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TANK 40 FINAL SB6 CHEMICAL CHARACTERIZATION RESULTS

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EXECUTIVE SUMMARY

A sample of Sludge Batch 6 (SB6) was taken from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)[i], and a portion of the sample was designated for SB6 processing studies. The SB6 WAPS sample was also analyzed for chemical composition including noble metals and fissile composition, 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 DWPF as SB6.

At the Savannah River National Laboratory (SRNL) the 3-L Tank 40 SB6 sample was transferred from the shipping container into a 4-L high density polyethylene vessel and solids were allowed to settle overnight. 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 485 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 in 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 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, and cold vapor atomic absorption (CV-AA) analysis for Hg. Equivalent dilutions of the peroxide fusion digestions and blank were submitted to AD for ICP-AES analysis.

Tank 40 SB6 supernate was collected from a mixed slurry sample in the SRNL Shielded Cells and submitted to AD for ICP-AES, ion chromatography (IC), and total inorganic carbon/total organic carbon (TIC/TOC) analyses. Weighted dilutions of slurry were submitted for IC, TIC/TOC, and total 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.[v]

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

- The ratios of the major elements for the SB6 WAPS sample, whose major Tank 51 Qualification sample component also underwent Al dissolution, are different from those measured for the SB5

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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., Bibler, N. E., and DiPrete, D. P. *Determination of Reportable Radionuclides for DWPF Sludge Batch 5 (Macrobatch 6)*, SRNL-STI-2009-000821, Savannah River Site, Aiken, SC 29808 (2009).

WAPS sample. There is more Al, Mn, and Th, and less Ca and U, 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 Ca/Fe, Mn/Fe, and U/Fe are in excellent agreement between this work and the DWPF Sludge Receipt and Adjustment Tank (SRAT) receipt analyses.

- Sulfur in the SB6 WAPS sample is 91% dissolved, similar to results reported for SB3 and SB4 samples and unlike the 50% percent undissolved sulfur observed in the SB5 WAPS sample.

- The average activities of the fissile isotopes of interest in the SB6 WAPS sample are (in µCi/g of total dried solids): 8.98E-02 U-233, 6.01E-04 U-235, 1.82E+01 Pu-239, and <8.3E+01 Pu-241.

- The fission product noble metal and Ag concentrations continue to increase with each successive DWPF sludge batch consistent with the increase in overall activity for each successive batch.

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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
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
SB4	Sludge Batch 4
SB5	Sludge Batch 5
SB6	Sludge Batch 6
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
WAPS	Waste Acceptance Product Specifications
Wt%	Weight Percent

1.0 Introduction

A sample of Sludge Batch 6 (SB6) was pulled from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)[1] and a portion of the sample was designated for SB6 processing studies. The SB6 WAPS sample was also analyzed for chemical composition, including noble metals, and fissile composition, 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 DWPF as SB6.

Savannah River National Laboratory (SRNL) analyses on SB6 were requested by DWPF via Technical Task Request (TTR) HLW-DWPF-TTR-2009-0014[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 June 22, 2010 following slurry operations. Four slurry pumps were operated for 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 158.6 inches after the pumps were secured and when the sample was pulled.

2.0 Experimental Procedure

At SRNL, the 3-L Tank 40 SB6 sample was transferred from the shipping container into a 4-L high density polyethylene vessel, and solids were allowed to settle overnight. 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 485 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 in 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 Na_2O_2 are not determined 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. 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 81-209 and 230-252, and cold vapor atomic absorption (CV-AA) analysis for Hg. Equivalent dilutions of the peroxide fusion digestions and blank were submitted to AD for ICP-AES analysis.

