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Tank 40 Final Sludge Batch 9 Chemical and Fissile Radionuclide Characterization Results

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EXECUTIVE SUMMARY

A sample of Sludge Batch (SB) 9 was pulled from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)[i]. The SB9 WAPS sample was also analyzed for chemical composition, including noble metals, and fissile constituents, and these results are reported here. These analyses along with the WAPS radionuclide analyses will help define the composition of the sludge in Tank 40 that is fed to the Defense Waste Processing Facility (DWPF) as SB9.

At the Savannah River National Laboratory (SRNL), the 3-L Tank 40 SB9 sample was transferred from the shipping container into a 4-L high density polyethylene bottle and solids were allowed to settle. Supernate was then siphoned off and circulated through the shipping container to complete the transfer of the sample. Following thorough mixing of the 3-L sample, a 547 g sub-sample was removed. This sub-sample was then utilized for all subsequent slurry sample preparations.

Eight separate aliquots of the slurry were digested, four with HNO_3/HCl (aqua regia[ii]) in sealed Teflon® vessels and four with NaOH/Na_2O_2 (alkali or peroxide fusion[iii]) using Zr crucibles. Three Analytical Reference Glass – 1[iv] (ARG-1) standards were digested along with a blank for each preparation. Each aqua regia digestion and blank was diluted to 1:100 with deionized water and submitted to Analytical Development (AD) for inductively coupled plasma – atomic emission spectroscopy (ICP-AES) analysis, inductively coupled plasma – mass spectrometry (ICP-MS) analysis, atomic absorption spectroscopy (AA) for As and Se, and cold vapor atomic absorption spectroscopy (CV-AA) for Hg. Equivalent dilutions of the alkali fusion digestions and blank were submitted to AD for ICP-AES analysis.

Tank 40 SB9 supernate was collected from a mixed slurry sample in the SRNL Shielded Cells and submitted to AD for ICP-AES, ion chromatography (IC), total base/free OH^-/other base, total inorganic carbon/total organic carbon (TIC/TOC) analyses. Weighted dilutions of slurry were submitted for IC, TIC/TOC, and total base/free OH^-/other base analyses.

Activities for U-233, U-235, and Pu-239 were determined from the ICP-MS data for the aqua regia digestions of the SB9 WAPS slurry using the specific activity of each isotope. The Pu-241 value was determined from a Pu-238/-241 method developed by SRNL AD and previously described.[v]

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[i] *Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms*, US DOE Document DOE/EM-0093, Rev. 2, Office of Environmental Restoration and Waste Management (1996).

[ii] *Aqua Regia Dissolution of Sludge for Elemental Analysis (U)*, Manual L16.1, Procedure ADS-2226, Rev. 10, Savannah River Site, Aiken, SC (2013).

[iii] *Alkali Fusion Dissolutions of Sludge and Glass for Elemental and Anion Analysis (U)*, Manual L16.1, Procedure ADS-2502, Rev. 7, Savannah River Site, Aiken, SC (2013).

[iv] Smith, G. L. *Characterization of Analytical Reference Glass – 1 (ARG-1)*, PNL-8992, Pacific Northwest (National) Laboratory, Richland, WA (1993).

[v] Bannochie, C. J., DiPrete, D. P. *Determination of Reportable Radionuclides for DWPF Sludge Batch 6 (Macrobatch 7)*, SRNL-STI-2011-00189, Rev. 0, Savannah River National Laboratory, Aiken, SC (2011).

The following conclusions were drawn from the analytical results reported here:

- The solids reported were 14.06 wt% total, 9.13 wt% insoluble, and 10.60 wt% calcined. With a slurry density of 1.09 mg/mL and supernate density of 1.05 mg/mL.

- The ratios of the major elements for the SB9 WAPS sample are very similar to those measured for the SB8 WAPS sample. There is less Al and U, and more Mn relative to Fe than in early sludge batches.

- The elemental composition of this sample and the analyses conducted here are reasonable and consistent with DWPF batch data measurements in light of SRAT product heel and variable line flush contributions to the DWPF SRAT receipt sample. The element ratios for Al/Fe, Ca/Fe, Mn/Fe, and U/Fe agree within 5% between this work and the DWPF SRAT receipt analyses.

- Sulfur in the SB9 WAPS sample is 82% soluble, the same as that reported for SB7b, but slightly less than the results reported for SB3, SB4, SB6, and SB8, and unlike the 50% insoluble sulfur observed in the SB5 WAPS sample. In addition, 6% of the soluble sulfur is not present as sulfate in SB9, which is the lowest difference seen in recent sludge batches.

- The average activities of the fissile isotopes of interest in the SB9 WAPS sample are (in µCi/g of total dried solids): 6.66E-02 U-233, 6.63E-04 U-235, 5.50E+00 Pu-239, and 2.69E+01 Pu-241. The full radionuclide composition will be reported in a future document.

- The fission product noble metal and Ag concentrations appear to have largely peaked in previous DWPF sludge batches. The concentration of Ru has decreased further in SB9.

