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Evaporation of Hanford Waste Treatment Plant Direct Feed Low Activity Waste Effluent Management Facility Core Simulant

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Savannah River National Laboratory™

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EXECUTIVE SUMMARY

The Hanford Waste Treatment and Immobilization Plant (WTP) Low Activity Waste (LAW) vitrification facility will generate an aqueous condensate recycle stream (LAW Melter Off-Gas Condensate, LMOGC) from the off-gas system. The baseline plan for disposition of this stream during full WTP operations is to send it to the WTP Pretreatment Facility, where it will be blended with LAW, concentrated by evaporation, and recycled to the LAW vitrification facility. However, during the Direct Feed LAW (DFLAW) scenario, planned disposition of this stream is to evaporate it in a new evaporator, in the Effluent Management Facility (EMF), and then return it to the LAW melter. It is important to understand the composition of the effluents from the melter, and new evaporator so that the disposition of these streams can be accurately planned and accommodated. Furthermore, alternate disposition of the LMOGC stream would eliminate recycling of problematic components, and would reduce the need for closely integrated operation of the LAW melter and the Pretreatment Facilities. Long-term implementation of this option after WTP start-up would decrease the LAW vitrification mission duration and quantity of glass waste, amongst the other operational complexities such a recycle stream presents. In order to accurately plan for the disposition path, it is key to experimentally determine the fate of contaminants. To do this, testing is needed to accurately account for the buffering chemistry of the components, determine the achievable evaporation end point, identify insoluble solids that form, and determine the distribution of key regulatory-impacting constituents.

The LAW Melter Off-Gas Condensate stream will contain components that are volatile at melter temperatures, have limited solubility in the glass waste form, and represent a materials corrosion concern, such as halides and sulfate. Because this stream will recycle within WTP, these components will accumulate in the Melter Condensate stream, exacerbating their impact on the number of LAW glass containers that must be produced. Diverting the stream reduces the halides and sulfates in the recycled Condensate and is a key outcome of this work. This overall program examines the potential treatment and immobilization of this stream to enable alternative disposal. The objective of this task was to demonstrate evaporation of a simulant of the LAW Melter Off-gas Condensate expected during DFLAW operations, in order to predict the composition of the effluents from the EMF evaporator to aid in planning for their disposition. This document describes the results of that test using the core simulant. This simulant formulation is designated as the “core simulant”; other additives will be included for specific testing, such as volatiles for evaporation or hazardous metals for measuring leaching properties of waste forms.

The results indicate that the simulant can easily be concentrated via evaporation. During that the pH adjustment step in simulant preparation, ammonium is quickly converted to ammonia, and most of the ammonia was stripped from the simulated waste and partitioned to the condensate. Additionally, it was found that after concentrating (>12x) and cooling that a small amount of LiF and $Na_3(SO_4)F$ precipitate out of solution. With the exception of ammonia, analysis of the condensate indicated very low to below detectable levels of many of the constituents in the simulant, yielding very high decontamination factors (DF).

TABLE OF CONTENTS

LIST OF TABLES vii
LIST OF FIGURES vii
1.0 Introduction 1
    1.1 Testing Basis and Objective 1
    1.2 Simulant Formulation 5
2.0 Experimental Procedure 6
    2.1 Evaporator Test Apparatus 6
    2.2 Quality Assurance 11
3.0 Results and Discussion 11
    3.1 Evaporator operation 11
    3.2 Sample Analysis Results 16
4.0 Conclusions 24
5.0 Future Work 25
6.0 References 25
Appendix A A-1

LIST OF TABLES

Table 1-1. EMF Core Condensate Simulant Formulation 5

Table 1-2. EMF Core Condensate Simulant Filtrate Analysis Results.. 6

Table 2-1. M&TE Equipment used for testing 9

Table 2-2. Named vs. Actual Pot Sample Concentrations... 11

Table 3-1. Ammonia Condensate Data... 22

Table A-1. Measured Concentrate Data.. A-1

Table A-2. Measured Condensate Data A-2

LIST OF FIGURES

Figure 1-1. Simplified LAW Off-gas System.. 3

Figure 1-2. Simplified Schematic of the Direct Feed LAW (DFLAW) Scenario 4

Figure 2-1. EMF Evaporator Test Apparatus 7

Figure 2-2. Image of EMF Evaporator Operating 8

Figure 2-3. Chiller used to cool water recirculating in the EMF Condenser............................... 8

Figure 2-4. Temperature vs Saturated Water Pressure 9

Figure 2-5. Simulant filtration step.. 10

Figure 3-1. Simulant Boiling in the evaporator pot 12

Figure 3-2. 9.08X Boil-down (left) and 12.56X Boil-down (right) Simulant Samples.............. 13

Figure 3-3. Settled Solids in the 12.56X Boil-down Simulant Sample 13

Figure 3-4. Condensate removed from Condensate Tank during the evaporation test............... 14

Figure 3-5. Evaporator Concentrate (12.56X) at the End of Boil-down 15

Figure 3-6. Filter Paper (dried) used to Filter Concentrate... 16

Figure 3-7. Test Conditions, Temperature and Pressure.. 17

Figure 3-8. Simulant Concentration during Boil-off 18

Figure 3-9. Measured Concentrate Results (mg/L) for Concentrated Simulant 19

Figure 3-10. XRD Pattern of Dried Filter Paper.. 20

Figure 3-11. Concentrate Analysis for Concentrated Simulant Samples 21

Figure 3-12. Analysis of Condensate.. 23

Figure 3-13. Wt% Solids in Concentrate 24

LIST OF ABBREVIATIONS

ACTL	Aiken Count Technology Laboratory
AD	Analytical Development Department in SRNL
DFLAW	Direct Feed Low-Activity Waste
DOE	Department of Energy
EMF	Effluent Management Facility
ETF	Effluent Treatment Facility
g	grams
hr	hour
HTWOS	Hanford Tank Waste Operations Simulator
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
Kg	kilogram
L	Liter
LAW	Low-Activity Waste
LMOGC	LAW Melter Off-Gas Condensate
mg	milligram
mL	milliliter
PSAL	Process Science Analytical Laboratory in SRNL
SBS	Submerged Bed Scrubber
Sim	Simulant
SRNL	Savannah River National Laboratory
Std. Dev	Standard Deviation
VSL	Vitreous State Laboratory – Catholic University
WESP	Wet Electrostatic Precipitator
WRPS	Washington River Protection Solutions
WTP	Waste Treatment Plant
DF	Decontamination Factor

1.0 Introduction

The Hanford Low-Activity Waste Melter Off-Gas Condensate (LMOGC) stream will be generated in the Waste Treatment Plant (WTP) by condensation and scrubbing of the Low-Activity Waste (LAW) melter off-gas system by a Submerged Bed Scrubber (SBS) and Wet Electrostatic Precipitator (WESP), as shown in Figure 1-1. This stream, which will contain substantial amounts of chloride, fluoride, ammonium, and sulfate ions, and technetium and other radionuclides will get recycled to the LAW melter after evaporation. During Direct Feed LAW (DFLAW) operations, the evaporation will be performed in the planned Effluent Management Facility (EMF), as shown in Figure 1-2. Most of the evaporator bottoms will normally be returned to the LAW melter, but this stream may be returned to the tank farm without evaporation when the EMF evaporator is unavailable [1]. The volatile halide and sulfate components that accumulate in this stream are only marginally soluble in glass, and often dictate the LAW glass waste loading, thereby impacting the total quantity of glass canisters produced. The principal radionuclides present in this stream that are not compatible with current onsite disposal limits are ^{99}Tc and ^{129}I. These radionuclides are volatile in the melter and accumulate in the LAW system. Diverting this LAW Melter Off-Gas Condensate stream to an alternate disposal path would have substantial beneficial impacts on the cost, life cycle, and operational complexity of WTP [2], but disposition of ^{99}Tc and ^{129}I must be appropriately managed.

1.1 Testing Basis and Objective

The scope of this task is to support Washington River Protection Solutions (WRPS) in determining the composition and behavior of the waste streams to determine compatibility with existing facilities and make plans for disposition options [3]. Analytical results of melter off-gas condensate sample results from two DuraMelter-10 (DM-10) tests at Vitreous State Laboratory (VSL) at the Catholic University of America were used as the basis for the simulant of this stream [4]. This melter is a small-scale melter that has been used extensively in testing for the Hanford WTP. The off-gas system is a scaled-down version of the system for WTP, and includes a submerged bed scrubber (SBS) and wet electrostatic precipitator (WESP), which generate the aqueous condensate stream used as the basis for this simulant. At the time that the condensate samples were generated, the simulant melter feed to the DM-10 was similar to actual wastes that are expected during the Direct Feed LAW operations. Preparation and analysis of the simulant has been described elsewhere [5]. For this test, a vacuum evaporator system was assembled and is similar in construction to a prior system [6] since design details of the future EMF evaporator are not yet available. Details of the experimental apparatus are described in Section 2.0 below. Evaporator conditions were selected to be comparable to those used in prior testing, which are also consistent with the operating conditions of the 242-A evaporator at Hanford.

