

# **EXAMINATION OF SULFUR MEASUREMENTS IN DWPF SLUDGE SLURRY AND SRAT PRODUCT MATERIALS**

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November 2012

Savannah River National Laboratory  
Savannah River Nuclear Solutions, LLC  
Aiken, SC 29808

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contract number DE-AC09-08SR22470.



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## EXECUTIVE SUMMARY

This report was requested via an email amendment<sup>a</sup> to the Technical Task Request (TTR)<sup>b</sup> for the Sludge Batch 7b (SB7b) Qualification effort. This work was initiated as a result of interest in the reported sulfur (S) content of the SB7b Waste Acceptance Product Specifications (WAPS) sample<sup>c</sup>. More total S was observed in this sample than in previously reported blend and confirmation samples<sup>d,e,f</sup>. The values reported for the weight percent (wt. %) solids and S in the SB7a Tank 40 WAPS sample and the SB7b Tank 51 Sept. 2011 Confirmation sample predict SB7b Tank 40 WAPS sample values different from those reported on the original SB7b WAPS material.

During meetings with the Defense Waste Processing Facility (DWPF), the Savannah River National Laboratory (SRNL) was asked to re-sample the received SB7b WAPS material for wt. % solids, perform an aqua regia digestion and analyze the digested material by inductively coupled plasma – atomic emission spectroscopy (ICP-AES), as well as re-examine the supernate by ICP-AES. The new analyses were requested in order to provide confidence that the initial analytical subsample was representative of the Tank 40 sample received and to replicate the S results obtained on the initial subsample collected. The ICP-AES analyses for S were examined with both axial and radial detection of the sulfur ICP-AES spectroscopic emission lines to ascertain if there was any significant difference in the reported results. The outcome of this second subsample of the Tank 40 WAPS material is the first subject of this report.

After examination of the data from the new subsample of the SB7b WAPS material, a team of DWPF and SRNL staff looked for ways to address the question of whether there was in fact insoluble S that was not being accounted for by ion chromatography (IC) analysis. The question of how much S is reaching the melter was thought best addressed by examining a DWPF Slurry Mix Evaporator (SME) Product sample, but the significant dilution of sludge material, containing the S species in question, that results from frit addition was believed to add additional uncertainty to the S analysis of SME Product material. At the time of these discussions it was believed that all S present in a Sludge Receipt and Adjustment Tank (SRAT) Receipt sample would be converted to sulfate during the course of the SRAT cycle. A SRAT Product sample would not have the S dilution effect resulting from frit addition, and hence, it was decided that a DWPF SRAT Product sample would be obtained and submitted to SRNL for digestion and sample preparation followed by a round-robin analysis of the prepared samples by the DWPF Laboratory, F/H Laboratories, and SRNL for S and sulfate. The results of this round-robin analytical study are the second subject of this report.

The following conclusions can be drawn from this examination of sampling and S in the Tank 40 SB7b WAPS sample and the DWPF SB7b SRAT Product #632:

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- a. Fellingner, T. L. "Request for Documenting Sulfate Results", Email, Savannah River Site, Aiken, SC (2012).
  - b. Bricker, J. M. *Sludge Batch 7b Qualification Studies*, HLW-DWPF-TTR-2011-0004, Savannah River Site, Aiken, SC (2011).
  - c. Bannochie, C. J. *Tank 40 Final SB7b Chemical Characterization Results*, SRNL-STI-2012-00097 Rev. 1, Savannah River Site, Aiken, SC (2012).
  - d. Washington, A. L. *Chemical Characterization Results of the Sludge Batch 7b Tank 51 Confirmation Sample*, SRNL-L3100-2011-00149, Savannah River Site, Aiken, SC (2011).
  - e. Pareizs, J. M. *Stable and Radioactive Constituents in the September 2011 Tank 51 Sludge Batch 7b Confirmation Sample (HTF-51-11-100)*, SRNL-L3100-2011-00189, Savannah River Site, Aiken, SC (2011).
  - f. Reboul, S. H., Click, D. R. *Stable Constituents in SB7a Tank 40 WAPS Sample*, SRNL-L3100-2011-00133, Savannah River Site, Aiken, SC (2011).

1. The initial subsampling of the Tank 40 SB7b WAPS sample was representative of the sample pulled in the tank farm and received by SRNL on January 19, 2012.
2. More total S was measured in the original and resampled Tank 40 SB7b WAPS material than was determined in the DWPF SB7b SRAT Product #632 sample. For  $\text{SO}_4^{2-}$  on a wt. % calcined solids basis, the WAPS sample yielded 1.83 - 1.87, whereas the SRAT Product #632 sample yielded 1.63, a difference which is close to the  $\pm 10\%$  uncertainty in the measurements.
3. The total S value reported for the initial subsample of the Tank 40 SB7b WAPS material via ICP-AES with radial detection for S was essentially identical to that determined from the re-sampled material via ICP-AES with axial detection for sulfur. This indicates that both viewing positions for the ICP-AES (axial vs. radial) produce acceptable results, with the axial position being more sensitive and having a lower method reporting limit (MRL).
4. The DWPF SRAT Product Batch #632 analyzed by SRNL, DWPF, and F/H Laboratories for S and  $\text{SO}_4^{2-}$  yielded the same results within  $\pm 10\%$  of the cross-laboratory averages.
5. Comparing the average of the soluble S with the soluble  $\text{SO}_4^{2-}$ , both expressed in terms of S as a weight percent of total solids, indicates that essentially no soluble S is present that is not sulfate.
6. Based on the cross-laboratory average, up to approximately 24% of the total S in the DWPF SRAT Product Batch #632 may be insoluble.
7. A method for total S measured as  $\text{SO}_4^{2-}$  by IC needs further method development and testing to ascertain its potential to replace the current aqua regia digestion and ICP-AES analysis.
8. When there is a concern over the detection limit that is possible with an ICP-AES radial torch configuration or when very low S values are suspected, the measurements should be made with an axial configuration of the torch to improve the sensitivity of the measurements.

