Evaluation and Impacts of Mercury in the SRS Liquid Waste System – 16121

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ABSTRACT

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 in many ways including: 1) the Tank Farm evaporator condensates; 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); and it is immobilized in the low-level, grout waste form. An integrated, system-wide evaluation and assessment of mercury behavior in the LWS is being performed.

The recently completed Phase I evaluation focused on mercury inventory and speciation in the LWS; mercury holdup and chemical processing behavior; mercury impact Identification, including worker safety and equipment degradation; and mercury removal and disposal options. The mercury removal system at the DWPF has been unable to remove mercury successfully due to equipment and chemistry challenges since the 2008 timeframe. Phase I evaluations indicate that approximately 43 percent of the mercury in waste sent to the DWPF is now returning to the Tank Farm in the recycle stream and is concentrating to higher than expected levels (~500 mg/l) around the 2H evaporator system. The chemical behavior of mercury is further complicated by the formation of higher than expected quantities of organomercury species, specifically methyl mercury, now present in the DWPF recycle evaporator system (2H Tank farm evaporator), which is used to volume-reduce the recycle stream.

Phase II activities are building on the Phase I mercury activities, including additional sampling and characterization activities, a re-assessment of overall system knowledge, ranking and prioritizing critical gaps/information in mercury

behavior across the flowsheet, assessing impacts of mercury removal and disposal options, and documenting an action plan for overall mercury management in the LWS. Phase II activities include two System Engineering Evaluations to 1) "Re-Establish Mercury removal Capability within DWPF," and 2) "Determine the Best Alternative Mercury Removal Location with the LWS." This paper provides the results of the Phase I and II mercury evaluations for the SRS 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 in many ways including: 1) the Tank Farm evaporator condensates; 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); and 4) it is immobilized in the low-level, grout waste form. Fig. 1 shows the flow for mercury through the LWS while Fig. 2 shows the estimated quantities of mercury in the LWS.

The mercury removal system at the DWPF was designed to remove the majority of the mercury inventory from the sludge waste. However, since the 2008 timeframe, it has been unable to successfully remove mercury due to both equipment and chemistry challenges. Phase I evaluations indicate that at least 40 percent of the mercury in waste sent to DWPF is now returning to the tank farm in the recycle stream and is concentrating to higher than expected levels (~500 mg/l) around the 2H evaporator system. Chemical behavior of mercury is further complicated by the formation of higher than expected quantities of organomercury species, specifically monomethylmercury (MMHg), now present in the DWPF recycle evaporator system (2H Tank farm evaporator), which is used to volume-reduce the recycle stream.

A Mercury Program Team was established to conduct an integrated, system-wide evaluation of mercury behavior in the LWS including

