

**Contract No:**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-09SR22505 with the U.S. Department of Energy (DOE) National Nuclear Security Administration (NA).

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## Long-Term Management of Mercury at the Savannah River Site Liquid Waste System – 17364

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### ABSTRACT

Mercury in the Savannah River Site Liquid Waste System (LWS) originated from decades of canyon processing where it was used as a catalyst for dissolving the aluminum cladding of reactor fuel. Approximately 60 metric tons of mercury (Hg) is currently present throughout the LWS. Mercury has long been a consideration in the LWS, from both hazard and processing perspectives. In February 2015, a Mercury Program Team (MPT) was established at the request of the Department of Energy to *"take an integrated, system-wide approach to evaluating the movement, monitoring, and collection of mercury through the entire Liquid Waste System/Facilities..."*. The key objective of the Mercury Program Team was to evaluate mercury in the LWS and develop a comprehensive action plan for long term management and removal of mercury. After completion of Phase I and II, a comprehensive action plan for long-term management and removal of mercury was developed and recommendations for actions are categorized under three broad categories – Plant Operations, Technology Development, and Sampling and Monitoring. The resolution of these Action Items will provide long term management and removal of mercury through the LWS.

### INTRODUCTION

The Savannah River Site (SRS) Liquid Waste System (LWS) stores radioactive waste in 43 underground tanks. The radionuclides in the waste are removed through a series of separation processes and the low-level fraction is immobilized in a grout waste form while the high-level fraction is disposed in a glass waste form. Mercury originated from decades of canyon processing (used as a catalyst for dissolving the aluminum cladding of reactor fuel) and is present throughout the LWS (~60 metric tons). Mercury has long been a consideration in the LWS, from both hazard and processing perspectives. Mercury is removed from the LWS (Fig. 1) in many ways including: 1) the Tank Farm Evaporators condensate; 2) at the Defense Waste Processing Facility (DWPF), where it is steam-stripped and removed during the feed preparation processes; 3) it is removed at the Effluent Treatment Plant (ETP) via ion-exchange process; and it is immobilized in the low-level, grout waste form. 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) to “... 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]

