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Review of Mercury in the SRS Tank Waste Storage and Treatment Processes for Applicability to Hanford Waste Processing

The Savannah River Site (SRS) and Hanford produced large quantities of plutonium and other radioisotopes. The separations processes recovered plutonium and produced large quantities of High-Level Waste (HLW) that accumulated at each site in large, underground storage tanks. SRS has been retrieving the stored HLW, pretreating the waste for immobilization, and immobilizing the waste in glass or grout waste forms since the mid-1990s. Treatment of the waste at Hanford is expected to start in the early 2020s. Mercury is present in both the SRS and Hanford tank waste. SRS has recently completed an evaluation of mercury speciation throughout the tank waste treatment and immobilization flowsheet[1]. This study was reviewed to determine what information from the study can be applied to the Hanford tank waste treatment program.

Summary

After an extensive sampling and analysis effort at SRS, the chemistry of mercury in tank waste was found to be quite complex. Originally, insoluble mercury was assumed present at SRS as HgO, but recent analysis of HM sludge mercury indicates at least two forms: predominately HgO but some is likely HgS and other unidentified forms. Soluble mercury speciation efforts at SRS indicate that significant amounts of organic mercury, primarily methyl mercury (CH_3Hg^+ ion), are present in SRS tank waste. These findings suggest that small amounts of organomercury are likely to be present in the Hanford tank waste, but the differences in the waste chemistry makes it difficult to use the SRS data in a more definitive manner. The amounts of elemental mercury at Hanford are expected to be small, typically seen at SRS in concentrations similar to organic mercury in tanks that have not been processed through a high-temperature evaporation system. Figure 1 shows the diversity of mercury species across the tank farms. Similarly, differences in the tank waste processing flow sheets between SRS and Hanford also makes it difficult to draw definitive projections about the fate and speciation of mercury at Hanford.
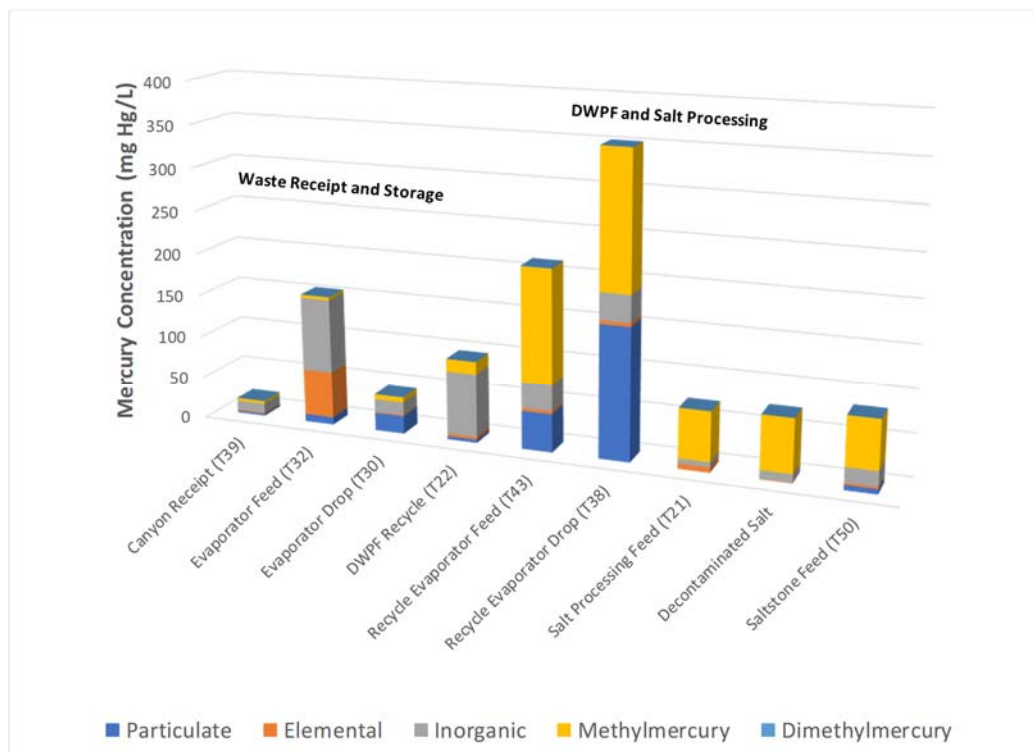

