We put science to work.™

Savannah River
National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Evaporator Feed Qualification Analysis of Tank 38H and 43H Samples: January 2010 through April 2013

C. J. Martino
C. J. Coleman

August 2013

SRNL-STI-2012-00464, Revision 0

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2012-00464
Revision 0

Keywords:
Sodium Aluminosilicate, Evaporator Scale, Characterization

Retention: *Permanent*

Evaporator Feed Qualification Analysis of Tank 38H and 43H Samples: January 2010 through April 2013

C. J. Martino
C. J. Coleman

August 2013

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

REVIEWS AND APPROVALS

AUTHORS:

C. J. Martino, Advanced Characterization and Processing Date

C. J. Coleman, Analytical Development, Spectroscopy and Separations Date

TECHNICAL REVIEW:

M. S. Hay, Advanced Characterization and Processing Date

APPROVALS:

F. M. Pennebaker, Manager Date
Advanced Characterization and Processing

S. L. Marra, Manager Date
Environmental & Chemical Process Technology Research Programs

D. J. Martin, Manager Date
Tank Farm/ETP Process Engineering

EXECUTIVE SUMMARY

This report provides the results of analyses that focused on the chemical species that pertain to the sodium aluminosilicate formation potential for archived Tank 38H and 43H subsurface samples from January 2010 through April 2013. Analyses included warm acid strike preparation followed by analysis of silicon, aluminum, and sodium and water dilution preparation followed by analysis for anions.

The Tank 43H and 38H supernatant liquid silicon measurements for the January 2010 through April 2013 time period exhibit a slight increasing trend. Over this time period, the silicon concentration in the Tank 43H and Tank 38H samples averaged 179 mg/L and 235 mg/L, respectively.

Comparison of Tank 43H sample results from 2005 through April 2013 to the previously developed process control models indicates that the current formation of sodium aluminosilicate in the 2H system is due to the seeded direct precipitation of cancrinite and sodalite.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CI	Confidence Interval
EFQ	Evaporator Feed Qualification
HTF	H Tank Farm
IC	Ion Chromatography
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

1.0 Introduction

Savannah River Remediation (SRR) periodically samples from two locations (one from the liquid surface and one from the sub-surface) within the 2H-Evaporator feed tank (Tank 43H) and drop tank (Tank 38H). The Savannah River National Laboratory (SRNL) analyzes the samples per the requirements Nuclear Criticality Safety Evaluation for operation of the 2H Evaporator[1] and the Corrosion Control program. SRR has requested that SRNL on a yearly basis analyze the subsurface samples from Tank 38H and 43H for the remaining Evaporator Feed Qualification (EFQ) analytes that are required for the 2F- and 3H-Evaporator systems.[2] For the 2F and 3H systems, the measurement of silicon, aluminum, sodium, hydroxide, and ionic strength provide the information required to judge the sodium aluminosilicate formation potential. The EFQ program currently uses the method adapted by Wilmarth for the application of Gasteger's sodium aluminosilicate solubility data to the SRS HLW evaporator systems.[3,4,5]

This report documents the analytical results that pertain to sodium aluminosilicate formation potential for archived Tank 38H and 43H sub-surface samples from January 2010 through April 2013, as outlined in the Task Technical and Quality Assurance Plan (TTQAP) for the project.[6] Through previous efforts using a wider range of sodium aluminosilicate solubility data, SRNL developed a series of process control models for sodium aluminosilicate formation potential in SRS HLW evaporators.[7,8 9,10] This report uses the most recently issued process control model as a basis for comparison of the relative sodium aluminosilicate formation potential of the Tank 38H and 43H samples. This analysis discusses the applicability of the process control model to the 2H-evaporator system, which is seeded with sodium aluminosilicate solids.

2.0 Samples

Samples used in this study include HTF-38-10-8 and HTF-43-10-10;[11] HTF-43-10-113;[12] HTF-38-10-178 and HTF-43-10-180;[13] HTF-43-11-72;[14] HTF-38-12-52 and HTF-43-12-54,[15] and HTF-38-13-48 and HTF-43-13-50.[16] This analysis was limited to subsurface samples rather than the surface samples, as the subsurface samples would be more representative of material sent to the evaporator. Several Tank 38H samples with excessive insoluble solids were excluded from this analysis. The exception is sample HTF-38-12-52, which contained excessive insoluble solids in the bulk material but supernatant liquid was decanted for analysis. Table 2-1 contains sample details including sampling location, sampling date, and the previously reported specific gravity (SpG). The SpG data are averages of duplicate measurements with standard deviations in parentheses. SpG measurements were determined as the density of the sample material at the SRNL shielded cell temperature normalized to the density of water at the same temperature. For the purpose of this report, SpG is used interchangeably with the Tank 38H and 43H material density (ρ, in g/mL).

Table 2-1: Tank 38H and 43H Analytical Samples

Sample Name	Tank	Tank Location	Date Sampled	Specific Gravity
HTF-38-10-8	38H	Supernatant liquid mid-height	1/14/2010	1.259 (0.003)
HTF-43-10-10	43H	Pump suction height	1/14/2010	1.198 (0.003)
HTF-43-10-113	43H	Pump suction height	8/19/2010	1.231 (0.009)
HTF-38-10-178	38H	Supernatant liquid mid-height	12/21/2010	1.313 (0.010)
HTF-43-10-180	43H	Pump suction height	12/21/2010	1.253 (0.011)
HTF-43-11-72	43H	Pump suction height	6/15/2011	1.264 (0.013)
HTF-38-12-52	38H	Supernatant liquid mid-height	5/1/2012	1.348 (0.011)
HTF-43-12-54	43H	Pump suction height	5/1/2012	1.238 (0.001)
HTF-38-13-48	38H	Supernatant liquid mid-height	4/2/2013	1.291 (0.004)
HTF-43-13-50	43H	Pump suction height	4/2/2013	1.221 (0.003)

3.0 Experimental Procedure

Two preparation methods were used on sub-samples of the original material. The first method was the 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.[17] In addition to a dissolution blank, three silicon standards and a matrix blank were prepared in parallel to sample processing. After the dissolution process, neither the samples nor the standards contained visible solids. Following the warm acid dissolution preparations, inductively coupled plasma – emission spectroscopy (ICP-ES) was used to determine sodium, aluminum, and silicon.

The second sample preparation method was dilution with deionized water, which was performed in triplicate and yielded an approximately 10-fold dilution. The water dilution preparations were analyzed for hydroxide by titration, for anions by ion chromatography (IC), and for carbonate by total inorganic carbon (TIC).

4.0 Analytical Results

Table 4-1 through Table 4-8 contain the analytical results for the EFQ analysis of the Tank 38H and 43H samples. The tables contain the results of the three individual sample preparations and measurements and the averages and standard deviations of the determinations. Values proceeded by "<" are the detection limits for the cases where analytes were not present at detectable levels.

Assuming that the measurements do not contain biases or systematic errors, the reported standard deviations reflect a combination of the variances in subsampling, analytical preparations, and measurements. For some analytes, the standard deviations were used to calculate the 95% confidence intervals (CI) bounding the true averages. Table 4–11 contains a summary of the average and 95% CI for sodium, hydroxide, aluminum, and silicon measurements for the Tank 38H and 43H samples. Figure 4-1 contains a plot of the silicon concentration for the samples analyzed. The error bars on the silicon concentrations are the two-sided 95% CI for the silicon measurement averages, based on replicate warm acid strike preparations and analyses.

As seen in Table 4-7, the silicon results for the supernatant portion of sample HTF-38-12-52 were scattered and are not considered to be reliable. Thus, the results for HTF-38-12-52 supernatant are not considered in the data summary and in the subsequent model comparisons.

