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Analysis of Tank 23H Samples in Support of Salt Batch Planning

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EXECUTIVE SUMMARY

Savannah River Remediation obtained three samples from different heights within Tank 23H. The samples were analyzed by Savannah River National Laboratory to support salt batch planning. The results from the analysis indicate the top two samples from the tank appear similar in composition. The lowest sample from the tank contained significantly more solids and a more concentrated salt solution. The filtered supernate from the bottom sample showed ~60% lower Sr-90 and Pu-238 concentrations than the decanted (unfiltered) supernate results which may indicate the presence of some small amount of entrained solid particles in the decanted sample. The mercury concentrations measured in the filtered supernate were fairly low for all three samples ranging from 11.2 to 42.3 mg/L.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DI	De-ionized
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
%RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation

1.0 Introduction

Savannah River Remediation (SRR) obtained three samples from different heights within Tank 23H. The samples were received by the Savannah River National Laboratory (SRNL) Shielded Cells on June 8, 2015. The analysis of these samples provides information necessary for salt batch planning. The sample characterization was requested via a Technical Task Request[1] and conducted based on a Task Technical and Quality Assurance Plan.[2]

2.0 Experimental Procedure

The three samples were opened in the SRNL Shielded Cells and poured into clear plastic beakers. The beakers were photographed and the mass of the samples determined, however, some material was removed for the Hg Speciation program prior to the determination of the mass. Table 2-1 provides the sampling height and mass of each sample. Figure 2-1 shows photographs of the samples. The top two samples from the tank (HTF-23-15-55 and HTF-23-15-56) showed little to no visible undissolved solids when poured into the clear beakers. The third sample (HTF-23-15-57) contained visible undissolved solids. After sitting undisturbed overnight, a few dark particles settled to the bottom of the poly bottle containing HTF-23-15-56 and a thick layer of brown solids settled out of HTF-23-15-57.

Triplicate density measurements were made on decanted (unfiltered) aliquots of the samples using 2 mL volumetric tubes at ambient cell temperature (29 °C).

De-ionized (DI) water dilutions were made in triplicate from decanted (unfiltered) liquid from each sample and submitted to Analytical Development (AD) for analysis. A blank of the DI water was also prepared along with the samples. The water dilutions were analyzed by ion chromatography, total inorganic carbon, and free hydroxide methods. A special sample preparation was conducted in the Shielded Cells on triplicate, decanted (unfiltered) aliquots of the samples for I-129 analysis. The aliquots for the I-129 analysis were spiked with a potassium iodide solution, decontaminated using cesium/strontium removal resins, filtered, and treated with a sodium hydroxide solution before sending to AD for analysis. Acid dilutions of filtered liquid from the samples were made in triplicate and submitted to AD for analysis by liquid scintillation for Sr-90, mercury analysis (CV Hg digested), and plutonium isotopics. A blank of the diluting acid (2 M HNO_3) was also prepared along with the samples.

Triplicate aliquots of decanted (unfiltered) liquid from each sample were also prepared for analysis using the warm acid strike method. A reagent blank and three silicon standard solutions were submitted for analysis with the samples. The samples prepared by warm acid strike were submitted to AD for analysis by inductively coupled plasma-emission spectroscopy (ICP-ES), by inductively coupled plasma-mass spectrometry (ICP-MS), gamma spectroscopy, plutonium isotopics, Sr-90 liquid scintillation, and Tc-99 methods.

The weight percent undissolved (insoluble) solids were determined on the Tank 23H samples by filtering a known weight of the sample through a weighed Nylon filter disk, drying any solids on the filter disk at 100 °C, and then reweighing the filter disk. The solids on the filter disk were not washed in any way so the results will be biased high by the amount of salt left from evaporation of any supernate trapped in the pores of the filter disk. The magnitude of this bias was measured by repeating the same weight percent undissolved solids measurement using the previously

filtered sample. The reported weight percent undissolved solids results were corrected for this bias.