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AA	Atomic Absorption (Spectroscopy)
AD	Analytical Development
AF	Alkali Fusion
ARG – 1	Analytical Reference Glass – 1
ASP	Analytical Study Plan
CC	Cold Chemistry (Digestion)
CV-AA	Cold Vapor Atomic Absorption Spectroscopy
DWPF	Defense Waste Processing Facility
HLW	High Level Waste
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
L	Liter
μCi	Microcuries
M	Molar
NA	Not Available (e.g. Not Measured)
PRFT	Precipitate Reactor Feed Tank
RSD	Relative Standard Deviation
SB	Sludge Batch
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
Std. Dev.	Standard Deviation
TC	Total Carbon
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TS	Total Dried Solids
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAPS	Waste Acceptance Product Specifications
Wt.%	Weight Percent

1.0 Introduction

A sample of Sludge Batch (SB) 9 was pulled from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)[1]. The SB9 WAPS sample was also analyzed for chemical composition, including noble metals, and fissile constituents, and these results are reported here. These analyses along with the WAPS radionuclide analyses will help define the composition of the sludge in Tank 40 that is fed to the Defense Waste Processing Facility (DWPF) as SB9.

Savannah River National Laboratory (SRNL) analyses on SB9 were requested by DWPF via Technical Task Request (TTR) U-TTR-S-00009, Rev. 1.[2] The sample preparation work and analyses are governed by a Task Technical and Quality Assurance Plan (TTQAP).[3]

A 3-L sample of Tank 40 (HTF-40-17-5) was pulled and delivered to the SRNL Shielded Cells on February 16, 2017 following slurry operations. Four slurry pumps were operated for nine hours and seven minutes (from last pump start up until first pump shutdown) preceding sample collection. The sample was collected within 30 minutes after discontinuing slurry operations. The general protocol for transferring Tank 40 material to DWPF is for all four slurry pumps to run for eight hours prior to transfer and to be kept running during the transfer, but due to the need to pull a sample, the pumps had to be shut down. The Tank 40 level was 152.6 inches after the pumps were secured and when the sample was pulled. No Al foil was utilized on the sampler for Tank 40.

2.0 Experimental Procedure

2.1 Sample Handling and Preparations

At SRNL, the 3-L Tank 40 SB9 sample was transferred from the shipping container into a 4-L high density polyethylene bottle and solids were allowed to settle. Supernate was then siphoned off and circulated through the shipping container to complete the transfer of the sample. No visible solids were observed in the sampler following transfer. Following thorough mixing of the 3-L sample, a 547 g sub-sample was removed. This sub-sample was then utilized for all subsequent slurry sample preparations.[4]

Eight separate aliquots of the slurry were digested, four with HNO_3/HCl (aqua regia[5]) in sealed Teflon® vessels and four with NaOH/Na_2O_2 (alkali or peroxide fusion[6]) using Zr crucibles. Due to the use of Zr crucibles and Na in the alkali fusions (AF), Na and Zr cannot be determined from this preparation. Additionally, other alkali metals, such as Li and K that may be contaminants in the NaOH/Na_2O_2 are not utilized from this preparation. Three Analytical Reference Glass – 1[7] (ARG-1) standards were digested along with a blank for each preparation. The ARG-1 glass allows for an assessment of the completeness of each digestion. A multielement metal ion standard was submitted with each digestion, and the elemental checks were within ± 10% of the expected values for those elements from digestions selected for the final reporting. Each aqua regia digestion, of nominally 0.25 g total solids, and blank were diluted to 100 mL with deionized water and submitted to Analytical Development (AD) for inductively coupled plasma – atomic emission spectroscopy (ICP-AES) analysis, inductively coupled plasma – mass spectrometry (ICP-MS) analysis of masses 82-208 and 230-244, atomic absorption spectroscopy (AA) for As and Se, and cold vapor atomic absorption spectroscopy (CV-AA) analysis for Hg. Since CV-AA

Hg measurements were done on AR digested material, no further permanganate digestion was done at the instrument. Equivalent dilutions of the AF digestions and a blank were submitted to AD for ICP-AES analysis.

Tank 40 SB9 supernate was collected from a mixed slurry sample in the SRNL Shielded Cells and submitted to AD for ICP-AES, ion chromatography (IC), total inorganic carbon/total organic carbon (TIC/TOC), and total base/free OH^-/other base analyses. Weighted dilutions of slurry were submitted for IC, TIC/TOC, and total base/free OH^-/other base analyses.

Activities for U-233, U-235, and Pu-239 were determined from the ICP-MS data for the aqua regia digestions of the SB9 WAPS slurry using the specific activity of each isotope. The Pu-241 value was determined from a Pu-238/-241 method developed by SRNL AD and previously described.[8]

2.2 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

Table 3-1 presents the measured SB9 density and weight percent solids data[9,10] collected for the SB9 WAPS sample taken in February 2017. Table 3-1 also contains data from the DWPF Sludge Receipt and Adjustment Tank (SRAT) receipt sample data for Batch #782 as a comparison. Batch #782 was selected because it was the last DWPF batch received from Tank 40 prior to the pulling of HTF-40-17-5. The wt.% total solids for the SB9 WAPS sample is higher than that seen for Batch #782, as well as the average DWPF measured for all SB9 batches received. Batches #774 through #782 have an average wt% total solids of 13.8%. Generally, it would be expected to be lower than the total solids observed for the DWPF SRAT receipt batch due to the impacts of the SRAT heel and transfer line flush water. The SRAT heel contributes approximately 13 – 19% of the volume of slurry in the SRAT vessel. Calcine factors were also calculated by taking the ratio of the weight percent calcined solids and the weight percent total solids. The SB9 WAPS sample has a value of 0.754 grams of calcined solids per gram of dried solids.

