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Analysis of Sludge Batch 10 Samples from Tank 51H (HTF-51-18-94, -95)

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EXECUTIVE SUMMARY

Savannah River National Laboratory characterized sludge samples from Tank 51H that is being used to generate Sludge Batch 10. The composite slurry sample from Tank 51H was analyzed and determined to contain a concentrated salt solution with a sodium concentration of 5.79 M (1.33E+05 mg/L) and insoluble sludge solids content of 7.20 wt% (using all nine replicates from the 3 wt% total solids measurements). Hydroxide is the main anionic species in the salt solution with a concentration of 3.00 M followed by nitrate (0.728 M) and nitrite (0.657 M). The sum of the major cations versus the sum of the major anions from the analysis of the filtered supernatant liquid phase shows a difference of <5% indicating good data quality. The results from the analysis of the digestions of the well mixed composite slurry sample show sodium to be the main component of the total dried solids of the sample followed by aluminum, iron, manganese, and thorium. Additional measurements of the weight percent total solids and density using hand shaking of the sample bottle and recirculation through a peristaltic pump indicate both methods provide adequate mixing of the sludge slurry sample.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DI	De-ionized
GS	Gamma Scan
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
RSD	Relative Standard Deviation
SB10	Sludge Batch 10
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TIC	Total Inorganic Carbon
TT	Titration
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

Savannah River Remediation (SRR) requested that Savannah River National Laboratory (SRNL) characterize sludge samples from Sludge Batch 10 (SB10) material assembled in Tank 51H. The samples were taken after transfer of aluminum dissolution leachate from Tank 51H to Tank 8F. The characterization activities were directed by a Task Technical and Quality Assurance Plan (TTQAP) that was developed from a subset of the analyses listed in the Technical Task Request (TTR) for analysis of sludge samples comprising SB10.[1,2]

2.0 Experimental Procedure

The two ~200 mL dip samples from Tanks 51H (HTF-51-18-94 and -95) were received at SRNL on November 11, 2018 and opened in the SRNL Shielded Cells. Both samples were composited into a single bottle. The resulting composite was a dark brown slurry containing significant sludge solids.

Density measurements were made on aliquots of the well mixed slurry and on the filtered supernatant liquid of the composite sample using calibrated tubes at ambient cell temperature (17 °C). All measurements were conducted in triplicate. The weight percent total solids in the composite slurry sample and the weight percent dissolved solids of the filtered supernatant liquid were determined by drying weighed aliquots to constant weight (+/- 0.005 g) in a conventional drying oven at 110 °C. The weight percent insoluble solids and weight percent soluble solids of the slurry were calculated from these results. Additional measurements of the density and weight percent total solids were conducted using a recirculation pump to mix the slurry as a comparison to hand shaking the sample bottle.

The filtered supernatant liquid of the composite sample was prepared for analysis by diluting triplicate aliquots with de-ionized (DI) water and diluting triplicate aliquots with 2.0 M nitric acid. The water dilutions were submitted to Analytical Development (AD) for determination of free hydroxide by titration (TT), ion chromatography (IC), and total inorganic carbon (TIC). A blank of the DI water was also prepared along with the samples. The acid dilutions of the filtered supernatant liquid were submitted to AD for analysis by gamma spectroscopy (GS) and inductively coupled plasma-emission spectroscopy (ICP-ES).

Aliquots of the well mixed composite slurry sample were prepared for analysis using the aqua regia and sodium peroxide fusion digestion methods by AD. Triplicate aliquots of the slurry were prepared with each digestion method along with a reagent blank. The digested samples were submitted to AD for analysis by ICP-ES.

Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This review meets the acceptable criteria to comply with the TTR classification for this work as safety class. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-28.

