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Simulated Waste Testing of Glycolate Impacts on the 2H-Evaporator System

C. J. Martino

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EXECUTIVE SUMMARY

Glycolic acid is being studied as a total or partial replacement for formic acid in the Defense Waste Processing Facility (DWPF) feed preparation process. After implementation, the recycle stream from DWPF back to the high-level waste tank farm will contain soluble sodium glycolate. Most of the potential impacts of glycolate in the tank farm were addressed via a literature review, but several outstanding issues remained.

This report documents the non-radioactive simulant tests impacts of glycolate on storage and evaporation of Savannah River Site high-level waste. The testing for which non-radioactive simulants could be used involved the following: the partitioning of glycolate into the evaporator condensate, the impacts of glycolate on metal solubility, and the impacts of glycolate on the formation and dissolution of sodium aluminosilicate scale within the evaporator. The following are among the conclusions from this work:

- Evaporator condensate did not contain appreciable amounts of glycolate anion. Of all tests, the highest glycolate concentration in the evaporator condensate was 0.38 mg/L. A significant portion of the tests had glycolate concentration in the condensate at less than the limit of quantification (0.1 mg/L).

- At ambient conditions, evaporator testing did not show significant effects of glycolate on the soluble components in the evaporator concentrates.

- Testing with sodalite solids and silicon containing solutions did not show significant effects of glycolate on sodium aluminosilicate formation or dissolution.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CW	Chilled Water
DWPF	Defense Waste Processing Facility
ETF	Effluent Treatment Facility
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma – Emission Spectrometry
PSAL	Process Science Analytical Laboratory
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TIC/TOC	Total Inorganic Carbon / Total Organic
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

Glycolic acid is being studied as an alternate reductant in the Defense Waste Processing Facility (DWPF) feed preparation process. It will either be a total or partial replacement for the formic acid that is currently used. A literature review was conducted recently on the impact of glycolate on two post-DWPF downstream systems – the 2H Evaporator system and the Effluent Treatment Facility (ETF).[1] The DWPF recycle stream serves as a portion of the feed to the 2H Evaporator. Glycolate enters the evaporator system from the glycolate in the recycle stream. The overheads (i.e., condensate) from the 2H Evaporator serves as a portion of the feed to the ETF.

The literature search revealed glycolic acid or glycolate have the ability to complex many multivalent metals and increase their solubility. The complexing ability of glycolate at high pH has been shown for the lanthanides and several actinides. This complexing or solubilizing ability of glycolate may be a potential criticality concern for the 2H Evaporator system. Further, a determination of the amount or fraction of the glycolate in the evaporator overhead is crucial to more accurately assess its impact on the ETF.

This report documents non-radioactive simulant tests for glycolate partitioning and cation solubility. Tests where simulants could be used involve partitioning of glycolate into the evaporator condensate, impacts on non-radioactive metal solubility in the evaporator concentrate, and the formation or dissolution of sodium aluminosilicate scale within the evaporator. Actual-waste tests are being performed in parallel to this work in order to determine the storage and evaporator impacts of glycolate in the tank farm, where glycolate will be in contact with radioactive components of the tank sludge and the evaporator scale. These tasks are derived from the scope outlined in the Technical Task Request and further detailed in the Task Technical and Quality Assurance Plan (TT&QAP).[2,3]

1.1 Background

From a review of the literature, there is not a large amount of vapor-liquid equilibrium data for glycolate anion and complexes applicable to the 2H evaporator system conditions.[1] Glycolic acid would have a reasonably high vapor pressure at salt solution evaporation temperatures and thus could partition significantly into the condensate. However, in the high pH salt solutions typical of 2H evaporator feed, the glycolate vapor pressure is expected to be very low, similar to other salt species at evaporator temperatures. Most salt anions are present in the evaporator condensate due to small amounts of entrainment rather than through evaporation. For the evaporator concentrate, the glycolate is expected to remain soluble when cooled after the single-pass evaporation, although data directly related to this concentrated salt mixture is not available.

There are industrial uses of glycolic acid to remove certain types of evaporator mineral scale. At the high pH conditions of the 2H evaporator, however, there is no compelling evidence that glycolate would be effective at removing or preventing sodium aluminosilicate evaporator scale. The experiments that we performed were designed to detect potential effects of glycolate on both sodium aluminosilicate formation and dissolution..

1.2 Objectives

This report addresses non-radioactive simulant tests. Tests where simulants could be used involve partitioning of glycolate into the evaporator condensate, impacts on non-radioactive metal solubility, and the formation or dissolution of sodium aluminosilicate scale within the evaporator. The objectives of this study are to perform tests to address the following:

- Determine the fate of glycolate in the 2H Evaporator system including the amount of glycolate that may be in the overhead (condensate) and potential solubility impacts of metals in the concentrate.

- Determine the extent to which existing sodium aluminosilicate solids that may be present in the Evaporator system are dissolved by glycolate.

- Determine whether glycolate impedes or increases the formation of sodium aluminosilicate solids in the evaporator system.

The data generated will be used in the OLI modeling task as appropriate.[4]

2.0 Experimental

2.1 Waste Simulants

Waste simulants were developed that are based on samples from the 2H evaporator system. First, the recent composition data for salt supernate in Tank 43H, the 2H evaporator feed tank, was reviewed.[5] Because Tank 43H is part of an active evaporator system, there are some fluctuations of composition with time. A Nominal Salt composition was selected from these sample data. Additional simulant variations were created by increasing and decreasing the hydroxide concentrations to extremes that are outside of those expected in Tank 43H. The impact of the specific sample concentrations used for the Nominal Salt simulant is outweighed by the variability introduced by using a wide range of hydroxide concentrations.

After comparing recent sample compositions, the Nominal Salt simulant composition was based on sample HTF-43-11-72.[6] As an individual sample, HTF-43-11-72 appeared representative of the Tank 43H concentration from 2010 to 2012. The components in HTF-43-11-72 were not at the extremes of the sample-to-sample variation and the sample data showed a relatively good cation/anion balance. Sample HTF-43-11-72 had a density of 1.264 g/mL.