Two recommendations for possible future work were suggested during discussions between DWPF and SRNL held to review the results reported in this document. The first was to identify the insoluble S species (singular or plural) present in these samples. At this time, it is unclear if this/these species can be quantified due to the fact that they collectively represent only 24%, or less, of the relatively small total S in the sample.

The second path of future work was a desire by DWPF to quantify the  $\text{SO}_4^{2-}$  loss in the DWPF melter so as to increase the limit of S in the melter feed. It is known that melter processing results in some volatilization of  $\text{SO}_4^{2-}$  and it is believed that the melter bubblers result in greater volatilization of  $\text{SO}_4^{2-}$  salt from the melt pool. Another suggestion was to examine the next DWPF pour stream glass sample more carefully for S to determine if a measurable value can be determined – previous samples have yielded results below the detection limit for sulfur.

A couple observations from previous work are possibly relevant to this discussion of the path forward. The first is from the sample of cells prepared SB7b Tank 40 material<sup>g</sup> (shown in Table 1-1) that was processed into glass and yielded a measurable  $\text{SO}_4^{2-}$  value in the glass of 0.345 wt.% at 36% waste

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g. Pareizs, J. M. *Chemical and Fissile Characterization Results of the SRNL Prepared Sludge Batch 7b Tank 51 and Tank 40 Samples*, SRNL-L3100-2011-00128, Savannah River Site, Aiken SC (2011).

loading. This corresponds to 0.958  $\text{SO}_4^{2-}$  as a wt% calcined solids and 0.234 S as a wt% total solids.<sup>h</sup> Thus compared to the starting material shown in Table 1-1, there was a 50% loss of S during the SRNL simulated DWPF operations. The second observation concerns the rinsates from SB5 and SB6 pour stream glass samples that have been positive for  $\text{SO}_4^{2-}$  thus indicating there is S in the melter that is not being incorporated into the glass matrix or forming on the glass surface upon cooling.<sup>ij</sup> The latter was observed throughout DWPF cold runs.

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h. Pareizs, J. M., Billings, A. L., Reboul, S. H., Lambert, D. P., Click, D. R. *Sludge Batch 7b Qualification Activities with SRS Tank Farm Sludge*, SRNL-STI-2011-00548, Savannah River Site, Aiken, SC (2011).

i. Johnson, F. C. *Analysis of DWPF Sludge Batch 6 (Macrobatches 7) Pour Stream Glass Samples*, SRNL-STI-2011-00555, Savannah River Site, Aiken, SC (2012).

j. Reigel, M. M., Bibler, N. E. *Analysis of Sludge Batch 4 (Macrobatches 5) for Canister S02902 and Sludge Batch 5 (Macrobatches 6) for Canister S03317 DWPF Pour Stream Glass Samples*, SRNL-STI-2010-00435, Savannah River Site, Aiken, SC (2010).



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## LIST OF ABBREVIATIONS

AA	Atomic Absorption Spectroscopy
AD	Analytical Development
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
Kg	Kilogram
L	Liter
LRM	Low-Activity Reference Material
MRL	Method Reporting Limit
mg	Milligram
mL	Milliliter
NA	Not Applicable
RSD	Relative Standard Deviation
SB7a	Sludge Batch 7a
SB7b	Sludge Batch 7b
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TTR	Technical Task Request
WAPS	Waste Acceptance Product Specifications
WSE	Waste Solidification Engineering
Wt. %	Weight percent

## 1.0 Introduction

This report was requested via an email amendment<sup>1</sup> to the Technical Task Request (TTR)<sup>2</sup> for the Sludge Batch (SB7b) Qualification effort. This work was initiated as a result of interest in the reported sulfur (S) content of the SB7b Waste Acceptance Product Specifications (WAPS) sample<sup>3</sup>. More insoluble S was observed in this sample than in previously reported blend and confirmation samples<sup>4,5,6</sup>. Table 1-1 summarizes the values for weight percent (wt. %) solids and S reported in the Tank 40 SB7a WAPS sample, the Tank 51 SB7b July 2011 Confirmation sample, the Tank 51 SB7b Sept. 2011 Confirmation sample, the predicted Tank 40 SB7b WAPS sample composition, and the reported values in the original SB7b WAPS material.

The terminology used throughout this report is important to understanding the work and conclusions made in the report. Ion chromatography (IC) currently reports only the soluble portion of S present as sulfate. Inductively coupled plasma – atomic emission spectroscopy (ICP-AES) measures the amount of S present in a sample. The source of that sample leads to further distinctions. “Total S” refers to a value derived from complete digestion of a slurry sample and measurement of the resulting solution by ICP-AES. “Total Soluble S” refers to a value derived from ICP-AES analysis of a supernate solution which has been separated from the sludge solids prior to analysis. “Soluble S” refers to a value derived from IC measurement of  $\text{SO}_4^{2-}$  expressed on a S basis. The term “Soluble Sulfate” may also be used to designate an IC measured  $\text{SO}_4^{2-}$  value.