3.0 Results and Discussion

The following tables contain the results from the analysis of the samples. The tables show the average concentrations and the percent relative standard deviations (RSD) for the triplicate sample preparations unless otherwise noted. Results preceded by "<" indicate the analyte was below the limits of quantification for all three replicate aliquots of the sample. Results preceded by "≤" indicate that at least one of the replicates for the sample was above the limits of quantification while one or more of the replicates analyzed were below detection. The percent RSD presented in the table only includes the uncertainty associated with sub-sampling and sample preparation in the Shielded Cells and the analytical method. The percent RSD does not include tank sampling uncertainty. The estimated one sigma percent uncertainty provides an indication of the uncertainty associated with the analytical method as reported by AD. Neither of these measures of uncertainty includes the uncertainty associated with sampling a large waste tank. Previous investigations indicate the uncertainty from taking a small sample from a large waste tank can be significant.[3,4,5]

The results in Table 3-1 provide the physical properties of the composite sample from Tank 51H. The slurry sample contains 7.75 wt% insoluble sludge solids and dissolved solids in the filtered supernatant liquid phase of 26.9 wt%. The measured densities for the slurry and the filtered supernatant liquid are in the range typically expected for slurries with the measured weight percent total solids and weight percent dissolved encountered at Savannah River Site (SRS). The results for the wt% total solids and density of the slurry in Table 3-1 show the initial measurement for these properties. Additional measurements of these properties are discussed below.

Table 3-2 provides the results from the analysis of the filtered supernatant liquid of the composite slurry sample from Tank 51H. The results show the supernatant liquid to be a concentrated salt solution with a sodium concentration of 5.79 M (1.33E+05 mg/L). Hydroxide is the main anionic species in the salt solution with a concentration of 3.00 M. The other main anions in the salt solutions are nitrate, nitrite, aluminate (0.560 M), and carbonate. The sum of the major cations versus the sum of the major anions shows a difference of <5% indicating good data quality.

The results from the analysis of the digestions of the well mixed composite slurry sample are shown in Table 3-3. Sodium is the main component of the total dried solids of the composite slurry sample followed by Na>Al>Fe>Mn>Th>S>U. The calculated averages and RSD's for most elements used all six replicates from the two digestion methods. The sodium and zirconium result utilized only the aqua regia digestion method data since the sodium peroxide fusion method adds sodium as a reagent and is conducted in a zirconium crucible. The silicon result used only the sodium peroxide fusion method results since the aqua regia method does not effectively dissolve silicon species. The titanium result used only the sodium peroxide fusion method data because the aqua regia method results were below detection.

As a check of the reliability of hand shaking the sample bottle to thoroughly mix the composite slurry sample prior to removing aliquots for the various analyses, additional measurements of the weight percent total solids and density were made using a recirculation pump to mix the slurry. An additional measurement of the weight percent total solids using hand shaking was also conducted. Table 3-4 provides the additional results from the measurement of the weight percent total solids and density of the composite slurry sample.

The original density measurement of the slurry of 1.29 g/mL (Table 3-1) using hand shaking of the bottle for mixing, and the density of 1.33 g/mL (Table 3-4) measured using the recirculation pump for mixing show good agreement with a difference of ~3%. The average of all six replicates from the two measurements of the slurry density yields a value of 1.31 g/mL (1.9% RSD).

The two measurements of the weight percent total solids of the slurry using hand shaking of the sample bottle for mixing show good agreement with values of 32.5 wt% (Table 3-1) and 31.8 wt% (Table 3-4). The measurement of the weight percent total solids of the slurry using a recirculation pump of 32.1 wt% also shows good agreement with the two values obtained using hand shaking. The average of all nine replicates from the three measurements of the weight percent total solids of the slurry yields a value of 32.1 wt% (2.1% RSD). Using the average value from the three weight percent total solids measurements (32.1 wt%) and the weight percent dissolved solids of the supernate (26.9 wt%) to calculate the weight percent insoluble solids and weight percent soluble solids yields 7.20 wt% insoluble solids and 24.9 wt% soluble solids.

These additional physical property results show that hand shaking the sample bottle or using a recirculation pump for mixing the slurry sample yield the same results for weight percent solids and density measurements indicating a well mixed slurry in both cases. For small samples, hand shaking the sample bottle is faster and provides adequate mixing for these slow settling sludge slurry samples. The recirculation pump takes additional time to setup and may provide incorrect (low biased) results if not applied carefully. On this small sample, the sample bottle was hand shaken to mix the slurry prior to starting the recirculation through the pump to maintain suspension. The results indicate this method provided adequate mixing. However, recirculation through a peristaltic pump is not a very good mixing method by itself. With larger samples a mechanical mixer in addition to the recirculation pump would likely be required to obtain adequate mixing.

