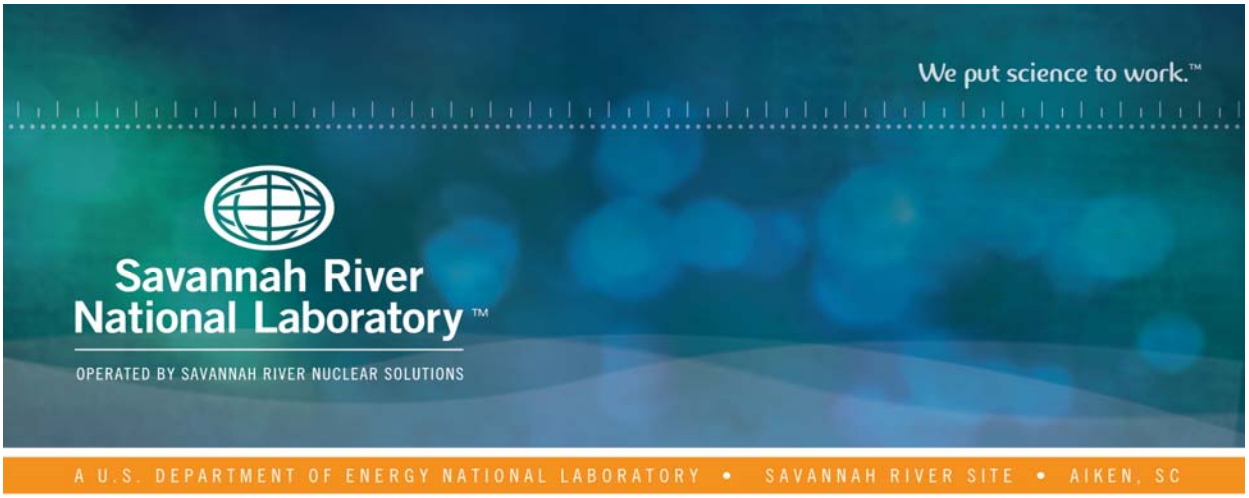

Analysis of Tank 38H (HTF-38-14-6, 7) and Tank 43H (HTF-43-14-8, 9) Samples for Support of the Enrichment Control and Corrosion Control Programs

C.J. Martino

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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EXECUTIVE SUMMARY

SRNL performed analysis on Tanks 38H and 43H surface and subsurface supernate samples to support ECP and CCP.

The U-235 mass divided by the total U mass ranged from 0.0059 to 0.0060. Uranium concentration ranged from 53.1 mg/L in the Tank 43H surface sample to the 85.1 mg/L in the Tank 38H subsurface sample. The U-235/U and uranium concentration are in line with the prior 2H-Evaporator System ECP samples.

For the Tank 43H samples, the aluminum (0.0198 M), sodium (3.61 M), and density (1.16 g/mL) are all trending downward and are significantly below the range of measurements for the Tank 43H samples from January 2010 through April 2013. The measured silicon (149 mg/L) and hydroxide (1.60 M) are at the low end of the range of Tank 43H measurements over that period.

In analyses performed to support 2H evaporator foaming and carryover recovery, Sr-90 measured 1.63×10^6 and 1.80×10^6 dpm/mL in the Tank 43H surface and subsurface samples, respectively. Measurement of the semi-volatile organic compounds suspected of contributing to foaming revealed that all were below the detection limit of 6 mg/L in the Tank 43H samples.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

calc.	Calculation
CCP	Corrosion Control Program
ECP	Enrichment Control Program
EFQ	Evaporator Feed Qualification
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectrometry
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
n.d.	Not determined
PDD	Program Description Document
RSD	Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semivolatile Organics Analysis
VDS	Variable Depth Sample

1.0 Introduction

A Nuclear Criticality Safety Evaluation (NCSE) establishes the barriers to ensure that a nuclear criticality remains incredible for the 2H Evaporator.[1] The barriers include the Enrichment Control Program (ECP), requiring sampling to determine the equivalent enriched uranium at two locations in Tanks 38H and 43H every 26 weeks. The Corrosion Control Program Description Document establishes concentration and temperature limits for key constituents and periodic sampling and analysis to confirm that waste supernate is within these limits.