Tank 40 SB6 supernate was collected from a mixed slurry sample in the SRNL Shielded Cells and submitted to AD for ICP-AES, ion chromatography (IC), and total inorganic carbon/total organic carbon (TIC/TOC) analyses. Weighted dilutions of slurry were submitted for IC, TIC/TOC, and total 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 SB6 density and weight percent solids data[9] collected for the SB6 WAPS sample taken in June 2010. Table 3-1 also contains data from the DWPF Sludge Receipt and Adjustment Tank (SRAT) receipt sample data for Batch #535 as a comparison. Batch #535 was selected because it was the fifth DWPF batch received from Tank 40 following the start of SB6 processing and both the SRAT heel and receipt material should represent SB6 material. The wt % total solids for the Tank 40 – WAPS sample is similar to that seen for Batch #535, and it would be expected to be lower then 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 0.78 grams of calcined solids per gram of dried solids.

Table 3-1. Weight Percent Solids and Density for Tank 40 SB6 WAPS Samples and DWPF SRAT Receipt Batch 535 [Number of Samples Included in Average]

Property	Tank 40 – WAPS (% RSD*)	DWPF SRAT Receipt for Batch 535[a]
Slurry Density	1.12 (0.5) [4]	1.08
Supernate Density	1.05 (0.5) [4]	NA
Wt % Total Solids	16.24 (0.1) [3]	17.3
Wt % Calcined Solids	12.73 (0.8) [4]	NA
Wt % Dissolved Solids[b]	6.10 (0.6) [4]	NA
Wt % Insoluble Solids	10.80	NA
Wt % Soluble Solids[c]	5.44	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

Table 3-2 provides the anion results for the Tank 40 WAPS sample and the available DWPF SRAT receipt data for Batch #535. It should be noted that the oxalate value determined in the prepared IC standard submitted with these samples was low compared to the expected value, but the AD check standard was within allowable tolerances. In order to compare the data from the two labs it was necessary to put the SRNL data on a slurry basis. The supernate sulfur result given for SRNL is calculated from total sulfur detected in the supernate by ICP-AES and is slightly 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.[10] 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 SB6 WAPS Samples and DWPF SRAT Receipt Batch 535 [Number of Samples Included in Average]

Analyte	Tank 40 – WAPS (%RSD*) Molar	Tank 40 – WAPS (%RSD*) mg/kg slurry	Method	SRAT Receipt for Batch 535 mg/kg slurry
NO_3^-	0.0962 (0.5) [4]	5070 (0.5) [4]	IC	7810
NO_2^-	0.235 (0.3) [4]	9190 (0.3) [4]	IC	8490
SO_4^{2-}	0.0102 (0.4) [4]	832 (0.4) [4]	IC	1090
PO_4^{3-}	<0.00036	<29	IC	NA
Br^-	<0.0042	<290	IC	NA
Cl^-	0.00155 (1.2) [4]	46.6 (1.2) [4]	IC	NA
CHO_2^-	0.00112 (1.0) [4]	43.0 (1.0) [4]	IC	7210
$C_2O_4^{2-}$	0.00114 (2.5) [4]	85.2 (2.5) [4]	IC	<505
F^-	<0.0018	<29	IC	NA
Al	0.0519 (0.2) [4]	1190 (0.2) [4]	ICP-AES	NA
Ca	0.000151 (0.5) [4]	5.15 (0.5) [4]	ICP-AES	NA
Cr	0.000379 (0.3) [4]	16.8 (0.3) [4]	ICP-AES	NA
K	0.00135 (1.9) [4]	44.9 (1.9) [4]	ICP-AES	NA
Mo	0.0000330 (3.1) [4]	2.69 (3.1) [4]	ICP-AES	NA
Na	0.945 (0.1) [4]	18500 (0.1) [4]	ICP-AES	NA
S	0.0125 (1.4) [4]	341 (1.4) [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 #535 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. Previous new 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 0.210 wt% S for the Tank 40 – SB6 WAPS sample. Comparing this value with the total slurry sulfur value in Table 3-5 indicates that ~91% of the sulfur in the WAPS sample is soluble. For

SB3[11] and SB4[12], 95% and 93% of the sulfur was soluble, respectively. But 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 SB6. When the SB6 WAPS supernate sulfur value by ICP-AES (Table 3-2) is put on a slurry sulfate basis, the result is 1010 mg sulfate/kg slurry. This compares well with the DWPF sulfate analysis for Batch #535 of 1090 mg sulfate/kg slurry.