Figure 1. Overall Mercury Inventory at SRS

Testing was done years ago to select materials of construction to determine corrosion susceptibility induced by mercury and halides in the acidic chemical processing cell at DWPF. Given the expected levels of Hg in the Hanford LAW waste feed are much lower than supernate at SRS, it is not expected that

mercury-induced corrosion will be a significant factor for processing the Hanford waste or the LAW melter condensate.

Discussion

SRS Mercury Evaluation Results

SRS has large quantities (60 metric tons) of mercury in the HLW, primarily from modifications to the PUREX process made in the H-Canyon facility. Overall inventories and expected concentration in selected locations are shown in Figure 2, taken from the SRS mercury review. Note that the Salt Waste Processing Facility (SWPF) will replace the ARP/MCU process, performing the same functions with the same unit operations but at larger scales.
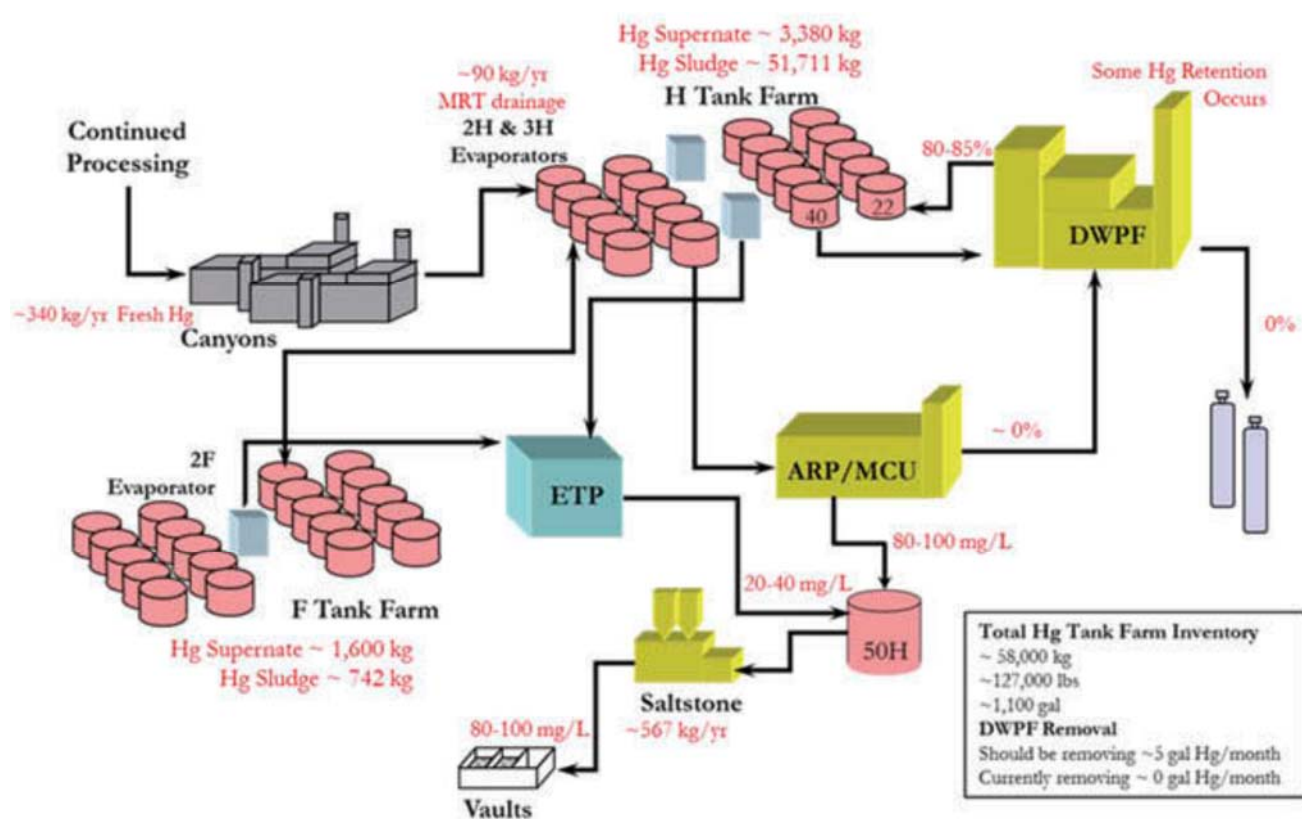