The predicted SB7b data in Table 1-1 is based on the SB7a WAPS data and the Sept. 2011 SB7b Confirmation sample data using the gallons of material reported for the transfer between Tank 51 and Tank 40 and the existing heel of Tank 40 at the time of the transfer. A range is given for the insoluble solids because the calculation was done based both on volume and on mass of insoluble solids transferred. One observation that should be noted is that the total S value in the SB7a WAPS sample (0.23 wt. % TS) cannot be less than the soluble S value (0.30 wt. % TS) determined from  $\text{SO}_4^{2-}$  measured by ion chromatography (IC). This reported total S value had a %RSD of 14, indicating there was a large amount of scatter in the replicate measurements possibly as a result of being near the detection limit for sulfur.

If one takes the soluble S value for the SB7a WAPS material and the higher soluble S value for the Sept. 2011 SB7b Confirmation sample and predicts the soluble S as a wt. % TS, the resulting value lies between the soluble S and total S values reported for the original SB7b WAPS subsample. However, the predicted total S value is considerably below that reported for the original SB7b WAPS subsample.

Another observation for this previously published data from the July 2011 SB7b Confirmation sample is that the total soluble S was 17% higher than either the total S or soluble S measured for the sample. A total soluble S value higher than the soluble S measurement was also seen in the SB7b WAPS sample. These results hint that the actual total S for this July 2011 sample may actually be higher than reported.

**Table 1-1. Comparison of Predicted and Measured SB7b Wt. % Solids and Sulfur Measurements**

Property	SB7a WAPS <sup>6</sup>	SB7b Confirmation <sup>4</sup> July 2011	SB7b Confirmation <sup>5</sup> Sept 2011	SB7b Tank 40 Cells Prep <sup>7</sup>	SB7b Predicted	SB7b WAPS Original <sup>3</sup>
Total Solids	17.2	18.2	20.4	16.1	18.0	15.6
Calcined Solids	13.5	14.8	16.5	11.8	NA	12.5
Dissolved Solids <sup>a</sup>	5.4	14.2	8.3	6.1	6.1	5.5
Insoluble Solids	12.5	4.7	13.2	10.6	12.6 – 12.7	10.8
Soluble Solids <sup>b</sup>	4.7	13.5	7.2	5.5	5.3	4.9
Total S Wt. % TS	0.23	1.2	0.54	0.46	0.30	0.49
Total Soluble S Wt. % TS	NA	1.4	NA	NA	NA	0.40
Soluble S Wt. % TS	0.30	1.2	0.56	0.37	0.36	0.31

\* 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.

<sup>a</sup> Also known as Uncorrected Soluble Solids

<sup>b</sup> Also known as Corrected Soluble Solids

The SB7b Cells Prep<sup>7</sup> is a characterization of a blend of Tanks 7, 51 (SB7a), and H Canyon Pu solution, washed to an anticipated April 2011 Tank Farm projection (i.e., the Tank 51 SB7b Qualification Sample), blended with a portion of SB7a Tank 40 WAPS material. The resulting sludge blend showed a larger projected total S composition than the later SB7b Predicted value shown in the table, and its total S value more closely matches the original SB7b WAPS determination. The glass produced from this study also provided a measureable S value which will be discussed in the context of future work later in this report.

During meetings with the Defense Waste Processing Facility (DWPF), the Savannah River National Laboratory (SRNL) was asked to re-sample the received SB7b WAPS material for wt. % solids, perform an aqua regia digestion and analyze the digested material by ICP-AES, as well as re-examine the supernate by ICP-AES. The new analyses were requested in order to provide confidence that the initial analytical subsample was representative of the Tank 40 sample received and to replicate the S results obtained on the initial subsample collected. The ICP-AES analyses for S were examined with both axial and radial detection of the sulfur ICP-AES spectroscopic emission lines to ascertain if there was any significant difference in the reported results. The outcome of this second subsample of the Tank 40 WAPS material is the first subject of this report.

After examination of the data from the new subsample of the SB7b WAPS material, which is described in detail later in Section 3.1, a team of DWPF and SRNL staff looked for ways to address the question of whether there was in fact insoluble S that was not being accounted for by IC analysis. The question of how much S is reaching the melter was thought best addressed by examining a DWPF Slurry Mix Evaporator (SME) Product sample, but the significant dilution of sludge material, containing the S species in question, that results from frit addition was believed to add additional uncertainty to the analysis of SME Product material. At the time of these discussions it was believed that all S present in a Sludge Receipt and Adjustment Tank (SRAT) Receipt sample would be converted to SO<sub>4</sub><sup>2-</sup> during the

course of the SRAT cycle. A SRAT Product sample would not have the S dilution effect resulting from frit addition, and hence, it was decided that a DWPF SRAT Product sample would be obtained and submitted to SRNL for digestion and sample preparation followed by a round-robin analysis of the prepared samples by the DWPF Laboratory, F/H Laboratories, and SRNL for S and sulfate. The results of this round-robin analytical study are the second subject of this report.

## 2.0 Experimental Procedure

### 2.1 Second Subsample of Tank 40 SB7b WAPS Material

The initial receipt, handling, and subsampling of the SB7b WAPS sample has been described<sup>3</sup>. The sample labeled “HTF-40-12-10 Tank 40 SB7b WAPS” was mixed with a spatula to suspend any packed solids at the bottom of the sample. A mixer motor was set up and the sample was vortex mixed with a clean shaft/blade for 30 minutes to ensure the suspension of any solids at the bottom of the container. The shaft speed was set so as to show evidence of sludge movement along the side of the container. The mixer was stopped and both ends of clean Tygon® tubing attached to a peristaltic pump were inserted into the sludge and the material recirculated through the tubing for two minutes. The exit end of the Tygon® tube was then inserted into a subsample bottle with the metal dip leg end remaining in the main sample container positioned approximately halfway up the sludge layer from the bottom. A 533.70 g subsample of the Tank 40 SB7b WAPS material was collected for the analyses.

