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Iodine Distribution During Evaporation of Hanford Waste Treatment Plant Direct Feed Low Activity Waste Effluent Management Facility Simulant

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October 2019

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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 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 involves concentrating the condensate in a new evaporator at the Effluent Management Facility (EMF) and returning it to the LAW melter.

The LAW melter condensate stream will contain components, e.g. halides and sulfates, that are volatile at melter temperatures, have limited solubility in glass waste forms, and present a material corrosion concern. Further, some minor constituents in the melter condensate, such as volatile organic compounds and iodine, have been found to be at least partially volatile in the EMF. The condensate from the EMF will be sent to the Hanford Effluent Treatment Facility (ETF). The presence of some recalcitrant organics and iodine, as ^{129}I , are expected to be problematic in the ETF. In order to better predict and prepare for the distribution of organics and ^{129}I in the flowsheet, it is key to understand their chemistry and experimentally determine their behavior during evaporation. To do this, modeling and testing were performed to examine the speciation of iodine under relevant conditions, as well as determine partitioning of iodine and the organics in the EMF evaporator.

This overall program examines the potential treatment and immobilization of the LAW melter condensate stream to enable alternative disposal. The objective of this task was to (1) perform modeling to determine the speciation and fate of iodine species, (2) prepare a simulant of the LAW Melter Off-gas Condensate expected during DFLAW operations, (3) spike in the key volatile organics and non-radioactive iodine, and (4) demonstrate evaporation in order to predict the final composition of the effluents from the EMF evaporator to aid in planning for their disposition.

The results of the modeling of iodine speciation indicate that the iodine is expected to remain in the evaporator pot as iodide and possibly iodate ion if the pH is raised to 11.5-12, which is the planned condition for the EMF. Experimental testing confirmed that the iodide remained in the evaporator concentrate and was below detection limits in all condensate and knock-out pot samples, indicating it was not volatile. The organic nitrile compounds that were added to the simulant were absent from the evaporator feed solution, either lost through evaporation, or more likely, decomposition. The acetone and methylene chloride were below the target values in the feed and condensate samples, and were presumably lost to evaporation or decomposition.

TABLE OF CONTENTS

LIST OF TABLES	viii
1.0 Introduction	1
1.1 Testing Basis and Objective	1
1.2 Thermodynamic-Equilibrium Prediction of Volatiles Emission during DM10 Test with AP-107 Simulant Blended with DFLAW Melter Off-Gas Recycle	5
1.2.1 FactSage Run	5
1.2.1.1 Identification of Feed Batch to Model	5
1.2.1.2 Feed Composition Vector	6
1.3 OLI Modeling.....	10
1.4 Simulant Formulation.....	11
2.0 Experimental Procedure.....	11
2.1 Simulant Preparation	11
2.2 Evaporator Test Apparatus	12
2.3 Quality Assurance	15
3.0 Results and Discussion	15
3.1 Results of FactSage Model.....	15
3.1.1 Equilibrium Speciation of Glass and Calcine Gases at 1,150 °C	15
3.1.1 Equilibrium Speciation of Calcine Gases at 300 °C	16
3.1.2 Equilibrium Speciation of Off-Gas at 45 °C.....	18
3.2 OLI modeling	19
3.3 Simulant Analysis	25
3.4 Evaporator Operation	26
3.5 Sample Analysis Results	28
4.0 Conclusions.....	33
5.0 Future Work	34
6.0 References	35
7.0 Appendices.....	38
7.1 Appendix A. Analysis Results.....	38
7.2 Appendix B. M&TE used for this testing.....	39

LIST OF TABLES

Table 1-1. DM10 Feed Batch Blending Ratios.....	5
Table 1-2. DM10 Batch 1 Feed Composition without Off-Gas Recycle.	7
Table 1-3. DM10 Batch 2 Feed Composition with Off-Gas Recycle.	8
Table 1-4. Pre-Decomposed DM10 Feed Input for FactSage Run.	10
Table 2-1. EMF Core Condensate Simulant Formulation.	12
Table 2-2. Pot Sample Concentrations.....	14
Table 3-1. Predicted Equilibrium Partitioning of DM10 Feed Using FactSage at 1,150 °C.	17
Table 3-2. Predicted Equilibrium Speciation of DM10 Melter Exhaust Using FactSage at 300 °C.....	18
Table 3-3. Predicted Equilibrium Speciation of DM10 Off-Gas Using FactSage at 45 °C.....	19
Table 3-4. SBS-WESP Composition used for OLI modeling.....	20
Table 3-5. EMF Core Simulant Filtrate Analysis Results.....	26
Table 3-6. Evaporator Concentrate Analytical Results.....	29
Table 3-7. Condensate Analytical Results.	30
Table 3-8. Knock-Out Pot Analytical Results.	31
Table 3-9. Total Volume and Ammonium and Iodide Balance.	32
Table 3-10. Knock-Out Pot Organic Analysis Results.	33
Table A-1. Analytical Results for Simulant Samples.	38
Table B-1. M&TE Equipment used during the EMF Evaporator Testing.....	39

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.....	13
Figure 3-1. OLI modeling output of SBS-WESP Stream with Iodine added as KI.....	21
Figure 3-2. OLI Modeling output of SBS-WESP stream with Iodine added as I ₂	22
Figure 3-3. OLI Modeling output of SBS-WESP stream with Iodine added as KI with reduced O ₂	23
Figure 3-4. OLI Modeling output of SBS-WESP stream with Redox for Iodine and Nitrogen.	24
Figure 3-5. Test Conditions, Temperature and Pressure.....	27
Figure 3-6. Simulant Boiling in the Evaporator Pot.	27
Figure 3-7. Evaporator Concentrate (~5.6X) at the End of Boil-down.....	28

LIST OF ABBREVIATIONS

BBI	Best Basis Inventory (BBI)
DFLAW	Direct Feed Low-Activity Waste
EMF	Effluent Management Facility
ETF	Effluent Treatment Facility
g	grams
gmole	gram-mole
hr	hour
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
inHg	Inches of mercury (pressure)
kg	kilogram
KOP	Knock-out Pot
L	Liter
LAW	Low Activity Waste
M&TE	Measurement and Test Equipment
mg	milligram
mL	milliliter
SBS	Submerged Bed Scrubber
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
Std. Dev.	Standard Deviation
VSL	Vitreous State Laboratory – Catholic University
WESP	Wet Electrostatic Precipitator
WRPS	Washington River Protection Solutions
wt %	Weight percent
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

The Hanford Low Activity Waste (LAW) Melter Off-Gas Condensate waste stream will be produced in the Waste Treatment and Immobilization Plant (WTP) by condensation and scrubbing of the LAW melter off-gas system by a Submerged Bed Scrubber (SBS) and Wet Electrostatic Precipitator (WESP), as shown in Figure 1-1. This condensate stream, which will contain substantial amounts of chloride, fluoride, ammonium, and sulfate ions, as well as technetium-99 (^{99}Tc) 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 Effluent Management Facility (EMF), as shown in Figure 1-2 [1]. Under normal operations, the evaporator bottoms will be returned to the LAW melter, however, the condensate may be returned to the tank farm without evaporation when the EMF evaporator is unavailable [2]. The evaporator overhead condensate is sent to the Effluent Treatment Facility (ETF). The volatile halide and sulfate components that accumulate in the evaporator bottoms stream are only partially retained in the glass, and often dictate the LAW glass waste loading [3], thereby impacting the total quantity of glass canisters produced. This accumulation of halide and sulfate then further impacts WTP by increasing the number of glass canisters produced, extending the mission duration. The radionuclides present in this stream that are key contributors to the long-term dose consequences for onsite disposal are ^{99}Tc and ^{129}I [4]. These two radionuclides are partially 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 beneficial impacts on the long-term cost, life cycle, and operational complexity of WTP [5]. Additionally, the LAW melter produces some volatile organic species due to the decomposition and reaction of sugar, which is added as a reductant, and the salts in the waste. The organics can have consequences in down-stream treatment processes. This work examines the behavior of non-radioactive iodine as a surrogate for ^{129}I and the volatile organics in the EMF evaporator.

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 concentrate and condensate waste streams produced during evaporation of the LAW Melter Condensate, determining waste stream compatibility with existing facilities, and planning alternate disposition options [6]. Analytical results of melter off-gas condensate samples from two DuraMelter-10 tests at Vitreous State Laboratory (VSL) at the Catholic University of America were used as the basis for the simulant of this stream [7]. This small-scale melter has been used extensively in testing for the Hanford WTP. The off-gas system is a scaled-down version of the system for WTP, including a SBS and WESP, which generated the aqueous condensate stream used as the basis for this simulant. At the time condensate samples used for the basis of the simulant were generated, the simulants being fed to the DuraMelter-10 were based on actual wastes expected during the DFLAW operations. Preparation and analysis of the core simulant by Savannah River National Laboratory (SRNL) has been described elsewhere [8]. This work added iodide ion, acetonitrile, acrylonitrile, methylene chloride, and acetone to the composition in order to quantify their fate and disposition. A vacuum evaporator system used in previous testing was used for this work [9, 10]. A description of the experimental apparatus is described in Section 2.0 below, and is described in additional detail in previous a report [10]. Evaporator conditions were selected to be similar to those used in prior testing for comparison and are consistent with the operating conditions of the 242-A evaporator at Hanford [11]. The target concentration for evaporation was ~5-6X the simulant feed concentration. This is consistent with the modeling performed for the EMF, which indicates that the evaporator bottoms will be ~4 wt % [Na] for the first three years of operation [12]

During tests at VSL, the SBS and WESP condensate is typically found to be near neutral pH. Prior to evaporation in the EMF evaporator during DFLAW operations, the pH will be raised to 12 to minimize corrosion of the evaporator material [13]. However, in recent tests at VSL, the condensate from the simulant tests was evaporated without pH adjustment. At the conclusion of that test, two issues identified in melter off-gas system testing of this flow-sheet by VSL [14] were the presence of organic species and iodine in

the evaporator condensate. The partitioning of organics to the condensate would be expected, but the volatility of iodine in the EMF evaporator would not generally be expected.