Table 3-1. Weight Percent Solids and Density for SB9 WAPS Samples, Tank Farm Projections, and DWPF SRAT Receipt Batch #782 [Number of Samples Included in Average]

Property	SB9 WAPS (% RSD*)	Tank Farm Projection[11]	DWPF SRAT Receipt for Batch #782[c]
Slurry Density (g/mL)	1.09 (1.9) [4]	1.13	1.09
Supernate Density (g/mL)	1.05 (0.2) [3]	1.05	NA
Total Solids (Wt.% in Slurry)	14.06 (0.5) [4]	15.46	13.3
Calcined Solids (Wt.% in Slurry)	10.60 (1.5) [4]	12.05	NA
Dissolved Solids[a] (Wt.% in Supernate)	5.42 (1.9) [4]	NA	NA
Insoluble Solids (Wt.% in Slurry)	9.13	10.68	NA
Soluble Solids[b] (Wt.% in Slurry)	4.93	NA	NA

NA ≡ not measured
* Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.
[a] Also known as Uncorrected Soluble Solids
[b] Also known as Corrected Soluble Solids
[c] Measured in DWPF

Table 3-2 provides the anion results for the SB9 WAPS sample and the available DWPF SRAT receipt data for Batch #782. In order to compare the data from the two labs it was necessary to put the SRNL data on a slurry basis. SRNL data in Columns 2 and 3 of the table are presented on a supernate basis, i.e. moles/L of supernate, but were the result of weighted dilutions of slurry and weighted dilutions of supernate, respectively. Columns 4 and 5 in the table are presented on a slurry basis, i.e. mg/kg slurry, but were the result of weighted dilutions of slurry and weighted dilutions of supernate, respectively. As a result, Columns 2 and 4 are from the same set of weighted dilutions of slurry, and Columns 3 and 5 are from a separate set of weighted dilutions of supernate.

The supernate sulfur result is calculated from total sulfur detected in the supernate by ICP-AES and is about 6% higher, on a molar basis, than sulfate sulfur determined by IC, this is considerably lower than the approximately 21% difference seen for SB8[18] and the approximately 23% difference seen for SB7b.[12] This difference between total soluble sulfur and sulfate soluble sulfur was observed throughout SB6 washing[13] but appears to be greatly reduced for SB9. As was shown, this non-sulfate, soluble sulfur does not appear to persist following SRAT cycle processing.[14] The Al, Cr, Hg, Na and S values also shown in this table were calculated from the ICP-AES data (except for Hg, which is from CV-AA data) for the supernate and placed on a slurry basis using the insoluble solids content from Table 3-1. Other supernate elements measured were below the ICP-AES detection limits or present at equivalent levels in the blank.

Table 3-2. Supernate Analyses for SB9 WAPS Samples and DWPF SRAT Receipt Batch #782 [Number of Samples Included in Average]

1	2	3	4	5	6	7
Analyte	SB9 WAPS (%RSD*) Mol/L super. Wt'd Dil. Slurry	SB9 WAPS (%RSD*) Mol/L super. Wt'd Dil. Super.	SB9 WAPS (%RSD*) mg/kg slurry Wt'd Dil. Slurry	SB9 WAPS (%RSD*) mg/kg slurry Wt'd Dil. Super.	Method	SRAT Receipt for Batch #782 mg/kg slurry
NO_3^-	0.108 (1.9) [4]	0.102 (2.3) [4]	5840 (1.9) [4]	5490 (2.3) [4]	IC	6270
NO_2^-	0.300 (0.8) [4]	0.281 (1.2) [4]	12000 (0.8) [4]	11200 (1.2) [4]	IC	8490
SO_4^{2-}	0.0102 (1.1) [4]	0.00935 (0.7) [4]	847 (1.1) [4]	780 (0.7) [4]	IC	525
PO_4^{3-}	<0.0013	<0.0010	<110	<79	IC	NA
Br^-	<0.016	<0.011	<1100	<790	IC	NA
Cl^-	<0.0034	<0.0026	<110	<79	IC	NA
CHO_2^-	<0.0027	<0.0020	<110	<79	IC	4630
$C_2O_4^{2-}$	0.0289 (3.8) [4]	0.0282 (5.4) [4]	2210 (3.8) [4]	2150 (5.4) [4]	IC	725
F^-	<0.0064	<0.0048	<110	<79	IC	NA
Al	NA	0.0313 (0.7) [4]	NA	733 (0.7) [4]	ICP-AES	NA
Cr	NA	0.000527 (0.9) [4]	NA	23.8 (0.9) [4]	ICP-AES	NA
Hg	NA	0.000461 (1.5) [4]	NA	88.5 (1.5) [4]	CV-AA	NA
Na	NA	0.835 (0.7) [4]	NA	16700 (0.7) [4]	ICP-AES	NA
S	NA	0.0109 (0.5) [4]	NA	304 (0.5) [4]	ICP-AES	NA

NA ≡ not measured
* Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.

A comparison of anion data, shown in Table 3-2, for this sample and the DWPF SRAT Receipt Batch #782 is difficult due to a number of factors. The DWPF SRAT receipt nitrite ion concentration would be expected to be reduced relative to the incoming sludge since the heel in the SRAT is reduced in nitrite ion. Similarly, the SRAT formate and nitrate ion concentrations would be expected to be elevated relative to the sludge since the heel in the SRAT is greatly increased in these anions. The nitrite to nitrate ratio observed is considerably different, but is likely due to the large residual heel in the SRAT vessel. This pre-concentration of the SRAT receipt material, prior to sampling and analysis, makes a comparison of anion levels very difficult for this sludge batch. Some past sludge batches have been higher in incoming insoluble solids and did not require this caustic boil prior to routine SRAT processing.