Table 3-3 provides the TIC and TOC measured for the SB6 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 are reported on a slurry basis. Due to the lower activity of the supernate, a larger sample of supernate can be diluted into a given volume of water as compared with the slurry dilution, thus attainment of TOC value above the method quantification limit was possible. 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. Since the slurry TOC value could not be determined, the TC was reported by AD at the same level as the TIC value, but there is at least 141 mg TOC/kg slurry based on the supernate dilution results, hence the TC value for the slurry would be at least 1140 mg TC/kg slurry. 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 all of the insoluble TIC, hence the 168 mg/kg insoluble TIC observed is a lower bound on the actual insoluble TIC value. The slurry TIC value measured for SRAT Batch #535 is only 11% higher 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 SB6 WAPS Samples and DWPF SRAT Receipt Batch 535 [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 535[a]
Total Inorganic Carbon	900 (3.8) [4]	732 (0.2) [4]	1003
Total Organic Carbon	<36	141 (0.4) [4]	NA
Total Carbon	900 (3.8) [4]	873 (0.1) [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 SB6 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. The total base measured for DWPF Batch #535 was in reasonable agreement.

Table 3-4. Base Analysis for Tank 40 SB6 WAPS Samples and DWPF SRAT Receipt Batch 535 [Number of Samples Included in Average] (mol/kg slurry)

Analyte	Tank 40 – WAPS (%RSD)	SRAT Receipt for Batch 535[a]
Total Base	0.380 (2.1) [4]	0.423
Free OH^-	0.168 (14) [4]	NA
Other Base	0.074 (1.9) [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

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 0.15 moles base/kg slurry, while the TIC value from the supernate weighted dilution gives 0.12 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) was derived from a weighted dilution of slurry and thus is in excellent agreement with the measured TIC carbonate.

The elemental concentrations determined from ICP-AES, ICP-MS, 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. Due to the use of Zr crucibles and 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 and Zn since the ARG-1 glass value for Cr by alkali fusion was biased high, as was one of the Zn 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. In the case of Ce and Nd the distribution of isotopes was not natural 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 3.58 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 excellent agreement between the ICP-MS and ICP-AES results. SRNL is currently working on 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 SB6 WAPS Samples in Wt % of Total Dried Solids (%RSD) [Number of Samples Included in Average]**

Element	Tank 40 – WAPS	Element	Tank 40 – WAPS
Al	10.6 (0.5) [4]	Mo	0.00579 (4.3) [4]
B	<0.0090	Na	13.2 (1.1) [4]
Ba	0.0930 (3.9) [8]	Ni	1.83 (1.0) [8]
Be	<0.00087	Nd‡‡	0.0262 (0.4) [4]
Ca	0.868 (1.5) [4]	P	0.0764 (10) [4]
Cd‡	0.0314 (2.9) [4]	Pb‡	0.0242 (7.0) [4]
Ce‡‡	0.147 (0.3) [4]	S	0.230 (7.0) [4]
Co	0.00869 (1.5) [4]	Sb	<0.055
Cr	0.0419 (1.0) [4]	Si	0.844 (1.8) [4]
Cu	0.0598 (6.1) [8]	Sn	<0.017
Fe	14.0 (1.8) [8]	Sr	0.0449 (2.7) [8]
Gd‡	0.0825 (3.4) [4]	Th‡	2.23 (0.9) [4]
Hg^	3.17 (3.3) [4]	Ti	0.0189 (5.1) [8]
K	<0.064	U‡‡	3.68 (0.7) [4]
La‡	0.0742 (2.2) [4]	V	<0.0042
Li	0.0237 (3.7) [8]	Zn	0.0432 (1.0) [4]
Mg	0.447 (1.4) [8]	Zr	0.0822 (15) [4]
Mn	4.30 (0.9) [8]		

* 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; 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

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 #535 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. The agreement between the SB6 WAPS sample and the DWPF Batch #535 data is excellent. The Ca/Fe, Mn/Fe and U/Fe ratios are in excellent agreement with DWPF data. The lower Al/Fe ratio for DWPF is probably due to the use of a DWPF Al value resulting from the cold chemical digestion method that is known to be biased low for Al when the Al is present as boehmite. At the time of this report, the DWPF Al value determined from alkali fusion data for the first 10 SRAT receipt batches was not available.

