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Analysis of Tank 7 Surface Supernatant Sample (FTF-7-15-26) in Support of Corrosion Control Program

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EXECUTIVE SUMMARY

This report provides the results of analyses on Savannah River Site Tank 7 surface supernatant liquid sample in support of the Corrosion Control Program (CCP).

The measured nitrate, nitrite and free-hydroxide concentrations for the Tank 7 surface sample averaged, 3.74E-01 ± *1.88E-03*, 4.17E-01 ± *9.01E-03* and 0.602 ± *0.005* M, respectively. The Tank 7 surface cesium-137, sodium and silicon concentrations were, respectively, 3.99E+08 ± *3.25E+06* dpm/mL, 2.78 M and <3.10 mg/L. The measured aluminum concentration in the Tank 7 surface sample averaged 0.11 M.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CCP	Corrosion Control Program
DWPF	Defense Waste Processing Facility
ECP	Enrichment Control Program
HTF	H-Area Tank Farm
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-ES	Inductively Coupled Plasma-Emission Spectrometry
SpG	Specific Gravity
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TIC	Total Inorganic Carbon
TTQAP	Task Technical and Quality Assurance Plan
WAC	Waste Acceptance Criteria

1.0 Introduction

Compositional feed limits have been established to ensure that a nuclear criticality event for the 2H and 3H Evaporators[i] is not possible. The limits are established by the Enrichment and Corrosion Control Programs. The Enrichment Control Program (ECP) requires feed sampling to determine the equivalent enriched uranium content prior to transfer of waste other than recycle transfers.[ii] The Corrosion Control Program (CCP) establishes concentration and temperature limits for key constituents and periodic sampling and analysis to confirm that waste supernate is within these limits.[iii]

In August 2015, Savannah River Remediation (SRR) retrieved tank samples from two locations within the Savannah Rivers Site (SRS) Tank 7. These two supernatant samples were delivered to the Savannah River National Laboratory (SRNL) on August 19, 2015 for analyses to support the ECP, CCP and Evaporator Feed Qualification (EFQ) Programs. This analysis request was later changed by SRR to only include analysis of the Tank 7 surface sample in support of CCP for now. As summarized in Table 1, the two Tank 7 samples were identified as FTF-7-15-26 (surface sample) and FTF-7-15-25 (subsurface sample), respectively. The surface sample was collected from a height of 109.92 inches from the tank bottom and the variable depth sample or subsurface sample was collected 34 inches from the tank bottom.

This work is governed by the Technical Task Request and the detailed experimental plan is presented in the Task Technical and Quality Assurance Plan.[iv,v, vi] 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.

2.0 Experimental

As shown in Figure 1, one of the two Tank 7 supernatant samples (Subsurface sample FTF-7-15-25) contained visible fine solid particles while the surface sample (FTF-7-15-26) was essentially free of any visible insoluble solids and the solutions was relatively clear and transparent with no cloudy appearance. In general, the visual appearance of the two samples was consistent with supernatant liquid containing <1 wt. % insoluble solids based on experience with these sample types. Measured masses, approximate volumes and sample descriptions are provided in Table 2. The analysis performed here for the corrosion control program, was performed only on the Tank 7 surface sample (FTF-7-15-26).

The CCP analyses requirements for the Tank 7 supernatant sample is summarized in Table 1. The CCP analysis included ion chromatography (IC) for anions (nitrate and nitrite), acid titration for free hydroxide, and gamma scan for detectable gamma-emitting isotopes. The sample preparation for IC, titration, and gamma analysis involved dilution with de-ionized water. The density of each “as-received” sample was measured by determining the weight of 1.0 mL sample portions in triplicate and the specific gravity (SpG) was calculated from these density measurements relative to the density of water.

All of the analyses were performed and reported in triplicate as shown in Appendix A and the averages and standard deviations for the analytical results are presented in Table 3.

Table 1 Tank 7 Sample Description and Analysis Suite.

