysis	ETP	Completed - Covered in presentation Hg Analytical Methods used at SRS	Close[redacted]
2	How many ETP transfers were made from WCHT to Tank 50 between Dec-14 and March-15	ETP	None. It was Verified using the Process Information Management System (PIMS)	Closed
3	Evaluate need to pull the sample from WCHT for Hg Speciation and data comparison	ETP	WCHT sample was pulled on 3/16/15 and sent to Eurofin for Hg Speciation Analysis[23]	Closed
3a	What species to analyze for Organo Hg? ETP Timeline, History Mercury Column Change out, carbon beds	ETP	Total Hg, Ionic Hg, Dimethyl Hg, Methyl Hg, elemental Hg, and Ethyl Hg	Closed
4	Investigate High Hg peak in 2006	ETP	Two off normal influents, R-basin trucked transfers and an H-Canyon upset were the cause for the Hg peak	Closed
5	What type of Hg, mercury columns remove?	ETP	GT-73 removes ionic mercury; some evidence it may remove organomercury[21]	Closed
6	Estimate mass of Hg from resin removed in the past	ETP	Data is not available- Not relevant for this team-	Closed
7	Do you measure Hg in Treated Water Storage Tanks?	ETP	Yes. Below detection limit.	Closed
8	Understand resin regeneration Solution Stream	ETP	There is no regeneration. GT-73/GT-74 is disposed of once the column is loaded with radioactivity	Closed
9	Document equipment problems related due to Hg	ETP	Completed - No Hg related equipment problems at ETP	Closed
10	Investigate and document WCT peak in Hg between 2011 and 2013	ETP	Information not needed.	Close[redacted]
11	Interpret CME (carbon mid data) data	ETP	Complete. Email dated 10/14/2015 from Eric Harrison. Information stored: PITDATA:\HG TEAM 2015	Close[redacted]
12	Revise ETP Block diagram to show pH changes and Hg flow in the process	ETP	Not Needed.	Closed
13	Why there is 86% mercury removal in the ETP process? Reexamine the data presented and investigate any process upsets	ETP	At this time, this information is not needed.	Closed

	Issue/Recommendation	Facility	Resolution Remarks	Status
14	Pull the SRAT sample during the caustic boiling step of the SRAT cycle while PRFT material is added.	DWPF	Pulled samples during SRAT #738 caustic boiling	Close[redacted]
15	Several samples would be pulled and set off to the side of for shipment to SRNL and then to Eurofins for Hg speciation[1].	DWPF	Pulled samples during SRAT #738 caustic boiling	Closed
16	Pull the SMECT samples during different steps of the SRAT Cycle (SRAT Batch # 735)	DWPF	Pulled samples during SRAT #738 caustic boiling	Closed
17	Pull the SMECT samples during different steps of the SME Cycle (SRAT Batch # 735)	DWPF	Pulled samples during SRAT #738 caustic boiling	Closed
18	Pull the OGCT baseline and prior to transfer to RCT samples (SRAT Batch # 735)	DWPF	Pulled samples during SRAT #738 caustic boiling	Closed
19	Pull RCT baseline and prior to Tank Farm transfer samples (SRAT Batch # 735)	DWPF	Pulled samples during SRAT #738 caustic boiling	Closed
20	Document the DWPF Lab results of the analyzed samples of the vessels listed in action item 14 thru 19 (SRAT Batch # 735)	DWPF	Completed (Analytical Results for the condensate samples for SRAT Batch 735[24])	Closed
21	Determine what samples needs to be sent to Eurofins and SRNL for Hg Speciation(SRAT Batch # 735)	DWPF	Completed[24]	Closed
22	Complete the time- line of hand written chart on Visio/ Power Point software	Sludge and Salt Batch Transfer History	Completed. Figure 7 of Reference 4	Closed
23	Come up with the plan to incorporate sub-component with the time line	Sludge and Salt Batch Transfer History	Completed- Plan has been developed	Closed
24	Receive the data from all presenters to input into the plan	Sludge and Salt Batch Transfer History	All the required information for the assessment of mercury in the LWS obtained	Closed
25	Input the data as per the developed plan and link it to time line	Sludge and Salt Batch Transfer History	Data not linked to time-line yet. However, the data has been collected and placed in the PITDATA folder. Required information for mercury assessment obtained.	Closed

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

	Issue/Recommendation	Facility	Resolution Remarks	Status
26	Determine fraction of DWPF recycle in each Salt Batch	Sludge and Salt Batch Transfer History	Figure 6 of Reference 4. PITDATA:\HG TEAM 2015\Shah\Presentations and Action Items\Action Items Database	Closed
27	Investigate the need to sample 2H ECP sample for Total Hg/ soluble?	TK 22, 41 and RCT	Completed –No Need to analyze Total Hg/Soluble Hg for 2H ECP Sample. Email from Christie Sudduth	Closed
28	Investigate the need to sample 3H EFQ sample for Total/ Soluble Hg?	TK 22, 41 and RCT	Not Needed	Closed
29	Obtain Tank 41 sample for Total and Soluble Hg data (part of Salt Batch 9 make-up)	TK 22, 41 and RCT	Completed[25]	Closed
30	Obtain Tank 13 sample for Total and Soluble Hg data (may be a recommendation from 2H/ 3H/ 2F Presentation)	TK 22, 41 and RCT	Completed[26]	Closed
31	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	TK 22, 41 and RCT	Completed[27]	Closed
32	Investigate the feasibility of sampling RCT for TOC? Formate?	TK 22, 41 and RCT	RCT: Formate and TOC are analyzed for on every 10th batch (batches ending in 0s)	Closed
33	Obtain RCT soluble Mercury data and Track soluble and Total Hg in the RCT (Long Term)	TK 22, 41 and RCT	Added in the Sample Schedule. RCT-8 has mercury data as required once a month. Hg Speciation Data: References [28] and [29].	Closed
34	Obtain Tank 22 sample for Soluble Hg Data	TK 22, 41 and RCT	Samples were pulled on 3/23 and received by SRNL	Closed
35	Obtain TK 22 sample for Hg Speciation	TK 22, 41 and RCT	Samples were pulled on 3/23 and received by SRNL	Closed
36	Include samples from source tanks for soluble and total Hg that is used for salt batch make up.	TK 22, 41 and RCT	Sampling complete	Closed
37	Check TOC analytical data of Salt Batch # 3	Salt Batch Make up and TK 49	Based on blend Calculation	Closed
38	Check Phenol analytical data of Salt Batch # 3	Salt Batch Make up and TK 49	Based on blend Calculation	Closed
39	Compare Tank 50 TCLP Hg data vs Salt Batch Hg	Salt Batch Make up and TK 49	Complete[30]	Closed
40	Document a narrative of Tank 50 TCLP Hg data vs Salt Batches Hg	Salt Batch Make up and TK 49	Complete[30]	Closed

