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Analysis of Tank 30H (HTF-30-18-96, -97), Tank 32H (HTF-32-18-98, -99), and Tank 37H (HTF-37-18-100, -101) Samples for Support of the Evaporator Feed Qualification and Corrosion Control Programs for the 3H-Evaporator

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Savannah River National Laboratory™
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EXECUTIVE SUMMARY

SRNL analyzed samples from Tank 30H, Tank 32H, and Tank 37H to support the Evaporator Feed Qualification and Corrosion Control Programs for the 3H-Evaporator system. The six samples from Tanks 30H, 32H, and 37H all contain highly concentrated salt solutions with sodium concentrations ranging from 11.8 M to 15.7 M. The samples from Tank 30H show somewhat higher concentrations of the major cations and anions in the sub-surface sample than the surface sample indicating some stratification within the tank. The two Tank 32H samples show similar concentrations of the major anions and cations between the surface and sub-surface samples. The sub-surface sample from Tank 37H shows higher concentrations for most species than the surface sample indicating some stratification within this tank as well.

For all six samples, the sum of the major cations versus the sum of the major anions shows a difference of <10% providing an indication of good data quality. The VDS and surface samples from Tank 30H, Tank 32H, and Tank 37H all show silicon concentrations below 30 mg/L except for the Tank 30H VDS with a concentration of 87 mg/L.

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LIST OF ABBREVIATIONS

AD	Analytical Development
DI	De-ionized
CCP	Corrosion Control Program
EFQ	Evaporator Feed Qualification
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
NAS	Sodium Aluminosilicate
%RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TIC	Total Inorganic Carbon
VDS	Variable Depth Sample

1.0 Introduction

Feed limits have been established for the 3H-Evaporator system to ensure nuclear criticality is not possible by preventing the accumulation of sodium aluminosilicate (NAS) solids in the evaporator and that corrosion is minimized. These limits are protected by the Evaporator Feed Qualification Program (EFQ) and the Corrosion Control Program (CCP) that require periodic sampling and analysis to confirm that the waste supernate composition stays within the limits.[1,2]

Savannah River Remediation (SRR) obtained samples from two different heights within each of the three waste tanks supporting the 3H-Evaporator operations on November 23, 2018. The Tank 30H (evaporator drop tank), Tank 32H (evaporator feed tank), and Tank 37H (alternate evaporator drop tank) samples were received by the Savannah River National Laboratory (SRNL) Shielded Cells on November 26, 2018. The analysis of these samples provides information necessary for determining compliance with the EFQ and CCP. The sample characterization was requested via a Technical Assistance Request.[3]

2.0 Experimental Procedure

The samples from Tanks 30H, 32H, and 37H were opened in the SRNL Shielded Cells and poured into clear plastic beakers. The beakers were photographed, and the masses of the samples determined. Table 2-1 provides a description and the measured mass of each of the six samples. Figures 2-1, 2-2, and 2-3 show photographs of each set of samples in clear beakers. Figure 2-4 shows all the tank samples together in poly bottles. The variable depth sample (VDS) from Tank 30H, Tank 32H, and Tank 37H and the surface sample from Tank 30H contained solids that were clearly precipitated salts based on observations during the transfer of the samples from the clear beakers to the poly storage bottles. No indication of any dark colored solids was observed in any of the samples.

All six samples received the analyses required by the EFQ that includes determination of Cs-137 by gamma spectroscopy and inductively coupled plasma-emission spectroscopy (ICP-ES) to determine Na, Al, Si, and other metals. All six samples also received the analyses required by the CCP. The CCP analysis suite includes determination of free hydroxide, ion chromatography (IC), and total inorganic carbon (TIC).

Density measurements were made on decanted (unfiltered) aliquots of the samples using calibrated tubes at ambient cell temperature (18 °C).

For the CCP analysis, de-ionized (DI) water dilutions were made in triplicate from a well-mixed (unfiltered) sample and submitted to Analytical Development (AD) for analysis. A blank of the DI water was also prepared along with the samples.

For the EFQ analysis, triplicate aliquots of the well mixed (unfiltered) sample from each sample were prepared for analysis using the warm acid strike method.[4] A reagent blank and three silicon standard solutions were submitted for analysis with the samples.

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 Y7081-00081-29.