The VSL testing of the melter [14] used potassium iodide in the feed, but their results indicated that the iodine species in the liquid tank waste simulant are converted to molecular iodine (I_2) in the melter based on the observation that iodine was found in an alkaline impinger off-gas sample but not a preceding particle filter or acidic impinger. At melter temperature, any iodine species in the feed would be expected to disproportionate to the same, most thermodynamically stable species in the gas phase, although this has not been demonstrated by experiment with these simulants. Although both impinger samples were measured for iodine content using ion chromatography for the iodide ion (I^-), the molecular iodine is assumed to disproportionate to iodide once captured in the aqueous solution. The molecular iodine was partially scrubbed by the SBS and WESP [14]. When the aqueous SBS/WESP condensate was evaporated, a significant fraction of the iodine and organic species were found in the evaporator condensate; over 20% of the overall amount fed to the melter. The presence of a significant fraction of iodine in the evaporator condensate, as ^{129}I , would be challenging to process at the ETF.

The objective of this task is to examine the chemistry of the iodine and organics in this stream and determine if they are expected to partition the same as in the integrated testing at VSL and end up in the evaporator condensate that will be processed at ETF. An attribute of the integrated testing that deviated from the intended operations within the EMF evaporator, and that is suspected to have impacted iodine speciation and partitioning, was the lack of pH adjustment. This task will utilize computer modeling with FactSage (for melter off-gas speciation) and OLI Studio (EMF evaporation speciation) to determine what caused the iodine to partially volatilize in both the melter and the evaporator during the integrated testing, i.e., what species of iodine was present under the test conditions and whether the pH adjustment (which was not done in the testing) would be expected to prevent it. It was also important to understand the speciation of iodine in the melter off-gas and in the EMF in order to determine which species of iodine should be used in the simulant formulation for EMF testing at SRNL. Subsequent testing was performed to confirm the fate of iodine during evaporation. The test will also include organics identified in previous melter testing by VSL to determine the partitioning of these species in the EMF evaporator.

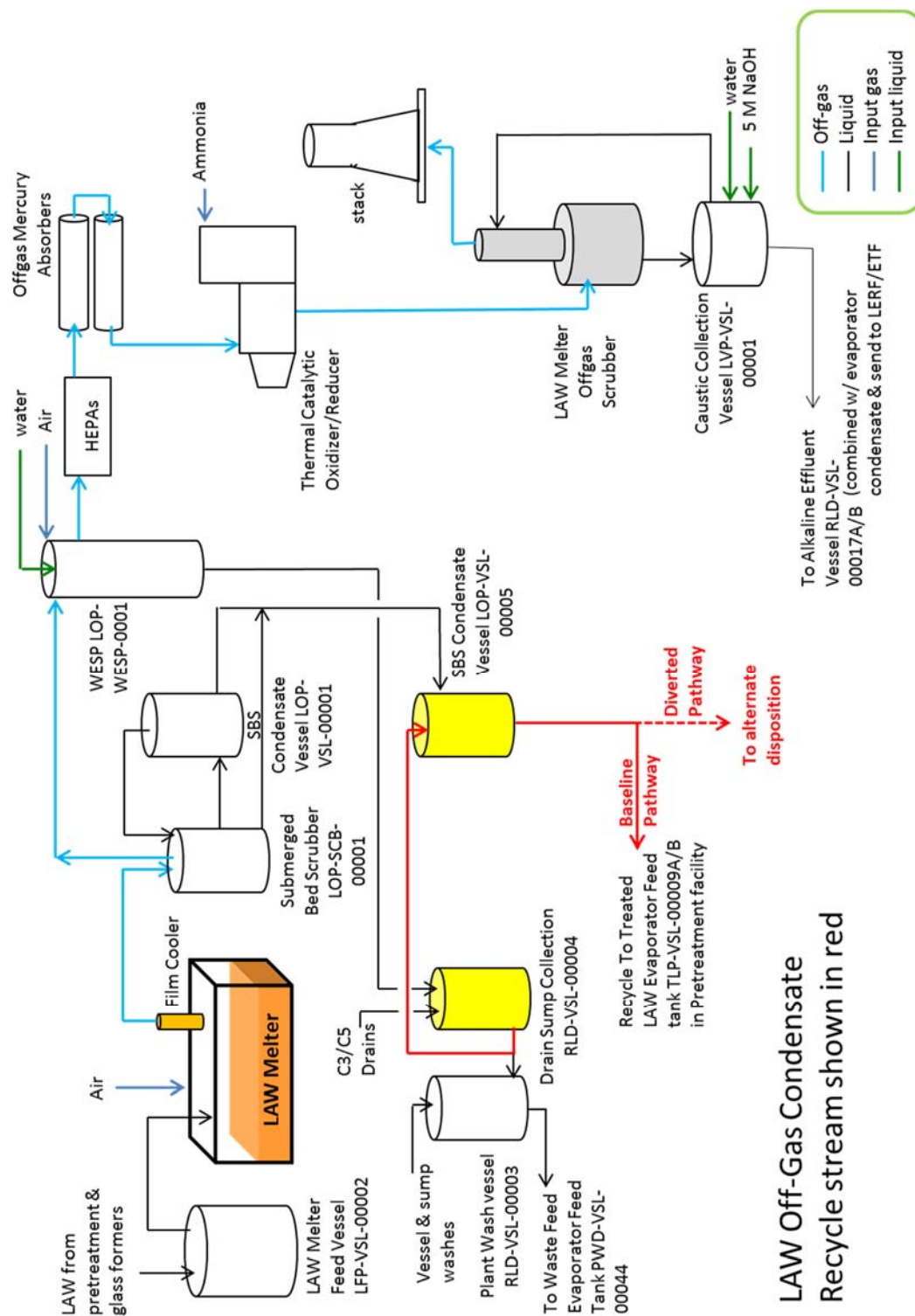


Figure 1-1. Simplified LAW Off-gas System.

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)

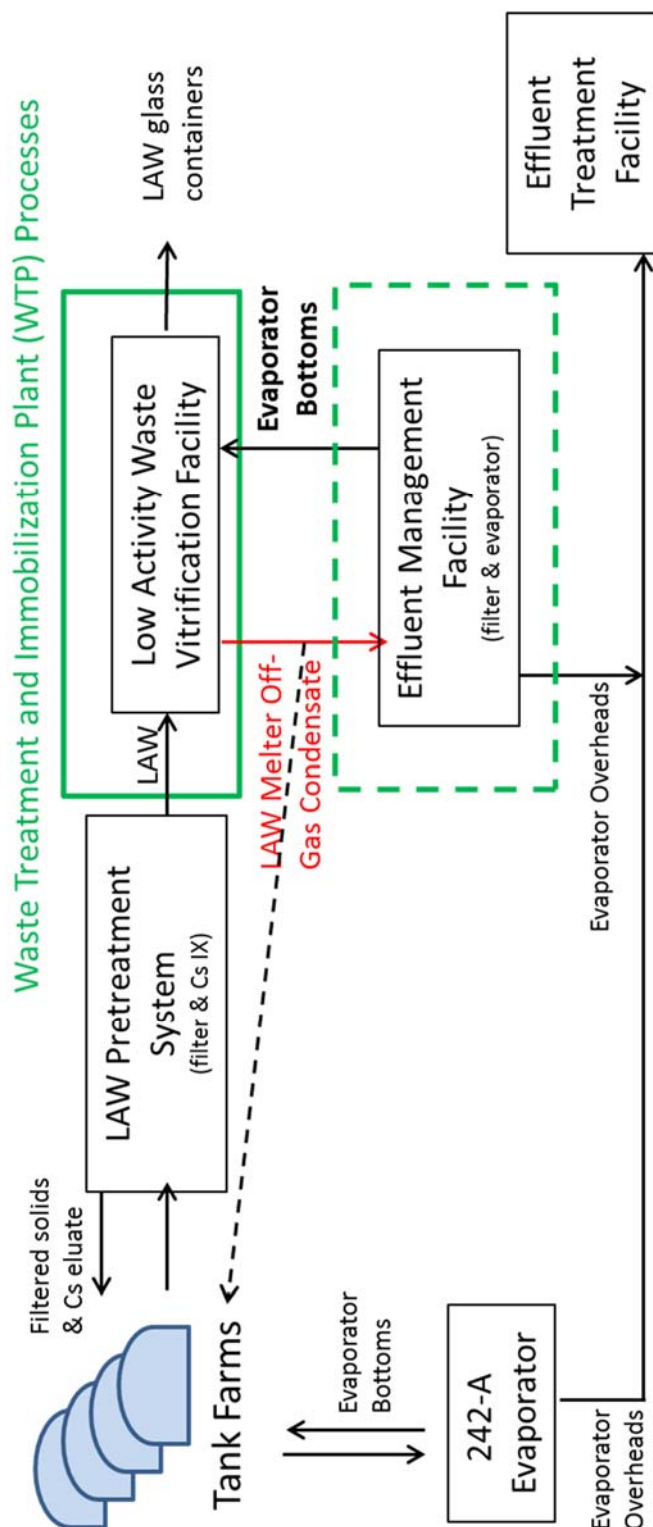


Figure 1-2. Simplified Schematic of the Direct Feed LAW (DFLAW) Scenario.