During tests at VSL, the SBS and WESP condensate was found to be near neutral pH. Prior to evaporation in the EMF evaporator, the pH will be raised to 12 to minimize corrosion [7]. Note that a significant cation in the LMOGC is ammonium, which will largely convert to ammonia during this adjustment (>98% at pH=11 [8]) and will then largely vaporize in the evaporator. It is important to determine the distribution of ammonium and ammonia in the evaporator because the overhead condensate will be dispositioned in the Effluent Treatment Facility (ETF). This task will provide evidence of the partitioning of ammonia and other components to the ETF, so that the effects on the facility can be anticipated. Additionally, a significant component is boric acid, which will consume one equivalent of hydroxide ions to reach pH 11. It is important to experimentally determine the total equivalents of hydroxide consumed by the ammonium to ammonia conversion, and the boric acid reaction, to determine the amount needed to overcome any other buffers, such as forming zinc hydroxides, and actually raise the pH to the target. Then, during evaporation, it is important to determine that the target pH is high enough to maintain the high pH in the evaporator, which will then allow obtaining an accurate characterization of the bottoms. Since solids can precipitate from the bottoms, it is important to experimentally validate the evaporation end point so that it can be determined if insoluble solids form, particularly if they impact the handling and disposition options.

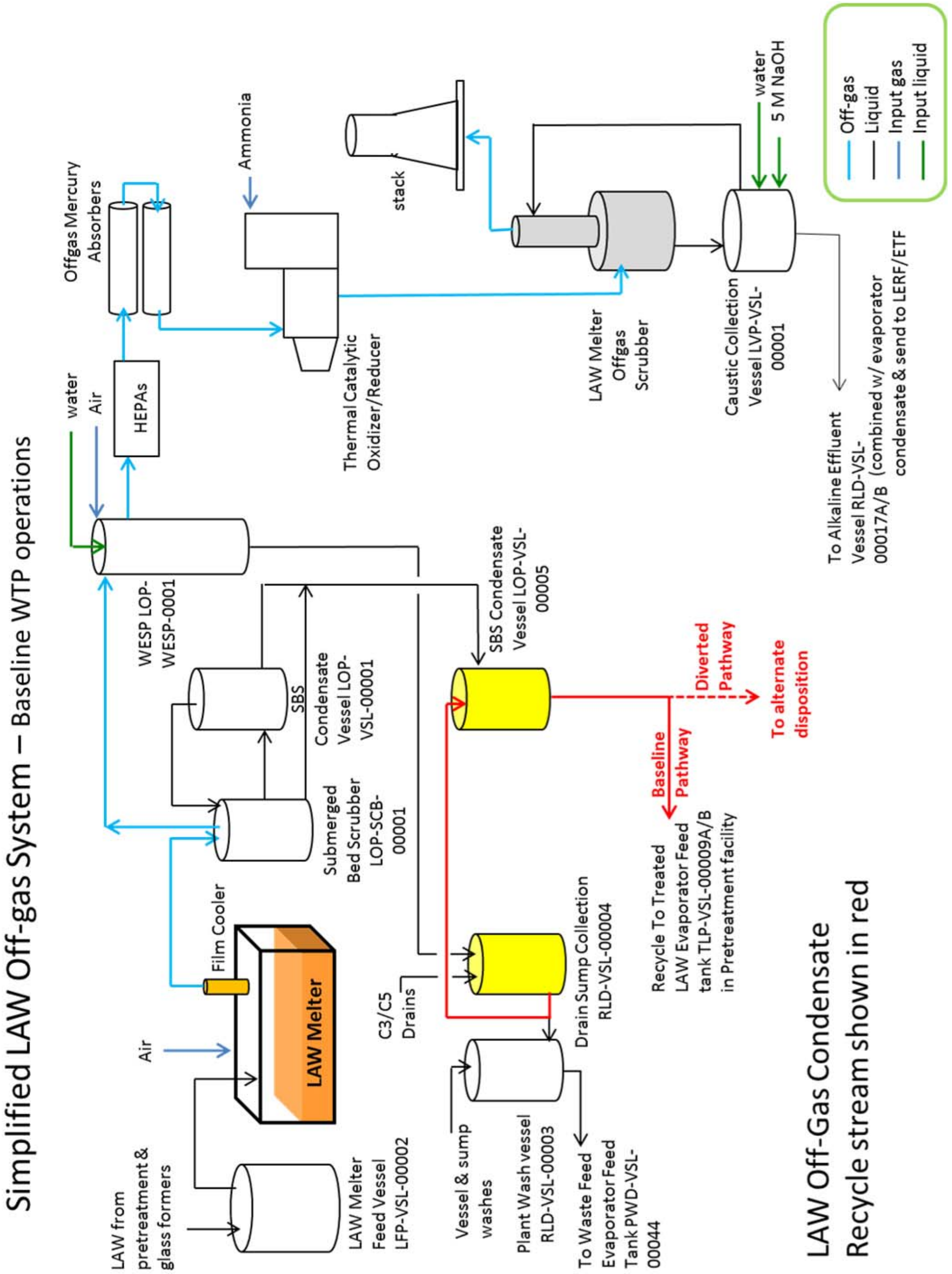

Figure 1-1. Simplified LAW Off-gas System

Note: (adapted from 24590-WTP-RPT-PT-02-005, Rev. 6; yellow indicates SBS/WESP LAW Off-Gas Condensate collection tanks, red lines indicate the collected off-gas condensate pathway)

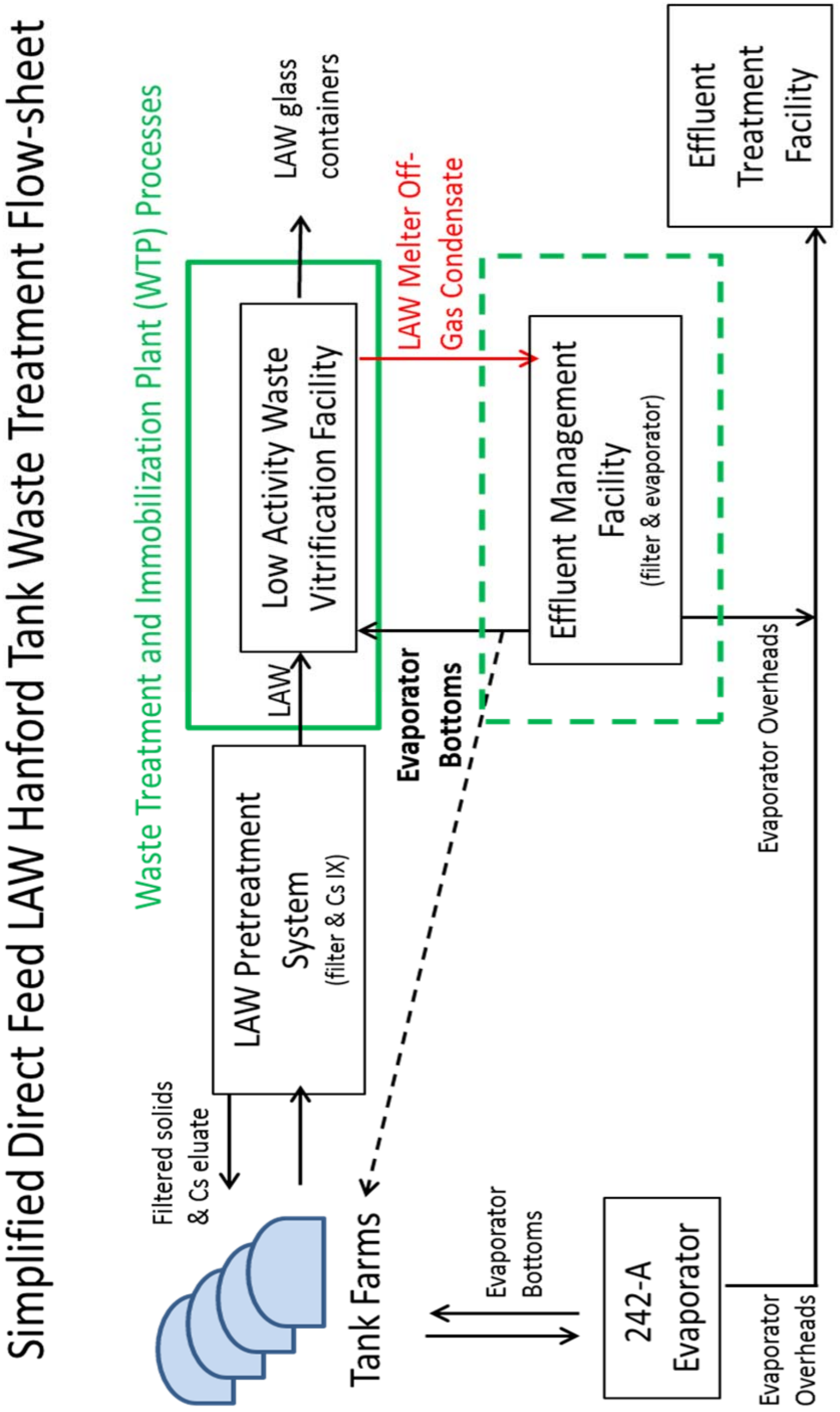

Figure 1-2. Simplified Schematic of the Direct Feed LAW (DFLAW) Scenario

1.2 Simulant Formulation

Results of the Off-Gas Condensate stream analysis from VSL tests 4 and 6 were used as the basis for the chemical composition, and the preparation and analysis were previously reported [4]. The target formulation is shown in Table 1-1. Analytical results of the simulant used for this test are shown in Table 1-2. The results represent duplicate analyses of two samples; the first was collected when the simulant was first prepared and the second was collected and analyzed in the course of this evaporation test.