Table 2-1. Sampling Description and Mass of the Tank 30H, 32H, and 37H Samples

Tank	Sample ID	Sample Type	Sample Mass (g)	Description
Tank 30H	HTF-30-18-96	Surface	102.7	Blue tinted solution with ~1/8" of settled white crystalline solids
Tank 30H	HTF-30-18-97	VDS	315.4	Blue tinted solution with ~3/4 by volume white crystalline solids
Tank 32H	HTF-32-18-98	Surface	101.6	Yellow tinted solution with no solids
Tank 32H	HTF-32-18-99	VDS	310.5	Yellow tinted solution with ~1/4" of settled white crystalline solids
Tank 37H	HTF-37-18-100	Surface	114.6	Gray tinted solution with no solids
Tank 37H	HTF-37-18-101	VDS	326.6	Gray tinted solution with ~1/3 by volume white crystalline solids

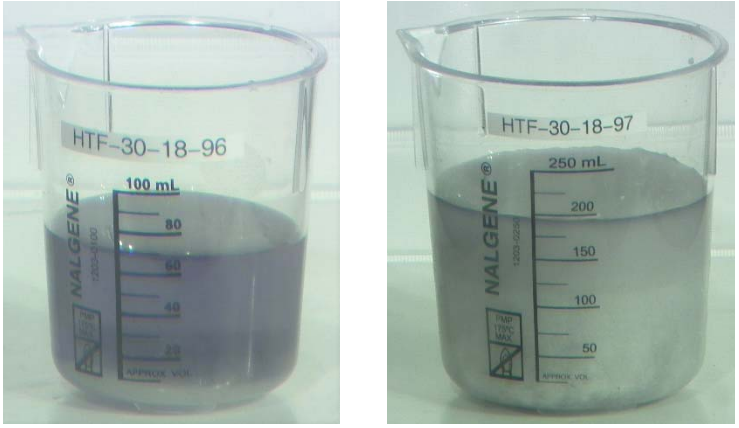

Figure 2-1. 3H-Evaporator Samples from Tanks 30H

Figure 2-2. 3H-Evaporator Samples from Tanks 32H

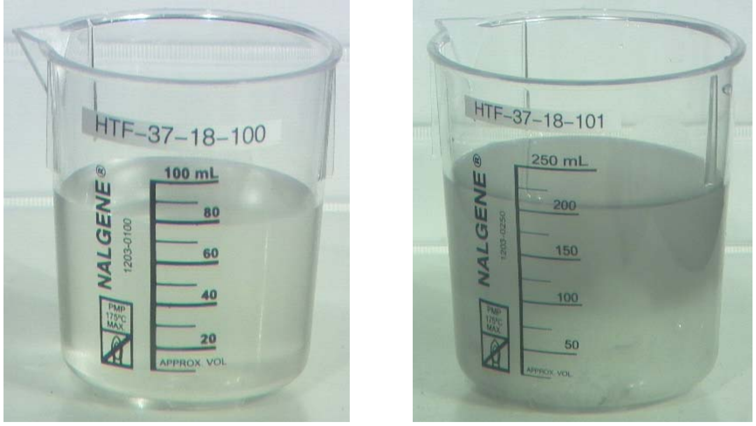

Figure 2-3. 3H-Evaporator Samples from Tanks 37H

Figure 2-4. View of the 3H-Evaporator Samples

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. 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. 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.[5,6,7]

The results in Table 3-1 for the two samples from Tank 30H show both samples to be highly concentrated salt solutions with a sodium concentration of 14.1 M in the surface sample and 15.7 M in the VDS. Hydroxide is the main anionic species in both solutions with a concentration of 9.18 M in the surface sample and 8.40 M in the VDS. The other main anions in the two solutions are nitrate and nitrite. Except for the hydroxide concentration, most of the other species in Table 3-1 show higher concentrations in the VDS than in the surface sample indicating some stratification in the tank. The sum of the major cations versus the sum of the major anions shows a difference of <10% for each of the two Tank 30H samples providing an indication of good data quality. The surface sample from Tank 30H is similar to the previous surface sample while the VDS shows significantly higher aluminum, carbonate, nitrate and silicon than the previous sample.[8]