The subsample was prepared and analyzed in quadruplicate. Total solids and density on the slurry sample were determined. A 0.45 µm disposable filter cup was used to collect supernate for dissolved solids, density, and ICP-AES analysis. Approximately 10 g of supernate was diluted with 1M HNO<sub>3</sub> to a final volume of 50 mL for soluble elemental analysis by ICP-AES. Approximately 0.25 g of total solids was digested with aqua regia and diluted to a final volume of 100 mL<sup>8</sup> for total elemental analysis by ICP-AES.

### 2.2 Round-Robin Analyses of DWPF SB7b SRAT Product #632

DWPF collected a 200 mL doorstep of SRAT Product #632 and transferred this material to the SRNL Shielded Cells. The doorstep material was transferred to a 250 mL polyethylene bottle and allowed to settle overnight. Supernate from the transferred material was used to rinse the doorstep and the rinsate was added to the initially collected material. A total of 241.30 g of SRAT Batch #632 was received. The material was thick, but not clumpy.

The sample was prepared and analyzed in quadruplicate. Total solids and density on the slurry sample were determined. A 0.45 µm disposable filter cup was used to collect supernate for dissolved solids, density, and ICP-AES analysis. Approximately 10 g of supernate was diluted with 1M HNO<sub>3</sub> to a final volume of 50 mL for soluble elemental analysis by ICP-AES. Additionally, approximately 10 g of slurry was diluted with deionized H<sub>2</sub>O to a final volume of 50 mL and then filtered through a 0.45 µm filter to remove remaining solids prior to IC analysis. Approximately 1.25 g of slurry was digested with aqua regia and diluted to a final volume of 100 mL<sup>8</sup> for total elemental analysis by ICP-AES. Another 1.25 g of slurry was dried and then digested with Na<sub>2</sub>O<sub>2</sub>/NaOH. The digest was taken up in deionized H<sub>2</sub>O to a final volume of 100 mL for determination of SO<sub>4</sub><sup>2-</sup> by IC.

## 3.0 Results and Discussion

### 3.1 Second Subsample of Tank 40 SB7b WAPS Material

The initial concern was that if the original WAPS subsample was low in insoluble solids and therefore supernate rich, the amount of S could be elevated in the sample. A careful resampling of the original

WAPS sample was undertaken as described in the Experimental section. Comparing the insoluble solids determined for each of these samples in Table 3-1 shows that the insoluble solids value did not change between the initially reported value<sup>3</sup> and that obtained here. The fourth column of Table 3-1 provides the solids data determined for DWPF SRAT Batch #632 which will be discussed in the Section 3.2 of this report.

**Table 3-1. Weight Percent Solids<sup>9</sup> for Tank 40 WAPS Samples and DWPF SRAT Product #632 (% RSD\*) [Number of Samples Included in Average]**

Property	Original WAPS	Resampled WAPS	DWPF SRAT #632
Total Solids	15.64 (0.2) [4]	16.05 (0.3) [4]	20.27 (0.8) [4]
Calcined Solids	12.50 (2.8) [4]	NA	14.85 (0.6) [4]
Dissolved Solids <sup>a</sup>	5.48 (0.2) [4]	5.93 (0.8) [4]	9.47 (0.4) [4]
Insoluble Solids	10.75	10.76	11.93
Soluble Solids <sup>b</sup>	4.89	5.29	8.34

\* 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.

<sup>a</sup> Also known as Uncorrected Soluble Solids

<sup>b</sup> Also known as Corrected Soluble Solids

The supernate samples sent for ICP-AES were analyzed twice radially for a full suite of elements and once axially for sulfur. The results of these analyses, for those elements measured above their detection limit, are given in Table 3-2 along with those reported for the original subsample. Within the uncertainty of the measurements, the new determinations for the soluble elemental species as well as the determination of S via axial mode detection yield the same results as those reported in the WAPS Chemical Characterization report<sup>3</sup>.

**Table 3-2. Supernate ICP-AES Elemental Results for Tank 40 SB7b WAPS Samples in mg/kg Slurry (%RDS) [Number of Samples Included in Average]**

Analyte	Original SB7b WAPS	Resampled SB7b WAPS	Resampled SB7b WAPS	Resampled SB7b WAPS
	Radial <sup>3</sup>	Radial-1	Radial-2	Axial
Al	820 (0.1) [4]	788 (0.3) [4]	811 (1.7) [4]	NA
B	NA	3.37 (2.0) [4]	3.82 (1.5) [4]	NA
Ca	3.97 (3.6) [4]	2.31 (9.8) [4]	2.11 (10) [4]	NA
Cr	19.6 (0.6) [4]	19.1 (0.5) [4]	19.3 (0.6) [4]	NA
Fe	0.513 (12) [2]	5.89 (NA) [1]	0.847 (8.5) [2]	NA
K	62.8 (17) [3]	42.9 (2.9) [4]	58.5 (8.5) [4]	NA
Mg	NA	0.0486 (17) [3]	0.0441 (14) [3]	NA
Mo	4.05 (9.7) [2]	3.61 (4.6) [4]	3.75 (6.6) [4]	NA
Na	19200 (0.5) [4]	18500 (0.4) [4]	18800 (1.3) [4]	NA
P	NA	11.1 (4.6) [4]	12.1 (3.8) [4]	NA
S	632 (3.1) [4]	615 (4.5) [4]	610 (1.6) [4]	629 (1.7) [4]
Zn	NA	0.419 (NA) [1]	0.374 (NA) [1]	NA

NA ≡ not measured or below the detection limit

\* 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.