Table 1-1. EMF Core Condensate Simulant Formulation

Chemical	Formula	Target Mass (g)/L simulant*	Target Molarity
Potassium fluoride	KF	1.252	0.0216
Sodium chloride	NaCl	0.275	0.0047
Ammonium nitrate	NH_4NO_3	0.910	0.0114
Ammonium sulfate	$(NH_4)_2SO_4$	0.642	0.0049
Sodium sulfate	Na_2SO_4	0.963	0.0068
Potassium sulfate	K_2SO_4	2.20	0.0126
Ammonium chloride	NH_4Cl	2.343	0.0438
Silica	SiO_2	0.305	0.0051
Boric acid	$B(OH)_3$	5.250	0.0849
Zinc nitrate	$Zn(NO_3)_2$	0.241	0.0013
Sodium oxalate	$Na_2C_2O_4$	0.077	0.0006
Potassium hydroxide	KOH	0.980	0.0175
NaOH (50 wt%)	NaOH	Adjust to pH 11.9	
Sodium chromate	Na_2CrO_4	0.108	0.0007
Sodium nitrite	$NaNO_2$	8.350	0.1210
Lithium carbonate	Li_2CO_3	0.213	0.0029

*calculated weights assumes anhydrous reagent is used

Table 1-2. EMF Core Condensate Simulant Filtrate Analysis Results

Species	Target (mg/L)	Result average (mg/L)	Std. Dev.*
B	918	916	53
Cr	35	35	3
K	2511	2667	148
Li	40	47	5
Na	6765	7635	397
Si	143	3	1
Zn	83	82	12
NH_4^+	1171	1005	163**
Cl^-	1720	1711	17
F^-	409	402	5
NO_3^-	863	920	86
NO_2^-	5568	5850	182
SO_4^{-2}	2331	2189	82
CO_3^{-2}	173	NA	-
oxalate	50	43	6

* std deviation of 4 values shown in table 1-2
**Two measurements
NA = not analyzed

This simulant was slightly cloudy prior to filtration, which was evidently due to the insoluble silica. To prepare the simulant, an amorphous form of silica had been used, and it was first mixed with concentrated potassium hydroxide in an attempt to dissolve it. However, it did not completely dissolve in the potassium hydroxide solution, and evidently did not dissolve or further precipitated in the final simulant mixture. Also note that sodium is slightly higher than calculated, but variance in sodium concentration was expected, since sodium hydroxide was used to adjust the pH. The final, measured pH was 12.2 (which was slightly above target, but was assessed as acceptable), since the difference in ammonia-ammonium ratio is <0.1%[a]. Density of the solution was 1.0186 g/mL. The total amount of 50 wt% sodium hydroxide solution added to achieve this pH was 14.39 g/L and the equivalent of 0.98 g/L of potassium hydroxide.

2.0 Experimental Procedure

2.1 Evaporator Test Apparatus

Figure 2-1 is a schematic of the EMF Evaporator Test Apparatus. The glass apparatus was constructed inside a fume hood at SRNL's Aiken County Technology Laboratory (ACTL). The

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[a] Ammonium is 99.82% converted to ammonia at pH = 12.0 and 99.88% at pH 12.2 based on calculations in [8].

evaporator pot was a 1,000 mL modified glass beaker. The contents of the pot were heated using a hotplate (Torrey Pines Scientific) and were continuously stirred using a magnetic stir-bar.

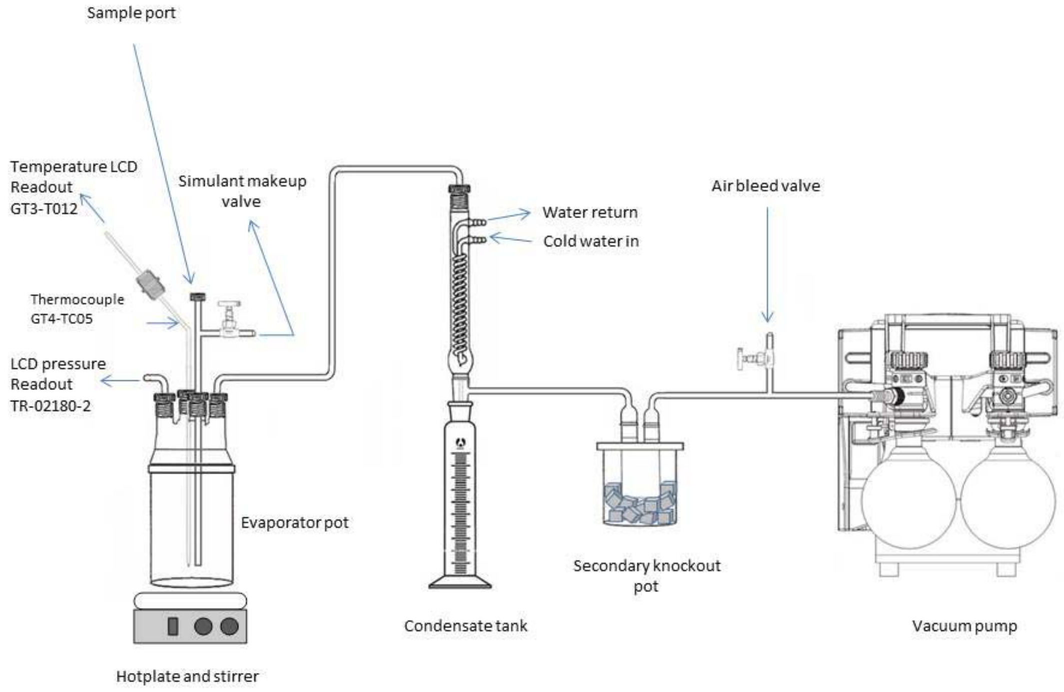

Figure 2-1. EMF Evaporator Test Apparatus

The contents of the pot were under a vacuum, typically keeping the pot at 2.4” Hg pressure. Since the pressure was low the liquid boiled at approximately 42 °C (incorrectly measured at ~50 °C, see description below).

As the contents of the pot boiled, the vapors traveled unrestricted to the condenser where the vapors were condensed. There was no engineered demisting element designed into the off-gas line to knock out entrained particles. The condensate then gravity drained into the Condensate Tank.

The Condenser was cooled using a Haake$^{®}$ Chiller (Model K20). The chiller maintained the cooling water at approximately 13 °C. Any vapors that passed through the condenser were condensed in the Secondary Knockout Pot. The knockout pot was continuously submersed in an ice bath where the temperature was approximately 0 °C.

The vacuum was created by the Vacuubrand$^{®}$ Diaphragm Vacuum pump, Type: MZ 2C. Figure 2-2 is an image of the EMF Evaporator Test Apparatus.

Figure 2-2. Image of EMF Evaporator Operating

A Haake® Chiller was used to provide continuous cold flow of liquid through the condenser to cool the off-gas. The chiller shown in Figure 2-3 was located on the floor outside the fume hood.

Figure 2-3. Chiller used to cool water recirculating in the EMF Condenser

Table 2-1 is a list of M&TE equipment used during the EMF Evaporator testing.

Table 2-1. M&TE Equipment used for testing

Equipment	M&TE
Thermocouple, K type	GT4-TC05
Pressure Transducer	TR-02180-2
Temperature LCD Readout	GT3-T012
Thermocouple, K type *	ITS TC0060

* Replaced GT4-TC05 during simulant testing

The evaporator was checked for operation using deionized water. Figure 2-4 shows the expected versus observed boiling point results of temperature versus pressure for deionized water from the literature [9] versus water check test results (P = 2.42" Hg) with this evaporation apparatus and the boiling point of the simulant after one hour (P = 2.32" Hg). The observed results do not match the expected literature results. All instruments were re-checked for calibration and found within limits. Erratic behavior of the LCD readout was observed and was traced to a faulty wire between the thermocouple and the LCD readout. It was determined that the discrepancy could not be reproduced accurately, so the data could not be corrected. However, note that the objective of this report, the characterization of the distribution of species between the condensate and evaporator bottoms, is not expected to be measurably impacted by this discrepancy. Since the measured vacuum pressure was correct, the evaporation actually occurred under the planned conditions, it was just that the measured boiling temperature is approximately 8 ºC too high.

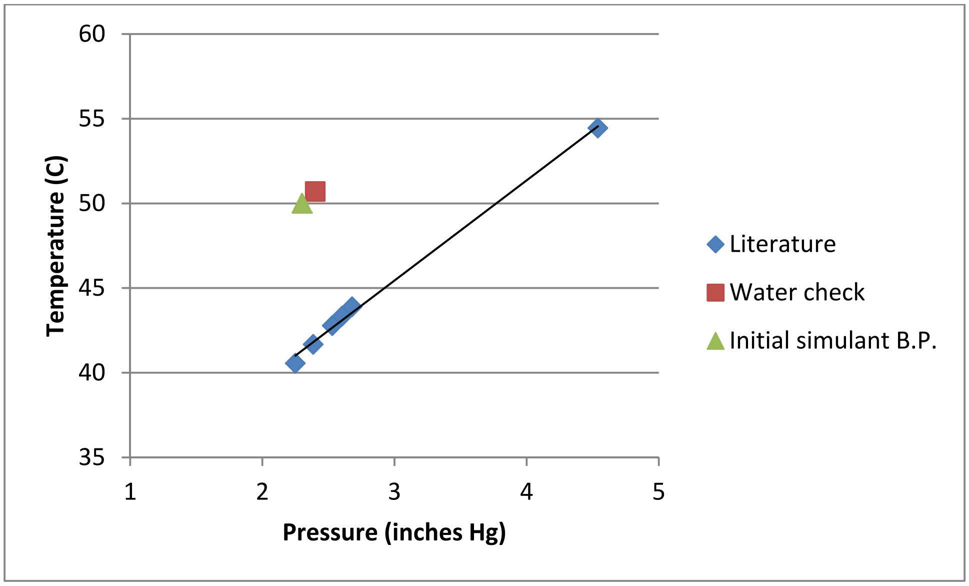

Figure 2-4. Temperature vs Pressure for literature values, water check, and simulant

The simulant used for the EMF testing was previously prepared and analyzed with an ICP-ES for metals and Ion Chromatography for anions and cations (ammonium). Before Bench-scale EMF Evaporator testing began, the 2 liters of simulant was filtered using a 0.45 micron filter as shown in Figure 2-5 below. The feed simulant was filtered to remove the visible insoluble solids.