Table 1 contains the seven recipes used for the 2H evaporator feed solution simulants. The Nominal Salt simulant (with 0 g/L glycolate) was based directly on the analytical results for sample HTF-43-11-72. Two glycolate-containing Nominal Salt simulants (with 5 g/L and 10 g/L glycolate respectively) were formulated by replacing a portion of the sodium nitrite with sodium glycolate. Two High Salt simulants (with 0 g/L and 10 g/L glycolate respectively) were formulated from the analogous Nominal Salt recipes by increasing the sodium hydroxide concentration to 6.0 M. Two Low Hydroxide simulants (with 0 g/L and 10 g/L glycolate respectively) were formulated from the analogous Nominal Salt recipes by reducing the hydroxide concentration to 0.01 M and eliminating aluminum/aluminate from the recipe. Analysis of the feeds was performed for confirmation and the results are presented in Section 3.1.

Table 1: Evaporator feed simulant recipes used in glycolate impact testing (mol/L)

	Nominal Salt			High Salt		Low Hydroxide	
Glycolate:	0 g/L	5 g/L	10 g/L	0 g/L	10 g/L	0 g/L	10 g/L
Na^+	6.58	6.58	6.58	9.88	9.88	3.85	3.85
OH^-	2.71	2.71	2.71	6.01	6.01	0.01	0.01
NO_2^-	1.78	1.71	1.65	1.78	1.65	1.78	1.65
NO_3^-	1.06	1.06	1.06	1.06	1.06	1.06	1.06
CO_3^{2-}	0.453	0.453	0.453	0.453	0.453	0.453	0.453
AlO_2^-	0.0379	0.0379	0.0379	0.0379	0.0379	0.0000	0.0000
CHO_2^-	0.0354	0.0354	0.0354	0.0354	0.0354	0.0354	0.0354
SO_4^{2-}	0.0192	0.0192	0.0192	0.0192	0.0192	0.0192	0.0192
PO_4^{3-}	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042
$C_2O_4^{2-}$	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019
$C_2H_3O_3^-$	0.000	0.067	0.133	0.000	0.133	0.000	0.133

The salt solution simulants did not contain sludge components. The sludge components used in this testing were contributed from an archived portion of washed Sludge Batch 4 simulant. Table 2 contains the results of a chemical analysis of the Sludge Batch 4 simulant. The total and calcined solids of this material were 95.5 wt % and 72.9 wt %, respectively. This archived material did not contain the mercury component.

Table 2: Analysis of calcined solids from washed Sludge Batch 4 simulant

elemental (wt %)				oxide (wt %)			
Al	16.3	Mn	7.2	Al_2O_3	30.8	MnO_2	11.4
B	< 0.10	Na	1.5	B_2O_3	--	Na_2O	2.0
Ba	0.20	Ni	4.0	BaO	0.23	NiO	5.1
Ca	2.3	P	< 0.10	CaO	3.2	P_2O_5	--
Ce	0.01	Pb	< 0.10	CeO_2	0.01	PbO_2	--
Cr	0.21	Pd	< 0.10	Cr_2O_3	0.30	PdO	--
Cu	0.10	S	0.06	Cu_2O	0.12	SO_4	0.19
Fe	27.3	Si	1.7	Fe_2O_3	39.0	SiO_2	3.6
K	0.18	Ti	0.03	K_2O	0.22	TiO_2	--
Li	< 0.10	Zn	0.15	Li_2O	--	ZnO	0.18
Mg	1.2	Zr	0.38	MgO	2.0	ZrO_2	0.51

2.2 Evaporation Tests

The partitioning of glycolate between the overheads (condensate) and the bottoms (concentrate) in the 2H evaporator system was determined through a series of tests with non-radioactive simulated waste. To answer the basic question of partitioning due to vaporization, the test system was not prototypic in design to the 2H evaporator. Instead, the apparatus was a small-scale batch evaporation apparatus constructed of laboratory glassware and designed to provide data for a single equilibrium stage. The laboratory system was operated at the same pressure as the 2H evaporator, nominally atmospheric pressure, and the operating temperature was the temperature required for atmospheric evaporation of the salt simulant mixtures.

An objective of this test is to determine the partitioning of glycolate into the evaporator condensate only by means of vaporization. The system was designed and operated to minimize liquid and aerosol entrainment into the condensate. Thus, the presence or absence of entrainment in this test will not be representative of the level of entrainment in the 2H evaporator.

Figure 1 is a diagram of the batch evaporator used in the simulant tests of glycolate. The evaporator system consists of a 500 mL round bottom glass flask, a heating mantle, a chilled water (CW) glass condenser unit, and a 40 mL glass tube for condensate collection. One of the two evaporator units included a type K thermocouple in the vapor space of the round bottom flask. The top portion of the evaporator flask was insulated to minimize condensation prior to the condenser. Figure 2 shows two of these units assembled side-by-side in a fume hood.

The round bottom flask is initially charged with 100 mL of salt simulant and a much smaller amount of washed and dried sludge simulant (0.01 g to 1.0 g). Glass beads are added to help aid in maintaining boiling in a controlled manner. The CW is set to 15 °C and CW flow is initiated. Heating is initiated via power to the heating mantle, and heating is regulated to control boiling. During evaporation, the measured vapor temperatures ranged from 99 to 101 °C.

Evaporation continued until the volume of condensate collected was 25 to 30 mL, after which power to the heating element was switched off. The concentrate (the portion remaining in the round bottom flask) and the condensate (the cooled evaporator overheads) were weighed and collected for analysis.

