**Mercury Speciation in Savannah River Site High-Level Waste:
Determination and Implications for Waste Handling and Disposal**

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ABSTRACT

As part of a larger program to address mercury issues at the Savannah River Site, a number of samples from across the salt processing flowsheet have been collected and analyzed for several mercury species. The results indicate the presence of organomercury species, predominately methylmercury cation. This result was not expected, and it represents a significant paradigm shift in the understanding of mercury chemistry in high-level tank waste. Concentrations of total and soluble mercury have been measured as high as 0.5 g/L with methylmercury concentrations of at least fifty percent of that value. The distribution of mercury species being observed have ramifications to waste processing strategies. In particular, the mercury behavior across the cesium solvent extraction process has been examined. Leachates, from toxicity testing of the cementitious waste form used for decontaminated salt waste at Savannah River, have been tested and shows methylmercury as the dominant extractable species.

INTRODUCTION

The Department of Energy's Savannah River Site (SRS) utilizes vitrification for the disposition of high-level nuclear waste in the Defense Waste Processing Facility (DWPF) and cementitious grout (also called saltstone) for the immobilization of low-level nuclear waste in the Saltstone Production/Disposal Facility. The low-level stream is producing by removing radionuclides (e.g., strontium, cesium and some actinides) from the liquid, salt waste at the interim Alpha Removal Project (ARP) and the Modular Caustic-Side Solvent Extraction Unit (MCU) facilities.

Mercury catalyzes the dissolution of aluminum clad fuels during processing, and it became an integral part of high-level waste stored in SRS waste tanks. Initially, the vitrification plant or Defense Waste Processing Facility (DWPF) operations were designed to remove and collect Hg from the incoming sludge waste, but due to a variety of factors, Hg collection has not occurred as initially envisioned. The result has been ever increasing amounts of Hg in liquid waste effluents destined for low-level waste saltstone disposition. A higher than anticipated Hg concentration was measured in the leachate from a Toxicity Characteristic Leaching Procedure (TCLP) [1] on a saltstone sample initiated an effort to characterize and, for the first time, establish the forms of Hg present in SRS liquid waste streams. Initially, saltstone's suitability as a disposition pathway was established based on formulation testing using inorganic mercuric nitrate salt as this was the expected mercury species in the salt waste. The behavior of other forms of mercury, e.g., organomercury species, has not been studied and the expected behavior is not well understood in the cementitious waste form. It is well known that the environmental mobility (or extractability) of mercury in a soil profile depends on its speciation, with

alkylmercury species such as methylmercury at least an order of magnitude more mobile than inorganic mercury species [2]. The efforts of Savannah River Remediation, LLC, the tank waste contractor, and the Savannah River National Laboratory (SRNL) have focused on the salt processing flowsheet from production of large, million gallon batches of salt feed, through the ARP/MCU facility, into the decontaminated salt hold tank, and in the leachate from saltstone in the Saltstone facility.

DESCRIPTION OF METHODS

Samples from the various salt processing facilities and waste tanks were predominately collected from the waste tank in small stainless steel bottles. It is recognized that there could be large uncertainties with such small samples from such a large volume. Every attempt was made by operations personnel to obtain a zero headspace sample. The bottle are capped, packaged for transfer to SRNL, and received into 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 the shielded cells, an intermediate dilution of 1:100 was made into a Teflon bottle and immediately removed from the cells for refrigerated storage prior to final dilution and shipment. Those samples received in a radiological fume hood were subsampled for radionuclide characterization, if necessary, and then placed in refrigerated storage. 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.

Dissolved versus total Hg

The samples are filtered through 0.45 µm disposable filtration devices for dissolved mercury. When using filtration, an unquantifiable fraction of the dissolved volatile species can be lost, and so understate the dissolved total Hg concentration. Analysis directly of the filter post filtration can also be used to quantify particulate mercury if higher relative concentrations of volatile mercury are found.

