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Speciation of Mercury in Sludge Solids: Unwashed Sludge

C. J. Bannochie

June 2020

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Speciation of Mercury in Sludge Solids: Unwashed Sludge

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EXECUTIVE SUMMARY

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), originally developed by (Eurofins) Frontier Global Sciences (FGS) and adapted by the Savannah River National Laboratory (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 an unwashed sample of high-level radioactive waste sludge.

The Savannah River Site's 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 the 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".

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

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

Step	Extractant	Description of Hg Species	Typical Compounds	Performed on SRS Unwashed Sludge	Result from this Study
F-0	Air	Free Gaseous Elemental Hg	Hg(0), Hg(II), Gaseous Hg	No, parameters for this test were not established following foaming issues with a prior Washed Sludge	NA
F-1	Deionized Water	Water Soluble Hg Salts	HgCl ₂ , HgSO ₄	No, sludge solids were already washed with inhibited water during collection	NA
F-2	HCl/HOAc	Low pH Soluble Salts of Hg	HgO	No, 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	Yes	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	Hg amalgam
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 unwashed sludge drawn from Tank 51 during assembly of SB10, it, along with the washed sludge reported previously, have demonstrated that oxides of mercury or coprecipitated Hg-metal oxides are 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 Hg species such as mercury amalgams.

Historical insoluble sulfur measurements conducted on incoming DWPF sludge batches^{15,16,17,18,19,20} have indicated that between 5% and 50% (depending upon sludge batch) of the incoming sulfur is insoluble, but we can now conclude that this sulfur is not bound as HgS. This result was determined by examining the post-extracted F-3 and F-4 sludge solids, which showed no indication of S associated with Hg. Since the non-oxide Hg is likely not a sulfide, the composition of the insoluble sulfur species remains elusive. The highest level of insoluble sulfur was the SB5 material, which was subjected to Al dissolution prior to

processing in the DWPF. As a high 'H-Area Modified' (HM) Plutonium-Uranium Redox Extraction (PUREX) sludge batch with a high Hg content, the relationship between this high Hg containing sludge and sulfur is unclear.

To date, all processing studies for DWPF have been conducted with simulants that are based on only the addition of HgO. In the washed sludge sample studied previously, 21% of the Hg was present as a non-oxide species¹³. In the unwashed sludge sample studied here, 19% of the Hg was present as a non-oxide species that is now suspected to be a mercury amalgam.

Previously, we proposed examining an unwashed sludge slurry from the SRS Tank Farm in order to determine the amount of soluble Hg present and the amount that is mobilized prior to the introduction of sludge into the DWPF as a result of sludge washing. That has now been accomplished. About 4% of the Hg is present in the sludge supernate, but another 12% is likely solubilized during sludge washing and transferred to the salt waste stream before DWPF processing begins.

The initial scope of this work proposed looking at three, SRS tank sludge samples, the first washed, the second unwashed, and the third from an unwashed, high HM-containing sludge prior to transfer for sludge batch preparation. Applying the lessons learned from the first two SSE studies on the final sludge is still recommended. With a sufficiently sized sample an examination of volatile Hg species would also be possible as was initially attempted with the first washed sludge until excessive foaming prohibited completion of the experiment.

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LIST OF ABBREVIATIONS

CVAFS	Cold Vapor Atomic Fluorescence Spectrometer
DI	Deionized
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EDS	Energy Dispersive Spectroscopy
EM	Environmental Management
FGS	(Eurofins) Frontier Global Sciences
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
XRF	X-Ray Fluorescence 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), originally developed by (Eurofins) Frontier Global Sciences (FGS)^{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 an unwashed sample of high-level radioactive waste sludge.

The Savannah River Site's 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 the 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. The intended fate of Hg in sludge processed through the DWPF is to reduce all Hg species to Hg(0) and steam strip the elemental mercury out of the sludge for collection before it is vitrified into glass. Thus understanding the mercury species associated with radioactive sludge is important. 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" (Oak Ridge National Laboratory (ORNL) Lead), "WP 2.2 Approaches for Managing Technetium Issues" (Pacific Northwest National Laboratory (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 a 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 FGS under SRR Subcontract No. SRRA074197.

2.0 Experimental Procedure

Savannah River Remediation collected a 3 L sample of sludge slurry from Tank 51 [HTF-51-17-112] on November 28, 2017 for the purposes of studying aluminum dissolution. A 200 mL subsample was obtained for this study. At the time of collection, Tank 51 contained pre-Sludge Batch (SB) 10 material, or unwashed material being prepared for eventual processing by the Defense Waste Processing Facility (DWPF).

2.1 Sludge Solids Preparation

Approximately 200 mL of pre-SB10 Tank 51 sludge slurry was filtered through a 0.45 μm filter to collect the solids. The collected solids were transferred to a clean PMP beaker to which was added 50 mL inhibited H_2O (0.011M NaNO_3 /0.01M NaOH) and allowed to soak for approximately 90 minutes. The slurried solids were transferred to a clean, disposable nylon filter cup and filtered under vacuum. A second 50 mL portion of inhibited H_2O was used to transfer any remaining solids to the filter cup and rinse the solids on the disposable filter, where they were vacuum dried overnight, then transferred to a clean, previously weighed beaker and dried at 103°C until a constant weight was achieved. The final mass of dried insoluble solids was 13.29 g.

Approximately 40 mL of SB9 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 . The solids were then dried at 105 °C until a constant weight of 6.714 g was achieved.

2.2 Supernate Mercury Fraction

One mL (1.133 g) of the pre-SB10 Tank 51 sludge supernatant liquid was transferred to a 100 mL volumetric flask and diluted to the mark with Eurofins FGS 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 °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 shipment purposes.

Utilizing Eurofins FGS supplied DI H_2O and pre-cleaned 250 mL clear and amber glass bottles and SRNL supplied 1.2 mL Ultrapure concentrated HCl preservative for each dilution destined for methyl Hg and ethyl Hg determination, 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 samples were 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 within the sealed samples. In total 16 bottles were prepared on July 17, 2018 and shipped the following day by next-day air to Eurofins FGS where they were received on July 19, 2018. Eurofins FGS reported the aqueous sample results in units of ng Hg/L sample on August 28, 2018.

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

Each of five Oak Ridge centrifuge tubes were filled with ~0.4 g of pre-SB10 Tank 51 dried sludge solids. Another ~0.4 g of each Kaolin Clay Hg standard (HgO , HgS , and Hg_2Cl_2 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 SB9 Tank 40 simulant dried sludge solids was added to a tenth Oak Ridge centrifuge

tube. The final amount of material added into each Oak Ridge centrifuge tube is given in Table 2-1. The two sample numbers that include an 'R' are replicates prepared during the extractions.

Table 2-1. Mass of dried solids in each replicate, standard, and blank.

	Sample Description	Sample Mass (C)
1	Pre-SB10 TK51 #1	0.457
2	Pre-SB10 TK51 #2	0.420
2R	Pre-SB10 TK51 #2	0.451
3	Pre-SB10 TK51 #3	0.445
4	Pre-SB10 TK51 #4	0.416
5	Pre-SB10 TK51 #5	0.406
6	SB9 TK40 Simulant	0.396
7	KC HgO	0.425
8	KC HgS	0.450
8R	KC HgS	0.434
9	KC Hg ₂ Cl ₂	0.413
10	KC Blank	0.401

To each tube, 40 mL 1M KOH was added, the tube capped and mixed on a on a Mixi-Max vortex mixer in order to suspend the solids. Once all samples, standards and blanks were suspended in 1M KOH, the tubes were placed in a Thermolyne Rotator on a setting '40' (maximum rotation) and end-over-end rotation occurred for 16 hours. See Figure 2-1. When the rotation period ended, each tube was centrifuged for 30 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 of 1M KOH was added to each tube, the solids suspended with a vortex mixer, and centrifuged to pack the solids, prior to a second transfer of the supernatant liquid. The second supernate fraction was added to the first fraction in a 100 mL thick-walled glass volumetric flask. The volume of each flask was brought to the mark with 8% HCl. Following dilution, the contents of each flask containing non-radioactive material was transferred to a pre-cleaned, labelled 125 mL glass storage bottle with Teflon-lined cap and removed from the shielded cell. Those containing radioactive material were left in their volumetric flasks until diluted for final speciation analysis.

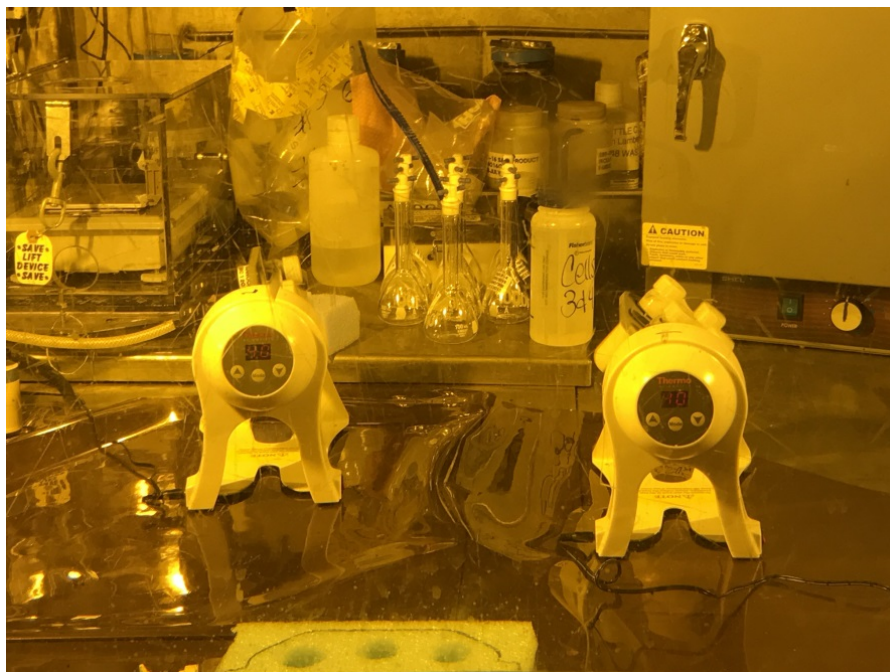


Figure 2-1 Thermolyne Rotators in the SRNL Shielded Cells Facility during Hg extractions

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

Using the solid samples left over from each F-3 extraction in Section 2.3, 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. When the rotation period ended, each tube was centrifuged for 30 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 containing non-radioactive material was transferred to a pre-cleaned, labelled 125 mL glass storage bottle with Teflon-lined cap and transferred out of the shielded cell. Those containing radioactive material were left in their volumetric flasks until diluted for final speciation analysis.