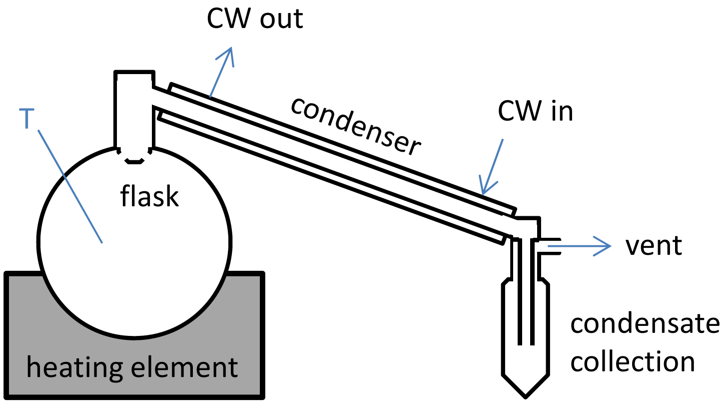

Figure 1: Diagram of batch evaporation apparatus

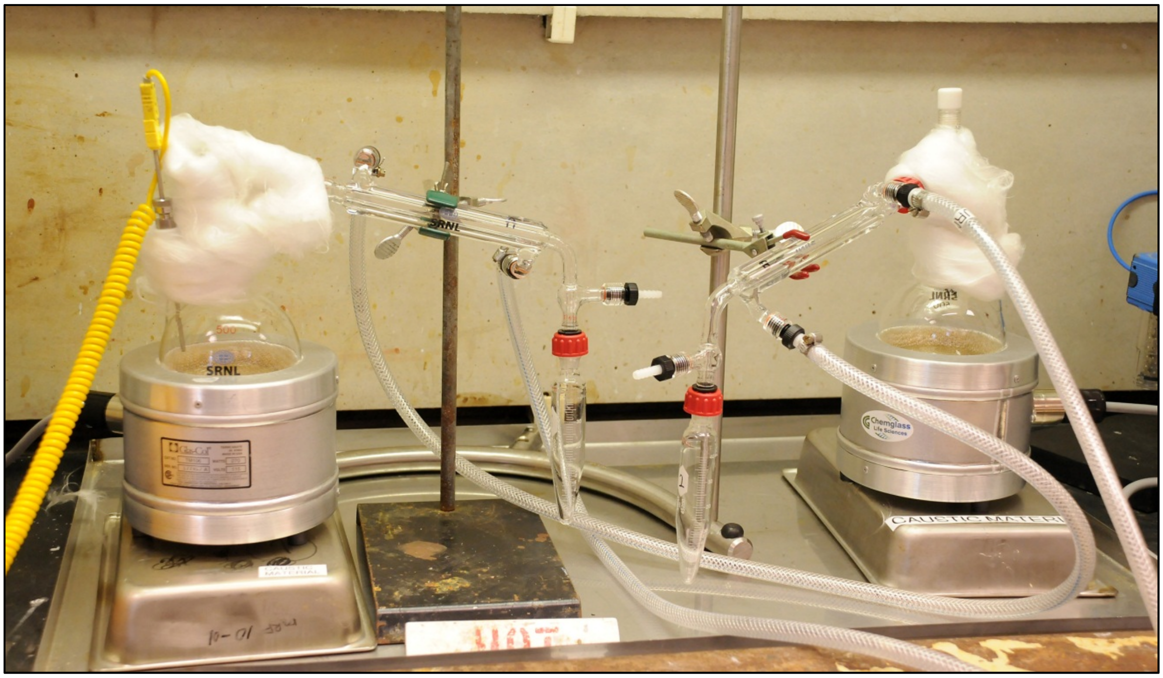

Figure 2: Two evaporator apparatuses assembled within a chemical fume hood at 999-1W

2.3 Sodium Aluminosilicate Formation and Dissolution Tests

Sodium aluminum formation and dissolution tests were performed on a small scale with the non-radioactive Nominal Salt simulants (0, 5 and 10 g/L of glycolate) described in Section 2.1. The sodium aluminosilicate formation and dissolution tests did not include sludge components.

Sodium aluminosilicate dissolution tests were performed to determine whether the presence of glycolate promotes or inhibits the dissolution of sodium aluminosilicate solids at evaporator conditions. For the dissolution tests, salt simulant feed (100 mL) was charged with 1.88 grams of nitrated sodalite solids ($Na_8Al_6Si_6O_{24} \cdot 2NO_3 \cdot 2.5H_2O$, prepared and analyzed by J. Addai-Mensah[7]). This quantity of sodalite, if solubilized, is equivalent to a silicon concentration of 3000 mg/L in the mixture.

Sodium aluminosilicate formation tests were performed to determine whether the presence of glycolate inhibits or promotes the formation of sodium aluminosilicate solids at evaporator conditions. For the formation tests, salt simulant feed (100 mL) was charged with 0.364 grams of PQ sodium silicate solution D®. This quantity of sodium silicate solution is equivalent to a silicon concentration of 500 mg/L in the mixture. A small amount of sodalite solids (0.01 g) was included for the purpose of seeding.

For all formation and dissolution tests, materials were combined in 125 mL Teflon® bottles and heated to 90 °C for approximately 18 to 24 hours (quiescent). At the end of the test, the material was filtered with a 0.45 micron cellulose nitrate filter. The collected solids were washed with deionized water and oven-dried on the filter. The quantity of solids formed and collected were used to determine differences in aluminosilicate formation or dissolution with relation to the variable sodium glycolate concentration.

2.4 Analysis Methods

Glycolate and other anions in the evaporator condensate were measured using ion chromatography (IC) and performed by the SRNL Process Science Analytical Laboratory (PSAL). The pH of the evaporator condensate was measured by PSAL using a pH probe.

The simulated evaporator feed solutions and the soluble portion of the concentrates from the evaporation tests were measured by several methods at PSAL. Metals were measured by inductively coupled plasma – emission spectroscopy (ICP-ES), anions were measured by IC Additionally, several analyses of the evaporator feeds and concentrates were measured by SRNL Analytical Development (AD), including free hydroxide by titration; and carbonate and organic carbon by total inorganic carbon/total organic carbon (TIC/TOC) analysis. Solids were not analyzed.

3.0 Evaporation Test Results

3.1 Test Performance

Table 3 contains a description of the eighteen evaporator runs that were performed, presented in time sequential order. The feed simulant is identified as well as the amount of sludge added. Table 3 also contains a mass balance of the feed and product materials. In general, 1 to 2 grams of material used in the feed was not accounted for in the products when using the Nominal Salt and Low Hydroxide salt simulants. This loss of material increases to 3 to 7 grams for the High Salt simulant due to inefficiencies in transferring concentrate out of the round bottom flask because of salt precipitation.

In the SRS tank farm, it is expected that only a small amount of sludge is suspended in the supernatant liquid and sent to the evaporator. The first two tests used 100 mg/L of dried sludge solids. Because 0.01 g of dried sludge was found to be too small an amount to regularly measure and add to the 100 mL of salt solution, the nominal sludge content used in this evaporator testing was increased to 500 mg/L. Subsequently, to determine if additional sludge had an effect on the results, some evaporator tests were repeated with 10 g/L of sludge, which is near the maximum allowable amount of sludge in the evaporator feed.