Table 3-1. Physical Properties of the Tank 51H Composite Sample

Property	Units	Average	RSD
Mass of Composite Sample	g	539.5	--
Density of Supernate (17 °C)	g/mL	1.25	0.6%
Density of Slurry (17 °C)	g/mL	1.29	0.4%
Wt% Total Solids	wt%	32.5%	3.6%
Wt% Dissolved Solids*	wt%	26.9%	0.6%
Wt% Insoluble Solids (calc.)	wt%	7.75%	--
Wt% Soluble Solids (calc.)	wt%	24.8%	--

*wt% Dissolved Solids uses as the mass basis the filtered supernatant liquid

Table 3-2. Filtered Supernate Analytical Data for the Tank 51H Composite Sample. (Averages and RSD values are of triplicate measurements)

Analyte	Method	Units	Est. 1σ	Average	RSD
Cs-137	GS	dpm/mL	5%	3.18E+08	4.4%
OH^-	TT	M	10%	3.00E+00	2.2%
F^-	IC	M	10%	<1.09E-02	--
CHO_2^-	IC	M	10%	<4.60E-03	--
Cl^-	IC	M	10%	<5.84E-03	--
NO_2^-	IC	M	10%	6.57E-01	3.3%
Br^-	IC	M	10%	<2.59E-03	--
NO_3^-	IC	M	10%	7.28E-01	3.1%
PO_4^{3-}	IC	M	10%	<2.18E-03	--
SO_4^{2-}	IC	M	10%	2.42E-02	3.5%
$C_2O_4^{2-}$	IC	M	10%	<2.35E-03	--
CO_3^{2-}	TIC	M	10%	2.69E-01	1.1%
Organic	TOC	mg C/L	10%	<4.14E+02	--
Ag	ICP-ES	mg/L	10%	<2.85E-01	--
Al	ICP-ES	mg/L	10%	1.51E+04	1.9%
B	ICP-ES	mg/L	10%	2.82E+01	7.0%
Ba	ICP-ES	mg/L	10%	<4.14E-01	--
Be	ICP-ES	mg/L	10%	<1.38E-01	--
Ca	ICP-ES	mg/L	10%	2.64E+01	64%
Cd	ICP-ES	mg/L	10%	<3.03E-01	--
Ce	ICP-ES	mg/L	10%	<6.39E+00	--
Co	ICP-ES	mg/L	10%	<9.39E-01	--
Cr	ICP-ES	mg/L	10%	8.01E+01	5.7%
Cu	ICP-ES	mg/L	10%	≤2.36E+00	--
Fe	ICP-ES	mg/L	10%	4.92E+00	22%
Gd	ICP-ES	mg/L	10%	<8.41E-01	--
K	ICP-ES	mg/L	10%	3.89E+02	3.4%
La	ICP-ES	mg/L	10%	<2.67E-01	--
Li	ICP-ES	mg/L	10%	<9.18E-01	--
Mg	ICP-ES	mg/L	10%	2.31E+00	55%
Mn	ICP-ES	mg/L	10%	<1.04E-01	--
Mo	ICP-ES	mg/L	10%	<2.60E+01	--
Na	ICP-ES	mg/L	10%	1.33E+05	3.2%
Ni	ICP-ES	mg/L	10%	<4.14E+00	--
P	ICP-ES	mg/L	10%	<7.45E+01	--
Pb	ICP-ES	mg/L	10%	<6.15E+00	--
S	ICP-ES	mg/L	10%	9.70E+02	0.4%
Sb	ICP-ES	mg/L	10%	<5.62E+00	--

Table 3-2. Filtered Supernate Analytical Data for the Tank 51H Composite Sample Continued. (Averages and RSD values are of triplicate measurements)

Analyte	Method	Units	Est. 1σ	Average	RSD
Si	ICP-ES	mg/L	10%	<4.55E+00	--
Sn	ICP-ES	mg/L	10%	<4.97E+00	--
Sr	ICP-ES	mg/L	10%	≤9.02E-02	--
Th	ICP-ES	mg/L	10%	<2.80E+00	--
Ti	ICP-ES	mg/L	10%	<2.59E-01	--
U	ICP-ES	mg/L	10%	<6.37E+01	--
V	ICP-ES	mg/L	10%	<1.61E+00	--
Zn	ICP-ES	mg/L	10%	6.28E+00	46%
Zr	ICP-ES	mg/L	10%	<1.88E-01	--
Cations (sum)	--	M	--	5.79E+00	--
Anions (sum)	--	M	--	5.55E+00	--