2.5 Post F-4 Extraction Solids Analysis

Pre-SB10 Tank 51 Replicate #2 solids were set aside following the F-4 extraction in order to examine the solids for HgS. Erroneously, 8% HCl was added to this set aside solids sample prior to work up, so a replicate sludge sample, and this time also a Kaolin Clay Standard with HgS, were carried through the F-3 and F-4 extractions and the solids once again set aside. These solids were resuspended in 40 mL Eurofins FGS deionized H₂O with the Mixi-Max vortex mixer then collected on a 0.45 µm Millipore Fluoropore filter and air dried for 90 minutes under vacuum. The dried solids were submitted for x-ray diffraction

(XRD), x-ray fluorescence (XRF), and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) analyses.

2.6 1:4 Aqua Regia Soluble Mercury Fraction (F-5)

To each of the remaining solid samples 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 30 minutes at nominally 1200 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 for each sample 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. Following dilution, the contents of each flask containing non-radioactive material was transferred to a pre-cleaned, labelled 125 mL glass storage bottle with Teflon-lined cap and transferred out of the shielded cell. Those containing radioactive material were left in their volumetric flasks until diluted for final speciation analysis.

2.7 Mineral Bound Mercury (F-6)

The solids remaining from each F-5 extraction in Section 2.6 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. Following dilution, the contents of each flask containing non-radioactive material was transferred to a pre-cleaned, labelled 125 mL glass storage bottle with Teflon-lined cap and transferred out of the shielded cell. Those containing radioactive material were left in their volumetric flasks until diluted for final speciation analysis.

2.8 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

2.9 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 15 °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.

2.10 Radiochemical Analysis and Shipping

The F-3, F-4, F-5, and F-6 fractions from the sample with the largest initial mass 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 FGS radioactive material

license limitations. The final dilutions of the radioactive samples were 200 μ L 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 FGS.

2.11 Total Mercury Analysis

Eurofins FGS conducted total mercury analyses on each of the 38 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).

2.12 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-51-17-112 Properties

The weight percent total solids, dissolved solids (supernate basis), insoluble solids, as well as the supernate and slurry densities were reported previously on this pre-SB10 Tank 51 sample¹¹ and are summarized in Table 3-1

**Table 3-1 Measured solids and densities for pre-SB10 Tank 51 Sample¹¹
(%RSD) [No. of Replicates]**

Property	Tank 51 pre-SB10 SSE [HTF-51-17-112]
Slurry Density (g/mL)	1.221 (0.4) [3]
Supernate Density (g/mL)	1.170 (<0.1) [3]
Total Solids (Wt.% in Slurry)	26.99 (0.3) [3]
Dissolved Solids (Wt.% in Supernate)	20.45 (0.3) [3]
Insoluble Solids (Wt.% in Slurry)	8.3 (N/A)
Soluble Solids (Wt.% in Slurry)	18.7 (N/A)

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

There was insufficient sample to apply Purge & Trap methods to this second tank slurry sample. Since it was not possible to measure volatile mercury species via purge and trap on the parent sample, the volatile species were measured on diluted samples of supernatant liquid as discussed in the next section.

3.3 Supernate Mercury Fraction

The speciation of mercury found in the supernate fraction of the Tank 51 pre-SB10 sample is shown in Table 3-2. The SRNL measured Tank 51 supernate density of 1.170 g/mL was used in the calculations. Total Hg was 182 mg Hg/L supernate and the species recovery as a fraction of total Hg is about 100%. 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 51 pre-SB10 supernate expressed as mg Hg/L (ppm) [%RSD] (No. of Replicates)¹²

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
182 [3.9] (3)	90.6 [2.9] (3)	89*	2.59 [20] (3)	87.7 [3.3] (3)	3.10 [NA] (1)**	<1.8	<0.051	100 – 101%

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

** Replicates were at the detection limit.

3.4 Selective Sequential Extractions

The Hg species that can be expected in various extraction fractions are described in Table 3-3. The F-3 1M KOH extraction was conducted on this unwashed sludge, whereas the previous washed sludge was not subjected to this extraction,¹³ to ensure removal of any calomel (Hg₂Cl₂) in the sludge, but also to extract calomel in the Kaolin Clay standard, so that it would not co-extract with HgS in the F-5 fraction. Since fraction F-4 was the first acidic extraction that these dried solids materials were exposed to, the HgO was expected to dissolve exclusively into this fraction as it had for the washed sludge.¹³

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	1M KOH	Organic Bound Hg Compounds (Hg(II) Bound to Sludge/Humics)	Hg Humics, Hg ₂ Cl ₂	Mobility Varies‡
F-4	12M HNO ₃	All Other Non-Sulfide or Silicate Bound Hg Compounds	Mineral lattice, Hg(0)	Low Mobility
F-5	1:4 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 (see text for final concentration)	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

The results of the total mercury measurements on the extraction fractions for five replicates (four after sacrificing one replicate following extraction F-4) of pre-SB10 Tank 51 insoluble solids, the insoluble solids from a SB9 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. This table also includes the results from the washed sludge¹³ for comparison. One replicate of the fraction F-5 extractions with Tank 51 insoluble solids had a measured total mercury value that was about four times the average of the other three replicates, so it is not included in the average calculated and given 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 3-4 Concentrations of Hg in SSE fractions F-3, F-4, F-5, and F-6 for Washed and Unwashed sludge solids, SSE Hg standards, blank, and simulant sludge solids

Sample	Washed Sludge Tank 40 SB8 Total Hg (mg Hg / g insoluble solids) [%RSD] (No. of Replicates)	Washed Sludge Percent of Total Hg Measured from All Fractions	Unwashed Sludge Tank 51 Pre-SB10 Total Hg (mg Hg / g insoluble solids) [%RSD] (No. of Replicates)	Unwashed Sludge Percent of Total Hg Measured from All Fractions
Rad Sludge – F-3	N/A	N/A	5.13 [11] (5)	12.4
HgS Std – F-3	N/A	N/A	0.00384	0.5
Hg₂Cl₂ Std – F-3	N/A	N/A	0.632	60.1
HgO Std – F-3	N/A	N/A	1.02	70.1
Blank – F-3	N/A	N/A	0.000317	26.1
Simulant – F-3	N/A	N/A	8.43	43.2
Rad Sludge – F-4	22.2 [5.8] (4)	78.7	28.3 [4.2] (5)	68.6
HgS Std – F-4	0.0219	2.1	0.0163	2.1
Hg₂Cl₂ Std – F-4	0.174	12.4	0.400	38.0
HgO Std – F-4	1.44	98.5	0.421	29.0
Blank – F-4	0.00224	74.5	0.000374	30.9
Simulant – F-4	30.7	99.8	10.9	56.0
Rad Sludge – F-5	5.91 [3.6] (5)	21.0	7.73 [15] (3)	18.7
HgS Std – F-5	1.03	97.9	0.756	96.9
Hg₂Cl₂ Std – F-5	1.23	87.4	0.0188	1.8
HgO Std – F-5	0.0214	1.5	0.0129	0.9
Blank – F-5	0.000403	13.4	0.000329	27.1
Simulant – F-5	0.0546	0.2	0.167	0.9
		Continued Next Page		

Sample	Washed Sludge Tank 40 SB8 Total Hg (mg Hg / g insoluble solids) [%RSD] (No. of Replicates)	Washed Sludge Percent of Total Hg Measured from All Fractions	Unwashed Sludge Tank 51 Pre-SB10 Total Hg (mg Hg / g insoluble solids) [%RSD] (No. of Replicates)	Unwashed Sludge Percent of Total Hg Measured from All Fractions
Rad Sludge – F-6	0.00850 [10] (5)	0.03	0.0781 [18] (4)	0.2
HgS Std – F-6	0.000237	0.02	0.00400	0.5
Hg ₂ Cl ₂ Std – F-6	0.00290	0.2	0.000366	0.03
HgO Std – F-6	0.00104	0.1	0.000238	0.02
Blank – F-6	0.000364	12.1	0.000193	15.9
Simulant – F-6	0.000529	0.002	0.00106	0.01

The data from Table 3-4 for the unwashed sludge extractions is presented graphically in Figure 3-1 and Figure 3-2. In Figure 3-1, the mass of Hg, relative to the mass of insoluble solids, released during each extraction from each sample is shown. This allows one to clearly see that the starting amount of Hg in the pre-SB10 Tank 51 and simulant samples are much larger relative to those found in the Kaolin Clay standards and the blank.

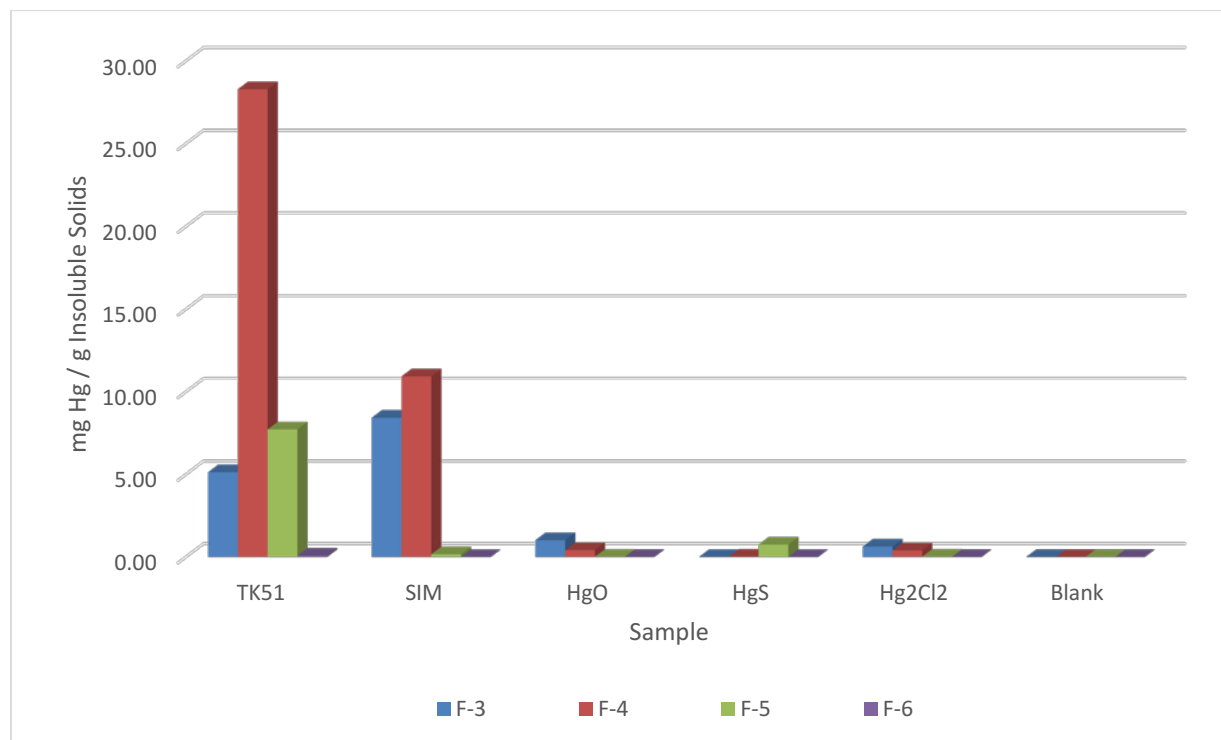


Figure 3-1 Mass of total Hg released (mg Hg / g Insoluble Solids) from each sample into each extraction fraction (F-x).