Table 3: Evaporator test runs and mass balance

Test Details		Simulant Feed				Mass Balance (g)		
Run	Date	Salt	Glycolate	Amount	Sludge	Feed	Condensate	Concentrate
1	2/11/2013	Nominal	0 g/L	100 mL	0.01 g	126.6	27.1	97.3
2	2/11/2013	Nominal	10 g/L	100 mL	0.01 g	126.6	26.2	99.2
3	2/12/2013	Low OH^-	10 g/L	100 mL	0.05 g	117.3	27.9	88.7
4	2/12/2013	Low OH^-	0 g/L	100 mL	0.05 g	117.0	26.9	88.8
5	2/12/2013	High Salt	0 g/L	100 mL	0.05 g	134.7	26.1	105.1
6	2/12/2013	High Salt	10 g/L	100 mL	0.05 g	134.9	24.9	107.0
7	2/12/2013	Low OH^-	10 g/L	100 mL	0.05 g	117.4	24.9	91.0
8	2/12/2013	High Salt	10 g/L	100 mL	0.05 g	135.3	24.3	106.9
9	2/12/2013	Nominal	10 g/L	100 mL	0.05 g	126.4	26.3	98.6
10	2/12/2013	Nominal	0 g/L	100 mL	0.05 g	126.0	26.4	98.0
11	2/14/2013	Nominal	0 g/L	100 mL	1.0 g	126.1	25.5	98.8
12	2/14/2013	Nominal	10 g/L	100 mL	1.0 g	126.5	25.2	100.1
13	2/14/2013	Nominal	5 g/L	100 mL	0.05 g	123.6	23.0	99.0
14	2/14/2013	Nominal	5 g/L	100 mL	1.0 g	123.1	25.1	96.5
15	2/14/2013	High Salt	0 g/L	100 mL	1.0 g	135.9	26.2	102.2
16	2/14/2013	High Salt	10 g/L	100 mL	1.0 g	134.4	25.9	103.1
17	2/14/2013	Low OH^-	0 g/L	100 mL	1.0 g	117.5	26.7	88.5
18	2/14/2013	Low OH^-	10 g/L	100 mL	1.0 g	117.5	25.8	89.9

Table 4 contains an analysis of the soluble portions of the simulant feed solutions. Visual inspections suggest that the Nominal Salt and Low Hydroxide simulants were completely soluble, while some solid salts were present in the High Salt simulant even prior to evaporation. A larger quantity of water than the recipe called for was added during preparation of the 5 g/L glycolate Nominal Salt simulant, thus lowering the concentration of all salts by approximately 10%. The sodium analysis appears to be biased low in the Nominal Salt case, but the anions are in better agreement with the recipe. Glycolate analysis matched the target levels for the 0 g/L and 10 g/L simulants.

Table 4: Analysis of soluble portions of feed solutions, for comparison with Table 1

	Glycolate:	0 g/L	5 g/L	10 g/L	0 g/L	10 g/L	0 g/L	10 g/L
Analyte	Units	Nominal Salt			High Salt		Low Hydroxide	
Na^+	M	5.70	5.05	5.81	8.29	8.24	3.53	3.58
K^+	M	1.6E-04	1.2E-04	1.6E-04	1.2E-04	1.7E-04	9.5E-05	1.6E-04
cations	*N*	*5.70*	*5.05*	*5.81*	*8.29*	*8.24*	*3.53*	*3.58*
OH^-	M	2.52	2.31	2.63	5.80	5.85	<0.10	<0.10
NO_2^-	M	1.87	1.62	1.75	1.87	1.73	1.85	1.73
NO_3^-	M	1.09	0.97	1.10	1.08	1.10	1.07	1.07
CO_3^{2-}	M	0.390	0.416	0.394	0.391	0.392	0.363	0.366
AlO_2^-	M	0.0376	0.0342	0.0371	0.0372	0.0380	6.5E-06	3.8E-06
CHO_2^-	M	0.0361	0.0334	0.0410	0.0354	0.0409	0.0352	0.0401
SO_4^{2-}	M	0.0179	0.0160	0.0178	0.0174	0.0180	0.0181	0.0181
PO_4^{3-}	M	0.0054	0.0045	0.0052	0.0054	0.0086	0.0048	0.0048
$C_2O_4^{2-}$	M	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011
$C_2H_3O_3^-$	M	<0.013	0.058	0.132	<0.013	0.132	<0.013	0.129
anions	*N*	*6.38*	*5.90*	*6.52*	*9.66*	*9.73*	*3.73*	*3.75*
density	g/mL	1.266	1.241	1.270	1.354	1.357	1.174	1.177
solids	wt %	30.2	27.5	30.5	37.1	37.4	22.6	23.0
TOC	mg C/L	522	1600	3010	502	3000	501	2920
B	mg/L	0.4	0.2	0.3	0.7	0.7	0.1	0.1
Ca	mg/L	1.6	<0.1	1.8	0.3	1.5	2.1	2.4
Cu	mg/L	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	mg/L	<0.1	0.2	0.4	<0.1	0.3	<0.1	<0.1
Mn	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Si	mg/L	2.9	0.8	2.4	2.3	2.6	2.4	2.4
Ti	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zr	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Tests proceeded with no visual indication of liquid entrainment into the evaporator condensate. Once the 100 mL of salt solution was boiling, the collection of 25 to 30 mL of condensate took 10 to 15 minutes.

Figure 3 contains a photograph of condensation on the inner surface of a 500 mL flask during evaporation of salt solution. Worthy of note, during some of the tests, beading of condensed vapor was noted on the evaporator bulb (as seen in Figure 3). In other cases, beading was not evident in the condensation on the inner surface of the flask. It was not clear whether the presence or absence of glycolate contributed to this observation, as these observations were not rigorous and a correlation was not evident.