1.2 Thermodynamic-Equilibrium Prediction of Volatiles Emission during DM10 Test with AP-107 Simulant Blended with DFLAW Melter Off-Gas Recycle

The DFLAW melter test was conducted at the Vitreous State Laboratory (VSL) using the DM10 melter, which has a melt surface area of 0.021 m² and holds approximately 8 kg of glass.[14] The LAW simulant used was prepared based on the AP-107 supernatant composition from the Best Basis Inventory (BBI) and pre-mixed with the glass-forming chemicals at the vendor's facility before being shipped to VSL. The as-received feed was then blended with varying amounts of off-gas recycle and further constituted with additional chemicals, including iodine (added as KI), as shown in Table 1-1.[14] The main goal of the 2018 DM10 run was to demonstrate the DFLAW melter operation at the WTP with an off-gas condensate recycle loop consisting of a WTP prototypic vacuum evaporator to concentrate the effluents from the SBS and WESP; it was the evaporator bottom that was recycled back to the melter. No off-gas recycle was added to the first batch (Batch 1), since the SBS/WESP effluents had not been fully processed through the recycle loop yet. Thus, the presence of off-gas recycle in Batch 1 was simulated by adding larger quantities of key recycle species such as rhenium, iodine, chlorine, and sulfur, as shown in Table 1-1, and the amounts to be added were determined based on the recycle factors derived in previous VSL tests.[14] Of particular interest was how the retention of rhenium (added as a surrogate for technetium) in glass would be impacted by the off-gas recycle. For that, it was necessary to determine what species would likely volatilize during the calcination/fusion of feed solids and end up in the off-gas stream and the FactSage code was run to predict the resulting glass and off-gas chemistry.

Table 1-1. DM10 Feed Batch Blending Ratios.

Feed Batch	1	2 to 15	16
Start of Feeding	4/18/2018 11:00 AM	4/19/2018 3:00 AM	4/26/2018 4:35 AM
As-Received Feed (kg)	42.6	28.3	33.1
Off-Gas Recycle (kg)	0	14.4	16.8
Boric Acid (kg)	5.759	3.759	4.39
Li ₂ CO ₃ (g)	704	469	548
Perrhenic Acid (50 wt % Re) (g)	42.38	18.01	21.03
KI (g)	63.5	27.58	32.21
NaCl (g)	81	0	0
Na ₂ SO ₄ (g)	6	0	0
Sugar (g)	1876	1244	1453
DI water (kg)	21.6	0	0

1.2.1 *FactSage Run*

A high-temperature, thermodynamic-equilibrium code, called FactSage Version 7.0,[15] was used to predict the chemistry of volatiles emission from the DM10, which consisted of three steps. In Step 1, the recipes for the AP-107 supernatant simulant/glass forming chemicals and further adjustments outlined in Table 1-1 were followed to construct the DM10 feed composition vectors. In Step 2, the actual input to the FactSage code was developed by pre-decomposing the salt species such as nitrate/nitrite, hydroxide, and carbonate into the corresponding oxides and calcine gases. In Step 3, the FactSage code was run using the input from Step 2 in conjunction with the oxide solution (FToxid) as well as the pure substance (FactPS) databases of FactSage.

1.2.1.1 *Identification of Feed Batch to Model*

A total of 16 feed batches were processed during the 200-hour test from 4/18/2018 to 4/26/2018, while collecting a large quantity of glass and off-gas effluent samples throughout the DM10 off-gas system. However, the most crucial melter exhaust (from the melter volatility standpoint) was sampled only twice,

once near the beginning and again near the end of the test. In addition, the first set of melter exhaust samples taken was determined to be within the isokinetic sampling limits of 90-110% but not the second set due to anomalous instrument readouts. This instrument anomaly, which occurred near the end of the 200-hour test had no impact on the FactSage modeling results since 1) the feed composition vector for the model run was constructed based on the feed makeup recipe used early in the test and 2) the melter exhaust data collected during that time did not meet the isokinetic sampling protocols and thus was not used in this study. This means that only the first set of melter exhaust samples could be used to estimate retention of feed elements (in glass) and recycle concentrations of key species of interest such as rhenium, halides, and sulfate. Specifically, the first set of melter exhaust samples was taken at the midpoint of Batch 2 feeding which lasted for 12 hours. However, noting that the glass composition at the time of sampling would not be the same as that of Batch 2 being fed due to the mixing delay in the melt pool, it was necessary to first estimate the melter turnover at the time of sampling, where melter turnover is defined as the time it takes to produce one melt pool volume of glass. For example, under ideal mixing conditions, it would take 4.6 melter turnovers to flush out 99% of the initial glass in the melt pool.[16]

The average glass production rate (\dot{m}_g) during DM10 test is calculated from measured melt fluxes and the melt surface area of DM10:

$$\dot{m}_{glass} = \left(\frac{1,974 + 2,007}{2} \frac{kg}{m^2 day} \right) (0.021 m^2) = 41.8 \frac{kg}{day} = 1.74 \frac{kg}{hr} \quad (1)$$

Based on DM10 glass inventory of 8 kg, melter turnover is then calculated to be 4.6 hr (= 8/1.74), which means that the first set of melter exhaust samples was taken after 1.3 melter turnovers (= 12 hr/2/4.6 hr) since Batch 2 feeding began.

Under the assumption of ideal mixing of melt pool with no off-gas carryover, the ratio of concentration of species i in glass at $t = t_{n+1}$ to that at $t = t_n$ is related to the melter turnover N over that time increment as follows:[16]

$$\ln \left[\frac{x_{g,i}(t_{n+1})}{x_{g,i}(t_n)} \right] = -N \quad (2)$$

Per Eq. (2), the concentration ratio is 0.27 at $N = 1.3$, which means that at the time of first melter exhaust sampling, 73% of Batch 1 glass would have been flushed out of DM10 and the melt pool was likely made up of 27% Batch 1 and 73% Batch 2 glasses. Thus, the input vector to the steady state FactSage code should be based on a blend of Batch 1 and Batch 2 recipes given in Table 1-1 at a 27:73 ratio, respectively.

1.2.1.2 Feed Composition Vector

The DM10 feed was made up of four groups; (1) AP-107 supernatant simulant, (2) glass-forming chemicals, (3) off-gas recycle, and (4) VSL additives, including sugar and KI. The recipes used to prepare the AP-107 simulant and the glass-formers (GF) were followed to develop the composition of the as-received feed, which was then blended with additional chemicals at VSL according to the ratios given in Table 1-1. The resulting Batch 1 composition is shown in Table 1-2 on a per liter (L) simulant basis; the total solids was quite high at 58.1 wt %. The as-received feed composition used for Batch 1 was also used for Batch 2 following the blending ratios in Table 1-1 for Batches 2 to 15. The composition of the off-gas recycle produced during the Batch 1 feeding shown in Table 1-3 was developed from the analytical data of the first evaporator concentrate sample taken during the DM10 run (Sample ID: 10Q1-E1-120A) during the span of 15 hours.[12] It is noted that although the amount of recycle added to Batch 2 was close to 50% of the as-received feed per Table 1-1, nearly all of it (>99%) was H₂O. The resulting Batch 2 composition is shown in Table 1-3 on a per-liter simulant basis; the amount of H₂O added was adjusted so that the total solids remained at 58.1 wt %.

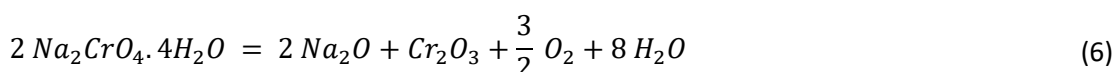
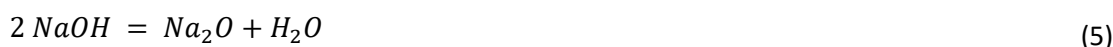
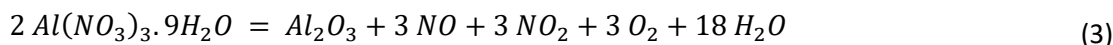
Table 1-2. DM10 Batch 1 Feed Composition without Off-Gas Recycle.

Simulant:	(g/L simulant)	Glass Formers (GF) & VSL Additions:	(g/L simulant)
Al(NO ₃) ₃ ·9H ₂ O	136.54	Al ₂ SiO ₅ (Kyanite)	70.42
Ca(NO ₃) ₂ ·4H ₂ O	0.31	CaSiO ₃ (Wollastonite)	87.57
Fe(NO ₃) ₃ ·9H ₂ O	0.18	Mg ₂ SiO ₄ (Olivine)	30.03
NaNO ₃	70.88	ZrSiO ₄ (Zircon)	45.62
NaNO ₂	76.66	ZnO (Kadox)	35.45
Na ₂ CO ₃	56.97	Fe ₂ O ₃	53.92
Na ₂ SO ₄	7.70	SiO ₂	359.63
Na ₃ PO ₄ ·12H ₂ O	6.92	TiO ₂ (Rutile)	15.02
Na ₂ CrO ₄ ·4H ₂ O	2.34	H ₃ BO ₃ (US Borax)	198.33
NaCl	7.13	Li ₂ CO ₃	24.24
NaF	0.90	KI	2.19
KOH	4.63	HReO ₄ (Perrhenic Acid)	1.46
NaOH	86.13	C ₁₂ H ₂₂ O ₁₁ (Sucrose)	64.61
Ni(OH) ₂	0.04	GF & Additives	988.49
PbO	0.02	H ₂ O	743.87
SiO ₂	0.07	Total GF & VSL Additions	1,732.36
Na ₂ C ₂ O ₄	0.97		
CH ₃ COONa	5.68	Final Batch 1 Feed:	2,504.56
NaCOOH	3.68	- total solids	1,456.26
Total Solids	467.77	- H ₂ O	1,048.31
H ₂ O & Impurities	304.44	- wt % solids	58.1
Total Simulant Slurry	772.21		

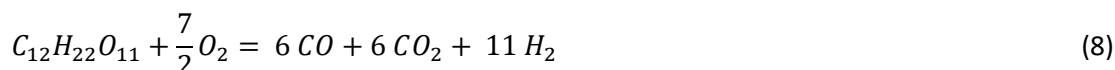
Table 1-3. DM10 Batch 2 Feed Composition with Off-Gas Recycle.

