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TANK 40 FINAL SB7b CHEMICAL CHARACTERIZATION RESULTS

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EXECUTIVE SUMMARY

A sample of Sludge Batch 7b (SB7b) was taken from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)[i]. The SB7b 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 currently being fed to the Defense Waste Processing Facility (DWPF) as SB7b.

At the Savannah River National Laboratory (SRNL) the 3-L Tank 40 SB7b sample was transferred from the shipping container into a 4-L high density polyethylene bottle and solids were allowed to settle over the weekend. 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 558 g sub-sample was removed. This sub-sample was then utilized for all subsequent analytical samples.

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. Two 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 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, 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 SB7b 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, and Cs-137 gamma scan[v]. 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 Tank 40 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.[vi]

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

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[i] Office of Environmental Restoration and Waste Management, *Waste Acceptance Product Specifications for Vitrified High-Level Waste Forms*, US DOE Document DOE/EM-0093, Rev. 2, (12/96).

[ii] Coleman, C. J. *Aqua Regia Dissolution of Sludge for Elemental Analysis*, Manual L16.1, Procedure ADS-2226, Rev. 9, Savannah River Site, Aiken, SC 29808 (2009).

[iii] Coleman, C. J. *Alkali Fusion Dissolutions of Sludge and Glass for Elemental and Anion Analysis*, Manual L16.1, ADS-2502, Rev. 6, Savannah River Site, Aiken, SC 29808 (2008).

[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-2011-000189, Savannah River Site, Aiken, SC 29808 (2011).

[vi] Bannochie, C. J., DiPrete, D. P. *Determination of Reportable Radionuclides for DWPF Sludge Batch 6 (Macrobatch 7)*, SRNL-STI-2011-000189, Savannah River Site, Aiken, SC 29808 (2011).

- The ratios of the major elements for the SB7b WAPS sample are different from those measured for the SB7a WAPS sample. There is less Al and Mn relative to Fe than the previous sludge batch.

- The elemental composition of this sample and the analyses conducted here are reasonable and consistent with DWPF batch data measurements in light of DWPF pre-sample concentration and SRAT product heel contributions to the DWPF SRAT receipt analyses. The element ratios for Al/Fe, Ca/Fe, Mn/Fe, and U/Fe agree within 10% between this work and the DWPF Sludge Receipt and Adjustment Tank (SRAT) receipt analyses.

- Sulfur in the SB7b WAPS sample is 82% soluble, slightly less than results reported for SB3, SB4, and SB6 samples but unlike the 50% insoluble sulfur observed in the SB5 WAPS sample. In addition, 23% of the soluble sulfur is not present as sulfate in SB7b.

- The average activities of the fissile isotopes of interest in the SB7b WAPS sample are (in µCi/g of total dried solids): 4.22E-02 U-233, 6.12E-04 U-235, 1.08E+01 Pu-239, and 5.09E+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, with the exception of Ru, which still shows a slight increase in SB7b.

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LIST OF ABBREVIATIONS

AD	Analytical Development
ARG – 1	Analytical Reference Glass – 1
ASP	Analytical Study Plan
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)
RSD	Relative Standard Deviation
SB3	Sludge Batch 3
SB4	Sludge Batch 4
SB5	Sludge Batch 5
SB6	Sludge Batch 6
SB7a	Sludge Batch 7a
SB7b	Sludge Batch 7b
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 7b (SB7b) was pulled from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)[1]. The SB7b 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 currently being fed to the Defense Waste Processing Facility (DWPF) as SB7b.

Savannah River National Laboratory (SRNL) analyses on SB7b were requested by DWPF via Technical Task Request (TTR) HLW-DWPF-TTR-2011-0004[2]. The sample preparation work is governed by a Task Technical and Quality Assurance Plan (TTQAP)[3], and analyses were controlled by an Analytical Study Plan[4].

One 3-L sample of Tank 40 was pulled and delivered on January 19, 2012 following slurry operations. Four slurry pumps were operated for a minimum of eight out of the 10 hours preceding sample collection, and the sample was collected not more than one hour after discontinuing slurry operations. The general protocol is for all four slurry pumps to run for eight hours before a DWPF 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 level was 206.2 inches after the pumps were secured and when the sample was pulled.