The conversion of the total supernate sulfur value, as shown in Table 3-2, from molar to wt.% of total solids, yields 0.216 wt.% (0.5 %RSD) S for the SB9 WAPS sample. Comparing this value with the total slurry sulfur value in Table 3-5 (0.263 wt.%, 0.7 %RSD) indicates that ~82% of the sulfur in the SB9 WAPS sample is soluble. For SB3[15], SB4[20], SB6[21], SB7b[12] and SB8[18], 95%, 93%, 91%, 82% and 86% of the sulfur was soluble, respectively. However, the SB5[22] WAPS sample had only 50% of the sulfur present in the supernate phase. Since the total sulfur content does not exceed any glass limits for anticipated waste loadings[16], there should not be any negative consequences to the speciation of the sulfur in SB9. When the SB9 WAPS supernate sulfur value by ICP-AES (Table 3-2) is put on a slurry sulfate basis, the result is 909 mg sulfate/kg slurry. This compares reasonably well with the DWPF average sulfate analysis for Batches #774 - 782 of 719 mg sulfate/kg slurry considering the latter measurement would not include the soluble, non-sulfate sulfur contribution. The SRNL sulfate/kg slurry value was 847 mg sulfate/kg slurry which is closer still. There is also some variability in the DWPF values batch to batch, which range from 522 to 863 mg/kg across all SB9 batches, and from 522 to 775 mg/kg for the last five batches (less influenced by SB8 heal material).

Table 3-3 provides the TIC and TOC measured for the SB9 WAPS sample along with the total carbon (TC) value which is reported as the sum of the TIC and TOC values. The first column of values resulted from a weighted dilution of the slurry into water, while the second column of values resulted from a weighted dilution of supernate into water. Note that both sets of results are reported on a slurry basis. The slurry value of TIC is needed for current SRAT processing acid calculations while the supernate TIC value has been used in developmental work on a revised acid calculation, hence both dilution methods were undertaken. The data does support earlier observations that there is an undissolved slurry TIC component that is not measured if only the supernate TIC is measured. It does not demonstrate, however, that the current slurry TIC measurement actually succeeds in dissolving the entire insoluble TIC; hence the 500 mg/kg insoluble TIC observed is a lower bound on the actual insoluble TIC value. The slurry TIC value measured for SRAT Batch #782 is ~40% lower than the slurry value determined in SRNL, but no TOC or TC values are available for comparison.

Table 3-3. Carbon Analysis for SB9 WAPS Samples and DWPF SRAT Receipt Batch #782 [Number of Samples Included in Average] (mg C/kg slurry)

Analyte	Slurry Wt'd Dilution SB9 WAPS (%RSD*)	Supernate Wt'd Dilution SB9 WAPS (%RSD*)	SRAT Receipt for Batch #782[a]
Total Inorganic Carbon	1670 (2.2) [4]	1170 (1.4) [4]	929
Total Organic Carbon	590 (2.3) [4]	563 (5.6) [4]	NA
Total Carbon	2260 (0.9) [4]	1730 (1.0) [4]	NA

NA ≡ not measured
* Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.
[a] Measured in DWPF

Table 3-4 provides the base measurements made on the SB9 WAPS sample. Total base represents the value determined from an inflection endpoint titration to pH 7. Free OH^- represents the value determined after precipitation of carbonate with $BaCl_2$ and titration to the first inflection endpoint between pH 11 and 8. Further titration of this treated sample to pH 7 yields the value for 'other base'.

Table 3-4. Base Analysis for SB9 WAPS Samples and DWPF SRAT Receipt Batch #782 [Number of Samples Included in Average] (mol/kg slurry)

Analyte	Slurry Wt'd Dilution SB9 WAPS (%RSD)	Supernate Wt'd Dilution SB9 WAPS (%RSD)	SRAT Receipt for Batch #782[a]
Total Base	0.326 (0.3) [3]	0.237 (13) [4]	0.250
Free OH^-	0.318 (2.1) [3]	0.190 (9.7) [4]	NA
Other Base	< 0.30	<0.079	NA

NA ≡ not measured
* Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.
[a] Measured in DWPF

The total base value when free OH^- and 'other base' are removed should correspond to the carbonate base equivalents determined via titration. This value, 0.047 moles base/kg slurry derived from the supernate dilutions, should correspond to the TIC base equivalents for carbonate determined from the data in Table 3-3. The value of TIC for the slurry weighted dilution gives 0.28 moles base/kg slurry, while the TIC value from the supernate weighted dilution gives 0.19 moles base/kg slurry. The supernate determined value would be expected to be lower than the slurry value if there are undissolved carbonates in the solids that are dissolved when the slurry is diluted into water. The carbonate base value (determined from the data in Table 3-4) that was derived from a weighted dilution of slurry is low even if the 'other base' value is assumed to be zero. In other words, the carbonate base value derived from a weighted dilution of slurry is effectively zero, which implies that one or both of the reported free OH- or the 'other base' values is too high, i.e. a sum of the two exceeds the total base value without consideration of the contribution from carbonate species.