Simulant:	(g/L simulant)	Off-Gas Recycle:	(g/L simulant)
Al(NO ₃) ₃ ·9H ₂ O	136.54	- soluble	
Ca(NO ₃) ₂ ·4H ₂ O	0.31	Al(NO ₂) ₃	2.37E-02
Fe(NO ₃) ₃ ·9H ₂ O	0.18	Ca(NO ₂) ₂	3.44E-02
NaNO ₃	70.88	Fe(NO ₂) ₃	<1.30E-04
NaNO ₂	76.66	KNO ₂	2.05E-01
Na ₂ CO ₃	56.97	LiNO ₂	6.49E-02
Na ₂ SO ₄	7.70	Mg(NO ₃) ₂	4.97E-03
Na ₃ PO ₄ ·12H ₂ O	6.92	NaNO ₃	2.48E-02
Na ₂ CrO ₄ ·4H ₂ O	2.34	NaNO ₂	5.24E-01
NaCl	4.34	Ni(NO ₃) ₂	4.18E-04
NaF	0.90	Na ₃ PO ₄	3.48E-03
KOH	4.63	Pb(NO ₃) ₂	<1.19E-04
NaOH	86.13	Na ₂ SO ₄	2.12E-01
Ni(OH) ₂	0.04	NaCl	2.65E-02
PbO	0.02	NaF	6.35E-02
SiO ₂	0.07	NaI	4.02E-01
Na ₂ C ₂ O ₄	0.97	NH ₄ Cl	5.47E-01
CH ₃ COONa	5.68	Na ₂ B ₄ O ₇	3.44E-01
NaCOOH	3.68	NaReO ₄	3.14E-01
Glass Formers (GF) & VSL Additions:		Na ₂ SiO ₃	4.87E-02
Al ₂ SiO ₅ (Kyanite)	70.42	Zn(NO ₃) ₂	3.18E-02
CaSiO ₃ (Wollastonite)	87.57	ZrF ₄	4.10E-05
Mg ₂ SiO ₄ (Olivine)	30.03	- insoluble	
ZrSiO ₄ (Zircon)	45.62	Al ₂ O ₃	7.26E-03
ZnO (Kadox)	35.45	B ₂ O ₃	<2.40E-05
Fe ₂ O ₃	53.92	CaO	1.90E-03
SiO ₂	359.63	Cr ₂ O ₃	3.38E-04
TiO ₂ (Rutile)	15.02	Fe ₂ O ₃	5.19E-03
H ₃ BO ₃ (US Borax)	194.87	K ₂ O	2.34E-04
Li ₂ CO ₃	24.31	Li ₂ O	<1.61E-05
KI	1.43	MgO	1.11E-04
HReO ₄ (Perrhenic Acid)	0.93	Na ₂ O	5.84E-04
C ₁₂ H ₂₂ O ₁₁ (Sucrose)	64.49	NiO	<9.50E-06
		P ₂ O ₅	<1.71E-05
Simulant+GF+VSL Additions	1,753.11	Re ₂ O ₇	6.80E-05
- Total Solids	1,448.67	SiO ₂	2.11E-02
- H ₂ O & Impurities	304.44	TiO ₂	4.23E-04
		ZnO	3.70E-03
Final Batch 2 Feed:	2,499.61	ZrO ₂	8.07E-04
- Total Solids	1,451.62	Total Recycled Solids	2.95
- H ₂ O	1,047.99	H ₂ O	743.55
- wt % solids	58.1	Total Recycle	746.50

The final DM10 feed composition for the FactSage run was derived by blending the Batch 1 and Batch 2 compositions at a 27:73 ratio, respectively. The resulting blend feed has a total of 62 chemical species, excluding H₂O, as shown in Table 1-3, and a half of those species are to represent the soluble and insoluble species of the evaporator concentrate despite the fact that the recycle contains only 0.2 wt % of the total solids in the DM10 feed. Thus, in an effort to reduce the number of feed species to be input into the FactSage model, the nitrate/nitrite salts, hydroxides and organic species in Table 1-3 were pre-decomposed to their respective oxides and calcine gases as follows:



Sugar was oxidatively pre-decomposed as:



In Eq. (8), sugar is shown to exert its reducing potential by consuming O₂, while producing reducing gases, CO and H₂. The resulting pre-decomposed DM10 feed composition is shown in

Table 1-4 on a per liter simulant basis; it consists of a total of 42 species, including 16 oxides, 13 salts and minerals, 6 halides, and 7 gas species. The impurities represented the balance of the added chemicals per the AP-107 simulant recipe after subtracting the sum of pure compounds based on the assay data; [14] ~99% of them originated from the addition of NaOH (50%) and Al(NO₃)₃·9H₂O (60%). So, the impurities were treated as H₂O and constituted ~17% of the total H₂O.

The salts and minerals in

Table 1-4 were further decomposed to the oxides and calcine gases to obtain the final glass composition. Although not shown here, it was determined that 43.1 wt % of the DM10 slurry feed would be converted to glass. This compares well with the measured calcination ratio of 44.1 wt % based on the average DM10 feed rate and melt flux of 3.98 kg/hr and 2,007 kg/m²/day, respectively; note that the latter is equivalent to the glass pour rate of 1.7562 kg/hr, i.e., (2,007 kg/m²/day)(0.021 m²)/(24 hr/day). The good agreement between the calculated and measured calcine ratios gives credence to the calculated feed compositions given in Table 1-4.

Finally, based on the measured DM10 feed rate of 3.98 kg/hr,[14] the feed composition given in

Table 1-4 was converted into the instantaneous feed rates by multiplying the concentration of each component by 1.592, which was obtained by dividing the feed rate by the weight of the feed on a per L simulant basis, i.e., (3.98 kg/hr)/(2.5 kg/L simulant) = 1.592 L simulant/hr. The resulting instantaneous molar feed rates of all 42 species were input into the FactSage model.

Table 1-4. Pre-Decomposed DM10 Feed Input for FactSage Run.

Oxides:	(g/L simulant)	(gmole/L simulant)	Halides:	(g/L simulant)	(gmole/L simulant)
Fe ₂ O ₃	53.9594	0.3379	NaCl	5.1163	0.0875
Al ₂ O ₃	18.5662	0.1821	NaF	0.9454	0.0225
CaO	0.0855	0.0015	KI	1.6342	0.0098
MgO	0.0009	2.12E-05	NaI	0.2935	0.0020
NiO	0.0324	0.0004	NH ₄ Cl	0.3991	0.0075
Cr ₂ O ₃	0.7595	0.0050	ZrF ₄	3.00E-05	1.79E-07
TiO ₂	15.0203	0.1880	Total	8.3886	0.1293
SiO ₂	359.7147	5.9868	Calcine Gases:		
Na ₂ O	132.1459	2.1598	H ₂ O	83.9846	4.6619
ZnO	35.4627	0.4357	CO	34.5793	1.2345
K ₂ O	3.9702	0.0421	CO ₂	54.3310	1.2345
B ₂ O ₃	0.1736	0.0025	NO	45.7654	1.5252
Li ₂ O	0.0134	0.0004	NO ₂	70.1677	1.5252
PbO	0.0201	0.0001	O ₂	8.1042	0.2533
Re ₂ O ₇	0.0000	1.02E-07	H ₂	4.4436	2.2044
ZrO ₂	0.0006	4.78E-06	Total	301.3759	12.6390
Total	619.9253	9.3148			
Salts & Minerals:			Free H ₂ O	871.6641	48.3849
Na ₂ CO ₃	56.9745	0.5376	Impurities	176.4124	9.7924
Na ₃ PO ₄	2.9883	0.0182	Total Slurry Feed	2,500.8408	86.6709
Na ₂ SO ₄	7.7604	0.0546			
Na ₂ B ₄ O ₇	0.2508	0.0012			
NaReO ₄	0.2295	0.0008			
Na ₂ SiO ₃	5.86E-02	3.35E-05			
H ₃ BO ₃	195.8024	3.3501			
Li ₂ CO ₃	24.2946	0.3288			
HReO ₄	1.0756	0.0043			
Al ₂ SiO ₅	70.4200	0.4346			
CaSiO ₃	87.5700	0.7539			
Mg ₂ SiO ₄	30.0300	0.2134			
ZrSiO ₄	45.6200	0.7128			
Total	523.0746	6.4104			

1.3 OLI Modeling

OLI Systems, Inc. chemical thermodynamic software programs are used in calculating aqueous electrolyte chemistry. One of the components of this software system, the Stream Analyzer (SA), is used to reconcile chemical analyses, calculate thermodynamic parameters, and predict phase splits. SA provides complete speciation of all phases that are in the databank for a given aqueous chemistry composition, along with the thermodynamic parameters and reduction-oxidation chemistry (only the SA component of the software was used in this work). The software program is a chemical thermodynamic simulator using the OLI Engine, which is used for approximating aqueous electrolyte chemistry. The results from this software can be used

in many ways, such as estimating aqueous waste chemistry for development of flow sheets and material balances. The OLI databanks (which are part of the OLI Engine and used by SA) have been evaluated and used previously.[17, 18] For this work, the SA software was utilized by SRNL to calculate the expected speciation and behavior of iodine during evaporation under various conditions. The results will be utilized to help explain what happened during VSL testing and to decide which iodine species to use in the simulant testing.