The S results reported in Table 3-2 have been converted to S as a weight percent of total dried solids (wt. % TS) and SO<sub>4</sub><sup>2-</sup> as a weight percent of calcined solid (wt. % CS) in Table 3-3. These values will be useful when comparing the results of the Tank 40 WAPS sample with those obtained from the DWPF SRAT Product Sample in Section 3.2.

**Table 3-3. Sulfur Determined in Supernate by ICP-AES in Tank 40 SB7b WAPS Samples**

Analyte	Original SB7b WAPS Radial	Resampled SB7b WAPS Radial-1	Resampled SB7b WAPS Radial-2	Resampled SB7b WAPS Axial
S (wt. % TS)	0.407	0.396	0.392	0.405
SO <sub>4</sub> <sup>2-</sup> (wt. % CS)	1.52	1.47	1.46	1.51

Data from the analysis of the aqua regia digestions of the resampled SB7b WAPS material appears in Table 3-4. It should be noted that the initial data set represents a combination of aqua regia and peroxide fusion digestion results, whereas only the aqua regia digestion was performed on the resampled material. Additionally, the list of elements has been reduced to remove elements originally determined by atomic absorption (AA) or cold vapor atomic absorption (CV-AA) spectroscopies. Elements originally determined by inductively coupled plasma – mass spectrometry (ICP-MS) including Cd, Ce, Gd, La, Pb, Th, and U have been included if they were also reported from the ICP-AES. Nd, for example, is not reported via ICP-AES and therefore is not included in the table.

Agreement between the two data sets is generally excellent with the exception of some trace elements, such as Cr, which could be subject to sampling uncertainties. Variation is seen in K, which is often reported from the AA data, and P, which shows a high %RSD between the replicates in the resampled material. The only major element with a fairly large discrepancy is U, which was previously reported from the ICP-MS data, but even with this difference the reported results for the two samples are still within the ± 10% uncertainty anticipated in the measurements.



**Table 3-4. Elemental Concentrations in Tank 40 SB7b WAPS Samples in Wt. % of Total Dried Solids for Original WAPS Subsample and the Resampled Material (%RSD\*\*) [Number of Samples Included in Average]**

Element	Original SB7b WAPS <sup>3</sup>	Resampled SB7b WAPS	Element	Original SB7b WAPS <sup>3</sup>	Resampled SB7b WAPS
B	<0.016	<0.0090	Mo	0.00547 (10) [2]	0.00632 (0.9) [4]
Ba	0.0979 (1.1) [8]	0.0958 (0.3) [4]	Na	14.4 (0.7) [4]	14.2 (0.6) [4]
Ca	0.699 (0.6) [4]	0.637 (0.2) [4]	Ni	2.69 (0.6) [8]	2.60 (0.6) [4]
Cd	0.0288 (4.0) [4] ‡	0.0295 (0.3) [4]	P	0.115 (1.1) [4]	0.0679 (19) [4]
Ce	0.135 (0.3) [4] ††	0.144 (1.0) [4]	Pb	0.0261 (5.7) [4] ‡	0.0289 (2.7) [4]
Co	0.0135 (5.5) [8]	0.0124 (1.0) [4]	S	0.490 (1.7) [4]	0.486 (8.9) [4]
Cr	0.0405 (1.0) [4]	0.0595 (0.9) [4]	Sb	<0.084	<0.13
Cu	0.0437 (4.0) [8]	0.415 (0.6) [4]	Sn	<0.044	<0.072
Fe	13.9 (0.5) [8]	13.9 (0.6) [4]	Sr	0.0443 (1.9) [8]	0.0450 (0.3) [4]
Gd	0.0736 (1.5) [4] ‡	0.0829 (0.4) [4]	Th	1.08 (5.8) [4] ‡	1.12 (0.9) [4]
K	0.0536 (9.1) [4]	0.166 (4.5) [4]	Ti	0.0181 (6.9) [8]	0.0165 (1.4) [4]
La	0.0730 (1.1) [4] ‡	0.0726 (0.3) [4]	U	4.78 (1.9) [4] ††	5.20 (1.3) [4]
Li	0.0247 (2.1) [8]	0.0254 (0.9) [4]	V	<0.00037	<0.00066
Mg	0.296 (1.8) [8]	0.291 (0.2) [4]	Zr	0.176 (10) [4]	0.187 (12) [4]
Mn	3.09 (0.6) [8]	3.10 (0.2) [4]			

\*\* 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; U: U-233, U-234, U-235, U-236 and U-238

The agreement observed for S is excellent between the two samples lending confidence to the value originally reported for the SB7b WAPS sample. Converting the S from a wt. % TS basis to SO<sub>4</sub><sup>2-</sup> on a wt.% CS basis by using the individually determined wt. % TS values in Table 3-1 for the two samples, but the wt. % CS value determined for the original WAPS subsample, yields the results shown in Table 3-5. If the total S determined from the aqua regia digestions is compared to the soluble S values shown in Table 3-3, 83% of the total S in both samplings of the SB7b WAPS sample is soluble, with the balance presumably an insoluble species that has not yet been identified.