On January 15, 2014, Savannah River Remediation (SRR) sampled from two locations within Tanks 38H and 43H. The samples were delivered to the Savannah River National Laboratory (SRNL) for analyses to support the Enrichment Control and Corrosion Control Programs. Tanks 38H and 43H are the drop tank and the feed tank, respectively, of the 2H-evaporator system.

This work is governed by the Technical Task Request and the experimental details are presented in the Task Technical and Quality Assurance Plan.[2,3] Analysis of this set of Tank 38H and 43H samples also includes components that relate to the formation of sodium aluminosilicate evaporator scale.

Additional analysis for Sr-90 and semi-volatile organics were performed in an effort to understand high beta/gamma activity in the evaporator overheads and foaming in the evaporator pot.[4]

2.0 Experimental Procedure

Analysis for ECP was performed on all four samples. Analysis for the Corrosion Control Program (CCP) was performed on the two surface samples. Analysis for components that contribute to sodium aluminosilicate evaporator scale was performed on the two subsurface samples.

The ECP analysis includes inductively-coupled plasma – mass spectroscopy (ICP-MS) for uranium isotopics and radiochemical separation and counting methods for Pu-238, Pu-239/240, and Pu-241. The CCP analysis includes ion chromatography (IC) for anions (nitrate and nitrite), acid titration for free hydroxide, and gamma scan for detectable gamma-emitting isotopes. The preparation of samples for ECP and gamma scan analyses was by dilution with 2M nitric acid. The preparation of samples for IC and titration analyses was by dilution with water. Density of the as-received samples was measured gravimetrically at the ambient temperature of the SRNL shielded cells by weighing portions of sample material in pre-calibrated tubes. Preparation for ECP and CCP analytes were performed in duplicate. Additional analytes are reported when they are available from the analytical methods used. For each Tank 43H sample, additional Sr-90 analysis and semivolatile organics analysis (SVOA) were performed on acid and water dilutions, respectively.

Preparation of samples for inductively-coupled plasma – emissions spectroscopy (ICP-ES) measurement for silicon and other elements was performed by warm acid strike, which was performed in triplicate and yielded an approximately 50-fold dilution. Twenty milliliters of 3 M nitric acid were added to two milliliters of sample, and the mixture was heated at 90 °C for four

hours before dilution to 100 milliliters. This method was previously determined to be the optimal method for accurate silicon measurement in this waste matrix.[5]

3.0 Samples

Table 3-1 contains a description of the sampling location and the quantity of material received. As seen in Figure 3-1, the two Tank 43H samples and the Tank 38H surface sample had a slight haze, while the Tank 38H subsurface sample HTF-38-14-7 was turbid but had good light transmittance. The visual appearance of all samples was consistent with supernatant liquid containing <<1 wt. % insoluble solids.

Table 3-1. Sample Description

Sample Name	Tank	Tank Location	Volume	Mass
HTF-38-14-6	38H	Supernate surface (336" from tank bottom)	~ 80 mL	97.0 g
HTF-38-14-7	38H	Supernate mid-height (287" from tank bottom)	~ 70 mL	87.1 g
HTF-43-14-8	43H	Supernate surface (315" from tank bottom)	~ 80 mL	88.4 g
HTF-43-14-9	43H	Pump suction height (161" from tank bottom)	~ 60 mL	69.3 g

