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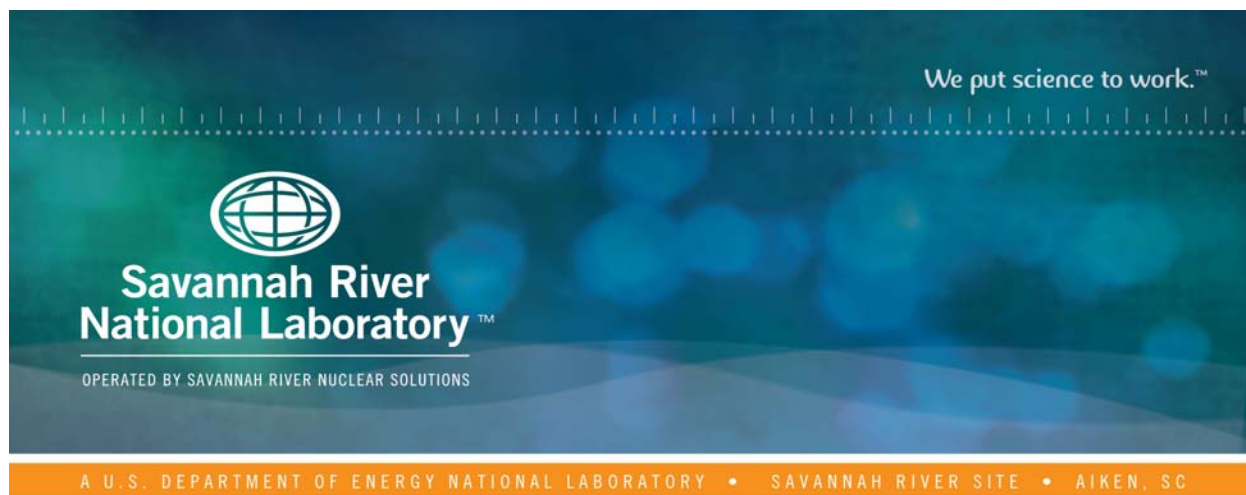
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Speciation of Mercury in Sludge Solids: Washed Sludge

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October 2017

SRNL-STI-2017-00398, Revision 0



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EXECUTIVE SUMMARY

The objective of this applied research task was to study the type and concentration of mercury compounds found within the contaminated Savannah River Site Liquid Waste System (SRS LWS). A method of selective sequential extraction (SSE), developed by Eurofins Frontier Global Sciences^{1,2} and adapted by SRNL, utilizes an extraction procedure divided into seven separate tests for different species of mercury. In the SRNL's modified procedure four of these tests were applied to a washed sample of high level radioactive waste sludge.

The Savannah River Site's continual use of mercury as a catalyst in the dissolution of aluminum cladding has led to the distribution of ~60,000 kg of mercury into the SRS LWS. The concentration of mercury in the salt waste continues to increase and propagate from solid phase waste sludge. This research aims to complete the speciation of the mercury within the sludge in order to better understand the chemical behavior and properties of said mercury. A better understanding of the mercury within the LWS will allow for the development of more accurate and effective waste simulants and treatment techniques.

Table E-1 summarizes the extraction protocol performed on the washed SRS sludge and a high-level summary of the results obtained in this first ever examination of radioactive sludge mercury speciation.

Table E-1. Summary of Extraction Protocol Performed* and Results from Washed SRS Sludge

Step	Extractant	Description of Hg Species	Typical Compounds	Performed on SRS Washed Sludge	Result
F-0	Air	Free Gaseous Elemental Hg	Hg(0), Hg(II), Gaseous Hg	Yes	Inconclusive Due to Foaming
F-1	Deionized Water	Water Soluble Hg Salts	HgCl ₂ , HgSO ₄	No, sludge was already washed	NA
F-2	HCl/HOAc	Low pH Soluble Salts of Hg	HgO	No, initially thought to be unnecessary on caustic dried sludge solids	NA
F-3	KOH	Organic Bound Hg Compounds (Hg(II) Bound to Sludge/Humics)	Hg Humics, Hg ₂ Cl ₂	Existing Supernate Analyzed	Hg(I), Hg(II), predominately dissolved species
F-4	HNO ₃	All Other Non-Sulfide or Silicate Bound Hg Compounds	Mineral lattice, Hg(0)	Yes	HgO
F-5	HNO ₃ /HCl	Sulfide Bound Hg Compounds Only – Cinnabar (Can Include Hg Amalgams)	HgS, M-HgS, HgSe, HgAu	Yes	HgS, possible Hg ₂ Cl ₂ based on standard behavior
F-6	HNO ₃ /HCl/HF	Silicate or Aluminosilicate Bound Hg Compounds – Mineral Bound	Hg in Crystal Lattice	Yes	No Hg Species

*Adapted from information supplied by Eurofins Frontier Global Sciences

The SSE method is an effective way to differentiate potential mercury species in SRS sludge samples. While this study was limited to a single washed sludge drawn late in its processing cycle, prepared in 2013 and sampled in 2016, it has demonstrated that HgO is not the only insoluble Hg species in SRS sludge solids. This is significant because the basis of all processing decisions is the simulant testing conducted by SRNL – to date, this testing has not included insoluble sulfur as HgS.

Historical insoluble sulfur measurements conducted on incoming Defense Waste Processing Facility (DWPF) sludge batches coupled with the observations of this study, indicate that between 5% and 50% (depending upon sludge batch) of the incoming mercury to the DWPF facility may have been HgS. The amount varies depending upon the source tanks utilized for a given sludge batch. The highest level of insoluble sulfur, and possibly HgS, was the Sludge Batch 5 (SB5) material, which was subject to Al dissolution prior to processing in the DWPF. As a high H-Area Modified Plutonium Uranium Redox Extraction (HM) sludge batch, this is consistent with sludge material that would have a high Hg content.

What is less clear is the source or mechanism of potential sulfide formation in the SRS Tank Farm. Additional data will be necessary to definitively identify HgS as the primary insoluble sulfur-containing compound in sludge and what impact HgS has on the new glycolic acid flowsheet. Clear identification of HgS as a sludge constituent would provide increased understanding of mercury and sulfur fate, and would facilitate more representative demonstrations during sludge batch qualification activities, which can reduce costly processing delays due to unexpected behavior.