The SA software program is produced by OLI Systems, Inc. and procured by SRNS. The databanks contain thermodynamic parameters on thousands of chemicals, with the parameters derived primarily from open technical literature. These fundamental parameters are then used by the software in a thermodynamic framework based on Revised Helgeson Equation of State to predict the physical and chemical properties of aqueous or multiphase systems. Calculation of the composition and phases is accomplished by solving the equilibrium equations with parameters from the included databanks.[18] SRNL used this software and databanks without modification. OLI version 9.6 was used for this work.

1.4 Simulant Formulation

The basis for the core simulant chemical composition has been previously reported [8]. The amount of added silica was decreased compared to the previous formulation in order to add only the measured soluble amount. Selection of the iodine species to add was based on the outcome of the modeling and the observation that the VSL analysis method was capable of only detecting iodide, indicating that the iodine converted to iodide in the aqueous solution. The VSL report indicated that the feed to the evaporator was 78.9 mg/L of iodine, as measured using Ion Chromatography (IC) (Table 4.13 of [14]). The selection of organic chemicals was based on prior melter testing that identified species that can form in the melter and are collected in the SBS and WESP liquids.

2.0 Experimental Procedure

2.1 Simulant Preparation

The target simulant formulation is shown in Table 2-1.^a

^a Combining iodine species and ammonia, under certain conditions, can form nitrogen triiodide. Nitrogen triiodide is a dark solid that is a shock sensitive explosive. No dark solids were observed in this testing. However, caution is urged in preparing these simulants.

Table 2-1. 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 ₄ NO ₃	0.910	0.0114
Ammonium sulfate	(NH ₄) ₂ SO ₄	0.642	0.0049
Sodium sulfate	Na ₂ SO ₄	0.963	0.0068
Potassium sulfate	K ₂ SO ₄	2.20	0.0126
Ammonium chloride	NH ₄ Cl	2.343	0.0438
Silica	SiO ₂	0.005	0.0001
Boric acid	B(OH) ₃	5.250	0.0849
Zinc nitrate	Zn(NO ₃) ₂	0.241	0.0013
Sodium oxalate	Na ₂ C ₂ O ₄	0.077	0.0006
Potassium hydroxide	KOH	0.980	0.0175
Sodium hydroxide (50 wt %)	NaOH	Adjust to pH 11.5-12.0	
Sodium chromate	Na ₂ CrO ₄	0.108	0.0007
Sodium nitrite	NaNO ₂	8.350	0.1210
Lithium carbonate	Li ₂ CO ₃	0.213	0.0029
Sodium iodide	NaI	0.088	5.9E-4
Acetone	(CH ₃) ₂ CO	0.010**	1.3E-4
Acetonitrile	CH ₃ CN	0.010**	1.9E-4
Acrylonitrile	CH ₂ CHCN	0.010**	1.5E-4
Methylene chloride	CH ₂ Cl ₂	0.010**	1.6E-4

*calculated weights assume anhydrous reagent is used

** units for organics are mL/L

The simulant was prepared in one 3-L batch. The simulant was clear yellow but was filtered through a 0.45-μm Nylon filter prior to use although there were no visible insoluble solids. The organics were added to the filtered simulant within 24 hours of the beginning of the evaporation test to minimize evaporative losses.

2.2 Evaporator Test Apparatus

Figure 2-1 is a schematic of the EMF Evaporator Test Apparatus used for the simulant testing. During the design and construction, care was taken to have as few polymer parts as practicable. This would prevent the simulant in the evaporator pot and the off-gas from coming into contact with polymeric materials. This was as a precautionary measure to minimize loss of key components that might absorb into such materials and thereby avoid detection in the aqueous phases. The apparatus was constructed almost entirely with glass and stainless steel tubing. All testing was conducted inside a fume hood in a laboratory in SRNL. The evaporator pot was a 1-L modified glass beaker. The simulant was heated using a hot plate/stirrer and continuously stirred with a Teflon-coated magnetic stir bar.

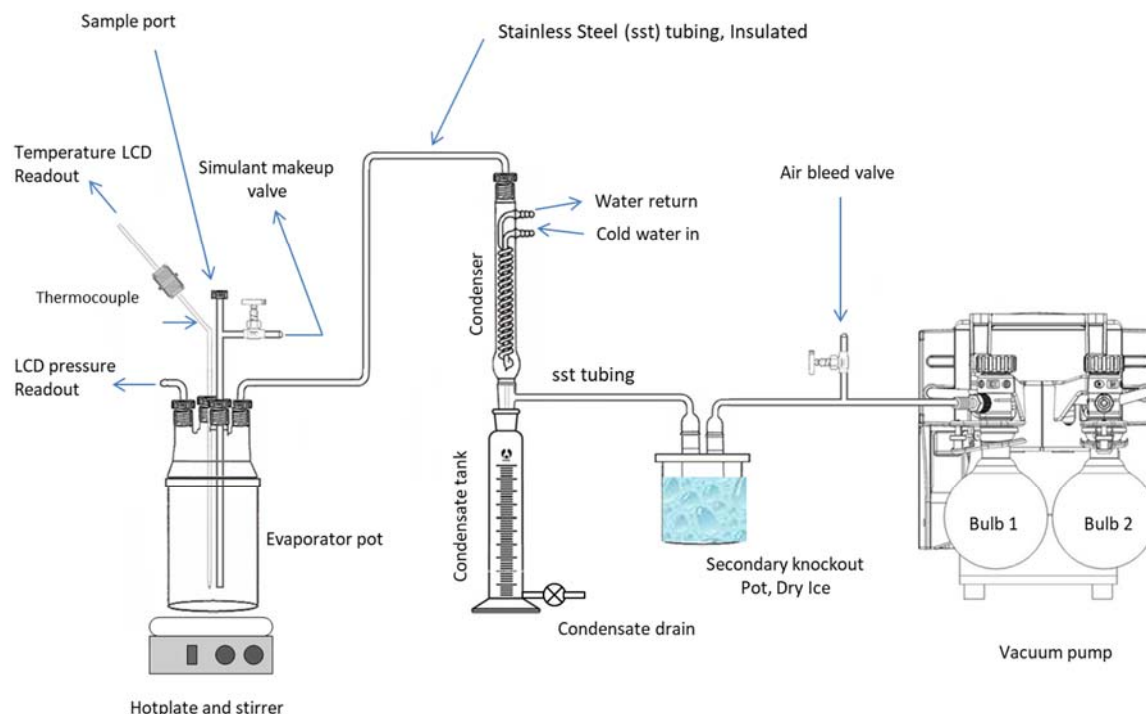


Figure 2-1. EMF Evaporator Test Apparatus.

The contents of the pot were kept under a vacuum, typically at an absolute pressure of 2.4 inches of Hg (inHg) (equivalent to 60 torr) as measured by a pressure transducer. As a result, the simulant boiled at approximately 42 °C. The vapors traveled unrestricted to the glass condenser. There was no engineered demisting element designed into the off-gas line to knock out entrained particles, but the stainless steel line was approximately 58 cm high, which should have precluded entrainment based on engineering judgement. As the gases cooled in the condenser, the condensate drained into the glass Condensate Tank.

The Condenser was cooled using a VWR Scientific recirculating water bath. The chiller, supplemented with periodic additions of ice, maintained the cooling water at approximately 4 °C. Any vapors that passed through the condenser were condensed in the glass secondary Knock-out Pot (KOP). The KOP was submersed in a Dewar with dry ice, where the temperature was maintained at approximately -78 °C. The vacuum in the system was created by a Vacuubrand® Diaphragm Vacuum pump, Type: MZ 2C. Images of the EMF evaporator test apparatus and components are available in the previous report [10].

The contents collected inside the KOP were always frozen when it was disconnected and had to be thawed before they could be poured into the sample collection bottle. Care was taken to transfer the liquid as soon as it had thawed to minimize vapor losses. During the test campaign, two separate KOPs were used, one to allow time to thaw the collected contents and the other placed back into the dry ice to allow testing to continue.

Before simulant testing, water runs were performed to ensure that all of the equipment and instruments were operating correctly. The system operated under a vacuum at approximately 2.4 inHg and a temperature of 42 °C. This compares well with CRC Steam Tables [19] that show a boiling point of water at 108.0 °F (42.2 °C) at 1.2030 psia (2.45 inHg). All equipment and instruments that made up the test apparatus operated as expected, as indicated by calibrated instrument readings and no evidence of pressure leaks.

The simulant used for the EMF testing was previously prepared and analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) for metals and Ion Chromatography for anions and cations (ammonium).

Initially, 400 mL of feed simulant was loaded into the evaporator pot. The pressure was adjusted to approximately 2.4 inHg (equivalent 8.1 kPa; 60 torr, absolute), comparable to conditions used for previous boil-down tests performed by SRNL [9, 10, 20].

The simulant was heated using a hot plate and stirred continuously with a Teflon-coated magnetic stir-bar. The pressure in the system was 60 ± 5 torr and the solution boiled at approximately 42 °C. In order to achieve the desired concentration factor of ~5-6X, and mimic a semi-continuous process, each time ~200 mL of condensate was collected ~200 mL of fresh simulant was added to the evaporator pot. During the first “concentration phase”, a portion of the simulant was initially concentrated to the target concentration factor. As this phase progressed, after evaporating 200 mL from the evaporator pot, an additional 200 mL of (room temperature) feed simulant was added to the pot to replenish the liquid level. This cycle was repeated until ~1250 mL of simulant was evaporated down to an equivalent of 250 mL (accounting for extracted samples). At this point, boiling was paused and a ~ 50 mL sample was withdrawn from the evaporator pot, and the accumulated condensate was collected. Fresh simulant was then added to the remaining concentrate in the evaporator pot and boiling resumed. This was the “production phase,” where some concentrated liquid from the evaporator pot was periodically removed, and fresh simulant were added to restore the liquid level. At the end of the test campaign, the concentrated simulant density was 1.11 g/mL. No insoluble solids were visible in any samples.