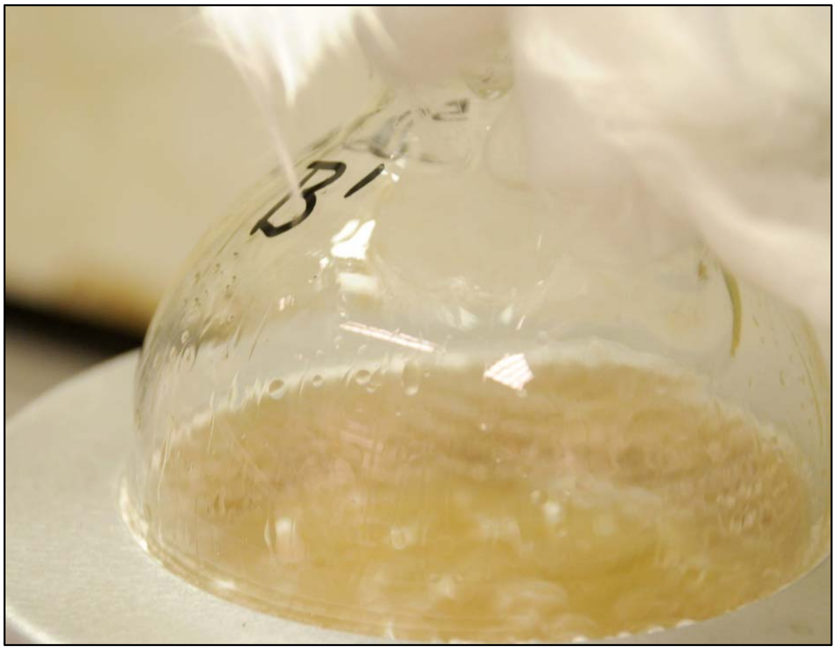

Figure 3: Salt mixture during evaporation

3.2 Condensate Analysis

Figure 4 is a photograph of typical condensate collected during evaporation tests. Condensates appeared visually clear, colorless, and free of solids or other liquid phases. There were no visual indications that the condensate was anything other than distilled water. Nominally 25 to 30 mL of condensate was produced and collected from each evaporation test.

Figure 4: Condensate collected during evaporation

The condensate was collected in a poly bottle and analyzed by PSAL for anions and pH. Table 5 contains the results of the condensate analysis. For most cases, the condensate had a slightly acidic pH (5.6 to 6.9) and a very small salt anion content (less than 1 mg/L). Most of the cases with salt concentrations above the limit of quantification had nitrate concentration slightly higher than nitrite concentration, which differs from the salt solution feed. This observation suggests that the salt content in the condensate is mostly due to volatilization rather than entrainment for most cases. Based on the nitrate, nitrite, and pH results, runs 5 and 17 appear to have experienced a small amount of entrainment of salt-containing liquid into the condensate. These two runs did not have glycolate in the feed.

Glycolate was only noted in the evaporator condensate at low concentration. Four of the 11 runs that included glycolate in the feed had glycolate measured in the condensate at greater than the 0.1 mg/L limit of quantification, ranging from 0.12 to 0.38 mg/L. This is in contrast to the much higher level in the feed solutions (5000 to 10000 mg/L). Glycolate was noted in one of the seven runs in which glycolate was not present in the feed solution (run 4, 0.21 mg/L glycolate), possibly due to sample cross contamination. There is no readily apparent correlation of glycolate concentration in the condensate to the evaporator test feed parameters.

The highest glycolate level observed in evaporator condensate during this testing (0.38 mg/L) is well within the 33 mg/L of glycolate used in the analysis of impacts to ETF.[1]

Table 5: Condensate analysis

Simulant:	Nominal Salt			High Salt		Low Hydroxide		Nominal Salt		Nominal Salt			High Salt			Low Hydroxide		
glycolate (g/L):	0	0	0	0	0	0	0	5	5	10	10	10	10	10	10	10	10	10
sludge (g/L):	0.1	0.5	10	0.5	10	0.5	10	0.05	1	0.01	0.05	1	0.05	0.05	1	0.05	0.05	1
Condensate / Feed:	0.214	0.209	0.202	0.194	0.193	0.230	0.227	0.186	0.204	0.207	0.208	0.199	0.185	0.180	0.193	0.238	0.212	0.219
Run:	1	10	11	5	15	4	17	13	14	2	9	12	6	8	16	3	7	18
NO_2^- (mg/L)	**0.13**	<0.10	**0.26**	**2.23**	**0.55**	<0.10	**2.39**	**0.52**	**0.18**	<0.10	**0.31**	**0.11**	**0.27**	**0.49**	**0.47**	**0.20**	**0.29**	**0.44**
NO_3^- (mg/L)	<0.10	**0.51**	**0.38**	**1.57**	**0.68**	**0.22**	**2.17**	**0.63**	**0.44**	<0.10	**0.40**	**0.40**	**0.21**	**0.58**	**0.66**	**0.34**	**0.31**	**0.68**
CHO_2^- (mg/L)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
SO_4^{2-} (mg/L)	<0.10	<0.10	<0.10	<0.10	<0.10	**0.39**	0.10	<0.10	**0.27**	<0.10	<0.10	**0.17**	<0.10	<0.10	**0.15**	**0.27**	<0.10	<0.10
PO_4^{3-} (mg/L)	**0.10**	<0.10	**0.10**	<0.10	<0.10	**0.12**	<0.10	<0.10	**0.12**	**0.11**	<0.10	**0.11**	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
$C_2O_4^{2-}$ (mg/L)	<0.10	**0.12**	<0.10	<0.10	<0.10	**0.37**	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
$C_2H_3O_3^-$ (mg/L)	<0.10	<0.10	<0.10	<0.10	<0.10	**0.21**	<0.10	<0.10	<0.10	<0.10	**0.12**	<0.10	<0.10	**0.22**	<0.10	**0.38**	**0.12**	<0.10
pH	6.13	6.51	5.99	9.22	6.58	6.18	6.81	5.76	6.06	5.93	6.27	5.60	6.88	6.52	6.90	5.97	5.87	5.76

3.3 Concentrate Analysis

After completion of the evaporation runs, the concentrate was transferred out of the volumetric flask and into a poly bottle for analysis. Figure 5 contains photographs of some evaporator test concentrates, arranged as a function of salt simulant and feed glycolate concentration. As seen in this figure, supernatant liquid in the concentrates that contained glycolate tended to be darker. This visual difference may be due to the dissolution of a greater quantity of some sludge components for evaporation runs with glycolate. This effect, however, may have been temporary as precipitation of brown solids was noted on the inner surface of the bottle wall when the solution was allowed to cool. Subsequent analysis of the solutions after cooling did not show appreciable soluble components originating from the sludge.