2.0 Experimental Procedure

At SRNL, the 3-L Tank 40 SB7b sample was transferred from the shipping container into a 4-L high density polyethylene bottle and solids were allowed to settle over the weekend. 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 558 g sub-sample was removed. This sub-sample was then utilized for all subsequent analytical samples.

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 peroxide fusions, 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 determined from this preparation. Two 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 generally within ± 5% of the expected value. Each aqua regia digestion and blank was diluted to 1:100 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. Equivalent dilutions of the alkali fusion digestions and blank were submitted to AD for ICP-AES analysis.

Tank 40 SB7b 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), total base/free OH^-/other base analyses, and Cs-137 gamma scan[8]. 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 Tank 40 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]

3.0 Results and Discussion

Table 3-1 presents the measured SB7b density and weight percent solids data[9,10] collected for the SB7b WAPS sample taken in January 2012. Table 3-1 also contains data from the DWPF Sludge Receipt and Adjustment Tank (SRAT) receipt sample data for Batch #614 as a comparison. Batch #614 was selected because it was the fifth DWPF batch received from Tank 40 following the start of SB7b processing and both the SRAT heel and receipt material should represent SB7b material. The wt. % total solids for the Tank 40 – WAPS sample is lower than that seen for Batch #614, and 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 DWPF pre-sample concentration of incoming Tank 40 transfers. The SRAT heel contributes approximately 13 – 19% of the volume of slurry in the SRAT vessel and can have total solids in the range of 20 wt. %. Calcine factors were also calculated by taking the ratio of the weight percent calcined solids and the weight percent total solids. The Tank 40 – WAPS Sample has a value of 0.80 grams of calcined solids per gram of dried solids.

Table 3-1. Weight Percent Solids and Density for Tank 40 SB7b WAPS Samples and DWPF SRAT Receipt Batch 614 [Number of Samples Included in Average]

Property	Tank 40 – WAPS (% RSD*)	DWPF SRAT Receipt for Batch 614[a]
Slurry Density	1.12 (0.6) [4]	1.11[d]
Supernate Density	1.05 (0.4) [5]	NA
Wt. % Total Solids	15.64 (0.2) [4]	18.05[d]
Wt. % Calcined Solids	12.50 (2.8) [4]	NA
Wt. % Dissolved Solids[b]	5.48 (0.2) [4]	NA
Wt. % Insoluble Solids	10.75	NA
Wt. % Soluble Solids[c]	4.89	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

[b] Also known as Uncorrected Soluble Solids

[c] Also known as Corrected Soluble Solids

[d] DWPF calculations give 16.05 wt.% total solids and a density of 1.09 when the effect of the SRAT heel and pre-concentration is removed.

Table 3-2 provides the anion results for the Tank 40 WAPS sample and the available DWPF SRAT receipt data for Batch #614. 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 supernate and weighted dilutions of slurry, 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 supernate and weighted dilutions of slurry, respectively. As a result, Columns 2 and 4 are from the same set of weighted dilutions, and Columns 3 and 5 are from a separate set of weighted dilutions.

The supernate sulfur result given for SRNL is calculated from total sulfur detected in the supernate by ICP-AES and is about 30 % higher, on a molar basis, than sulfate sulfur determined by IC. This difference between total soluble sulfur and sulfate soluble sulfur was observed throughout SB6 washing[11] and it appears to be true again for SB7b. The Al, Ca, Cr, K, Mo, Na, and S values also shown in this table were calculated from the ICP-AES 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.

Table 3-2. Supernate Analyses for Tank 40 SB7b WAPS Samples and DWPF SRAT Receipt Batch 614 [Number of Samples Included in Average]