Table 3-6. Comparison of Elemental Ratios for Major Insoluble Elements in the Tank 40 SB4, SB5 and SB6 Samples with DWPF Batch 535 SRAT Receipt Data

Element Ratio	Tank 40 – SB4 WAPS	Tank 40 – SB5 WAPS	Tank 40 – SB6 WAPS	DWPF SRAT Receipt Batch 535	% Difference SB6 WAPS – Batch 535
Al/Fe	0.67	0.60	0.76	0.64	19
Ca/Fe	0.099	0.092	0.062	0.061	2
Mn/Fe	0.22	0.23	0.31	0.32	-3
U/Fe	0.37	0.33	0.26	0.26	0

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 SB6 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 SB6 WAPS Sample in Wt% of Total Dried Solids

Element	Repl. 1	Repl. 2	Repl. 3	Repl. 4	Average	Instrument	Prep Method
Fe	14.0	13.6	14.1	13.9	13.9	ICP-AES	AR
Fe	13.9	13.9	14.5	14.1	14.1	ICP-AES	PF
Fe	-	-	-	-	14.0	ICP-AES	AR/PF

AR ≡ aqua regia digestion, PF ≡ peroxide fusion digestion

Table 3-8. Replicate Activities of Fissile Radionuclides for the Tank 40 SB6 WAPS Sample in µCi/g of Total Dried Solids

Radionuclide	Repl. 1	Repl. 2	Repl. 3	Repl. 4	Reported	%RSD**
U-233	8.19E-02	9.51E-02	1.06E-01	7.60E-02	8.98E-02	15
U-235	5.84E-04	5.66E-04	6.48E-04	6.06E-04	6.01E-04	5.9
Pu-239	1.81E+01	1.80E+01	1.87E+01	1.82E+01	1.82E+01	1.6
Pu-241‡	<8.3E+01	<1.0E+02	<8.6E+01	<1.2E+02	<8.3E+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.

This is the first Tank 40 WAPS sample to be enriched in U-235: 0.756 wt% enrichment, as compared to a normal U value of 0.711. Slight U enrichment has been seen in Tank 51 for several batches now, but previous heels in Tank 40 had lowered the enrichment of the final sludge batch to a "depleted U" level.

Table 3-9. Replicate Weight Percent Solids and Densities for Tank 40 SB6 WAPS Sample

Species (Wt% Solids are Slurry Basis)	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Average
Wt% Total Solids	16.22	16.27	16.24	NA	16.24
Wt% Calcined Solids	12.80	12.74	12.81	12.58	12.73
Slurry Density, g/mL	1.129	1.121	1.124	1.115	1.12
Supernate Density, g/mL	1.054	1.043	1.052	1.050	1.05

NA ≡ not applicable

The fission product noble metal and silver concentrations are given in Table 3-10. 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 (Tank 40)[12] sample and SB5 WAPS (Tank 40)[13] are also given in this table. The results indicate there has been an increase in fission product noble metal and silver concentrations over the past three sludge batches and that SB6 has the highest concentrations seen to date.

Table 3-10. Noble Metal Fission Product and Silver Concentrations in Tank 40 SB4, SB5, and SB6 WAPS Samples in Wt % of Total Solids (%RSD)

Element	Tank 40 – SB4 WAPS[12]	Tank 40 – SB5 WAPS[13]	Tank 40 – SB6 WAPS
Ag (-107, -109)	0.00987 (0.5)	0.0102 (2.0)	0.0138 (0.8)
Pd (-105, -106, -107, -108, -110)	0.00125 (6.0)	0.00252 (3.4)	0.00289 (2.6)
Rh (-103)	0.00840 (4.5)	0.0161 (1.1)	0.0205 (2.1)
Ru (-101, -102, -104)	0.0313 (0.7)	0.0733 (0.6)	0.0937 (0.6)

[12] Bannochie, C. J., *Tank 40 Final SB4 Chemical Characterization Results*, WSRC-STI-2007-00674, Savannah River Site, Aiken, SC 29808 (2008)

[13] 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).