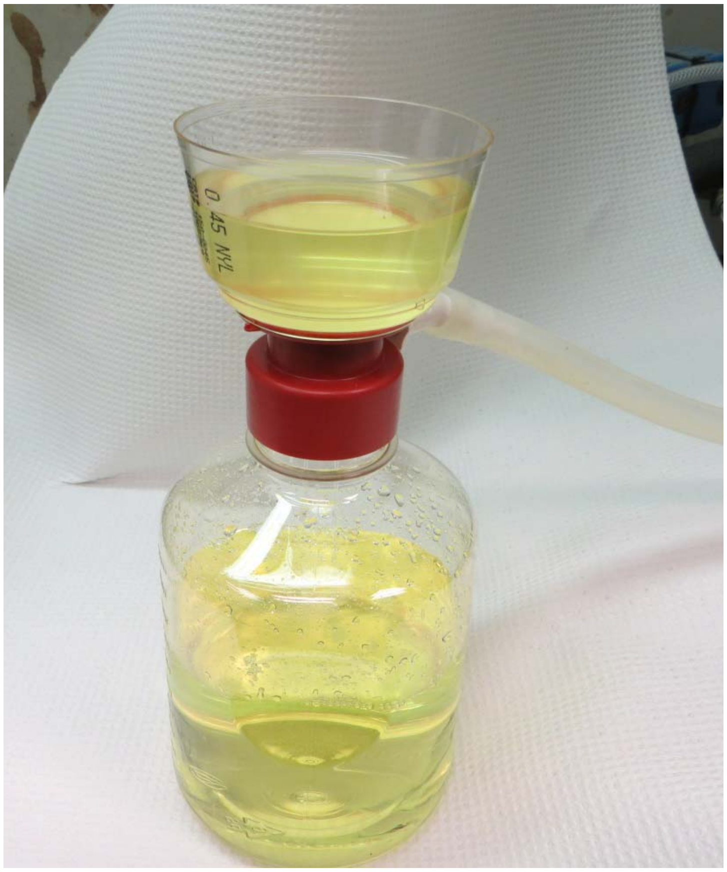

Figure 2-5. Simulant filtration step

As shown in the image, a vacuum was used to filter the simulant through the filter media. After filtering, there was 1,930.2 mL of feed simulant (losses were primarily due to removing samples for analysis) which was weighed into a separate container for use. Initially, 400 mL of feed simulant was loaded into the evaporator pot. The pressure was adjusted to approximately 8 kPa (60 torr, 2.35 inches of mercury absolute), comparable to conditions used for previous boil-down tests performed by SRNL [6] and comparable to the Hanford 242-A evaporator.

The simulant was heated using a hot plate and stirred continuously using a magnetic stir-bar. The solution boiled at approximately 42 °C (incorrectly measured at 50 °C). After evaporating 200 mL, an additional 200 mL of (room temperature) feed simulant was added to the pot to maintain the liquid level. This cycle was repeated until the 1,930 mL of simulant was evaporated down to an equivalent of 140 mL (accounting for extracted samples). At the end of the test campaign, the concentrated simulant density was 1.217 g/mL (including the solids that formed upon cooling).

Samples were collected at concentration points corresponding to 9.08X and 12.56X. These were higher than the original target values of 5.5 and 11X. The original sample names (5.5X and 11X) and condensate removal plan are shown in Table 2-2. However, measured masses and volumes were used to calculate actual concentrations in the pot and these are also shown in Table

2-2. Figures in this report that use sample concentration factors use the calculated value, but the labels in the photographs show the original target values. The reported quantities of simulant and condensate are based on the weight and measured density of the liquids. Densities were measured using volumetric flasks and measuring the weight of the liquid.

Table 2-2. Named vs. Actual Pot Sample Concentrations

Sample Name	Actual Calculated Concentration Factor	Total solution added to pot (g)	Total solution added to pot (mL)	Total volume condensate collected (mL)	Pot sample density (g/mL)
5.5X	9.08	1832	1796	1599	1.185
11X	12.56*	1969	1930	1767	1.217

*calculation accounts for solution volume removed from pot for 5.5X sample

2.2 Quality Assurance

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. Results are recorded in Electronic Laboratory Notebook #O8825-00233-01. This report documents completion of Task 3.3 in the Task Technical and Quality Assurance Plan SRNL-RP-2015-01038, Rev. 0 [3].

3.0 Results and Discussion

3.1 Evaporator operation

The evaporator was operated at 2.4” Hg and boiling at approximately 42 °C (incorrectly measured at 50 °C). The boil-off rate of the condensate was approximately 4.2 ml/min during the test. Figure 3-1 is an image of the simulant boiling in the evaporator pot. The evaporator pot was normally insulated during operation, but the insulation on the side was periodically moved to allow for visual observation.

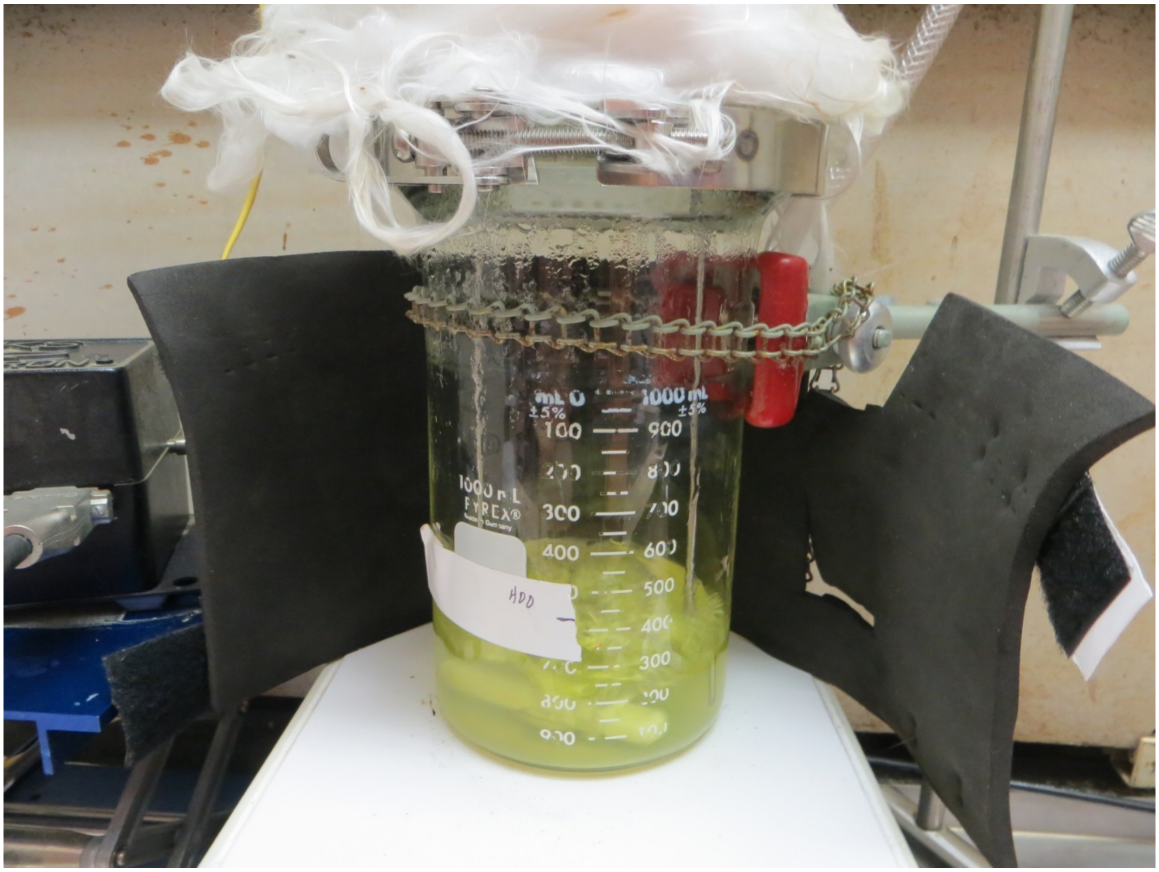

Figure 3-1. Simulant Boiling in the evaporator pot

The first sample was pulled from the evaporator pot after boiling down (concentrating) to 9.08X or boiling off approximately 1,600 mL of condensate from about 1800 mL of the simulant. The next sample was pulled from the evaporator pot at the end and after the simulant had been boiled down to the target concentration, which reached 12.56X concentration factor. An image of the two samples is shown in Figure 3-2. A small amount of insoluble solids appeared in 12.56X sample (sample on the right, labeled 11X) after cooling to room temperature.

Figure 3-2. 9.08X Boil-down (left) and 12.56X Boil-down (right) Simulant Samples

Solids continued to precipitate out in the 12.56X concentrated sample over time. Figure 3-3 below shows the solids settled to on the bottom of the vial after settling for a few days.

Figure 3-3. Settled Solids in the 12.56X Boil-down Simulant Sample

During the test, condensate was removed from the Condensate Tank when the volume reached approximately 500 ml for the first three samples, and then smaller aliquots were collected for the last two condensate samples in an effort to determine if the ammonia stripped early in the test. Each time the condensate tank was emptied, the vacuum pump was shut down and the heat turned off. Condensate sampling duration typically took less than 5 minutes from the time of shut down to restart.