Excluding sample HTF-38-12-52 supernatant, the Tank 43H and 38H silicon measurements for the January 2010 through April 2013 time period exhibited an increasing trend. Over this time period, the silicon concentration in the Tank 43H samples averaged 179 mg/L, with a low of 140 ± 20 mg/L in the January 2010 sample and a high of 217 ± 7 mg/L in the April 2013 sample. Silicon measurements for the Tank 38H samples averaged 235 mg/L with a high of 290 ± 2 mg/L in the April 2013 sample.

Several of the previous samples from Tanks 38H and 43H that were sent to SRNL for silicon analysis were routed to SRNL from F/H Laboratory because the samples contained solids. Such samples are not a very good basis for soluble silicon comparison because they may contain significant levels of insoluble silicon compounds that would not be intentionally sent to the evaporator. One previous set of Tank 38H and 43H samples analyzed by SRNL, samples HTF-38-07-24 and HTF-43-07-23 from February 2007, contained only small amounts of visible insoluble solids (similar to those analyzed in this report) and thus are valid for use in comparison.[18] Measurements of silicon in those 2007 samples showed 265 mg/L of silicon for Tank 38H and 184 mg/L for Tank 43H, which compare very well with the range of silicon measurements for the January 2010 to April 2013 samples.

As part of the quality control for the warm acid strike preparation methods, sub-samples of a stock solution containing 50 mg/L of soluble silicon was diluted to 0.5 mg/L, 1.0 mg/L and 2.0 mg/L and analyzed in parallel with the tank samples. The results of the analysis of the silicon standards are contained in Table 4-12. Based on the results of these standards, silicon analysis of the May 2012 samples may contain a slight high bias.

Trends in concentrations of hydroxide and aluminum in the Tank 38H and 43H samples are presented in Figure 4-2. The trends and relative change in magnitude of hydroxide and aluminum have mirrored each other over the period of this sample analysis.

Table 4-1: Analysis results for Tank 38H sample HTF-38-10-8

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	3.69E-02	4.05E-02	3.88E-02	3.87E-02	1.8E-03
Na	ICP-ES	M	5.86E+00	6.52E+00	6.46E+00	6.28E+00	3.6E-01
Si	ICP-ES	M	5.87E-03	6.41E-03	6.19E-03	6.16E-03	2.7E-04
		mg/L	1.65E+02	1.80E+02	1.74E+02	1.73E+02	8E+00
OH^-	titration	M	2.82E+00	2.76E+00	2.53E+00	2.70E+00	1.5E-01
CO_3^{2-}	TIC	M	4.28E-01	4.31E-01	4.23E-01	4.27E-01	4E-03
SO_4^{2-}	IC	M	1.88E-02	1.85E-02	1.82E-02	1.85E-02	3E-04
$C_2O_4^{2-}$	IC	M	<1.27E-03	<1.35E-03	<1.37E-03	<1.33E-03	--
PO_4^{3-}	IC	M	3.40E-03	3.50E-03	3.30E-03	3.40E-03	1.0E-04
NO_3^-	IC	M	1.14E+00	1.07E+00	1.17E+00	1.13E+00	5E-02
NO_2^-	IC	M	1.25E+00	1.26E+00	1.27E+00	1.26E+00	9E-03
Cl^-	IC	M	<3.15E-03	<3.35E-03	<3.40E-03	<3.30E-03	--
F^-	IC	M	<5.87E-03	<6.25E-03	<6.35E-03	<6.16E-03	--
CHO_2^-	IC	M	3.52E-02	3.51E-02	3.40E-02	3.48E-02	6E-04
Anions	sum	N	6.19E+00	6.07E+00	5.93E+00	6.06E+00	1.3E-01

Table 4-2: Analysis results for Tank 43H sample HTF-43-10-10

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	2.82E-02	3.16E-02	2.99E-02	2.99E-02	1.7E-03
Na	ICP-ES	M	4.91E+00	4.95E+00	4.98E+00	4.94E+00	3E-02
Si	ICP-ES	M	4.73E-03	5.29E-03	4.95E-03	4.99E-03	2.8E-04
		mg/L	1.33E+02	1.49E+02	1.39E+02	1.40E+02	8E+00
OH^-	titration	M	1.89E+00	2.06E+00	1.72E+00	1.89E+00	1.7E-01
CO_3^{2-}	TIC	M	3.30E-01	3.67E-01	3.27E-01	3.41E-01	2.2E-02
SO_4^{2-}	IC	M	1.42E-02	1.59E-02	1.40E-02	1.47E-02	1.1E-03
$C_2O_4^{2-}$	IC	M	<1.23E-03	<1.11E-03	1.25E-03	<1.20E-03	--
PO_4^{3-}	IC	M	2.62E-03	2.99E-03	2.90E-03	2.84E-03	1.9E-04
NO_3^-	IC	M	8.83E-01	1.01E+00	7.12E-01	8.70E-01	1.52E-01
NO_2^-	IC	M	9.51E-01	1.10E+00	1.12E+00	1.06E+00	9E-02
Cl^-	IC	M	<3.05E-03	<2.76E-03	<3.10E-03	<2.97E-03	--
F^-	IC	M	<5.70E-03	<5.15E-03	<5.79E-03	<5.55E-03	--
CHO_2^-	IC	M	2.62E-02	3.07E-02	2.66E-02	2.78E-02	2.5E-03
Anions	sum	N	4.48E+00	5.01E+00	4.30E+00	4.60E+00	3.7E-01

Table 4-3: Analysis results for Tank 43H sample HTF-43-10-113

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	2.98E-02	3.30E-02	3.08E-02	3.12E-02	1.7E-03
Na	ICP-ES	M	5.41E+00	5.32E+00	5.62E+00	5.45E+00	1.6E-01
Si	ICP-ES	M	5.87E-03	6.49E-03	6.00E-03	6.12E-03	3.2E-04
		mg/L	1.65E+02	1.82E+02	1.69E+02	1.72E+02	9E+00
OH^-	titration	M	1.98E+00	2.54E+00	2.39E+00	2.31E+00	2.9E-01
CO_3^{2-}	TIC	M	3.69E-01	3.71E-01	3.66E-01	3.69E-01	2E-03
SO_4^{2-}	IC	M	1.53E-02	1.48E-02	1.47E-02	1.49E-02	4E-04
$C_2O_4^{2-}$	IC	M	1.41E-03	1.28E-03	1.39E-03	1.36E-03	7E-05
PO_4^{3-}	IC	M	3.00E-03	2.97E-03	2.97E-03	2.98E-03	2E-05
NO_3^-	IC	M	8.25E-01	9.36E-01	8.55E-01	8.72E-01	5.7E-02
NO_2^-	IC	M	1.35E+00	1.53E+00	1.42E+00	1.43E+00	9E-02
Cl^-	IC	M	<3.49E-03	<2.65E-03	<3.46E-03	<3.20E-03	--
F^-	IC	M	<6.52E-03	<4.94E-03	<6.46E-03	<5.97E-03	--
CHO_2^-	IC	M	2.94E-02	3.00E-02	2.92E-02	2.96E-02	4E-04
Anions	sum	N	5.00E+00	5.85E+00	5.50E+00	5.45E+00	4.3E-01

