

# TANK 40 FINAL SB4 CHEMICAL CHARACTERIZATION RESULTS

C. J. Bannochie

January 2008

Process Science & Engineering Section  
Savannah River National Laboratory  
Aiken, SC 29808

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## REVIEWS AND APPROVALS

### AUTHOR(S):

---

C. J. Bannochie, Process Science & Engineering Section

Date

### TECHNICAL REVIEWERS:

---

D. C. Koopman, Process Science & Engineering Section

Date

---

N. E. Bibler, Process Science & Engineering Section

Date

### APPROVERS

---

R. E. Edwards, Jr., Manager, Process Science & Engineering Section

Date

---

C. C. Herman, Manager, Process Engineering & Technology

Date

---

J. E. Occhipinti, Manager, DWPF Process Engineering

Date

## EXECUTIVE SUMMARY

A sample of Sludge Batch 4 (SB4) was pulled from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)<sup>1</sup>. This sample was also analyzed for elemental and chemical composition including noble metals. These analyses along with the WAPS analyses will help define the composition of the sludge currently in Tank 40 which is currently being fed to DWPF and will become part of Sludge Batch 5 (SB5).

At SRNL the 3-L Tank 40 SB4 sample was transferred from the shipping container into a 4-L vessel and solids 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 280 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<sub>3</sub>/HCl in sealed Teflon<sup>®</sup> vessels and four in Na<sub>2</sub>O<sub>2</sub> 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. Three glass standards were digested along with a blank for each preparation. Each aqua regia digestion and blank was diluted 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. Equivalent dilutions of the peroxide fusion digestions and blank were submitted to AD for ICP-AES analysis.

Tank 40 SB4 supernate was collected from a mixed slurry sample in the SRNL Shielded Cells and submitted to AD for ICP-AES and ICP-MS. Weighted dilutions of slurry were submitted for ion chromatography (IC), total inorganic carbon/total organic carbon (TIC/TOC), and total base analyses.

A sample of Tank 40 SB4 decant was collected by carefully removing the supernate phase from a settled sample. This decant was not filtered prior to performing a warm nitric acid digestion of the material in order to measure the Si content by ICP-AES. Three Si standards, a blank, and a matrix standard were prepared and submitted along with the Tank 40 samples.

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

- The elemental composition of this sample and the analyses conducted here are reasonable and consistent with DWPF batch data measurements.
- There was no measurable Si in samples of Tank 40 decant.
- Ag and the Ru, Rh, and Pd noble metal concentrations agree well with the estimate used for the SB4 70/30 blend of SB3 and Tank 51 performed in the SRNL Shielded Cells.

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<sup>1</sup> 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).

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## LIST OF ACRONYMS/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
M	Molar
NA	Not Available (e.g. Not Measured)
RSD	Relative Standard Deviation
SB4	Sludge Batch 4
SC-1	Shielded Cells SRAT/SME Run 1
SRNL	Savannah River National Laboratory
Std. Dev.	Standard Deviation
TC	Total Carbon
TIC	Total Inorganic Carbon
WAPS	Waste Acceptance Product Specifications
Wt %	Weight Percent



## 1.0 INTRODUCTION AND BACKGROUND

A sample of Sludge Batch 4 (SB4) was pulled from Tank 40 in order to obtain radionuclide inventory analyses necessary for compliance with the Waste Acceptance Product Specifications (WAPS)<sup>1</sup>. This sample was also analyzed for elemental composition including noble metals. These analyses along with the WAPS analyses will help define the composition of the sludge currently in Tank 40 which is currently being fed to DWPF and will become part of Sludge Batch 5 (SB5).

SRNL analyses on SB4 were requested by DWPF via Technical Task Request (TTR) HLW-DWPF-TTR-2005-0034<sup>2</sup>. The sample preparation work is governed by Task Technical and Quality Assurance Plan (TTQAP)<sup>3</sup>, and analyses were controlled by an Analytical Study Plan<sup>4</sup>.

One 3-L sample of Tank 40 was pulled on October 10, 2007 following slurry operations. Four slurry pumps were started on October 10 and stopped at 11:22 am following eight hours of operation. 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 128.6 inches after the pumps were secured and when the sample was pulled. The sample was sent to SRNL on October 11, 2007.