The elemental concentrations determined from ICP-AES, ICP-MS, AA, and CV-AA analyses are presented in Table 3-5. For the SB9 WAPS sample, results from both digestions have been combined where appropriate. When both detection limits and actual values are measured for replicates, only the actual value(s) are included in the average shown in the table. Due to the use of Zr crucibles and $NaOH/Na_2O_2$ in the AF, Zr and Na values, as well as other alkali metals, were determined from the aqua regia digestion. In the case of B, Be, Mo, Sb, Sn, and V, both preparations yielded values below the detection limits; hence the lowest detection limit value was selected. Alkali fusion data was used to report values for Al and Si for the SB9 WAPS sample since the aqua regia preparation fails to dissolve all forms of these elements. The aqua regia data was used to report Sr since the ARG-1 glass value for Sr by AF was biased high. Based upon the ARG-1 glass determinations, the reported P value could be biased high, while the reported Ti and Zr values could be biased low. ICP-MS analysis of the aqua regia digestion was also used to determine the concentrations of Cd, Ce, Gd, La, Nd, Pb, Th, and U. The various isotopes used from the ICP-MS analysis are indicated in the footnotes to Table 3-5. In the case of Ce and Nd the distribution of isotopes was not according to their natural abundances but rather the result of fission product yields from U-235. Hence the sum of the respective isotopic masses was used to determine the reported concentrations for Ce, Nd, and U. The U value reported here from ICP-MS compares to a value determined by ICP-AES of 3.05 wt.% of total solids. For Cd, Gd, and Pb, the reported value was determined from all measured values calculated using the various isotopes' natural abundance. In the case of La-139 and Th-232, a single isotope has essentially 100% natural abundance and was used to calculate the values given in the table.

Where there are also ICP-AES results for elements reported in Table 3-5 based on their ICP-MS data, these have been included in Table A-1 in Appendix A. There is generally good agreement between the ICP-MS and ICP-AES results. SRNL is still developing a protocol to propagate the uncertainties for merging the data from the two instruments into a single value for future reports.

Table 3-5. Elemental Concentrations* in SB9 WAPS Samples in Wt. % of Total Dried Solids (%RSD) [Number of Samples Included in Average]**

Element	SB9 WAPS	Element	SB9 WAPS
Al	6.62 (2.1) [4]	Mo	<0.020
As^^	<0.0016	Na	15.6 (0.7) [4]
B	<0.027	Nd‡‡	0.133 (0.2) [4]
Ba	0.0678 (7.4) [8]	Ni	1.15 (3.3) [8]
Be	<0.000099	P‡‡‡‡	0.173 (9.6) [4]
Ca	0.927 (6.4) [8]	Pb‡	0.0302 (3.4) [4]
Cd‡	0.0142 (5.5) [4]	S	0.263 (0.7) [4]
Ce‡‡	0.223 (0.4) [4]	Se^^	<0.0031
Co	0.00623 (2.1) [4]	Sb	<0.025
Cr	0.0920 (9.0) [7]	Si	1.20 (4.5) [4]
Cu	0.0352 (0.5) [4]	Sn	<0.015
Fe	16.3 (4.4) [8]	Sr	0.0263 (0.7) [4]
Gd‡	0.0785 (2.2) [4]	Th‡‡	0.756 (0.6) [4]
Hg^	1.92 (8.8) [4]	Ti‡‡‡	0.0220 (1.1) [4]
K	0.123 (13) [4]	U‡‡	3.00 (0.6) [4]
La‡	0.0399 (1.4) [4]	V	<0.00069
Li	0.0401 (0.8) [4]	Zn	0.0274 (1.0) [4]
Mg	0.221 (0.7) [4]	Zr‡‡‡	0.0929 (20) [3]
Mn	5.32 (1.0) [8]		

* ICP-AES data unless specified otherwise. ^ Calc'd from CV-AA data. ^^ Calc'd from AA data
** Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.
‡ Calculated from MS data for Cd: Cd-111, Cd-112, Cd-114; La-139; Gd: Gd-155, Gd-156, Gd-157, Gd-158, Gd-160; Pb: Pb-206, Pb-207, Pb-208; and Th-232; respectively.
‡‡ Calculated from the sum of MS data for Ce: Ce-140 and Ce-142; Nd: Nd-143, Nd-144, Nd-145, Nd-146, Nd-148, and Nd-150; U: U-233, U-234, U-235, U-236, and U-238.
‡‡‡ Value may be biased low based upon the value obtained for the ARG standard.
‡‡‡‡ Value may be biased high based upon the value obtained for the ARG standard.

A comparison of the major elemental ratios of the insoluble solids using data from Table 3-5 is given in Table 3-6. SRAT Receipt Batch #782 data is from DWPF and was used to calculate the ratios of Fe to

Al, Ca, Mn, and U. These ratios should remain constant through batch processing unless an addition of material containing one or more elements of interest is made.

Generally, the elemental ratios observed for SB4 and SB5 are very similar for these major elements. SB6 has the highest Al/Fe ratio of the last seven sludge batches. SB7a[17] and SB7b are similar in the Ca and U ratios to Fe, but dissimilar in the ratios of Al and Mn. SB8 and SB9 have the lowest Al/Fe and U/Fe ratios observed for the last seven sludge batches and Mn/Fe ratios last observed for SB6. The agreement between the SB9 WAPS sample and the DWPF Batch #782 data is excellent. The Ca/Fe and Mn/Fe ratios are in reasonable agreement with the DWPF data from either their Cold Chem (CC) or AF digestion methods, but only the AF data is shown in the table. While there is generally a low bias in the CC method data for Al, the Al/Fe ratio is actually slightly better for the CC method for Batch #782 than from the AF digestion. However, the bias is more evident for data from Batches #780 (-9%) and #781 (-11%). A lower U/Fe ratio (0.16) is obtained from the DWPF AF method, and this low bias was also true for DWPF Batches #780 and #781, indicating that U is probably best determined from the CC method.