It is possible that radioactive sludge could contain ‘coprecipitate’ oxides of Hg that contain other sludge metals such as Fe, Mn, Ni, etc. All results from this study assume that any of the oxides of Hg (HgO or coprecipitated oxides) would extract with the same fraction expected for HgO.

By contrast, Figure 3-2 provides the same data as the percent of Hg released from each sample into any given extraction fraction. We can clearly see that HgS in the Kaolin Clay standard is released during extraction F-5. This figure allows us to see that about 12% of the Hg was released during extraction F-3 from the radioactive sludge sample, while >40% was released from the simulant, and 70% released from the Kaolin Clay HgO standard. The latter material was not expected to lose most of its Hg until the first acidic extraction, i.e. fraction F-4, but this standard released more than twice as much Hg into extractant F-3 as compared to F-4. This may indicate extraction F-2 is necessary in order to remove HgO prior to removing calomel.

The addition of extraction F-3 did prevent the majority of calomel from being released from the standard during extraction F-5, as had occurred with the first washed sludge. So while this improves the assertion of the presence of HgS in SRS Liquid Waste, other data has complicated this interpretation as shall be discussed in this report.

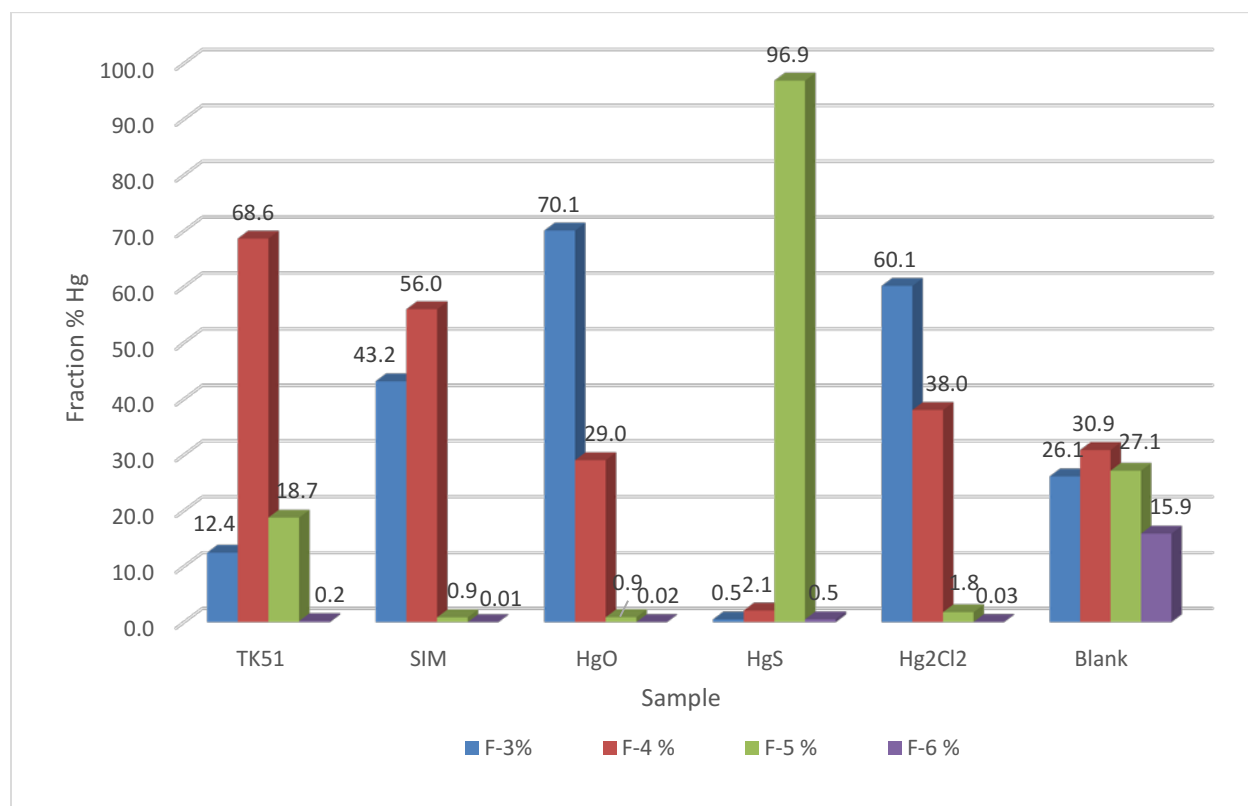


Figure 3-2 Percent of total Hg released from each sample into each extraction fraction (F-x)

The recovery of Hg from the three Kaolin Clay standards was not as high as for the washed sludge SSE experiment¹³, where in the recoveries differed by only a few percent from the accepted values¹⁴. In this experiment, while the HgO recovery was excellent, the HgS and Hg₂Cl₂ recoveries were about 20% low as can be seen in Table 3-5. The recovery of Hg from the SB9 simulant differed significantly from the

calculated value⁶ and was low by 46%. This may be a due to ineffective distribution of the HgO within the simulant sample prior to the selective sequential extraction experiments. 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. The recovery of Hg from the SB8 simulant utilized in the previous washed SSE experiment had a much better recover (18% low) even though the sludge simulant was made in a presumably similar manner. 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.

It was also not possible to calculate the amount of total Hg on a mg Hg/g IS basis in the Tank 51 pre-SB10 sample. Initially it was believed that the total Hg in the sample would be measured in another experiment since the subsample made available for this work contained an insufficient quantity of material to conduct the aqua regia digestions for this analysis. Unfortunately, Hg was not included in the analysis of the original sample¹¹.

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

Sample	Calculated	SSE#1 Measured	% Difference	SSE#2 Measured	% Difference
Tank 51 pre-SB10	Not measured	N/A	N/A	41.2*	
Tank 40 SB8	28.3**	28.2*	-0.2	N/A	N/A
HgS Standard	1.005	1.05	4.4	0.780	-22
Hg ₂ Cl ₂ Standard	1.363	1.40	3.1	1.05	-23
HgO Standard	1.40	1.46	4.6	1.45	3.6
Blank	N/A	0.00301	N/A	0.00121	N/A
Tank 40 SB9 Simulant	35.8	N/A	N/A	19.5	-46
Tank 40 SB8 Simulant	37.7	30.8	-18	N/A	N/A

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

** Includes a small contribution of soluble supernate Hg.

3.5 Examination of Sludge Solids Following Extractions F-3 and F-4

As noted in the Experimental section, after completing extractions F-3 and F-4, one replicate of pre-SB10 Tank 51 sludge solids was not carried forward to the F-5 extraction in order to examine the solids for the presence of HgS. Due to a handling error, the sample had to be reproduced, but this also provided the opportunity to examine a HgS Kaolin Clay standard after extractions F-3 and F-4. The dried solids from these two materials were submitted for XRD, XRF, and SEM analysis. The SEM analyses included both secondary electron and backscatter images, however the backscatter images were more useful for the comparison performed for this study.

In Figure 3-3 is the XRF and in Figure 3-4 is the XRD spectra of the Tank 51 pre-SB10 solids following extractions F-3 and F-4. A strong Hg signal is present in the XRF analysis at 10 and 12 keV even though 99% of the HgO in the Kaolin Clay standard containing HgO had been extracted per Figure 3-2. No sulfur signal was detected. There are also no crystalline Hg species observed in the XRD. If there was only HgO present in the waste sludge solids, there should have been no Hg signal following the F-4 12M HNO₃ extraction. This extraction does not dissolve HgS.

In Figure 3-5 is the XRF and in Figure 3-6 is the XRD spectra of the Kaolin Clay Standard with HgS following extractions F-3 and F-4. Again, there is a strong Hg signal in the XRF analysis at 10 and 12 keV, but no sulfur signal for the HgS known to be in this material. As with the waste sample, there are no crystalline Hg species observed in the XRD.

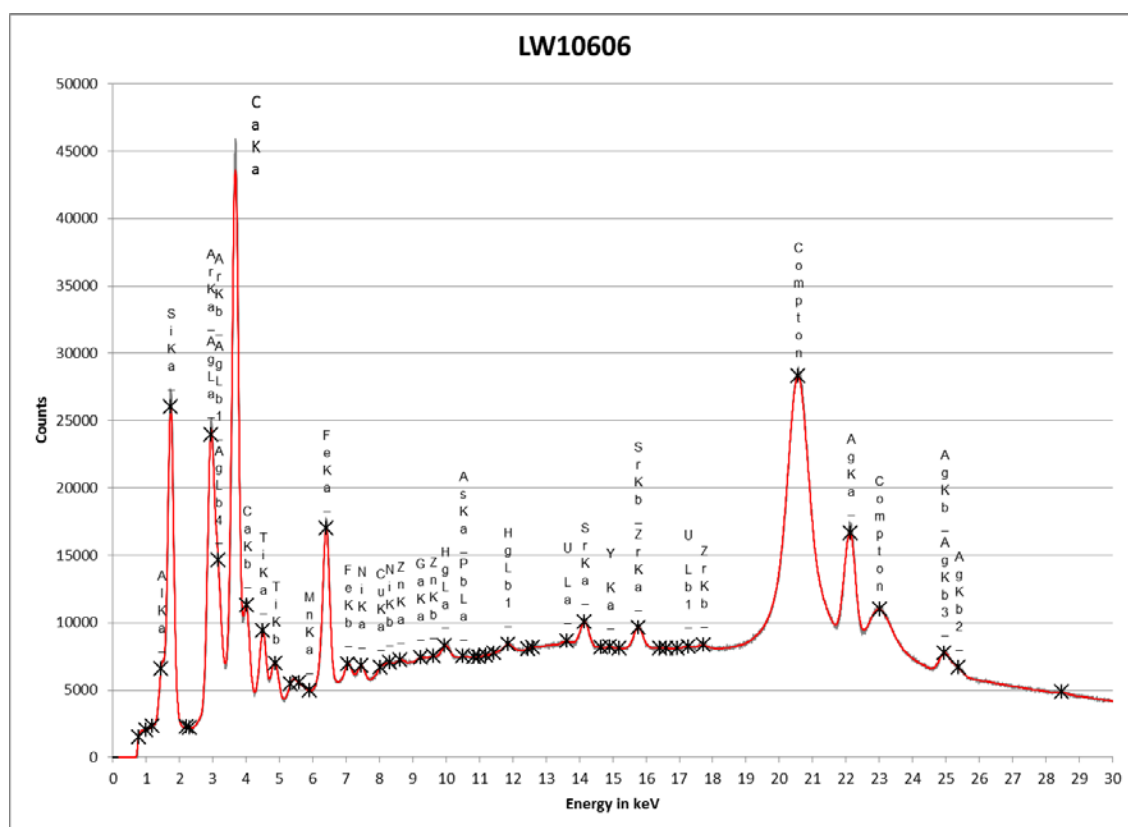


Figure 3-3 XRF Spectra of Unwashed Tank 51 Pre-SB10 Solids Following F-3 and F-4 Extractions