The results for the two samples from Tank 32H in Table 3-1 indicates the compositions remain consistent throughout the tank depth profile. The sodium concentration measured in the Tank 32H VDS of 12.9 M is only slightly higher (<10%) than the 11.8 M sodium concentration measured in the surface sample. As with Tank 30H samples, the anionic specie with the highest concentration is hydroxide followed by nitrite and nitrate. The data from the water dilution of the Tank 32H surface sample (titration, IC, and TIC data) used only a single replicate. The other two replicates of the Tank 32H surface sample showed anion concentrations that were unrealistically high with anion equivalents summing to >25 M. The high concentrations in these two replicates seems to indicate a dilution error during the sample preparations. The sum of the major cations versus the sum of the major anions indicates good data quality with a difference of <10% for each of the two Tank 32H samples. The surface sample from Tank 32H shows higher concentrations for most species compared to the previous sample while the VDS appears quite similar to the previous VDS.[8]

In the results from the two samples from Tank 37H in Table 3-1, the VDS sample shows higher concentrations for most species than found in the surface sample. As with the samples from the other two tanks, hydroxide is the predominant anion followed by nitrite and nitrate anions. Sodium is the dominant cation with a concentration of 11.8 in the Tank 37H surface sample and 14.9 in the VDS. Again, the sum of the major cations versus the sum of the major anions indicates good data quality with a difference of <10% for each of the two Tank 37H samples. Both the surface sample and the VDS from Tank 37H show higher concentrations for most species than measured in the previous sample.[8]

The silicon concentrations measured in the VDS and surface samples from Tank 30H, Tank 32H, and Tank 37H were all below 30 mg/L except for the Tank 30H VDS with a concentration of

87 mg/L. The standards used for the silicon analysis (50 mg/L silicon in the solution prepared by warm acid strike to final concentrations of 0.5, 1.0, and 2.0 mg/L) were all close to the target concentrations with differences from the targeted concentrations of 5.0%, 4.3%, and 3.6% respectively. The silicon concentration was below detectable levels in the process blank.

Table 3-1. ECP, CCP, and other Analytical Data for Tank 30H, 32H and 37H Samples. (Averages and %RSD values are of triplicate measurements)