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## 2.0 APPROACH AND RESULTS

### 2.1 Analytical Methods

At the Savannah River National Laboratory (SRNL) the 3-L Tank 40 SB4 sample was transferred from the shipping container into a 4-L vessel and solids 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 280 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  $\text{HNO}_3/\text{HCl}$  (aqua regia<sup>5</sup>) in sealed Teflon<sup>®</sup> vessels and four in  $\text{Na}_2\text{O}_2$  (alkali or peroxide fusion<sup>6</sup>) 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  $\text{Na}_2\text{O}_2$  are not determined from this preparation. Three Analytical Reference Glass – 1<sup>7</sup> (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 SB4 supernate was collected from a mixed slurry sample in the SRNL Shielded Cells and submitted to AD for ICP-AES and ICP-MS. Weighted dilutions of slurry were submitted for ion chromatography (IC), total inorganic carbon/total organic carbon (TIC/TOC), and total base analyses.

A sample of Tank 40 SB4 decant was collected by carefully removing the supernate phase from a settled sample. This decant was not filtered prior to performing a warm nitric acid digestion of the material (warm acid strike<sup>8</sup>) in order to measure the Si content by ICP-AES. Three Si standards, a blank, and a matrix standard were prepared and submitted along with the Tank 40 samples.

### 2.2 Results

Table 2-1 presents the measured SB4 density and weight percent solids data<sup>9</sup> collected for the final SB4 WAPS sample taken in October 2007. Table 2-1 also contains data from the DWPF Sludge Receipt and Adjustment Tank (SRAT) receipt data for Batch #416 as a comparison. Batch #416 was selected because this is the first DWPF batch received from Tank 40 following the Tank 40 sampling. The wt % total solids for the Tank 40 – WAPS sample are lower than seen for Batch #416. The higher total solids observed for the DWPF SRAT receipt batch probably reflect the impacts of the SRAT heel. The SRAT heel contributes approximately 13 – 19% of the volume of slurry in the SRAT vessel and can have total solids ranging from 24 – 27 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 0.75 grams of calcined solids per gram of dried solids.

**Table 2-1. Weight Percent Solids and Density for Tank 40 SB4 Samples and DWPF SRAT Receipt Batch 416 [Number of Samples Included in Average]**

<b>Property</b>	<b>Tank 40 – WAPS (Std. Dev., % RSD)</b>	<b>DWPF SRAT Receipt for Batch 416<sup>a</sup></b>
Slurry Density	1.084 [4] (0.008, 0.7)	1.135
Supernate Density	1.031 [4] (0.005, 0.5)	NA
Wt % Total Solids	14.44 [4] (0.08, 0.6)	17.25
Wt % Calcined Solids	10.77 [4] (0.09, 0.8)	NA
Wt % Dissolved Solids <sup>b</sup>	4.29 [4] (0.04, 0.9)	NA
Wt % Insoluble Solids	10.60	NA
Wt % Soluble Solids <sup>c</sup>	3.83	NA

NA = not measured

<sup>a</sup> Measured in DWPF<sup>b</sup> Also known as Uncorrected Soluble Solids<sup>c</sup> Also known as Corrected Soluble Solids

As shown in Table 2-2, there is generally reasonable agreement between the anion results for the Tank 40 WAPS sample and the available DWPF SRAT Receipt data for Batch #416. The Al, B, Ca, Cr, K, Mo, Na, and S values were calculated from the ICP-AES data for the supernate. The U value was determined from the ICP-MS supernate data. Other supernate elements measured were below the ICP-AES detection limits. The DWPF SRAT nitrite ion concentration would be expected to be reduced relative to the incoming sludge since the heel in the SRAT is greatly reduced in nitrite ion. Similarly, the SRAT formate and nitrate ion concentration would be expected to be elevated relative to the sludge since the heel in the SRAT is greatly increased in these anions. The supernate sulfur result given is calculated from total sulfur detected in the supernate by ICP-AES and is slightly higher than the sulfate value determined by IC, though likely within the uncertainty of the two measurements. The agreement with the DWPF value for sulfate is good.