Quantification of dimethylmercury

Dimethylmercury (DMHg) is first extracted from a sample aliquot (0.025 to 2.00 mL, depending upon expected concentration) by dilution into 50 mL of reagent water, and direct purging for 17 minutes at a flow rate of 200 mL/min from solution into Carbotrap columns. After collection on the Carbotrap, the columns were dried by passing nitrogen through for 7 minutes. For analysis, the loaded Carbotrap column is placed in-line with a packed column isothermal gas chromatograph (GC) (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]. In the column, the following species can be easily separated: elemental Hg, $(CH_3)_2Hg$, $CH_3HgC_2H_5$, and $(C_2H_5)_2Hg$. Under the conditions of these experiments, however, the only meaningful peak is $(CH_3)_2Hg$, which passes through the column with a retention time of approximately 2.5 minutes, after a meaningless "marker" peak of elemental Hg at about 1 minute [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]. The mass (ng) of Hg contained in each aliquot analyzed is quantified by comparison of measured peak heights to the slope of a calibration curve analyzed from aliquots of the $(CH_3)_2Hg$ stock solution analyzed in the same manner. The initial stock solution was custom prepared in isopropanol and certified for concentration by oxidization and analysis for total mercury after confirming the absence of other known species. A working solution of 1.0 ng/mL in methanol was prepared. Recertification of the concentration is performed annually by oxidation and analysis for total mercury.

Quantification of methyl- and ethylmercury
Methylmercury (MHg, CH_3Hg^+) and ethylmercury (EtHg, $C_2H_5Hg^+$) were analyzed similarly to the $(CH_3)_2Hg$ described above, except that the aliquot of sample was diluted with a pH 4.9 acetate buffer, and the sample first ethylated for 17 minutes with sodium tetraethyl borate for methylmercury [4], [6] or propylated with sodium tetrapropyl borate for ethylmercury. These reagents convert CH_3Hg^+, which is non-volatile, into methyl-ethylmercury ($CH_3HgC_2H_5$), which is volatile, or convert $CH_3CH_2Hg^+$, which is non-volatile, into ethyl-propylmercury ($CH_3CH_2HgC_3H_7$), which is volatile. Either species is then analyzed by purge and trap with Carbotrap, and isothermal GC-CVAFS. The initial calibration standard employed for methylmercury was a 100 µg/mL stock solution prepared by Absolute Standards (Hamden, CT), which was used to prepare a 1 ng/mL working standard. The accuracy of this standard was verified by daily comparison to a secondary standard prepared by Sigma Aldrich (St Louis, MO). The initial calibration standard employed for ethyl mercury was a 4.415 ug/mL stock solution prepared by Applied Isotope Technologies (Sunnyvale, CA). The accuracy of this standard was verified by daily comparison to a secondary standard prepared by Sigma Aldrich (St Louis, MO) and certified for concentration by oxidization and analysis for total mercury after confirming the absence of other known species.

Quantification of total, inorganic and elemental mercury
Prior to analysis for total Hg, bromine monochloride (0.2M BrCl in 12M HCl) was 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 (0.01 to 100 mL, depending upon concentration) 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 analyzed by thermal desorption at 450 °C into a cold vapor atomic fluorescence detector (CVAFS), using the dual amalgamation technique. Peak heights were accessed by chart recorder, and the mass (ng) present in the sample calculated by comparison to a standard curve spanning the range of 0-2.00 ng Hg. The calibration standard employed is 10,000 µg/mL Hg diluted to a working laboratory concentration (10 ng/mL). The accuracy of this standard is verified daily by the analysis of the National Institute of Standards and Technology (NIST) NIST-1641d (mercury in river water matrix) reference material, which is diluted 200x with 1% BrCl solution prior to use. Inorganic mercury is determined using the same procedure without the addition of BrCl that will give results of both ionic and elemental mercury. Elemental mercury is determined as well using the same procedure except without the addition of BrCl

and $SnCl_2$. Ionic mercury was calculated as the difference between inorganic and elemental mercury.

DISCUSSION

Figure 1 shows the flow of waste through the Liquid Waste processing facilities at the Savannah River Site. 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 of the form of concentrated supernate or dissolved saltcake which are prepared using water recycled streams from the DWPF. Additionally, the collected waste is adjusted to ensure carbon steel corrosion control requirements are met and routinely require additional hydroxide and this is added in the form of evaporator concentrate (Tank 38).