A comparison of the fission yield mass ratios for Ru:Rh, Ru:Pd, and Ru:Ag with those measured for the Tank 40 – SB6 WAPS sample is provided in Table 3-11. The Tank 40 SB4 WAPS and Tank 40 SB5 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 for all three 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.

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

Ratio	Fission Yield	Tank 40 – SB4 WAPS[12]	Tank 40 – SB5 WAPS[13]	Tank 40 – SB6 WAPS
Ru:Rh	3.7	3.7	4.6	4.6
Ru:Pd	6.9	25	29	32
Ru:Ag	342	3.2	7.2	6.8

11 Bannochie, C. J., *Tank 40 Final SB4 Chemical Characterization Results*, WSRC-STI-2007-00674, Savannah River Site, Aiken, SC 29808 (2008).

13 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).

The SB6 WAPS sample in Tank 40 was comprised of a blend of the Tank 51 material prepared during sludge washing and the heel of the SB5 WAPS sample remaining in Tank 40. The plant projected a total solids blend of 62% of Tank 51 and 38% of Tank 40 for the final SB6 WAPS sample. Unfortunately, due to variations between the Tank Farm and SRNL washing endpoints for the SB6 qualification sample and the fact that the Tank 51 SB6 confirmation sample was not digested and analyzed for fission product noble metal content, it is not possible to calculate the predicted noble metal content based on the Tank 51 SB6 confirmation sample and the SB5 heal in Tank 40 to compare this result to the measured values in Table 3-10 as has been done previously.[13]

4.0 Conclusions

- The ratios of the major elements for the SB6 WAPS sample, whose major Tank 51 Qualification sample component also underwent Al dissolution, are different from those measured for the SB5 WAPS sample. There is more Al, Mn, and Th, and less Ca and U, 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 Ca/Fe, Mn/Fe, and U/Fe are in excellent agreement between this work and the DWPF SRAT receipt analyses.

- Sulfur in the SB6 WAPS sample is 91% dissolved, similar to results reported for SB3 and SB4 samples and unlike the 50% percent undissolved sulfur observed in the SB5 WAPS sample.

- The average activities of the fissile isotopes of interest in the SB6 WAPS sample are (in µCi/g of total dried solids): 8.98E-02 U-233, 6.01E-04 U-235, 1.82E+01 Pu-239, and <8.3E+01 Pu-241. The full radionuclide composition will be reported in a future document.

- The fission product noble metal and Ag concentrations continue to increase with each successive DWPF sludge batch consistent with the increase in overall radioactivity for each successive batch.

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 SB6 WAPS Samples in Wt% of Total Dried Solids (%RSD) [Number of Samples Included in Average]**

Element	Tank 40 – WAPS
Cd	0.0328 (8.6) [8]
Ce	0.138 (3.4) [8]
Gd	0.0844 (6.7) [8]
La	0.0766 (5.4) [8]
Pb	0.0284 (3.1) [4]
Th	2.13 (3.0) [8]
U	3.58 (1.6) [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
D. A. Crowley, 773-43A
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
N. E. Bibler, 773-A
J. M. Pareizs, 773-A
S. H. Reboul, 773-A
A. L. Billings, 999-W
T. B. Edwards, 999-W
A. I. Fernandez, 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
B. R. Pickenheim 999-W
M. E Stone, 999-W
J. R. Zamecnik, 999-W

J. M. Bricker, 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
J. E. Occhipinti, 704-S
J. W. Ray, 704-S
D. C. Sherburne, 704-S

J. M. Gillam, 766-H
B. A. Hamm, 766-H
M. T. Keefer, 766-H
H. B. Shah, 766-H