Mercury in Aqueous Tank Waste at the Savannah River Site: Facts, Forms, and Impacts

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Abstract

Over the past two years, there has been an intense effort to understand the chemistry of mercury across the Savannah River Site's High-Level liquid waste flowsheet to determine the impacts of various mercury species. This effort began after high concentrations of mercury were measured in the leachates from a toxicity characteristic leaching procedure (TCLP) test on the low-level cementitious waste form produced in the Savannah River Saltstone facility. Speciation at specialized off-site laboratories showed the dominant form of leached mercury was the methylmercury cation. Neither the source of the methylmercury nor its concentration in the Saltstone feed was well established at the time of this testing.

Introduction

The primary source for mercury in the liquid waste streams originates from it use within the uranium and plutonium processing operations as a catalyst for acidic dissolution of aluminum cladding from targets and fuels, aluminum alloy fuels and aluminum-uranium cermets. This process has been used for over fifty years at the Savannah River Site (SRS). It is estimated that over 60 metric tons of mercury has been used and discharged to the Savannah River tank farms [1]. The spent acid streams from the canyons are neutralized with caustic prior to discharging to the tank farms and mercury partitions between the liquid phase and the precipitated sludge phase with the vast majority precipitating in the sludge phase. Figure 1 shows the expected distribution of mercury across the SRS liquid waste system. Originally, mercury was to be recovered primarily during vitrification operations in the Defense Waste Processing Facility (DWPF). However, the operation only operated for a few years following startup in 1996 [2].

Upon receipt of the mercury leachate data showing unexpected high levels of mercury from the 4th quarter sample for the low-level waste form exiting the liquid waste system, a significant effort has been expended to assess and speciate mercury (Hg(0), Hg(I), Hg(II), organomercury, and soluble versus insoluble mercury) within the liquid waste system. In particular, the discovery of methylmercury (MeHg) in the decontaminated salt feed [3] to the low-level waste operations resulted in additional mercury speciation activities throughout the liquid waste facilities and unit operations.

Evaluating the behavior of mercury within any waste unit operation requires an understanding of the mercury speciation within the waste. The speciation of the mercury strongly effects distribution of mercury in the various phases; i.e. aqueous, gas, or liquid, and the transfer of mercury between these phases. Important chemical properties such as the boiling point, density, vapor pressure, and solubility are all species dependent. A sound understanding of speciation within the waste is critical for evaluating the behavior and distribution within and across the unit operation. Typically, mercury can exist in three primary forms including the elemental, inorganic, and organic – the latter represented by at least one carbon-mercury covalent bond. In addition, significant quantities of mercury can be bound to a solid phase entrained with the flow or through accumulation from precipitation within the unit operation.

Experimental

Samples drawn from the various liquid waste processing facilities and waste tanks were predominately collected in small stainless steel bottles and every attempt was made to collect a zero headspace sample. The bottles were capped, packaged for transfer to ether a shielded cell or radiological fume hood depending on the activity of the sample and its associated radiation dose rate. For samples received into a shielded cell, an intermediate dilution of generally 1:100 was made into a Teflon bottle and immediately removed from the cell for refrigerated storage prior to final dilution and shipment. Final aliquot dilutions were prepared, packaged, and shipped to an offsite laboratory within 24-36 hours and maintained as close to 4 °C as possible.

Dimethylmercury (DMHg) is first extracted from a sample aliquot by dilution into 50 mL of reagent water, and direct purged onto Carbotrap columns. For analysis, the loaded Carbotrap column is placed in-line with a packed column isothermal gas chromatograph (1-m column, 4 mm ID, packed with 15% OV-3 on Chromasorb-WAW-DMSC; held at a constant 80 °C), and thermally desorbed into an argon stream which carries the Hg species into the GC column [4]. The gas stream from the GC column passes through a pyrolytic column held at approximately 800 °C, which breaks down all Hg species to elemental Hg, that are then quantified by cold vapor atomic fluorescence spectrometry (CVAFS), as detailed elsewhere [5].