Analyte	SB7b WAPS (%RSD*) Mol/L super. Wt'd Dil. Slurry	SB7b WAPS (%RSD*) Mol/L super. Wt'd Dil. Super.	SB7b WAPS (%RSD*) mg/kg slurry Wt'd Dil. Slurry	SB7b WAPS (%RSD*) mg/kg slurry Wt'd Dil. Super.	Method	SRAT Receipt for Batch 614 mg/kg slurry
NO_3^-	0.0953 (0.6) [4]	0.0975 (0.8) [4]	5030 (0.6) [4]	5150 (0.8) [4]	IC	8490
NO_2^-	0.232 (1.1) [4]	0.233 (0.7) [4]	9090 (1.1) [4]	9140 (0.7) [4]	IC	8790
SO_4^{2-}	0.0181 (1.0) [4]	0.0179 (1.4) [4]	1480 (1.0) [4]	1460 (1.4) [4]	IC	1880
PO_4^{3-}	<0.0052	<0.0033	<418	<268	IC	NA
I^- **	NA	1.19E-08 (8.5) [4]	NA	1.29 (8.5) [4]	ICP-MS	NA
Br^-	<0.0061	<0.0039	<418	<268	IC	NA
Cl^-	<0.014	<0.0089	<418	<268	IC	NA
CHO_2^-	<0.011	<0.0070	<418	<268	IC	6250
$C_2O_4^{2-}$	0.0399 (1.0) [4]	0.0394 (0.6) [4]	2990 (1.0) [4]	2950 (0.6) [4]	IC	3670
F^-	<0.026	<0.017	<418	<268	IC	NA
Al	NA	0.0357 (0.1) [4]	NA	820 (0.1) [4]	ICP-AES	NA
Ca	NA	0.000116 (3.6) [4]	NA	3.97 (3.6) [4]	ICP-AES	NA
Cr	NA	0.000442 (0.6) [4]	NA	19.6 (0.6) [4]	ICP-AES	NA
Fe	NA	0.0000108 (12) [2]	NA	0.513 (12) [2]	ICP-AES	NA
K	NA	0.00189 (17) [3]	NA	62.8 (17) [3]	ICP-AES	NA
Mo	NA	0.0000496 (9.7) [2]	NA	4.05 (9.7) [2]	ICP-AES	NA
Na	NA	0.979 (0.5) [4]	NA	19200 (0.5) [4]	ICP-AES	NA
S	NA	0.0231 (3.1) [4]	NA	632 (3.1) [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.
** Based on I-127 only, total I from mass 127 and 129 is approximately 2x this value.

A comparison of anion data, shown in Table 3-2, for this sample and the DWPF SRAT Receipt Batch #614 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 and the concentration of DWPF SRAT receipt material prior to sampling. 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 pre-concentration 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 0.403 wt.% (± 3.1 %RSD) S for the Tank 40 – SB7b WAPS sample. Comparing this value with the total slurry sulfur value in Table 3-5 (0.490 wt.% ± 1.7 %RSD) indicates that ~82% of the sulfur in the WAPS sample is soluble. For SB3[12], SB4[14] and SB6[15], 95%, 93%, and 91% of the sulfur was soluble, respectively, while the SB5 WAPS sample had only 50% of the sulfur present in the supernate phase. Since the total sulfur content does not exceed any glass limits, there should not be any negative consequences to the speciation of the sulfur in SB7b. When the SB7b WAPS supernate sulfur value by ICP-AES (Table 3-2) is put on a slurry sulfate basis, the result is 1890 mg sulfate/kg slurry. This compares well with the DWPF sulfate analysis for Batch #614 of 1880 mg sulfate/kg slurry.

Table 3-3 provides the TIC and TOC measured for the SB7b 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 however 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 is needed for 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 490 mg/kg insoluble TIC observed is a lower bound on the actual insoluble TIC value. The slurry TIC value measured for SRAT Batch #614 is 43% lower than the slurry value determined in SRNL, but no TOC or TC values are available for comparison.

Table 3-3. Carbon Analysis for Tank 40 SB7b WAPS Samples and DWPF SRAT Receipt Batch 614 [Number of Samples Included in Average] (mg C/kg slurry)

Analyte	Slurry Wt'd Dilution Tank 40 – WAPS (%RSD*)	Supernate Wt'd Dilution Tank 40 – WAPS (%RSD*)	SRAT Receipt for Batch 614[a]
Total Inorganic Carbon	1610 (5.8) [4]	1120 (3.1) [4]	918
Total Organic Carbon	1210 (6.1) [4]	1050 (1.3) [4]	NA
Total Carbon	2820 (5.8) [4]	2170 (0.9) [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 SB7b 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 Tank 40 SB7b WAPS Samples and DWPF SRAT Receipt Batch 614 [Number of Samples Included in Average] (mol/kg slurry)