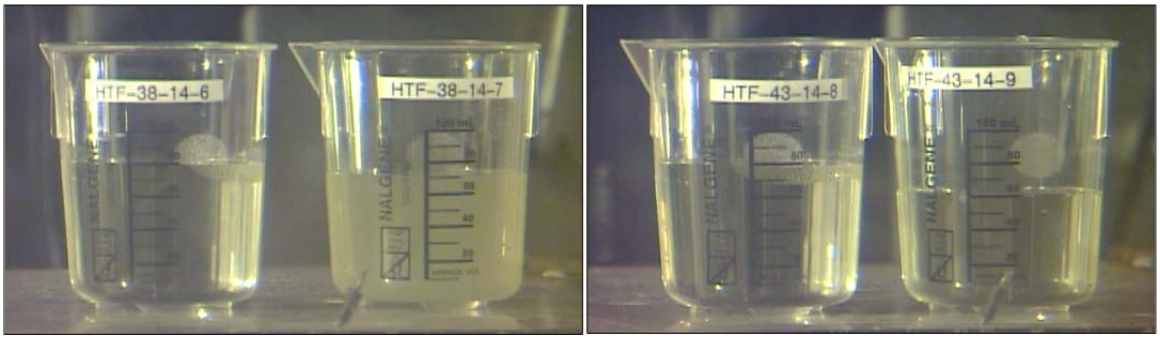

Figure 3-1. From left to right, samples from the Tank 38H supernate surface (Dip), Tank 38H supernate mid-point (VDS), Tank 43H supernate surface (Dip), and Tank 43H pump suction height (VDS)

4.0 Analysis Results

Table 4-1 contains the analytical results for the individual samples. Results are preceded by "<" when the analyte is below the limits of quantification. Results are preceded by "≤" when a combination of values above and below the limits of quantification are used. The average values

Table 4-1. ECP, CCP, and other analytical data for Tank 38H and 43H samples. Averages and RSD values are of duplicate measurements

analyte	method	units	HTF-38-14-6		HTF-38-14-7		HTF-43-14-8		HTF-43-14-9	
			average	RSD	average	RSD	average	RSD	average	RSD
density @18°C	grav.	g/mL	1.215	1.5%	1.240	0.2%	1.150	0.3%	1.160	0.2%
U-233	ICP-MS	mg/L	< 2.01E-02	--	< 2.06E-02	--	< 2.09E-02	--	< 2.07E-02	--
U-234	ICP-MS	mg/L	< 2.01E-02	--	< 2.06E-02	--	< 2.09E-02	--	< 2.07E-02	--
U-235	ICP-MS	mg/L	4.75E-01	0.8%	5.01E-01	1.2%	3.14E-01	0.6%	3.34E-01	4.3%
U-236	ICP-MS	mg/L	2.87E-02	5.4%	2.81E-02	0.2%	≤ 2.35E-02	16%	< 2.07E-02	--
U-238	ICP-MS	mg/L	7.84E+01	0.3%	8.46E+01	3.4%	5.28E+01	4.3%	5.53E+01	1.7%
Total U	calc.	mg/L	7.89E+01	0.3%	8.51E+01	3.3%	5.31E+01	4.3%	5.56E+01	1.7%
U-235 / U	calc.	%	0.60%	1.2%	0.59%	2.1%	0.59%	3.7%	0.60%	2.6%
Pu-238	PuTTA	mg/L	3.32E-04	0.4%	3.32E-04	3.8%	2.18E-04	4.6%	2.21E-04	4.2%
		dpm/mL	1.26E+04		1.26E+04		8.27E+03		8.38E+03	
Pu-239 [a]	PuTTA	mg/L	4.84E-03	6.8%	4.76E-03	1.9%	3.36E-03	1.3%	3.45E-03	4.5%
Pu-239/240	PuTTA	dpm/mL	6.68E+02		6.57E+02		4.64E+02		4.76E+02	
Pu-241	Pu238/41	mg/L	1.07E-05	3.7%	1.05E-05	11%	6.16E-06	6.3%	6.98E-06	3.4%
		dpm/mL	2.45E+03		2.39E+03		1.41E+03		1.60E+03	
Tc-99	ICP-MS	mg/L	9.59E-01	1.3%	8.91E-01	1.9%	6.21E-01	4.2%	6.34E-01	8.2%
		pCi/mL	1.63E+04		1.51E+04		1.05E+04		1.07E+04	
Cs-137	gamma scan	dpm/mL	7.87E+07	4.0%	8.15E+07	0.9%	5.19E+07	1.1%	5.46E+07	2.2%
Ba-137m			7.46E+07		7.72E+07		4.92E+07		5.17E+07	
Sr-90 [b]	Sr-90	dpm/mL	n.d.	--	n.d.	--	1.63E+06	--	1.80E+06	--
OH^-	titration	M	2.39E+00	0.8%	2.54E+00	1.7%	1.50E+00	0.3%	1.60E+00	0.6%
NO_2^-	IC	M	1.52E+00	1.9%	1.51E+00	0.9%	9.74E-01	1.5%	1.06E+00	0.0%
NO_3^-	IC	M	8.56E-01	0.9%	8.66E-01	0.9%	5.38E-01	5.9%	5.52E-01	0.3%
F^-	IC	M	< 3.19E-03	--	< 3.16E-03	--	< 3.17E-03	--	< 3.19E-03	--
CHO_2^-	IC	M	3.23E-02	1.5%	3.23E-02	0.3%	2.05E-02	4.7%	2.23E-02	0.1%
Cl^-	IC	M	4.04E-03	0.5%	4.62E-03	1.6%	2.17E-03	4.4%	2.34E-03	0.8%
PO_4^{3-}	IC	M	< 3.19E-03	--	< 3.16E-03	--	< 3.17E-03	--	< 3.19E-03	--
SO_4^{2-}	IC	M	1.83E-02	1.8%	1.85E-02	0.4%	1.16E-02	3.6%	1.25E-02	0.3%
$C_2O_4^{2-}$	IC	M	1.86E-03	0.1%	1.80E-03	0.9%	1.26E-03	6.2%	1.27E-03	3.7%
Br^-	IC	M	< 3.79E-03	--	< 3.76E-03	--	< 3.77E-03	--	< 3.79E-03	--
CO_3^{2-}	TIC/TOC	M	3.85E-01	0.8%	4.08E-01	3.1%	2.32E-01	1.1%	2.46E-01	0.1%
TOC	TIC/TOC	mg C/L	4.89E+02	1.3%	5.02E+02	1.7%	2.93E+02	1.2%	3.17E+02	1.0%
SVOA [b]	SVOA	mg/L	n.d.	--	n.d.	--	< 6.0E+00	--	< 6.0E+00	--