It is recommended that additional data be acquired to definitively determine if HgS is the primary insoluble sulfur-containing compound in sludge. Acquiring such data through alternative spectroscopic analysis techniques (including X-ray diffraction (XRD), X-ray fluorescence (XRF), and/or scanning electron microscopy (SEM)) and/or thermodynamic modeling would satisfy this need. Specifically, the solids should be examined following extraction F4 and again following extraction F5 of the SSE method. The vast majority of the radioactivity in the sample will be reduced, so it should be possible to rinse, dry, and remove all of the solids for further examination.

Determining the source and/or mechanism of sulfide formation in the SRS Tank Farm is also recommended. If sulfide is conclusively shown to be bound to mercury, it would be useful to understand the source term for this sulfur species.

As previously stated, all processing studies for DWPF have been conducted with simulants that are based on only the addition of HgO. In the SB8 sample studied here, 21% of the Hg was present as a non-oxide species, consistent with HgS based upon insoluble sulfur and selective extraction observations. If HgS is proven to be the primary insoluble sulfur-containing compound in sludge, it is recommended that the applicable amount of HgS be utilized in combination with HgO in future simulant formulations.

Under these conditions, it is also recommended that the ratio of HgS to HgO be evaluated for its impact on DWPF sludge processing mercury removal, as well as impacts throughout the entire LWS flowsheet. While there may be a number of questions, some immediate thoughts include the following: Is there a difference in mercury reduction potential when high HgS is present? How does the ratio of HgS to HgO impact this reduction? Does the proposed glycolic acid flow sheet impact HgS removal rates?

Sludge washing activities that occur during sludge batch preparations likely partition a significant quantity of mercury from the sludge to the salt waste streams. To quantify the amount of mercury that is mobilized prior to the introduction of sludge into the DWPF, SRNL proposes the examination of an unwashed sludge slurry from the SRS Tank Farms. This will allow SRNL to determine the amount of mercury that is already soluble, the amount that is solubilized as a result of sludge washing, and the speciation of the insoluble mercury that eventually will be transferred to the DWPF.

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LIST OF ABBREVIATIONS

CVAFS	Cold Vapor Atomic Fluorescence Spectrometer
DI	Deionized
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EM	Environmental Management
HM	H-Area Modified PUREX
IS	Insoluble Solids
LWS	Liquid Waste System
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PUREX	Plutonium Uranium Redox Extraction
RPM	Revolutions Per Minute
RSD	Relative Standard Deviation
SB	Sludge Batch
sccm	Standard Cubic Centimeters per Minute
SRAT	Slurry Receipt & Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SSE	Selective Sequential Extraction
TCR	Task Change Request
TTQAP	Task Technical & Quality Assurance Plan
TTR	Technical Task Request
WAPS	Waste Acceptance Product Specifications
WP	Waste Processing
XRD	X-Ray Diffraction Spectroscopy

1.0 Introduction

The objective of this applied research task is to study the type and concentration of mercury compounds found within the contaminated Savannah River Site Liquid Waste System (SRS LWS). A method of selective sequential extraction (SSE), developed by Eurofins Frontier Global Sciences^{1,2} and adapted by SRNL, utilizes an extraction procedure divided into seven separate tests for different species of mercury. In the SRNL's modified procedure four of these tests were applied to a washed sample of high level radioactive waste sludge.

The Savannah River Site's continual use of mercury as a catalyst in the dissolution of aluminum cladding has led to the distribution of ~60,000 kg of mercury into the SRS LWS. The concentration of mercury in the salt waste continues to increase and propagate from solid phase waste sludge. This research aims to complete the speciation of the mercury within the sludge in order to better understand the chemical behavior and properties of said mercury. A better understanding of the mercury within the LWS will allow for the development of more accurate and effective waste simulants and treatment techniques.

The customer for this work is the DOE Office of Technology Development (EM-3.2) and funding was provided through a Work Authorization / Task Change Request (TCR) – HQTD1002, “Alternative Waste Pretreatment”. This TCR covers a number of waste related topics, including “Waste Processing (WP) 2.1 At-Tank and In-Tank Treatment to Accelerate Salt and Sludge Processing” (ORNL Lead), “WP 2.2 Approaches for Managing Technetium Issues” (PNNL Lead), and “WP 2.3 Tank Waste Hg Mitigation/Management” (SRNL Lead).

A Task Technical & Quality Assurance Plan (TTQAP)³ was prepared under WP 2.3, which provides summary scope and funding for a number of separate mercury related tasks, including the subject mercury speciation in sludge (Task 2.3.5, excerpt as follows): Mercury is believed to be in the form of mercury oxide in sludge. There is evidence for oxide in sludge but there is no definitive data that all of the mercury is in the form of mercury oxide. Other species could be present such as elemental mercury, mercuric sulfide, etc. These different forms may have different behavior in the Defense Waste Processing Facility (DWPF) flowsheet and Tank Farm operations.⁴

The sludge sample utilized in this work was authorized in a Technical Task Request (TTR)⁵ from Savannah River Remediation, LLC (SRR) and mercury analyses were performed by Eurofins Frontier Global Sciences under SRR Subcontract No. SRRA074197.

2.0 Experimental Procedure

Savannah River Remediation collected a 200 mL dedicated sample of sludge slurry from Tank 40 [HTF-40-16-77] on August 25, 2016, which at the time of collection contained Sludge Batch (SB) 8 material being processed by the Defense Waste Processing Facility (DWPF).

2.1 Volatile Mercury via Purge & Trap (F-0)

Utilizing a Purge & Trap vessel constructed by the SRNL Glass Shop and shown in Figure 2-1, ~21 g of Tank 40 SB8 material was placed into each of five vessels and the exact mass determined. SB8 simulant was placed into the sixth vessel. One drop of Siovation Anti-Foam 747 was added to each vessel. After inserting the bubblers into each of the vessels, the red caps were tightened, and the vessels assembled as shown in the figure. The vessels were purged with Ar for 30 minutes at a rate of 300 – 320 sccm.