Analyte	Slurry Wt'd Dilution Tank 40 – WAPS (%RSD)	Supernate Wt'd Dilution Tank 40 – WAPS (%RSD)	SRAT Receipt for Batch 614[a]
Total Base	0.288 (3.4) [4]	0.283 (3.6) [4]	0.430
Free OH^-	0.184 (4.9) [4]	0.142 (12) [4]	NA
Other Base	0.112 (1.8) [4]	<0.134	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 difference between the total base value when free OH^- and 'other base' are removed should correspond to the carbonate base equivalents determined via titration. This value, 0.14 moles base/kg slurry, 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 0.27 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 supernate is low even if the 'other base' value is assumed to be zero. On the other hand, 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 Tank 40 – 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 alkali fusions, Zr and Na values, as well as other alkali metals, were determined from the aqua regia digestion. In the case of B, Be, 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 Tank 40 – WAPS sample since the aqua regia preparation fails to dissolve all forms of these elements. The aqua regia data was used to report Cr since the ARG-1 glass value for Cr by alkali fusion was biased high. For Zn, both the ARG-1 values by alkali fusion and aqua regia were biased high, so the alkali fusion value was used since it was the smaller of the two measured sample values. A similar bias was seen in the alkali fusion Sr data, but the actual sample results by alkali fusion were slightly lower than those found via aqua regia, so all eight measurements were averaged. 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 5.08 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 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 Tank 40 SB7b WAPS Samples in Wt. % of Total Dried Solids (%RSD) [Number of Samples Included in Average]**

Element	Tank 40 – WAPS	Element	Tank 40 – WAPS
Al	9.18 (0.4) [4]	Mn	3.09 (0.6) [8]
As^^	<0.0011	Mo	0.00547 (10) [2]
B	<0.016	Na	14.4 (0.7) [4]
Ba	0.0979 (1.1) [8]	Ni	2.69 (0.6) [8]
Be	<0.00063	Nd‡‡	0.191 (0.4) [4]
Ca	0.699 (0.6) [4]	P	0.115 (1.1) [4]
Cd‡	0.0288 (4.0) [4]	Pb‡	0.0261 (5.7) [4]
Ce‡‡	0.135 (0.3) [4]	S	0.490 (1.7) [4]
Co	0.0135 (5.5) [8]	Se^^	<0.0022
Cr	0.0405 (1.0) [4]	Sb	<0.084
Cu	0.0437 (4.0) [8]	Si	1.11 (0.4) [4]
Fe	13.9 (0.5) [8]	Sn	<0.044
Gd‡	0.0736 (1.5) [4]	Sr	0.0443 (1.9) [8]
Hg^	1.71 (3.9) [4]	Th‡	1.08 (5.8) [4]
I-127	0.00105 (3.8) [4]	Ti	0.0181 (6.9) [8]
K	0.0536 (9.1) [4]	U‡‡	4.78 (1.9) [4]
La‡	0.0730 (1.1) [4]	V	<0.00037
Li	0.0247 (2.1) [8]	Zn	0.0396 (5.0) [4]
Mg	0.296 (1.8) [8]	Zr	0.176 (10) [4]

* ICP-AES data unless specified otherwise
** 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; I-127; 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
^ Calculated from CV-AA data
^^ Calculated from AA data

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 #614 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 was the most unique of the last five sludge batches. SB7a[13] and SB7b are similar in the Ca and U ratios to Fe, but dissimilar in the ratios of Al and Mn. The agreement between the SB7b WAPS sample and the DWPF Batch #614 data is generally excellent. The Al/Fe, Mn/Fe and U/Fe ratios are in reasonable agreement with the DWPF data. The lower Ca/Fe ratio for DWPF is probably due mostly to the higher uncertainty in the measurement of this lower abundance metal ion.

Table 3-6. Comparison of Elemental Ratios for Major Insoluble Elements in the Tank 40 SB4, SB5, SB6, SB7a and SB7b Samples with DWPF Batch 614 SRAT Receipt Data

Element Ratio	SB4 WAPS[14]	SB5 WAPS[16]	SB6 WAPS[15]	SB7a WAPS[13]	SB7b WAPS	DWPF SRAT Receipt Batch 614	% Difference SB7b WAPS – Batch 614
Al/Fe	0.67	0.60	0.76	0.71	0.66	0.61	8
Ca/Fe	0.099	0.092	0.062	0.051	0.050	0.045	11
Mn/Fe	0.22	0.23	0.31	0.28	0.22	0.23	-4
U/Fe	0.37	0.33	0.26	0.34	0.34	0.35	-3