Table 4-4: Analysis results for Tank 38H sample HTF-38-10-178

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	4.86E-02	4.78E-02	4.30E-02	4.65E-02	3.0E-03
Na	ICP-ES	M	7.60E+00	8.51E+00	7.48E+00	7.86E+00	5.6E-01
Si	ICP-ES	M	9.12E-03	8.84E-03	7.99E-03	8.65E-03	5.8E-04
		mg/L	2.56E+02	2.48E+02	2.25E+02	2.43E+02	1.6E+01
OH^-	titration	M	3.57E+00	3.40E+00	3.26E+00	3.41E+00	1.5E-01
CO_3^{2-}	TIC	M	5.42E-01	5.60E-01	5.36E-01	5.46E-01	1.3E-02
SO_4^{2-}	IC	M	2.64E-02	2.42E-02	2.45E-02	2.50E-02	1.2E-03
$C_2O_4^{2-}$	IC	M	2.05E-03	2.22E-03	1.87E-03	2.05E-03	1.7E-04
PO_4^{3-}	IC	M	4.19E-03	4.63E-03	3.97E-03	4.26E-03	3.4E-04
NO_3^-	IC	M	1.25E+00	1.18E+00	1.47E+00	1.30E+00	1.5E-01
NO_2^-	IC	M	2.10E+00	1.99E+00	2.46E+00	2.18E+00	2.5E-01
Cl^-	IC	M	<3.40E-03	<3.44E-03	<3.32E-03	<3.39E-03	--
F^-	IC	M	<6.35E-03	<6.43E-03	<6.20E-03	<6.33E-03	--
CHO_2^-	IC	M	4.82E-02	4.48E-02	4.56E-02	4.62E-02	1.8E-03
Anions	sum	N	8.17E+00	7.84E+00	8.42E+00	8.14E+00	2.9E-01

Table 4-5: Analysis results for Tank 43H sample HTF-43-10-180

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	3.53E-02	3.35E-02	3.17E-02	3.35E-02	1.8E-03
Na	ICP-ES	M	5.72E+00	6.05E+00	5.89E+00	5.89E+00	1.6E-01
Si	ICP-ES	M	5.89E-03	5.49E-03	5.18E-03	5.52E-03	3.6E-04
		mg/L	1.65E+02	1.54E+02	1.45E+02	1.55E+02	1.0E+01
OH^-	titration	M	2.31E+00	2.12E+00	2.04E+00	2.16E+00	1.4E-01
CO_3^{2-}	TIC	M	3.91E-01	3.91E-01	4.43E-01	4.08E-01	3.0E-02
SO_4^{2-}	IC	M	1.72E-02	1.69E-02	1.74E-02	1.72E-02	3E-04
$C_2O_4^{2-}$	IC	M	1.88E-03	1.72E-03	1.49E-03	1.70E-03	1.9E-04
PO_4^{3-}	IC	M	3.95E-03	3.53E-03	3.02E-03	3.50E-03	4.6E-04
NO_3^-	IC	M	9.60E-01	8.79E-01	9.61E-01	9.33E-01	4.7E-02
NO_2^-	IC	M	1.64E+00	1.50E+00	1.64E+00	1.59E+00	8E-02
Cl^-	IC	M	<3.11E-03	<3.05E-03	<3.37E-03	<3.18E-03	--
F^-	IC	M	<5.80E-03	<5.69E-03	<6.29E-03	<5.93E-03	--
CHO_2^-	IC	M	3.21E-02	3.24E-02	3.45E-02	3.30E-02	1.3E-03
Anions	sum	N	5.81E+00	5.39E+00	5.64E+00	5.62E+00	2.1E-01

Table 4-6: Analysis results for Tank 43H sample HTF-43-11-72

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	3.75E-02	3.88E-02	3.76E-02	3.79E-02	7E-04
Na	ICP-ES	M	5.88E+00	6.87E+00	6.93E+00	6.56E+00	5.9E-01
Si	ICP-ES	M	6.62E-03	6.26E-03	6.03E-03	6.30E-03	3.0E-04
		mg/L	1.86E+02	1.76E+02	1.69E+02	1.77E+02	8E+00
OH^-	titration	M	2.85E+00	2.64E+00	2.64E+00	2.71E+00	1.2E-01
CO_3^{2-}	TIC	M	4.60E-01	4.39E-01	4.61E-01	4.53E-01	1.2E-02
SO_4^{2-}	IC	M	2.06E-02	1.86E-02	1.83E-02	1.92E-02	1.2E-03
$C_2O_4^{2-}$	IC	M	1.71E-03	2.17E-03	1.86E-03	1.91E-03	2.3E-04
PO_4^{3-}	IC	M	3.77E-03	4.90E-03	3.97E-03	4.21E-03	6.0E-04
NO_3^-	IC	M	1.09E+00	1.04E+00	1.04E+00	1.06E+00	3E-02
NO_2^-	IC	M	1.84E+00	1.77E+00	1.73E+00	1.78E+00	6E-02
Cl^-	IC	M	<2.66E-03	<3.36E-03	<3.55E-03	<3.19E-03	--
F^-	IC	M	<4.96E-03	<6.28E-03	<6.62E-03	<5.95E-03	--
CHO_2^-	IC	M	3.75E-02	3.23E-02	3.63E-02	3.54E-02	2.7E-03
Anions	sum	N	6.83E+00	6.45E+00	6.46E+00	6.58E+00	2.2E-01

Table 4-7: Analysis results for supernatant portion of Tank 38H sample HTF-38-12-52

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	4.10E-02	4.64E-02	4.69E-02	4.48E-02	3.3E-03
Na	ICP-ES	M	7.51E+00	9.15E+00	9.26E+00	8.64E+00	9.8E-01
Si	ICP-ES	M	5.86E-03	2.59E-03	3.23E-03	3.89E-03	1.7E-03
		mg/L	1.64E+02	7.28E+01	9.09E+01	1.09E+02	4.9E+01
OH^-	titration	M	3.79E+00	3.63E+00	--	3.71E+00	1.1E-01
CO_3^{2-}	TIC	M	5.97E-01	6.03E-01	--	6.00E-01	4E-03
SO_4^{2-}	IC	M	3.44E-02	3.16E-02	--	3.30E-02	2.0E-03
$C_2O_4^{2-}$	IC	M	3.17E-03	3.43E-03	--	3.30E-03	1.8E-04
PO_4^{3-}	IC	M	4.29E-03	5.13E-03	--	4.71E-03	5.9E-04
NO_3^-	IC	M	1.31E+00	1.43E+00	--	1.37E+00	8E-02
NO_2^-	IC	M	2.25E+00	2.22E+00	--	2.23E+00	2E-02
Cl^-	IC	M	4.84E-03	3.27E-03	--	4.06E-03	1.11E-03
F^-	IC	M	<5.65E-03	<6.10E-03	--	<5.88E-03	--
CHO_2^-	IC	M	4.77E-02	4.59E-02	--	4.68E-02	1.3E-03
Anions	sum	N	8.72E+00	8.66E+00	--	8.69E+00	5E-02

Table 4-8: Analysis results for Tank 43H sample HTF-43-12-54

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	3.36E-02	3.33E-02	3.28E-02	3.32E-02	4.2E-04
Na	ICP-ES	M	6.30E+00	6.35E+00	6.14E+00	6.26E+00	1.1E-01
Si	ICP-ES	M	7.63E-03	7.71E-03	7.54E-03	7.63E-03	8.8E-05
		mg/L	2.14E+02	2.17E+02	2.12E+02	2.14E+02	2.5E+00
OH^{-}	titration	M	2.48E+00	2.43E+00	--	2.45E+00	4E-02
CO_3^{2-}	TIC	M	3.70E-01	3.69E-01	--	3.69E-01	9E-04
SO_4^{2-}	IC	M	1.85E-02	2.42E-02	--	2.14E-02	4.0E-03
$C_2O_4^{2-}$	IC	M	2.52E-03	2.81E-03	--	2.67E-03	2.0E-04
PO_4^{3-}	IC	M	2.92E-03	3.79E-03	--	3.35E-03	6.1E-04
NO_3^{-}	IC	M	9.22E-01	1.08E+00	--	1.00E+00	1.1E-01
NO_2^{-}	IC	M	1.43E+00	1.67E+00	--	1.55E+00	1.7E-01
Cl^{-}	IC	M	3.13E-03	3.49E-03	--	3.31E-03	2.5E-04
F^{-}	IC	M	<5.85E-03	<5.91E-03	--	<5.88E-03	--
CHO_2^{-}	IC	M	3.01E-02	3.99E-02	--	3.50E-02	7.0E-03
Anions	sum	N	5.69E+00	6.06E+00	--	5.87E+00	2.6E-01