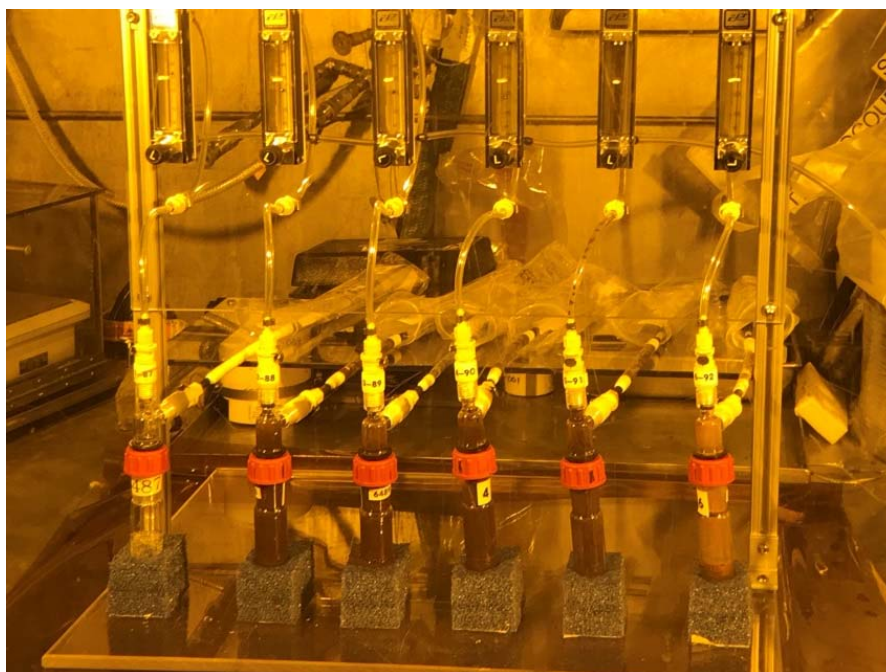


Figure 2-1 Purge & Trap Apparatus in the SRNL Shielded Cells Facility

2.2 Sludge Solids Preparation

Approximately 40 mL of SB8 Tank 40 sludge was filtered through a 0.45 μm filter cup and the collected solids rinsed twice with 50 mL inhibited H_2O (0.011M NaNO_3 /0.01M NaOH). Another ~40 mL of SB8 Tank 40 sludge simulant (non-rad)⁶ was filtered through a 0.45 μm filter cup and the collected solids rinsed twice with 50 mL inhibited H_2O . Both sets of solids were then dried at 105 $^\circ\text{C}$ until a constant weight was achieved.

2.3 1M Caustic Soluble Mercury Fraction (F-3)

The SB8 Tank 40 sludge was centrifuged for 15 minutes at nominally 1200 RPM. One mL (1.042 g) of the supernatant liquid was transferred to a 100 mL volumetric flask and diluted to the mark with Eurofins deionized (DI) H_2O . Two subsamples of this material were collected for Hg speciation in containers with zero headspace, one subsample was placed in a 30 dram glass vial with Teflon lined cap and the other in a 30 mL Teflon bottle. These two samples were transferred to refrigerated storage at 4 – 6 $^\circ\text{C}$ to await final dilution and shipment for mercury speciation. A third subsample was collected for radionuclide measurements including: gamma scan, Cs-removed gamma scan, Tc-99, Sr-90, I-129 and Pu-238/240 analyses needed for sample shipping purposes.

Utilizing Eurofins supplied DI H_2O and pre-cleaned 250 mL clear and amber glass bottles and SRNL supplied 1.2 mL concentrated HCl preservative per sample, triplicate samples were prepared for analysis. Each replicate was analyzed for seven Hg species: total Hg, dissolved Hg, elemental Hg [$\text{Hg}(0)$], ionic/inorganic Hg [$\text{Hg}(\text{I})$ and $\text{Hg}(\text{II})$], methyl Hg [$\text{CH}_3\text{Hg-X}$, where X is a counter anion], ethyl Hg [$\text{CH}_3\text{CH}_2\text{-Hg-X}$, where X is a counter ion], and dimethyl Hg [$(\text{CH}_3)_2\text{Hg}$] by methods described and referenced elsewhere.⁷ The analytes were determined from samples in four separate bottles: 1) methyl Hg and ethyl Hg; 2) dimethyl Hg; 3) total Hg and dissolved Hg; and 4) ionic Hg and elemental Hg.

Prior to shipment, the sample was diluted in a radiochemical hood with DI water and preservative (preservative for bottle set #1 only) to nominally 1:2500 by volume. SRNL DI water was employed as the blank. All containers were filled close to the maximum allowable volume to minimize headspace

with the sealed samples. In total 16 bottles were prepared on January 17, 2017 and shipped the following day by next-day air to Eurofins where 12 samples were received on January 19, 2017. FedEx delayed the delivery of the four acid preserved samples and they were held at their Memphis hub an extra day prior to delivery to Eurofins on January 20, 2017. Since the delayed samples were acid preserved, there was no loss of sample integrity. Eurofins reported the aqueous sample results in units of ng Hg/L sample on February 9, 2017 and the density measurement on February 10, 2017.

2.4 12M HNO₃ Soluble Mercury Fraction (F-4)

Each of five Oak Ridge centrifuge tubes were filled with ~0.4 g of SB8 Tank 40 dried sludge solids. Another ~0.4 g of each Kaolin Clay Hg standard (HgO, HgS, and Hg₂Cl₂ respectively) was added to three additional Oak Ridge centrifuge tubes. A Kaolin Clay blank was added to a separate Oak Ridge centrifuge tube, and ~0.4 g of SB8 Tank 40 simulant dried sludge solids was added to a tenth Oak Ridge centrifuge tube.

To each tube, 40 mL 12M HNO₃ was added, the tube capped and mixed on a Mixi-Max vortex mixer in order to suspend the solids. Once all samples, standards and blanks were suspended in 12M HNO₃, the tubes were placed in a Thermolyne Rotator on setting '40' (maximum rotation) and end-over-end rotation occurred for 16 hours. See Figure 2-2. When the rotation period ended, each tube was centrifuged for 15 minutes at nominally 1200 rpm or until the solids were hard packed. A pipette was employed to transfer ~90% of the supernatant liquid within each tube to a separately labeled and corresponding 100 mL glass volumetric flask with Teflon stopper. Following the supernatant liquid transfers, a second 40 mL 12M HNO₃ was added to each tube, the solids suspended with a vortex mixer, and centrifuged to pack the solids, prior to a second decant of the supernatant liquid. The second supernate fraction was added to the first fraction in a 100 mL glass volumetric flask. The volume of each flask was brought to the mark with 8% HCl. Following dilution, the contents of each flask was transferred to a pre-cleaned, labelled 125 mL glass storage bottle with Teflon-lined cap.