Figure 2. Overall Mercury Inventory at SRS

The dominant form of mercury in the SRS tank farms is insoluble HgO with some fraction of insoluble HgS with concentrations as high as several weight percent of the insoluble solids in the waste[2]. Soluble mercury was typically close to 100 mg/L in supernate. The chemical processing cell at DWPF is designed to remove the mercury from the melter feed, but has not been effective. An evaluation of soluble mercury at SRS was performed to address issues stemming from the lack of mercury removal at DWPF and the

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identification of elevated levels of methyl mercury in the feed to Saltstone[1]. Samples were analyzed for soluble mercury speciation from key processing tanks in the processing facilities and tank farms.

Key Findings from the SRS Studies

- Elevated levels of methyl mercury were noted in tanks that included DWPF recycle, indicating that DWPF is the primary source of methyl mercury in the tank farm
- Methyl mercury production in DWPF is likely from reactions of mercury with the antifoam agent added during DWPF processing
- Methyl mercury was found through-out the tank farm, therefore DWPF operations are not the only source of methylated mercury
- Dimethyl mercury was detectable in selected locations at very low concentrations (0.0002 mg/L)
- Dissolved mercury was typically 70-120 mg/L in the salt waste feed tank and processes
- Elemental mercury concentrations in the supernate were typically less than 2-3% of the total mercury
- Mercury losses to tank farm evaporator overheads is low, approximately 1-2% of the feed
- Ionic and methylmercury pass through the solvent extraction process that is used at MCU for removal of cesium

Application of the Results to Hanford Waste Processing

Several key differences need to be noted before addressing how the SRS results can be used to inform waste processing at Hanford:

1) Mercury amounts in the tank waste at SRS are orders of magnitude higher than the amounts in the Hanford tank waste[2,3] (There is more mercury in just the 3H evaporator feed and drop tanks than in the entire 18 Hanford tank farms).
2) The amount of organics in Hanford tank waste is much higher than SRS, with the difference in some tanks being orders of magnitude higher[4,5].
3) The types of organics contained in the Hanford waste are very different from the organics in SRS waste that were added as reductant (formate) or evaporator anti-foam[4,5]. These organics at SRS contain methyl functional groups that result in methylmercury.
4) Evaporation is performed at atmospheric pressure at SRS versus vacuum evaporation processes at Hanford, resulting in lower temperature at Hanford [4,6]
5) Chloride concentrations are much higher in Hanford waste versus SRS waste[7]

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Implications for Hanford

1) Like SRS, expect HgO to be the primary insoluble mercury species in tank waste.
2) Although differences exist, expect some of the mercury to be present as methylated mercury in the Hanford waste tanks and process systems

   The identification of methyl mercury in SRS tanks containing waste that has not been through DWPF or the tank farms evaporators indicate that methyl mercury formation can occur over time even at temperatures of approximately 50 degrees Celsius[8]. Thus, given the organics concentration in the Hanford tanks, methyl mercury and dimethyl mercury are likely present in the waste, but the concentrations are probably very low, given the lower concentrations of soluble mercury present in Hanford waste.