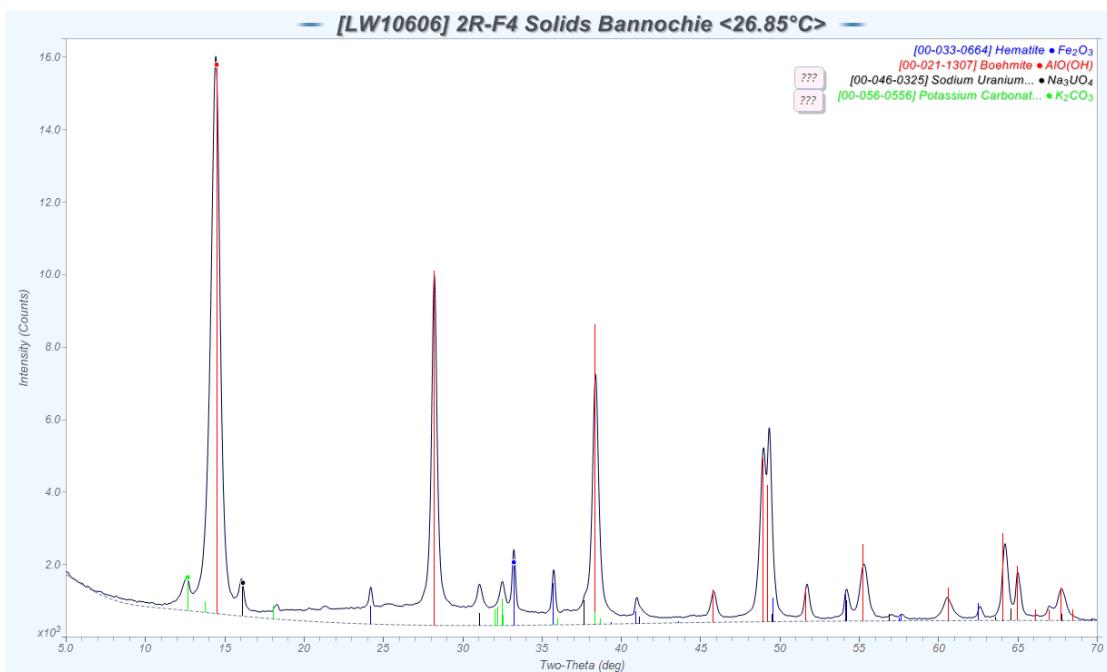


Figure 3-4 XRD Spectra of Unwashed Tank 51 Pre-SB10 Solids Following F-3 and F-4 Extractions

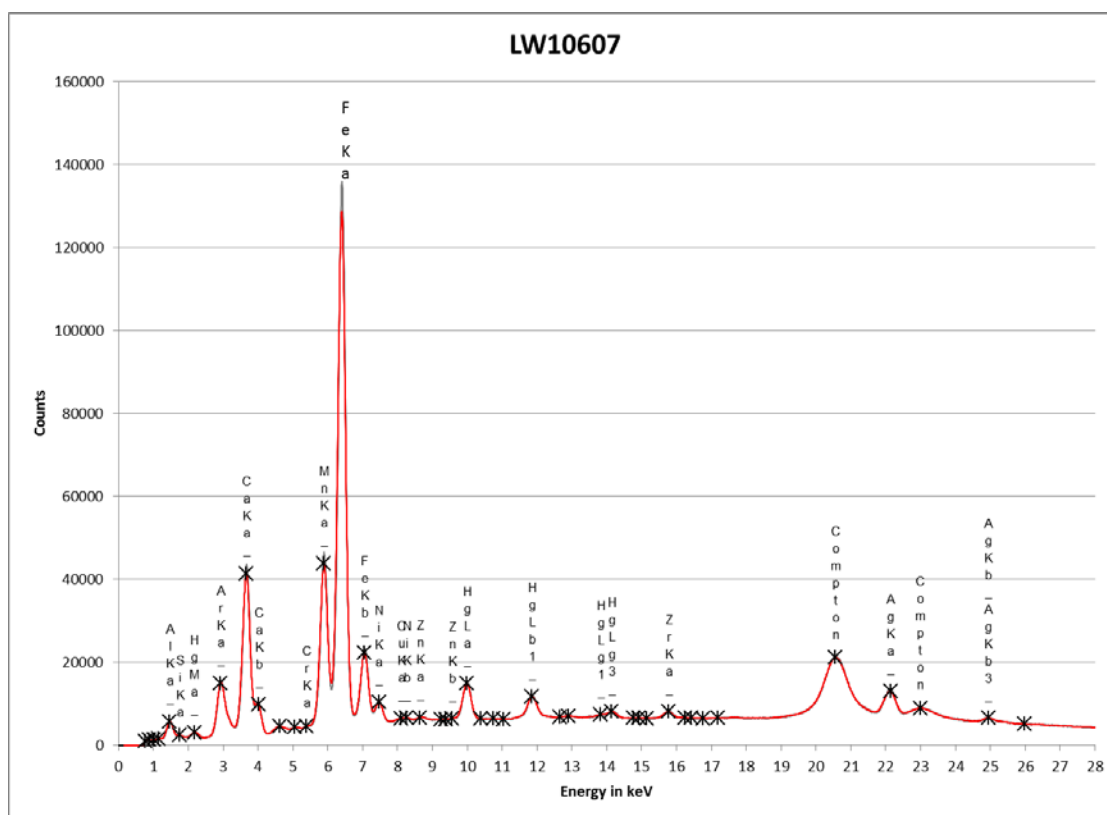


Figure 3-5 XRF Spectra of Kaolin Clay Standard with HgS Following Extractions F-3 and F-4

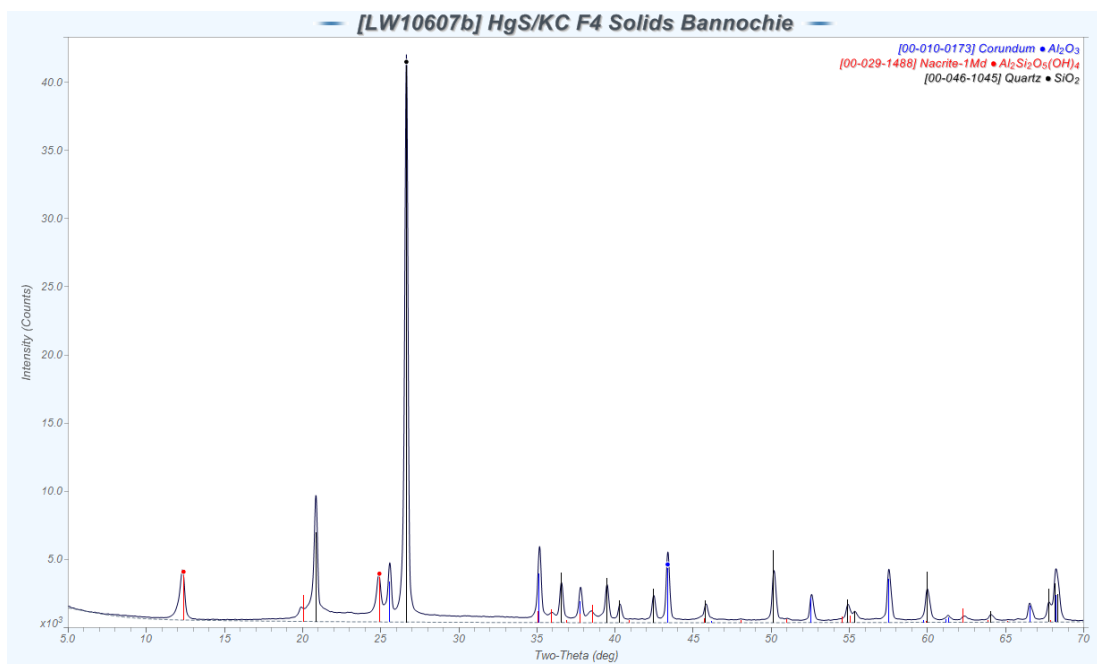


Figure 3-6 XRD Spectra of Kaolin Clay Standard with HgS Following Extractions F-3 and F-4

The backscatter SEM image in Figure 3-7 is the Tank 51 pre-SB10 solids that have been carbon coated to reduce charging. The EDS spectra for spots 1, 2, 7, and 9 show a signal for Hg in this material, but no S signal is associated with it. These spectra can be seen below in Figure 3-8 through Figure 3-11.