calc. = calculation; n.d. = not determined; [a] Pu-239 mass assumes entire Pu-239/240 activity is Pu-239; [b] single measurement

Table 4-2. Results of triplicate preparations of Tank 38H and 43H subsurface samples.

analyte	method	units	HTF-38-14-7		HTF-43-14-9	
			average	RSD	average	RSD
Al	ICP-ES	mg/L	8.49E+02	1.7%	5.35E+02	0.3%
		M	3.15E-02		1.98E-02	
B	ICP-ES	mg/L	1.33E+02	1.1%	9.08E+01	0.5%
Ca	ICP-ES	mg/L	3.34E+00	7.2%	3.36E+00	43%
Cr	ICP-ES	mg/L	3.85E+01	1.2%	2.60E+01	0.9%
Fe	ICP-ES	mg/L	7.09E+00	12%	5.23E+00	28%
K	ICP-ES	mg/L	3.59E+02	1.4%	2.37E+02	6.4%
Li	ICP-ES	mg/L	6.46E+01	3.2%	4.69E+01	0.2%
Mg	ICP-ES	mg/L	1.72E-01	12%	3.32E-01	78%
Na	ICP-ES	mg/L	1.26E+05	2.1%	8.30E+04	0.1%
		M	5.50E+00		3.61E+00	
P	ICP-ES	mg/L	1.08E+02	4.7%	7.20E+01	2.7%
S	ICP-ES	mg/L	8.10E+02	3.7%	< 7.90E+02	--
Si	ICP-ES	mg/L	2.20E+02	1.6%	1.49E+02	1.6%
		M	7.83E-03		5.30E-03	
Zn	ICP-ES	mg/L	3.96E+00	5.0%	2.83E+00	4.0%

and the relative standard deviations (RSD) are reported for the replicate sample preparations and measurements. The RSD values are not reported when all measurements are below the limits of quantification.