Figure 3-4 is an image comparing the condensate removed from the Condensate Tank during the run. The 1st Pull, 2nd Pull, and 3rd Pull contained 500 mL each. The 4th Pull was 115 mL and the 5th Pull was 170 mL. A sample from each condensate pull was submitted for analysis to determine if the condensate was changing as the contents of the pot concentrated with time. All of the condensate samples were clear and colorless. At the end of the test campaign, the Secondary Knockout Pot had only collected a total of 6.6 mL of cloudy condensate which was also submitted for analysis for ammonia only.

Figure 3-4. Condensate removed from Condensate Tank during the evaporation test.

Figure 3-5 is an image of the concentrated bottoms in the EMF Evaporator pot. At the conclusion of the test campaign, there were initially no insoluble solids visible in the pot. However; as the concentrate cooled, solids began to form and settle out of the concentrated simulant.

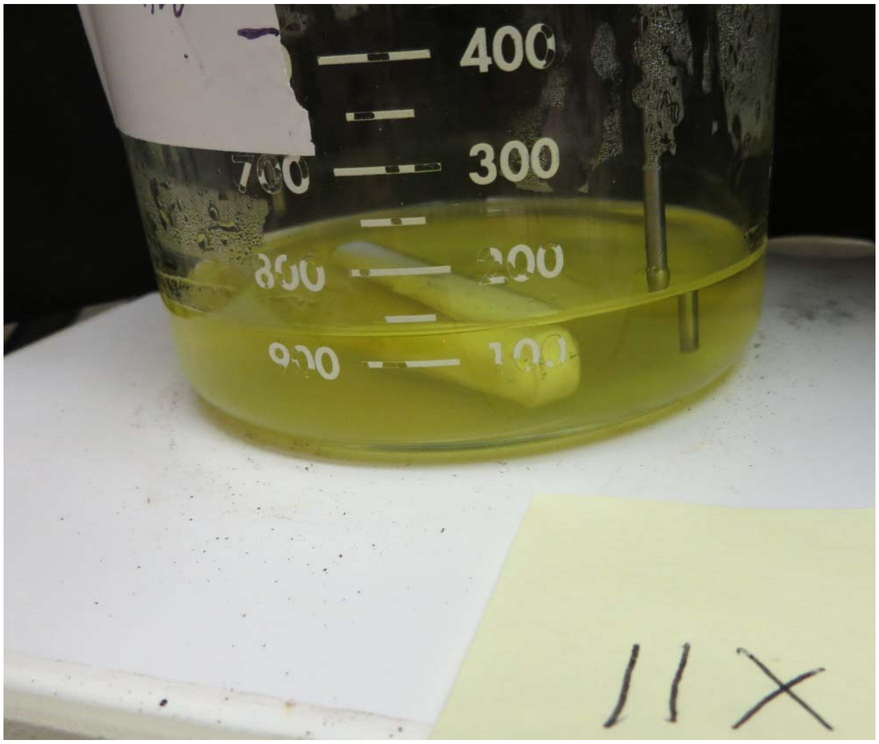

Figure 3-5. Evaporator Concentrate (12.56X) at the End of Boil-down

A portion of the concentrate in the evaporator pot at the end of the test campaign was filtered to remove solids. Figure 3-6 is an image of the dried filter paper after filtering approximately 40 mL of concentrate. No solids were visible to the naked eye on the filter after filtering the 40 mL of concentrated simulant. However, the slow filtration rate indicated that the filter media was plugging with solids from the concentrate. The filter was sent for particle analysis of filtered solids.

Figure 3-6. Filter Paper (dried) used to Filter Concentrate

3.2 Sample Analysis Results

The Evaporator was operated under vacuum at approximately 2.40” Hg as shown in Figure 3-7, along with the change in temperature during the test. The pressure varied a small amount over the entire test campaign, ranging from 2.32” Hg to 2.48” Hg. The decrease in temperature between the first and second data point is attributed partially to the decrease in pressure and partially to the faulty wire. Subsequent temperature data points varied with the small variation in pressure, with some variation also due to periodic additions of fresh feed to the pot, but with an overall upward trend. The change in temperature is plotted instead of the measured values because of the faulty reading. The “zero” point for the change in temperature is the lowest recorded temperature, which was the point after the system had stabilized, which was the 1-hour measurement. The observed temperature increase during the evaporation, measured at ~5 ºC, was expected and can be attributed to the increasing salt concentration in the pot causing boiling point elevation (i.e. simulant boiling point increased as concentration increased).

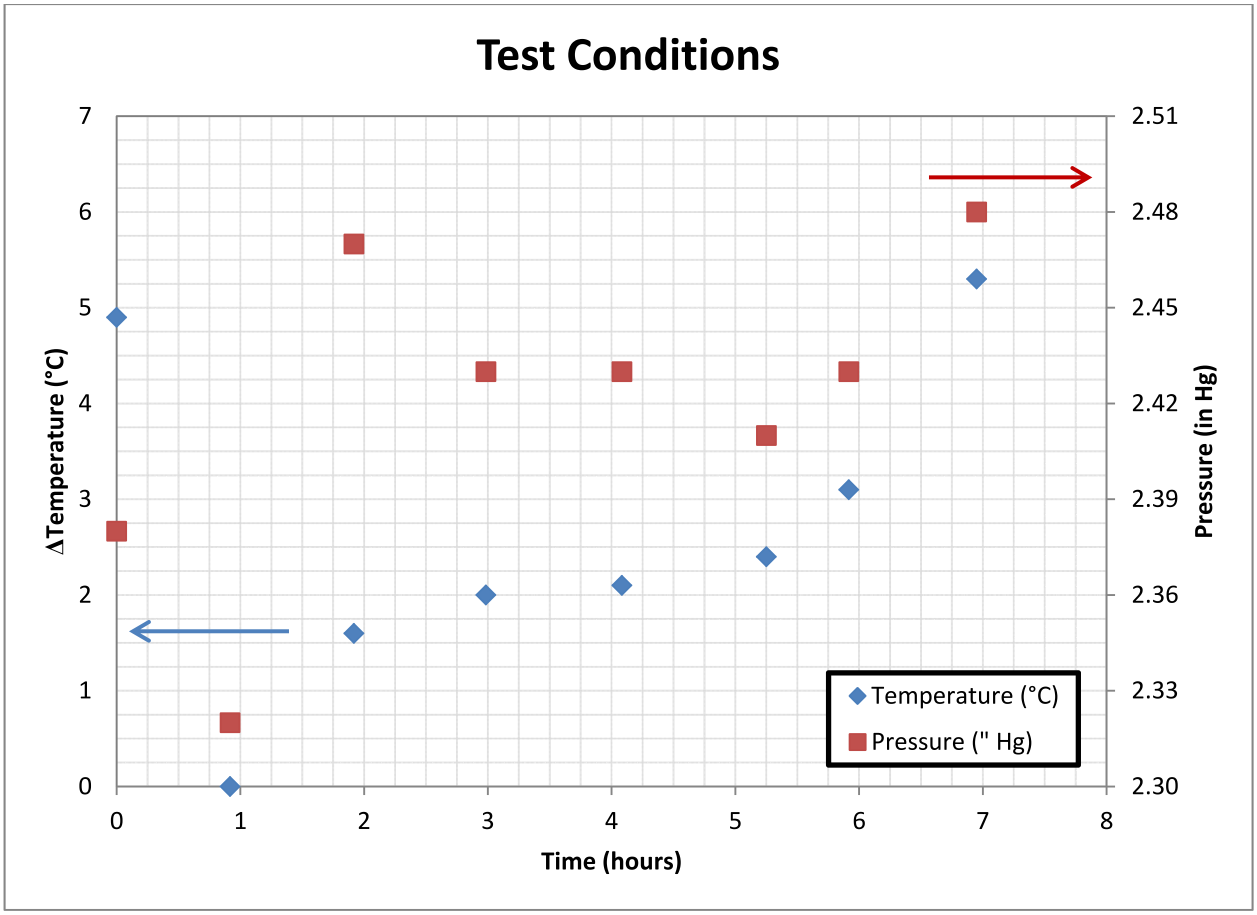

Figure 3-7. Test Conditions, ΔTemperature and Pressure

Because of the test apparatus configuration, fresh simulant was added to the pot periodically as the condensate was collected. This causes a discontinuous increase in the evaporator pot concentration. The calculated concentration in the pot at each condensate collection point is depicted in Figure 3-8. In between each point, the actual concentration in the pot would be higher or lower, depending on the periodic addition of fresh simulant. The small volume (6.64 mL) of condensate that was collected in the Secondary Knockout Pot was collected over time during the test campaign but was used only to calculate the final concentration of the simulant, 12.56X.