After the initial concentration phase, fresh feed was periodically added to the pot and five 50-mL concentrated samples were collected from the pot at various points during the campaign when the concentration was projected to correspond to ~6X. Detailed liquid addition and removal data are shown in Table 2-2. Correspondingly, five condensate samples, ~250 mL each, were pulled during the experiment. Each aliquot of feed and condensate were weighed, and those masses were used to calculate concentrations in the evaporator pot. In practice, the measured final concentration factors varied due to the ability to control the sample volume, and ranged from 5.3–5.6X and averaged 5.5X, based on volume, for the six concentrated pot samples collected.

Table 2-2. Pot Sample Concentrations.

Sample Name	Cumulative Total Simulant added to pot (mL)	Cumulative Condensate & KOP collected (mL)	Concentration Factor
Concentrate 1	1240	1010	5.4X
Concentrate 2	1517	1246	5.6X
Concentrate 3	1789	1468	5.6X
Concentrate 4	2072	1692	5.5X
Concentrate 5	2349	1913	5.4X
Concentrate 6	2629	2159	5.6X
Average			5.5X

2.3 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 #E7518-00211-42. This report documents completion of Task 3.1 and 3.2 in the Task Technical and Quality Assurance Plan SRNL-RP-2019-00204, Rev. 0 [6]. OLI modeling is controlled under Software Quality Assurance Plan X-SQP-A-00001, Rev. 0.

3.0 Results and Discussion

3.1 Results of FactSage Model

The FactSage model was run in conjunction with the FToxid and FactPS databases at three different temperatures.[15] First, the equilibrium speciation of the glass and calcine gases was calculated at the nominal melt pool temperature of 1,150 °C by simulating the calcination/fusion of the feed solids. Next, the resulting calcine gases were re-equilibrated along with free H₂O in the feed at the minimum vapor space temperature of 300 °C for the DFLAW melter. However, since the temperature of the DM10 off-gas at the film cooler outlet was controlled at ~310 °C,[14] the FactSage results at 300 °C would represent the equilibrium speciation in the DM10 vapor space as well as in the off-gas line leading to the SBS. Finally, the melter exhaust gases were cooled to 45 °C to simulate the off-gas exiting the SBS, ignoring the vapor-liquid contact in the SBS.

3.1.1 Equilibrium Speciation of Glass and Calcine Gases at 1,150 °C

The results of the FactSage run at 1,150 °C are shown in Table 3-1, where each species is identified by its molecular formula followed by the name of the database from which relevant thermochemical property data was pulled. All gas species were assumed to form an ideal gas mixture based on the FactPS database, which contains pure substances data from standard compilations. Only the gas species at higher than 10⁻⁵ gmole/hr are shown. All species in the Slag-liq#1 phase form a liquid solution optimized by the FToxid solution databases, which contain data for pure oxides and oxide solutions of 20 elements as well as for dilute solutions of S, SO₄, PO₄, H₂O/OH, CO₃, F, Cl and I in the molten (slag) phase.[15] Lithium disilicate (Li₂Si₂O₅) was the only pure liquid species predicted to form.

Table 3-1 shows that essentially 100% of the halides and sulfur fed would volatilize at 1,150 °C. Note that these results represent the thermodynamic limits and thus are higher than those measured during the melter tests with the cold cap present. Unlike Cl and F, iodine was predicted to volatilize as a monatomic iodine, I, while the loss of Cl and F was predicted to occur mainly as acid gases and alkali salts, e.g., HCl and NaCl. The predicted volatilities of Na, Li and K were 0.7%, 5.3% and 4.2%, respectively, and the losses would occur mainly in the form of halides and borates such as NaCl and LiBO₂, which is consistent with the analytical results of the DWPF melter off-gas deposit samples.[21] The calculated volatile loss of boron was 1.2%. Chromium and zinc were the only non-volatile species with a small but non-zero volatility at 0.2% and 0.1%, respectively. A recent mass balance analysis of the DWPF melter pour stream data showed that the losses of non-volatile feed components such as Fe, Al, and Si were an order of magnitude larger than the predicted volatilities of Cr and Zn, which was confirmed by the measurable quantities of carryover found in the off-gas from actual melters.[22] This was attributed to the physical entrainment due to the inherent cold cap instability of the slurry-fed melter as the main route of off-gas carryover, which is not accounted for by the thermodynamic modeling.

The predicted 100% volatilization of rhenium as Re₂O₇ was expected because the measured REDOX of the DM10 glass was highly oxidizing at 0.048 and it is well known that the volatility of technetium (Tc), for which rhenium was added as a surrogate, increases as glass becomes more oxidizing.[23] It is noted that the uncertainty associated with the measured REDOX value of 0.048 was not given in the VSL report.[14]

SRNL conducted a series of crucible tests in preparation for the upcoming flowsheet change at DWPF and produced 17 different test glasses by varying the relative amounts of reductants and oxidants in the feed. [24] The REDOX of all glass samples except for one was measured in triplicate and the results showed a 95% confidence interval of ± 0.04 or larger around the average REDOX value of each test glass. Thus, if we assume that the same 95% confidence interval would apply to the reported DM10 glass REDOX value, the calculated REDOX value of 0.075 using the FactSage code would lie inside the smallest 95% confidence interval of the measured REDOX, 0.008-0.088, gives credence to the calculated equilibrium speciation using the FactSage code. In fact, the predicted 100% volatility of rhenium at 0.075 REDOX is close to the estimated off-gas carryover rate of 84.3% for Tc-99 at the measured REDOX of 0.07 for the DWPF sludge batch 7b (SB7b) glass.[22] These comparisons are based on one implicit assumption – the REDOX is not impacted by the absolute difference in feed chemistry between the DWPF and AP-107 simulants, e.g., concentrations of major species such as Fe and Al or type of reductant used (sugar vs. glycolic acid), but by the relative concentrations of reductants and oxidants in each feed.

3.1.1 Equilibrium Speciation of Calcine Gases at 300 °C

The gas-phase output in Table 3-1 was input into the model and re-equilibrated at 300 °C along with the free H₂O that volatilized upon entering the melter. The potential air inleakage into the DM10 vapor space, which was maintained at -1.7 inches of H₂O column was not known and thus ignored. The calculated DM10 melter exhaust equilibrium speciation at 300 °C is shown in Table 3-2. Iodine was predicted to be present as iodine monochloride (ICl), hypoiodous acid (HIO) or diatomic iodine (I₂), but not monatomic iodine (I). Sulfur was predicted to be present as sulfuric acid or alkali sulfate. As expected, 100% of NO predicted at 1,150 °C was converted to N₂ at 300 °C, as the latter is thermodynamically more favorable at lower temperatures than the former. This contrasts with the measured concentration of NO in the range of 1,000 to 1,400 ppm during the 2016 Slurry-fed Melt Rate Furnace (SMRF) test at a comparable temperature,[25] which suggests the non-equilibrium nature of the vapor space reactions. It is also noted that the addition of free H₂O coupled with a lower temperature seemed to have resulted in a 2X increase in the total acidic gas flow, including HCl, HF and H₂SO₄.

Table 3-1. Predicted Equilibrium Partitioning of DM10 Feed Using FactSage at 1,150 °C.

PHASE: Gas	gmole/hr	PHASE: Gas	gmole/hr
H ₂ O_FactPS	1.89E+01	Li ₂ SO ₄ _FactPS	1.44E-05
CO ₂ _FactPS	5.31E+00	NO ₂ _FactPS	1.26E-05
N ₂ _FactPS	2.43E+00		
O ₂ _FactPS	1.35E+00	PHASE: Slag-liq#1	gmole/hr
SO ₂ _FactPS	8.58E-02	Na ₂ O_FToxid	2.04E+00
HCl_FactPS	6.06E-02	K ₂ O_FToxid	2.66E-02
NaCl_FactPS	4.91E-02	Al ₂ O ₃ _FToxid	4.42E-02
LiCl_FactPS	3.54E-02	SiO ₂ _FToxid	1.19E+01
HF_FactPS	3.50E-02	NaAlO ₂ _FToxid	1.78E+00
HBO ₂ _FactPS	2.11E-02	KAlO ₂ _FToxid	9.11E-02
I_FactPS	1.81E-02	CaO_FToxid	1.20E+00
LiBO ₂ _FactPS	1.73E-02	FeO_FToxid	8.11E-02
H ₃ BO ₃ _FactPS	1.28E-02	Fe ₂ O ₃ _FToxid	4.97E-01
NaBO ₂ _FactPS	7.95E-03	MgO_FToxid	6.79E-01
Re ₂ O ₇ _FactPS	4.00E-03	PbO_FToxid	1.42E-04
NO_FactPS	3.99E-03	ZnO_FToxid	6.93E-01
KCl_FactPS	3.47E-03	NiO_FToxid	6.90E-04
KBO ₂ _FactPS	2.10E-03	B ₂ O ₃ _FToxid	1.13E+00
OH_FactPS	2.00E-03	CrO_FToxid	2.08E-06
LiOH_FactPS	1.24E-03	Cr ₂ O ₃ _FToxid	7.98E-03
SO ₃ _FactPS	1.07E-03	Ti ₂ O ₃ _FToxid	1.81E-06
LiF_FactPS	5.12E-04	TiO ₂ _FToxid	2.99E-01
(NaCl) ₂ _FactPS	4.79E-04	ZrO ₂ _FToxid	1.13E+00
ZnCl ₂ _FactPS	4.29E-04	NaBO ₂ _FToxid	3.02E+00
NaOH_FactPS	2.89E-04		
HIO_FactPS	2.62E-04	PHASE: Liquid	gmole/hr
(LiCl) ₂ _FactPS	2.37E-04	Li ₂ Si ₂ O ₅ _liquid_FactPS	4.96E-01
Cl_FactPS	2.36E-04		
LiI_FactPS	2.23E-04	Calculated Glass REDOX:	
OBF_FactPS	1.24E-04	- Fe ²⁺ /ΣFe	0.075
HI_FactPS	1.21E-04	Calculated Volatility (% fed):	
NaF_FactPS	9.51E-05	Cl	100.0%
KI_FactPS	7.75E-05	F	100.0%
H ₂ _FactPS	5.48E-05	I	100.0%
Na ₂ SO ₄ _FactPS	4.55E-05	S	100.0%
(HBO ₂) ₃ _FactPS	4.13E-05	Re	100.0%
CO_FactPS	3.44E-05	Na	0.7%
ICl_FactPS	3.24E-05	Li	5.3%
CrO ₂ (OH) ₂ _FactPS	2.88E-05	K	4.2%
KOH_FactPS	1.96E-05	B	1.2%
I ₂ _FactPS	1.51E-05	Cr, Zn	0.1-0.2%

Table 3-2. Predicted Equilibrium Speciation of DM10 Melter Exhaust Using FactSage at 300 °C.