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

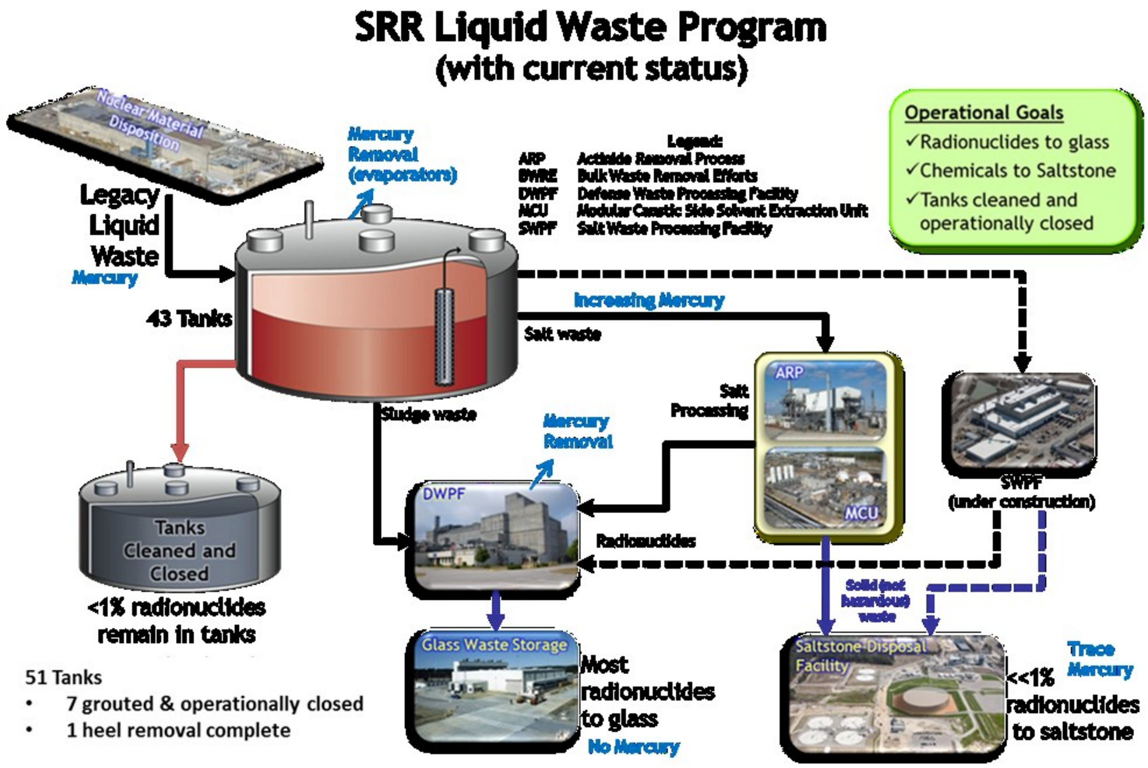

Fig. 1. Mercury in Liquid Waste Facilities.