3) Expect very little elemental mercury

   Despite the large concentrations of mercury in the SRS waste, very little elemental mercury was noted in the samples. However, it should be noted that this result could be partly caused by the inability to suspend very dense material and obtain representative samples containing elemental mercury. Concentrations of elemental mercury in those samples were routinely less than 5% of the total mercury.

4) Methyl mercury increases the total soluble mercury concentration

   Total soluble mercury was typically 30-100 mg/L in wastes with low concentrations of methyl mercury, but was as high as 325 mg/L in systems with elevated levels of methyl mercury.

Implications for Hanford Waste Processing

Overall, the implications of the SRS data for the overall treatment of the Hanford tank waste of the mercury speciation in the tank farm is not significant. This conclusion is based on the way mercury partitions through the overall flowsheet and the following observations:

1) Mercury is not retained in either the HLW or LAW glass products
2) Mercury speciation in the melter offgas is not dependent on the mercury speciation in the feed
   a. Chloride to mercury ratio will determine the mercury species in the melter offgas[3]
3) Based on testing at laboratory scale, nearly 90% of the mercury fed to the LAW and HLW melter system will be captured by the SBS[3]
4) Losses during recycle stream evaporation (SBS condensate) to the EMF overheads are expected to be small (<5%)[3]
5) The only credited purges of Hg from the flowsheet are the small losses to evaporator overheads, and absorption onto the HLW carbon bed, and the LAW carbon bed[9]

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a. It is noted that mercury could be captured on the HEPAs or could plate out on process lines, but these are assumed not to occur during modeling

6) Overall mercury levels at Hanford are low enough that soluble mercury (Hg^{+2}) can account for large fractions of the total mercury content in waste

7) HLW melter condensate handling could result in additional mercury being sent to the LAW system

8) Antifoams added to evaporator feed can contribute to organo mercury production but the temperatures of the vacuum evaporators used at Hanford are typically below the temperatures where large amounts of organomercury production was noted based on SRS waste testing[8].

Mercury in Tank Farm Waste

The total mercury concentration in much of the Hanford sludge waste is well below the amount of soluble mercury noted in SRS wastes with only(?) ~20 of the 177 Hanford tanks having mercury concentrations above 100 mg/L. Supernatant concentrations in the Hanford waste from the Best Basis Inventory are below 1 mg/L for all but one Hanford waste tank, much lower than found in SRS waste. Soluble mercury in all SRS waste was much higher, but some of the difference results from the elevated levels of methyl mercury noted after high temperature evaporation processes in the tank farm and DWPF.

Mercury in Melter Offgas Condensates

A key factor in how much mercury will be sent to the LAW facility is the handling of HLW condensate and whether mercury in the HLW condensate is soluble and remains soluble during recycle handling. As shown in Figure 3; two mercury "flywheels" are possible for the Hanford tank waste flowsheet[a]. Mercury fed to the HLW melter will be vaporized and most of the vaporized mercury (~90%) will be captured by the Submerged Bed Scrubber (SBS). The mercury in the HLW offgas condensate could be elemental, calomel (Hg_2Cl_2), or mercuric chloride ($HgCl_2$), with the amounts of each dependent on the ratio of mercury to chloride in the melter feed. Mercuric chloride would be expected from DFHLW processing assuming a flowsheet that has less washing than planned for WTP PT operation. Mercuric chloride is soluble in the SBS condensate but would likely form HgO if the condensate is pH adjusted with sodium hydroxide. The insoluble mercury would eventually be returned to the HLW process. However, any mercury that remains soluble during recycle handling would eventually be sent to the LAW process.