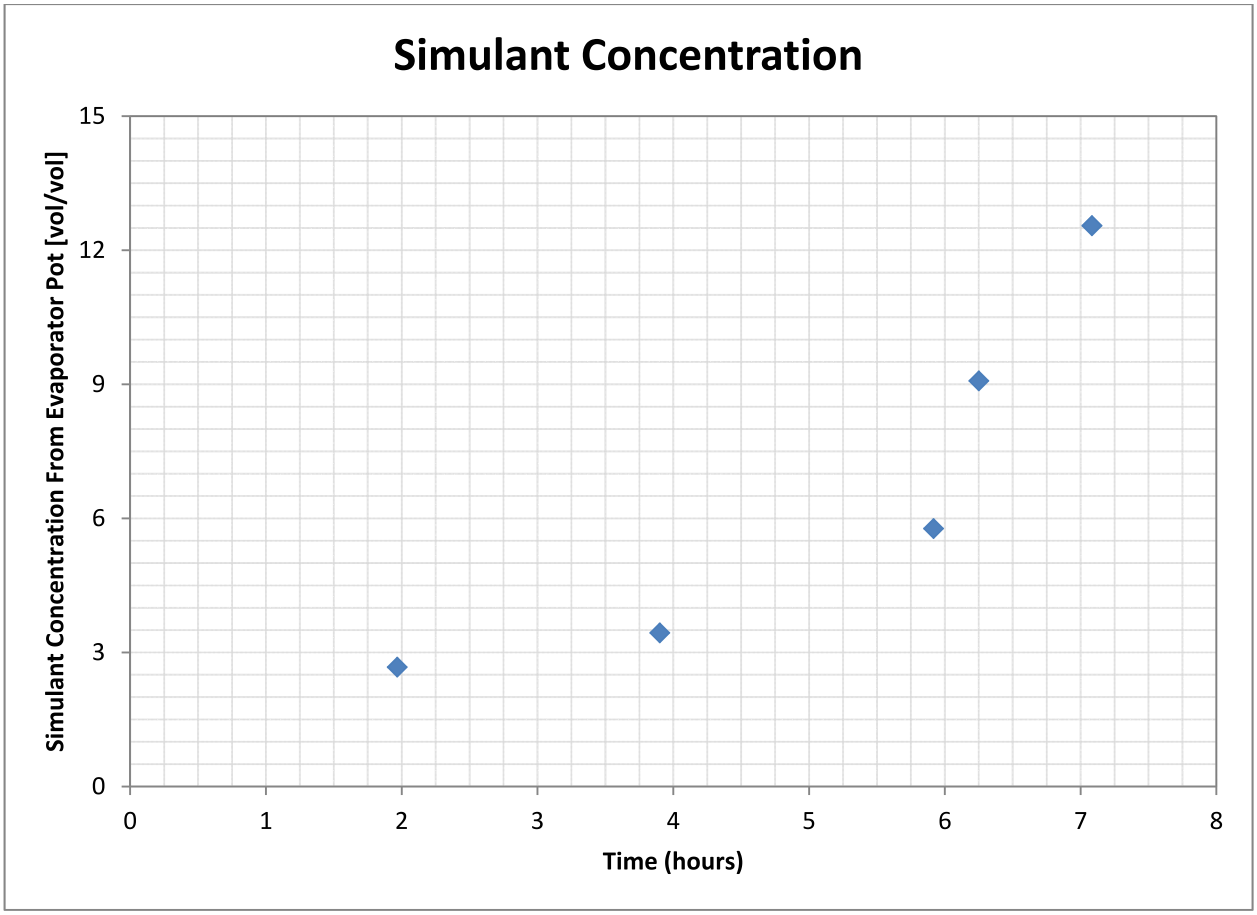

Figure 3-8. Simulant Concentration during Boil-off

The measured concentration of components in the filtered simulant are listed in Table 6.1 in the Appendix, and are shown as a function of concentration in Figure 3-9. The three vertical data sets correspond to the initial concentration (left-most column), 9.08X, and 12.56X (right-most column). As would be expected, the majority of components increase commensurately as the concentration increases. A few exceptions to this include NH_4, Li, F, S, and SO_4. This indicates that these precipitated or evaporated out of solution during testing, as depicted by level or decreasing concentrations between the 9.08X and 12.56X concentrations. Using the difference in concentration of components in the filtrate is an effective way to quantify precipitation of small concentrations of water-soluble salts, which would otherwise dissolve using traditional weight percent solids analysis methods.

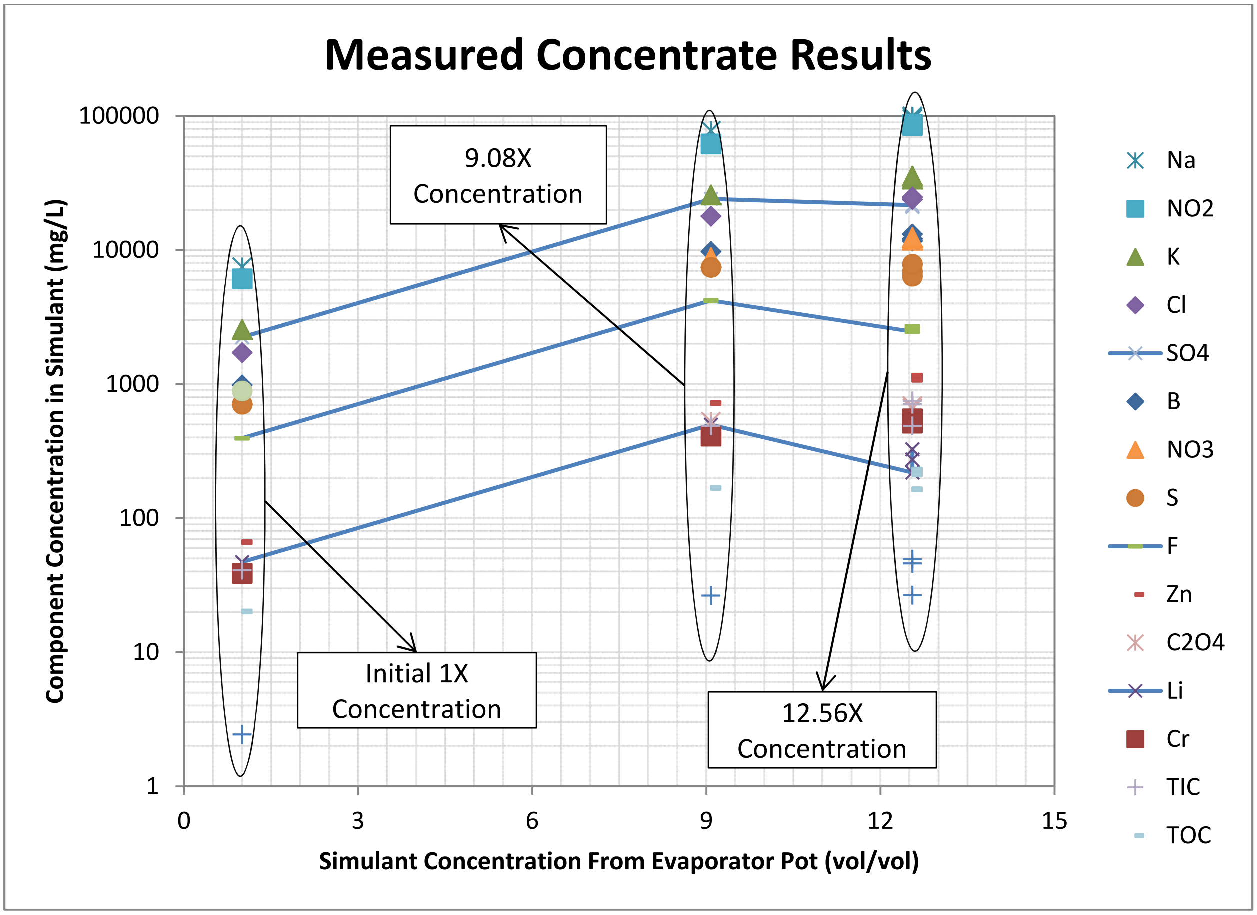

Figure 3-9. Measured Concentrate Results (mg/L) for Concentrated Simulant

Figure 3-10 below depicts the XRD results for the dried filter paper from filtration of the final pot sample. Two phases (LiF and $Na_3(SO_4)F$) are clearly identified, indicating that these insoluble solids form at higher concentrations after cooling.

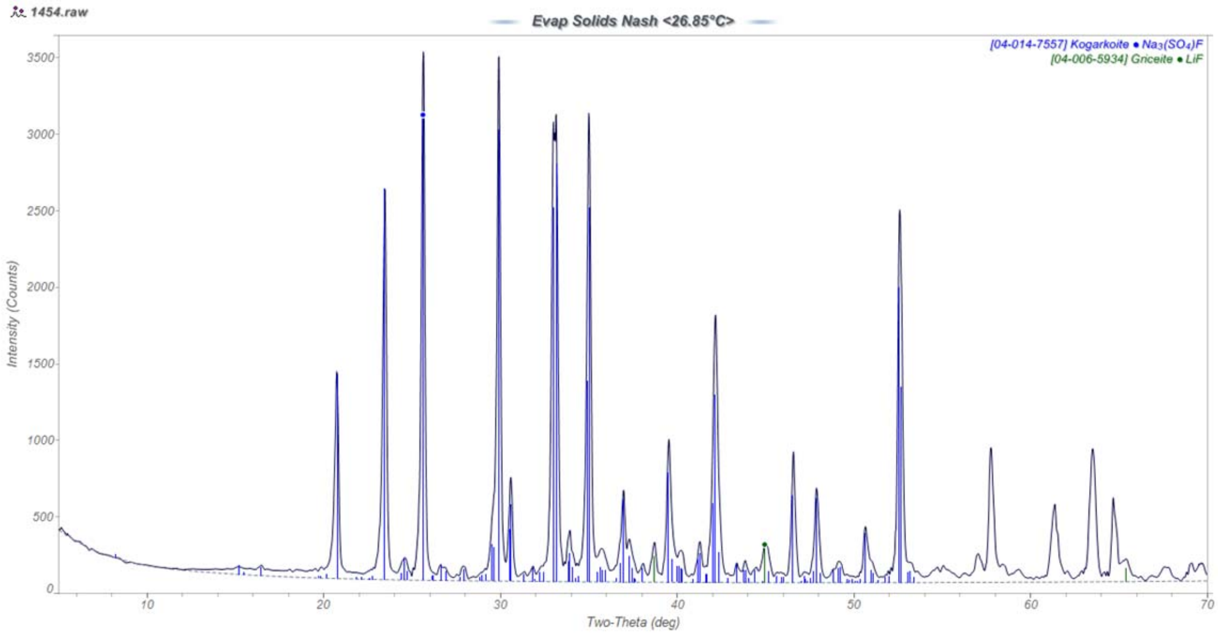

Figure 3-10. XRD Pattern of Dried Filter Paper

Figure 3-11 depicts the concentration of the system components normalized to the measured composition that was determined prior to evaporative testing. The scatter associated with the initial (1X) concentration is indicative of the variation between simulant batches and analytical analyses.