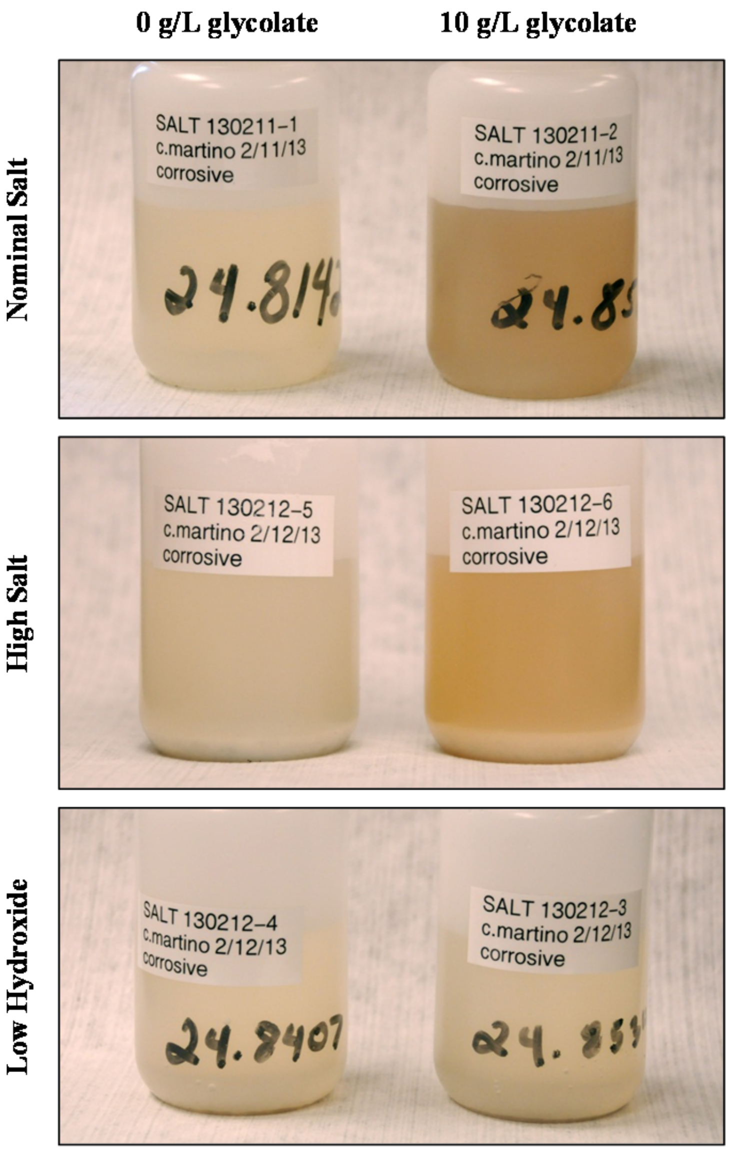

Figure 5: Appearance of concentrates after evaporation tests

Table 6: Concentrate analysis (soluble portion) for evaporation runs with 0 g/L glycolate

	Simulant:	Nominal Salt			High Salt		Low Hydroxide	
	Sludge (g/L):	0.1	0.5	10	0.5	10	0.5	10
	Condensate / Feed:	0.214	0.209	0.202	0.194	0.193	0.230	0.227
Analyte	Units	Run: 1	10	11	5	15	4	17
Na^+	M	8.13	7.83	7.85	10.77	10.35	4.96	4.65
K^+	M	4.2E-04	3.9E-04	9.5E-04	6.2E-04	1.2E-03	2.2E-04	8.4E-04
cations	*N*	*8.13*	*7.83*	*7.85*	*10.77*	*10.35*	*4.96*	*4.66*
OH^-	M	3.43	3.44	3.21	7.36	7.91	<0.10	<0.10
NO_2^-	M	2.56	2.35	2.31	2.37	2.31	2.42	2.51
NO_3^-	M	1.46	1.49	1.44	1.44	1.45	1.46	1.47
CO_3^{2-}	M	0.528	0.508	0.502	0.099	0.112	0.491	0.480
AlO_2^-	M	0.054	0.055	0.107	0.054	0.111	1.5E-04	0.0053
CHO_2^-	M	0.052	<0.022	<0.022	0.040	<0.022	0.047	0.049
PO_4^{3-}	M	0.0071	0.0071	0.0071	0.0075	0.0068	0.0065	0.0058
SO_4^{2-}	M	0.0241	0.0242	0.0239	0.0125	0.0121	0.0244	0.0245
$C_2O_4^{2-}$	M	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011
$C_2H_3O_3^-$	M	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013	<0.013
anions	*N*	*8.69*	*8.42*	*8.14*	*11.51*	*12.06*	*4.98*	*5.06*
density	g/mL	1.351	1.349	1.347	1.427	1.431	1.235	1.235
solids	wt %	38.7	38.5	38.2	44.7	45.0	29.6	29.5
TOC	mg C/L	751	696	665	588	592	699	661
B	mg/L	22.7	20.9	12.4	52.0	35.2	5.74	4.45
Ca	mg/L	1.47	1.50	0.81	0.26	<0.10	1.95	1.29
Cu	mg/L	<0.10	<0.10	1.1	0.17	4.05	<0.10	<0.10
Fe	mg/L	3.09	5.33	6.87	27.4	61.7	<0.10	<0.10
Mn	mg/L	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Si	mg/L	250	181	134	576	380	35.9	2.28
Ti	mg/L	<0.10	<0.10	8.71	<0.10	11.7	<0.10	<0.10
Zr	mg/L	1.88	<0.10	<0.10	1.00	0.36	<0.10	<0.10

Table 7: Concentrate analysis (soluble portion) for evaporation runs with 10 g/L glycolate