ARP -   Actinide Removal Process
DWPF- Defense Waste Processing Facility
MCU - Modular CSSX Unit
         SSFT – Salt Solution Feed Tank
         DSSHT – Decontaminate Salt Solution Hold Tank
         SHT – Solvent Hold Tank
         SEHT – Strip Effluent Hold Tank
SPF -   Saltstone Processing Facility
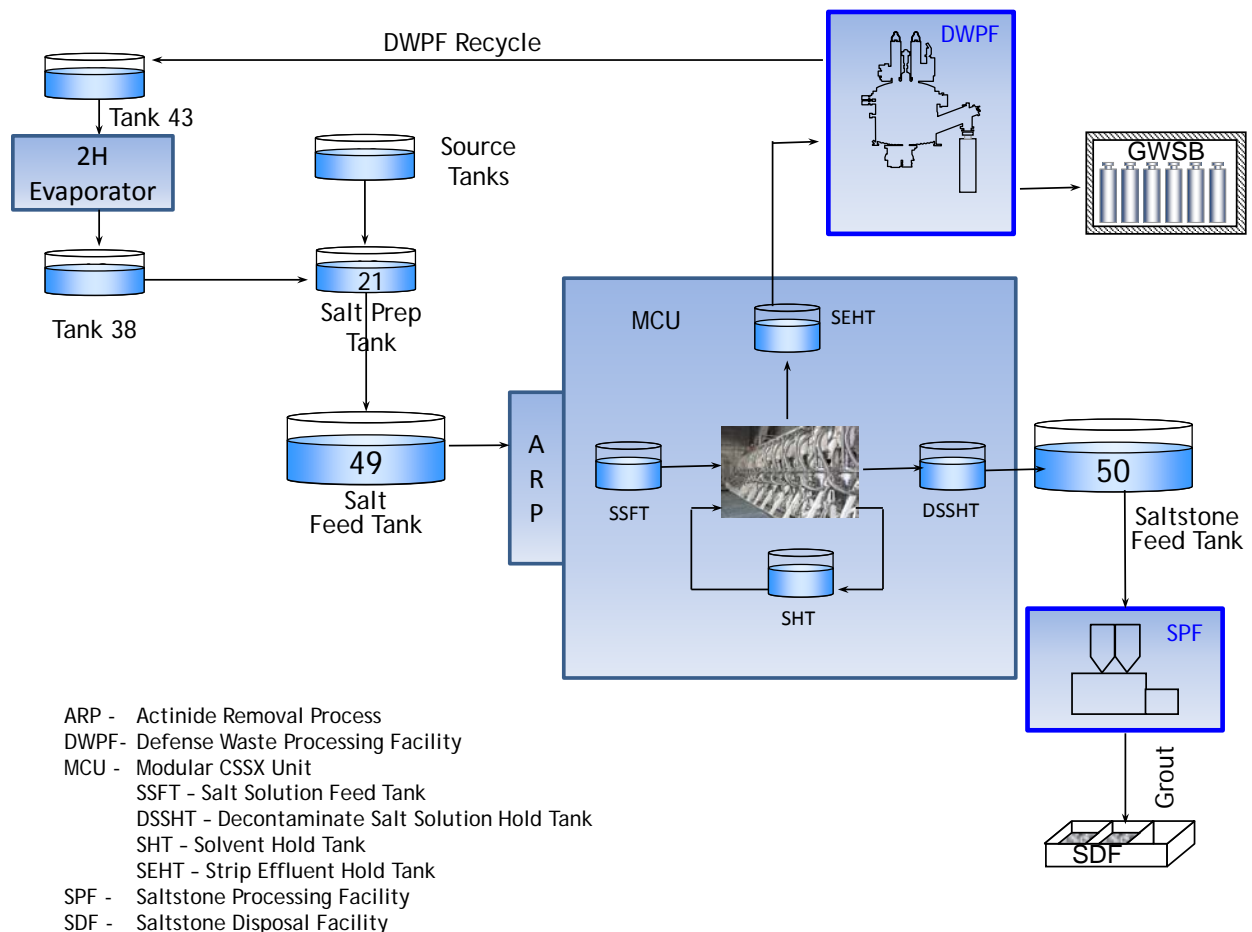SDF -   Saltstone Disposal Facility

Figure 1. Depiction of the Flow of Salt Waste through SRS Liquid Waste Facilities

Once qualified, the waste is fed to the 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 MCU

where cesium is removed using a solvent extraction process and the cesium is diverted to DWPF. The decontaminated salt solution is transferred from MCU to Tank 50 and is sent to Saltstone where the grout waste form is prepared and ultimately disposed in engineered vaults.