analyte	method	units	est. 1σ	HTF-30-18-96 average	RSD	HTF-30-18-97 average	RSD	HTF-32-18-98 average	RSD	HTF-32-18-99 average	RSD
sample type	--	--	--	surface		vds		surface		vds	
density @ 18°C	grav.	g/mL	5%	1.49	0.6%	1.61	2.2%	1.45	0.6%	1.48	1.7%
Cs-137	gamma scan	dpm/mL	5%	3.64E+09	5.0%	3.76E+09	1.9%	2.59E+09	7.5%	2.99E+09	1.3%
Ba-137m				3.44E+09		3.55E+09		2.45E+09		2.83E+09	
OH^-	titration	M	10%	9.18E+00	2.7%	8.40E+00	1.4%	6.34E+00	--[a]	6.82E+00	2.0%
F^-	IC	M	10%	<2.78E-02	--	<2.72E-02	--	<2.67E-02	--[a]	<2.75E-02	--
CHO_2^-	IC	M	10%	<1.17E-02	--	<1.15E-02	--	<1.13E-02	--[a]	<1.16E-02	--
Cl^-	IC	M	10%	2.24E-02	2.0%	2.02E-02	2.6%	1.63E-02	--[a]	1.80E-02	1.6%
NO_2^-	IC	M	10%	1.93E+00	5.5%	2.53E+00	2.6%	2.28E+00	--[a]	2.45E+00	0.2%
Br^-	IC	M	10%	<6.61E-03	--	<6.47E-03	--	<6.35E-03	--[a]	<6.55E-03	--
NO_3^-	IC	M	10%	1.35E+00	8.2%	2.50E+00	3.6%	1.78E+00	--[a]	1.63E+00	0.4%
PO_4^{3-}	IC	M	10%	1.01E-02	13%	1.10E-02	19%	<5.34E-03	--[a]	6.24E-03	7.1%
SO_4^{2-}	IC	M	10%	<5.50E-03	--	1.01E-02	3.1%	9.14E-03	--[a]	8.15E-03	1.9%
$C_2O_4^{2-}$	IC	M	10%	<6.00E-03	--	<5.88E-03	--	<5.77E-03	--[a]	<5.94E-03	--
CO_3^{2-}	TIC	M	10%	3.97E-02	5.6%	6.40E-02	1.8%	8.62E-02	--[a]	8.10E-02	1.3%
Al	ICP-ES	mg/L	10%	1.93E+04	5.7%	5.33E+04	3.1%	2.13E+04	0.7%	2.41E+04	4.3%
		M		7.16E-01		1.98E+00		7.90E-01		8.94E-01	
B	ICP-ES	mg/L	10%	2.79E+02	11%	2.86E+02	3.1%	2.32E+02	0.4%	2.57E+02	2.3%
Ca	ICP-ES	mg/L	10%	<1.32E+00	--	<2.98E+00	--	2.01E+01	24%	≤9.68E+00	--
Cr	ICP-ES	mg/L	10%	3.66E+02	3.7%	3.68E+02	2.2%	3.37E+02	0.2%	3.79E+02	3.4%
Fe	ICP-ES	mg/L	10%	2.73E+01	4.1%	4.65E+01	5.0%	2.50E+01	2.9%	2.85E+01	11%
K	ICP-ES	mg/L	10%	3.87E+03	2.6%	3.72E+03	2.9%	2.99E+03	1.1%	3.30E+03	3.0%
Li	ICP-ES	mg/L	10%	<2.99E+00	--	<4.05E+00	--	<2.55E+00	--	<2.58E+00	--
Na	ICP-ES	mg/L	10%	3.24E+05	5.8%	3.61E+05	1.4%	2.72E+05	0.6%	2.96E+05	4.2%
		M		1.41E+01		1.57E+01		1.18E+01		1.29E+01	
P	ICP-ES	mg/L	10%	4.95E+02	8.4%	5.43E+02	1.9%	1.74E+02	12%	3.00E+02	6.0%
Si	ICP-ES	mg/L	15%	<2.41E+01	--	8.66E+01	3.3%	<1.98E+01	--	2.43E+01	7.0%
Zn	ICP-ES	mg/L	10%	1.91E+01	6.4%	1.84E+01	8.4%	1.87E+01	6.2%	1.79E+01	19%
Anions	sum	M	--	1.33E+01	--	1.56E+01	--	1.14E+01	--	1.20E+01	--
Cations	sum	M	--	1.42E+01	--	1.58E+01	--	1.19E+01	--	1.30E+01	--

est.1σ = estimated one sigma percent uncertainty as reported by AD.

a = only a single replicate was used from the water dilution of HTF-32-18-98, the other two replicates being unrealistically high

Table 3-1. ECP, CCP, and other Analytical Data for Tank 30H, 32H and 37H Samples. (Averages and %RSD values are of triplicate measurements) Continued

analyte	method	units	est. 1σ	HTF-37-18-100 average	RSD	HTF-37-18-101 average	RSD
sample type	--	--	--	surface		vds	
density @ 18°C	grav.	g/mL	5%	1.47	0.3%	1.54	1.6%
Cs-137	gamma scan	dpm/mL	5%	2.47E+09	9.4%	3.74E+09	4.0%
Ba-137m				2.34E+09		3.54E+09	
OH^-	titration	M	10%	6.34E+00	0.9%	8.54E+00	1.8%
F^-	IC	M	10%	<2.81E-02	--	<2.79E-02	--
CHO_2^-	IC	M	10%	<1.18E-02	--	<1.18E-02	--
Cl^-	IC	M	10%	1.60E-02	1.1%	2.18E-02	0.9%
NO_2^-	IC	M	10%	2.11E+00	0.6%	2.76E+00	6.0%
Br^-	IC	M	10%	<6.67E-03	--	<6.64E-03	--
NO_3^-	IC	M	10%	1.82E+00	0.8%	2.07E+00	8.9%
PO_4^{3-}	IC	M	10%	9.12E-03	8.4%	1.35E-02	7.6%
SO_4^{2-}	IC	M	10%	≤5.55E-03	--	<5.52E-03	--
$C_2O_4^{2-}$	IC	M	10%	<6.06E-03	--	<6.02E-03	--
CO_3^{2-}	TIC	M	10%	1.29E-01	1.4%	4.32E-02	0.8%
Al	ICP-ES	mg/L	10%	2.17E+04	0.8%	3.06E+04	3.4%
		M		8.04E-01		1.13E+00	
B	ICP-ES	mg/L	10%	2.26E+02	1.1%	3.15E+02	4.0%
Ca	ICP-ES	mg/L	10%	<6.06E-01	--	≤1.40E+00	--
Cr	ICP-ES	mg/L	10%	3.35E+02	1.4%	4.69E+02	3.9%
Fe	ICP-ES	mg/L	10%	2.88E+01	24%	3.39E+01	7.1%
K	ICP-ES	mg/L	10%	2.92E+03	1.0%	4.15E+03	3.3%
Li	ICP-ES	mg/L	10%	<2.31E+00	--	<3.07E+00	--
Na	ICP-ES	mg/L	10%	2.71E+05	0.6%	3.42E+05	0.9%
		M		1.18E+01		1.49E+01	
P	ICP-ES	mg/L	10%	1.72E+02	4.3%	5.32E+02	4.1%
Si	ICP-ES	mg/L	15%	2.06E+01	3.2%	2.80E+01	0.6%
Zn	ICP-ES	mg/L	10%	1.43E+01	1.9%	1.99E+01	4.7%
Anions	sum	M	--	1.14E+01	--	1.46E+01	--
Cations	sum	M	--	1.19E+01	--	1.50E+01	--