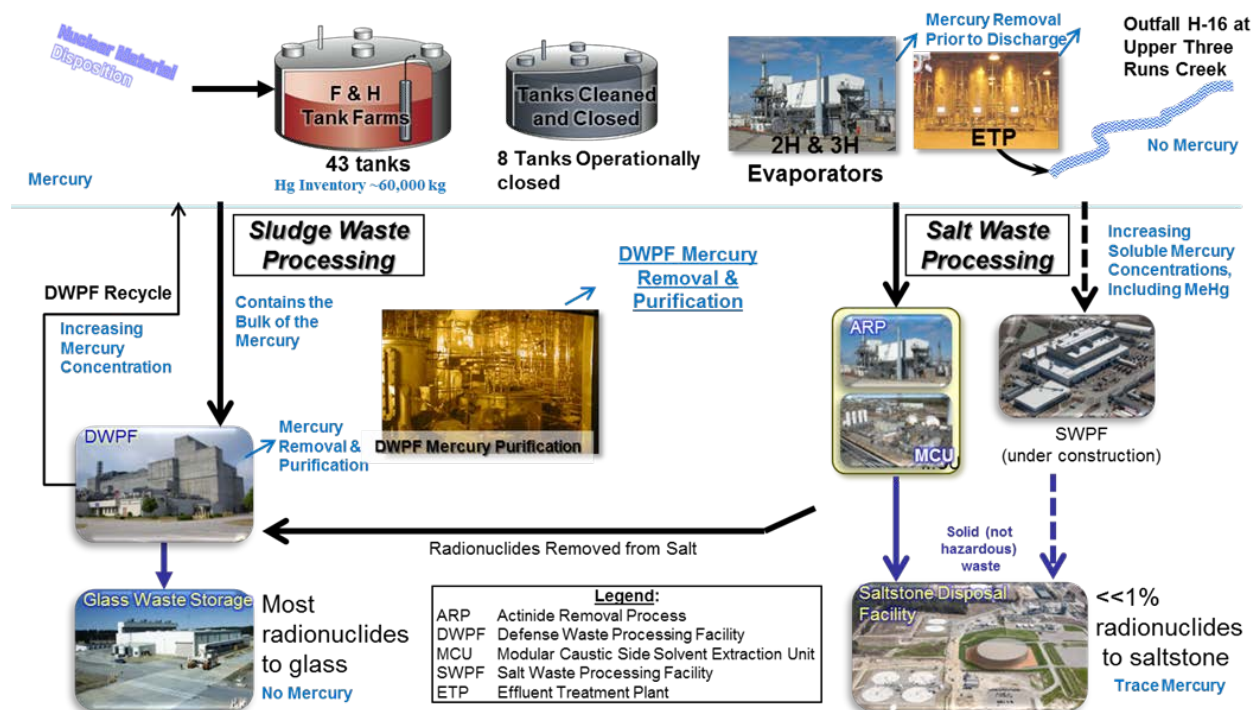


Fig. 1 Mercury in Liquid Waste System.

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).

## **EVALUATION OF MERCURY IN THE LWS**

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.

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 for speciation. 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 (SEEs) were performed using key SRR and Savannah River National Laboratory (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].

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.

## **RESULTS**

Some key findings from these studies include the following:

- 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.

- 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).
- Comparison of data between Tank 21/49, Salt Solution Feed Tank (SSFT), Decontaminated Salt Solution Hold Tank (DSSHT), and Tank 50 samples suggests that the total mercury as well as speciated forms in the assembled salt batches pass through the Actinide Removal Process (ARP) / Modular Caustic Side Solvent Extraction Unit (ARP/MCU) process to Tank 50 with no significant change in the mercury speciation. Some mercury does strip to the strip effluent and solvent hold tanks. However, the volume of strip effluent and solvent streams are small compared to Tank 49 solution processed through the ARP/MCU system.
- 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.

## **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
- 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 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 Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (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 Mercury Purification Process Cell (MPPC) to purge the mercury from the LWS as shown in Fig. 2. 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.

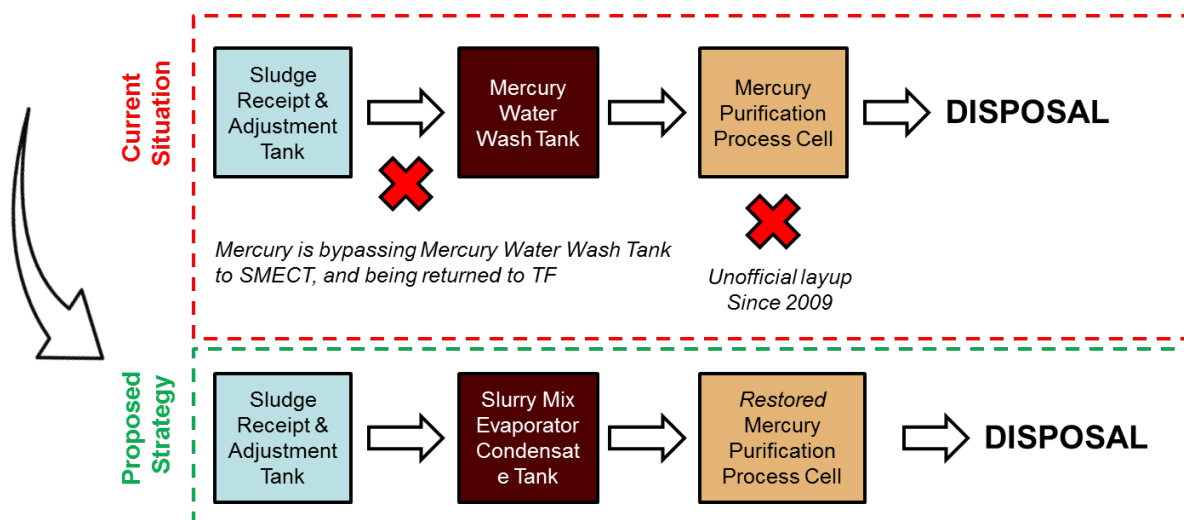


Fig.2. Proposed Mercury Removal from DWPF.