Table I provides the mercury speciation data, after adjusted for dilution, for several SRS tanks. The sample from Tank 22 (DWPF recycle tank) is over 100 mg/L of total and dissolved mercury consisting of elemental, ionic and methylmercury in decreasing amounts. Tank 38 surface and depth samples represent material that is a concentration of the DWPF recycle (as a result of evaporator operations) and show the highest concentrations of mercury of all the samples analyzed thus far, with concentrations of total mercury nearing 0.5 g/L. The results from the concentrated wastes show increases in methylmercury but do not show increases in elemental or ionic. This seems appropriate since it is known that reactions in the evaporator produce elemental mercury and some portion is collected in the condensation of the off-gas from the evaporator pot. If it were a direct concentration of the Tank 22 material, the increase in total mercury concentration would be slightly greater than a factor of four. Applying that concentration factor to the methylmercury concentration in Tank 22, one would expect the concentration in Tank 38 to be on the order of 130 mg/L, but the measured values are larger. However, since the estimated analytical uncertainty is approximately 20%, one cannot definitely conclude that methyl mercury is being produced across the evaporation process.

The samples from Tank 21 and Tank 49 represent salt feed to the ARP/MCU process. The mercury concentrations for total, dissolved and methylmercury are in reasonable agreement for two separate salt batches. It is striking that the ionic fraction in these samples are significantly reduced from the evaporator recycle tanks (38 and 43). The ionic mercury concentration for Tank 21 and 49 measured 5.9 and 15.6 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 is believed to be organomercury based on the measured ionic mercury and could represent a measurement low bias in the methylmercury 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 understand the MCU impact better, a single stage extraction was performed and the data are labeled "Tank 21 decon." in Table 1. A comparison of the data from this before and after extract shows a reduction in total, dissolved, and methylmercury indicating some interaction is possible between one of the solvent components and the mercury in the waste. Baseline studies by Delmau, et al. [8] showed a small extraction

distribution coefficient (D_{Hg} = 0.6) in the original extractant.   The data reported here showed a mercury concentration of 67 mg/L in the solvent which corresponds to a distribution coefficient of 0.8.

TABLE I. Mercury Concentrations (mg/L) across the Salt Waste Flowsheet
(Q=Calendar Quarter, S= surface, and D = depth)

Tank	Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg	Ionic Hg	MHg	DMHg	EtHg
22	119	111	8	77	56.5	31.2	--	--
38S	496	325	171	3.6	29.8	200	0.15	<35.1
38D	476	316	160	4.1	31.6	160	0.05	<34.3
43S	286	208	78	1.4	44.0	135	0.005	<8.7
43D	234	186	48	3.5	30.5	134	0.613	<8.4
21	101	120	--	<6.2	5.9	58.2	0.0156	<22
21 Decon	86.7	85	1.7	2.2	5.7	41.1	<0.00012	<4.4
49	110	109	1	6.35	15.6	58.1	0.471	<18
50 4Q14	78.7	--	--	0.57	1.2	37.6	--	--
50 1Q15	126	--	--	0.91	5.0	53.5	0.0022	--
50 2Q15	97.7	94.3	3.4	1	4.9	53.0	0.0235	<4.4
50 3Q15	113	99.6	13.4	2.2	10.2	53.3	0.143	<4.3

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 Hold Tank (SSFT). It if 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 II.

TABLE II. Mercury Concentrations (mg/L) across MCU
(* Dimethylmercury was detected but could not be quantified.)

Tank	Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg	Ionic Hg	MHg	DMHg	EtHg
SSFT	105	92.0	13	0.62	9.15	56.2	0.094	<13
SHT	14.2	13.5	ND	0.27	3.44	3.72	Detected*	--
SHT	11.0	12.3	0.64	0.25	3.10	2.30	Detected*	<0.03
SEHT	21.7	20.5	1.2	0.57	3.50	16.3	0.13	<18
DSSHT	125	125	0	0.74	12.2	77.7	0.0015	<8.6