	Simulant:	Nominal Salt			High Salt			Low Hydroxide		
	Sludge (g/L):	0.1	0.5	10	0.5	0.5	10	0.5	0.5	10
	Condensate / Feed:	0.207	0.208	0.199	0.185	0.180	0.193	0.238	0.212	0.219
Analyte	Units	Run: 2	9	12	6	8	16	3	7	18
Na^+	M	8.26	7.81	7.94	10.40	10.50	10.44	5.09	4.83	4.57
K^+	M	4.1E-04	4.1E-04	1.0E-03	6.8E-04	6.7E-04	1.3E-03	3.0E-04	2.7E-04	1.0E-03
cations	*N*	*8.26*	*7.81*	*7.94*	*10.40*	*10.51*	*10.44*	*5.09*	*4.83*	*4.57*
OH^-	M	3.37	3.52	3.37	7.35	7.65	7.63	<0.10	<0.10	<0.10
NO_2^-	M	2.27	2.14	2.12	2.10	2.10	2.33	2.25	2.13	2.31
NO_3^-	M	1.45	1.42	1.45	1.41	1.42	1.46	1.46	1.41	1.47
CO_3^{2-}	M	0.519	0.517	0.501	0.169	0.160	0.132	0.495	0.481	0.482
AlO_2^-	M	0.0528	0.0554	0.107	0.0521	0.0533	0.112	1.0E-04	1.7E-04	3.6E-03
CHO_2^-	M	0.055	0.057	0.057	0.053	0.054	0.056	0.055	0.054	0.056
SO_4^{2-}	M	0.0238	0.0241	0.0246	0.0120	0.0098	0.0114	0.0246	0.0239	0.0245
PO_4^{3-}	M	0.0068	0.0070	0.0067	0.0075	0.0074	0.0063	0.0066	0.0064	0.0058
$C_2O_4^{2-}$	M	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011	<0.011
$C_2H_3O_3^-$	M	0.173	0.176	0.171	0.174	0.175	0.176	0.176	0.172	0.172
anions	*N*	*8.49*	*8.49*	*8.36*	*11.53*	*11.82*	*12.07*	*5.11*	*4.91*	*5.17*
density	g/mL	1.346	1.353	1.352	1.423	1.426	1.434	1.240	1.233	1.236
solids	wt %	38.6	38.8	38.7	44.2	44.5	45.5	30.4	29.5	29.9
TOC	mg C/L	3940	3910	3780	3900	3740	3750	3940	3930	3800
B	mg/L	22.3	21.3	12.8	53.8	51.7	34.7	5.9	5.1	5.7
Ca	mg/L	3.78	5.44	2.98	1.56	1.52	<0.10	2.51	2.25	2.02
Cu	mg/L	<0.10	0.02	2.65	0.16	0.19	3.66	<0.10	<0.10	0.17
Fe	mg/L	3.88	6.15	5.95	20.1	19.3	33.1	<0.10	<0.10	0.15
Mn	mg/L	<0.10	<0.10	<0.10	2.43	2.44	7.12	<0.10	<0.10	<0.10
Si	mg/L	240	222	145	597	396	395	39.8	35.1	1.78
Ti	mg/L	<0.10	<0.10	9.22	<0.10	<0.10	12.0	<0.10	<0.10	<0.10
Zr	mg/L	0.98	0.17	<0.10	0.45	1.21	0.13	<0.10	<0.10	<0.10

Table 8: Concentrate analysis (soluble portion) for evaporation runs with 5 g/L glycolate

	Simulant:	Nominal Salt	
	Sludge (g/L):	0.5	10
	Condensate / Feed:	0.186	0.204
Analyte	Units	Run: 13	14
Na^+	M	6.81	6.85
K^+	M	3.0E-04	9.9E-04
cations	*N*	*6.81*	*6.85*
OH^-	M	2.93	2.86
NO_2^-	M	1.91	2.21
NO_3^-	M	1.25	1.28
CO_3^{2-}	M	0.435	0.451
AlO_2^-	M	0.0493	0.101
CHO_2^-	M	0.0434	0.0474
SO_4^{2-}	M	0.0210	0.0216
PO_4^{3-}	M	0.0058	0.0058
$C_2O_4^{2-}$	M	<0.011	<0.011
$C_2H_3O_3^-$	M	0.0742	0.0746
anions	*N*	*7.20*	*7.55*
density	g/mL	1.306	1.316
solids	wt %	34.1	35.2
TOC	mg C/L	2040	2080
B	mg/L	14.7	12.5
Ca	mg/L	4.01	1.55
Cu	mg/L	0.13	1.74
Fe	mg/L	4.99	5.69
Mn	mg/L	<0.10	<0.10
Si	mg/L	143	254
Ti	mg/L	<0.10	8.76
Zr	mg/L	0.77	<0.10

Table 6, Table 7, and Table 8 contain the analytical results for the evaporator concentrates, organized by the amount of glycolate included in the feed solution (0 g/L, 10, g/L, and 5 g/L, respectively). These materials were filtered prior to analysis, so the results do not contain components that were not soluble at the time of analysis. The analysis was performed more than a week after the test, so the results reflect solubilities at ambient conditions rather than at evaporator conditions.

In the evaporator concentrate, silicon and boron show increased soluble concentrations over their concentrations in the evaporator feeds. The concentrations of these components are related to the hydroxide content of the solutions and they are present at a ratio indicative of corrosion of the borosilicate glass evaporator flask. Regardless of the presence of glycolate, silicon in the nominal salt concentrates ranged from 134 to 254 mg/L, which is representative of silicon levels in the 2H-evaporator feed and drop tanks.[5]

Also apparent as a function of hydroxide content, a small amount of iron was dissolved from the sludge included in the tests. Neither iron, silicon, nor boron concentrations were influenced by the presence of glycolate.

There was not a great difference in the soluble components in the evaporator concentrate between the conditions with and without glycolate in the evaporator feed. This data will be expanded upon in the real waste testing, where more components are included and analysis.

Table 9: Glycolate recovered in the evaporator concentrate

Test Details		Glycolate Balance	
Run	Simulant	Feed	Recovery
2	Nominal Salt	10 g/L	98%
9	Nominal Salt	10 g/L	99%
12	Nominal Salt	10 g/L	98%
6	High Salt	10 g/L	103%
8	High Salt	10 g/L	103%
16	High Salt	10 g/L	102%
3	Low OH^-	10 g/L	98%
7	Low OH^-	10 g/L	100%
18	Low OH^-	10 g/L	99%
13	Nominal Salt	5 g/L	100%
14	Nominal Salt	5 g/L	97%

Table 9 contains the calculated percent recovery of sodium glycolate in the evaporator concentrate. The calculation uses the mass balance information of Table 3, the feed glycolate and density data of Table 4, and the concentrate glycolate and density data of Table 7 and Table 8. For the Nominal Salt and Low Hydroxide simulant runs, the measured recoveries of glycolate in the soluble portions of the concentrate ranged from 97% to 100%. Due to measurement uncertainties, these results are statistically indistinguishable from 100% recovery within the propagated uncertainty of the mass balance. There is a high bias for the glycolate recovery in the High Salt simulant runs because the mass balance did not include a separate measurements for quantity of salt solids formed and the salt slurry density.