	Issue/Recommendation	Facility	Resolution Remarks	Status
41	What % of DWPF recycle is in each sludge/ salt Batches? Show the data on pie chart batches Vs volumes	Salt Batch Make up and TK 49	Figure 6 of Reference 4. PITDATA:\HG TEAM 2015\Shah\Presentations and Action Items\Action Items Database.	Closed
42	Look into using membrane grade Caustic for the wash (impurities with electrolysis i.e. HgCl process a main concern)	241-96H and MCU	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.	Closed
43	SRNL to investigate any possibility of Hg in Boric Acid manufacturing	241-96H and MCU	Univar Vendor confirmed no mercury in boric acid	Closed
44	MCU is lacking Hg Data- Analyze SEHT, DSSHT, and SHT data and evaluate path forward	241-96H and MCU	Completed- Issued a memo[31] for the strategy to pull SSFT, SHT, SEHT and DSSHT samples for Salt Batch 7 @MCU	Closed
45	Quantify solvent degradation losses	241-96H and MCU	Complete[32]	Closed
46	Perform more thorough literature review of MCU process chemical interactions with various forms of Hg	241-96H and MCU	Accumulated enough information from the Hg speciation samples taken for MCU[33,34]	Closed
47	Is antifoam added to GPE bottoms?	H-Canyon to TK 39, 50, or 51	They have it in the past. Not used routinely.	Closed
48	Evaluate a need to analyze SRE stream for Total Hg, soluble Hg, and Hg speciation.	H-Canyon to TK 39, 50, or 51	Information is no longer required	Closed
49	Evaluate a need to analyze GPE Bottoms for Hg speciation.	H-Canyon to TK 39, 50, or 51	Total Hg was <0.36 mg/ L so it was decided not to analyze for Hg Speciation	Closed
50	Analyze Tank 39 supernate for soluble Hg and Hg speciation	H-Canyon to TK 39, 50, or 51	Completed[35]	Closed
51	Refine Historical Information as needed	H-Canyon to TK 39, 50, or 51	All required information for assessment obtained	Closed
52	Investigate why SRE batch 3, 4, 5 and 6 flowsheet now require more mercury	H-Canyon to TK 39, 50, or 51	Completed[36]. Modified SRE Dissolution Flowsheet.	Closed
53	Prepare a bar chart for Canyon Hg discharge over time	H-Canyon to TK 39, 50, or 51	Completed	Closed
54	Review Tom Britt's calculation that provided the basis to remove MMHg and DMHg Limits in Saltstone WAC	TK 50	Saltstone DSA[37] updated and technical basis[38]	Closed

	Issue/Recommendation	Facility	Resolution Remarks	Status
55	When salt batch make up started using Tank 41?	TK 50	Salt Batch 1had dissolved Tank 41 (720 kgal); Salt Batch 3 and 4 had some volume of Tank 41; and Salt Batch 5 had Tank 41 salt dissolution using DWPF recycle via Tank 23.	Closed
56	When Tank 41 started receiving DWPF recycle?	TK 50	After June 2010. During Salt Batch 3 processing	Closed
57	Standardize Hg analytical methods and what to analyze for DWPF, RCT, Tank 22, Tank 50, WCHT, DSSHT etc. ...for total and soluble Hg	TK 50	Discussed in Eurofin reports and DWPF flowsheet report[6]	Closed
58	Review Salt Batch 1 SRNL analytical data	TK 50	Not Required	Closed
59	Evaluate a need to determine Hg gradient in TK 50	TK 50	Depth samples from Tank 50 can't be obtained at this time	Closed
60	Evaluate results of Hg speciation analysis and SRNL variability studies and determine impact on Saltstone WAC	TK 50	Completed[39, 40]	Closed
61	Evaluate results of Tank 21 TCLP test to determine potential impacts from processing Salt Batch 8	TK 50	Completed[41]	Closed
62	Obtain Salt Batch 9 source tank samples to determine Hg concentration	TK 50	Completed	Closed
	a. Tank 23 samples to be obtained after completion of Tank 37 salt dissolution transfers into Tank 23	TK 50	Completed	Closed
	b. Tank 8 sample to be obtained	TK 50	Completed	Closed
	c. Tank 41 sample to be obtained	TK 50	Completed	Closed
63	Evaluate need to add TCLP testing to salt batch qualification (Based on Salt Batch 8 results)	TK 50	WAC has been revised to add TCLP testing if exceeds defined criteria	Closed
64	Analyze LWHT for soluble Hg and Hg Speciation. Also, have LWHT sample filtered and analyzed for Hg	512-S and Filter Cleaning	Hg Program team determined that there is no need for these samples because downstream process (MCU) information is available	Closed
65	Analyze LWPT for soluble Hg and Hg Speciation.	512-S and Filter Cleaning	Hg Program team determined that there is no need for these samples because downstream process (MCU) information is available	Closed
66	Identify if any sample left of LWPT-3(LWPT sample after filter cleaning) that can be analyzed for Hg Speciation	512-S and Filter Cleaning	Hg Program team determined that there is no need for these samples because downstream process (MCU) information is available	Closed