As can be clearly seen in Figure 3-11, there is a large variation between the expected and measured concentrations of Li, F, S, and SO_4 at the 12.56X target concentration. This difference can be explained by the formation of insoluble $Na_3(SO_4)F$ and LiF, and is consistent with the XRD results of the filtered solids. Two samples of the final evaporator pot liquid were collected and analyzed in duplicate, and the results of all 4 analyses are shown on Figure 3-11. Additionally, no ammonium was identified in pot samples other than in the initial 1X concentration, indicating that ammonia stripped off during evaporation to below detection limits (50 mg/L).

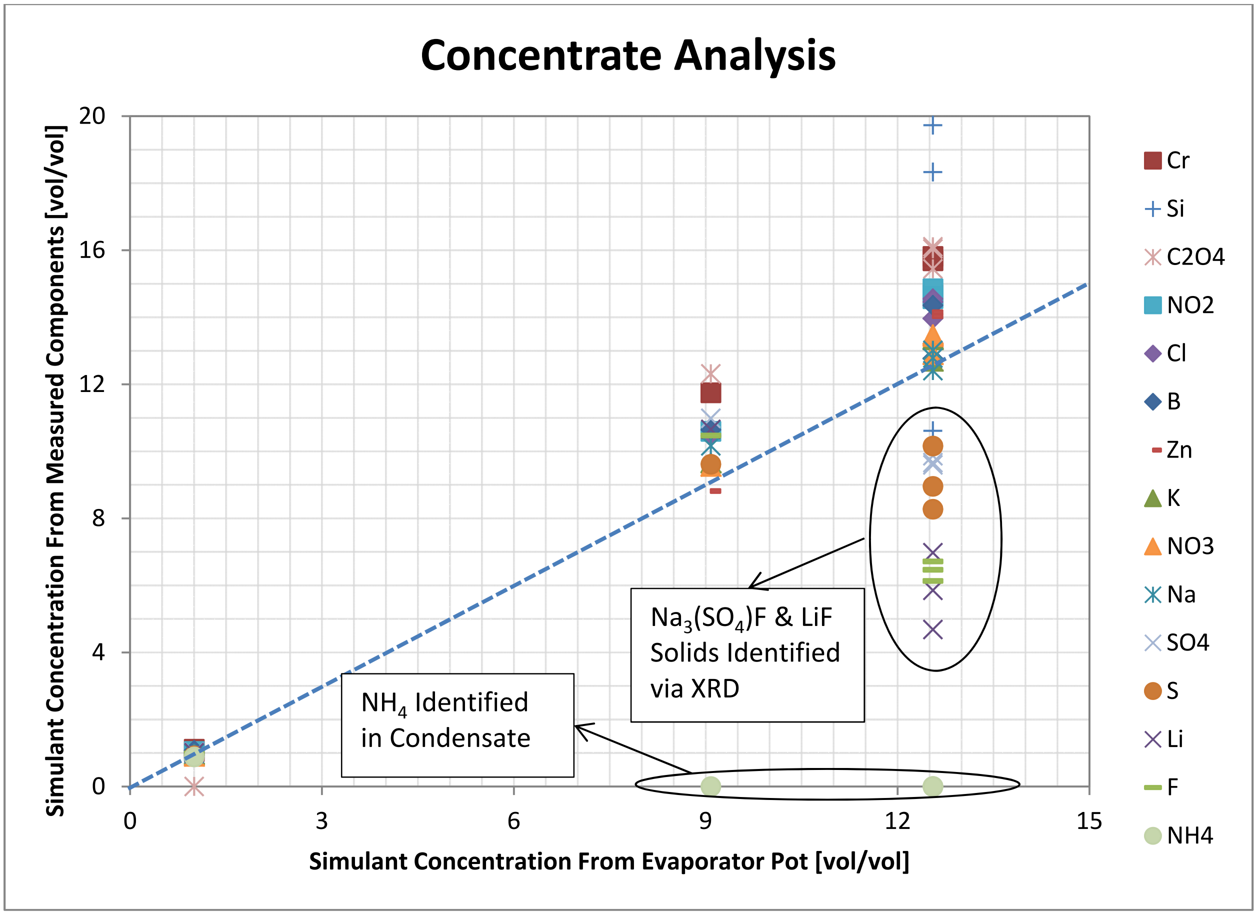

Figure 3-11. Concentrate Analysis for Concentrated Simulant Samples

As discussed above, the condensate tank was emptied five times during the run and stored in five separate poly bottles. These storage bottles were subsampled and 20 mL of each was submitted for analysis. Ammonium (NH_4^+) was present in all the condensate samples as depicted in Figure 3-12. This figure shows the fraction of ammonia recovered in each condensate aliquot versus the total amount that had been added to the pot prior to the condensate sampling event. Additionally, the condensate results provide good agreement with the normalized concentrate results since >95% of the ammonium present initially was found in the condensate before the simulant reached 3X concentration. The ammonium found in the condensate summed to 97% for the first sample and ~102% of the total added for each sample thereafter.

All condensate samples contained ammonia (as seen in Table 3-1 below), which suggests that ammonia continuously evolved during the test, but this is obscured by the fact that fresh simulant was added periodically, including near the end of the campaign, so it is not clear exactly how quickly the ammonia strips from the pot.

Table 3-1. Ammonia Condensate Data

Sample ID	Added Simulant Volume (mL)	Simulant Concentration from Evaporator Pot [vol\vol]	Condensate Volume (mL)	NH4 (mg/L)	NH4 (mg)	Accumulated Condensate			Accumulated Mass / Initial Batch Mass
						Mass (mg)	Volume (L)	Concentration (mg/L)	
EMF Condensate 1	796	2.67	498.1	1550	772	775	0.498	1550	96.5%
EMF Condensate 2	1,396	3.44	491.5	1320	649	1421	0.990	1436	101%
EMF Condensate 3	1,796	5.77	495.5	828	410	1831	1.485	1233	101%
EMF Condensate 4	1,796	9.08	113.4	138	16	1847	1.599	1155	102%
EMF Condensate 5	1,930	12.56	168.6	635	107	1954	1.767	1106	101%
Knockout Pot	1,930	12.56	6.64	635	4	1958	1.774	1104	101%

Of the total amount of ammonia in the simulant, ~100% was accounted for, as seen in Figure 3-12, in the condensate. The measurements that indicated >100% recovery of ammonia are attributed to analytical variability of the five condensate samples and high standard deviation of the initial feed sample analyses. The target initial ammonium concentration was 1170 mg/L, but the average of the two measurements was 1005 mg/L with a standard deviation of 163, indicating that the measured initial amount of ammonia used for the calculations may be biased low. The ammonium analysis of both of the evaporator pot liquid samples was below detectable limits, indicating that it readily strips to the condensate. Although it is theoretically possible that the ammonium could be destroyed during the analysis method in this matrix due to reactivity between ammonia and nitrite under acidic analysis preparation conditions, this was checked and found to not occur. The evaporator test conditions indicate that all of the ammonia partitions to the condensate, however, it cannot be ruled out that with a continuously-fed evaporator that some ammonia could remain in the bottoms, depending on conditions.

The condensate ICP-ES results gave very low to below detectable levels of many of the constituents in the simulant, shown in Table 6.2 in the Appendix. Other than ammonia, only a few measurements indicated that any species were present in the condensate, and these were all within 50% of the detection limit, so could be due to trace contaminants in equipment. Regardless, the highest DF calculated was from the analysis of Na^+, and was ~9.5E4. Other than ammonia, at this pH, all other species are expected to have minimal volatility, so would only be present in condensate due to entrainment. Since sodium is the dominant species, any entrainment would be most easily detected by analyzing sodium. Other non-volatile components would be expected to have comparable entrainment behavior, and thus comparable decontamination factors.