Table 4-9: Analysis results for Tank 38H sample HTF-38-13-48

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	3.62E-02	3.64E-02	3.60E-02	3.62E-02	2E-04
Na	ICP-ES	M	7.57E+00	7.78E+00	7.62E+00	7.66E+00	1.1E-01
Si	ICP-ES	M	1.04E-02	1.03E-02	1.03E-02	1.03E-02	3E-05
		mg/L	2.91E+02	2.90E+02	2.89E+02	2.90E+02	9E-01
OH^-	titration	M	3.06E+00	3.09E+00	3.08E+00	3.08E+00	2E-02
CO_3^{2-}	TIC	M	4.54E-01	4.51E-01	--	4.52E-01	2E-03
SO_4^{2-}	IC	M	2.37E-02	2.36E-02	2.34E-02	2.36E-02	2E-04
$C_2O_4^{2-}$	IC	M	2.89E-03	2.80E-03	2.75E-03	2.81E-03	7E-05
PO_4^{3-}	IC	M	< 1.22E-03	< 1.18E-03	< 1.22E-03	< 1.20E-03	--
NO_3^-	IC	M	1.15E+00	1.16E+00	1.16E+00	1.16E+00	5E-03
NO_2^-	IC	M	1.95E+00	1.95E+00	1.97E+00	1.95E+00	1E-02
Cl^-	IC	M	4.57E-03	4.42E-03	4.56E-03	4.52E-03	8E-05
F^-	IC	M	< 6.09E-03	< 5.89E-03	< 6.08E-03	< 6.02E-03	--
CHO_2^-	IC	M	4.58E-02	4.65E-02	4.62E-02	4.61E-02	4E-04
Anions	sum	N	7.20E+00	7.23E+00	7.26E+00	7.23E+00	3E-02

Table 4-10: Analysis results for Tank 43H sample HTF-43-13-50

Analyte	Method	Units	Prep 1	Prep 2	Prep 3	Average	Std. Dev.
Al	ICP-ES	M	2.86E-02	2.83E-02	2.85E-02	2.84E-02	2E-04
Na	ICP-ES	M	5.62E+00	5.45E+00	5.63E+00	5.56E+00	1.0E-01
Si	ICP-ES	M	7.80E-03	7.61E-03	7.77E-03	7.73E-03	1.0E-04
		mg/L	2.19E+02	2.14E+02	2.18E+02	2.17E+02	3E+00
OH^-	titration	M	2.19E+00	2.16E+00	--	2.18E+00	2E-02
CO_3^{2-}	TIC	M	3.35E-01	3.31E-01	--	3.33E-01	3E-03
SO_4^{2-}	IC	M	3.01E-02	3.07E-02	--	3.04E-02	5E-04
$C_2O_4^{2-}$	IC	M	1.89E-03	1.90E-03	--	1.90E-03	3E-06
PO_4^{3-}	IC	M	2.34E-03	2.35E-03	--	2.34E-03	4E-06
NO_3^-	IC	M	7.31E-01	7.22E-01	--	7.27E-01	6E-03
NO_2^-	IC	M	1.33E+00	1.32E+00	--	1.33E+00	8E-03
Cl^-	IC	M	< 3.13E-03	< 3.14E-03	--	< 3.14E-03	--
F^-	IC	M	< 5.85E-03	< 5.86E-03	--	< 5.86E-03	--
CHO_2^-	IC	M	3.04E-02	2.99E-02	--	3.02E-02	3E-04
Anions	sum	N	5.05E+00	5.00E+00	--	5.02E+00	4E-02

Table 4-11: Summary of Key Analytical Results

Tank 38H

Sample Name	Na (M)	OH (M)	Al (M)	Si (mg/L)
HTF-38-10-8	6.28 ± 0.91	2.70 ± 0.38	0.0387 ± 0.0045	173 ± 19
HTF-38-10-178	7.86 ± 1.40	3.41 ± 0.38	0.0465 ± 0.0075	243 ± 41
HTF-38-12-52*	8.64 ± 2.44	3.71 ± 0.28	0.0448 ± 0.0082	109 ± 121
HTF-38-13-48	7.66 ± 0.28	3.08 ± 0.04	0.0362 ± 0.0005	290 ± 2

Tank 43H

Sample Name	Na (M)	OH (M)	Al (M)	Si (mg/L)
HTF-43-10-10	4.94 ± 0.08	1.89 ± 0.42	0.0299 ± 0.0042	140 ± 20
HTF-43-10-113	5.45 ± 0.39	2.31 ± 0.72	0.0312 ± 0.0041	172 ± 23
HTF-43-10-180	5.89 ± 0.41	2.16 ± 0.35	0.0335 ± 0.0045	155 ± 25
HTF-43-11-72	6.56 ± 1.46	2.71 ± 0.30	0.0379 ± 0.0018	177 ± 21
HTF-43-12-54	6.26 ± 0.28	2.45 ± 0.32	0.0332 ± 0.0010	214 ± 6
HTF-43-13-50	5.56 ± 0.25	2.18 ± 0.18	0.0284 ± 0.0004	217 ± 7