	Issue/Recommendation	Facility	Resolution Remarks	Status
67	Determine Wt% of Hg in LWPT-1, 2 and 3 (2013 samples) are on insoluble or Total solids basis.	512-S and Filter Cleaning	Completed	Closed
68	Determine Hg in LWPT Samples pulled after completing Cycle 1 of salt batch 7B (2014)	512-S and Filter Cleaning	Hg Program team determined that there is no need for these samples because downstream process (MCU) information is available	Closed
69	What happens to Hg when the SMECT liquid is brought into caustic precharged RCT Heel?	DWPF and Sludge Batches (TK 40)	SRAT Batch 735 Samples have been sent to Eurofins for Hg Speciation Analysis	Closed
70	Should RCT be sampled for Hg (Total and Soluble) before the contents are transferred to Tank Farm?	DWPF and Sludge Batches (TK 40)	Continue with periodic sampling as currently planned	Closed
71	Pull Hg data of RCT during the cold runs	DWPF and Sludge Batches (TK 40)	Information not needed. Additional tank sampling was performed.	Closed
72	Redo the SMECT and RCT sampling during the SRAT and SME runs soon after the DWPF comes out of outage	DWPF and Sludge Batches (TK 40)	Completed[24]	Closed
73	Hg measurement for SRAT influent and Product	DWPF and Sludge Batches (TK 40)	Sampled and analyzed SRAT 738	Closed
74	RCT/ SMECT samples pulled for SRAT Batch 735 to be sent to SRNL for refrigeration	DWPF and Sludge Batches (TK 40)	Completed	Closed
75	Evaluate a need to send these (SRAT-735) samples to Eurofins for Hg speciation	DWPF and Sludge Batches (TK 40)	Completed. Samples sent to Eurofins.	Closed
76	Where is the air sparger located in the SMECT? Do air/ nitrogen have any impact on Hg Chemistry?	DWPF and Sludge Batches (TK 40)	Sparger is 2” from bottom of the tank.	Closed
77	What is the impact of antifoam and solvent degradation products on Hg speciation for DWPF recycle streams?	DWPF and Sludge Batches (TK 40)	SRAT 736 and 738 samples have been sent to SRNL[6]	Closed

	Issue/Recommendation	Facility	Resolution Remarks	Status
78	Why Hg is present in the two SEHT sample results?	DWPF and Sludge Batches (TK 40)	Discussed in Reference 5	Closed
79	Analyze PRFT sample to determine Hg	DWPF and Sludge Batches (TK 40)	Do not need it	Closed
80	Clean/ Replace the scrubber baskets to reduce the high delta P observed for SME and RCT/ MFT Scrubbers	DWPF and Sludge Batches (TK 40)	Included in Comprehensive Action Plan (Table 1)	Closed
81	Spare Hg pumps should be made available	DWPF and Sludge Batches (TK 40)	Pump is being repaired. Included in Comprehensive Action Plan (Table 1)	Closed
82	Sample and analyze the solids plugging the vessels in the Hg purification cell	DWPF and Sludge Batches (TK 40)	Samples sent to SRNL for analyses. Will be part of restoration of MPC (#83)	Closed
83	Restore operation of the Mercury Purification cell	DWPF and Sludge Batches (TK 40)	Included in Comprehensive Action Plan (Table 1)	Closed
84	Tank 37 Back flush valve corrosion- Was it attributed to Hg? Any evidence from SRNL testing?	2H, 3H and 2F Evaporators	There are no sample results	Closed
85	Investigate components degradation of 2H/ 3H systems due to Hg	2H, 3H and 2F Evaporators	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.	Closed
86	Pull the sodium aluminum silicate (NAS) data from the scale sample reports and determine Hg	2H, 3H and 2F Evaporators	Not Needed	Closed
87	Pull the process History on 1F/ 2H Systems	2H, 3H and 2F Evaporators	Complete. Assessment stored PITDATA:\HG TEAM 2015	Closed
88	When did we stop using antifoam in the Evaporators?	2H, 3H and 2F Evaporators	No antifoam has been used since 2003.	Closed

	Issue/Recommendation	Facility	Resolution Remarks	Status
89	Review SRNL report to determine whether Tank 38/ 43/ 51 samples for Hg were digested/ undigested and filtered?	2H, 3H and 2F Evaporators	Tank 38 and 43 samples were NOT filtered. Both 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.	Closed
90	Investigate 2H overhead Hg number. What analytical method was used at ETP? Digested/ undigested/ Filtered	2H, 3H and 2F Evaporators	The overhead samples analyzed at ETP are not filtered. A digested CVAA analysis is performed. This method has been used since the 1990s	Closed
91	Steam flow relation to Hg collected in 2H and 3H	2H, 3H and 2F Evaporators	Complete. Assessment stored PITDATA:\HG TEAM 2015	Closed
92	Look at 2H/ 3H Hg over heads volumes to ETP and compare to Hg collected from the MRT	2H, 3H and 2F Evaporators	Complete. Assessment stored PITDATA:\HG TEAM 2015	Closed
93	Perform digested analyses on tanks that are a part of the evaporators systems (Tanks 39, 32, 37, 30, 29, 51, 26, 25 and 44)	2H, 3H and 2F Evaporators	Tank 39 results are documented in Reference 35. Other listed tanks will not be sampled	Closed
94	Draw correlations between the undigested results in WCS and digested results then update WCS accordingly	2H, 3H and 2F Evaporators	All analysis were digested	Closed
95	Investigate Higher mass of Hg in 2H overheads	2H, 3H and 2F Evaporators	Complete (same as #92). Assessment stored PITDATA:\HG TEAM 2015	Closed