Methylmercury, CH_3Hg^+, and ethylmercury (EtHg), $C_2H_5Hg^+$, were analyzed similarly to the $(CH_3)_2Hg$ described above, except that the aliquot of the sample was diluted with a pH 4.9 acetate buffer, and the sample first ethylated with sodium tetraethyl borate for MeHg [4, 6] or propylated with sodium tetrapropylborate for EtHg. These reagents convert CH_3Hg^+ or $C_2H_5Hg^+$, which are non-volatile, into methylethylmercury $(CH_3HgC_2H_5)$ or propylethylmercury $(C_3H_7HgC_2H_5)$, respectively, which are volatile. These species are then analyzed by purge and trap using a Carbotrap, and isothermal GC-CVAFS.

Total mercury was determined using bromine monochloride (0.2M BrCl in 12M HCl) added to the samples in their collection containers, at level of 1 mL per 100 mL of sample for total mercury analysis. The samples were then allowed to digest overnight at room temperature. Aliquots of each digest were reduced to elemental Hg in reagent water by the addition of $SnCl_2$, and then the elemental Hg purged onto gold traps as a pre-concentration step [7]. The Hg contained on the gold traps was then thermally desorbed into a CVAFS. Following that procedure the samples were filtered through 0.45 µm disposable filtration devices and re-analyzed for dissolved mercury. Inorganic Hg is determined using the same procedure without the addition of BrCl after sparging to remove elemental Hg. Particulate Hg is

determined from the difference between the total and dissolved mercury analysis values after reducing this difference by the elemental Hg measurement.

Elemental mercury, Hg(0) was purged from the sample and collected onto gold traps, then thermally desorbed and reabsorbed on Carbotraps. The trapped Hg was digested with a heated mixture of nitric and sulfuric acids at 80 °C for two hours and brought to a 40 mL volume using bromine monochloride, with aliquots diluted and analyzed by CVAFS.

Results and Discussion

Even today, the nuclear material processing canyon uses mercuric ion to catalyze the dissolution of aluminum-based materials in nitric acid at elevated temperatures in dissolver vessels. Prior to discharging to the tank farms, the spent acid is evaporated to recover some of the nitric acid and remove the potential for large quantities of canyon-based organic species. The waste is then neutralized with caustic and discharged to Tank 39 where it is stored prior to evaporation. There are no other influents into Tank 39 from the tank farm facilities. The results of mercury speciation were expected to indicate that nearly 100 % of the mercury in Tank 39 was in the form of mercuric ion. Shown in Table 1 are the results from two samples taken from Tank 39. These results provide the first surprise identified in this characterization effort. Examination of the data in Table 1 indicates some minor difference between the samples taken at two depths in the tank. In general, the tank contained approximately 40 mg Hg/L, of which most is in a dissolved state. It is interesting that only about one fourth of the mercury is in the form of inorganic mercury, which was not expected. Additionally, there is a small, but measurable concentration of MeHg, on the order of 3 mg Hg/L, which is another surprise.

There were poor mass balances for this tank that are not completely understood. One could reason that the measurement for inorganic mercury was biased low. However, the presence of MeHg requires an additional hypothesis. In examining the tank farms historical data, Britt [8] indicated that Tank 39 was

considered an organic-containing tank due to the presence of partially dissolved resins from weapon materials production. There is a possibility that since this tank sees temperatures of 50 °C a methylation reaction could occur. Previous work by Wilmarth et al. [9] showed that the formation of DMHg was not supported at temperatures of 50 °C or lower but the testing failed to examine the formation of MeHg.