* decanted liquid analysis for HTF-38-12-52

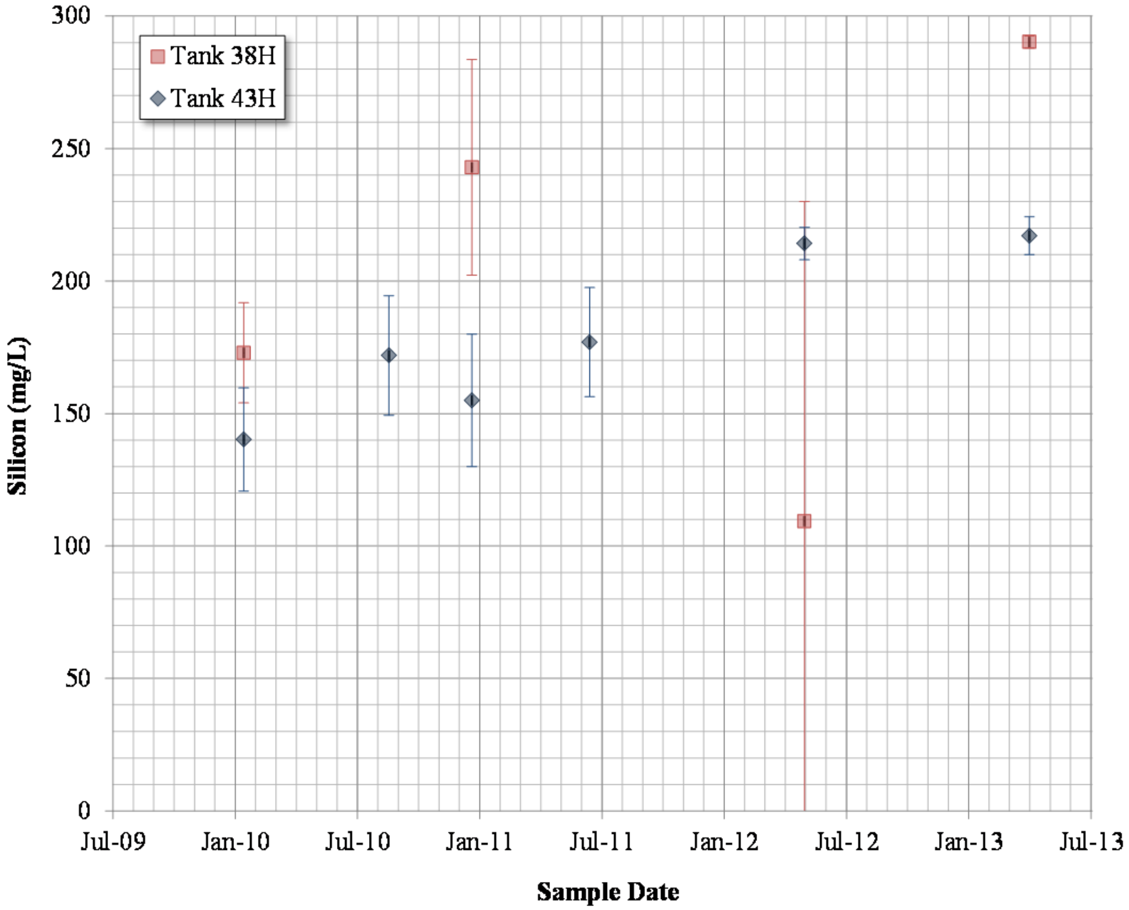

Figure 4-1: Silicon Concentration in Tank 38H and 43H Subsurface Samples

Table 4-12: 50 mg/L Si Standard Analysis

Si standard (50 mg/kg)	2010/2011 samples (mg/kg)		2012 samples (mg/kg)	2013 samples (mg/kg)
0.5 mg/L dilution	5.06E+01	5.25E+01	6.76E+01	5.19E+01
1.0 mg/L dilution	5.62E+01	5.62E+01	6.02E+01	5.25E+01
2.0 mg/L dilution	5.38E+01	5.05E+01	5.75E+01	5.19E+01

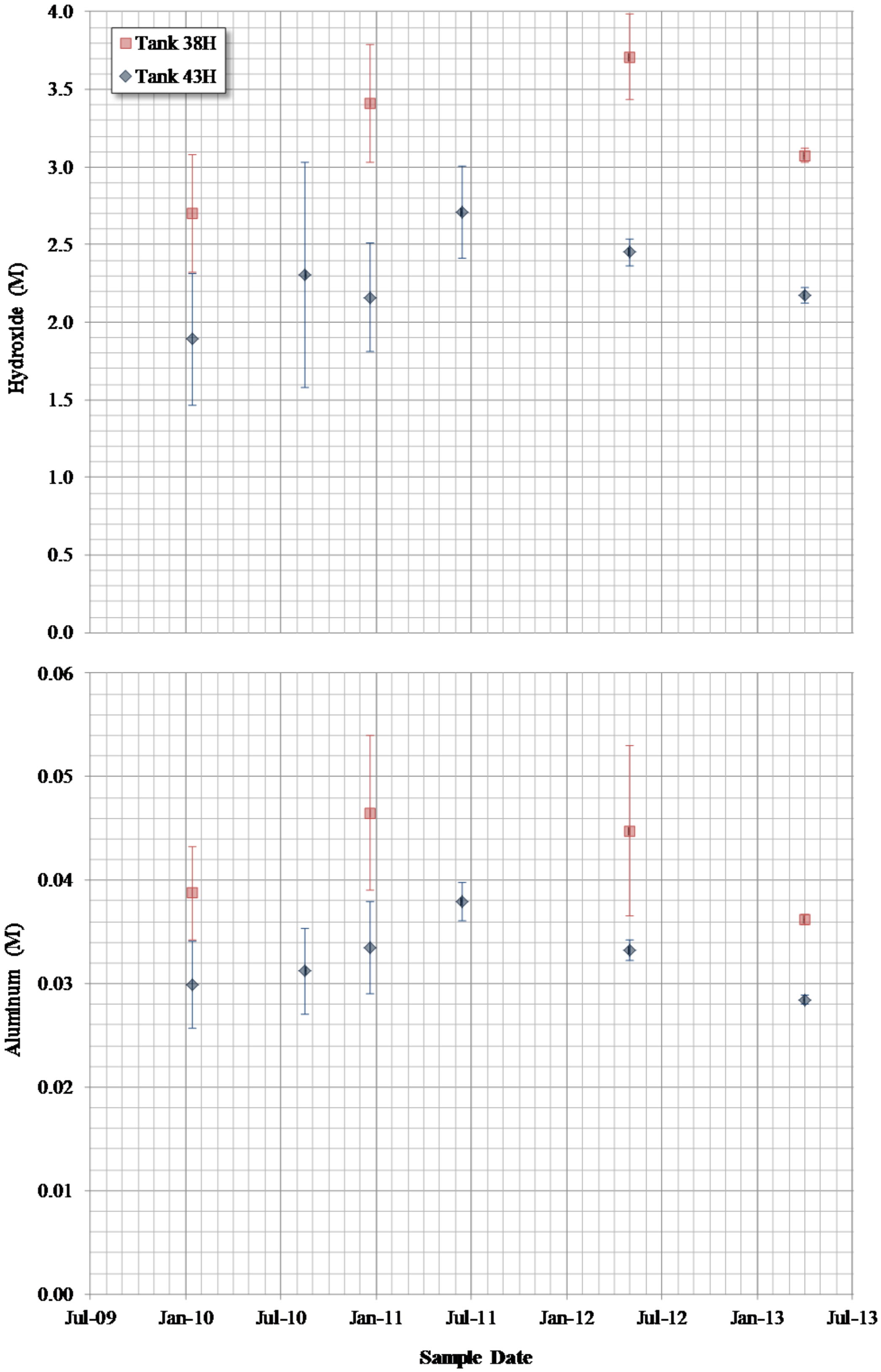

Figure 4-2: Hydroxide and Aluminum Concentrations in Tank 38H and 43H Subsurface Samples

5.0 Comparison with the Sodium Aluminosilicate Process Control Model

In the chemistry regimes applicable to SRS HLW evaporators, sodium aluminosilicate formation has been seen to progress through four phases, starting with amorphous sodium aluminosilicate gel and aging through the crystalline phases of zeolite A, nitrated sodalite, and nitrated cancrinite.[19,10] For sodium aluminosilicates, the most crystalline phases are thermodynamically favored, but the rate of transformation to the most thermodynamically favored phase is slow. The rate of the sodium aluminosilicate formation reaction increases with an increase in the temperature and the degree of supersaturation of the limiting reactant. The solubility of these aluminosilicate phases is inversely proportional to the order of progression, with cancrinite being the least soluble phase and sodium aluminosilicate gel being the most soluble phase. This means that the sodium aluminosilicate gel phase requires higher levels of silicon and aluminum than would the direct precipitation of sodalite or cancrinite, but the kinetics of direct precipitation of sodalite and cancrinite are considered to be too slow to be applicable to the evaporator systems. Thus, in a clean system, the formation of sodium aluminosilicate gel phase serves as a barrier to the deposition of more crystalline phases in the evaporator systems.

Through previous efforts, SRNL developed a series of process control models for sodium aluminosilicate formation potential in SRS HLW evaporators.[7,8,9,10] The models were based on the solubility parameter for the sodium aluminosilicate gel phase. The nominal process control models were developed by factoring in 40% evaporation and a temperature range of 120 to 140 °C. Use of the process control models requires knowledge of aluminum, silicon, and hydroxide concentrations, and enough understanding of the system to assure that tank chemistry and evaporator conditions are within the range used for model development.