Table 3. Status of Open Issues/Recommendations from Mercury Flowsheet Reviews (Phase II)

#	Issue/Recommendation	Source Document	Facility	Status	Action Plan	Priority
1	Evaluate if chemical consequences are bounding (DWPF)	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	DWPF	CLOSED	Analyzed volatilization & flammability characteristics of Hg and organic Hg compounds[38]. Requires functioning Hg removal system[6].	
2	Evaluate if chemical consequences are bounding (saltstone)	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	Tank Farm	CLOSED	Analyzed volatilization & flammability characteristics of Hg and organic Hg compounds[42]	
3	Ensure DMHg is addressed in saltstone flammability	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	Saltstone	CLOSED	Analyzed volatilization & flammability characteristics of Hg and organic Hg compounds[42]	
4	Define risk when using Tank 21 TCLP as basis for salt batch transition	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	Saltstone	CLOSED	Compared saltstone samples prepared with Tank 21 and Tank 50 solutions and measured TCLP release[5]	
5	Develop a position for >500 mg/L soluble Hg in Tank Farm	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	DWPF	CLOSED	Speciation studies show high-levels of soluble mercury in feed/drop tanks[7]. Requires Technology Development for long-term Hg management (see Table 1)	
6	Evaluate Pu concentration in DWPF recycle against NCSE	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	DWPF	CLOSED	N/A	
7	Determine if other metals (e.g. Cr) are changing and could impact LW flowsheet	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	Tank Farm	CLOSED	Reviewed - no significant changes were observed between previous salt batches	
8	Determine if Hg solids are concentrating in Tank 50 due to Isopar mixing strategy and impacting Hg concentration in the feed to saltstone or sample concentration	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	Tank Farm	CLOSED	Hg speciation data indicates that there is no significant concentration of Hg species in the salt processing flowsheet[5]	

#	Issue/Recommendation	Source Document	Facility	Status	Action Plan	Priority
9	Evaluate if Saltstone dry feeds are contributing to the TCLP variability	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	Saltstone	CLOSED	No dry feed variability study needed. Speciation data indicate MeHg accounts for almost all the Hg released during TCLP[5].	
10	Evaluate changing Saltstone permit to not require LDR limits at Saltstone	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	Saltstone	CLOSED	SCDHEC clarified – SRR is required to meet mercury hazardous waste limit of 0.2 mg/L[43]	
11	Determine best locations for Hg to be purged from the LWS	Hg Flowsheet Extent of Condition Review (Phase I Report[4]	LWS	CLOSED	Two SEE completed - identified various Hg purge points[8,9]	
12	Develop/justify how DMHg liquid samples are used to predict vapor space concentration	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	LWS	CLOSED	Used procedures identified by Eurofins	
13	Institute statistical process control methodology to identify changes early	Hg Flowsheet Extent of Condition Review (Phase I Report[4])	LWS	CLOSED	Long term monitoring plan at key locations provided in Table 1	
14	Develop a long-term sampling plan	Expert Panel Review (Phase I Report[4])	LWS	CLOSED	Sampling plan will be coordinated with the Comprehensive Action Plan (Table 1)	
15	More attention should be focused on DWPF recycle, evaporators and feed to saltstone	Expert Panel Review (Phase I Report[4])	LWS	CLOSED	Phase II reports focused on salt processing[5], DWPF[6] and Evaporators[7]	
16	Focus on alternate methods for Hg recovery from evaporators; solids removal/Hg removal from DWPF recycle	Expert Panel Review (Phase I Report[4])	LWS	CLOSED	Completed SEE which identified various Hg purge points and technologies[9]	
17	Organic is the main driver behind the increased soluble Hg concentration	Expert Panel Review (Phase I Report[4])	LWS	CLOSED	Confirmed via speciation studies[7,8,9]	

#	Issue/Recommendation	Source Document	Facility	Status	Action Plan	Priority
18	Pour fresh saltstone in the vault and measure DMHg	Expert Panel Review (Phase I Report[4])	Saltstone	CLOSED	Measured DMHg very small in Tank 50 compared to MeHg[5]. No action required to measure DMHg in saltstone vault.	
19	Develop in-house capability to measure organomercury. Lower dilution and could use headspace analyses to determine DMHg	Expert Panel Review (Phase I Report[4])	LWS	CLOSED	SRNL is procuring an instrument to measure organomercury species. Included in Comprehensive Action Plan (Table 1).	
20	Organomercury flammability evaluation	Expert Panel Review (Phase I Report[4])	LWS	CLOSED	Analyzed volatilization & flammability characteristics of Hg and organic Hg compounds[38]	
21	SRR negotiate with State to raise the limit above the current limit driven by LDR	Expert Panel Review (Phase I Report[4])	Saltstone	CLOSED	Same as #10	
22	Pursue particle size effect on TCLP	Expert Panel Review (Phase I Report[4])	Saltstone	CLOSED	Adopted removal of fine particles via sieving[39,40]	
23	Run certified laboratory-to-laboratory comparison on select tank samples for Hg speciation variability	Expert Panel Review (Phase I Report[4])	Saltstone	OPEN	Comparison between Eurofins and Brook Rand planned. Included in Comprehensive Action Plan (Table 1).	M
24	Analyze previous salt batches and correlate with Hg concentrations and observed Tank 50 results	Expert Panel Review (Phase I Report[4])	Tank Farm	CLOSED	Complete - No correlation was found.	
25	Provide Hg removal step (e.g. GT-74) before Tank 50 or decompose organomercury going to saltstone	Expert Panel Review (Phase I Report[4])	LWS	OPEN	Completed SEE which identified various Hg purge points and technologies[9]. Included in Comprehensive Action Plan (Table 1) as recommendation to EM for funding.	H