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. Technologies listed in Table 1 under 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 from 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  $\text{SnCl}_2$  or  $\text{H}_2\text{O}_2$ , 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 behave differently 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.

The below two programs, were not funded at this time:

- Wilmarth [11] 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 to mitigate the creation of organic mercury compounds. SRR included this recommendation as a part of the comprehensive action plan for completeness. This scope is being executed outside the mercury program.

In addition, the following three basic science research topics were considered important to address mercury issues at SRR:

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

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)
  - Completed worker communications
  - Completed methylmercury permeability testing of latex gloves and other materials
  - Precautions, such as 'sniffers', are taken to detect mercury should it be present prior to performing work
- Tank Farm Safety Analysis
  - Safety analysis changed, actions implemented, pending minor evaporator modifications which includes installation of sight glass [2]
- Saltstone Safety Analysis
  - Safety Analysis changed to address mercury levels that affect worker/facility safety [3]
- Saltstone Performance
  - Completed TCLP particle size variability study
  - Clarified hazardous waste landfill disposal limit
- Performance Assessment Impact (Tank Closure Grout and Saltstone)
  - Assessment completed and "No Impacts" documented

## **SUMMARY**

The comprehensive action plan identifies actions to reestablish and enhance mercury removal capability and to mitigate the increasing levels of mercury and organic mercury compounds returning to the tank farms in the DWPF recycle.

The comprehensive action plan categorizes actions into "Plant Operations" to continue to ensure worker safety and reestablish mercury removal within DWPF, "Technology Development" to investigate potential means to remove or enhance removal of mercury in both DWPF and in other locations throughout the LWS, and "Sampling and Monitoring" to continue to ensure proper monitoring of mercury and organomercury within the LWS.

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

Category	Facility	Status	Actions
Plant Operations	TF/ETP	Complete	Evaluate Industrial Hygiene (IH) and Worker Protection
	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
	DWPF	Complete	Raise pH in SMECT to keep mercury in elemental form
	DWPF	In Progress	Establish mercury pumping capability from SMECT and/or Mercury Water Wash Tank (MWWT) to Mercury Purification Process Cell (MPPC)
	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	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
	TF	In Progress	2H/3H Evaporators changes for mercury. Install sight glass to determine level of mercury.
	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
Technology Development	TF	In Progress	Removal of ionic mercury via reductant with a chemical additive to the evaporator (2H) system to enhance current mercury removal
	TF	In Progress	Removal of organic mercury via photoreaction (Tank 50)
	TF	In Progress	Develop methods to determine speciation of mercury in sludge

Category	Facility	Status	Actions
	TF	Not Funded	Hg absorbents/Ion exchange for organomercury
	TF	Not Funded	Mercury getters as additions to grout formulations
	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 [12].
	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.
Sampling and Monitoring	DWPF	In Progress	Monitor mercury in the SRAT sludge batches after concentration
	TF	In Progress	Monitor mercury collection from Evaporator System
	SS	In Progress	Monitor mercury speciation of Tank 50 quarterly samples
	SS	In Progress	Monitor mercury release from TCLP Tank 50 quarterly samples
	TF	In Progress	Monitor mercury in salt batch qualification samples
	SHT	In Progress	Monitor mercury in monthly MCU solvent sample
	All	In Progress	Develop in-house capability to measure organomercury.
	All	Complete	Run certified laboratory-to-laboratory comparison for select waste tank samples for mercury speciation variability
	LWS	Planned	Develop a conceptual and/or mass balance model for mercury in the LWS
	LWS	Planned	Add organic carbon analyses for potential alkylating agents to the suite of mercury analyses
	TF	In Progress	Update waste transfer time-line as new sludge and salt batches are prepared

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