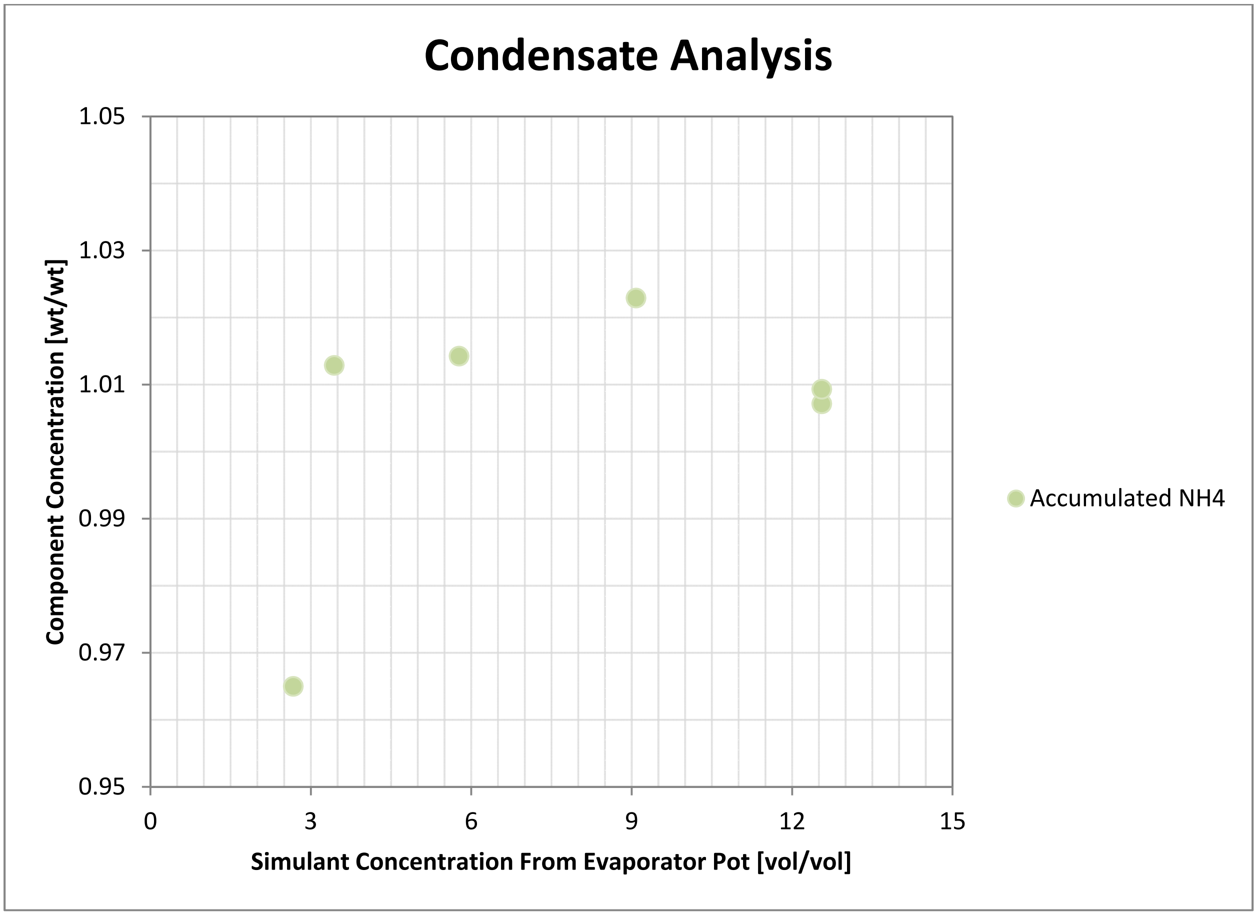

Figure 3-12. Analysis of Condensate

The wt% solids were determined by dividing the measured metals, cations, and anions by the total simulant mass. Additionally, the wt% insoluble solids were determined by comparing the expected simulant composition, based on the initial measured composition, and the measured composition post evaporative testing, and assuming that the differences indicated that the component either evaporated or solidified. These results, illustrated in Figure 3-13, show that the total dissolved solids increased from ~2.3 wt% to ~25 wt% as the simulant concentration increased to 12.56X. Figure 3-13 also shows that negligible solids form for all concentrations up to 9.08X, and then increased to ~0.8 wt% as the concentration increases to 12.56X. Two samples of the final evaporator pot liquid were collected and analyzed and the results are both shown on Figure 3-13. It should also be noted that these values don't include the ~140 mg/L of SiO_2 that was lost (due to filtering of simulant) prior to evaporative testing.

Figure 3-13. Wt% Solids in Concentrate

As seen in Table 6.1 in the appendix, the pH increased slightly from 12.2 to 13.1 with increasing concentration during evaporation, as measured with a pH meter. However, based solely on the amount of KOH and NaOH that was added to the simulant batch, the initial pH could be expected to be 13.3 and increase to a value of 14, but this does not account for buffers. During the preparation of the simulant, the boric acid consumes one equivalent of hydroxide when it converts to $NaB(OH)_4$, and likewise the ammonium consumes hydroxide in converting to ammonia and the extent of this reaction is based on the free OH^- concentration. The result is that the actual free OH^- concentration is lower than would be otherwise calculated without accounting for the buffers, resulting in a lower measured pH value. The measured value is comparable to the calculated value, after accounting for these buffering effects. However, note that measuring pH above 11 is beyond the recommended range for probes, and this is in very high ionic strength solution, so the measurements should be considered approximate values.

4.0 Conclusions

A simulant of the projected feed to the EMF evaporator at Hanford's WTP was successfully evaporated in the Bench-scale EMF Evaporator. The Feed simulant was found to be easily concentrated via low temperature boiling point evaporation with minimal solids formation. At the end of the test campaign, the simulant was concentrated to 12.56X with a density of 1.217 g/mL. Initially, no insoluble solids were visible in the concentrate at the end of the test campaign. However, as the concentrate cooled, insoluble solids were visible in the concentrated solution. The LiF and $Na_3(SO_4)F$ precipitated out of solution to form insoluble solids. During concentration of the simulant, the ammonia stripped and partitioned to the condensate stream. Ammonia continued to evolve during the test campaign, although the rate of evolution was obscured by the periodic addition of fresh simulant to the evaporator. Approximately 100% of ammonia was accounted for in the analysis of the condensate, and ammonia was below detection in the final evaporator pot sample. The objective of the test was to determine the distribution of components during vacuum evaporation. Although there was an issue with a faulty wire on a thermocouple which led to incorrect temperature measurements, the pressure was correct, so the evaporation conditions were correct, and the distribution of components is unaffected.

5.0 Future Work

Further testing is planned to augment this simulant with additional components. The simulant will be processed in the bench-scale EMF vacuum evaporator while measuring the distribution of species and examine the distribution and chemistry of the species.

6.0 References

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Appendix A

Table A-1. Measured Concentrate Data

Sample ID	Simulant Concentration from Evaporator Pot [vol\vol]	pH	Concentration in Concentrate (mg/L)																		
			B	Cr	Fe	K	Li	Mo	Na	S	Si	Zn	F	Cl	NO2	NO3	SO4	C2O4	NH4	TIC	TOC
EMF Evap Bottoms 1 (Unfiltered)	9.08	13.05	9520	408	<1.00	25400	495	<1.00	76400	7420	27	711	4250	18100	62200	8870	24300	535	<50	488	168
			9980	412	<1.00	26100	501	<1.00	78800	7420	26	728	4170	17700	61800	8700	23800	515			
EMF Evap Bottoms 2 (Unfiltered)	12.56	13.07	11700	528	<1.00	34000	211	<1.00	95300	6970	43	1050	2470	24000	91800	11900	21700	655	<50	488	164
			11700	567	<1.00	33700	227	<1.00	94200	6850	49	1100	2460	23800	82000	11800	21500	662			
EMF Evap Bottoms 3 (Unfiltered)	12.56	13.04	12100	560	<1.00	35700	277	<1.00	97600	6440	52	1150	2590	24300	84400	12100	20600	670	<50	708	212
			12100	544	<1.00	35400	270	<1.00	97600	6330	47	1160	2810	25200	86700	12600	21400	698			
EMF Evap Bottoms Feed (Unfiltered)	1.00	12.34	977	38	<1.00	2550	46	<1.00	7450	702	2	66	399	1730	6190	838	2210	<100	890	41	20
			995	40	<1.00	2560	48	<1.00	7500	715	3	66	392	1700	6030	823	2260	<100			
EMF Evap Bottoms Filtrate A	12.56	13.01	13200	514	<1.00	35500	327	<1.00	99000	7890	28	1140	2600	24900	84600	12400	21100	688	<50	748	230
			13100	510	<1.00	35700	325	<1.00	99700	7790	26	1150	2600	24900	85700	12400	21200	685			

Table A-2. Measured Condensate Data

Sample ID	Simulant Concentration from Evaporator Pot [vol\vol]	pH	Concentration in Condensate (mg/L)													
			B	Cr	K	Na	S	Si	Zn	F	Cl	NO2	NO3	SO4	C2O4	NH4
EMF Condensate 1	2.67	10.9	<1.00	<0.100	<1.00	1.16	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	1550
			<1.00	<0.100	<1.00	1.14	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	
EMF Condensate 2	3.44	10.7	<1.00	<0.100	<1.00	<1.00	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	1320
			<1.00	<0.100	<1.00	<1.00	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	
EMF Condensate 3	5.77	10.9	<1.00	<0.100	<1.00	<1.00	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	828
			<1.00	<0.100	<1.00	<1.00	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	
EMF Condensate 4	9.08	9.63	<1.00	<0.100	<1.00	<1.00	1.65	<0.100	<0.100	<100	<100	<100	<100	<100	<100	138
			<1.00	<0.100	<1.00	<1.00	1.80	<0.100	<0.100	<100	<100	<100	<100	<100	<100	
EMF Condensate 5	12.56	10.5	1.10	<0.100	<1.00	1.29	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	635
			1.16	<0.100	<1.00	1.32	<1.00	<0.100	<0.100	<100	<100	<100	<100	<100	<100	
Knockout Pot	12.56	10.53	-	-	-	-	-	-	-	-	-	-	-	-	-	635

Distribution:

D.E. Dooley. 773-A
T. B. Brown, 773-A
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
B. J. Wiedenman, 773-42A
W. R. Wilmarth, 773-A
A.D. Cozzi, 999-W
H. H. Burns, 773-41A
M. R. Poirier, 773-42A
Records Administration (EDWS)

P.A. Cavanah, WRPS
R.B Mabrouki, WRPS
D.J. Swanberg, WRPS
K. Subramanian, WRPS
M.G. Thien, WRPS
T. W. Crawford, WRPS
R. H. Davis, WRPS
S. T. Arm, WRPS

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B. M. Mauss, DOE-ORP
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