[13] Reboul, S. H., Click, D. R. *Stable Constituents in SB7a Tank 40 WAPS Sample*, SRNL-L3100-2011-00133, Savannah River Site, Aiken, SC 29808 (2011).
[14] Bannochie, C. J., *Tank 40 Final SB4 Chemical Characterization Results*, WSRC-STI-2007-00674, Savannah River Site, Aiken, SC 29808 (2008).
[15] Bannochie, C. J., *Tank 40 Final SB6 Chemical Characterization Results*, SRNL-STI-2010-00441, Savannah River Site, Aiken, SC 29808 (2010).
[16] Bannochie, C. J., Click, D. R. *Tank 40 Final SB5 Chemical Characterization Results Prior to Np Addition*, SRNL-STI-2009-00060, Rev. 2, Savannah River Site, Aiken, SC 29808 (2010).

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 SB7b 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 Tank 40 SB7b WAPS Sample in Wt.% of Total Dried Solids

Element	Repl. 1	Repl. 2	Repl. 3	Repl. 4	Average	Instrument	Prep Method
Fe	13.8	13.9	14.0	13.9	13.9	ICP-AES	AR
Fe	13.9	14.0	14.0	14.0	14.0	ICP-AES	PF
Fe	-	-	-	-	13.9	ICP-AES	AR/PF

AR ≡ aqua regia digestion, PF ≡ peroxide fusion digestion

Table 3-8. Replicate Activities of Fissile Radionuclides for the Tank 40 SB7b WAPS Sample in µCi/g of Total Dried Solids*

Radionuclide	Repl. 1	Repl. 2	Repl. 3	Repl. 4	Reported	%RSD**
U-233	4.00E-02	3.19E-02	4.28E-02	5.41E-02	4.22E-02	22
U-235	5.73E-04	6.18E-04	6.31E-04	6.24E-04	6.12E-04	4.3
Pu-239	1.06E+01	1.07E+01	1.10E+01	1.07E+01	1.08E+01	1.4
Pu-241‡	<3.0E+01	<1.5E+02	<1.8E+01	5.09E+01	5.09E+01	NA

NA ≡ not applicable
* 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 SB6[15] which was enriched to 0.756 wt.% U-235, both SB7a (0.658 wt.% enrichment) and SB7b (0.592 wt.% enrichment) are not enriched in U-235. Normal U enrichment is 0.711 wt.%.

Table 3-9. Replicate Weight Percent Solids and Densities for Tank 40 SB7b WAPS Sample

Species (Wt.% Solids are Slurry Basis)	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Average
Wt.% Total Solids	15.64	15.60	15.65	15.66	NA	15.64
Wt.% Calcined Solids	12.32	12.52	12.99	12.18	NA	12.50
Slurry Density, g/mL	1.109	1.120	1.125	1.120	NA	1.12
Supernate Density, g/mL	1.052	1.052	1.047	1.049	1.043	1.05

NA ≡ not applicable

Table 3-10 provides Tank Farm requested data on the amount of Cs-137 in the Tank 40 supernate needed for corrosion control activities.

Table 3-10. Cesium-137 Concentration in the Tank 40 SB7b WAPS Sample Supernate in dpm/mL (%RSD) [Number of Samples Included in Average]**

Isotope	Average
Cs-137	2.86E+06 (4.4) [4]

** Parenthetical %RSD value is relative to the true calculated average of the quantity in the table, while the average value reported has been rounded off to a reasonable number of significant figures.

The fission product noble metal and silver concentrations are given in Table 3-11 and Figure 3-1. The values were calculated from ICP-MS data using an Excel spreadsheet. This spreadsheet uses the fission yield for each isotope to account for the mass contribution from isotopes in the tank that could not be measured because isotopes of natural Cd interfere at this mass. 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 WAPS[14], SB5 WAPS[16], SB6 WAPS[15] and SB7a WAPS samples are also given in this table. The results indicate there has been a general leveling off in fission product noble metal and silver concentrations over the past five sludge batches. The silver concentration appears to have peaked in SB7a, [Pd] peaked in SB6, and [Ru] peaked in SB7b, while [Rh] has been fairly constant across SB6, SB7a, and SB7b.