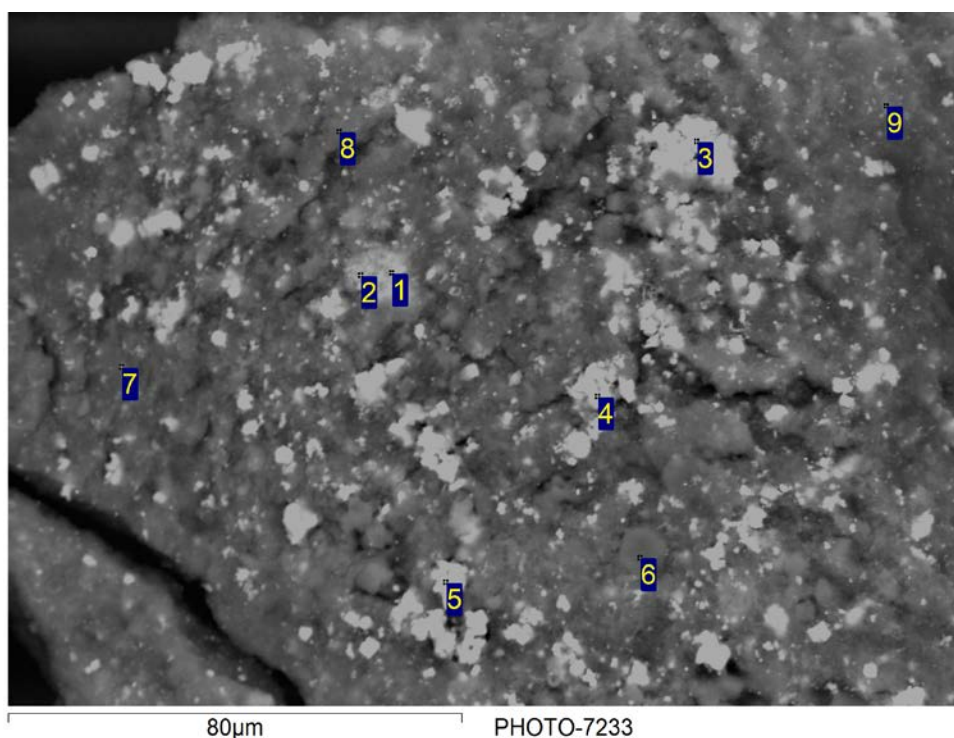


Figure 3-7 SEM Image of Carbon Coated Tank 51 Pre-SB10 Solids Following F-3 and F-4 Extractions

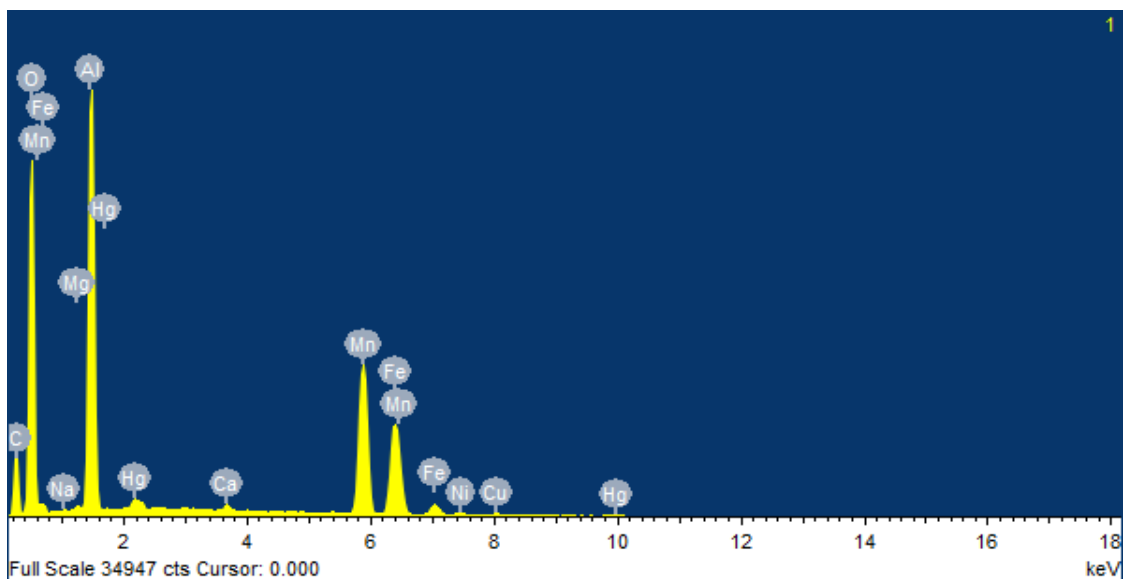


Figure 3-8 EDS Spectra of Spot 1 in Figure 3-7

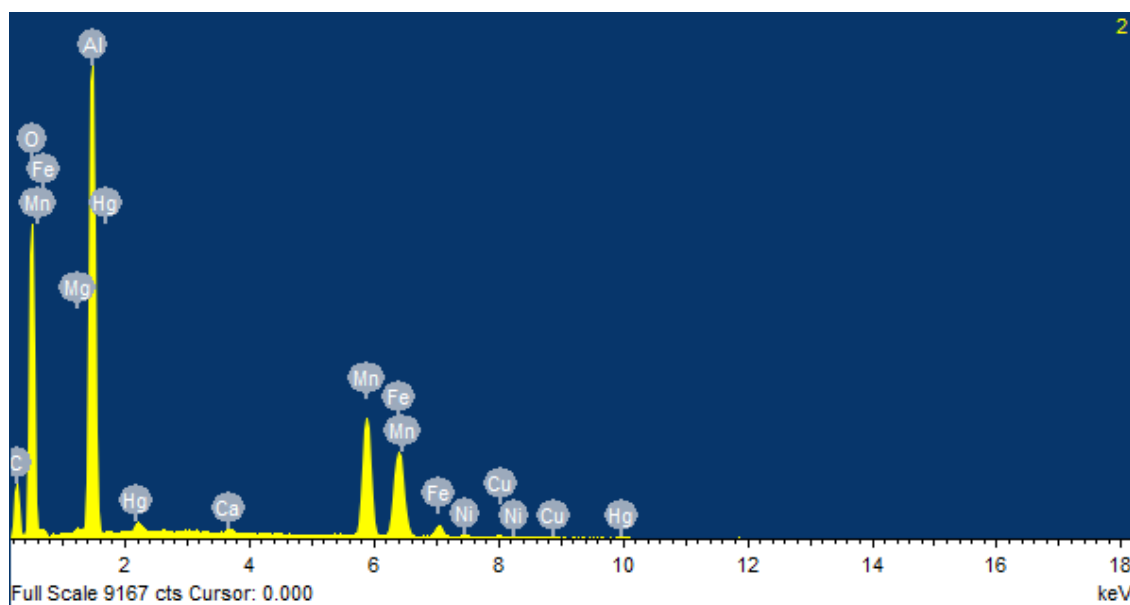


Figure 3-9 EDS Spectra of Spot 2 in Figure 3-7

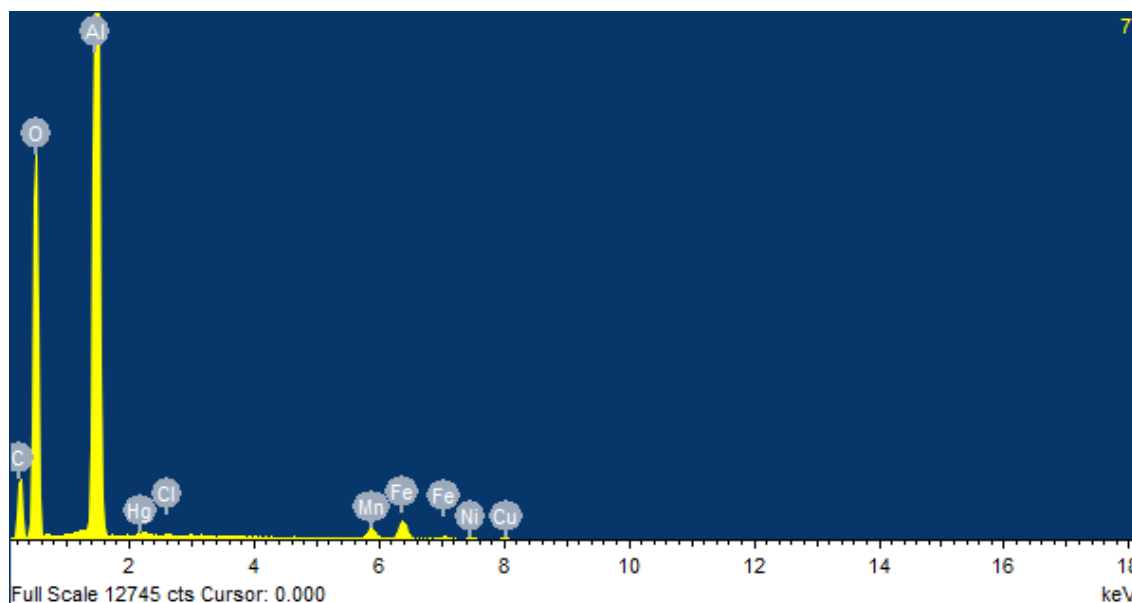


Figure 3-10 EDS Spectra of Spot 7 in Figure 3-7

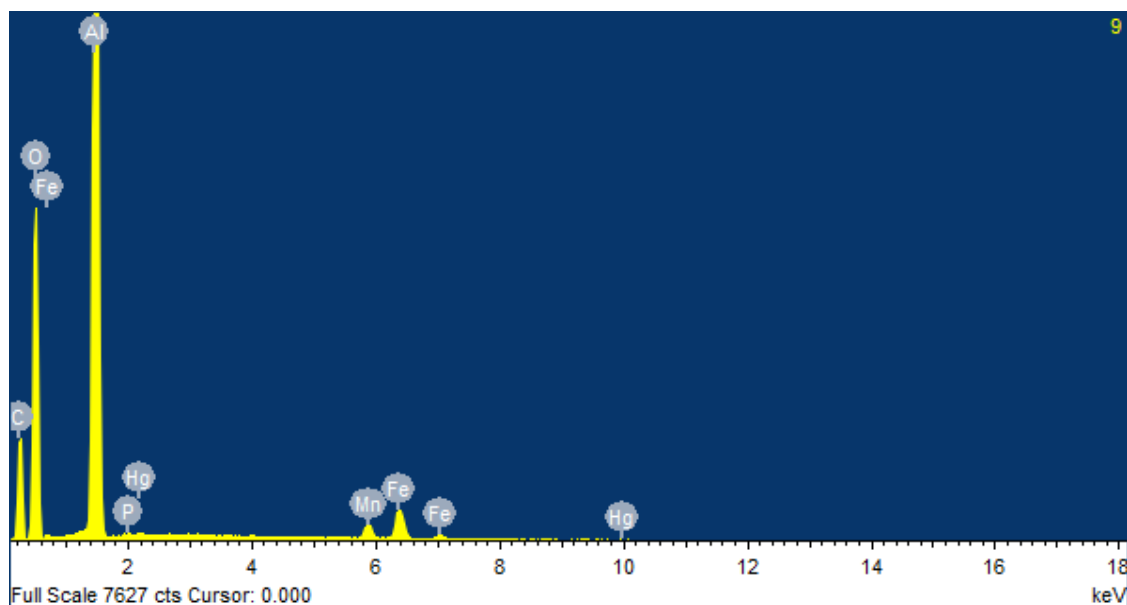


Figure 3-11 EDS Spectra of Spot 9 in Figure 3-7

The remaining spots shown in Figure 3-7 where typical HLW sludge components including Al, Fe, Mn, Cu, Ni, Ca and one weak signal for Cl in Spot 4.