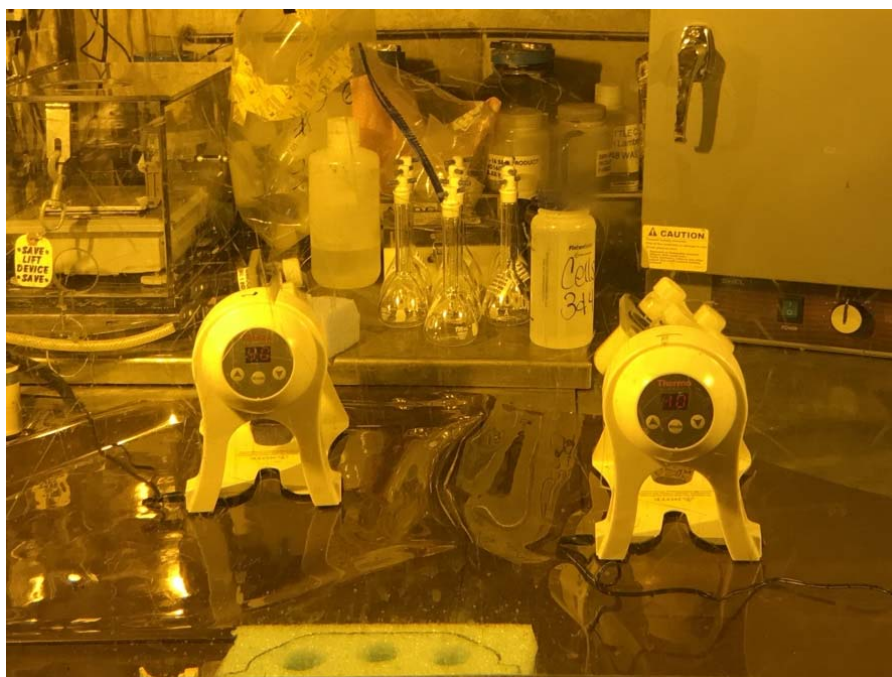


Figure 2-2 Thermolyne Rotators in the SRNL Shielded Cells Facility during soluble Hg (F-4) extractions

2.5 1:4 Aqua Regia Soluble Mercury Fraction (F-5)

To each solid sample left over from the F-4 extractions in Section 2.4, 8.0 mL concentrated HCl and 2.0 mL concentrated HNO₃ was added, the tubes swirled periodically over a four hour period, then left to digest at room temperature for a total elapsed time of eight hours. Each tube was then diluted to 40 mL with 8% HCl, capped tightly, shaken vigorously, and centrifuged for 15 minutes at ~1500 RPM. 90% of the supernatant liquid within each tube was transferred to a 100 mL glass volumetric flask with Teflon cap. The modified 1:4 aqua regia digestion was then repeated and the resulting diluted supernatant liquid combined with the first fraction in the volumetric flask, and the final volume brought to 100 mL with 8% HCl.

2.6 Mineral Bound Mercury (F-6)

The solids remaining from each F-5 extraction in Section 2.5 were transferred quantitatively and separately to a 125 mL Teflon digestion vessel using a portion of 18.75 mL of concentrated HNO₃. Following transfer, the balance of the concentrated HNO₃ was added to the vessel along with 6.25 mL of 48-50% HF, and 3 mL of concentrated HCl. A capping station was utilized to secure the digestion vessel lid and each vessel was placed in an oven at ~130 °C for 12 hours. The seal on each digestion vessel was examined and found to be intact at the end of 12 hours. After digestion, the contents were diluted to 40 mL with 8% HCl and transferred to a 100 mL glass volumetric flask with Teflon cap and brought to a final volume with additional 8% HCl.

2.7 Weight Percent Solids Measurements

Weight percent total and dissolved solids (also known as uncorrected soluble solids) were measured using an established procedure⁸ and then the soluble solids (also known as corrected soluble solids) and insoluble solids were calculated.⁹

2.8 Density Measurements

Density determinations on the final extraction fluids were made using a 10.00 mL volumetric flask that was standardized with deionized water at a temperature between 14 °C and 17 °C to determine a volume. The calibrated flask was then used to measure the mass of the sample and the density calculated using the previously determined volume.

2.9 Radiochemical Analysis and Shipping

The F-4, F-5, and F-6 fractions from the sample with the largest initial amount of sludge solids were subsampled into green shielded polyethylene bottles and submitted for radiochemical analysis including: gamma scan, Cs-removed gamma scan, Tc-99, Sr-90, I-129 and Pu-238/240. The resulting activity levels were then used in calculations for the final dilutions necessary to meet Eurofins radioactive material license limitations. The final dilutions of the radioactive samples were 200 µL brought to 100.00 mL in a volumetric flask.

Non-radioactive extractions for simulant, mercury standards, and blank samples did not undergo further dilution prior to shipment to Eurofins.

2.10 Total Mercury Analysis

Eurofins conducted total mercury analyses on each of the 30 samples submitted from the selective sequential extractions by oxidizing mercury to Hg(II) in each sample with bromine monochloride overnight and at room temperature. Aliquots of each digest were reduced to Hg(0) with SnCl₂, and then purged onto Au traps as a pre-concentration step,¹⁰ followed by thermal desorption into a cold vapor atomic fluorescence spectrometer (CVAFS).

2.11 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Site Manual E7 Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 HTF-40-16-77 Properties

The weight percent total solids, dissolved solids (supernate basis), and insoluble solids, as well as the supernate density were measured on the SB8 Tank 40 sample drawn for this study. There was not enough sample remaining to determine the density of the slurry, but this value was not needed for the calculations performed for this report. The values measured as well as those determined previously for the SB8 WAPS sample are given in Table 3-1. There was a significant drop in total and insoluble solids over the past three years. This is likely the result of bearing water in-leakage over the period since the original WAPS sample was pulled from Tank 40 in July 2013.