At SRS, bent tube evaporators are used to concentrate the waste and generate operating tank space. These evaporators operate between 130 and 150 °C under atmospheric pressure. Figure 2 shows a generalized schematic of the evaporator process. Typically, one High Level Liquid Waste (HLLW) tank is used as the feed tank to the evaporator in which the waste is boiled to a specific gravity of about 1.5 g/mL. This generates overheads which are condensed and collected in a couple of condensate tanks. The concentrated supernate is then transferred or "dropped" by gravity flow to the drop tank. Liquids can be recycled back to the feed tank for further concentration. There are two operating evaporators at Savannah River. The smaller 2H evaporator is used to concentrate water that is recycled from the vitrification plant, DWPF. The larger 3H evaporator is used to concentrate the wash water from the preparations of sludge batches for feed to DWPF.

During typical 2H evaporator system operations, DWPF recycle which is collected in Tank 22 is transferred into the evaporator feed tank, Tank 43. Following evaporation, waste is gravity drained to the concentrate tank, Tank 38. Periodically (~ every two weeks), waste is recycled without mixing back to the feed tank through a transfer jet in the concentrate tank. In this dynamic system, a mercury speciation analysis provides a snapshot of the process at a given point in time, but makes it difficult to establish a flowsheet. Samples were obtained from the feed (Tank 43), the concentrate tank (Tank 38) and the overhead tanks (OHT) and are contained in Table 2. Concentrations of total mercury in Tank 43 on the surface are similar to those taken at depth but are within the 20% measurement uncertainty and reflect a mercury concentration on the order of 260 mg/L Hg. The measured MeHg concentration was 135 mg/L Hg.

For the drop tank (Tank 38), the effect of evaporation is observed as total mercury concentrations increase by nearly 50% with total mercury concentrations rising to approximately 485 mg/L Hg on average across the surface and variable depth samples. The MeHg concentration increased to 180 mg/L Hg as expected due to the low volatility of the salt. The ratio of MeHg to total mercury in Tank 38 remains lower than in Tank 43 at 37%, indicating formation of MeHg in the evaporator does not appear to be occurring – though the impact of return transfers from Tank 38 back to Tank 43 cannot be accounted for in this assessment. What is not known is the degree to which MeHg is insoluble in the system. There is little elemental mercury in either the feed or drop tanks, as would be expected. It would be difficult to transfer any elemental mercury from Tank 22 due to the height of the transfer jet and the conditions in the feed and drop tanks. A decrease in DMHg is observed going from the feed to the drop tank at the lower elevation, as expected from the Henry's Law correlation, but the opposite is observed for the surface samples.

Table 2 also contains the results of mercury speciation from the 2H Evaporator's OHT-1 and OHT-2. These results show small mercury concentrations between 3.8 and 4.8 mg/L Hg as total mercury and between 2.4 and 5.6 mg/L Hg as MeHg. Almost no DMHg is measured in these samples as would be expected based on volatility. Table 3 contains data previously published [9] for samples taken in the early 2000s for DMHg. Note that for consistency, the concentration values reported have been converted to a mg Hg/L basis from the mg Hg-species/L basis that is given in the original reference document. The mercury behavior is not similar. Methylmercury is now a measurable species. The behavior of DMHg is different now too. For the current data set, the concentrations are 0.9 µg/L to 5.4 µg/L; whereas, the concentration in the 2000s was three orders of magnitude higher ranging from 0.013 mg/L to 1.9 mg/L. One potential explanation for this discrepancy is there is a different chemistry and utilization for the antifoam agent used in DWPF compared to the antifoam previously used in the evaporator system. From this data, one can claim that the DWPF antifoam is only singly methylating the mercury giving rise to

higher MeHg concentrations in the overhead tanks, i.e. the system is methyl limited, compared to the higher DMHg concentrations measured in the past. Alternatively, any DMHg formed in DWPF would likely be vented based upon the agitated vessels in use.

The 3H Evaporator is a comparable technology to the 2H Evaporator and is much larger and runs at higher steam flows and operating temperature. Following the discovery in the early 2000s that there was measurable DMHg present in the evaporator systems, both systems ceased the use of antifoam agents. The data for the 2H system indicates that antifoam breakdown products and the methylated byproducts of mercury are still entering the system from DWPF. This is not the case for the 3H system. The speciation data for the 3H system is shown in Table 4.