est.1σ = estimated one sigma percent uncertainty as reported by AD.

4.0 Conclusions

The six samples from Tanks 30H, 32H, and 37H all contain highly concentrated salt solutions with sodium concentrations ranging from 11.8 M to 15.7 M. The samples from Tank 30H show somewhat higher concentrations of the major cations and anions in the sub-surface sample than the surface sample indicating some stratification within the tank. The two Tank 32H samples show similar concentrations of the major anions and cations between the surface and sub-surface samples. The sub-surface sample from Tank 37H shows higher concentrations for most species than the surface sample indicating some stratification within this tank as well.

For all six samples, the sum of the major cations versus the sum of the major anions shows a difference of <10% providing an indication of good data quality. The silicon concentrations measured in the VDS and surface samples from Tank 30H, Tank 32H, and Tank 37H were all below 30 mg/L except for the Tank 30H VDS with a concentration of 87 mg/L.

5.0 Acknowledgements

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6.0 References

1. H. Bui, *CSTF Evaporator Feed Qualification Program*, WSRC-TR-2003-00055, Rev. 13, June 2018.

2. K. B. Martin., *CSTF Corrosion Control Program*, WSRC-TR-2002-00327, Rev. 9, December 2015.

3. B. A. Speight, Technical Assistance Request, X-TAR-H-00034, Savannah River Remediation, Aiken, SC 29808, June 7, 2018.

4. F.M. Pennebaker, C.J Coleman, M.A. Jones, W.R. Wilmarth, C.M. Jantzen and D.R. Click, *Evaluation of Warm Acid Strike Treatment for Silicon Analysis in High Level Waste*, WSRC-TR-2003-00036, Rev. 0, January 2003.

5. C.J Coleman, T. B. Edwards, C. A. Nash, *Statistical Analysis of Sample Data from Tank 48H*, WSRC-TR-95-0325, Rev. 0, September 29, 1995.

6. D. D. Walker, W. T. Boyce, C. J Coleman, D. P. Diprete, T. B. Edwards, A. A. Ekechukwu, C. W. Hsu, S. F. Peterson, L. L. Tovo, M. J. Whitaker, *Tank 48H Waste Composition and Results of Investigations of Analytical Methods*, WSRC-TR-97-00063, Rev. 0, April 2, 1997.

7. M. S. Hay, T. B. Edwards, *Statistical Analysis of ESP Verification Test Samples*, WSRC-RP-94-1224, Rev. 0, November 4, 1994.

8. M. S. Hay, C. J. Coleman, and D. P. Diprete, *Analysis of Tank 30H (HTF-30-18-54, -55), Tank 32H (HTF-32-18-56, -57), and Tank 37H (HTF-37-18-58, -59) Samples for Support of the Evaporator Feed Qualification and Corrosion Control Programs for the 3H-Evaporator*, SRNL-STI-2018-00455, Rev. 0, August 2018.

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