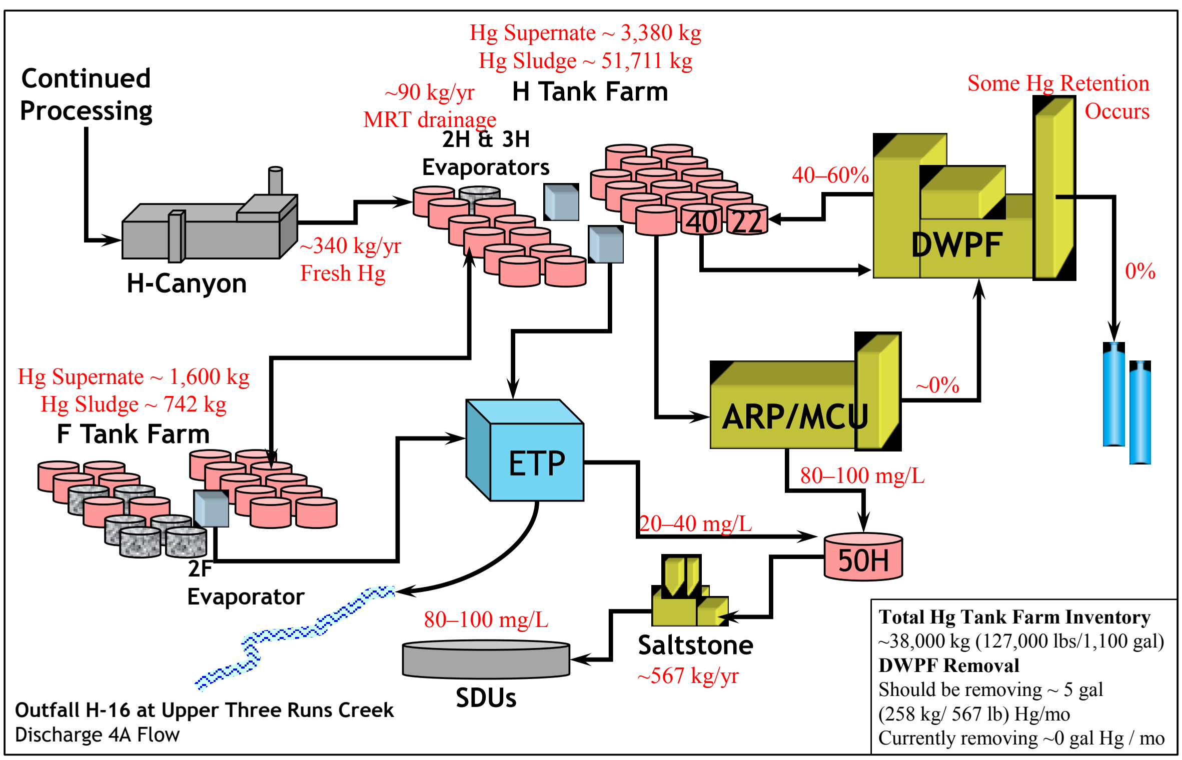

Fig. 2. Estimated Mercury Inventory in Liquid Waste Facilities

This evaluation was conducted in two phases. Phase I [1] activities included a review and assessment of the liquid waste inventory and chemical processing behavior of mercury using a system by system review methodology approach. Gaps in understanding mercury behavior as well as action items from the structured reviews are tracked and resolved. Phase II [2], [3]activities take an integrated approach to re-assess the overall system knowledge, to rank and prioritize critical gaps/information, assess impacts of removal and disposal options, and document an action plan needed to resolve overall mercury management. A key aspect of the mercury reviews has been the establishment of an outside Mercury Advisory Team, consisting of experts in mercury chemistry.

SYSTEMATIC LIQUID WASTE PROCESSING REVIEW

The Mercury Program Team reviewed the LWS flowsheet in a structured approach examining each of the twelve key systems/ processes that influence the chemical behavior of mercury. Reviews of these key systems/processes were conducted in a pre-determined format and were aimed at determining what was known about the behavior of mercury in the various process flowsheet operations which make-up the LWS and determine where significant gaps in knowledge or understanding in mercury behavior existed. Gaps and action items were captured for each of the 12 systems. With the discovery of higher than expected levels of MMHg in the decontaminated feed to the saltstone facility (Tank 50), a significant emphasis was placed on understanding the origins of MMHg within the LWS. Systematic reviews of the LWS resulted in 95 Gaps and identified actions. At the end of Phase I, 50% of these items were closed or resolved.

MERCURY PROCESSED in the LWS

The majority of the mercury present in the Tank Farm is mostly insoluble and processed with sludge through the DWPF. Fig. 3 shows the amount of mercury in the sludge batches fed to DWPF. Mercury concentration in the processed sludge batches range from 100 mg/kg to 3,600 mg/kg. To date, a total of 31.3 MT of Hg has been fed to DWPF. The concentration of mercury has increased substantially with time and, with the increased processing of H-Area waste (H-Area Tank Farm contains ~90% of the mercury) is expected to increase in future sludge batches since the majority of the sludge remaining is H-Area sludge. An appreciable amount of mercury is currently being returned to the tank farm in DWPF recycle.