The overall concentration of mercury in the 3H Evaporator system is currently lower than the 2H system except for the variable depth sample taken from Tank 32. The data from the surface samples show a general trend for total mercury: the feed tank (Tank 32) was 48 mg/L Hg, the drop tank (Tank 30) increased to ~76 mg/L Hg, and the spare drop tank (Tank 37) measured ~23 mg/L. There is little MeHg in the system, on the order of 2 – 8 mg/L Hg. The source of this MeHg could be from two sources. First, as discussed above, the canyon receipt tank contains low but measurable concentrations of MeHg and this being one of the feeds to 3H would bring MeHg into the system. Additionally very recently, there were transfers of wash water that were used in DWPF sludge batch preparation that contained significant quantities of Tank 22 supernate. Again, as discussed above, there is measurable MeHg in that tank system and it represents a source for the 3H evaporator system. The variable depth sample taken from Tank 32 shows a higher elemental and total mercury concentration than the surface sample, and is at a level comparable to the 2H evaporator system. One possible explanation for this observation is that mercury is being leached from the sludge layer that exists in this tank. By comparison, the Tank 30 variable depth data is in reasonably good agreement with that of the surface sample – Tank 30 does not contain a sludge layer.

There is considerable difference between the concentrations of DMHg seen in the current 3H evaporator overheads and that found previously as shown in Table 5 [9]. Previous concentrations of DMHg were 2 – 4 orders of magnitude higher when antifoam was being introduced into the 3H evaporator compared to the current values. The change in the level of MeHg measured is less significant, showing an inconsistent but minor reduction over earlier measurements. Similarly, total Hg is now lower by a factor of 3 – 8. Curiously, all the mercury that makes it into the overhead tanks is MeHg, which is unexpected since it is not a simple entrainment issue, this would result in a constant ratio of total to MeHg, and its low vapor pressure precludes evaporation. Looking at cesium levels as a measure of entrainment, the overheads are five orders of magnitude below those of the feed; however, the MeHg level does not show this degree of reduction in the overheads. Whatever mercury specie(s) that is (are) carried into the overheads appears to be converted to MeHg through a vapor phase or condensate phase reaction. In light of the significant compositional, temperature, and potential redox changes associated with moving from liquid in the evaporator pot to vapor and ultimately being condensed and retained as overhead liquids, there are means for such a transformation to occur in the system.

Figure 3 shows the flow of waste through the salt processing facilities at the Savannah River Site [10]. The salt batches, typically over a half million gallons in volume, are assembled in Tank 21; characterized to ensure compliance with waste acceptance criteria, and qualified to be processed. Waste from the source tanks are concentrated supernate or dissolved saltcake which are prepared using waste water streams recycled from the DWPF. Additionally, the collected waste is adjusted to ensure carbon steel corrosion control requirements are met and routinely require additional hydroxide, which is added in the form of evaporator concentrate (Tank 38).

Once qualified, the waste is fed to the Actinide Removal Process (ARP) where monosodium titanate (MST) is added to remove strontium and some actinides. The slurry is concentrated and the MST is diverted to the DWPF for vitrification. The filtrate is sent forward to the Modular Caustic Side Solvent Extraction Unit (MCU) where cesium is removed using a solvent extraction process and the cesium stream is diverted to DWPF. The decontaminated salt solution is transferred from MCU to Tank 50 and then sent to Saltstone where the grout waste form is prepared and ultimately disposed in engineered vaults.