Table 3-6. Comparison of Elemental Ratios for Major Insoluble Elements in the Tank 40 SB4, SB5, SB6, SB7a, SB7b, SB8 and SB9 Samples with DWPF Batch #782 SRAT Receipt Data

Element Ratio	SB4 WAPS[20]	SB5 WAPS[22]	SB6 WAPS[21]	SB7a WAPS[17]	SB7b WAPS[12]	SB8 WAPS[18]	SB9 WAPS	DWPF SRAT Receipt Batch #782[a]	% Difference SB8 WAPS – Batch #782	DWPF Method*
Al/Fe	0.67	0.60	0.76	0.71	0.66	0.41	0.41	0.39	-5	CC
Ca/Fe	0.099	0.092	0.062	0.051	0.050	0.057	0.057	0.058	2	AF
Mn/Fe	0.22	0.23	0.31	0.28	0.22	0.31	0.33	0.32	-0.5	AF
U/Fe	0.37	0.33	0.26	0.34	0.34	0.22	0.18	0.17	-5	CC

*CC ≡ cold chemical, PF ≡ alkali fusion

[a] Measured in DWPF

Table 3-7 and Table 3-8 provide the replicate measurements for Fe (whose average was reported in Table 3-5) and the fissile isotopes, U-233, U-235, Pu-239, and Pu-241 for the SB9 WAPS sample, respectively. This data along with the replicate solids and density measurements given in Table 3-9 are reported to allow for the verification of canister fissile limits in DWPF.

Table 3-7. Replicate Concentrations of Iron for the SB9 WAPS Sample in Wt.% of Total Dried Solids

Element	Repl. 1	Repl. 2	Repl. 3	Repl. 4	Average	Instrument	Prep Method
Fe	16.9	17.1	17.0	16.9	17.0	ICP-AES	AR
Fe	15.5	15.5	15.9	15.6	15.6	ICP-AES	AF
Fe	-	-	-	-	16.3	ICP-AES	AR/AF

AR ≡ aqua regia digestion, AF ≡ alkali digestion

Table 3-8. Replicate Activities of Fissile Radionuclides for the SB9 WAPS Sample in µCi/g of Total Dried Solids*

Radionuclide	Repl. 1	Repl. 2	Repl. 3	Repl. 4	Reported	%RSD**
U-233	6.73E-02	6.70E-02	6.51E-02	6.69E-02	6.66E-02	1.5
U-235	6.65E-04	6.64E-04	6.66E-04	6.56E-04	6.63E-04	0.7
Pu-239	5.52E+00	5.58E+00	5.49E+00	5.42E+00	5.50E+00	1.2
Pu-241‡	2.69E+01	3.02E+01	2.46E+01	2.60E+01	2.69E+01	8.8

* ICP-MS data unless specified otherwise

‡ Pu-238/-241 method. See Ref. 8 for description.

**Values in the %RSD column are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.

Unlike SB8, which was 0.643 wt.% U-235, i.e. it contained depleted U, SB9 has 1.022 wt% U-235 enrichment. Normal U enrichment is 0.7204 wt.%.[19]

Table 3-9. Replicate Weight Percent Solids and Densities for SB9 WAPS Sample

Species (Wt.% Solids are Slurry Basis)	Repl. 1	Repl. 2	Repl. 3	Repl. 4	Average
Wt.% Total Solids	14.01	14.10	14.14	13.98	14.06
Wt.% Calcined Solids	10.61	10.39	10.76	10.63	10.60
Slurry Density, g/mL	1.064	1.091	1.113	1.100	1.09
Supernate Density, g/mL	1.048	1.044	1.045	NA	1.05

NA ≡ not applicable

The fission product noble metal and silver concentrations are given in Table 3-10 and

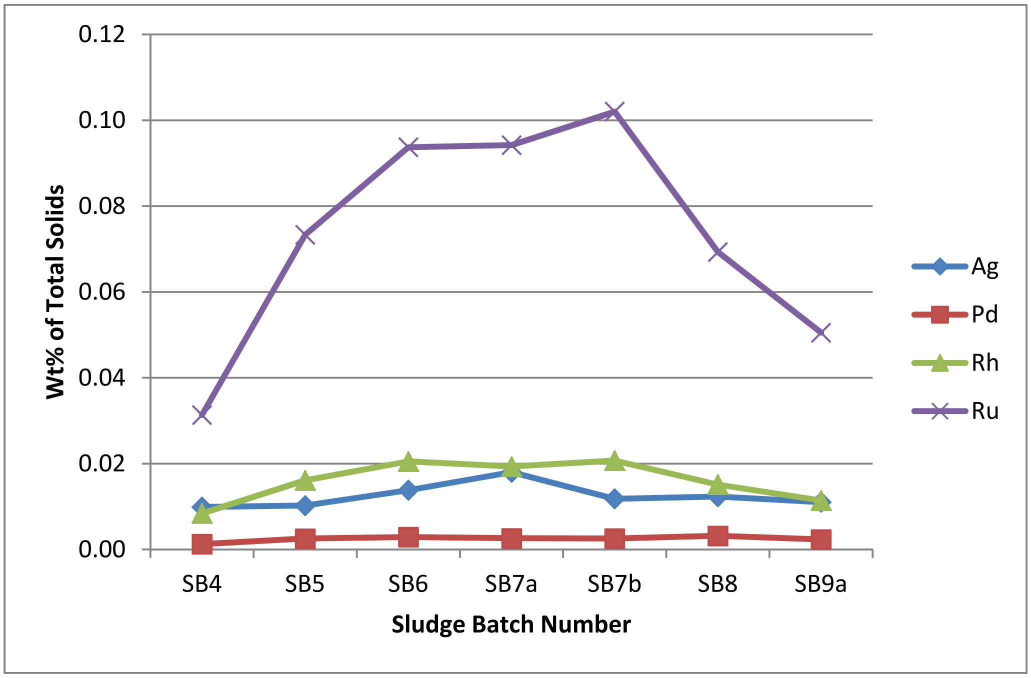

Figure 3-1. The values were calculated from ICP-MS data using an Excel spreadsheet. This spreadsheet uses the fission yield to account for the mass contribution from Pd isotopes in the tank that could not be measured because isotopes of natural Cd and Ag interfere. An example of this is the measurement at mass 110, which is comprised of Pd-110 and Cd-110. The uncertainties were analyzed using statistical techniques appropriate for replicate measurements of non-highly correlated data. For comparison purposes, the SB4[20], SB5[22], SB6[21], SB7a[12], SB7b[12] and SB8 WAPS[18] samples are also given in this table. The results indicate there had been a general leveling off in fission product noble metal and silver

