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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

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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 7.89 M to 15.0 M. The samples from Tank 30H show small differences in the concentrations of the major cations and anions between the surface sample and VDS. The two Tank 32H samples show significant differences in the concentrations of the major anions and cations with the VDS being nearly twice as concentrated as the surface sample. The surface sample and VDS from Tank 37H contain very similar compositions.

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 detectable levels. Based on visual observations the Tank 37H VDS appeared to contain insoluble sludge solids. The measured weight percent water insoluble solids on the Tank 37H VDS indicates the sample contains <0.03 wt% insoluble solids.

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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 June 16, 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 June 20, 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 sample in clear beakers. The variable depth sample (VDS) from Tank 30H and Tank 32H 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 the white crystalline solids during the transfer. The Tank 37H VDS, initially a cloudy dull brown solution, produced a thin layer of dark solids after settling overnight (see the photograph in Figure 2-4). Due to the presence of "sludge-like" solids, the weight percent water insoluble solids were measured on the Tank 37H VDS.

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 (29 °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.

The weight percent water insoluble solids were determined on the Tank 37H VDS by filtering a known weight of the sample through a weighed 0.45 µm Nylon filter disk, washing the solids with de-ionized water (3 x 50 mL) to remove water soluble solids, drying any solids on the filter disk at ~105 °C to constant weight, and then reweighing the filter disk.

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 Y7081-00081-26.

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-30-18-54	Surface	114.4	Clear solution with light blue tint, no solids
Tank 30H	HTF-30-18-55	VDS	323.8	Light blue solution with ~1/2" of settled white crystalline solids
Tank 32H	HTF-32-18-56	Surface	106.3	Clear solution, no solids
Tank 32H	HTF-32-18-57	VDS	302.8	Yellow tinted solution with ~1/4" of settled white crystalline solids
Tank 37H	HTF-37-18-58	Surface	112.6	Clear solution, no solids
Tank 37H	HTF-37-18-59	VDS	282.7	Cloudy dull brown solution. A thin layer of dark solids settled out overnight.