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[a] Note that even if WTP PT operation is assumed, the mercury pathways will be similar. Insoluble mercury in the HLW condensate will flywheel in the HLW system and soluble mercury will be passed to the LAW systems.
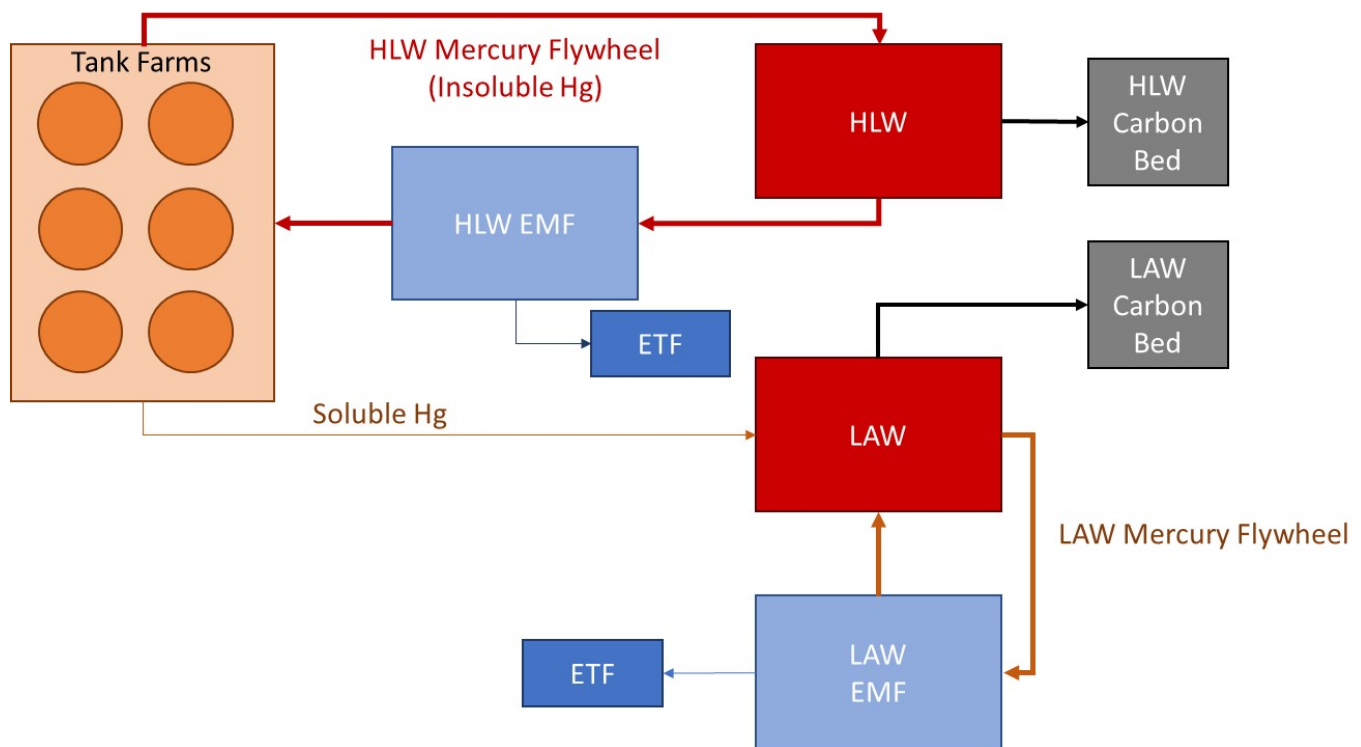
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Figure 3. Mercury Flywheels in the Hanford Direct Feed Flowsheets

The LAW mercury flywheel results from the recycle loop for EMF condensate. All of the mercury fed to the LAW melter is partitioned to the offgas and most of that mercury is condensed in the SBS condensate. During evaporation of the condensate, most of the mercury is retained in the concentrate and recycled back to the LAW melter feed. Mercury will accumulate in the LAW system until the quantity of mercury that passes through the SBS/WESP in the vapor phase is roughly equal to the amount of mercury in the LAW feed . Mercury in the off-gas that passes through the SBS is assumed to be metallic mercury vapor and pass through the WESP and HEPA, eventually being captured by the carbon bed.