By contrast the backscatter SEM image in **Figure 3-12** is from the Kaolin Clay standard containing HgS following F-3 and F-4 extractions. The solids have also been carbon coated to reduce charging. The EDS spectra for spots 2 through 5 show a signal for Hg in this material that is associated with S, unlike the Tank 50 solids shown above. These spectra can be seen below in Figure 3-13 through Figure 3-16. The fact that HgS is still present in this standard confirms that it is not removed until the modified F-5 aqua regia extraction. This can be seen clearly in Figure 3-2 when 97% of the Hg in this standard is extracted.

The fact that S is not seen associated with Hg in the Tank 51 sludge solids, but yet 18% of the Hg in this material extracts during the modified aqua regia extraction could lend support for this material being some type of mercury amalgam as shown in Table 3-3.

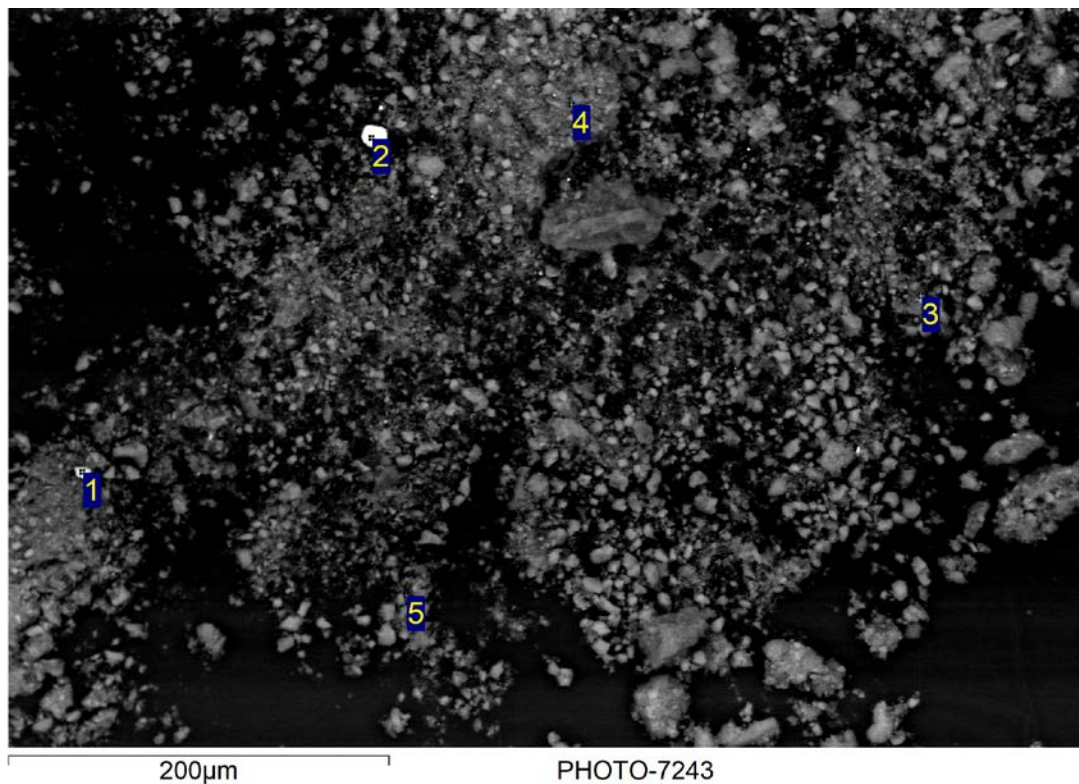


Figure 3-12 SEM Image of Carbon Coated Kaolin Clay Solids Containing HgS Following F-3 and F-4 Extractions