Table 3-11. Noble Metal Fission Product and Silver Concentrations in Tank 40 SB4, SB5, SB6, SB7a, and SB7b WAPS Samples in Wt. % of Total Solids (%RSD)

Element	SB4 WAPS[14]	SB5 WAPS[16]	SB6 WAPS[15]	SB7a WAPS	SB7b WAPS
Ag (-107, -109)	0.00987 (0.5)	0.0102 (2.0)	0.0138 (0.8)	0.0180 (2.3)	0.0118 (1.0)
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)
Rh (-103)	0.00840 (4.5)	0.0161 (1.1)	0.0205 (2.1)	0.0193 (1.8)	0.0207 (1.0)
Ru (-101, -102, -104)	0.0313 (0.7)	0.0733 (0.6)	0.0937 (0.6)	0.0942 (0.5)	0.102 (0.6)

[14] Bannochie, C. J., *Tank 40 Final SB4 Chemical Characterization Results*, WSRC-STI-2007-00674, Savannah River Site, Aiken, SC 29808 (2008)
[15] Bannochie, C. J., Tank 40 Final SB6 Chemical Characterization Results, SRNL-STI-2010-00441, Savannah River Site, Aiken, SC 29808 (2010).
[16] Bannochie, C. J., Click, D. R. *Tank 40 Final SB5 Chemical Characterization Results Prior to Np Addition*, SRNL-STI-2009-00060, Rev. 2, Savannah River Site, Aiken, SC 29808 (2010).

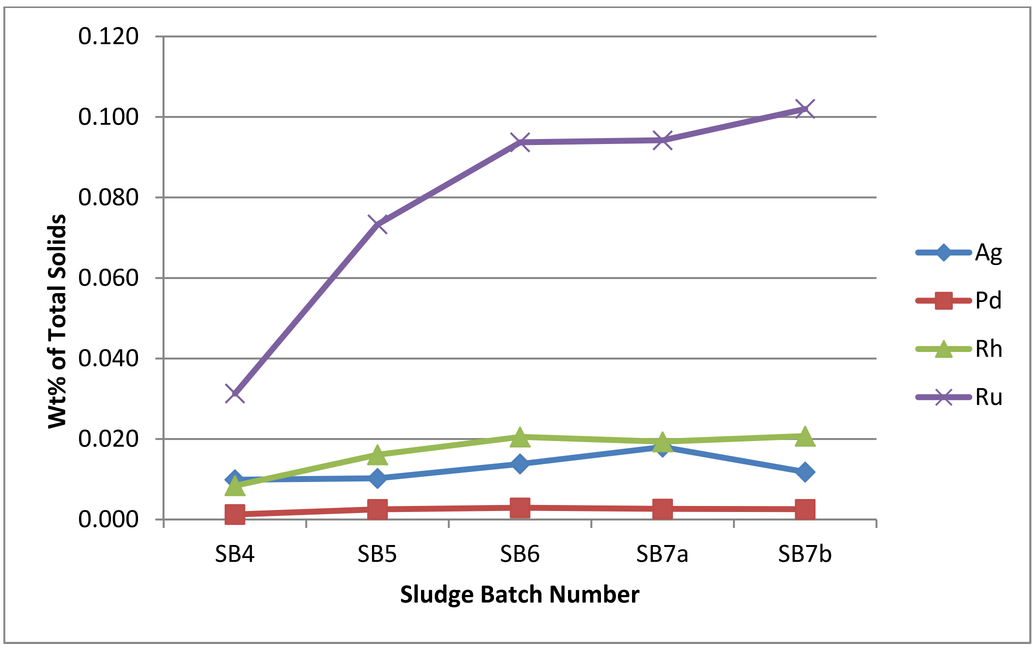

Figure 3-1. Noble Metal Fission Product and Silver Concentrations (Wt. % of Total Solids) in Tank 40 WAPS Samples for SB4 through SB7b

A comparison of the fission yield mass ratios for Ru:Rh, Ru:Pd, and Ru:Ag with those measured for the SB7b WAPS sample is provided in Table 3-12. The SB4, SB5, SB6, and SB7a 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 but does appear to be trending up across all five samples, 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 three 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 appears to be increasing over the last five sludge batches.