**Table 2-2. Supernate Analyses for Tank 40 SB4 Samples [Number of Samples Included in Average] (Molar or moles/L supernate)**

Analyte	Tank 40 – WAPS (Std. Dev., %RSD)	Method	SRAT Receipt for Batch 416
NO <sub>3</sub> <sup>-</sup>	0.130 [4] (0.001, 0.6)	IC	0.161 [4]
NO <sub>2</sub> <sup>-</sup>	0.289 [4] (0.003, 1.1)	IC	0.248 [4]
SO <sub>4</sub> <sup>2-</sup>	0.0144 [4] (0.0001, 0.6)	IC	0.0164 [4]
Br <sup>-</sup>	<0.0072	IC	NA
Cl <sup>-</sup>	<0.016	IC	NA
CHO <sub>2</sub> <sup>-</sup>	<0.013	IC	0.158 [4]
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	<0.0065	IC	NA
F <sup>-</sup>	<0.030	IC	NA
Al	0.00824 [4] (0.00011, 1.3)	ICP-AES	NA
B	0.000615 [4] (0.000007, 1.2)	ICP-AES	NA
Ca	0.0000556 [4] (0.0000023, 4.1)	ICP-AES	NA
Cr	0.000470 [4] (0.000034, 7.2)	ICP-AES	NA
K	0.00127 [4] (0.00001, 1.1)	ICP-AES	NA
Mo	0.0000104 [4] (0.0000002, 2.0)	ICP-AES	NA
Na	0.650 [4] (0.022, 3.4)	ICP-AES	NA
S	0.0161 [4] (0.0002, 1.0)	ICP-AES	NA
U	0.00014 [4] (0.00001, 4.5)	ICP-MS	NA

NA = Not measured

Table 2-3 provides the elemental concentrations determined for the Tank 40 decant (unfiltered) as compared with the 0.45 µm filtered material shown in Table 2-2.

**Table 2-3. Elemental Composition of Tank 40 SB4 Decant Samples [Number of Samples Included in Average] (Molar or moles/L supernate)**

Analyte	Tank 40 – WAPS (Std. Dev., %RSD)
Al	0.00810 [4] (0.00005, 0.7)
B	0.000762 [4] (0.000009, 1.1)
Cr	0.000479 [4] (0.000008, 1.6)
Fe	0.000237 [4] (0.000081, 34)
K	0.00121 [4] (0.00005, 4.1)
Mg	0.0000599 [4] (0.0000026, 4.4)
Mn	0.0000448 [4] (0.0000010, 2.2)
Na	0.641 [4] (0.00366, 0.6)
S	0.0164 [4] (0.0002, 1.3)
Si	<0.000565

Table 2-4 provides the total carbon (TC) and total inorganic carbon (TIC) measured for the SB4 WAPS sample. The TIC value measured for SRAT Batch #416 is 25% higher, but no TC value is available for comparison.

**Table 2-4. Carbon Analysis for Tank 40 SB4 Samples [Number of Samples Included in Average] (mg C/kg slurry)**

Analyte	Tank 40 – WAPS (Std. Dev., %RSD)	SRAT Receipt for Batch 416
Total Inorganic Carbon	897 [4] (29, 3.2)	1126 [4]
Total Carbon	1367 [3] (52, 3.8)	NA

NA ≡ Not measured

Table 2-5 provides the base measurements made on the SB4 WAPS sample. Total base represents the value determined from an inflection endpoint titration to pH 7. Free OH<sup>-</sup> represents the value determined after precipitation of carbonate with BaCl<sub>2</sub> 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 2-5. Base Analysis for Tank 40 SB4 Samples [Number of Samples Included in Average] (mol/kg slurry)**

Analyte	Tank 40 – WAPS (Std. Dev., %RSD)	SRAT Receipt for Batch 416
Total Base	0.121 [4] (0.008, 6.4)	0.113
Free OH	0.0392 [4] (0.0026, 6.7)	NA
Other Base	0.0248 [2] (0.0015, 5.9)	NA

NA ≡ Not measured

The elemental concentrations determined by ICP-AES, ICP-MS, and CV-AA analyses are presented in Table 2-6. For the Tank 40 – WAPS sample, results from both digestions have been combined where appropriate. In the case of Sb, only the peroxide fusion preparation was measured for this element. Also, due to the use of Zr crucibles and Na<sub>2</sub>O<sub>2</sub> 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, Ce, Mo, Sn, V, and Zn, both preparations yielded values below the detection limits, hence Ce was determined by ICP-MS and the lowest detection limit value was selected for the remaining elements. Peroxide 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. ICP-MS analysis of the aqua regia digestion was also used to determine the concentrations of Cd, Gd, La and U.