**Table 3-1 Measured solids and densities for SB8 Tank 40 Samples (%RSD)
[No. of Replicates]**

Property	Tank 40 SB8 SSE [HTF-40-16-77]	Tank 40 SB8 WAPS [HTF-40-13-177]¹⁷
Slurry Density (g/mL)	NA	1.16 (1.0) [4]
Supernate Density (g/mL)	1.05 (0.96) [3]	1.06 (0.2) [4]
Total Solids (Wt.% in Slurry)	13.70 (1.1) [4]	17.21 (0.9) [8]
Dissolved Solids (Wt.% in Supernate)	5.27 (3.3) [3]	6.64 (1.1) [4]
Insoluble Solids (Wt.% in Slurry)	8.90	11.32

3.2 Volatile Mercury via Purge & Trap (F-0)

The purge and trap methodology utilized for this experiment was mocked up using Tank 40 SB8 simulant sludge to test flow rates, headspace, and antifoam effectiveness. With the simulant sludge the vessel design and conditions were successfully demonstrated. However, when employed in the Shielded Cells, the actual sludge slurry quickly developed a persistent foam that rose rapidly up the vessel, through the soda lime drying trap, and into the Carbotraps designed to collect the elemental and dimethylmercury. The foam carried highly radioactive sludge solids into the traps, making them unsuitable for shipment to Eurofins for analysis.

In future sludge mercury speciation work, it will be necessary to redesign the containment vessels to provide additional headspace and to use significantly more antifoam agent to suppress foaming of the sludge. The design and testing work will need to be conducted with actual radioactive sludge in order to

ensure that the modifications to the system are adequate to protect the traps from contact with sludge solids.

Since it was not possible to measure volatile mercury species via purge and trap on the present sample, the volatile species were measured on diluted samples of supernatant liquid as discussed in the next section.

3.3 Caustic Soluble Mercury Fraction (F-3) Speciation

The speciation of mercury found in the supernate fraction of the Tank 40 SB8 sample is shown in Table 3-2. The SRNL measured Tank 40 supernate density of 1.048 g/mL was used in the calculations. Total Hg was 74.0 mg Hg/L supernate and the species recovery as a fraction of total Hg is between 80-83%, which is reasonable considering the uncertainties of the various individual measurements that go into this overall determination. As will be discussed in the next section, the total Hg in the supernatant phase is only a small fraction of the total Hg measured in the sludge sample.

Table 3-2 Average concentrations of various Hg species for Tank 40 SB8 supernate expressed as mg Hg/L (ppm) [%RSD] (No. of Replicates)¹¹

Total Hg	Dissolved Hg	Particulate Hg	Elemental Hg [Hg(0)]	Ionic Hg [Hg(I) & Hg(II)]	Methyl Hg	Ethyl Hg	Dimethyl Hg	Species Fraction of Total Hg
74.0 [1.1] (3)	65.4 [5.1] (3)	6.82*	1.73 [16] (3)	50.8 [17] (3)	<0.49	<1.7	<0.049	80 – 83%

* The particulate value is the difference of the total and dissolved Hg values after subtracting elemental Hg

3.4 Selective Sequential Extractions

The Hg species that can be expected in various extraction fractions are described in Table 3-3. Since fraction F-4 was the first acidic extraction that the dried solids materials were exposed to, the HgO would be expected to dissolve into this fraction. The results of the total mercury measurements on the extraction fractions for five replicates of SB8 Tank 40 insoluble solids, the insoluble solids from a SB8 Tank 40 simulant with HgO, a Kaolin Clay standard with HgO, a Kaolin Clay standard with HgS, a Kaolin Clay standard with Hg₂Cl₂, and a Kaolin Clay blank are given in Table 3-4. One replicate of the fraction F-4 extractions with Tank 40 insoluble solids had a measured total mercury value that was about one quarter of the other four replicates, so it was not included in the average shown in the table. To obtain the total recovery of each mercury species: HgO, HgS, and Hg₂Cl₂ shown in Table 3-5, the fractions for the respective standard were summed for each extraction.

Table 3-3 Expected Hg Fractions During Selective Sequential Extraction*

Step	Extractant	Description of Hg Species	Typical Compounds	Expected Mobility
F-0	Air	Free Gaseous Elemental Hg	Hg(0), Hg(II), Gaseous Hg	Relatively Low†
F-1	DI Water	Water Soluble Hg Salts	HgCl ₂ , HgSO ₄	Highly Mobile
F-2	HCl/HOAc	Low pH Soluble Salts of Hg	HgO	Relatively Low
F-3	KOH	Organic Bound Hg Compounds (Hg(II) Bound to Sludge/Humics)	Hg Humics, Hg ₂ Cl ₂	Mobility Varies‡
F-4	HNO ₃	All Other Non-Sulfide or Silicate Bound Hg Compounds	Mineral lattice, Hg(0)	Low Mobility
F-5	HNO ₃ /HCl	Sulfide Bound Hg Compounds Only – Cinnabar (Can Include Hg Amalgams)	HgS, M-HgS, HgSe, HgAu	Relatively Immobile
F-6	HNO ₃ /HCl/HF	Silicate or Aluminosilicate Bound Hg Compounds – Mineral Bound	Hg in Crystal Lattice	Relatively Immobile

*Adapted from information supplied by Eurofins Frontier Global Sciences

† Elemental gaseous Hg has low vapor pressure at room temperature – high volatility

‡ Dependent on factors including redox conditions and the presence of competing complexing agents

Table 3-4 Concentrations of Hg in SSE fractions F-4, F-5, and F-6 for Tank 40 SB8, SSE Hg standards, blank, and SB8 simulant sludge solids

Sample	Total Hg (mg Hg / g insoluble solids) [%RSD] (No. of Replicates)	Percent of Total Hg Measured
Tank 40 SB8 – F-4	22.2 [5.8] (4)	78.7
HgS Std – F-4	0.0219	2.1
Hg₂Cl₂ Std – F-4	0.174	12.4
HgO Std – F-4	1.44	98.5
Blank – F-4	0.00224	74.5
Tank 40 SB8 Simulant – F-4	30.7	99.8
Continues Next Page		