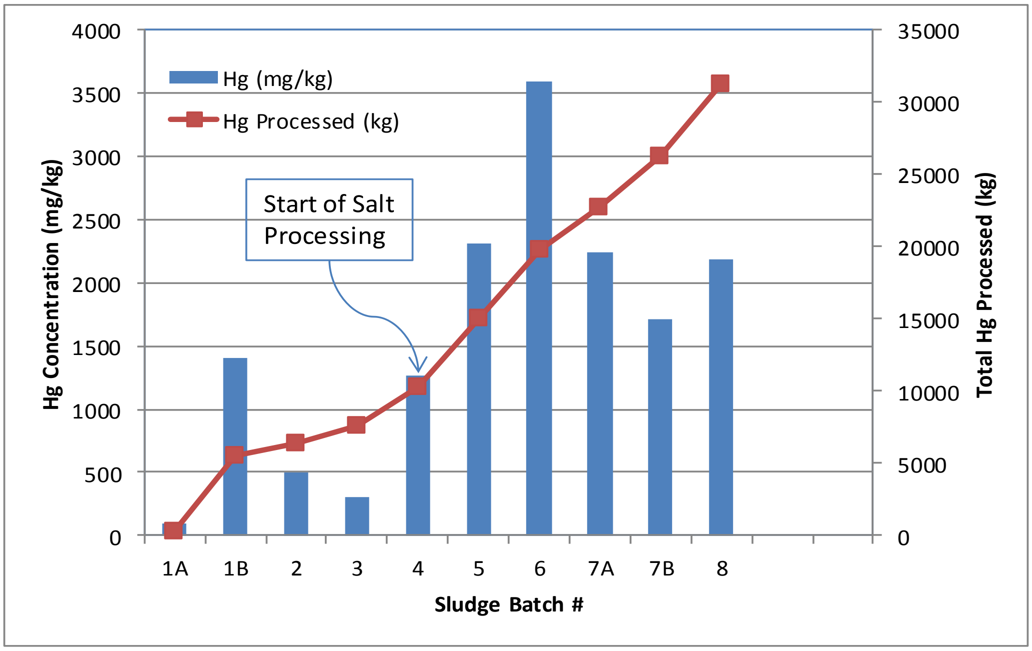

Fig. 3. Amount of Mercury in Sludge Batches Fed to the DWPF.

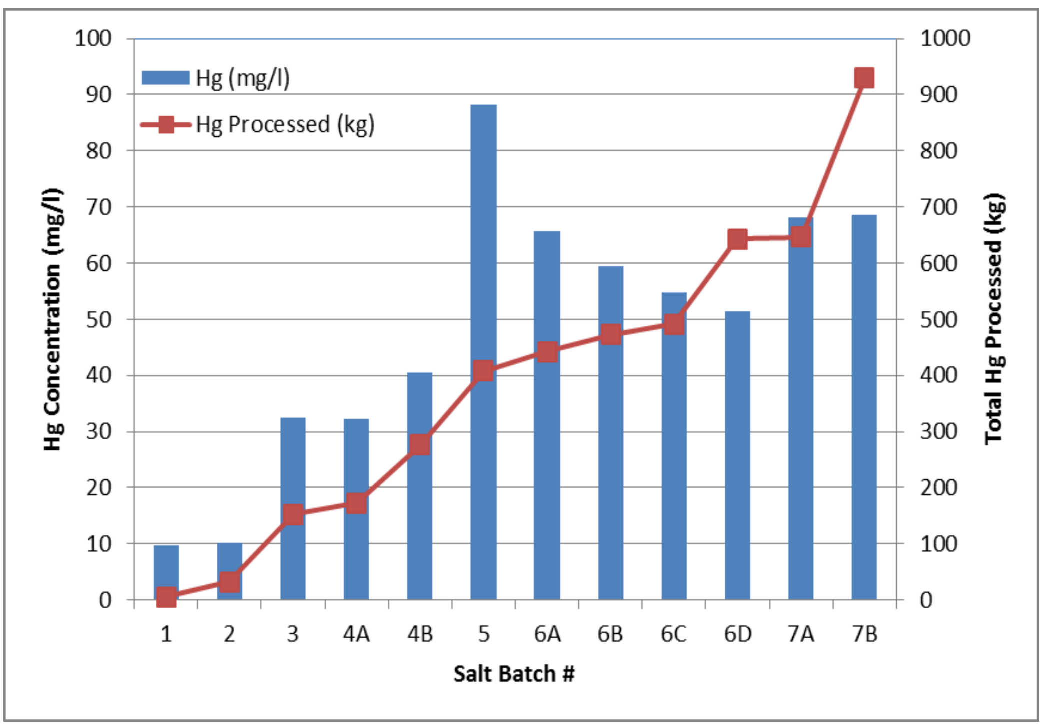

Fig. 4. Amount of Mercury in Salt Batches Processed through Saltstone Feed.