Table 2-1. Sampling Height in the Tank and Sample Mass of Tank 23H Samples

Sample ID	Sampling Height (inches from bottom)	Sample Mass (g)
HTF-23-15-55	353.7”	193.9
HTF-23-15-56	200”	163.6
HTF-23-15-57	60”	191.0

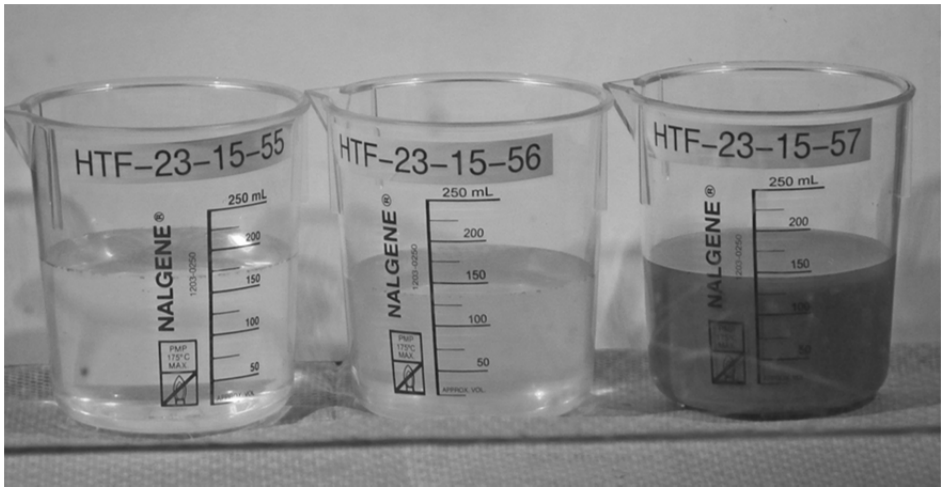

Figure 2-1. Samples from Tank 23H

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. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-04.

3.0 Results and Discussion

Tables 3-1, 3-2, and 3-3 contain the results of the Tank 23H sample analyses. The tables show the average concentration and the percent relative standard deviations (%RSD) for the triplicate sample preparations. Results preceded by “<” indicate the analyte was below the limits of quantification. Some of the data presented in the tables and the results of additional analyses of these samples were contained in previously issued memoranda.[3, 4, 5]

The results from the analysis indicate the top two samples (HTF-23-15-55 and HTF-23-15-56) from Tank 23H appear similar in composition. The lowest sample from the tank (HTF-23-15-57) contains significantly more solids and a more concentrated salt solution. HTF-23-15-57 has a higher density and a sodium molarity nearly 60% higher than the other two Tank 23H samples. The higher sodium molarity in HTF-23-15-57 results from a much higher sodium nitrate concentration than in the other two Tank 23H samples. Sample HTF-23-15-57 also contains somewhat lower concentrations of nitrite, oxalate, Tc-99, Cs-137, and plutonium and higher concentrations of phosphate and sulfate than the other two samples. The decanted supernate from sample HTF-23-15-57 also has Sr-90 and uranium concentrations ~2-3X higher than the decanted supernate from the top two samples (Table 3-1). The filtered supernate from HTF-23-15-57 (Table 3-2) shows higher Sr-90 and Hg concentrations than the filtered supernate from the top two samples but a lower plutonium concentration.

The filtered supernate from HTF-23-15-57 (Table 3-2) contains ~60% lower Sr-90 and Pu-238 concentrations than the decanted (unfiltered) supernate results (Table 3-1). This may indicate the decanted HTF-23-15-57 contained some small amount of entrained solid particles. The top two samples (HTF-23-15-55 and HTF-23-15-56) contain similar plutonium concentrations in the filtered and unfiltered samples while the Sr-90 concentration decreases by ~25-50% in the filtered supernate for both samples. The drop in the Sr-90 concentration from the decanted to filtered sample may be mostly due to the one sigma uncertainties of ~20% for all of the sample replicates. The mercury concentrations measured in the filtered supernate were fairly low for all three samples ranging from 11.2 to 42.3 mg/L.