The Pu-239 value reported in mg/L for the ECP analysis assumes that all of the activity measured as Pu-239/240 is from Pu-239. This assumption results in a high bias to the Pu-239 result and thus the assumption is conservative with respect to concentration of this fissile isotope.

Uranium-235 percentage enrichment, calculated as the U-235 mass divided by the total U mass multiplied by 100%, ranged from 0.59% to 0.60%. Uranium concentration ranged from 53.1 mg/L in the Tank 43H surface sample to the 85.1 mg/L in the Tank 38H subsurface sample. The uranium enrichment and concentration are in line with the prior 2H-evaporator ECP samples.[6]

Density, anions, plutonium and gamma results are in line with the previous set of 2H-evaporator system samples from August 2013.[6] However, the samples from August 2013 were more dilute than the previous Tank 38H and 43H samples.

Strontium-90 was measured in the Tank 43H samples to gain a more complete understanding of the beta and gamma emitting isotopes that may be contributing to the elevated dose levels in the evaporator overheads. Sr-90 was present in Tank 43H at approximately 3% of the activity level of Cs-137.

SVOA was performed on the Tank 43H samples to investigate the presence of organics that may be contributing to foaming in the 2H-evaporator system. No semi-volatile organic compounds were measured above the detection limit of 6 mg/L in the Tank 43H samples. Approximately 87% and 94% of the TOC in the Tank 38H and43H samples, respectively, can be accounted for by the concentration of carbon in the measured oxalate and formate, which indicates that there is not an appreciable amount of an unidentified organic compound present.

Table 4-2 contains the elemental results measured for the warm acid strike preparations of the Tank 38H and 43H subsurface samples. Results are only reported from ICP-ES for analytes where results are above the detection limit for at least one of the samples.

Silicon in Tank 38H and 43H supernate samples measured 220 mg/L and 149 mg/L, respectively. This is a reduction in silicon concentration from the April 2013 Tank 38H and 43H samples (290 mg/L and 217 mg/L, respectively) and are at the low end of silicon concentrations measured in Tank 38H and 43H samples from the time period of January 2010 through present.[7] For the Tank 43H samples, the aluminum (0.0198 M), sodium (3.61 M), and density (1.16 g/mL) are all trending downward and are significantly below the range of measurements for the samples from January 2010 through April 2013.

Figure 4-1 contains a plot of the silicon concentrations in the current sub-surface samples from January 15, 2014 compared with previous Tank 38H and 43H samples from January 2010 through April 2013. Figure 4-2 shows similar trends for hydroxide and aluminum. The error bars on the concentrations are the 95% two-sided confidence intervals for the replicate preparations and analyses.