Salt batches, which are expected to contain low levels of mercury (mostly soluble mercury), have seen substantial increases in concentration as shown in Fig. 4. Salt Batch 1 had a soluble mercury concentration of 9.75 mg/L while Salt Batches 4 through 7b ranged between 40 mg/L and 88 mg/L.

INTEGRATED EVALUATION of MERCURY SPECIATION in LWS

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 particular, the discovery of a higher than expected MMHg compound in the Tank 50 feed to saltstone resulted in additional mercury speciation activities to be performed on the various process streams that are constituent feed streams into Tank 50. Additional mercury speciation activities were also initiated around specific process flowsheet operations (i.e., DWPF Chemical Processing Cell (CPC) sludge preparation unit operations, Modular Caustic Side Solvent Extraction Unit (MCU) processing, Salt Batch feed preparation, 2H and 3H evaporator operations) in order to understand mercury processing behavior and also identify potential sources/location of MMHg formation. A number of sources of MMHg have been ruled out based on this sampling and analysis effort, however, completion of this effort will be required to determine the source.

Based on the review of the LWS process systems, a sampling plan for mercury speciation studies was developed. To date, samples have been analyzed for Total Hg, Total soluble Hg, Particulate Hg, Elemental Hg, Ionic Hg, MMHg, ethyl Hg, and dimethylmercury (DMHg). Sampling was prioritized based on operational considerations as well as the expected influence that the process stream and/ or system has on mercury behavior.

Fig. 5 provides a summary of mercury speciation results illustrating DWPF recycle (RCT) being transferred to the tank farm (Tank 22), evaporated in the 2H evaporator system (Feed Tank 43 and Drop Tank 38), becoming part of salt feed for Actinide Removal Process / Modular Caustic Side Solvent Extraction Unit (ARP/MCU) for actinide and cesium removal (Tank 49), and then processed into decontaminated salt solution to feed the saltstone low-level waste facility (Tank 50). Fig. 5 when read from left to right illustrates the sequence described above and shows the changing forms of mercury thru these processing operations. The data shows the presence of a significant amount of MMHg around the 2H evaporator system (Tanks 43 and 38).

Mercury speciation analysis confirms a change in the chemical nature of the mercury present in the LWS with a significant increase in organic mercury content around the 2H evaporator system. Results further show:

- Total mercury in Saltstone feed (Tank 50), based on multiple samples from various dates (4th Quarter 2014 to 3rd Quarter 2015) ranged from 78.7 mg/L to 126 mg/L. Speciation analyses indicates MMHg concentration ranging from 37.6 to 53.3 mg/L, DMHg concentration ranging from non-detectable (ND) to 0.143 mg/L, and ethyl mercury concentration <4.3 mg/L.