Sample	Total Hg (mg Hg / g insoluble solids) [%RSD] (No. of Replicates)	Percent of Total Hg Measured
Tank 40 SB8 – F-5	5.91 [3.6] (5)	21.0
HgS Std – F-5	1.03	97.9
Hg₂Cl₂ Std – F-5	1.23	87.4
HgO Std – F-5	0.0214	1.5
Blank – F-5	0.000403	13.4
Tank 40 SB8 Simulant – F-5	0.0546	0.2
Tank 40 SB8 – F-6	0.00850 [10] (5)	0.03
HgS Std – F-6	0.000237	0.02
Hg₂Cl₂ Std – F-6	0.00290	0.2
HgO Std – F-6	0.00104	0.1
Blank – F-6	0.000364	12.1
Tank 40 SB8 Simulant – F-6	0.000529	0.002

Table 3-5 SSE recovery of mercury (mg Hg / g IS)

Sample	Measured	Calculated	% Difference
Tank 40 SB8	28.2*	28.3**	-0.2
HgS Standard	1.05	1.005	4.3
Hg ₂ Cl ₂ Standard	1.40	1.363	3.1
HgO Standard	1.46	1.40	4.6
Blank	0.00301		
Tank 40 SB8 Simulant	30.8	37.7	-18

* Does not include a small contribution of soluble supernate Hg to Total Hg, see text.

** Includes a small contribution of soluble supernate Hg, see text.

Based upon Eurofins previous experience, HgO should extract in fraction F-4, and this is what was observed for both the Kaolin Clay standard with HgO and the SB8 Tank 40 simulant with HgO, where ~99% of the Hg is seen in fraction F-4. No appreciable extraction of the HgS standard occurred in fraction F-4, where only 2.1% of the Hg in this standard was measured. However, HgS did extract into the F-5 fractions, where ~98% of the Hg in the Kaolin Clay HgS standard was recovered and most significantly, 21% of the Hg in the SB8 Tank 40 insoluble solids was recovered.

The total Hg measured for the simulant was about 18% lower than the calculated total mercury. This difference may be due to the fact that the HgO was added to the simulant after it was precipitated, rather than co-precipitated with the other metal ions. This simulant was then subsampled, the solids collected, washed with inhibited H₂O, and dried. If the HgO was not evenly distributed within the simulant, it is possible that we isolated some solids that were high in Hg relative to the bulk solids. If this method of mercury introduction is done again, the simulant should be sonicated following addition to help ensure the even distribution of the oxide throughout the slurry.

We observed that there was a considerable difference in the appearance of the SB8 Tank 40 sludge simulant and the actual SB8 Tank 40 material following extraction F-5. Shown in Figure 3-1 is a side-by-side comparison of the remaining solids following the modified aqua regia extractions. The simulant solids are now white and the actual sludge solids are still dark brown. The reason for this difference is unclear, but the behavior of the solids through the first two extractions has resulted in a modification of the simulant relative to the actual waste.

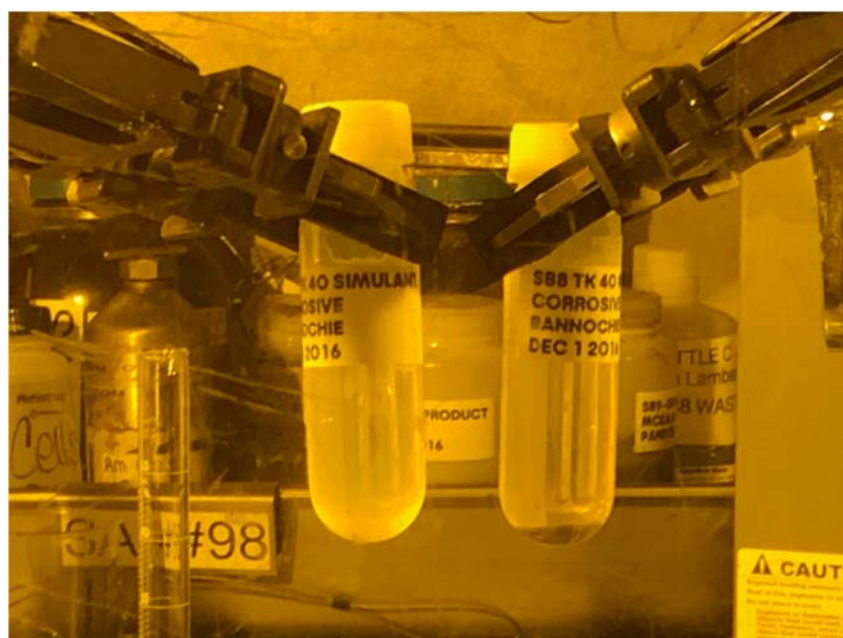


Figure 3-1. Difference in remaining solids following completion of extraction F-5. The left sample (white solids) is the SB8 Tank 40 Simulant and the right sample (brown solids) is the SB8 Tank 40 Waste.

Since SB3, we have monitored the insoluble sulfur content of the Tank 40 WAPS samples.^{12,13,14,15,16,17} In SB8, it was noted that 14% of the total sulfur in the sample was insoluble.¹⁷ Insoluble sulfur reached a high of 50% of total sulfur in SB5.¹⁴ If the 14% insoluble sulfur measured in SB8 WAPS sample is placed on an insoluble solids basis, it becomes 0.745 mg S / g IS. This is enough sulfur to form 5.41 mg

HgS / g IS, or 79% of the HgS suspected to be present in the SB8 Tank 40 sample measured in this experiment. This is excellent agreement considering we are comparing two different samples of SB8 Tank 40, one from July 2013 and one from August of 2016, and there are analytical uncertainties in both the sulfur measurements and the mercury measurements. Previously SRNL could only conjecture on what form of sulfur we were dealing with in the WAPS samples. A 2012 report examined sulfur measurements during DWPF processing of SB7b.¹⁸ This cross-laboratory study involved SRNL, F/H Labs, and the DWPF Lab and confirmed that up to approximately 24% of the sulfur in SB7b may be insoluble. Future work was proposed to identify the insoluble sulfur species present in the two examined samples, Tank 40 SB7b Waste Acceptance Product Specifications (WAPS) sample and the DWPF SB7b Slurry Receipt & Adjustment Tank (SRAT) product #632 sample, but limitations were evident in our ability to speciate this small amount of insoluble sulfur in an already small amount of total sulfur. Non-sulfate sulfur species in DWPF sludge slurry and SRAT product samples was the subject of an additional SRNL study in 2013.¹⁹ This work was able to show that non-sulfate, soluble sulfur was not thiosulfate, which was observed in Hanford Salt Waste.²⁰ It can be concluded from the SSE work conducted here that a possible candidate for insoluble sulfur species in DWPF sludge batches is HgS.