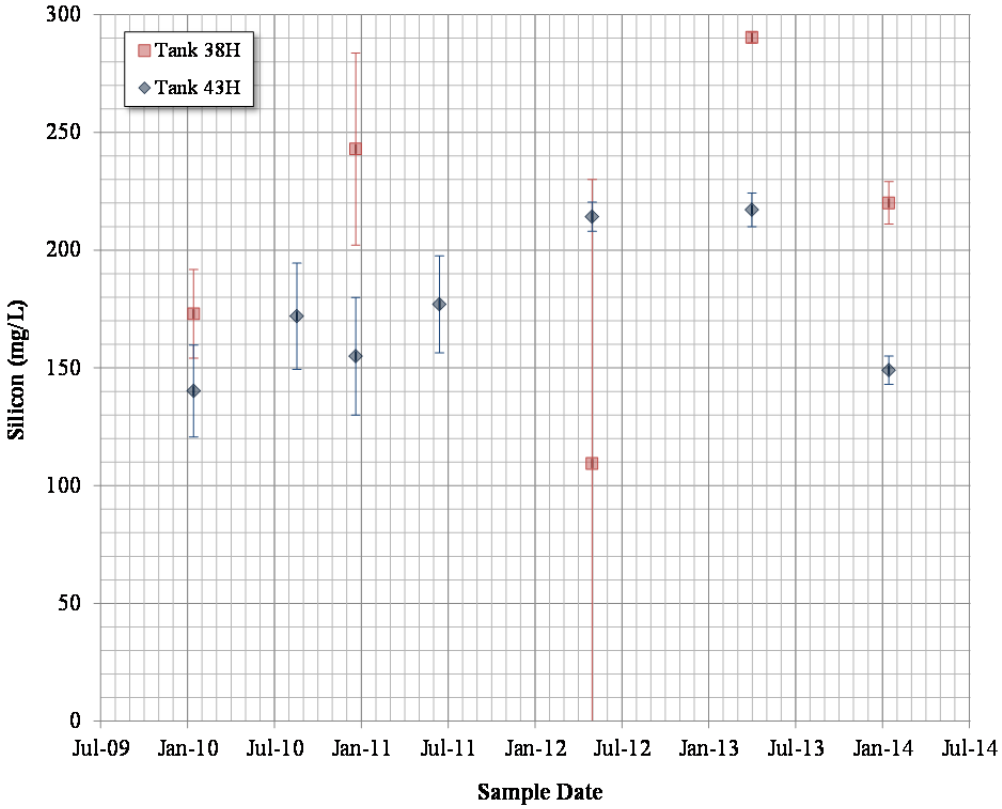

Figure 4-1. Silicon concentrations in Tank 38H and 43H subsurface samples

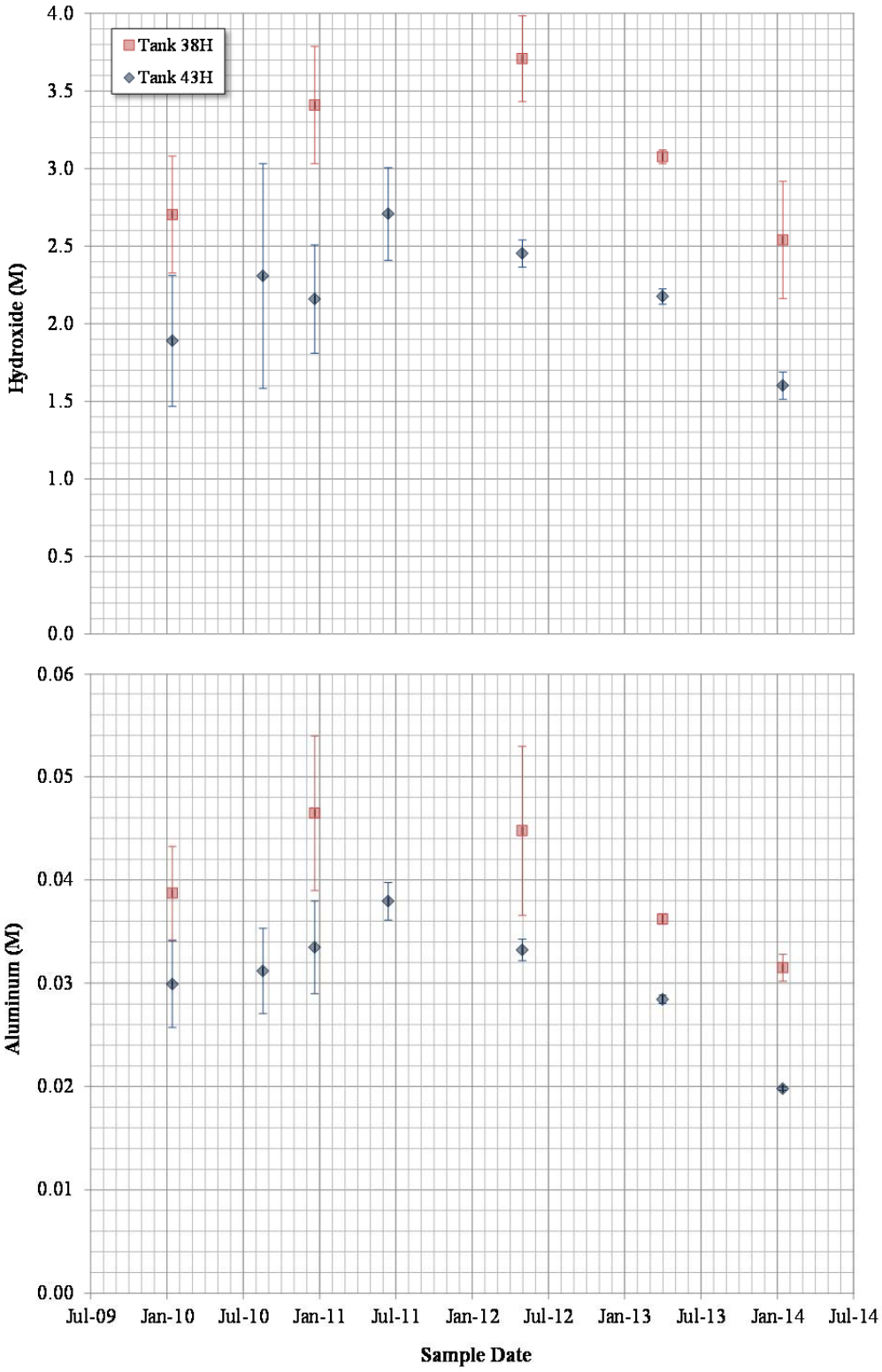

Figure 4-2. Hydroxide and aluminum concentrations in Tank 38H and 43H subsurface samples

The 50 mg/L standards used for the silicon analysis (50 mg/L silicon in solution prepared by warm acid strike to three final concentrations of 0.5, 1.0, and 2.0 mg/L for the instrument) were measured as 54, 89, and 60 mg/L, respectively. Thus, the silicon standards showed a potential high bias in the silicon measurements of an average of 17 mg/L or ~35%, which is beyond the 10% method uncertainty. The silicon concentration was below the detectible level in the process blank.

For the subsurface samples, the measured anions and cations are in good agreement, with the sum of the anions approximately 6% higher than the sodium molarity. Anions in HTF-38-14-7 summed to 5.84 M versus the sodium measurement of 5.50 M. Anions in HTF-43-14-9 summed to 3.78 M versus the sodium measurement of 3.61 M.

Nominal 1σ method uncertainties are 10% for IC, ICP-ES,TIC/TOC and OH^-; 5% for Pu-238 and gamma scan; 7% for Pu-239/240, 16% for Pu-241and Sr-90; and 20% for ICP-MS.

5.0 Conclusions

SRNL performed analysis on Tanks 38H and 43H surface and subsurface supernate samples to support ECP and CCP. The U-235 mass divided by the total U mass ranged from 0.0059 to 0.0060. Uranium concentration ranged from 53.1 mg/L in the Tank 43H surface sample to the 85.1 mg/L in the Tank 38H subsurface sample. The U-235/U and uranium concentration are in line with the prior 2H-Evaporator System ECP samples.

For the Tank 43H samples, the aluminum (0.0198 M), sodium (3.61 M), and density (1.16 g/mL) are all trending downward and are significantly below the range of measurements for the Tank 43H samples from January 2010 through April 2013. The measured silicon (149 mg/L) and hydroxide (1.60 M) are at the low end of the range of Tank 43H measurements over that period.

In analyses performed to support 2H evaporator foaming and carryover recovery, Sr-90 measured 1.63×10^6 and 1.80×10^6 dpm/mL in Tank 43H surface and subsurface samples, respectively. Measurement of the semi-volatile organic compounds suspected of contributing to foaming revealed that all were below the detection limit of 6 mg/L in the Tank 43H samples.

6.0 Quality Assurance

Data are recorded in the electronic laboratory notebook system as notebook/experiment number A6583-00032-40. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 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.

7.0 Acknowledgements

I acknowledge the contributions of Nan Stanley for preparing the samples, and Chuck Coleman, Mark Jones, Tom White, Amy Ekechukwu, David DiPrete, Mira Malek, and John Young for providing analytical services.

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