Thus, the concentrate analysis results are consistent with the expectation that the glycolate remains in the soluble evaporator concentrate. Consistent with the condensate analysis, the concentrate analysis confirms that glycolate compounds do not partition into the evaporator overheads and condensate. There is no indication of glycolate decomposition during the short duration of these non-radioactive simulant tests.

4.0 Sodium Aluminosilicate Formation and Dissolution Test Results

4.1 Sodalite Dissolution Tests

Glycolic acid is used in some industrial applications for evaporator scale removal. Glycolate and glycolic acid has also been shown to form complexes with some metals. For these reasons, it was requested that SRNL test whether processing glycolate-containing salt supernate through the 2H evaporator system would dissolve some of the nitrated sodalite and cancrinite scale. Short term tests were performed to investigate if there was an effect of glycolate concentration on nitrated sodalite dissolution. Sodalite was used in these tests because it would be faster to dissolve than cancrinite and thus more likely to indicate an effect.

Table 10 contains the mass of scale dissolved during testing based on the quantity of solids collected. Dissolution was noted in all tests, ranging from 6% to 11% of the original scale material. The resulting silicon concentration in the supernate, calculated from the amount of solids dissolved, ranged from 170 to 330 mg/L. The test-to-test variation in dissolution and the experimental method uncertainty masked any small effect of glycolate on increasing the dissolution of scale. This limited set of tests did not demonstrate a statistically significant effect of glycolate on the dissolution of nitrated sodalite.

Table 10: Dissolution of sodalite at 90 °C

feed glycolate (g/L)	solids dissolved (g/L)			final solution Si (mg/L)			RSD
	test 1	test 2	average	test 1	test 2	average	
0	1.308	1.927	**1.617**	208	307	**258**	27%
5	1.056	1.980	**1.518**	168	315	**242**	43%
10	1.996	2.075	**2.036**	318	331	**324**	3%

4.2 Seeded Sodium Aluminosilicate Precipitation Tests

There was not previous evidence suggesting that glycolate in tank waste would influence the formation of sodium aluminosilicate solids in the evaporator. Short term precipitation tests were performed using nominal salt solutions loaded with 500 mg/L of soluble silicon and contacted with sodalite seed material at 90 C. Table 11 contains the amount of solids collected from the formation tests. One of the formation tests at 0 g/L glycolate failed due to loss of a considerable quantity of the solids during the filtration and washing process, and thus its result is not included in the table.

At the end of the formation tests, approximately 2.0 to 2.3 grams of washed and dried solids were isolated per liter of feed. This is a significant increase to the 0.1 g/L of sodalite included as a seed in each test. However, the test-to-test variation is large enough to outweigh the dependence of the solids formed on the glycolate content. The potential effect of glycolate on aluminosilicate solids formation appears to be small enough as to not warrant further testing.

Table 11: Formation of sodium aluminosilicate precipitates at 90 °C

feed glycolate (g/L)	final solids (g/L)			final solution Si (mg/L)			RSD
	test 1	test 2	average	test 1	test 2	average	
0	--	2.058	**2.058**	--	328	**328**	--
5	2.144	2.020	**2.082**	342	322	**332**	4%
10	2.314	2.136	**2.225**	369	340	**354**	6%

The resulting silicon concentration in the supernate, calculated from the amount of solids precipitated, ranged from 320 to 370 mg/L. From the data in Tables 10 and 11, soluble silicon concentrations in both tests appeared to converge to an equilibrium value of roughly 300 mg/L.

5.0 Conclusions

The following are the concussions from this work:

- Evaporator condensate did not contain appreciable amounts of glycolate anion. Of all tests, the highest glycolate concentration in the evaporator condensate was 0.38 mg/L. A significant portion of the tests had glycolate concentration in the condensate at less than the limit of quantification (0.1 mg/L).
- At ambient conditions, evaporator testing did not show significant effects of glycolate on the soluble components in the evaporator concentrates.
- Testing with sodalite solids and silicon containing solutions approached an equilibrium and did not show large effect sizes of glycolate impacts towards sodium aluminosilicate formation or dissolution.

6.0 Recommendations

Part of the TTQAP for updating the OLI database for glycolate species includes the identification of “limitations of the updated OLI database for use in the simulation of HLW process chemistry” and specifically mentions the application for “the prediction of evaporator overheads.” Based on the results of this testing, comparison of data generated during this report to the OLI model will provide little value with respect to glycolate effects and thus is not recommended.

As summarized in the conclusions section, no appreciable glycolate was measured in the evaporator condensate. This was the expected result for high pH evaporator solutions, and thermodynamic modelling will provide no additional information, as slightly volatile free glycolic acid completely dissociates under alkaline conditions. The small amount of glycolate in some evaporator condensate samples was likely due to physical entrainment which is outside the scope of a thermodynamic model such as OLI.

Comparing solubilities in evaporator feeds and condensates with and without added glycolate, there were no appreciable differences noted in the concentrations of soluble species and the amount of sodium aluminosilicate formed or dissolved. Comparison of the OLI model with the radioactive solubility test data has already shown that model predicts no appreciable impact from the presence of up to 10 g/L glycolate.[8] Rigorous comparison of the OLI model with the data generated in this report will not provide additional value and thus is not recommended. Comparison of the updated OLI database would be more valuable for situations where glycolate has been shown to have an influence on species solubilities.

7.0 Quality Assurance

Data are recorded in electronic laboratory notebooks A6583-00032-11 and A6583-00032-14. 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 support of D. Healy and several other technicians for performing the evaporation and aluminosilicate formation tests. C. Sexton and G. Dobos of the SRNL glass shop assisted in the design and fabricated the evaporation apparatus.

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