#	Issue/Recommendation	Source Document	Facility	Status	Action Plan	Priority
26	Removal of ionic Mercury via reductant with a chemical additive to the evaporator (2H) system to enhance current mercury removal	LWS SEE Report[9]	Tank Farm	OPEN	EM 30 Technology Development Funded a program to develop the technology. Included in Comprehensive Action Plan (Table 1).	H
27	Removal of organic mercury via photoreaction (Tank 50)	LWS SEE Report[9]	Tank Farm	OPEN	EM 30 Technology Development Funded a program to develop the technology. Included in Comprehensive Action Plan (Table 1).	H
28	Develop methods to measure mercury in sludge	LWS SEE Report[9]	Tank Farm	OPEN	EM 30 Technology Development Funded a program to develop the technology. Included in Comprehensive Action Plan (Table 1).	H
29	Hg Absorbents/Ion exchange for organomercury	LWS SEE Report[9]	Tank Farm	OPEN	Not funded. Included in Comprehensive Action Plan (Table 1).	M
30	Mercury getters as additions to grout formulations	LWS SEE Report[9]	Saltstone	OPEN	Not funded. Included in Comprehensive Action Plan (Table 1).	M
31	Deploy methods to removal elemental Hg from the process tanks (opportunistic)	LWS SEE Report[9]	Tank Farm	OPEN	Not funded. Included in Comprehensive Action Plan (Table 1).	L
32	DMHg could be formed in contactors could be carried away with air purge and released. Measure DMHg in vent systems	Salt Processing Flowsheet Report[5]	MCU	CLOSED	Last measured in 2010. DMHg was at non-detect (< 0.000002 mg/m^3)	

#	Issue/Recommendation	Source Document	Facility	Status	Action Plan	Priority
33	MeHg may built up in solvent or strip effluent	Salt Processing Flowsheet Report[5]	MCU	CLOSED	Both concentration of Hg and volume of strip effluent are small compared to Tank 49 solution processed through ARP/MCU. SHT monitored on a monthly basis[44]. Captured in Sampling and monitoring section of the plan (Table 1)	
34	Raise pH in SMECT to minimize mercury solubility, and collect mercury primarily in the SMECT sump then pump out (repair or replace SMECT mercury pump)	DWPF SEE Report[8]	DWPF	OPEN	Action plan to reduce acid addition in small steps (5 gal) in progress[45]. Included in Comprehensive Action Plan (Table 1).	H
35	Re-establish existing system for mercury removal and purification	DWPF SEE Report[8]	DWPF	OPEN	Action plan to re-establish mercury removal and purification system via SMECT is in progress[45]. Included in Comprehensive Action Plan (Table 1).	H
36	Continue with the SRAT product analyses	DWPF Flowsheet[6]	DWPF	OPEN	Continue to sample future batches. Included in Comprehensive Action Plan (Table 1).	H

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APPENDIX A

Expert External Advisory Panel Review

Mercury Program Phase II

EXPERT EXTERNAL ADVISORY PANEL REVIEW

MERCURY PROGRAM PHASE 2

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Lucien M. Papouchado, Ph.D., Independent Consultant, GES
Dennis G. Jackson, P.E., Savannah River National Laboratory

AUGUST 16, 2016

Expert Advisory Panel Review Scope

Provide targeted suggestions, recommendations and insights on the proposed path forward and recommendations to address long-term management and removal of mercury from liquid waste system.

1. Liquid Waste System (LWS)
    a. Approach addresses the overall mercury behavior in the LWS
    b. Sampling of the system is sufficient to support long-term action plan
    c. Speciation data supports long-term action plan
    d. Path forward/recommendations provides adequate control on mercury reduction/removal from the LWS

2. Mercury Behavior in the Salt Processing Flowsheet
    a. Speciation data supports conclusions reached in the report
    b. Sampling of the system is sufficient to support long-term action plan
    c. Proposed technologies adequately addresses pathways for removal/reduction/conversion of mercury in the salt processing flowsheet
    d. ARP/MCU impacts are adequately analyzed

3. Mercury Behavior in the DWPF Mercury Flowsheet
    a. Speciation data supports conclusions reached in the report
    b. Sampling of the system is sufficient to support long-term action plan
    c. Proposed removal of mercury from SMECT instead of MMWT adequately addresses pathways for reduction/removal of mercury in the DWPF

4. Mercury Behavior in the Tank Farm Evaporators
    a. Speciation data supports conclusions reached in the report
    b. Sampling of the system is sufficient to support long-term action plan
    c. Proposed technologies adequately addresses pathways for removal/reduction/conversion of mercury in the TF Evaporators
    d. WAC controls adequate to protect high concentration of mercury in salt and/or sludge batches

EXTERNAL REVIEW TEAM CHARTER
MERCURY PROGRAM

JULY 28, 2016

At SRS 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). In 2015, a Mercury Program Team (MPT) was formed to evaluate mercury in the LWS and develop a comprehensive action plan for long term management and removal of mercury. Mercury Program Team divided the scope in two phases.

In Phase I, two major reviews were completed. 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.

Phase II activities looked at 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 MPT also recognized that since the designed mercury removal process located at the DWPF only had limited success during earlier sludge batches and substantial improvements may be required to bring the existing system back to its original operation, the team identified the best approach was the perform two separate System Engineering Evaluations (SEE). The first SEE was directed towards a recommended system to remove the majority of the mercury that is fed and reduced to its elemental form at the DWPF. The second SEE examined the remainder of the LWS (Tank Farm evaporator(s), MCU, Saltstone feed, etc.) and determine what system(s) could be put in place to supplement the system designed and operated at the DWPF.

The current Expert Panel Mercury Program Review Team is assembled to review and provide independent assessment of the Phase I and II activities and provide the MPT a proposed path forward/recommendations to address long-term management and removal of Hg from the LWS.