Sample	Sample ID	Sample location	SRNL Receipt Date	Date Sample was transferred into Shielded Cells
Tank 7 surface	FTF-7-15-26	Collected 109.92 inches from the tank bottom.	8/19/2015	8/24/2015
Tank 7 subsurface	FTF-7-15-25	Collected 34 inches from the tank bottom.	8/19/2015	8/24/2015

Sample location	Analysis Suite summary
Tank 7 Surface sample	**CCP analysis only**
Tank 7 Subsurface sample (variable depth sample)	NOT analyzed

Table 2 Tank 7 Sample Volume, Mass and Appearance

Tank Sample ID	Sample location	Approx. Volume, mL	Mass, g	Clarity of supernate
FTF-7-15-26	surface sample	80	89.219	clear supernate, no visible solids
FTF-7-15-25	subsurface sample	80	89.052	not a clear supernate, suspended brown particles visible

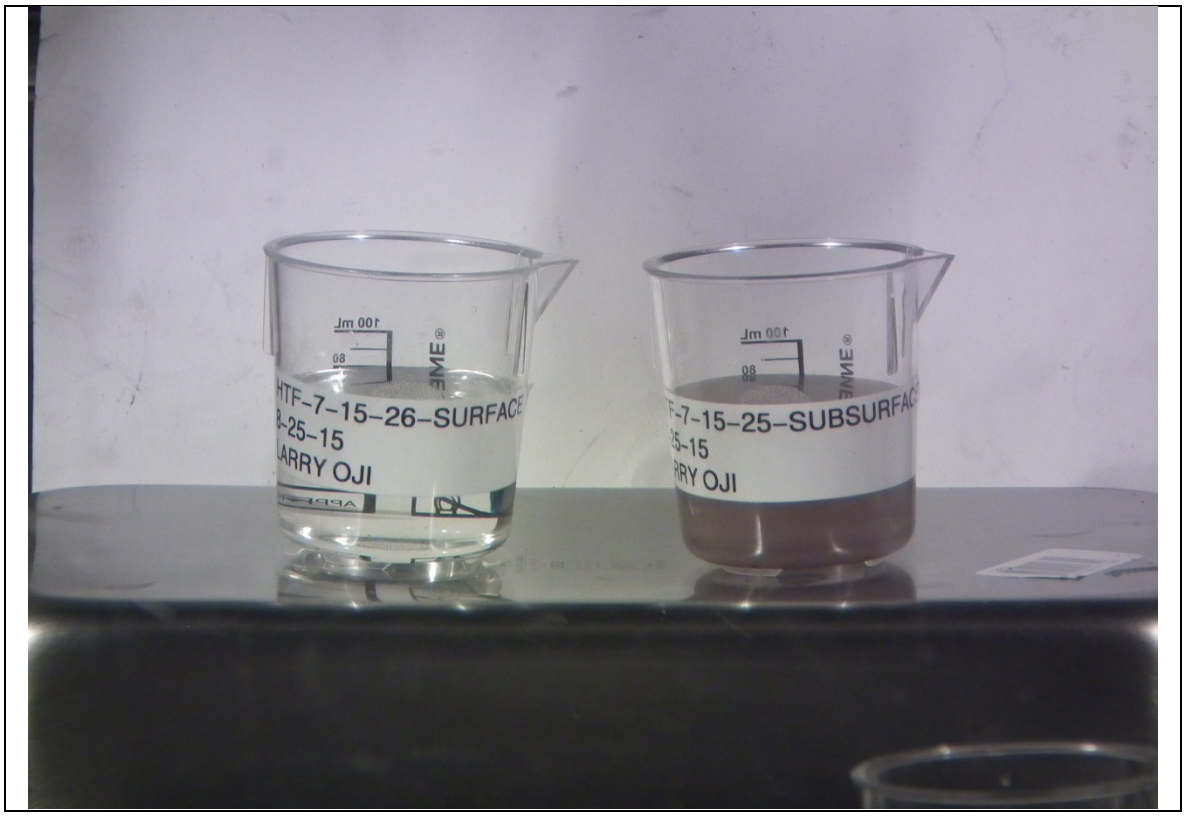

Figure 1 Tank 7 Supernate Surface (FTF-7-15-26, left) and Subsurface (FTF-7-15-25 right). Samples.

3.0 Analytical Results

Table 2 contains a description of the sampling location and the quantity of material received for the "as-received" Tank 7 surface and subsurface samples. As shown in Figure 1, only the Tank 7 surface sample (FTF-7-15-26) was essentially free of any visible or settled insoluble solids. It was relatively clear and without a cloudy appearance. The Tank 7 subsurface sample (FTF-7-15-25), on the other hand, contained brown suspended particles.

Table 3 contains a summary of the CCP analytical results for the Tank 7 surface sample. This summary table includes only the average values for the analytes and the standard deviations for each triplicate analysis. Analyses for selected cations in the Tank 7 supernatant samples, which were not requested by the customer, are also reported (performed to support cation/anion balance calculations).