Table 3-3. Digested Total Dried Solids Analytical Data for Tank 51H Composite Sample. (Averages and RSD values calculated on the number of replicates indicated)

Analyte	Method	Units	Est. 1σ	Average	RSD	# Reps
Ag	ICP-ES	wt%	10%	<1.42E-03	--	6
Al	ICP-ES	wt%	10%	9.17E+00	10%	6
B	ICP-ES	wt%	10%	<1.48E-03	--	6
Ba	ICP-ES	wt%	10%	1.77E-02	5.2%	6
Be	ICP-ES	wt%	10%	<1.12E-04	--	6
Ca	ICP-ES	wt%	10%	1.72E-01	51%	6
Cd	ICP-ES	wt%	10%	≤4.84E-04	--	6
Ce	ICP-ES	wt%	10%	<8.01E-03	--	6
Co	ICP-ES	wt%	10%	<1.02E-03	--	6
Cr	ICP-ES	wt%	10%	3.05E-02	4.1%	6
Cu	ICP-ES	wt%	10%	1.35E-02	4.2%	6
Fe	ICP-ES	wt%	10%	2.31E+00	2.7%	6
Gd	ICP-ES	wt%	10%	<1.31E-03	--	6
K	ICP-ES	wt%	10%	<1.34E-01	--	6
La	ICP-ES	wt%	10%	1.05E-02	11%	6
Li	ICP-ES	wt%	10%	<3.21E-03	--	6
Mg	ICP-ES	wt%	10%	3.78E-02	5.8%	6
Mn	ICP-ES	wt%	10%	6.17E-01	2.1%	6
Mo	ICP-ES	wt%	10%	<1.47E-02	--	6
Na	ICP-ES	wt%	10%	3.33E+01	0.5%	3

Table 3-3. Digested Total Dried Solids Analytical Data for Tank 51H Composite Sample Continued. (Averages and RSD values calculated on the number of replicates indicated)

Analyte	Method	Units	Est. 1σ	Average	RSD	# Reps
Ni	ICP-ES	wt%	10%	9.60E-02	7.5%	6
P	ICP-ES	wt%	10%	≤2.42E-02	--	6
Pb	ICP-ES	wt%	10%	<2.85E-02	--	6
S	ICP-ES	wt%	10%	2.49E-01	5.8%	6
Sb	ICP-ES	wt%	10%	<1.01E-02	--	6
Si	ICP-ES	wt%	10%	1.36E-01	5.9%	3
Sn	ICP-ES	wt%	10%	<2.46E-03	--	6
Sr	ICP-ES	wt%	10%	9.58E-03	2.9%	6
Th	ICP-ES	wt%	10%	4.93E-01	36%	6
Ti	ICP-ES	wt%	10%	4.07E-03	2.3%	3
U	ICP-ES	wt%	10%	1.75E-01	11%	6
V	ICP-ES	wt%	10%	<1.56E-03	--	6
Zn	ICP-ES	wt%	10%	5.49E-03	16%	6
Zr	ICP-ES	wt%	10%	4.11E-02	1.6%	3

Table 3-4. Additional Physical Property Measurements on the Tank 51H Composite Sample

Property	Units	Average	RSD
Density of Slurry (17 °C, with recirculation pump)	g/mL	1.33	1.4%
Wt% Total Solids (with hand shaking)	wt%	31.8%	0.2%
Wt% Total Solids (with recirculation pump)	wt%	32.1%	0.5%

4.0 Conclusions

The composite slurry sample from Tank 51H was analyzed and determined to contain a concentrated salt solution with a sodium concentration of 5.79 M (1.33E+05 mg/L) and insoluble sludge solids content of 7.20 wt% (using all nine replicates from the 3 wt% total solids measurements). Hydroxide is the main anionic species in the salt solution with a concentration of 3.00 M followed by nitrate (0.728 M) and nitrite (0.657 M). The sum of the major cations versus the sum of the major anions from the analysis of the filtered supernatant liquid phase shows a difference of <5% indicating good data quality. The results from the analysis of the digestions of the well mixed composite slurry sample show sodium to be the main component of the total dried solids of the sample followed by aluminum, iron, manganese, and thorium. Additional measurements of the weight percent total solids and density using hand shaking of the sample bottle and recirculation through a peristaltic pump indicate both methods provide adequate mixing of the sludge slurry sample.

5.0 Acknowledgements

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