PHASE: Gas	gmole/hr	PHASE: Gas	gmole/hr
H ₂ O_FactPS	1.11E+02	I ₂ _FactPS	2.48E-04
CO ₂ _FactPS	5.31E+00	(HBO ₂) ₃ _FactPS	1.07E-04
N ₂ _FactPS	2.43E+00	CrO ₂ (OH) ₂ _FactPS	2.63E-05
O ₂ _FactPS	1.31E+00	Zn ₂ Cl ₄ _FactPS	1.53E-05
HCl_FactPS	1.30E-01	I_FactPS	1.01E-05
H ₃ BO ₃ _FactPS	6.12E-02	BF ₂ OH_FactPS	4.97E-06
HF_FactPS	3.58E-02	CrO ₂ Cl ₂ _FactPS	3.61E-06
H ₂ SO ₄ _FactPS	2.57E-02	HSO ₃ F_FactPS	2.63E-06
ICl_FactPS	1.78E-02	SO ₂ _FactPS	1.18E-06
Re ₂ O ₇ _FactPS	4.00E-03		
SO ₃ _FactPS	1.52E-03	PHASE: Liquid	gmole/hr
Cl ₂ _FactPS	1.03E-03	Na ₂ SO ₄ _liquid_FactPS	2.93E-02
HIO_FactPS	4.69E-04	Li ₂ SO ₄ _liquid_FactPS	2.76E-02
ZnCl ₂ _FactPS	3.99E-04	K ₂ SO ₄ _liquid_FactPS	2.84E-03

3.1.2 Equilibrium Speciation of Off-Gas at 45 °C

The composition of the melter exhaust gases in Table 3-2 was input into the model and re-equilibrated at the measured SBS outlet temperature of 45 °C during the DM10 test.[14] As stated earlier, the calculation was simplified by ignoring the vapor-liquid contact in the SBS, thereby focusing solely on the effect of cooling on the equilibrium speciation of the off-gas. The calculated DM10 off-gas equilibrium speciation at 45 °C is shown in Table 3-3. Essentially, 100% of the halides, sulfur and rhenium and >99% of H₂O in the off-gas were predicted to condense out in the SBS. The resulting condensate would be very acidic at pH ≈ 1 since the concentration of acid gases (HCl, HF and HIO) in the off-gas was high. Chlorine would dissolve completely as Cl⁻, while fluoride would either dissolve as undissociated HF or form borates, BF₄⁻ and BF₃OH⁻, where the latter seems unlikely. Rhenium would dissolve as perrhenate (ReO₄⁻), while iodine would dissolve as iodate (IO₃⁻) and undissociated hypoiodous acid (HIO).

Table 3-3. Predicted Equilibrium Speciation of DM10 Off-Gas Using FactSage at 45 °C.

PHASE: Gas	gmole/hr	PHASE: Liquid	gmole/hr
CO ₂ _FactPS	5.2871	H ₂ O_liquid_FactPS	110.3900
N ₂ _FactPS	2.4292	H[+]_FactPS	0.2111
O ₂ _FactPS	1.2811	Cl[-]_FactPS	0.1512
H ₂ O_FactPS	0.9362	H ₃ BO ₃ _FactPS	0.0548
HF_FactPS	2.73E-05	HSO ₄ [-]_FactPS	0.0260
ICl_FactPS	1.04E-05	CO ₂ _FactPS	0.0211
HCl_FactPS	2.82E-07	HF_FactPS	0.0128
H ₃ BO ₃ _FactPS	1.74E-07	IO ₃ [-]_FactPS	0.0103
HIO_FactPS	1.50E-07	HIO ₃ _FactPS	0.0085
Cl ₂ _FactPS	3.25E-08	ReO ₄ [-]_FactPS	0.0080
I ₂ _FactPS	2.68E-08	NO ₃ [-]_FactPS	0.0075
		BF ₃ OH[-]_FactPS	0.0040
	% condensation	BF ₄ [-]_FactPS	0.0027
I	99.99	SO ₄ [2-]_FactPS	0.0011
Cl	99.99	Zn[2+]_FactPS	0.0004
F	99.92	O ₂ _FactPS	0.0003
S	100.00	N ₂ _FactPS	0.0002
Re	100.00	ZnSO ₄ _FactPS	7.01E-05
H ₂ O	99.15	F[-]_FactPS	5.85E-05
		Cr[3+]_FactPS	2.72E-05
Calculated pH	0.9741	CrCl ₂ [+]_FactPS	2.57E-06
Ionic Strength	0.1074	HF ₂ [-]_FactPS	1.01E-06

3.2 OLI modeling

As discussed above, the VSL report [14] stated that the iodine was present in the vapor phase as molecular iodine (I₂). OLI modeling was used to determine the speciation of iodine once it is dissolved in the aqueous SBS-WESP stream. The composition of the stream was calculated based on results in the VSL report, with adjustment of Na ion to account for cation-anion imbalance. The flow-volume-weighted average composition was derived from results shown in Tables 4.2, 4.5, and 4.6 in VSL 18R4500-1 [14]. The resulting charge-balanced composition input used for the OLI modeling is shown below as molecular species. OLI calculated that the pH of this composition matched the measured average evaporator feed, pH = 7.31. Note that the species identified in the FactSage modeling of the condensate, iodine, iodate, and iodic acid, are all included in the OLI databank used for this work.

Table 3-4. SBS-WESP Composition used for OLI modeling.

Species	Moles
H ₂ O	55.5082
NaF	1.4E-3
NH ₄ Cl	6.9E-3
NaCl	1.8E-3
NaNO ₂	4.8E-3
NaNO ₃	1.0E-4
Na ₂ SO ₄	1.4E-3
KI	1.1E-3
NaOH	7.0E-5
HNO ₃	0*
N ₂	0.08
O ₂	0.02
I ₂	0**

*nitric acid was used to adjust pH in some modeling runs

**iodine was added in some modeling runs, and KI was deleted

OLI calculations were performed at 0.079 atmospheres of pressure (60 torr) and 41.6 °C, which was the condition needed to vaporize ~90% of the water and concentrate the liquid by 11X, consistent with the VSL conditions. Sufficient oxygen was also included to exceed the stoichiometric amount of iodine species by 9X (and was mixed with nitrogen in a 20:80 ratio). Redox was turned “on” for iodine only (oxygen is on by default). The source of iodine in this case was potassium iodide (KI). Results are shown below and indicate that the dominant iodine species at low pH (<~4.0) is molecular iodine (I₂) vapor, but above pH 5.0, the iodine is present in the liquid phase as iodate ion (IO₃⁻). The conversion of iodide ion to molecular iodine by oxidation in air under acidic solutions is a well documented reaction [26], so the OLI results appear consistent with literature. It is believed that if molecular iodine was formed in the evaporator at VSL, it would be volatile and would explain the observation of enhanced iodine concentration in the condensate. However, the VSL analysis method was by ion chromatography, which would only detect iodide in this matrix. So the iodine would have converted to iodide, probably by reaction with a reductant, such as ammonia, or by hydrolysis. Note that the evaporator bottom solution in the VSL testing was pH 6.4, not the ~1 as predicted by the FactSage. Although other iodine species may have also been present in the off-gas and/or in the scrubber solution, they would not have been identified and would not have led to the observation that the iodine partitions to the EMF condensate because they would not have been measured.

For Figures 3-1 through 3-4, the left axis shows the ionic and molecular iodine-containing species molar amount in the aqueous phase. The right axis shows the molecular iodine-containing species molar amount in the vapor phase. The calculation input was 1 L of the composition shown in Table 3-4 above and vaporized at 0.079 atmospheres and 41.6 °C. The same conditions were used for all OLI calculations; albeit with different iodine species.