List of Presentations received:

- Fortenberry, K, RE Edwards, and V Jain. 2016. Evaluation and Impacts of Mercury in the SRS Liquid Waste System – Overview.
- Bannochie, CJ and WR Wilmarth. 2016. Mercury Related Technology Development Needs for Tank Waste.
- Bannochie, CJ, CL Crawford, DG Jackson, HB Shah, V Jain, JE Occhipinti, and WR Wilmarth. 2016. Mercury Phase II Study – Mercury Behavior across the High-Level Waste Evaporator System.
- Fellinger, TL and Bannochie, CJ. 2016. Phase II – Mercury Update for DWPF.
- Jain, V. 2016. System Engineering Evaluation – Reduce Mercury in LWS (Alternate to DWPF)
- Jain, V. 2016. Managing Mercury in LWS – Long Term Action Plan.
- Jain, V. 2016. Mercury Behavior During Salt Processing.

List of Reports received:

- Bannochie, CJ, CL Crawford, DG Jackson, HB Shah, V Jain, JE Occhipinti, and WR Wilmarth. 2016. Mercury Phase II Study – Mercury Behavior across the High-Level Waste Evaporator System. Savannah River National Laboratory, Report Numbers SRNL-STI-2016-00163 and SRR-STI-2016-00293, Savannah River Site, Aiken, SC 29808
- Jain, V, H Shah, CJ Bannochie, and WR Wilmarth. 2016. Mercury Phase II Study – Mercury Behavior in Salt Processing Flowsheet. SRR-CES-2016-00005, Rev.1. Savannah River Remediation, Savannah River Site, Aiken, SC 29808
- Fellinger, TL and CJ Bannochie. 2016. Phase 2 Report-Mercury Behavior in the Defense Waste Processing Facility. X-ESR-S-00279, Savannah River Remediation, Savannah River Site, Aiken, SC 29808
- Winship, G. 2015. Liquid Waste System Mercury Removal Study. Y-AES-G-00013, Rev.0, Savannah River Remediation, Savannah River Site, Aiken, SC 29808
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EXPERT PANEL REPORT

COMMENTS ON THE PRESENTATIONS:

- SRR provided excellent presentations with a lot of new work and results being presented.
- SRR followed up and addressed a large number of the panel recommendations from the Phase I review.

RECOMMENDATIONS SUMMARY:

- Develop a conceptual model for mercury in the LW system that is followed with a simple mass balance model based upon measured and observed process conditions.
- Expedite the current plan for on-site mercury speciation measurement capability.
- Proceed expeditiously with the TD plan to identify the mercury species in the H area sludge and sludge washes.
- Add organic analyses for potential alkylating agents to the suite of mercury analyses
- Pursue more stable antifoams for the pH conditions of the CPC but consider all upstream and downstream impacts.
- Add investigation of mercury removal ion exchange columns for methylmercury cation to the current program to use UV treatment of DSS.
- The Panel fully supports the MPT plan to bring the mercury recovery in DWPF on-line by March 2017. The amounts of mercury recovered from this system should be used in the conceptual and mass balance models.
- During outages, continue to remove mercury collected in sumps and feed into the conceptual and mass balance models.
- The Panel fully supports the MPT plan to improve the elemental mercury recovery at the tank farm evaporators. Use these amounts to feed into the conceptual and mass balance models.
- The Panel fully supports MPT's plan to continue the mercury vapor control and mitigation program at ETP.

OVERARCHING PROGRAM CONCLUSIONS:

- SRR has a reasonable path forward plan and should proceed expeditiously to implement the current MPT plan with an emphasis placed on bringing the DWPF Mercury Removal System on-line. In addition, the Panel would like the MPT to consider the additional recommendations provided in this report.
- The Panel agrees that sampling across the LW system is adequate and that mercury speciation data presented supports the conclusions presented to the panel.

- The Panel recommends adding organic analyses for potential alkylating agents to the suite of mercury analyses to better understand their distribution and contribution to formation of the organomercury compounds.
- Dr. Pierce on the Panel recommends developing a Conceptual Model for mercury in the LW system. He is prepared to provide follow-up instructions. Dr. Papouchado and Mr. Jackson recommend developing a simple mass balance model for mercury in the LW System. These developments are not intended to be independent activities and should be linked.

  Mass balance calculations should couple measured concentrations from key process points with flowrate data. While the analyses to date have adequately focused on the concentration of the various mercury species across all the LW unit operations, a mass balance across the unit operation or system is lacking. Both concentrations and mass balances are necessary to fully understand the system, to be able to predict trends in the overall system, and to assess the effectiveness of the proposed new and improved mercury purge points. The model should include all liquid (dissolved and elemental), vapor and solid (sludge) phases even if some of the phases are estimates.
- The measurement capability for mercury speciation is such an essential part of the success of this program that the panel recommends expediting the on-site mercury speciation measurement capability.
- It is obvious to the panel that the mercury chemistry in the LW system is very complex. However, a lack of complete understanding of all the reactions should not prevent SRR from capitalizing on the new and improved current purge points identified in their plan.
- SRNL should proceed expeditiously to identify the mercury species in sludge and any potential organomercury compounds released during sludge washing.
- Dr. Pierce recommended reduction or elimination of new mercury discharges from H-canyon to the tank farm because it would benefit the mercury problem in the Tank Farm. He understands that the amount is small relative to the existing mercury inventory, but it would still be beneficial to reduce that additional mercury input.

PANEL MEMBER OBSERVATIONS AND RECOMMENDATIONS RELATED TO SPECIFIC PROCESSES

The observations and recommendations include comments from individual panel members as a result of the one-day meeting and reviewing supporting documentation. Each of the observations and recommendations provided below are a combination of panel member inputs and may not represent a consensus panel view.