From Reference 10, the process control model is based on the sodium aluminosilicate gel solubility parameter of Equation 1.

$$\log Q\,(\mathrm{NAS_{gel}})_{25°\mathrm{C}} = 12 \log_{10}[\mathrm{Al\,(M)}] + 12 \log_{10}[\mathrm{Si\,(M)}] - 12 \log_{10}[\mathrm{OH\,(M)}] \quad [1]$$

The nominal model was expanded to be independent of the degree of evaporation through correlation with the evaporation temperature (T) and solution density (ρ), resulting in Equation 2.

$$\log (Q/K)_{\mathrm{NAS}} = 9.8691 + 13.04 \log_{10}[\mathrm{Al\,(M)}] + 11.09 \log_{10}[\mathrm{Si\,(M)}] - 13.51 \log_{10}[\mathrm{OH\,(M)}] + 15.84\,\rho\,(\mathrm{g/mL}) + 0.0163\,T\,(°\mathrm{C}) \quad [2]$$

Precipitation of sodium aluminosilicate in the evaporator, as initiated through the gel phase, would be expected only when log $(Q/K)_{\mathrm{NAS}}$ calculated by Equation 2 is greater than or equal to zero.

Figure 5-1 (from Reference 10) is the comparison of the values calculated for Equation 2 using evaporator feed and drop tank data from the three systems from 1994 through 2002. The practical operational limits (proposed but not implemented) for the 2F and 3H system were established by high-point samples. The value labeled the "Wilmarth Experimental Limit" of 3.5×10^{-4} refers to the K_{SP} for the formation of sodium aluminosilicate based on the work of Gasteiger et. al.,[5] which is currently used within the EFQ program.[3] From this comparison, it is clear that Tank 43H has experienced periods where the formation of sodium aluminosilicate gel would be expected.

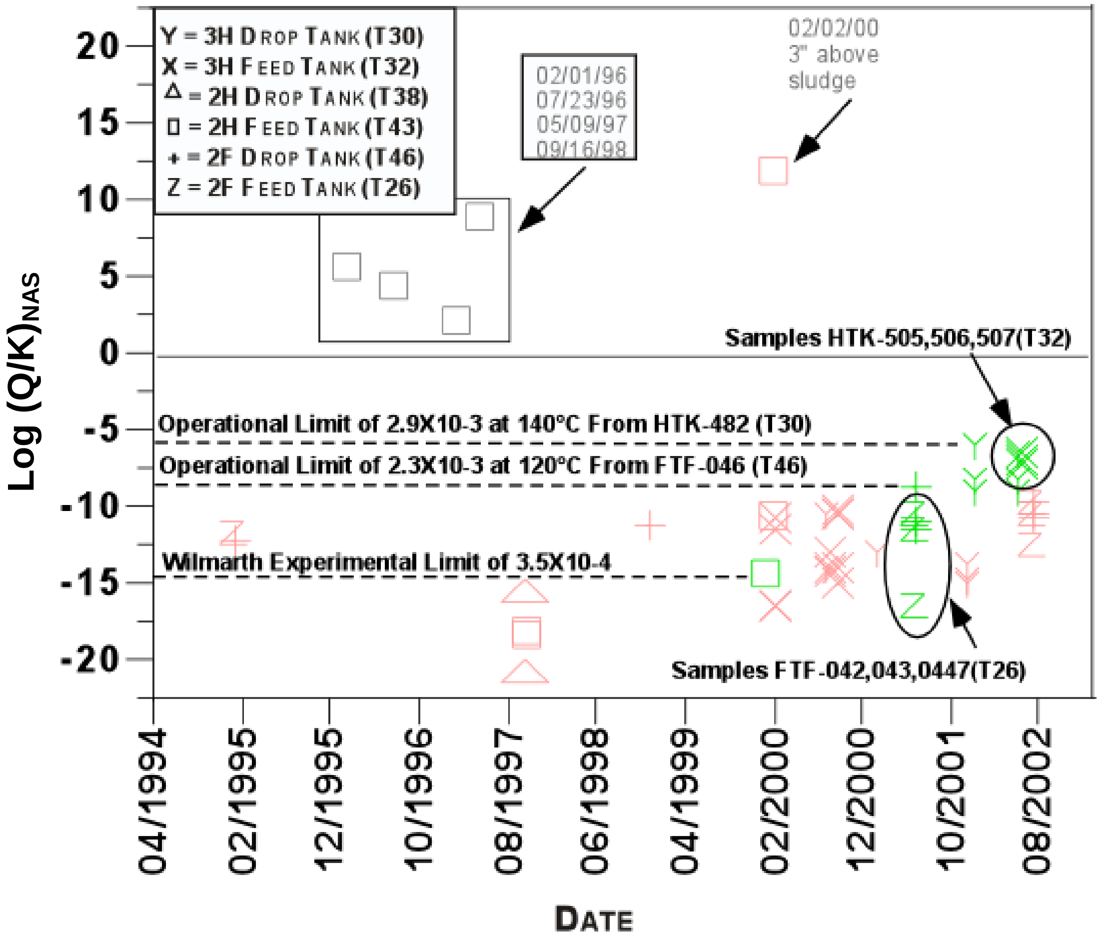

Figure 5-1: The evaporator process control model (Equation 2) compared with historic sample analysis, from Reference 9.

Table 5-1 contains the calculation of log $(Q/K)_{NAS}$ values from the process control model of Equation 2, evaluated at an evaporation temperature of 120 °C. In addition to the data acquired during the characterization featured in this report, Table 5-1 includes past data from SRNL results memoranda[18, 20] and from F/H Lab data compiled in the SRS HLW tank chemistry spreadsheets.[21,22] The data selected are for samples taken after 2H restart in late 2001 and where measured values are reported for all three model parameters (aluminum, silicon, and hydroxide). Values are based on the reported averages for the model parameters. For data in this report, where uncertainty information is known, one sided 95% CI maxima are approximated for log $(Q/K)_{NAS}$ by evaluating Equation 2 using aluminum and silicon concentrations at their one sided 95% CI maxima and hydroxide at its one sided 95% CI minimum.

Table 5-1: Evaporator process control model (Equation 2) results for Tank 38H and 43H sample analysis, 2003 to present samples

Tank 38H

Sample Name	Date Sampled	Ref.	Al (M)	Si (M)	OH (M)	ρ (g/mL)	log(Q/K)$_{NAS}$
HTF-38-13-48	4/2/2013	***	3.62E-02	1.03E-02	3.08E+00	1.291	-15.1 (-15.0*)
200565518	4/7/2011	21	5.79E-02	3.00E-03	3.96E+00	1.3276	-19.3
HTF-38-10-178	12/21/2010	***	4.65E-02	8.65E-03	3.41E+00	1.313	-14.8 (-13.3*)
HTF-38-10-8	1/14/2010	***	3.87E-02	6.16E-03	2.70E+00	1.259	-17.0 (-15.6*)
HTF-38-07-78	6/4/2007	20	7.19E-02	1.45E-02	4.20E+00	1.329	-10.9****
HTF-38-07-24	2/14/2007**	18	5.80E-02	9.44E-03	4.20E+00	1.320	-14.3