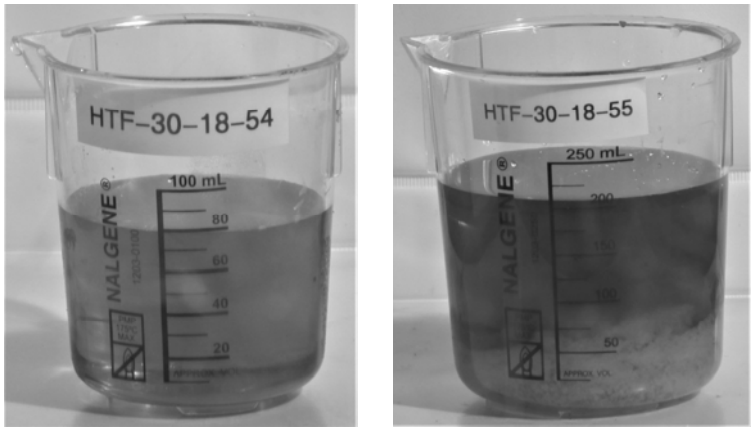

Figure 2-1. 3H-Evaporator Samples from Tanks 30H

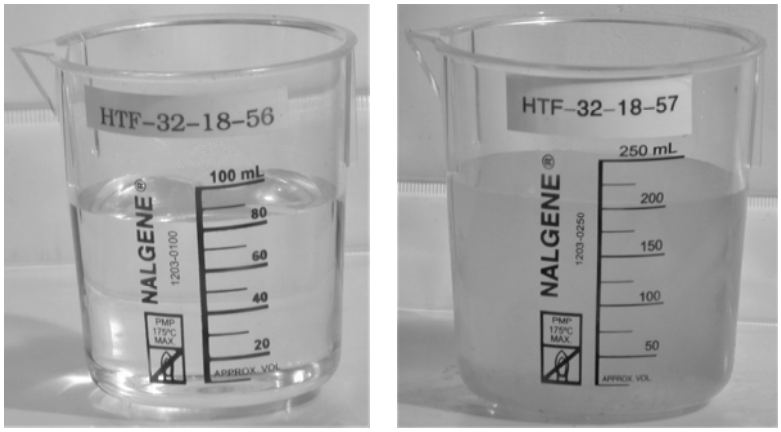

Figure 2-2. 3H-Evaporator Samples from Tanks 32H

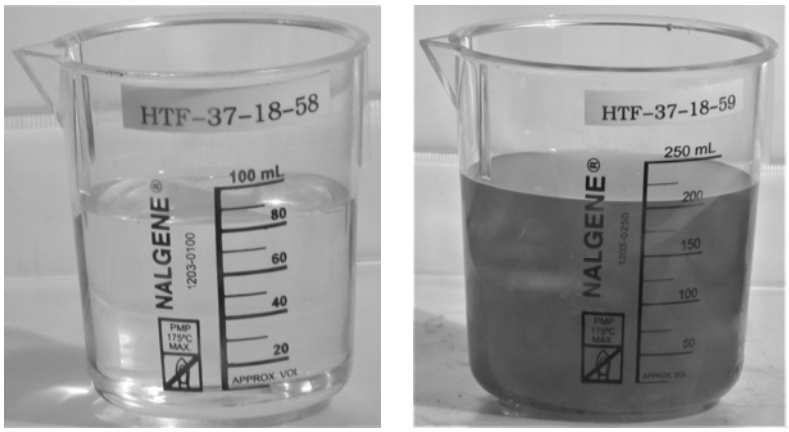

Figure 2-3. 3H-Evaporator Samples from Tanks 37H

Figure 2-4. View of settled solids in the Tank 37H VDS

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 13.7 M in the surface sample and 15.0 M in the VDS. Hydroxide is the main anionic species in both solutions with a concentration of 8.28 M in the surface sample and 9.34 M in the VDS. The other main anions in the two solutions, nitrate and nitrite show similar concentrations in both samples with differences of 5% or less. The Cs-137 as well as most of the other species in Table 3-1 show concentrations about 10-15% higher in the VDS than in the surface sample. 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 results for the two samples from Tank 32H in Table 3-1 show significant stratification in the tank with the concentration of most species in the VDS much higher than in the surface sample. The sodium concentration measured in the Tank 32H VDS of 13.1 M is significantly higher than the 7.89 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. All three of these anions show significantly higher concentrations in the VDS than in the surface sample. 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 two samples from Tank 37H show similar concentrations for most species in the surface sample and VDS with differences of <10% for the major constituents. 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.

The silicon concentrations measured in the VDS and surface samples from Tank 30H, Tank 32H, and Tank 37H were all below detectable levels. 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 9%, 14%, and 13% respectively. The silicon concentration was below detectable levels in the process blank.

The measurement of the weight percent water insoluble solids on the Tank 37H VDS found the sample contained <0.03 wt% insoluble solids. The wt% insoluble solids value is indicated as below detection since less than 30 mg of dried, water insoluble solids were obtained during the measurement. With less than 30 mg of solids on the filter paper, the weighing errors in the shielded

cells can be significant. Therefore, a less than value is reported for the measurement. Table 3-2 provides the total gamma, total (non-volatile) beta, and total alpha measured on the Tank 37H VDS. The total gamma result of 2.03E+09 dpm/mL agrees well with the value of 2.08E+09 dpm/mL for Cs-137 in the Tank 37H VDS in Table 3-1.