The samples from Tank 21 and Tank 49 represent salt feed to the ARP/MCU process. The mercury concentrations for total, dissolved, and MeHg are in reasonable agreement for two separate salt batches. It is striking that the inorganic fraction in these samples are significantly reduced from the evaporator recycle tanks (38 and 43). The inorganic mercury concentration for Tank 21 and 49 measured 5.9 and 15.0 mg Hg/L, respectively. The reason for this reduced inventory is not completely understood; but, it is known that several transfers from a number of uncharacterized source tanks were blended to make the salt feeds. However, simple dilution does not explain the low concentrations. Methylmercury concentrations approached 60 mg Hg/L and account for over fifty percent of the soluble mercury in the salt feed for salt batch 7. The remaining mercury species are believed to be organomercury based on the measured inorganic mercury and could represent a low measurement bias in the MeHg analysis. The results from Tank 50, the Saltstone feed tank, show a general trend of increasing total and dissolved mercury concentrations, which is expected based on the types of waste being retrieved. There is very good agreement between the distributions of mercury species analyzed in the Tank 49 samples and the Tank 50 samples taken in third quarter 2015. This indicates the ARP/MCU process has little effect on the mercury chemistry of the salt waste. However, in an effort to better understand the impact of MCU on the distribution of mercury compounds, SRNL performed a series of organic-aqueous phase contacts with two extraction stages, one scrub and one strip stage, using actual Tank 21H samples, and freshly prepared solvent. The mercury content of the cesium-decontaminated Tank 21H sample is listed in Table 1 as the

"21 Decon." result. A comparison of the data from this before and after extract shows a reduction in total, dissolved, and MeHg indicating some interaction is possible between one of the solvent components and the mercury in the waste. In addition, Peters reports distribution values for the scrub of ~0.8 and the strip of ~2 as measured without temperature correction [11]. A distribution value <1 indicates a preferential distribution into the aqueous phase, while a value >1 indicates preferential distribution into the organic phase.

In order to better understand this interaction, samples were taken from the process vessels within MCU, which operates in batch mode so the samples were taken at one time and represent a "snapshot" of the facility during operation. Within MCU, salt waste is received and stored in the Salt Solution Feed Tank (SSFT). It is fed to banks of centrifugal contactors where the salt and an organic solvent, Isopar L, containing a calixerene-based extractant, are mixed. After the solvent is scrubbed the cesium is removed from the solvent via a stripping operation and stored in the Strip Effluent Hold Tank (SEHT). The decontaminated salt is then transferred to the Decontaminated Salt Solution Hold Tank (DSSHT). The solvent continues through a washing step and is returned to the Solvent Hold Tank (SHT). Samples were obtained from each of these tanks and are presented in Table 7.

Comparison of the mercury concentration in the SSFT and the DSSHT exhibits similar concentrations for each of the mercury species and similar species distributions, but in general the concentrations in the decontaminated salt solution are slightly lower than the feed. However, they are certainly within the analytical uncertainty of the measurements. There is one effect that should be acknowledged in this comparison. For DMHg, the reporting limits have been significantly lowered (from <0.12 mg Hg/L to <0.0012 mg Hg/L) between the feed and the decontaminated salt solution. We are unsure whether the actual concentration of DMHg has decreased over time or remains the same. However, some of the DMHg partitions to the strip effluent. Since DMHg is fairly volatile, it would also make sense that some

partitions to the contactor air purge and is discharged through the vessel vent system. Efforts are underway to measure the DMHg in these vent systems.

However, the measurements from the solvent hold tank (SHT) and the strip effluent hold tank (SEHT) indicate the chemistry is more complicated. The SEHT shows total mercury and dissolved mercury at concentrations of ~ 20 mg/L, with inorganic species measuring 3.5 mg/L and MeHg measuring 16.3 mg Hg/L. The only way for mercury to make it to the SEHT is to be extracted into the solvent and be stripped into the effluent stream. The solvent composition has been changed to improve overall processing parameters, but the effect on mercury has not been studied. Results from the SHT show slightly lower mercury concentrations with similar distribution of species. These findings indicate that mercury is not building up in the solvent, and it appears that the strip and wash steps limit the inventory of mercury in the solvent. However, the data does have implications for the intended solvent disposition pathway once it is spent.