Tank 43H

Sample Name	Date Sampled	Ref.	Al (M)	Si (M)	OH (M)	ρ (g/mL)	log(Q/K)$_{NAS}$
HTF-43-13-50	4/2/2013	***	2.84E-02	7.77E-03	2.18E+00	1.221	-17.0 (-16.6*)
HTF-43-12-54	5/1/2012	***	3.32E-02	7.63E-03	2.45E+00	1.242	-16.5 (-16.0*)
HTF-43-11-72	6/15/2011	***	3.79E-02	6.30E-03	2.71E+00	1.264	-16.9 (-15.9*)
HTF-43-10-180	12/21/2010	***	3.35E-02	5.52E-03	2.16E+00	1.253	-17.1 (-15.4*)
HTF-43-10-113	8/19/2010	***	3.12E-02	6.12E-03	2.31E+00	1.231	-17.8 (-15.5*)
HTF-43-10-10	1/14/2010	***	2.99E-02	4.99E-03	1.89E+00	1.198	-18.3 (-16.4*)
200480763	6/16/2008	22	5.00E-02	5.70E-03	3.10E+00	1.2753	-16.5
200472473	3/25/2008	22	4.00E-02	4.50E-03	3.07E+00	1.2587	-19.1
200456916	9/27/2007	22	4.00E-02	5.10E-03	2.55E+00	1.2284	-17.9
HTF-43-07-79	6/5/2007	20	7.41E-02	1.27E-02	2.75E+00	1.255	-10.0****
HTF-43-07-23	2/14/2007**	18	4.33E-02	6.55E-03	2.75E+00	1.220	-16.8
200436183	9/8/2006	22	4.00E-02	5.50E-03	3.04E+00	1.2486	-18.2
200419852	3/10/2006	22	1.00E-01	1.50E-03	3.49E+00	1.2495	-20.1
200402913	9/14/2005	22	4.00E-02	3.80E-03	2.30E+00	1.1591	-19.8
200388295	3/29/2005	22	4.00E-02	5.60E-03	2.47E+00	1.2821	-16.4
200367847	10/19/2004	22	1.10E-01	4.60E-03	5.18E+00	1.3050	-15.6
200345718	5/9/2004	22	1.20E-01	1.07E-02	5.14E+00	1.3040	-11.0
200317062	11/6/2003	22	1.20E-01	6.70E-03	4.24E+00	1.2570	-12.9
200276136	2/18/2003	22	1.70E-01	6.80E-03	5.12E+00	1.35	-10.4

* upper 95% CI ** approximate date *** this report **** contained sodalite solids

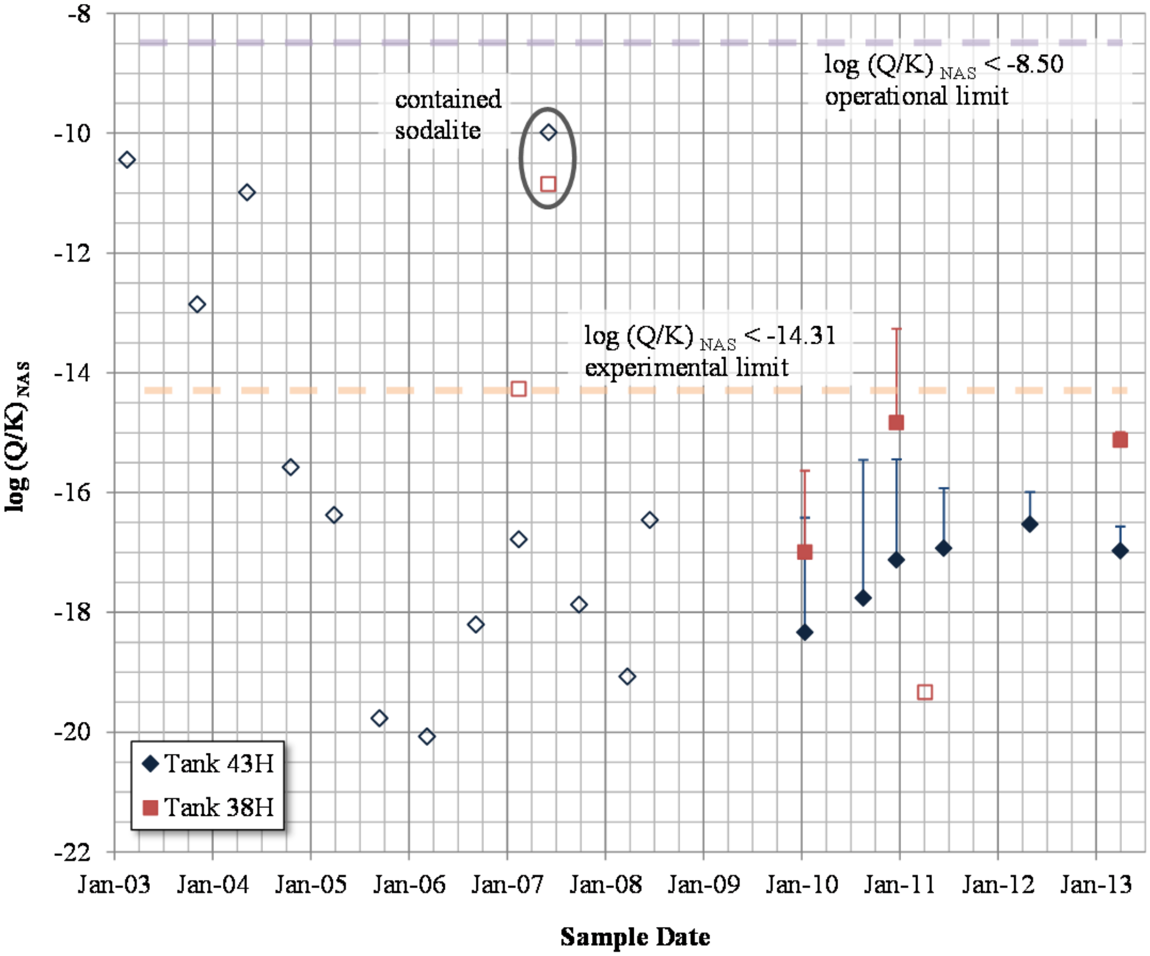

Figure 5-2: The evaporator process control model of Equation 2 using data from 2003 to present. Open symbols are data from Ref. 18, 20, 21, and 22; and solid symbols are data from this report.

Figure 5-2 contains a plot of results for the process control model of Equation 2, as seen in Table 5-1, as a function of the sample date. The filled symbols are results for the data from this report and the open symbols are the results for the previously obtained data. Figure 5-2 can be seen as analogous to and an extension of Figure 5-1, utilizing the more-recent 2H-Evaporator system data. Figure 5-2 contains two reference values: the proposed operational limit of log $(Q/K)_{NAS} \leq -8.5$ based on historic levels in Tank 46F, and Wilmarth's proposed experimental limit of log $(Q/K)_{NAS} \leq -14.31$ based on a solubility product determined by Gasteiger et. al. Using either operational limit adds conservatism to the expected precipitation of sodium aluminosilicate gel at log $(Q/K)_{NAS} \geq 0$.

Examining the data in Figure 5-2, log $(Q/K)_{NAS}$ based on F/H-Lab analyses from early 2003 to mid 2004 show that Tank 43H had a log $(Q/K)_{NAS}$ of greater than -14.31, increasing the potential for sodium aluminosilicate precipitation in the 2H evaporator. The samples from June 2007, which were analyzed by SRNL because they contained a significant amount of insoluble solids including nitrated sodalite, also had a log $(Q/K)_{NAS}$ of greater than -14.31.[20] The log $(Q/K)_{NAS}$ values do not show a clear trend from 2005 through the present samples, with most log $(Q/K)_{NAS}$

values below -14.31. The current Tank 38H and 43H samples have log $(Q/K)_{NAS}$ values below both the apparent operational limit and Wilmarth's experimental limit. When taking the upper CI into account, only one of the current samples (HTF-38-10-178) challenges Wilmarth's experimental limit. However, the Tank 38H samples are of less importance toward sodium aluminosilicate formation in the evaporator pot because that drop-tank material is not fed directly to the evaporator.

Cancrinite and sodalite continue to be deposited within the 2H evaporator pot and gravity drain line, and removal of the scale buildup from the 2H evaporator pot has been necessary every two to three years.[23,24,25] Comparison of sample results with the process control model indicates that sodium aluminosilicate formation through the gel phase is not expected. The sample results are just outside the region where direct sodalite precipitation is expected and are likely within the region where direct cancrinite precipitation is expected. Typically, precipitation of these crystalline phases are slow processes unless seeds of sodalite or cancrinite are present.