The standards used for the silicon analysis (50 mg/L silicon in solution prepared by warm acid strike to final concentrations of 0.5, 1.0, and 2.0 mg/L) were all somewhat higher than the target concentration except for the 2.0 mg/L standard that was within 10% of the target concentration. The silicon concentration was below detectible levels in the process blank. The three decanted (unfiltered) samples show silicon concentrations of approximately 11-20 mg/L.

The sum of the major cations versus the sum of the major anions shows a difference of ~5% for all three Tank 23H samples providing an indication of good data quality for these species.

The significantly different supernate composition in the lowest sample from Tank 23H indicates some stratification of the liquid waste in the tank. The composition of the lowest sample HTF-23-15-57 shows some similarity to the composition of a sample obtained from Tank 23H at the same elevation in 2013 prior to the addition of material from other tanks.[6] The current composition of the material in the lowest part of the tank may be the result of incomplete mixing of the previous material in the tank with the new material added on top. The trend of the plutonium concentration being lower in the HTF-23-15-57 sample versus the other two samples was seen in both the decanted (unfiltered) and filtered supernate analysis. These analyses used two separate sample preparations making the lower plutonium concentration unlikely to be the result of a dilution error.

4.0 Conclusions

Three Tank 23H samples were analyzed by SRNL to support salt batch planning. The results from the analysis indicate the top two samples from the tank appear similar in composition. The lowest sample from the tank contained significantly more solids and a higher sodium nitrate concentration. The filtered supernate from the bottom sample showed ~60% lower Sr-90 and Pu-

238 concentrations than the decanted (unfiltered) supernate results which may indicate the presence of some small amount of entrained solid particles in the decanted sample. The mercury concentrations measured in the filtered supernate were fairly low for all three samples ranging from 11.2 to 42.3 mg/L.

5.0 Acknowledgements

The contributions of Rita Sullivan for preparing the samples, Amy Ekechukwu, Leigh Brown, John Young, and Tom White for providing analytical services are appreciated and acknowledged.

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Table 3-1. Concentrations of Components of Tank 23H Decanted (Unfiltered) Liquid