**Table 2-6. Elemental Concentrations in Tank 40 SB4 Samples in Wt % of Total Solids [Number of Samples Included in Average] (Std. Dev., %RSD)**

<b>Element</b>	<b>Tank 40 – WAPS</b>	<b>Element</b>	<b>Tank 40 – WAPS</b>
Al	9.52 [4] (0.04, 0.4)	Mo	<0.014
B	<0.011	Na	11.0 [4] (0.07, 0.6)
Ba	0.0479 [8] (0.0005, 1.1)	Ni	0.894 [8] (0.017, 1.9)
Ca	1.41 [8] (0.09, 6.6)	P	0.297 [4] (0.022, 7.5)
Cd	0.194 [4]‡ (0.007, 3.4)	Pb	0.0417 [3] (0.0046, 11)
Ce	0.0401[4]‡ (0.0008, 2.0)	S	0.332 [4] (0.016, 4.7)
Cr	0.0767 [4] (0.0004, 0.5)	Sb	<0.069
Cu	0.0331 [4] (0.0006, 1.8)	Si	0.899 [4] (0.018, 2.0)
Fe	14.3 [8] (0.2, 1.6)	Sn	<0.20
Gd	0.0147 [4]‡ (0.0009, 5.8)	Sr	0.0235 [8] (0.0011, 4.6)
Hg	0.814^ [4] (0.028, 3.4)	Ti	0.0166 [4] (0.0001, 0.9)
La	0.0300‡ [4] (0.0007, 2.3)	U	5.29‡‡ [4] (0.17, 3.1)
Li	0.0221 [4] (0.0005, 2.3)	V	<0.0055
Mg	1.17 [8] (0.05, 4.0)	Zn	<0.045
Mn	3.18 [8] (0.04, 1.2)	Zr	0.04 [4] (0.02, 54)

‡ Calculated from MS data for Cd-113, La-139, Ce-140, Gd-157, respectively

‡‡ Calculated from MS data for U-234, -235, -236 and -238

^ Calculated from CV-AA data



The fission product noble metal and silver concentrations are given in Table 2-7. The values were calculated from ICP-MS data using a spreadsheet developed by Ned Bibler (SRNL). 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. For comparison purposes, data for the SB4 Qualification Sample and the estimated concentrations for Shielded Cells SRAT Cycle 1 (SC-1) Blend Sample (70% Tank 40 (SB3) / 30% Tank 51 (SB4 Qualification Sample)) are also given<sup>10</sup>. The values for each noble metal are in reasonably good agreement considering the low concentrations being measured to calculate them. Additionally, the SB4 Qualification Sample results do not include an estimate for the impact on the noble metals concentrations as a result of the SB3 heel in Tank 40. The calculated SC-1 Blend Sample values did take into consideration the impact of this heel and show excellent agreement with the measured values.

**Table 2-7. Noble Metal Fission Products and Silver Concentrations in Tank 40 SB4 WAPS and Qualification Samples in Wt % of Total Solids**

Element	Tank 40 – WAPS	SB4 Qualification Sample <sup>10</sup>	SC-1 Blend Sample <sup>10*</sup>
Ag (-107, -109)	0.00987	0.00292	0.00950
Pd (-105, -106, -107, -108, -110)	0.00124	0.000857	0.00132
Rh (-103)	0.00840	0.0104	0.00824
Ru (-101, -102, -104)	0.0313	0.0427	0.0348

\* Calculated

<sup>10</sup> Pareizs, J. M., Bannochie, C. J., Barnes, M. J., Bibler, N. E., Click, D. R., Hansen, E. K., Lambert, D. P., Stone, M. E. *Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells in Support of Sludge Batch 4 Qualification*, WSRC-STI-2007-00053, Savannah River Site, Aiken, SC 29808 (2007).

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### 3.0 DISCUSSION

#### 3.1 Carbonate

Subtracting the free  $\text{OH}^-$  and other base values from the total base measurement should yield the carbonate contribution to the base equivalents. The carbonate contribution determined from the titration measurements is 0.057 mol carbonate/kg slurry. This compares to a carbonate concentration via the TIC measurement of 0.075 mol carbonate/kg slurry. The agreement is good considering the large uncertainty in determining carbonate via titration.