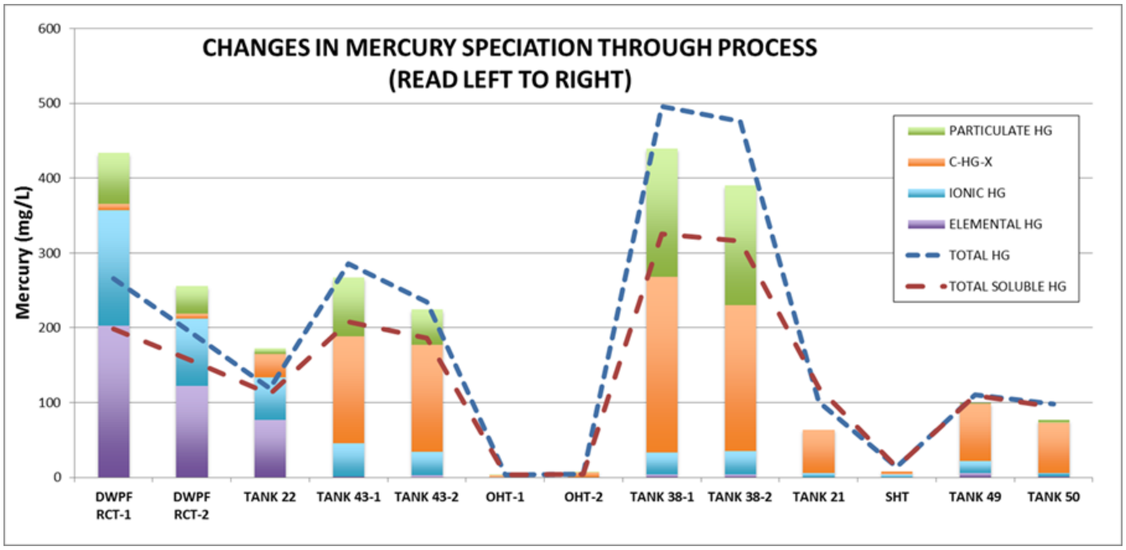

Fig. 5. Speciation profile of Hg in various tanks (C-HG-X is organomercury).

- Total mercury in Salt Feed to ARP/MCU (Tank 49), was 101 mg/L. Speciation analyses indicates MMHg concentration of 58.2 mg/L, DMHg concentration of 0.015 mg/L, and ethyl mercury was not detected. Even though Tank 50 analyses is based on Salt Batch 7 and undergoes 15 – 20 % dilution when processed through ARP/MCU, the comparison of data between Tank 49 feed and Tank 50 product samples suggests that the total mercury as well as organic mercury forms pass through the ARP/MCU process with no significant change in the chemical nature of mercury. A small fraction of the mercury does strip to the strip effluent (21.7 mg/L) and some is present in the solvent (14.2 mg/L total Hg) at MCU. It should be noted that the mass/volumes of strip effluent and solvent are very small compared to the solution processed through the ARP/MCU system. For illustration, Salt Batch 8 feed was determined to have MMHg concentration of 58.2 mg/L compared to the 2nd Quarter Tank 50 product MMHg concentration of 53 mg/L.
- Mercury speciation analyses of Toxicity Characteristics Leaching Procedure (TCLP) leached solutions of the saltstone grout samples show the majority of the released mercury has a chemical form of MMHg. MMHg, therefore, is preferentially released from the saltstone waste form during TCLP product performance testing.

- Total mercury in Tank 22, which is the DWPF recycle receipt tank, was 119 mg/L. Speciation analyses indicates a MMHg concentration of 31.2 mg/L with no detectable DMHg and ethyl mercury.
- As shown in Fig. 3, DWPF processes significant amounts of mercury in sludge batches. To understand the distribution of mercury in the DWPF vessels, sampling and analysis activities were also conducted within DWPF during CPC processing of Slurry Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) Batch 735. This was a first step to better understand mercury behavior during CPC processing operations and to understand chemistry issues with both mercury recovery in the Mercury Wash Water Tank (MWWT) and the high fraction of mercury being returned to the tank farm in DWPF recycle. Data indicate ~43% of the mercury was being returned to the tank farm during Batch 735 processing versus prior estimates of over 80%.

Currently several samples are at various stages of sample collection/analyses. As the sample analysis is complete, it is expected that a better understanding of the source of MMHg formation will emerge, as well as, a better understanding of potential issues with mercury recovery in DWPF.

SYSTEM ENGINEERING EVALUATIONS (SEE)

The Mercury Program Team 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 would be 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 would be to examine 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 process used for SEE evaluation was a structured alternative analysis with weighted evaluation criteria. This methodology is commonly used to select an alternative from two or more options which would be available to meet specific functions, selection criteria, and requirements. The SEE process is shown in Fig. 6.