		HTF-23-15-55		HTF-23-15-56		HTF-23-15-57	
Analyte	Units	Average	%RSD, n	Average	%RSD, n	Average	%RSD, n
F^-	M	<0.017	-	<0.016	-	<0.016	-
CH_2O^-	M	<0.011	-	<0.010	-	<0.010	-
Cl^-	M	<0.009	-	<0.009	-	<0.009	-
NO_2^-	M	0.554	1.6%, 3	0.558	1.1%, 3	0.314	0.4%, 3
Br^-	M	<0.004	-	<0.004	-	<0.004	-
NO_3^-	M	1.24	1.6%, 3	1.25	1.1%, 3	3.59	0.4%, 3
PO_4^{3-}	M	<0.003	-	<0.003	-	0.008	1.6%, 3
SO_4^{2-}	M	0.039	1.4%, 3	0.040	2.5%, 3	0.114	0.6%, 3
$C_2O_4^{2-}$	M	0.008	2.7%, 3	0.009	8.5%, 3	0.006	0.9%, 3
CO_3^{2-}	M	0.256	3.5%, 3	0.254	3.2%, 3	0.273	1.7%, 3
$OH^-_{(free)}$	M	1.00	2.5%, 3	1.02	7.2%, 3	1.01	9.5%, 3
Al	M	0.206	0.8%, 3	0.210	0.2%, 3	0.194	0.1%, 3
K	M	0.010	2.8%, 3	0.010	4.6%, 3	0.013	2.0%, 3
Na	M	3.82	0.5%, 3	3.84	0.3%, 3	6.11	0.5%, 3
P	M	0.004	3.0%, 3	0.004	4.2%, 3	0.009	0.3%, 3
Si	mg/L	20.4	5.9%, 3	20.4	6.0%, 3	11.1	6.4%, 3
Density (29°C)	g/mL	1.16	0.8%, 3	1.17	0.3%, 3	1.27	0.8%, 3
Radioactive Species							
Sr-90	dpm/mL	3.87E+05	23%, 3	2.71E+05	2.0%, 3	9.23E+05	14%, 3
	µCi/mL	1.74E-01	-	1.22E-01	-	4.16E-01	-
Cs-137	dpm/mL	3.31E+08	0.9%, 3	3.54E+08	1.9%, 3	1.63E+08	1.6%, 3
	µCi/mL	1.49E+02	-	1.60E+02	-	7.36E+01	-
Tc-99	dpm/mL	9.24E+04	0.8%, 3	9.30E+04	8.3%, 3	5.90E+04	0.9%, 3
	µCi/mL	4.16E-02	-	4.19E-02	-	2.66E-02	-
I-129	dpm/mL	8.89E+01	18%, 3	9.07E+01	12%, 3	3.15E+01	15%, 3
	µCi/mL	4.00E-05	-	4.08E-05	-	1.42E-05	-
Pu-238	dpm/mL	1.77E+04	3.3%, 3	1.65E+04	5.7%, 3	1.39E+04	29%, 3
	µCi/mL	7.96E-03	-	7.41E-03	-	6.28E-03	-
Pu-239/240	dpm/mL	4.66E+02	45%, 2	3.82E+02	5.2%, 3	4.13E+02	65%, 3
	µCi/mL	2.10E-04	-	1.72E-04	-	1.86E-04	-
Pu-241	dpm/mL	<6.83E+03	-	<6.12E+03	-	<4.08E+03	-
	µCi/mL	<3.08E-03	-	<2.76E-03	-	<1.84E-03	-
Pu-Total	dpm/mL	1.81E+04	-	1.68E+04	-	1.43E+04	-
	µCi/mL	8.17E-03	-	7.59E-03	-	6.46E-03	-
U-235	mg/L	4.87E-02	0.3%, 3	4.89E-02	1.9%, 3	1.04E-01	1.8%, 3
U-238	mg/L	4.51E+00	0.8%, 3	4.57E+00	1.4%, 3	9.96E+00	0.7%, 3
U-total	mg/L	4.56E+00	-	4.63E+00	-	1.01E+01	-

Table 3-2. Concentrations of Components of Tank 23H Filtered Liquid

		HTF-23-15-55		HTF-23-15-56		HTF-23-15-57	
Analyte	Units	Average	%RSD, n	Average	%RSD, n	Average	%RSD, n
Hg	mg/L	13.5	2.2%, 3	11.2	0.5%, 3	42.3	2.6%
Radioactive Species							
Sr-90	dpm/mL	2.77E+05	19%, 3	1.30E+05	15%, 3	3.73E+05	8.0%, 3
	µCi/mL	1.25E-01	-	5.85E-02	-	1.68E-01	-
Pu-238	dpm/mL	1.82E+04	6.6%, 3	1.51E+04	8.5%, 3	5.06E+03	3.4%, 3
	µCi/mL	8.20E-03	-	6.79E-03	-	2.28E-03	-
Pu-239/240	dpm/mL	3.92E+02	47%, 3	3.75E+02	28%, 3	<1.37E+02	-
	µCi/mL	1.77E-04	-	1.69E-04	-	<6.17E-05	-
Pu-241	dpm/mL	<8.06E+03	-	<6.34E+03	-	<1.17E+03	-
	µCi/mL	<3.63E-03	-	<2.85E-03	-	<5.26E-04	-

Table 3-3. Weight Percent Undissolved (Insoluble) Solids of Tank 23H Samples

Sample ID	Wt% Undissolved Solids*
HTF-23-15-55	<0.04 wt%
HTF-23-15-56	<0.05 wt%
HTF-23-15-57	3.56 wt%

* Results were corrected for the salt from supernate entrained in the pores of the filter disk.

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