#### 3.2 Warm Acid Strike for Soluble Silica

The warm acid strike method<sup>8</sup> was utilized to measure the concentration of Si in a Tank 40 decant. The amount of Si measured was below the detection limit and below the lowest standard value of 0.5 ppm Si. There was excellent agreement between the values for the elements Al, Cr, K, Na, and S which were detected in both the warm acid strike treated decant and the filtered supernate (Table 2-2), indicating there is no significant contribution to the concentrations of these elements from suspended fine particles that may be present in the decant.

#### 3.3 Sulfur

The conversion of the total supernate sulfur values, as shown in Table 2-3, from molar to wt% of total solids, yields 0.310 wt% S for the Tank 40 – WAPS sample. Comparing this value with the total slurry sulfur value in Table 2-6 indicates that 93% of the sulfur in the WAPS sample is soluble. Within the uncertainty of the measurements, it is reasonable to assume that virtually all of the sulfur remains as soluble species in the sludge.

#### 3.4 Elemental Ratios

A comparison of the elemental ratios of the major insoluble solids using data from Table 2-6 is given in Table 3-1. SRAT Product Batch #416 data is from DWPF and was used to calculate the ratios of Fe to Al, Ca, Mn, and U since receipt data on these elements is not available. These ratios should remain constant through batch processing unless an addition of material containing one or more elements of interest is made. Generally, the agreement between the Tank 40 – WAPS sample and the DWPF Batch #416 data is good, differing by less than 10% except for U, which is within the analytical uncertainty of the measured data. The U value reported for DWPF SRAT Batch #416 is from ICP-AES rather than ICP-MS, and it is likely biased low. Using the U value determined by ICP-AES for the WAPS sample (5.01 wt% TS) yields a U/Fe ratio of 0.35 which is 18% higher than that observed in DWPF. Generally, the U values determined in DWPF have been lower than those determined at SRNL.

**Table 3-1. Comparison of Elemental Ratios of Major Insoluble Elements in Tank 40 SB4 Sample with DWPF Batch 416 SRAT Product Data**

<b>Element Ratio</b>	<b>Tank 40 – WAPS</b>	<b>DWPF SRAT Product Batch 416</b>	<b>% Difference WAPS – Batch 416</b>
Al/Fe	0.67	0.67	0
Ca/Fe	0.099	0.091	9
Mn/Fe	0.22	0.22	0
U/Fe	0.37	0.30	23

### 3.5 Noble Metal Ratios

A comparison of the fission yield ratios for Ru:Rh, Ru:Pd, and Ru:Ag with those measured for the Tank 40 – WAPS sample is provided in Table 3-2. The SB4 Qualification Sample results and estimated values for the SC-1 Blend Sample are provided for comparison. The 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 since 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 by the relative concentration of Ag, the fission products are not expected to be in proportion to their fission yields. The Ru:Pd ratios agree for the WAPS and the estimated SC-1 Blend 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 fractionated off into the salt waste, thus increasing the ratio of Ru to Pd in the sludge waste.

**Table 3-2. Fission Yield Ratios and Measured Noble Metal Ratios in Various SB4 Samples**

<b>Ratio</b>	<b>Fission Yield</b>	<b>Tank 40 - WAPS</b>	<b>SB4 Qualification Sample<sup>10</sup></b>	<b>SC-1 Blend Sample<sup>10</sup></b>
Ru:Rh	3.7	3.7	4.1	4.2
Ru:Pd	6.9	25	50	26
Ru:Ag	342	3.2	15	3.7

<sup>10</sup> Pareizs, J. M., Bannochie, C. J., Barnes, M. J., Bibler, N. E., Click, D. R., Hansen, E. K., Lambert, D. P., Stone, M. E. *Demonstration of the DWPF Flowsheet in the SRNL Shielded Cells in Support of Sludge Batch 4 Qualification*, WSRC-STI-2007-00053, Savannah River Site, Aiken, SC 29808 (2007).

## **4.0 CONCLUSIONS**

- The elemental composition of this sample and the analyses conducted here are reasonable and consistent with DWPF batch data measurements.
- There was no measurable Si in samples of Tank 40 decant.
- Ag and the Ru, Rh, and Pd noble metal concentrations agree well with the estimate used for the SB4 70/30 blend of SB3 and Tank 51 performed in the SRNL Shielded Cells.

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## 5.0 REFERENCES

- <sup>1</sup> 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).
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