A- DWPF OBSERVATIONS:

- The plan to remove mercury from the SMECT is a good approach. Nitric acid additions should be tailored to minimize the amount of nitric acid added to the SMECT to minimize oxidation of elemental mercury present in the tank's sump and trench.
- The need identified by the MPT to restore the functionality of the MPC to allow collection and removal of mercury from DWPF is supported by the Panel. The restoration plan should be pursued with a high sense of urgency.
- The MPT states that the major source of methyl mercury returned to the tank farm from DWPF occurs in the CPC from reactions of mercury with antifoam degradation products. The panel agrees that this is the likely the source of the methyl-groups for MeHg formation.
- The question posed was if the recovery (and holdup) of mercury in DWPF from the current 40% were increased to the original flowsheet value of about 70%, would that resolve the higher concentrations of leachable methylmercury seen in Saltstone? It will improve this important purge point recovery of mercury at DWPF but it may not reduce the leachable methylmercury at Saltstone.
- The total contribution of the mercury to the DWPF coupled operations is less than 1% during Actinide Removal Process (ARP)/Modular Caustic Side Solvent Extraction (MCU) operations. This percentage increases to around 4% during Salt Waste Processing Facility (SWPF) operations. Based on speciation analysis, SE is also a source of methylmercury (MeHg+). The likely source of MeHg+ is the salt solution fed to ARP/MCU which contains a small fraction of DWPF recycle material.
- The majority of the reactions related to the mercury chemistry, presented in the Phase 2 mercury behavior report for DWPF, were consistent with the mercury analysis of the products and condensate streams. The exception to this was the reaction chemistry for the OGCT and the identification of methyl and ethyl mercury (via sample analysis) in the SMECT.
- The mercury mass balances performed during SRAT and SME cycles indicate that a significant amount of elemental mercury potentially resides in the SMECT and is not removed via the MWWT.

- The concentration of mercury in the OGCT appears to depend on the mercury reduction/strip efficiency of the Chemical Process Cell (CPC) [i.e. SRAT and SME processing]. Mercury not removed during the CPC process volatilizes in the melter and is condensed in the OGCT which is then fed to the RCT.

B- <u>DWPF RECOMMENDATIONS:</u>

- The Panel supports the MPT plans to implement the improved recovery of mercury in DWPF from the SMECT and bring the MPC back into operation to meet the needs of the current flowsheet by March 2017. This is a key to improving the overall recovery of mercury in the LW system.
- Pursue more stable antifoams for the pH conditions of the CPC, and minimize antifoam amounts added during CPC processing, when possible, since this appears to be the major source of methylmercury formation. Consider all upstream and downstream impacts.

A- <u>TANK FARM OBSERVATIONS:</u>

- A technology development effort was presented to the Panel to improve the recovery of mercury in the tank Farm Evaporators by about 25% by using a reducing agent such a stannous chloride. While this would increase the mercury purge points and is a worthwhile objective, it may not be effective in necessitating having to introduce a methylmercury cation removal step in tank 50 to keep leachable mercury within limits at the Saltstone disposal vaults. The mass balance model proposed below should help answer the question of the effectiveness of the various purge points being evaluated.
- One of the questions that needs to be addressed is whether the H area sludge containing the higher levels of mercury discharged from H-canyon has reacted over the years with organic alkylating agents in the waste to form methylmercury compounds. The plan below to characterize the mercury species in the sludge should be able to answer that question.
- Sample results from the evaporator unit operation indicate that the behavior of mercury is consistent with thermodynamic understanding of mercury partitioning between liquid, vapor, and dissolved phases.
- Of the two evaporator systems, the 2H system had the higher mercury concentrations and a large fraction of the mercury in this system is methylmercury. The source of the methylmercury in the 2H system is postulated to be from the DWPF recycle. The evaporator then concentrates methylmercury that creates undesirable downstream impacts at Saltstone.
- The MPT has data that indicates that stopping the use of antifoam in the Tank Farm (TF) evaporators has reduced the formation of dimethylmercury in these systems.

B- <u>TANK FARM RECOMMENDATIONS:</u>

- The Panel supports the MPT's plan to proceed expeditiously with testing the improved mercury recovery in the TF evaporators. If MPT intends to use a reducing agent or some other enhancement for mercury recover, the upstream and downstream impacts should be considered.
- Proceed with the mass model to determine the overall impact of this evaporator mercury recovery enhancement on the overall LW system.
- The Panel supports the MPT's plan to proceed with the feasibility of using UV light to demethylate methylmercury in DSS coupled to a reduction method such as stannous chloride so that it meets Saltstone mercury release limits. These steps should also consider potential upstream and downstream impacts prior to implementation.
- The Panel also recommends considering a simpler and proven approach as an alternate to the UV light decomposition which is to use GT-74 (mercury removal) ion exchange columns either at tank 50 or at the Salstone receipt tanks (if needed) to reduce the levels of this leachable mercury species to acceptable levels. The DFs required to meet Saltstone limits are not high which should greatly simplify that removal process. A cost and technology maturity comparison between the two technologies needs to be performed.
- The program for SRNL to complete studies related to mercury speciation in SRS H area sludge is supported by the Panel. They should also identify any soluble organic mercury species released to the wash water when sludge is washed. From the concentrations measured, and the volumes still to be generated, a mass balance can be determined. It is important from a mass balance perspective to determine if the methyl mercury species in the LW system is only created in DWPF or what the contribution, if any, may be from the H area sludge.
- Analytical capability is needed to monitor mercury removal efficiency and it is key to the long-term LWS treatment success, especially given the anticipated volume that will be received from SWPF (once on-line). Thus the creation of a dedicated on-site capability is needed to support LWS and DWPF plant operations. Although sample analyses will be limited to support operations, Hg speciation analyses are challenging thus the need for dedicated capability. This was a recommendation from a previous committee review that was only initiated but not fulfilled, almost certainly a result of competing priorities. This activity should be prioritized and expedited. This type of capability will also aide in refinements to the LW model.