concentrations over the first five sludge batches shown in

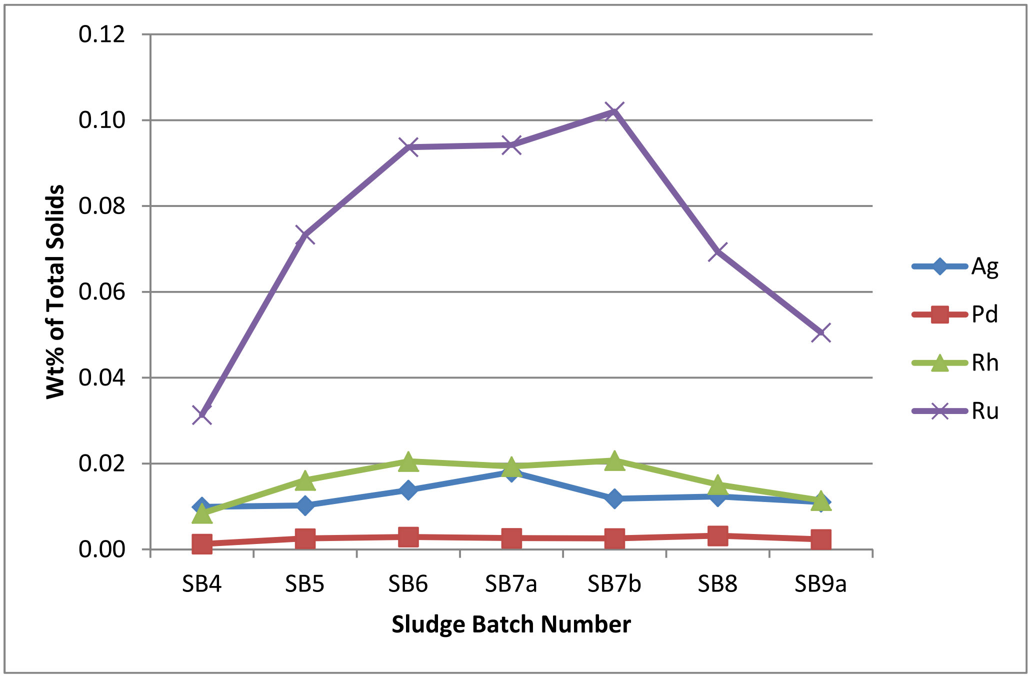

Figure 3-1. However, with SB9, the [Ru] continues to drop, back below SB5 levels. The silver concentration appears to have peaked in SB7a, [Pd] peaked in SB6, and [Ru] peaked in SB7b, while [Rh] had been fairly constant across SB6, SB7a, and SB7b, it now continues to decrease like that of Ru to below SB5 levels.

Table 3-10. Noble Metal Fission Product and Silver Concentrations in SB4, SB5, SB6, SB7a, SB7b, SB8, and SB9 WAPS Samples in Wt. % of Total Solids (%RSD)

Element	SB4 WAPS[20]	SB5 WAPS[22]	SB6 WAPS[21]	SB7a WAPS[12]	SB7b WAPS[12]	SB8 WAPS[18]	SB9 WAPS
Ag (-107, -109)	0.00987 (0.5)	0.0102 (2.0)	0.0138 (0.8)	0.0180 (2.3)	0.0118 (1.0)	0.0123 (2.5)	0.0110 (0.4)
Pd (-105, -106, -107, -108, -110)	0.00125 (6.0)	0.00252 (3.4)	0.00289 (2.6)	0.00261 (2.7)	0.00254 (3.9)	0.00317 (5.1)	0.00233 (0.80)
Rh (-103)	0.00840 (4.5)	0.0161 (1.1)	0.0205 (2.1)	0.0193 (1.8)	0.0207 (1.0)	0.0151 (3.4)	0.0114 (1.2)
Ru (-101, -102, -104)	0.0313 (0.7)	0.0733 (0.6)	0.0937 (0.6)	0.0942 (0.5)	0.102 (0.6)	0.0693 (0.7)	0.0505 (0.2)