As noted in a review of the SBS system, high DFs for mercury in that system would reduce the purge of mercury to the carbon beds and increase the concentrations of mercury in the recycle stream as well as the amount of mercury sent to the LERF/ETF facility. In addition, capture of mercury by the WESP is assumed to be very low, otherwise, any removal of mercury in the WESP would significantly reduce the mercury purge to the carbon beds. It should be noted that no current operational controls exist that could impact mercury partitioning in the LAW vitrification facility, so the only way to address issues with higher than allowable mercury in the LERF-ETF or stack effluents is to blend down high mercury feeds. Given

the overall lack of options for mitigation of mercury issues for LAW, the design and operation of the LAW facility must ensure robustness for handling mercury.

It is not possible to use the SRS data to directly correlate the expected partitioning or speciation of mercury in the HLW or LAW melter condensate since the amount of chloride in the SRS waste is far lower than the Hanford waste and the amount of mercury is far higher. Thus, chloride interactions with mercury are not significant at SRS but testing has shown these interactions are dominant for much of the Hanford waste. Further, the SRS melter runs a slightly reducing redox condition, as opposed to the WTP melters that run oxidizing. Also, the DWPF process reduces and strips mercury from the sludge in the chemical processing cell which changes the speciation of mercury in the melter feed, and there is no comparable unit operation in WTP. Lastly, SRS does not vitrify the decontaminated liquid phase (LAW), so comparable data does not exist.

Corrosion from elevated mercury levels

During the initial materials selection for DWPF performed in the 1980s, tests were performed for various DWPF processing tanks with significant quantities of mercuric ion (1,000 to 28,000 mg/L)[10]. In these mostly acidic environments, with mercuric ion and chloride present, severe pitting and crevice corrosion was observed for a number of stainless-steel alloys (304L, 316L, Alloy 20). The facility switched to Hastelloy C276 for these vessels and there have been no know issues with corrosion during processing. More recent testing on C276 has been performed to evaluate changing to a glycolic acid flowsheet at DWPF[11]. Testing was performed in solutions with mercury concentrations between 0 and 300 mg/L. At concentrations on the order of 300 mg/L Hg^{+2}, the open circuit potential shifted significantly in the positive direction, which may suggest that the material will be more susceptible to pitting. However, at Hg concentrations of less than 60 mg/L the open circuit potential did not increase significantly. Even the presence of up to 300 mg/L Hg^{+2} in the glycolate based simulants also did not increase the susceptibility of C276 to localized corrosion. There was a slight increase in the general corrosion rate as compared to the formic acid flow sheet, but it was not significant.

A couple of items were noted during the testing related to materials selection for DWPF. Alloys that contained more than 0.5 wt.% copper (e.g., Alloy 20) pitted severely in Hg containing solutions while all alloys with a total Cr + Mo content greater than 30% were resistant to crevice corrosion at pH 6 and 40 ⁰C. Only nickel-based alloys with more than 9% molybdenum were able to resist crevice attack at pH 1.6 and 40 ⁰C for the simulated DWPF process streams. C276 was resistant to crevice corrosion at pH 6 and 90 ⁰C. Alloy C276 had some evidence of crevice attack at pH 1.6 and 90 ⁰C. Only ALLCORR had no visible attack at this latter concentration and temperature. ALLCORR was superior for the off-gas solutions, however C276 was deemed acceptable for the DWPF process.

Given that the expected levels of Hg in the LAW waste feed are relatively low compared to the SRNL test data that indicated corrosion problems, it is not expected that mercury will accelerate corrosion of the materials of construction due to exposure to the Hanford waste or the LAW melter condensate.

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