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-30-18-54		HTF-30-18-55		HTF-32-18-56		HTF-32-18-57	
				average	RSD	average	RSD	average	RSD	average	RSD
density @ 29°C	grav.	g/mL	5%	1.49	0.1%	1.53	0.4%	1.33	0.3%	1.48	0.3%
Cs-137	gamma scan	dpm/mL	5%	3.65E+09	0.6%	4.17E+09	1.7%	1.61E+09	4.1%	3.24E+09	5.6%
Ba-137m				3.45E+09		3.94E+09		1.52E+09		3.07E+09	
OH^-	titration	M	10%	8.28E+00	2.0%	9.34E+00	1.6%	3.47E+00	1.7%	6.48E+00	2.6%
F^-	IC	M	10%	<2.78E-02	--	<3.59E-02	--	<2.51E-02	--	<3.30E-02	--
CHO_2^-	IC	M	10%	<1.17E-02	--	<1.51E-02	--	<1.06E-02	--	<1.39E-02	--
Cl^-	IC	M	10%	2.01E-02	2.5%	2.39E-02	0.7%	<1.34E-02	--	1.82E-02	1.4%
NO_2^-	IC	M	10%	2.27E+00	4.7%	2.20E+00	3.0%	1.48E+00	17%	2.42E+00	1.1%
Br^-	IC	M	10%	<6.60E-03	--	<8.53E-03	--	<5.97E-03	--	<7.85E-03	--
NO_3^-	IC	M	10%	1.70E+00	4.7%	1.62E+00	2.7%	1.84E+00	17%	2.07E+00	1.2%
PO_4^{3-}	IC	M	10%	1.27E-02	4.3%	1.49E-02	4.2%	≤5.15E-03	--	1.01E-02	1.9%
SO_4^{2-}	IC	M	10%	<5.49E-03	--	<7.09E-03	--	1.82E-02	4.0%	1.09E-02	2.5%
$C_2O_4^{2-}$	IC	M	10%	<5.99E-03	--	<7.74E-03	--	<5.42E-03	--	<7.12E-03	--
CO_3^{2-}	TIC	M	10%	3.01E-02	10%	2.74E-02	20%	2.17E-01	0.6%	1.16E-01	36%
Al	ICP-ES	mg/L	10%	1.84E+04	0.5%	2.09E+04	2.1%	1.14E+04	1.1%	2.21E+04	7.0%
		M		6.83E-01		7.75E-01		4.22E-01		8.17E-01	
B	ICP-ES	mg/L	10%	2.98E+02	0.8%	3.40E+02	1.8%	1.32E+02	0.5%	2.75E+02	6.2%
Ca	ICP-ES	mg/L	20%	<7.86E+00	--	<8.34E+00	--	<7.67E+00	--	1.58E+01	56%
Cr	ICP-ES	mg/L	10%	3.55E+02	0.4%	4.11E+02	2.0%	1.77E+02	1.1%	4.09E+02	4.2%
Fe	ICP-ES	mg/L	10%	2.59E+01	1.1%	2.85E+01	1.4%	1.36E+01	4.0%	2.95E+01	8.4%
K	ICP-ES	mg/L	10%	3.82E+03	1.6%	4.30E+03	3.1%	1.71E+03	1.6%	3.49E+03	7.5%
Li	ICP-ES	mg/L	10%	<1.50E+01	--	<1.59E+01	--	<1.46E+01	--	<1.44E+01	--
Na	ICP-ES	mg/L	10%	3.16E+05	0.5%	3.45E+05	1.0%	1.81E+05	1.1%	3.01E+05	6.2%
		M		1.37E+01		1.50E+01		7.89E+00		1.31E+01	
P	ICP-ES	mg/L	10%	5.76E+02	2.4%	6.62E+02	3.7%	2.38E+02	2.8%	5.10E+02	3.9%
Si	ICP-ES	mg/L	10%	<2.04E+01	--	<2.17E+01	--	<1.99E+01	--	<1.97E+01	--
Zn	ICP-ES	mg/L	10%	1.90E+01	1.6%	2.24E+01	2.0%	8.29E+00	0.6%	2.12E+01	5.9%