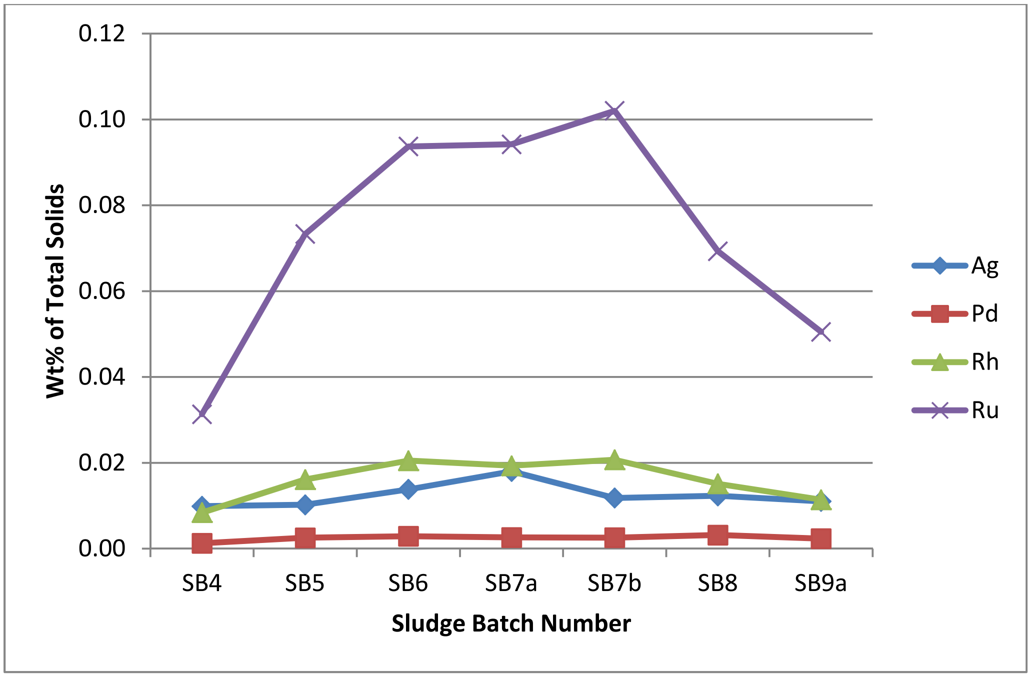

Figure 3-1. Noble Metal Fission Product and Silver Concentrations (Wt. % of Total Solids) in SB4 through SB9 WAPS Samples

A comparison of the fission yield mass ratios for Ru:Rh, Ru:Pd, and Ru:Ag with those measured for the SB9 WAPS sample is provided in Table 3-11. The SB4, SB5, SB6, SB7a, SB7b and SB8 WAPS sample results are also provided for comparison. The mass ratios are based upon Ru due to its relatively high concentration in the sludge as compared with the other noble metals. The Ru:Rh ratio agrees reasonably well, while the Ru:Ag ratios differ significantly from the fission yield ratios. This lack of agreement for the Ag ratios is not unexpected. The majority of the Ag is natural Ag originating from Ag saddles used in the dissolvers to scavenge radioactive iodine, while the noble metals are fission products of U-235. Consequently, the relative concentration of Ag is not expected to be in proportion to the fission yields of its two isotopes. The Ru:Pd ratios agree reasonably well amongst the samples but not with that predicted by the fission yield. A possible explanation for this is that a portion of the Pd is soluble and hence has fractioned off into the salt waste, thus increasing the ratio of Ru to Pd in the sludge waste. This fractionation appeared to be increasing over the past five sludge batches, but has dropped off significantly for SB8 and SB9.

Table 3-11. Fission Yield Ratios and Measured Noble Metal Ratios in SB4, SB5, SB6, SB7a, SB7b, SB8 and SB9 WAPS Samples

Ratio	Fission Yield	SB4 WAPS[20]	SB5 WAPS[22]	SB6 WAPS[21]	SB7a WAPS[12]	SB7b WAPS[12]	SB8 WAPS[18]	SB9 WAPS
Ru:Rh	3.7	3.7	4.6	4.6	4.9	4.9	4.6	4.4
Ru:Pd	6.9	25	29	32	36	40	22	22
Ru:Ag	343	3.2	7.2	6.8	5.2	8.6	5.6	4.6

4.0 Conclusions

- The solids reported were 14.06 wt% total, 9.13 wt% insoluble, and 10.60 wt% calcined. With a slurry density of 1.09 mg/mL and supernate density of 1.05 mg/mL.

- The ratios of the major elements for the SB9 WAPS sample are very similar to those measured for the SB8 WAPS sample. There is less Al and U, and more Mn relative to Fe than in early sludge batches.

- The elemental composition of this sample and the analyses conducted here are reasonable and consistent with DWPF batch data measurements in light of SRAT product heel and variable line flush contributions to the DWPF SRAT receipt sample. The element ratios for Al/Fe, Ca/Fe, Mn/Fe, and U/Fe agree within 5% between this work and the DWPF SRAT receipt analyses.

- Sulfur in the SB9 WAPS sample is 82% soluble, the same as that reported for SB7b, but slightly less than the results reported for SB3, SB4, SB6, and SB8, and unlike the 50% insoluble sulfur observed in the SB5 WAPS sample. In addition, 6% of the soluble sulfur is not present as sulfate in SB9, which is the lowest difference seen in recent sludge batches.

- The average activities of the fissile isotopes of interest in the SB9 WAPS sample are (in µCi/g of total dried solids): 6.66E-02 U-233, 6.63E-04 U-235, 5.50E+00 Pu-239, and 2.69E+01 Pu-241. The full radionuclide composition will be reported in a future document.

- The fission product noble metal and Ag concentrations appear to have largely peaked in previous DWPF sludge batches. The concentration of Ru has decreased further in SB9.

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Appendix A: Supplemental Data

Table A-1. ICP-AES Results for Elements Reported Based on ICP-MS Data in Table 3-5 for SB9 WAPS Samples in Wt.% of Total Dried Solids (%RSD) [Number of Samples Included in Average]**

Element	SB9 WAPS
Cd	0.0126 (0.9) [4]
Ce	0.226 (0.4) [4]
Gd	0.0747 (1.6) [4]
La	0.0439 (1.6) [4]
Th	0.894 (11) [8]
U	3.05 (7.1) [8]

** Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.

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