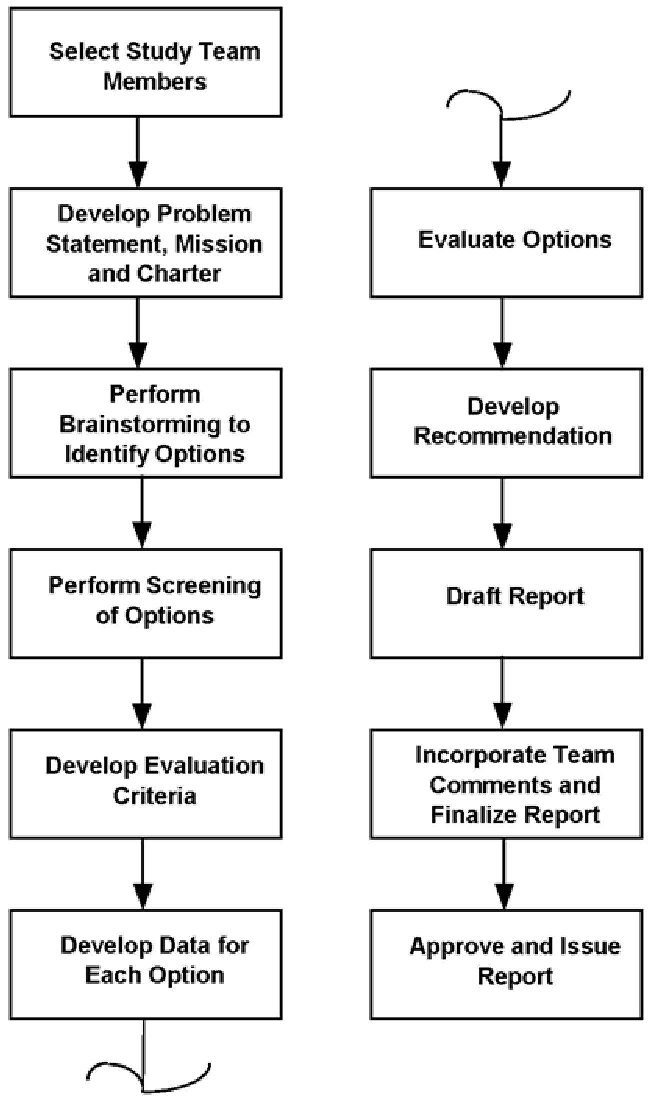

Fig. 6. SEE Study Process

Re-establish Mercury Removal Capability within DWPF

A review of past mercury related events and corresponding corrective actions taken within DWPF indicates that mercury collection and recovery was successful during sludge-only operations between 1996 and 2008, however, with the start of salt processing in conjunction with HM sludge feeds, a shift in mercury behavior occurred. The shift in behavior resulted in less mercury collection in the Mercury Water Wash Tank (MWWT) than previously experienced and the mercury that was recovered was “dirty” mercury (i.e. sludge/mercury mix) which could not be successfully processed in the DWPF Mercury Purification Process (MPP). Comprehensive testing [4] was performed; however, an exact cause for the change in mercury behavior was not identified. Recent analysis following successful sampling of the Slurry Mix Evaporator Condensate Tank (SMECT), Slurry Receipt and Adjustment Tank (SRAT) and MWWT sumps indicate that the mercury in the MWWT is still "dirty" (i.e. sludge containing) mercury, but the mercury being recovered in the SMECT is relatively clean mercury, analogous to the mercury being collected and recovered from the MWWT during sludge-only operations. The SMECT mercury pump, however, has not functioned properly thus preventing mercury recover from this vessel. Following pump removal, the 2013 video inspection of the SMECT mercury pump revealed that the high pressure water lines for the pump had been severed; the cause has not been determined. With the change in mercury chemistry behavior, the failure of the SMECT mercury pump, and the plugging of the MPP with dirty mercury, all efforts to collect and recover mercury have been unsuccessful since the time frame of salt processing through DWPF. A SEE was conducted to brainstorm and assess potential options to re-establish mercury removal capability taking advantage of the relatively clean collection of mercury in the SMECT.