Table 3-12. Fission Yield Ratios and Measured Noble Metal Ratios in SB4, SB5, SB6, SB7a, and SB7b WAPS Samples

Ratio	Fission Yield	SB4 WAPS[14]	SB5 WAPS[16]	SB6 WAPS[15]	SB7a WAPS	SB7b WAPS
Ru:Rh	3.7	3.7	4.6	4.6	4.9	4.9
Ru:Pd	6.9	25	29	32	36	40
Ru:Ag	342	3.2	7.2	6.8	5.2	8.6

[14] Bannochie, C. J., *Tank 40 Final SB4 Chemical Characterization Results*, WSRC-STI-2007-00674, Savannah River Site, Aiken, SC 29808 (2008).
[15] Bannochie, C. J., *Tank 40 Final SB6 Chemical Characterization Results*, SRNL-STI-2010-00441, Savannah River Site, Aiken, SC 29808 (2010).
[16] Bannochie, C. J., Click, D. R. *Tank 40 Final SB5 Chemical Characterization Results Prior to Np Addition*, SRNL-STI-2009-00060, Rev. 2, Savannah River Site, Aiken, SC 29808 (2010).

4.0 Conclusions

- The ratios of the major elements for the SB7b WAPS sample are different from those measured for the SB7a WAPS sample. There is less Al and Mn relative to Fe than the previous sludge batch.

- The elemental composition of this sample and the analyses conducted here are reasonable and consistent with DWPF batch data measurements in light of DWPF pre-sample concentration and SRAT product heel contributions to the DWPF SRAT receipt analyses. The element ratios for Al/Fe, Ca/Fe, Mn/Fe, and U/Fe agree within 10% between this work and the DWPF SRAT receipt analyses.

- Sulfur in the SB7b WAPS sample is 82% soluble, slightly less than results reported for SB3, SB4, and SB6 samples but unlike the 50% insoluble sulfur observed in the SB5 WAPS sample. In addition, 23% of the soluble sulfur is not present as sulfate in SB7b.

- The average activities of the fissile isotopes of interest in the SB7b WAPS sample are (in µCi/g of total dried solids): 4.22E-02 U-233, 6.12E-04 U-235, 1.08E+01 Pu-239, and 5.09E+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, with the exception of Ru, which still shows a slight increase in SB7b.

5.0 References

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Appendix A

Table A-1. ICP-AES Results for Elements Reported Based on ICP-MS Data in Table 3-5 for Tank 40 SB7b WAPS Samples in Wt.% of Total Dried Solids (%RSD) [Number of Samples Included in Average]**

Element	Tank 40 – WAPS
Cd	0.0309 (4.1) [8]
Ce	0.138 (12) [8]
Gd	0.0698 (23) [8]
La	0.0628 (5.9) [8]
Pb	0.0313 (1.1) [4]
Th	1.08 (5.0) [8]
U	5.08 (0.8) [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.

Distribution:

S. L. Marra, 773-A
A. B. Barnes, 999-W
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
F. M. Pennebaker, 773-42A
J. P. Vaughan, 773-41A
C. M. Jantzen, 773-A
C. L. Crawford, 773-42A
J. M. Pareizs, 773-A
S. H. Reboul, 773-A
T. B. Edwards, 999-W
K. M. Fox, 999-W
F. C. Johnson, 999-W
D. C. Koopman, 999-W
D. P. Lambert, 999-W
J. D. Newell, 999-W
D. K. Peeler, 999-W
M. E Stone, 999-W
J. R. Zamecnik, 999-W
J. W. Amoroso, 999-W
P. R. Jackson, 703-46A

J. M. Bricker, 704-27S
A. Samadi-Dezfouli, 704-27S
M. A. Broome, 704-29S
T. L. Fellinger, 704-26S
R. N. Hinds, 704-S
E. W. Holtzscheiter, 704-15S
J. F. Iaukea, 704-30S
R. T. McNew, 704-27S
A. V. Staub, 704-27S
J. E. Occhipinti, 704-S
J. W. Ray, 704-S
D. C. Sherburne, 704-S
H. H. Elder, 704-24S

J. M. Gillam, 766-H
D. A. McIlmoyle, 766-H
M. T. Keefer, 766-H
H. B. Shah, 766-H
M. A. Rios-Armstrong, 241-156H
A. R. Shafer, 241-197H
K. H. Subramanian, 249-8H

A. W. Wiggins, 705-1C