- New Mercury discharges from H-Canyon to the tank farm: Dr. Pierce understands that the volume of Hg discharges to the tank farms is small in comparison to the current large mercury inventory in the LWS. While this may be true, constant Hg inputs from H-Canyon will continue to plague the LWS and he believes that it is prudent that Hg used in the H-Canyon process should be reduced, recycled or removed prior to reaching the tank farms.

A- <u>SALT PROCESSING OBSERVATIONS:</u>

- For recent salt batches, methylmercury (MHg+) contributed over 50% to the total mercury present. This fraction was attributed to DWPF recycle being used to prepare the salt batches.
- The Panel agrees with MPT's findings that the chemistry of the mercury does not change through the Actinide Removal Process (ARP) and the Modular Caustic Side Solvent Extraction Unit (MCU) process.
- The Panel also agrees with MPT that the Decontaminated Salt Solution (DSS) from the ARP/MCU is the major contributor to the total mercury in Saltstone feed material.

B- <u>SALT PROCESSING RECOMMENDATIONS:</u>

- None

A- <u>SALTSTONE OBSERVATIONS:</u>

- The Panel agrees with MPT that the majority of the mercury released as leachate from TCLP analysis is methylmercury cation.
- The Waste Acceptance Criteria (WAC) for Tank 50 were revised to include individual limits for total mercury (325 mg/L), elemental mercury (18.2 mg/L) and methylmercury (350 mg/L). MPT is pursuing a substantial increase in the elemental mercury limit which will help disposal of the mercury inventory.

B- <u>SALTSTONE RECOMMENDATION:</u>

- The current program to pursue mercury getters as additives to the Saltstone formulations to solving the mercury problem in the LW system is reasonable. However, other options to remove problematic mercury species prior to the disposal vaults should be considered first. There are options available, described previously, to accomplish that objective.

A- <u>ETP OBSERVATIONS:</u>

- The MPT has recently initiated additional investigations at the Effluent Treatment Project (ETP) due to the presence of airborne concentrations of mercury that have been identified in this facility (X-EPF-H-00016). The MPT has recognized three problem areas related to operations in the ETP. These problem areas are the process building sumps, the organics

removal area, and the ETP evaporator feed tanks. The MPT has identified several potential solutions with the intention of maintaining vapors within the processes so as to minimize vapor concentrations in the breathing zones, thus limiting potential vapor inhalation exposure.

B- <u>ETP RECOMMENDATIONS:</u>

- The Panel fully supports the MPT's plan to continue the mercury vapor control and mitigation program. Implementation of the closing funnel and, in addition, consideration of other less intrusive mitigation strategies (e.g., increased air circulation) is reasonable.

FURTHER DISCUSSION ON MERCURY MODELS AND RECOMMENDATIONS:

Dr. Papouchado and Mr. Jackson recommend that a simple heuristic mercury mass balance model be developed for the LW system. On the other hand, Dr. Pierce proposes that a very simple Conceptual Model of the LW system be developed. The Panel members would be glad to assist in either or both of these model development efforts. These developments are not intended to be independent activities and should complement each other.

During the early stages of creation, developers of the Conceptual Model should assume steady-state conditions (ignore aspects regarding partition factors between LWS unit operations, sludge batch-to-batch variations, and dynamic transfers between LWS unit operations). Attempting to capture these complex processes during the development stage will simply complicate tool development. These complexities can be added during future iterations. The initial approach to developing the conceptual model should be as simple as possible.

This should enable the team to estimate build-up of mercury in each LWS unit operation. A significant portion of the data required to create the "Conceptual Model" is listed in report number "X-ESR-S-00279" and mercury partitioning is introduced in SRNL-STI-2016-00163/SRR-STI-2016-00293. The "Conceptual Model" will need to be refined over time as additional data is obtained.

The Mass Balance effort, on the other hand, would provide a more complete mercury picture. In addition to the liquid species (aqueous and elemental), an estimate of the vapor and solid (sludge) phase species should be included as well as hold-up inventory to complete the balance. In determining the fate of the different mercury species across the LW system, two sets of values

are needed at a minimum. The first, which SRR has actively pursued, is to measure the concentrations of the different species across unit operations such as the 2H and 3H evaporators, DWPF, ARP/MCU, and recently ETF. While this data provide invaluable information with respect to conversion of the mercury species from the input of the unit operation to the output, it does not provide a mass balance picture, In other words, if we generate organomercury compounds in a unit operation, we need to multiply that concentration by the expected volumes of that stream over the LW lifetime to get a true picture of the whole system. For example, the recycle stream from DWPF may be high in organomercury compounds which we generate by using antifoam in the CPC but the total mass may be small compared to the sludge washings which are lower in concentration but far larger in volume. We believe that the current main source of organomercury compounds in the LW system is from DWPF recycle. However, H area sludge washings have shown low levels of methylmercury so they contribute, but to a lesser degree, to the organomercury inventory. Since halting the use of antifoam in the TF evaporators, it appears that that source of organomercury compounds has been halted. TD has funded a program to identify the mercury species coming from sludge which will be very useful in completing this important balance of mercury compounds. A useful tool should leverage mercury characterization and concentration activities with existing waste volume inventories and liquid flux projections with projected waste volumes from the current system plan to support future projections. We recognize that a 100% mass balance is not achievable so the model should highlight data gaps & uncertainties.

Another value of this mass balance model is to assess where the largest mass of undesirable mercury species will be created (or exists), how they will concentrate over time and how they may cause potential downstream problems at Saltstone and ETP. It will also provide a guide of where future data collection efforts should focus. In addition, it would provide the MPT with an indication of how beneficial some of the proposed mercury removal or conversion processes that are being pursued will be and allow the MPT to select the most effective solutions.