Once the salt waste has been decontaminated it is collected in Tank 50 and sent in batches to the Saltstone Production Facility (SPF) where it is mixed with fly ash, blast furnace slag, and Portland cement to form a cementitious waste form, also known as grout, that is poured into engineered vaults in the Saltstone Disposal Facility (SDF). Langton and Wilhite [12] had previously studied the behavior of mercury as one of the major contaminants of concern in this cementitious waste form and found acceptable performance versus regulatory testing employed to determine the waste form's toxicity level. This test is the Toxicity Characteristic Leaching Procedure (TCLP) in which a crushed sample of the waste form is contacted with a reference solution and the leachates are measured for the contaminant of concern.

As such, Tank 50 represents one location in the liquid waste system where mercury trends can be analyzed. Figure 4 shows the results for sampling and analysis for mercury species since the fourth quarter of 2014. Total mercury concentrations reached a maximum measured value of 105 mg Hg/L, but

have risen from a lower value in the first quarter of 2015 to nearly the same high level over 100 mg Hg/L. There has been variation, but MeHg has steadily increased from 25 mg Hg/L to nearly 60 mg Hg/L. Plotted in Figure 5 is the ratio of the specific mercury species to total mercury, e.g., ratio of MeHg to total mercury. The ratios for elemental and inorganic mercury have been relatively flat, prior to the last quarterly sample, but the ratio of MeHg to total has generally risen over the past eight quarters. It is not well understood when this increasing ratio will cause operational problems. Examination of these data strongly indicates that the mercury in the TCLP leachate is predominately MeHg. The measured total Hg leachate concentrations are low and have been well below the Land Disposal toxicity limit of 0.2 mg/L and have been both above and below the TCLP Universal Treatment Standard (UTS) of 0.025 mg/L, but the values in the leachate have continued to increase across this timeframe. However, a firm technical understanding of the binding mechanisms for organomercury within the waste form is warranted to ensure compliance of the form to its regulatory requirements.

As part of the assessment of the liquid waste inventory and chemical processing behavior of mercury through a system by system review, the SRS vitrification plant systems were examined and speciation measurements made on a series of condensate samples collected at various times during the processing of three separate sludge batches identified as DWPF Batches 735, 736, and 738 [2]. Samples were collected from the Slurry Mix Evaporator Condensate Tank (SMECT), Off-Gas Condensate Tank (OGCT), and Recycle Condensate Tank (RCT). Condensates collected from the SMECT and OGCT are combined in the RCT and return to the SRS Tank Farm through Tank 22. The selected batches allowed for various processing conditions in the Slurry Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) tank to be assessed since Batch 736 followed a facility shutdown and de-inventory operations on the condensate collection tanks.

Figure 6 shows the mercury concentration (mg Hg/L) for various mercury species in the SMECT at the start (initial/baseline), after acid addition and initial concentration, and at the end of the SRAT processing

cycle for Batch 736. This batch contained no SEHT addition from MCU and hence there was no caustic boiling conducted prior to the start of acid addition and steam stripping of Hg(0). The growth in the concentration of MeHg from <1 mg/L to 138 mg/L is evident. The methylation source is believed to be IIT747 (composed of two siloxane polyalkyleneoxide wetting agents) antifoam degradation products that include two volatile species, hexamethyldisiloxane and trimethylsilanol, as shown in Figure 7. What is unclear is whether this MeHg generation is occurring through a vapor phase reaction with elemental mercury, in the SMECT vessel itself through reaction of these antifoam degradation products with inorganic mercury species present in the condensate, or via entrainment. Further work with simulant products should address the question of whether entrainment is a significant factor.

The variety of mercury species identified in these SMECT samples points to the complexity of the processing situation since by initial DWPF design, the only expected species is elemental mercury resulting from the formic acid reduction in the SRAT vessel. Instead we find inorganic mercury, MeHg, and EtHg along with the elemental mercury. Ethylmercury was identified in one sample from two SRAT batches, but it is difficult to measure because the concentration is overwhelmed by the level of MeHg present.