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

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-37-18-58		HTF-37-18-59	
				average	RSD	average	RSD
density @ 29°C	grav.	g/mL	5%	1.39	0.1%	1.39	0.1%
Cs-137	gamma scan	dpm/mL	5%	2.00E+09	2.5%	2.08E+09	2.7%
Ba-137m				1.89E+09		1.96E+09	
OH^-	titration	M	10%	4.04E+00	2.6%	4.01E+00	1.6%
F^-	IC	M	10%	<2.73E-02	--	<3.15E-02	--
CHO_2^-	IC	M	10%	<1.15E-02	--	<1.33E-02	--
Cl^-	IC	M	10%	<1.46E-02	--	<1.69E-02	--
NO_2^-	IC	M	10%	1.78E+00	0.3%	1.91E+00	13%
Br^-	IC	M	10%	<6.48E-03	--	<7.49E-03	--
NO_3^-	IC	M	10%	2.16E+00	0.6%	2.32E+00	15%
PO_4^{3-}	IC	M	10%	6.06E-03	1.2%	≤6.31E-03	--
SO_4^{2-}	IC	M	10%	2.07E-02	2.0%	2.00E-02	3.0%
$C_2O_4^{2-}$	IC	M	10%	<5.89E-03	--	<6.80E-03	--
CO_3^{2-}	TIC	M	10%	2.37E-01	4.7%	2.28E-01	2.4%
Al	ICP-ES	mg/L	10%	1.49E+04	0.5%	1.51E+04	0.5%
		M		5.53E-01		5.58E-01	
B	ICP-ES	mg/L	10%	1.74E+02	0.8%	1.71E+02	0.5%
Ca	ICP-ES	mg/L	20%	<7.75E+00	--	<6.78E+00	--
Cr	ICP-ES	mg/L	10%	2.57E+02	0.8%	2.86E+02	0.5%
Fe	ICP-ES	mg/L	10%	1.92E+01	4.2%	3.24E+01	10%
K	ICP-ES	mg/L	10%	2.21E+03	0.7%	2.27E+03	0.7%
Li	ICP-ES	mg/L	10%	<1.47E+01	--	<1.29E+01	--
Na	ICP-ES	mg/L	10%	2.22E+05	0.0%	2.24E+05	0.4%
		M		9.67E+00		9.75E+00	
P	ICP-ES	mg/L	10%	3.06E+02	2.9%	3.00E+02	1.8%
Si	ICP-ES	mg/L	10%	<2.01E+01	--	<1.76E+01	--
Zn	ICP-ES	mg/L	10%	1.05E+01	3.7%	1.12E+01	2.0%

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

Table 3-2. Results for Total Gamma, Total Beta, and Total Alpha for the Tank 37H VDS

Analysis	Average dpm/mL	RSD
Total Gamma	2.03E+09	1.4%
Total Non-volatile Beta	2.48E+09	1.8%
Total Alpha	<2.64E+05	--

4.0 Conclusions

The six samples from Tanks 30H, 32H, and 37H all contain highly concentrated salt solutions with sodium concentrations ranging from 7.89 M to 15.0 M. The samples from Tank 30H show small differences in the concentrations of the major cations and anions between the surface and sub-surface sample. The two Tank 32H samples show significant differences in the concentrations of the major anions and cations with the VDS being nearly twice as concentrated as the surface sample. The surface sample and VDS from Tank 37H contain very similar compositions.

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 detectable levels. Based on visual observations the Tank 37H VDS appeared to contain insoluble sludge solids. The measured weight percent water insoluble solids on the Tank 37H VDS indicates the sample contains <0.03 wt% insoluble solids.

5.0 Acknowledgements

The contributions of Dee Wheeler and Monica Jenkins, in preparing the samples, and those of Amy Ekechukwu, Mark Jones, John Young, and Tom White, for providing analytical services, are appreciated and acknowledged.

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