SEE identified 33 potential options which were subsequently reduced to 14 through a screening process. The evaluation of the 14 final options resulted in the recommendation to deploy the two highest ranking options concurrently, monitor the recycle stream for mercury content, and develop add on enhancements to be selected and ready for deployment if the desired mercury removal capability is not being observed. The two highest options were

- Raise pH in SMECT, collect mercury in SMECT then pump out
- Re-establish existing mercury removal system

In conjunction with the two options selected, a prioritized list of contingency design and process changes was developed should the options above provide less than satisfactory results.

Determine the Best Alternative Mercury Removal Location within the LWS

Soluble mercury levels within the LWS are being encountered which are higher than previously predicted. This may be attributed to ineffective removal of mercury from the sludge feed to the DWPF. The original flowsheet design had DWPF as the major purge point for mercury in its elemental form. It is possible that removal of mercury in DWPF may not be sufficient to meet system removal requirements and also prevent significant recycling of mercury to the Tank Farm. Therefore, as part of an overall strategy to reduce the LWS mercury level, a team was chartered to identify and examine options to determine the best possible alternative means to remove mercury from the LWS (excluding DWPF) and provide a recommendation for implementation of a preferred option(s).

The SEE team identified the following purge and collection points for mercury: 1) Elemental mercury removed at the DWPF (outside the scope of this evaluation); 2) Elemental mercury collected at the bottom of process vessels; 3) Elemental mercury collected at the H-area evaporators; 4) MMHg sent to Saltstone (TCLP tests have shown that the organomercury cation is the major mercury species in the leachate). This could be a potential concern in Saltstone if the concentration of soluble mercury in the LWS increases over time.

Twenty potential options were initially identified to remove mercury from the LWS. The 20 options were subsequently reduced to 13 options through a screening process. The evaluation of the 13 final options resulted in three recommendations by the team to because of the different forms of mercury in the LWS:

- Deploy Option 8: Target process vessels (e.g., overheads tank) for mechanical removal of elemental mercury observed to collect at the bottom of process tanks (opportunistic)
- Deploy Option 5a: Enhanced Removal of ionic mercury at the H-area Evaporators using chemical addition of a reducing agent to enhance the reduction of ionic mercury to elemental mercury for collection the enhanced Evaporator (minimal chemical addition option)
- Pursue the removal conversion of the MMHg in tank 50 (feed to Saltstone) to ionic and elemental mercury using ultraviolet (UV-C) light by testing the photo reactor Option 10 (Photoreactor on Tank 50), and maturing the technology for deployment.

In parallel initiate testing to mature Option 7 (Enhanced retention of mercury in Saltstone). This initiative would potentially allow Saltstone to pass the mercury TCLP even if the UV-C treatment is not successful.

SRR is currently evaluating the recommended options from the two SEE reports as part of the overall action plan development to address mercury issues for the entirety of the LWS.

SUMMARY

Mercury removal is necessary within the SRS LWS. Systematic reviews and mercury speciation activities were performed to understand current mercury behavior.

Creation of organomercury compounds, predominately MMHg is occurring within the LWS and is causing higher than previously experienced concentrations of soluble mercury. Understanding the creation and behavior of MMHg is necessary to develop a path forward to effectively address removal of mercury from the LWS. Additional sampling and speciation studies are underway and are expected to be completed in FY16.

Two SEE's were performed to address options to restore mercury removal capability in DWPF and provide additional options for mercury recovery elsewhere in the LWS. SRR is currently evaluating the recommended options from the two SEE reports as part of the overall action plan development to address mercury issues for the entirety of the LWS.

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