Mercury mass balances performed during the SRAT and SME cycles indicated that a significant amount of elemental mercury resides in the SMECT and is not removed via the Mercury Water Wash Tank (MWWT). This elemental mercury can be dissolved by the nitrous/nitric acid by-products of the SRAT neutralization reactions and by the nitric acid additions made to the SMECT to maintain an acidic pH. Efforts are underway to reduce the added nitric acid and, hopefully, minimize the dissolution of elemental mercury in this system, as well as improve the MWWT efficiency so that less elemental mercury is deposited in the SMECT.

In Figure 8, we see the concentrations of mercury compounds in the SMECT following both SRAT and SME operations for another batch designated, Batch 738. A dilution of the MeHg concentration is observed following the receipt of SME condensate in the SMECT, indicating that most of the generation is likely occurring around SRAT operations where the mercury levels are much higher before the sludge slurry is steam stripped and transferred to the SME. Total mercury levels continue to rise in the SMECT during the SME processing cycle since mercury continues to steam strip from the concentrating slurry of sludge and glass frit. Mercury that is not removed from the SME moves on to the Melter Feed Tank (MFT) and is fed to the glass melter where it volatilizes and is condensed in the OGCT. Based on the limited data available to date, the SMECT condensate appears to be the larger contributor, relative to OGCT condensate, to the mercury collected in the RCT where, after caustic addition, it is returned to the Tank Farm. The presence of elemental mercury in the RCT supports the baseline assumptions that elemental mercury only slowly dissolves in caustic, and hence, most of the dissolution occurs during Tank Farm storage.

Conclusions

The predictability of the behavior of mercury across the liquid waste systems requires knowledge about the particular mercury species contained in each thermodynamic state. The partitioning between the liquid, solid, and vapor phases is directly correlated to the speciation. The major contribution of this work is to provide an initial analytical speciation for various aspects of the waste systems.

Mercury enters the liquid waste system from plutonium and uranium operations conducted in H-canyon at the Savannah River Site. Mercury, in the form of mercuric nitrate, is used as a catalyst for aluminum dissolution. New insight has been gained that indicates there is a possibility that methylation reactions are occur as early in the liquid waste processes as this canyon waste receipt tank.

As the waste is processed through the waste evaporators and is concentrated into salt cake and supernatant liquids, mercury partitions into the neutralized sludge solids due to its limited solubility in the high sodium alkaline wastes. Originally, organomercury formation was thought to be limited to the evaporator systems as it was here that organic antifoam agents were found to react with the soluble mercury in the waste to produce methyl and DMHg. The cessation of antifoam additions to the evaporators removed this production source. Today, the source appears to be slightly different. Now the data suggest that MeHg is formed during sludge processing, but again it is due to antifoam usage. After formation, the MeHg is returned to the tank farm in recycled water from the vitrification plant. There are significant gaps in the understanding of the partitioning and formation of organomercury across the off-gas systems within the vitrification plant that need further study.

Methylmercury is concentrated in the 2H evaporator system and the concentrate and recycle are used in salt batch preparations. The MeHg is feed to the cesium solvent extraction process and partitions to a small degree into the eluent and decontaminated salt streams. The decontaminated salt stream contains the majority of the MeHg and from here it is sent to the low-level waste operations where a cementitious waste form is produced. This waste form has a capacity for binding the MeHg, but it has also been shown to leach some MeHg during regulatory-required testing.

The 3H evaporator system appears to be slightly different and contains only minute quantities of organomercury species. The source of these methylated mercury species is likely in-tank formation resulting from the co-discharge of mercury-containing canyon wastes with wastes containing organic species from resin digestion operations. Another likely source is feed to this evaporator system that contains wash waters from vitrification facility sludge batch preparation, which would transfer MeHg into this evaporator system.

Although much of the data sets reported herein represent single point speciation at various points within the liquid waste system, the flow, speciation, and chemistry is understandable and can be predicted. A complete data set is not realistically possible considering all of the configurations and processing options that will be proposed and evaluated over the life of the Savannah River Site. Sufficient science and engineering work can be used to make sound engineering judgements as to the potential effects and side effects on mercury chemistry based on the results from this work.

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