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 higher than the feed. However, they are certainly within the analytical uncertainty of the measurements. This is a second instance where there does not appear to be a major impact by the process on the mercury waste chemistry. There is one effect that should be acknowledged in this comparison. For dimethylmercury, the measure concentration is reduced almost two orders of magnitude (from 0.094 mg Hg/L to 0.0015 mg Hg/L) between the feed and the decontaminated salt solution. Some of the dimethylmercury partitions to the strip effluent hold tank.   Since dimethylmercury 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 dimethylmercury 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 ionic species measuring 3.5 mg/L and methylmercury 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. This indicates 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 that is poured into engineered vaults in the Saltstone Disposal Facility (SDF). Langdon and Wilhite [9] had previously studied the behavior of mercury in this cementitious waste form and found acceptable performance versus regulatory testing, which was 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. Table III shows the mercury concentrations in TCLP leachates from the second quarter Tank 50 sample and the leachate from a Tank 21 sample of saltstone grout prepared as part of the overall mercury program. Two samples of saltstone grout were prepared from each aqueous waste sample and crushed into two particle distributions (normal at < 9.5 mm and large at <9.5 mm and > 5.6 mm).

TABLE III. Mercury Concentrations (mg/L) from Saltstone Leachates
(Q=Calendar Quarter, L = Large Particle Fraction, N = Normal Particle Fraction)

Tank	Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg	Ionic Hg	MHg	DMHg	EtHg
50 (2Q-L)	0.0135	0.012	0.0016	0.0002	0.0002	0.016	0.00034	<0.0058
50 (2Q-N)	0.016	0.014	0.0015	0.00054	0.0002	0.017	0.0008	<0.004
21 (L)	0.012	0.011	0.00014	0.00001	0.00006	0.014	0.00012	<0.006
21 (N)	0.012	0.012	0.0002	0.0001	0.00009	0.014	0.00013	<0.0056

Examination of these data strongly indicates that the mercury in the TCLP leachate is predominately methylmercury. The measured total Hg leachate concentrations are low and well below the Land Disposal toxicity limit of 0.2 mg/L and are slightly below the TCLP Universal Treatment Standard of 0.025 mg/L. 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.

CONCLUSIONS
Following the speciation of a number of samples from across the Savannah River Site salt waste flowsheet, several conclusions can be drawn, and while additional sampling efforts will reveal how any flowsheet changes impact Hg concentrations, these conclusions apply to salt batches 7 through 9:
- Organomercury species enter the salt flowsheet from several sources including DPWF recycle used to dissolve saltcake, 2H evaporator concentrate used to adjust the salt feed chemistry, and dissolved saltcake feeds.
- Organomercury is predominantly in the aqueous phase and has relatively high solubility (perhaps as high as 0.5 g/L or more) based on Tank 38 data.

- Methylmercury represents about 50% of the total organomercury. The remaining species have not been identified.
- Ionic mercury (either mercurous or mercuric) in the salt feed to MCU is around 15% of the total.
- Ethylmercury analysis has been performed on a number of salt-related samples, but it has not been found at levels above the method reporting limit.
- Methylmercury is several orders of magnitude more abundant than dimethylmercury.
- Methylmercury and ionic mercury do not appear to be extracted by the MCU solvent to a large degree based on speciation of before and after contacts with the solvent.
- Dimethylmercury, methylmercury and ionic mercury are detected in the solvent hold tank samples, but dimethylmercury has so far not been quantified in this stream.
- Some form of mercury is extracted into the solvent and is stripped into the boric acid strip solution based on samples from the strip effluent hold tank and is transferred to DWPF.
- Data indicates that dimethylmercury removed from the salt phase during MCU operation is likely partitioning to the vapor phase and discharged through the vessel vent system.
- Saltstone predominately incorporates both ionic and organomercury species. However, methylmercury preferentially leaches during the performance of the TCLP.

SRNL continues to examine waste tanks and process systems to gain further insight into the Hg cycle in the high-level waste systems at SRS. Currently underway is examinations of the Hg speciation in both the DWPF recycle streams and a second evaporator system. To examine our long-standing assumptions about the form of Hg in incoming DWPF feed, a speciation study of Hg in insoluble, precipitated, HLW tank solids (i.e. sludge) is planned. To date, all simulant sludge processing studies have assumed that Hg is present as insoluble mercuric oxide, and processing conditions for reduction of Hg and steam stripping have been established accordingly.

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