Results for the analytes that were below the limits of quantification are preceded by "<" and values proceeded by "≤" (less than or equal to sign) indicate that at least one of the analytical replicates was above the instrument detection limit and at least one of the analytical results was below the detection limit or was an upper limit. Thus, where replicate analyses gave values both above and below the detection limit, the average of all replicates above and below the detection limit is given and a "≤ " sign precedes the average value. The standard deviations were calculated and provided only for values that were all above the detection limits. To check the results, a cation-anion normality balance was performed. The normal concentrations of cations (mainly Na^+ and K^+) were summed, as were the anions (NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, CO_3^{2-}, PO_4^{3-}, AlO_2^-, $C_2O_4^{2-}$ and free OH^-). The two sums were compared.

For the Tank 7 surface sample the cations summed to 2.78 M, while the anions summed to 2.59 M. Thus, the anions summed to about 93.1 %. The difference between the cation and anion molarity values are within 10% of each other, which is relatively good when one takes into consideration the nominal uncertainties (1 sigma) for the analytical methods. The difference can be attributed to the analytical uncertainties and the cation/anion concentrations are considered to be the same based on the uncertainties.

Tables 4 through 7 in Appendices A contain all the analytical results for the characterization of Tank 7 surface sample.

Table 3 CCP Average Analytical Data for Tank 7 Supernatant Sample.

Analytes	Tank 7 Surface HTF-7-15-26		Methods	Units
	Average	Stdev.		
Cs-137	**3.99E+08**	*3.3E+06*	gamma scan	dpm/mL
Ba-137m	**3.77E+08**	*3.1E+06*	gamma scan	dpm/mL
OH^-	**0.60**	*0.01*	Titration	M
NO_2^-	**4.2E-01**	*9.0E-03*	IC	M
NO_3^-	**3.7E-01**	*1.9E-03*	IC	M
F^-	**<6.1E-03**	-	IC	M
CHO_2^-	**<2.6E-03**	-	IC	M
Cl^-	**6.5E-03**	*1.8E-04*	IC	M
PO_4^{3-}	**<1.2E-03**	-	IC	M
SO_4^{2-}	**1.0E-01**	*1.7E-03*	IC	M
$C_2O_4^{2-}$	**2.9E-02**	*1.2E-04*	IC	M
Br^-	**<7.2E-03**	-	IC	M
CO_3^{2-}	**0.41**	*0.001*	TIC	M
Al	**2998**	*5.3*	ICP-ES	mg/L
B	**14.5**	*0.04*	ICP-ES	mg/L
Ba	**≤0.04**	-	ICP-ES	mg/L
Ca	**1.7**	*0.01*	ICP-ES	mg/L
Cr	**87.0**	*0.1*	ICP-ES	mg/L
Fe	**1.9**	*0.1*	ICP-ES	mg/L
K	**320**	*8.3*	ICP-ES	mg/L
Na	**63803**	*170.4*	ICP-ES	mg/L
P	**58.4**	*0.4*	ICP-ES	mg/L
S	**3731.5**	*86.1*	ICP-ES	mg/L
Si	**<3.1**	-	ICP-ES	mg/L
Zn	**0.6**	*0.1*	ICP-ES	mg/L
Na	**2.8**	*0.01*	ICP-ES	M
Total cation	**2.8**	*7.6E-03*	Calc.	M
Total anion	**2.6**	-	Calc.	M
SpG 25 °C	**1.12**	*0.004*	Calc.	-

4.0 Conclusions

This report provides the results of analyses on Savannah River Site Tank 7 surface supernatant liquid sample in support of the Corrosion Control Program (CCP).

The measured nitrate, nitrite and free-hydroxide concentrations for the Tank 7 surface sample averaged, 3.74E-01 ± *1.88E-03*, 4.17E-01 ± *9.01E-03* and 0.602 ± *0.005* M, respectively. The Tank 7 surface cesium-137, sodium and silicon concentrations were, respectively, 3.99E+08 ± *3.25E+06* dpm/mL, 2.78 M and <3.10 mg/L. The measured aluminum concentration in the Tank 7 surface sample averaged 0.11 M.

5.0 Quality Assurance

Data are recorded in SRNL Electronic Notebook: L5575-00080-07 SRNL Electronic Notebook (Production); SRNL, Aiken, SC 29808 (2014) and various AD notebooks contain the analytical/experimental data.