**Table 3-5. Sulfate as a Wt. % of Calcined Solids Based on Tank 40 SB7b WAPS Samples Total Sulfur Values**

Original SB7b WAPS	Resampled SB7b WAPS
1.83	1.87

### 3.2 Round-Robin Analyses of DWPF SB7b SRAT Product #632

The wt. % solids data for the DWPF SB7b SRAT Product #632 (henceforth “SRAT #632”) was reported in Table 3-1. Only SRNL did a complete elemental suit on both the supernate and aqua regia digested slurry samples, so comparison among the different laboratory results are limited for elements other than sulfur. The common soluble elements determined by ICP-AES and analyzed by both SRNL and F/H Laboratory are given in Table 3-6, while Table 3-7 contains the common soluble anions determined by IC between SRNL and F/H Laboratory. The ICP-AES in F/H Labs was operated axially for all elements reported, whereas the SRNL ICP-AES was only operated axially for the S results reported, other elements were collected radially.

**Table 3-6. Common Soluble Supernate Elements by ICP-AES from SRNL and F/H Laboratory for DWPF SB7b SRAT Product #632**

Analyte	SRNL mg/kg slurry	F/H Labs mg/kg slurry
Ca	20.8	21.9
Mn	133	132
Na	25700	24100
S	650	607

**Table 3-7. Common Soluble Supernate Anions by IC from SRNL and F/H Laboratory for DWPF SB7b SRAT Product #632**

Analyte	SRNL Wt.% TS	F/H Labs Wt.% TS
HCO <sub>2</sub> <sup>-</sup>	15.3	15.0
Cl <sup>-</sup>	0.319	0.397
NO <sub>3</sub> <sup>-</sup>	11.1	11.2
SO <sub>4</sub> <sup>2-</sup>	0.899	0.900
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.116	0.110

Table 3-8 provides the common elements determined for the total digestion of the SRAT #632 sample. The agreement between the two labs was generally very good. F/H Labs did find more total S than did SRNL, however an average of the three laboratory determinations gives a value of 0.398 wt. % TS, so each lab is within ±10% of the cross-laboratory average. The results for total and soluble S, as well as total and soluble SO<sub>4</sub><sup>2-</sup> are summarized in Table 3-9 and in Appendix A, where the results are presented on other bases.

**Table 3-8. Common SRNL and F/H Laboratory Total Elemental Measurements by ICP-AES for DWPF SB7b SRAT Product #632**

Element	SRNL Wt. % TS	F/H Labs Wt. % TS	Element	SRNL Wt. % TS	F/H Labs Wt. % TS
Ca	0.615	0.625	Ni	2.58	2.75
Fe	13.7	13.4	S	0.376	0.429
Mn	2.94	2.88	Th	1.14	1.15
Na	14.0	13.4			

**Table 3-9. Summary of Laboratory Round-Robin Study of Sulfur and Sulfate in DWPF SRAT Product #632**

<i>Analysis/Laboratory</i>	<b>S Wt. % TS</b>
<b><i>Total Sulfur Measurement (AR<sup>a</sup>/ICP-AES axial)</i></b>	
SRNL	0.376
DWPF	0.390
F/H Labs	0.429
<b><i>Average</i></b>	<b><i>0.398</i></b>
<b><i>Total Soluble Sulfur Measurement (Supernate/ICP-AES)</i></b>	
SRNL (radial)	0.296
SRNL (axial)	0.321
DWPF (axial)	0.287
F/H Labs (axial)	0.299
<b><i>Average (axial)</i></b>	<b><i>0.302</i></b>
<b><i>Soluble Sulfate Measurement (Filtered Diluted Slurry/IC)</i></b>	
SRNL	0.300
DWPF	0.298
F/H Labs	0.300
<b><i>Average</i></b>	<b><i>0.299</i></b>
<b><i>Total Sulfate Measurement (PF-H<sub>2</sub>O<sup>b</sup>/IC)</i></b>	
SRNL	0.199
DWPF	0.017
F/H Labs	0.295

<sup>a</sup> AR ≡ aqua regia digestion

<sup>b</sup> PF-H<sub>2</sub>O ≡ peroxide fusion digestion with water uptake

Each laboratory analyzed the samples submitted to them from SRNL utilizing their individual protocols for calibration and instrument check standards. The reproducibility of the results between the laboratories adds additional support that the values reported reflect the likely values for S or SO<sub>4</sub><sup>2-</sup> in the samples. In three of the four preparation/analysis combinations, results from all three laboratories agreed to within

±10% of the average reported value. For the fourth, trial, preparation/analysis, there was considerable variation between the laboratories.

To determine the values in the section of Table 3-9 labeled “Total Sulfur Measurement”, the SRAT #632 sample was digested in aqua regia and analyzed by ICP-AES with axial detection to maximize the signal for sulfur. Supernate was diluted into 1M HNO<sub>3</sub> and analyzed by ICP-AES to obtain the results reported in the section labeled “Soluble Sulfur Measurement”. Based upon the reported results in these two sections of the table, a difference ranging from 15 – 30% (average 24%) of the S determined by ICP-AES is an insoluble species, which has not yet been identified. The data in the section labeled “Soluble Sulfate Measurement” was obtained from weighted dilutions of slurry into water, which were then filtered and analyzed for SO<sub>4</sub><sup>2-</sup> by IC. Comparing the average of the soluble S with the soluble SO<sub>4</sub><sup>2-</sup>, both expressed in terms of S as a weight percent of total solids, indicates that essentially no soluble S is present that is not sulfate.