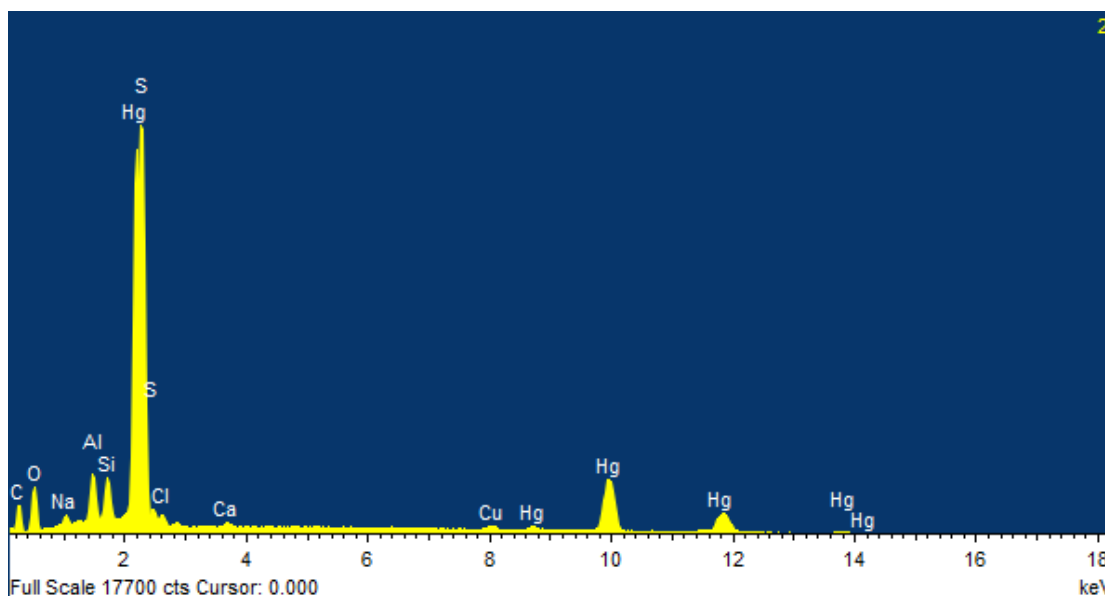


Figure 3-13 EDS Spectra of Spot 2 in Figure 3-12

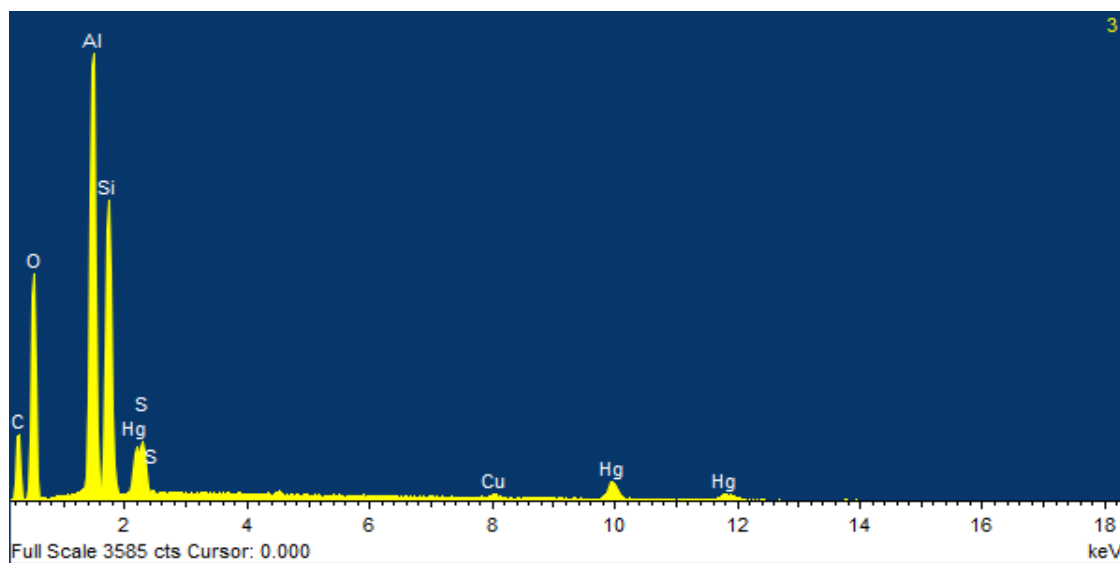


Figure 3-14 EDS Spectra of Spot 3 in Figure 3-12

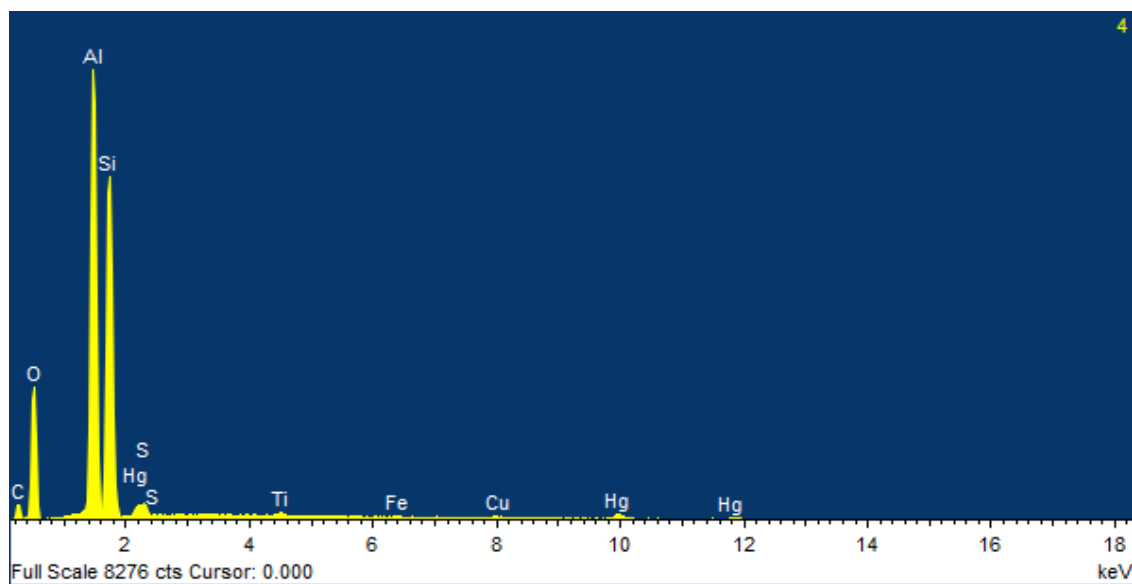


Figure 3-15 EDS Spectra of Spot 4 in Figure 3-12

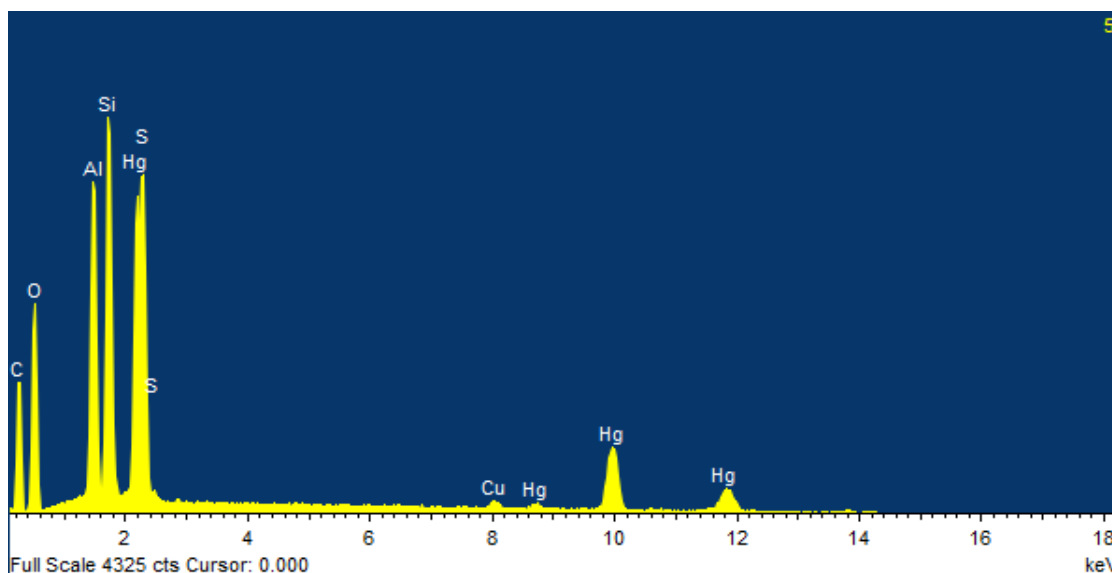


Figure 3-16 EDS Spectra of Spot 5 in Figure 3-12

A second image was analyzed to confirm the association between Hg and S observed in the spots analyzed from Figure 3-12. This second image is shown in Figure 3-17. Figure 3-18 through Figure 3-22 provide the EDS spectra for five of the eight analyzed spots (#1, #2, #3, #5, and #6) which had Hg associated with S. The remaining spots contained mostly Al and Si.

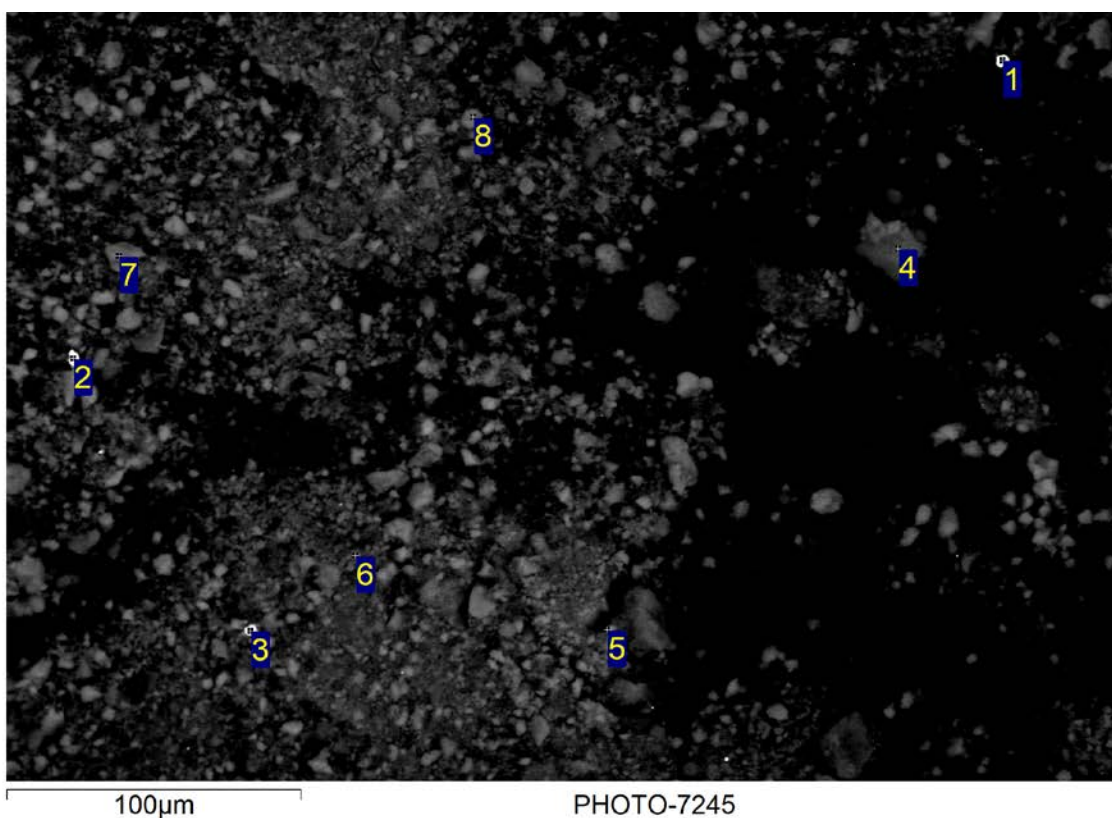


Figure 3-17 SEM Image of Carbon Coated Kaolin Clay Solids Containing HgS Following F-3 and F-4 Extractions