6.0 Acknowledgements

I acknowledge the contributions of R. Sullivan and J. Mixon for preparing the samples in the SRNL Shielded cells and Mark Jones, Tom White, Amy Ekechukwu, Mira Malek and David DiPrete for providing analytical services.

7.0 References

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[v] C. J. Martino, "Task Technical and Quality Assurance Plan for Analysis of Tank 38H and Tank 43H Enrichment Control Program and Corrosion Control Samples," SRNL-RP-2013-00522, Rev. 0, August 2013.

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Appendix A. Tank 7 Surface samples (FTF-7-15-26)

Table 4 Tank 7 Surface Sample FTF-7-15-26: CCP Results

Analytes	Analysis-1	Analysis-2	Analysis-3	Average	St. Deviation	Units
NO_3^-	3.75E-01	3.74E-01	3.71E-01	**3.74E-01**	*1.88E-03*	Mole/L
NO_2^-	4.26E-01	4.19E-01	4.08E-01	**4.17E-01**	*9.01E-03*	Mole/L
OH^{-1}	0.605	0.603	0.596	**0.602**	*0.005*	Mole/L
SpG @ 25 °C	1.11	1.12	1.12	**1.12**	*0.004*	-
Cs-137	4.00E+08	4.01E+08	3.95E+08	**3.99E+08**	*3.25E+06*	dpm/mL
Ba-137m	3.79E+08	3.79E+08	3.74E+08	**3.77E+08**	*3.07E+06*	dpm/mL

SpG = Specific gravity

Table 5 Tank 7 Surface Sample FTF-7-15-26: Other Results from CCP

Analytes	Analysis-1	Analysis-2	Analysis-3	Average	St. Deviation	Units
SO_4^{2-}	1.04E-01	1.02E-01	1.00E-01	**1.02E-01**	*1.74E-03*	Mole/L
CHO_2^-	<2.54E-03	<2.52E-03	<2.64E-03	**<2.57E-03**	-	Mole/L
Cl^-	6.45E-03	6.70E-03	6.35E-03	**6.50E-03**	*1.79E-04*	Mole/L
F^-	<6.03E-03	<5.96E-03	<6.25E-03	**<6.08E-03**	-	Mole/L
PO_4^{3-}	<1.21E-03	<1.19E-03	<1.25E-03	**<1.22E-03**	-	Mole/L
$C_2O_4^{2-}$	2.93E-02	2.95E-02	2.93E-02	**2.93E-02**	*1.15E-04*	Mole/L
Br^-	<7.17E-03	<7.09E-03	<7.43E-03	**<7.23E-03**	-	Mole/L
Inorganic carbon	4.88E+06	4.88E+06	4.91E+06	**4.89E+06**	*1.55E+04*	µgC/L
Organic carbon	7.86E+05	7.86E+05	7.91E+05	**7.88E+05**	*2.50E+03*	µgC/L
Total carbon	5.66E+06	5.66E+06	5.69E+06	**5.67E+06**	*1.80E+04*	µgC/L
CO_3^{2-}	0.406	0.407	0.409	**0.407**	*0.001*	Mole/L

Table 6 Tank 7 Surface Sample (FTF-7-15-26): Selected Elemental Analysis Results

Analytes	Analysis-1	Analysis-2	Analysis-3	Average	St. Deviation	Units
Al	3000	3001	2992	**2998**	*5.31*	mg/L
B	14.43	14.50	14.48	**14.47**	*0.04*	mg/L
Ba	<0.034	0.036	0.038	**≤0.04**	-	mg/L
Ca	1.72	1.72	1.71	**1.72**	*0.01*	mg/L
Cr	87.02	87.10	86.89	**87.01**	*0.10*	mg/L
Fe	1.91	1.77	1.90	**1.86**	*0.08*	mg/L
K	310.31	323.93	325.28	**319.84**	*8.28*	mg/L
Na	63665	63993	63750	**63803**	*170.4*	mg/L
P	58.17	58.90	58.17	**58.41**	*0.42*	mg/L
S	3790	3772	3633	**3731**	*86.1*	mg/L
Si	<3.07	<3.04	<3.18E	**<3.10**	-	mg/L
Zn	0.55	0.60	0.50	**0.55**	*0.05*	mg/L

Distribution:

T. B. Brown, 773-A
D. E. Dooley, 999-W
A. P. Fellinger. 773-42A
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
M. E. Stone, 999-W
W. R. Wilmarth, 773-A
T. B. Peters, 773-42A
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