The SB8 WAPS sample was shown to have 1.86 wt.% Hg on a total solids basis.¹⁷ Converting the 28.2 mg Hg/g IS for the total Hg measured in the SSE sample to a wt.% TS basis and adding the 74.0 mg Hg/L supernate, also converted to a total solids basis, would project 1.89 wt.% Hg in the WAPS sample. If one converts these measured Hg values to a wt.% total solids basis using the measured properties from Table 3-1 for the SSE Tank 40 sample, one finds 1.88 wt.% Hg on a total solids basis. This indicates that there has been no change in the amount of total mercury on a total solids basis over the course of processing.

If we look at the fraction F-5 mercury content from the perspective of how much HgS could this represent in the original WAPS sample, as opposed to the amount of HgS it represents based upon the sulfur in the WAPS sample as a limiting reagent, we find that there is enough Hg in fraction F-5 to account for 6.86 mg HgS/g IS. The ratio of HgS to HgO could change over time - repeated slurry and transfer operations, as well as water in-leakage to the tank, could increase the percentage of HgS to HgO. The K_{sp} of HgS is $2E-54$ (red form) and $2E-53$ (black form),²¹ 27 orders of magnitude more insoluble than HgO (K_{sp} $3.6E-26$).²¹ It has been noted that the solubility of HgO in water depends upon the particle size,²² which also could change over time with tank slurry operations. The thermal decomposition temperatures of HgS and HgO also differ. HgS decomposes at a temperature between 265°C and 345°C²³ and HgO decomposes at 500°C²⁴.

According to Eurofins' experimental experience, the calomel, Hg_2Cl_2 , should also have extracted in fraction F-4. Normally, it is removed during the 1M KOH extraction (F-3), but since washed SRS tank waste is nominally 1 M hydroxide, there was no reason to conduct this extraction. Hence, the calomel would be expected to dissolve in the first (F-4) fraction, but instead, the calomel standard extracted in fraction F-5. There is currently no explanation for this observation. The recovery of calomel matches closely the actual amount in the standard (see Table 3-5), so this suggests that neither two HgS standards were mistakenly prepared by Eurofins, nor two HgS standards were measured out by the SRNL Shielded Cells technicians. However, since calomel extracted with fraction F-5, other species could also have extracted too. These other species could include mercury halides and mercury amalgams formed between elemental Hg and noble metals. Sulfur should compete favorably for Hg present in amalgams since one of the methods for removing Hg adsorbed onto Au (thus forming an amalgam) is to place the amalgam into sulfur, which draws the Hg out of the Au.

No appreciable Hg was measured in the fraction F-6 samples. This indicates there was no silicate trapped Hg species in this sludge sample. The F-6 samples contained only 0.03% ($0.00850/28.2 \times 100$) of the SB8 Tank 40 Hg. Following the final dilution of fraction F-6 with 8% HCl, we observed the formation of a white crystalline solids in the volumetric flasks following transfer of the solution to 125 mL storage

bottles, and then further white, crystalline solids formation after the storage bottles sat overnight in the Shielded Cells, likely brought on by cooler evening temperatures in the cells in December. See Figure 3-2. The initial concern was that these solids may pull mercury out of solution. The solids were collected on a 0.45 μm filter cup filter, rinsed with DI water, and allowed to air dry with suction for several hours. A subsample of the solids was then collected and submitted for x-ray diffraction analysis (XRD).

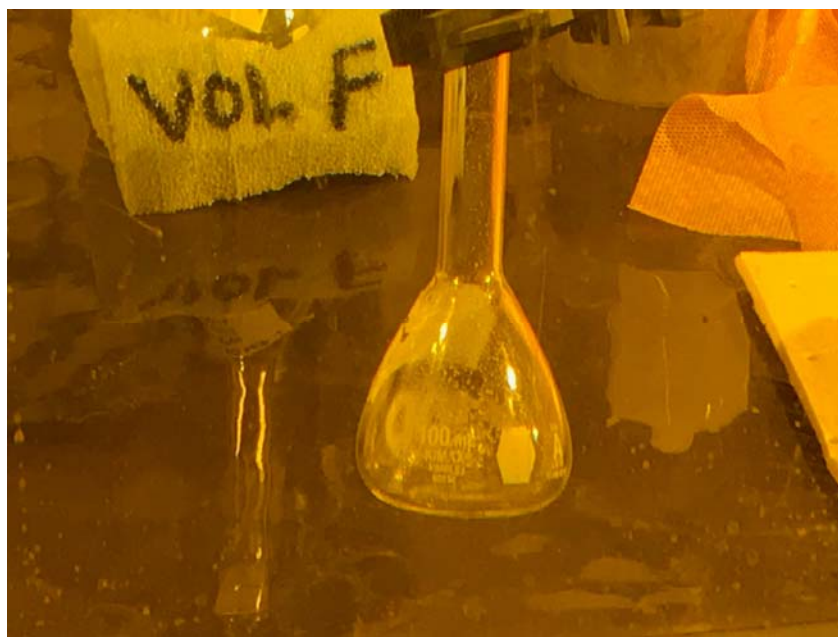


Figure 3-2 Solids precipitated in the final dilution flasks for fraction F-6.

The XRD analysis spectrum for the white crystalline solids collected is shown in Figure 3-3. The pattern was a very clean match to Na_2SiF_6 (Malladrite). This was not an unexpected precipitate, but it did confirm that the solids did not contain significant mercury. Upon dilution of the $\text{HNO}_3/\text{HF}/\text{HCl}$ digestion solution with 8% HCl , the silicon fluoride precipitated. Normally, this dilution would have been done with bromine monochloride, but this chemical is banned from air transport, so a substitution was made that allowed the precipitation to occur.