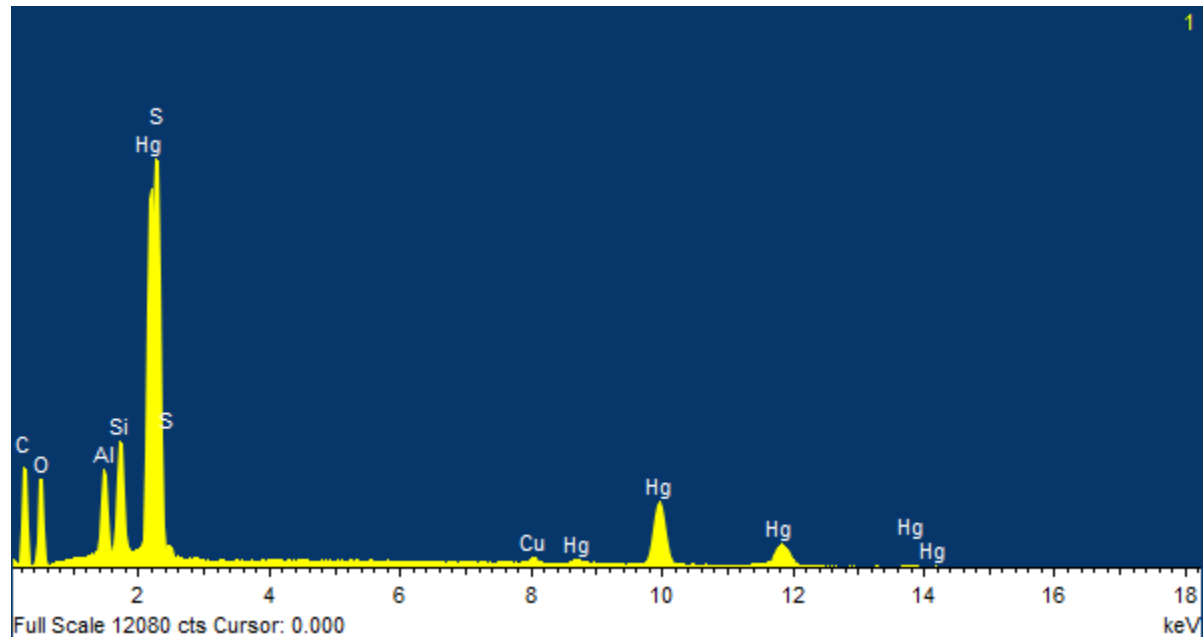


Figure 3-18 EDS Spectra of Spot 1 in Figure 3-17

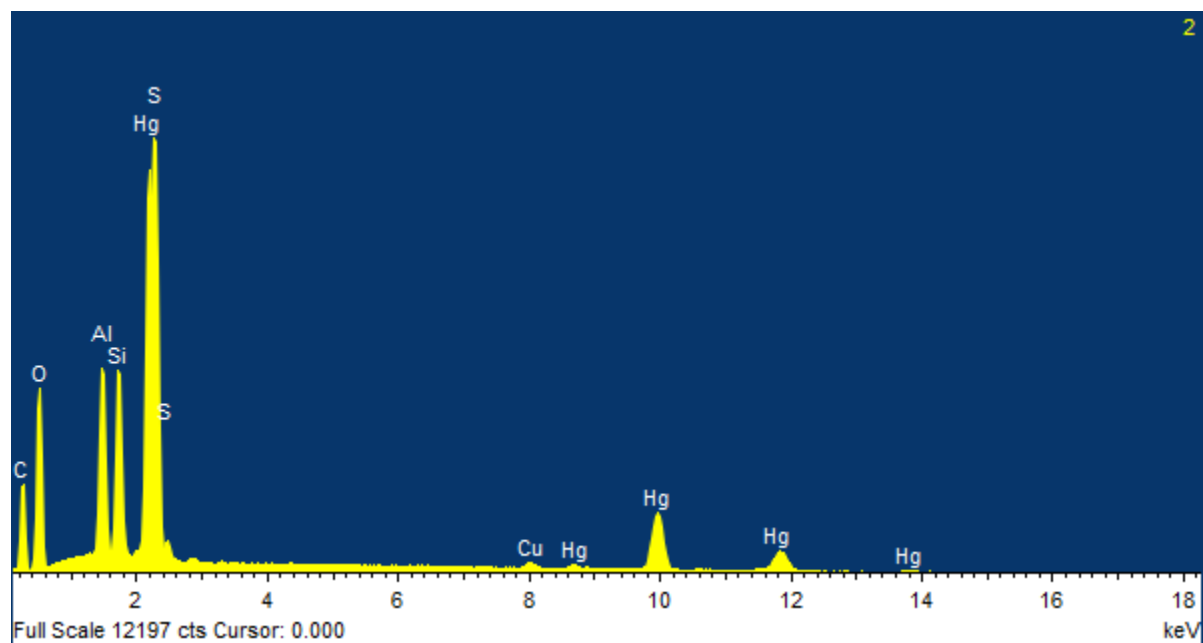


Figure 3-19 EDS Spectra of Spot 2 in Figure 3-17

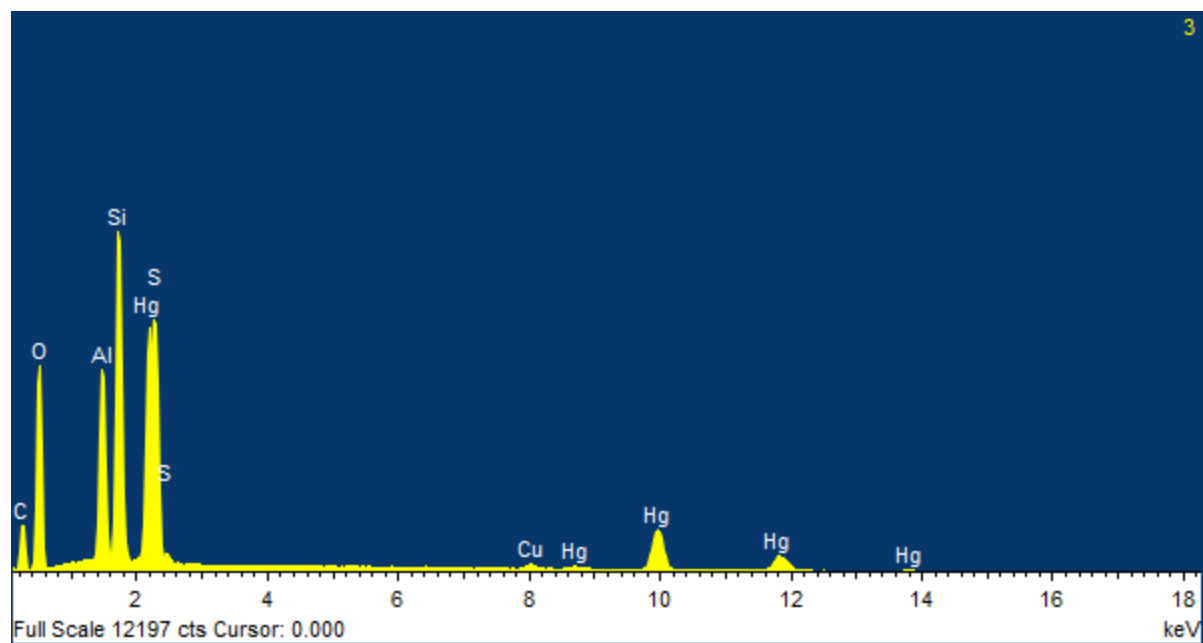


Figure 3-20 EDS Spectra of Spot 3 in Figure 3-17

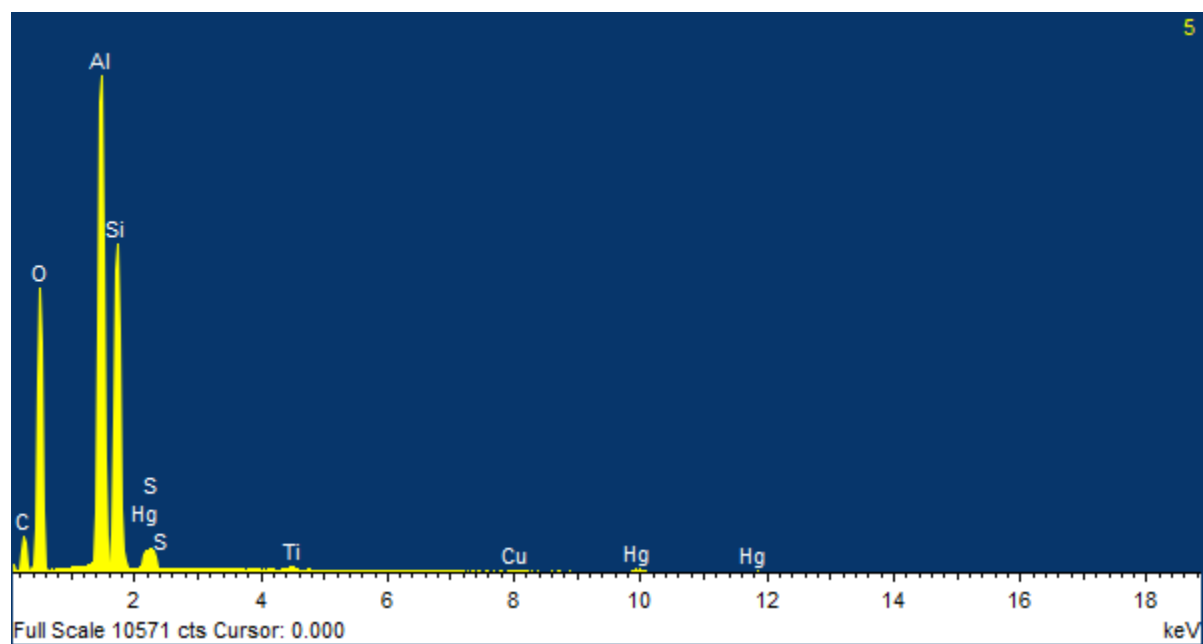


Figure 3-21 EDS Spectra of Spot 5 in Figure 3-17

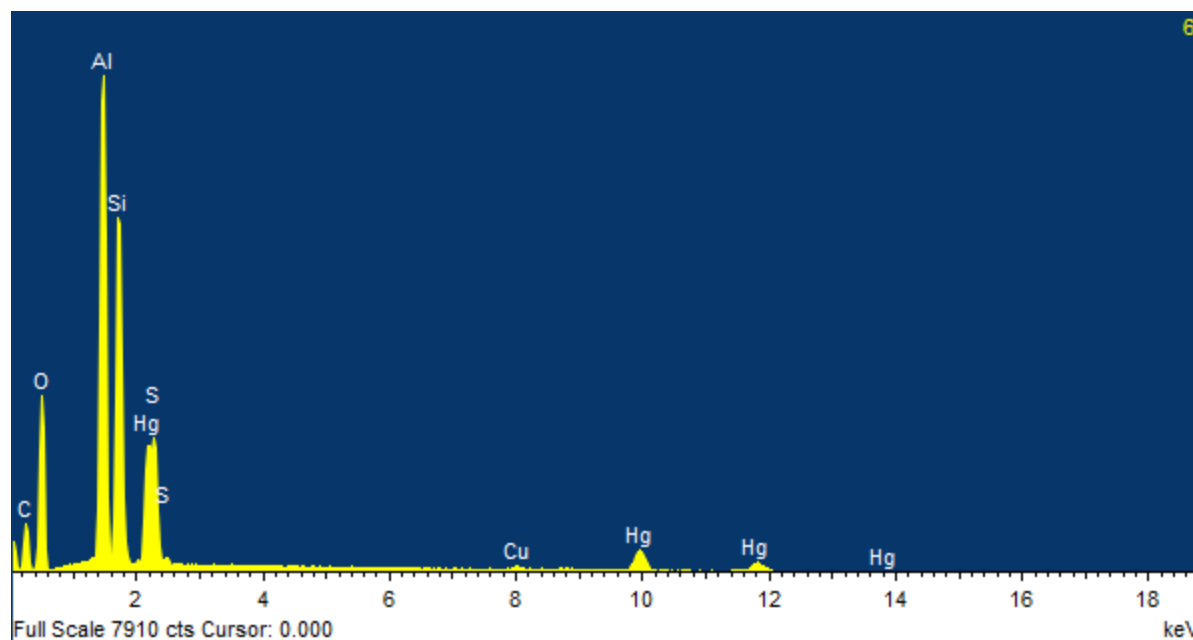


Figure 3-22 EDS Spectra of Spot 6 in Figure 3-17

Since SB3, we have monitored the insoluble sulfur content of the Tank 40 WAPS samples.^{15,16,17,18,19,20} In SB8, it was noted that 14% of the total sulfur in the sample was insoluble.²⁰ Insoluble sulfur reached a high of 50% of total sulfur in SB5.¹⁷ 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 previously analyzed by selective sequential extraction.¹³ This was excellent agreement considering we were comparing two different samples of SB8 Tank 40, one from July 2013 and one from August of 2016, and there were 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.²¹ 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 2013.²² That work was able to show that non-sulfate, soluble sulfur was not thiosulfate, which had been observed in Hanford Salt Waste.²³ It can be concluded from the SSE work reported here that a possible candidate for insoluble sulfur species in DWPF sludge batches is not mercury sulfide. The non-oxide insoluble mercury may be a mercury amalgam, which is another species known to extract in fraction F-5.

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 0.19% (0.0781/41.2*100) of the pre-SB10 Tank 51 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. As was demonstrated in the previous SSE work on washed SB8 sample¹³, the solids are likely Na₂SiF₆ (Malladrite), so there is no anticipated loss of Hg in the precipitate.

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 unwashed sludge drawn from Tank 51 during assembly of SB10, it, along with the washed sludge reported previously, have demonstrated that oxides of mercury or coprecipitated Hg-metal oxides are 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 Hg species such as mercury amalgams.

Historical insoluble sulfur measurements conducted on incoming DWPF sludge batches^{15,16,17,18,19,20} have indicated that between 5% and 50% (depending upon sludge batch) of the incoming sulfur is insoluble, but we can now conclude that this sulfur is not bound up as HgS. This result was determined by examining the post-extracted F-3 and F-4 sludge solids, which showed no indication of S associated with Hg. Since the non-oxide Hg is likely not a sulfide, the composition of the insoluble sulfur species remains elusive. The highest level of insoluble sulfur was the SB5 material, which was subjected to Al dissolution prior to processing in the DWPF. As a high ‘H-Area Modified’ (HM) Plutonium-Uranium Redox Extraction (PUREX) sludge batch with a high Hg content, the relationship between this high Hg containing sludge and sulfur is unclear.

5.0 Recommendations and Future Work

To date, all processing studies for DWPF have been conducted with simulants that are based on only the addition of HgO. In the washed sludge sample studied previously, 21% of the Hg was present as a non-oxide species¹³. In the unwashed sludge sample studied here, 19% of the Hg was present as a non-oxide species that is suspected to be a mercury amalgam.

Previously, we proposed examining an unwashed sludge slurry from the SRS Tank Farm in order to determine the amount of soluble Hg present and the amount that is mobilized prior to the introduction of sludge into the DWPF as a result of sludge washing. That has now been accomplished. About 4% of the Hg is present in the sludge supernate, but another 12% is likely solubilized during sludge washing and transferred to the salt waste stream before DWPF processing begins.

The initial scope of this work proposed looking at three, SRS tank sludge samples, the first washed, the second unwashed, and the third from an unwashed, high HM-containing sludge prior to transfer for sludge batch preparation. Applying the lessons learned from the first two SSE studies on the final sludge is still recommended. With a sufficiently sized sample an examination of volatile Hg species would also be possible as was initially attempted with the first washed sludge until excessive foaming prohibited completion of the experiment.

6.0 References

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