An attempt was made to analyze total S via IC. This instrumental method is desirable for the DWPF laboratory since it generally does not perform an aqua regia digestion on SRAT feed or product samples and the current cold chem digestion<sup>10</sup> performed has too great a dilution factor (5000X) to consistently analyze for the low levels of S usually contained in these sample matrices. For this round-robin study a peroxide fusion with water uptake was employed to produce a digestion matrix compatible with IC, i.e. free of excessive amounts of acid interferants such as Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>. To help ascertain the effectiveness of the method a low-activity reference material (LRM) glass<sup>11</sup> was subjected to the same digestion and analysis. The standard value for SO<sub>4</sub><sup>2-</sup> as a wt. % of glass reported in LRM is 0.36 (23% RSD), but this value was never obtained via peroxide fusion with water uptake, so it was not possible to ascertain if this method is suitable for this analyte in the reference material. The results of the round-robin study for total sulfate shown in Table 3-9 yielded mixed results. Only F/H Labs reported a S value approaching the expected 0.398 wt. % TS, the average total S value by AR digestion and ICP-AES reported for the SRAT Product #632 samples. Only SRNL reported (as a detection limit) a value close to the expected LRM SO<sub>4</sub><sup>2-</sup> value as shown in Table 3-10. If this digestion method is to be considered further, additional method development and verification will be necessary to ascertain if it can yield total S results approaching those determined via the aqua regia digestion and subsequent ICP-AES analysis.

**Table 3-10. Reported LRM Sulfate as a Wt. % of Calcined Solids**

Analyte	S wt. % CS	SO <sub>4</sub> <sup>2-</sup> wt. % CS
SRNL	<0.104	<0.313
DWPF	0.012	0.036
F/H Labs	0.23	0.68
Std. Value	0.12	0.36

#### 4.0 Conclusions

The following conclusions can be drawn from this examination of sampling and S measurements in the Tank 40 SB7b WAPS sample and the DWPF SB7b SRAT Product #632:

1. The initial subsampling of the Tank 40 SB7b WAPS sample was representative of the sample pulled in the tank farm and received by SRNL on January 19, 2012.

2. More total S was measured in the original and resampled Tank 40 SB7b WAPS material than was determined in the DWPF SB7b SRAT Product #632 sample. For  $\text{SO}_4^{2-}$  on a wt. % calcined solids basis, the WAPS sample yielded 1.83 - 1.87, whereas the SRAT Product #632 sample yielded 1.63, a difference which is close to the  $\pm 10\%$  uncertainty in the measurements.
3. The total S value reported for the initial subsample of the Tank 40 SB7b WAPS material via ICP-AES with radial detection for S was essentially identical to that determined from the re-sampled material via ICP-AES with axial detection for sulfur. This indicates that both viewing positions for the ICP-AES (axial vs. radial) produce acceptable results, with the axial position being more sensitive and having a lower method reporting limit (MRL).
4. The DWPF SRAT Product Batch #632 analyzed by SRNL, DWPF, and F/H Laboratories for S and  $\text{SO}_4^{2-}$  yielded the same results within  $\pm 10\%$  of the cross-laboratory averages.
5. Comparing the average of the soluble S with the soluble  $\text{SO}_4^{2-}$ , both expressed in terms of S as a weight percent of total solids, indicates that essentially no soluble S is present that is not sulfate.
6. Based on the cross-laboratory average, up to approximately 24% of the total S in the DWPF SRAT Product Batch #632 may be insoluble.
7. A method for total S measured as  $\text{SO}_4^{2-}$  by IC needs further method development and testing to ascertain its potential to replace the current aqua regia digestion and ICP-AES analysis.
8. When there is a concern over the detection limit that is possible with an ICP-AES radial torch configuration or when very low S values are suspected, the measurements should be made with an axial configuration of the torch to improve the sensitivity of the measurements.

## 5.0 Path Forward

Two recommendations for possible future work were suggested during discussions between DWPF and SRNL held to review the results reported in this document. The first was to qualitatively identify the insoluble S species (singular or plural) present in these samples. At this time, it is unclear if this/these species can be quantified due to the fact that they collectively represent only 24%, or less, of the relatively small total S in the sample.

The second path of future work was a desire by DWPF to quantify the  $\text{SO}_4^{2-}$  loss in the DWPF melter so as to increase the limit of S in the melter feed. It is known that melter processing results in some volatilization of  $\text{SO}_4^{2-}$  and it is believed that the melter bubblers result in greater volatilization of  $\text{SO}_4^{2-}$  salt from the melt pool. Another suggestion was to examine the next DWPF pour stream glass sample more carefully for S to determine if a measurable value can be determined – previous samples have yielded results below the detection limit for sulfur.

A couple of observations from previous work are possibly relevant to this discussion of the path forward. The first is from the sample of cells prepared SB7b Tank 40 material<sup>7</sup> (shown in Table 1-1) that was processed into glass and yielded a measurable  $\text{SO}_4^{2-}$  value in the glass of 0.345 wt.% at 36% waste loading. This corresponds to 0.958  $\text{SO}_4^{2-}$  as a wt% CS and 0.234 S as a wt% TS.<sup>12</sup> Thus compared to the starting material shown in Table 1-1, there was a 50% loss of S during the SRNL simulated DWPF operations. The second observation concerns the rinsates from SB5 and SB6 pour stream glass samples that have been positive for  $\text{SO}_4^{2-}$  thus indicating there is S in the melter that is not being incorporated into

the glass matrix or forming on the glass surface upon cooling.<sup>13,14</sup> The latter was observed throughout DWPF cold runs.