The continued buildup of cancrinite and sodalite in the 2H evaporator system is likely due to the presence of these crystalline sodium aluminosilicate phases at levels that allow for the seeding and direct formation of the crystalline phases. Based on the experiments by Addai-Mensah, the seeded growth of sodalite and cancrinite can occur on time scales on the order of the residence time of material in the evaporator pot.[19]

6.0 Conclusions

The Tank 43H and 38H supernatant liquid silicon measurements for the January 2010 through April 2013 time period exhibit a slight increasing trend. Over this time period, the silicon concentration in the Tank 43H and Tank 38H samples averaged 179 mg/L and 235 mg/L, respectively.

Comparison of Tank 43H sample results from 2005 through April 2013 to the previously developed process control models indicates that the current formation of sodium aluminosilicate in the 2H system is due to the seeded direct precipitation of cancrinite and sodalite.

7.0 Quality Assurance

Data are recorded in laboratory notebooks SRNL-NB-2010-00038 and SRNL-NB-2011-00114; and in the SRNL electronic notebook A6583-00032.

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.

8.0 Acknowledgements

I acknowledge the contributions of Nan Stanley and Monica Jenkins for preparing the samples and Boyd Wiedenman, Amy Ekechukwu and Tom White for providing analytical services. Carol Jantzen and John Pareizs provided helpful insight into applying and interpreting results from the evaporator process control models.

9.0 Recommendations for Future Work

SRR Tank Farm Engineering has expressed an interest in having a practical model that relates changes in 2H evaporator feed chemistry to the rate or cumulative quantity of sodium aluminosilicate scale. Not all of the sodium aluminosilicate scale is deposited in the evaporator pot, but on a relative basis such a model can be formed from results of thermodynamic modeling. Because the most thermodynamically favored phase (cancrinite) has been shown to deposit in the evaporator, using a thermodynamic model such as OLI should be feasible.

10.0 Reference

[1] D. A. Eghbali, "Nuclear Criticality Safety Evaluation: Operation of the 2H Evaporator System (U)," N-NCS-H-00180, Rev. 0, September 2008.

[2] C. Duffey, "SRNL Tank 43 and Tank 38 ECP Samples," HLE-TTR-2008-69, Revision 1, August 25, 2010.

[3] T. T. Le, "CSTF Evaporator Feed Qualification Program: Program Description Document," WSRC-TR-2003-00055, Revision 7, March 22, 2010.

[4] W. R. Wilmarth, "Technical Requirements for Dispositioning Tank 40H Decants," SRT-LWP-2001-00032, Revision 1, March 20, 2001.

[5] H. A. Gasteiger, W. J. Frederick and R. C. Streisel, "Solubility of Aluminosilicates in Alkaline Solutions and a Thermodynamic Equilibrium Model," *Ind. Eng. Chem. Res.*, **31**, 1183 – 1190, 1992.

[6] C. J. Martino, "Task Technical and Quality Assurance Plan for Analysis of Tank 38H and Tank 43H Enrichment Control Program and Corrosion Control Samples", SRNS-RP-2008-00208, Revision 1, July 27, 2011.

[7] C. M. Jantzen, J. E. Laurinet, and K. G. Brown, "Thermodynamic Modeling of the SRS Evaporators: Part I. The 2H and 2F Evaporators (U)," WSRC-TR-2000-00293, Rev. 1, April 4, 2002.

[8] C. M. Jantzen, J. E. Laurinet, and K. G. Brown, "Thermodynamic Modeling of the SRS Evaporators: Part II. The 3H System (U)," WSRC-TR-2001-00155, Rev. 1, April 8, 2002.

[9] C. M. Jantzen, T. B. Edwards, and J. M Pareizs, "Thermodynamic Modeling of the SRS Evaporators: Part III. Temperature, Evaporation, and Composition Effects on Process Control Strategy (U)," WSRC-TR-2002-00318, Rev. 1, March 31, 2003.

[10] C. M. Jantzen, J. M. Pareizs, and T. B. Edwards, "Thermodynamic Modeling of the SRS Evaporators: Part IV. Incorporation of High Caustic Aluminosilicate Solubility Data (U)," WSRC-TR-2002-00330, Rev. 0, March 15, 2003.

[11] C. J. Martino, "Analysis of Tank 38H (HTF-38-10-7,8) and Tank 43H (HTF-43-10-9,10) Samples for Support of the Enrichment Control and Corrosion Control Programs," SRNL-L3100-2010-00022, Revision 1, March 4, 2010.

[12] C. J. Martino, "Analysis of Tank 38H (HTF-38-10-110, 111) and Tank 43H (HTF-43-10-112, 113) Samples for Support of the Enrichment Control and Corrosion Control Programs," SRNL-L3100-2010-00197, Revision 0, September 28, 2010.

[13] C. J. Martino, "Analysis of Tank 38H (HTF-38-10-177,178) and Tank 43H (HTF-43-10-179,180) Samples for Support of the Enrichment Control and Corrosion Control Programs," SRNL-L3100-2011-00022, Revision 0, February 9, 2011.

[14] C. J. Martino, "Analysis of Tank 38H (HTF-38-11-69, 70) and Tank 43H (HTF-43-11-71, 72) Samples for Support of the Enrichment Control and Corrosion Control Programs," SRNL-L3100-2011-00147, Revision 0, July 25, 2011.

[15] C. J. Martino, "Analysis of Tank 38H (HTF-38-12-51, 52) and Tank 43H (HTF-43-12-53, 54) Samples for Support of the Enrichment Control and Corrosion Control Programs," SRNL-L3100-2012-00076, Revision 0, June 12, 2012.

[16] C. J. Martino, "Analysis of Tank 38H (HTF-38-13-47, 48) and Tank 43H (HTF-43-13-49, 50) Samples for Support of the Enrichment Control and Corrosion Control Programs," SRNL-L3100-2013-00068, Revision 0, May 15, 2013.

[17] 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, Revision 0, March 20, 2003.

[18] C. J. Martino, "Analysis of Tank 38H and 43H Samples HTF-38-07-24 and HTF-43-07-23," SRNL-CST-2007-00103, Revision 0, October 17, 2007.

[19] J. Addai-Mensah, J. Li, M. Zbik, and S. Rosencrance, "The Chemistry, Crystallization, Physiochemical Properties and Behaviors of Sodium Aluminosilicate Solid Phases: Final Report," WSRC-M-2002-00907, Rev. 0, November 20, 2002.

[20] C. J. Martino, "Analysis of Tank 38H and 43H Samples from June 2007," SRNL-CST-2007-00075, Rev. 0, September 26, 2007.

[21] \\wg08\WASTE8\SAMPLES\HLW Tank Chemistry\NTANK38.xls, July 1, 2012.

[22] \\wg08\WASTE8\SAMPLES\HLW Tank Chemistry\NTANK43.xls, July 1, 2012.

[23] C. J. Martino and W. R. Wilmarth, "Analysis of 2H-Evaporator Pot Scale Samples HTF-137 – 139," SRNL-CST-2006-00001, Rev. 0, January 25, 2006.

[24] K. B. Martin and C. J. Martino, "The 2H Evaporator Pot & Gravity Drain Line Scale Nuclear Criticality Analysis Suite," WSRC-STI-2008-00185, Rev. 0, April 21, 2008.

[25] C. J. Martino, "Analysis of 2H-Evaporator Scale Samples (HTF-10-116 – 117)," SRNL-TR-2010-00264, Rev. 0, September 21, 2010.