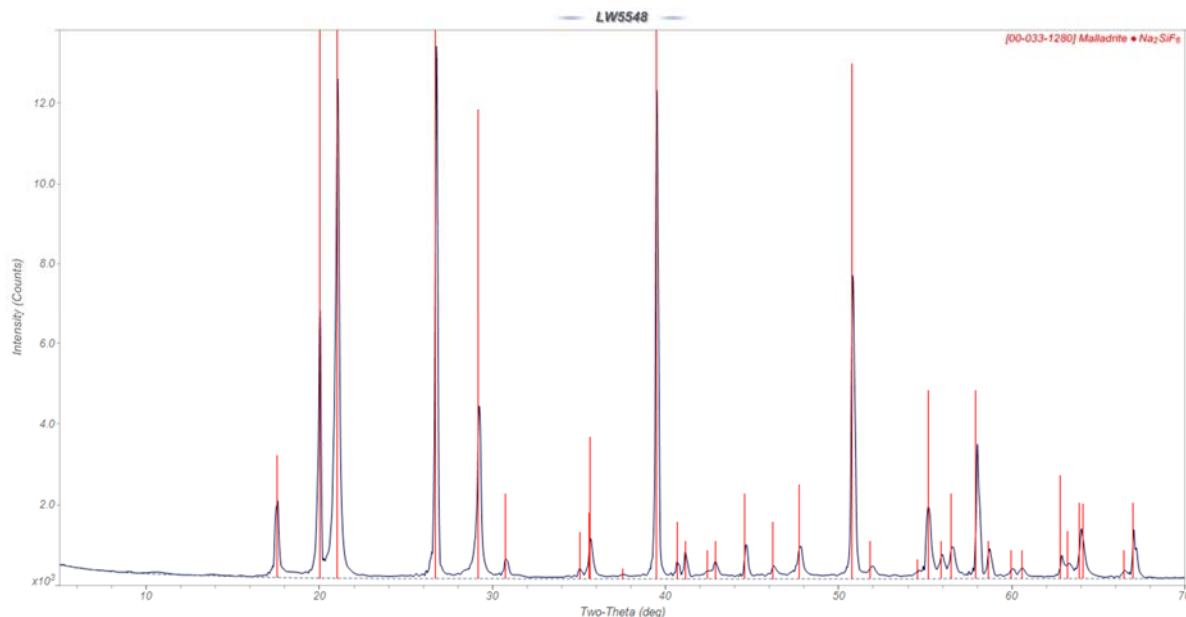


Figure 3-3 XRD of fraction F-6 reprecipitated solids confirming Na_2SiF_6 .

4.0 Conclusions

The SSE method is an effective way to differentiate potential mercury species in SRS sludge samples. While this study was limited to a single washed sludge drawn late in its processing cycle, prepared in 2013 and sampled in 2016, it has demonstrated that HgO is not the only insoluble Hg species in SRS sludge solids. This is significant because the basis of all processing decisions is the simulant testing conducted by SRNL – to date, this testing has not included insoluble sulfur species such as HgS .

Historical insoluble sulfur measurements conducted on incoming DWPF sludge batches^{12,13,14,15,16,17} coupled with the observations of this study, indicate that between 5% and 50% (depending upon sludge batch) of the incoming mercury to the DWPF facility may have been HgS . The amount varies depending upon the source tanks utilized for a given sludge batch. The highest level of insoluble sulfur and possibly HgS was the SB5 material, which was subject to Al dissolution prior to processing in the DWPF. As a high HM-sludge batch, this is consistent with sludge material that would have a high Hg content.

What is less clear is the source or mechanism of potential sulfide formation in the SRS Tank Farm. Additional data will be necessary to definitively identify HgS as the primary insoluble sulfur-containing compound in sludge and what impact HgS has on the new glycolic acid flowsheet. Clear identification of HgS as a sludge constituent would provide increased understanding of mercury and sulfur fate, and would facilitate more representative demonstrations during sludge batch qualification activities, which can reduce costly processing delays due to unexpected behavior.

5.0 Recommendations and Future Work

Acquire additional data to definitively determine if HgS is the primary insoluble sulfur-containing compound in sludge. Acquire such data through alternative spectroscopic analysis techniques (including X-ray diffraction (XRD), X-ray fluorescence (XRF), and/or scanning electron microscopy (SEM)) and/or thermodynamic modeling. Specifically, the solids should be examined following extraction F4 and again following extraction F5. The vast majority of the radioactivity in the sample will be reduced, so it should be possible to rinse, dry, and remove all of the solids for further examination.

Determine the source and/or mechanism of sulfide formation in the SRS Tank Farm. If sulfide is conclusively shown to be bound to mercury, it would be useful to understand the source term for this sulfur species.

To date, all processing studies for DWPF have been conducted with simulants that are based on only the addition of HgO. In the SB8 sample studied here, 21% of the Hg was present as a non-oxide species, consistent with HgS based upon insoluble sulfur and selective extraction observations. If HgS is proven to be the primary insoluble sulfur-containing compound in sludge, it is recommended that applicable amounts of HgS be utilized in combination with HgO in future simulant formulations.

Under these conditions, it is also recommended that the ratio of HgS to HgO be evaluated for its impact on DWPF sludge processing mercury removal, as well as impacts throughout the entire LWS flowsheet. While there may be a number of questions, some immediate thoughts include the following: Is there a difference in mercury reduction potential when high HgS is present? How does the ratio of HgS to HgO impact this reduction? Does the proposed glycolic acid flow sheet impact HgS removal rates?

Sludge washing activities that occur during sludge batch preparations likely partition a significant quantity of mercury from the sludge to the salt waste streams. To quantify the amount of mercury that is mobilized prior to the introduction of sludge into the DWPF, we propose the examination of an unwashed sludge slurry from the SRS Tank Farms. This will allow us to determine the amount of mercury that is already soluble, the amount that is solubilized as a result of sludge washing, and the speciation of the insoluble mercury that eventually will be transferred to the DWPF.

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