## 6.0 References

1. Fellingner, T. L. "Request for Documenting Sulfate Results", Email, Savannah River Site, Aiken, SC (2012).
2. Bricker, J. M. *Sludge Batch 7b Qualification Studies*, HLW-DWPF-TTR-2011-0004, Savannah River Site, Aiken, SC (2011).
3. Bannochie, C. J. *Tank 40 Final SB7b Chemical Characterization Results*, SRNL-STI-2012-00097 Rev. 1, Savannah River Site, Aiken, SC (2012).
4. Washington, A. L. *Chemical Characterization Results of the Sludge Batch 7b Tank 51 Confirmation Sample*, SRNL-L3100-2011-00149, Savannah River Site, Aiken, SC (2011).
5. Pareizs, J. M. *Stable and Radioactive Constituents in the September 2011 Tank 51 Sludge Batch 7b Confirmation Sample (HTF-51-11-100)*, SRNL-L3100-2011-00189, Savannah River Site, Aiken, SC (2011).
6. Reboul, S. H., Click, D. R. *Stable Constituents in SB7a Tank 40 WAPS Sample*, SRNL-L3100-2011-00133, Savannah River Site, Aiken, SC (2011).
7. Pareizs, J. M. *Chemical and Fissile Characterization Results of the SRNL Prepared Sludge Batch 7b Tank 51 and Tank 40 Samples*, SRNL-L3100-2011-00128, Savannah River Site, Aiken SC (2011).
8. 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).
9. Marek, J. C. *Correction Factor for Soluble and Insoluble Solids*, SRTC-PTD-92-0040, Savannah River Site, Aiken, SC (1992).
10. Savannah River Remediation, "Cold Chem Preparation", *Analytical Cells System Operating Manual*, SW4-15.201, Section 2.1, Savannah River Site, Aiken, SC (2010).
11. Ebert, W. L., Wolf, S. F. An Interlaboratory Study of a Standard Glass for Acceptance Testing of Low-Activity Waste Glass. *J. of Nucl. Mater.* **2000**, 282, 112-124.
12. Pareizs, J. M., Billings, A. L., Reboul, S. H., Lambert, D. P., Click, D. R. *Sludge Batch 7b Qualification Activities with SRS Tank Farm Sludge*, SRNL-STI-2011-00548, Savannah River Site, Aiken, SC (2011).
13. Johnson, F. C. *Analysis of DWPF Sludge Batch 6 (Macrobatches 7) Pour Stream Glass Samples*, SRNL-STI-2011-00555, Savannah River Site, Aiken, SC (2012).
14. Reigel, M. M., Bibler, N. E. *Analysis of Sludge Batch 4 (Macrobatches 5) for Canister S02902 and Sludge Batch 5 (Macrobatches 6) for Canister S03317 DWPF Pour Stream Glass Samples*, SRNL-STI-2010-00435, Savannah River Site, Aiken, SC (2010).

**Appendix A**



**Table A-1. Summary of Laboratory Round-Robin Study of Sulfur and Sulfate in DWPF SRAT Product #632**

<i>Analysis/Laboratory</i>	<b>S Wt. % CS</b>	<b>SO<sub>4</sub><sup>2-</sup> Wt. % TS</b>	<b>SO<sub>4</sub><sup>2-</sup> Wt. % CS</b>
<b><i>Total Sulfur Measurement</i></b> <b><i>(AR<sup>a</sup>/ICP-AES axial)</i></b>			
SRNL	0.514	1.13	1.54
DWPF	0.532	1.17	1.59
F/H Labs	0.586	1.29	1.76
<b><i>Average</i></b>	<b><i>0.544</i></b>	<b><i>1.19</i></b>	<b><i>1.63</i></b>
<b><i>Total Soluble Sulfur Measurement</i></b> <b><i>(Supernate/ICP-AES)</i></b>			
SRNL (radial)	0.404	0.888	1.21
SRNL (axial)	0.428	0.961	1.31
DWPF (axial)	0.392	0.861	1.18
F/H Labs (axial)	0.409	0.897	1.22
<b><i>Average (axial)</i></b>	<b><i>0.413</i></b>	<b><i>0.906</i></b>	<b><i>1.24</i></b>
<b><i>Soluble Sulfate Measurement</i></b> <b><i>(Filtered Diluted Slurry/IC)</i></b>			
SRNL	0.410	0.899	1.23
DWPF	0.407	0.893	1.22
F/H Labs	0.410	0.900	1.23
<b><i>Average</i></b>	<b><i>0.409</i></b>	<b><i>0.897</i></b>	<b><i>1.22</i></b>
<b><i>Total Sulfate Measurement</i></b> <b><i>(PF-H<sub>2</sub>O<sup>b</sup>/IC)</i></b>			
SRNL	0.272	0.597	0.815
DWPF	0.024	0.052	0.071
F/H Labs	0.403	0.885	1.21

<sup>a</sup> AR ≡ aqua regia digestion<sup>b</sup> PF-H<sub>2</sub>O ≡ peroxide fusion digestion with water uptake

**Distribution:**

K. M. Fox, 999-W  
S. D. Fink, 773-A  
B. J. Giddings, 786-5A  
C. C. Herman, 999-W  
S. L. Marra, 773-A  
F. M. Pennebaker, 773-42A  
F. C. Johnson, 999-W  
D. P. Lambert, 999-W  
J. R. Zamecnik, 999-W  
D. C. Koopman, 999-W  
J. D. Newell, 999-W  
J. W. Amoroso, 999-W  
M. E. Stone, 999-W  
D. K. Peeler, 999-W  
J. M. Pareizs, 773-A  
C. L. Crawford, 773-42A  
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J. M. Bricker, 704-27S  
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J. M. Gillam, 766-H  
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E. W. Holtzscheiter, 704-15S  
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