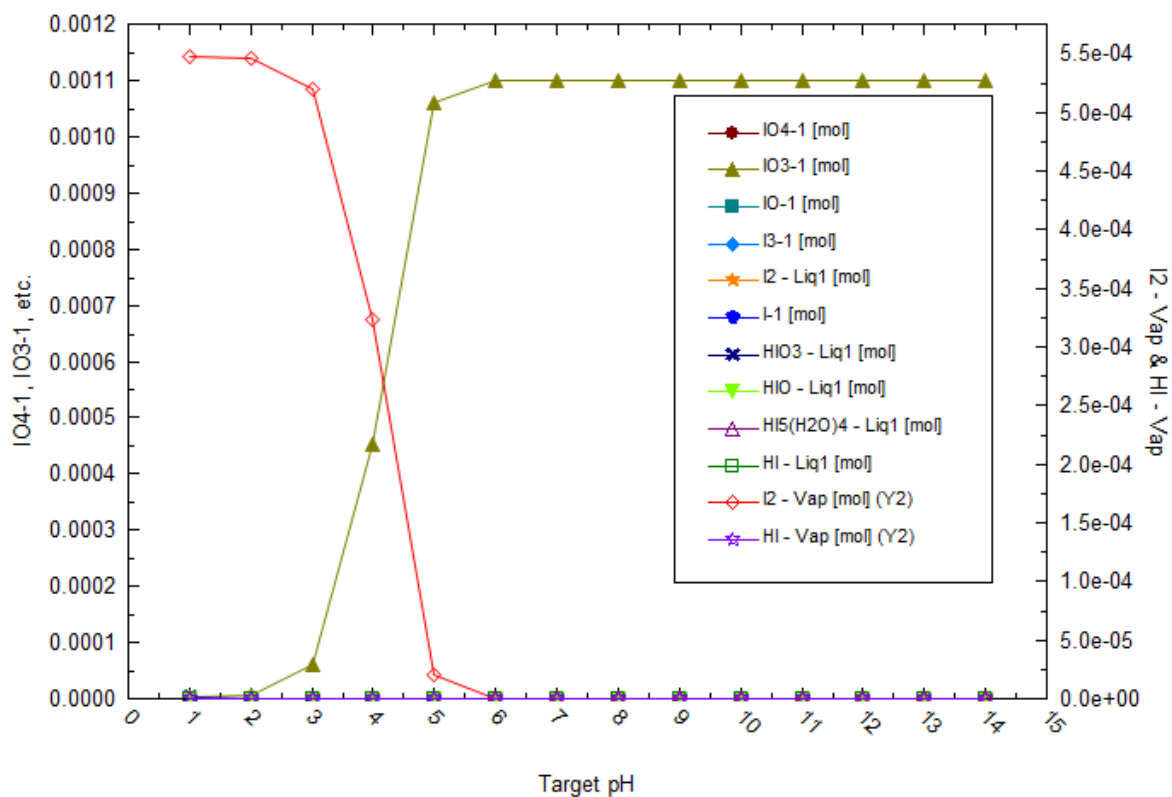


Figure 3-1. OLI modeling output of SBS-WESP Stream with Iodine added as KI.

An identical calculation was performed, except the source of iodine was molecular iodine (I_2). Results are shown below. Results indicated that the speciation was identical, regardless of which iodine species was used.

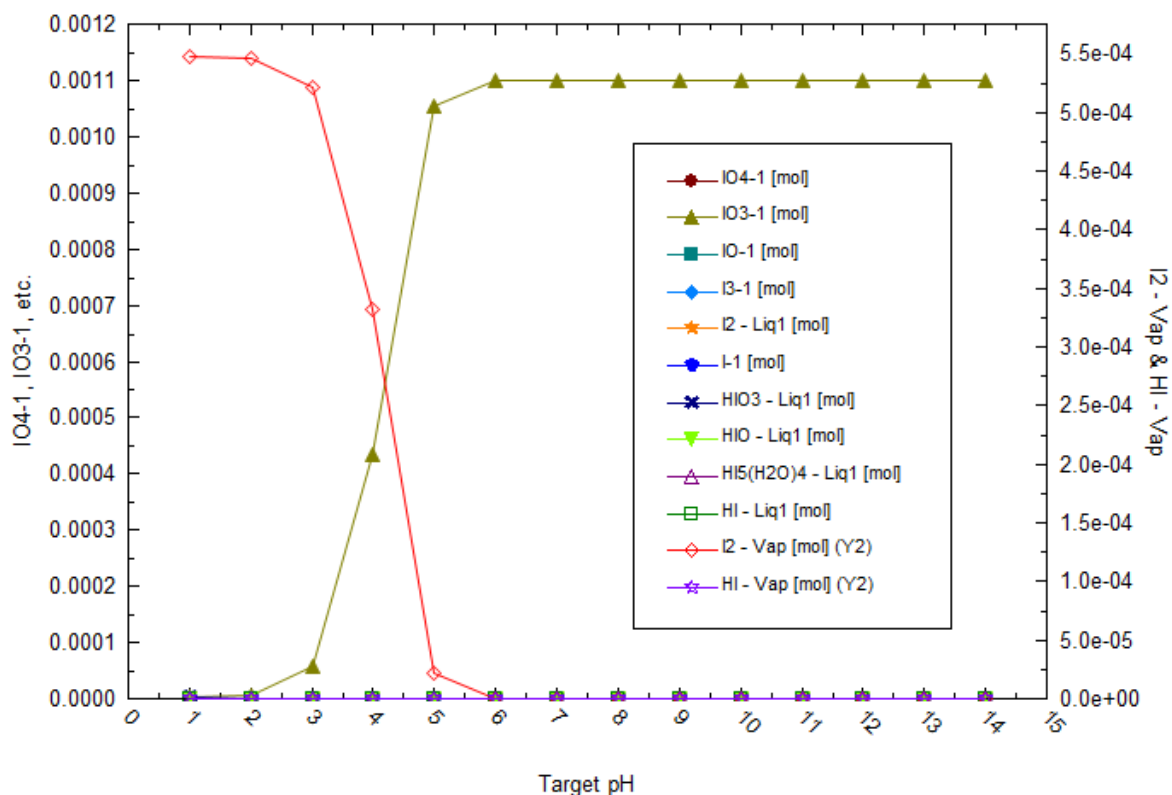


Figure 3-2. OLI Modeling output of SBS-WESP stream with Iodine added as I₂.

A subsequent calculation was performed with KI as the source of iodine, but the amount of oxygen was decreased to near equimolar with KI, making the condition “oxygen depleted”. Results are shown below. This indicates that the amount of iodine that vaporizes is a strong function of the amount of oxygen available for reaction. It also shows that this condition would be expected to have a significant fraction of iodine partition to the vapor phase at the pH of the evaporator bottoms (6.4).

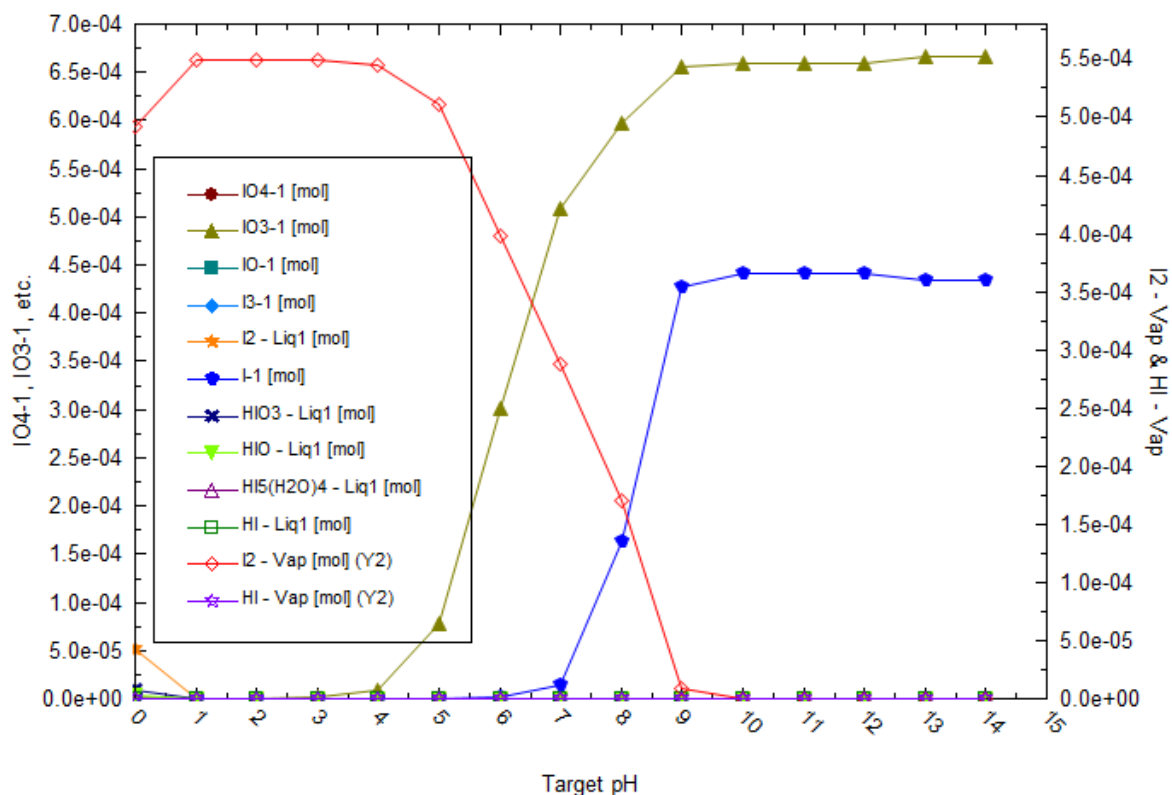


Figure 3-3. OLI Modeling output of SBS-WESP stream with Iodine added as KI with reduced O₂.

Another calculation was performed where the redox was turned on for both iodine and nitrogen. Results are shown below. Recognize that this calculation indicates that the ammonia is completely destroyed by reaction with either nitrate ion, nitrite ion, and/or oxygen. The results indicate that at higher pH, the iodate converts to iodide, presumably because it is a strong enough oxidizer to react with the remaining nitrite. However, note that this simulant has been evaporated at this temperature in previous experiments, and the ammonia-nitrite reaction does not actually occur at any appreciable rate at alkaline pH.

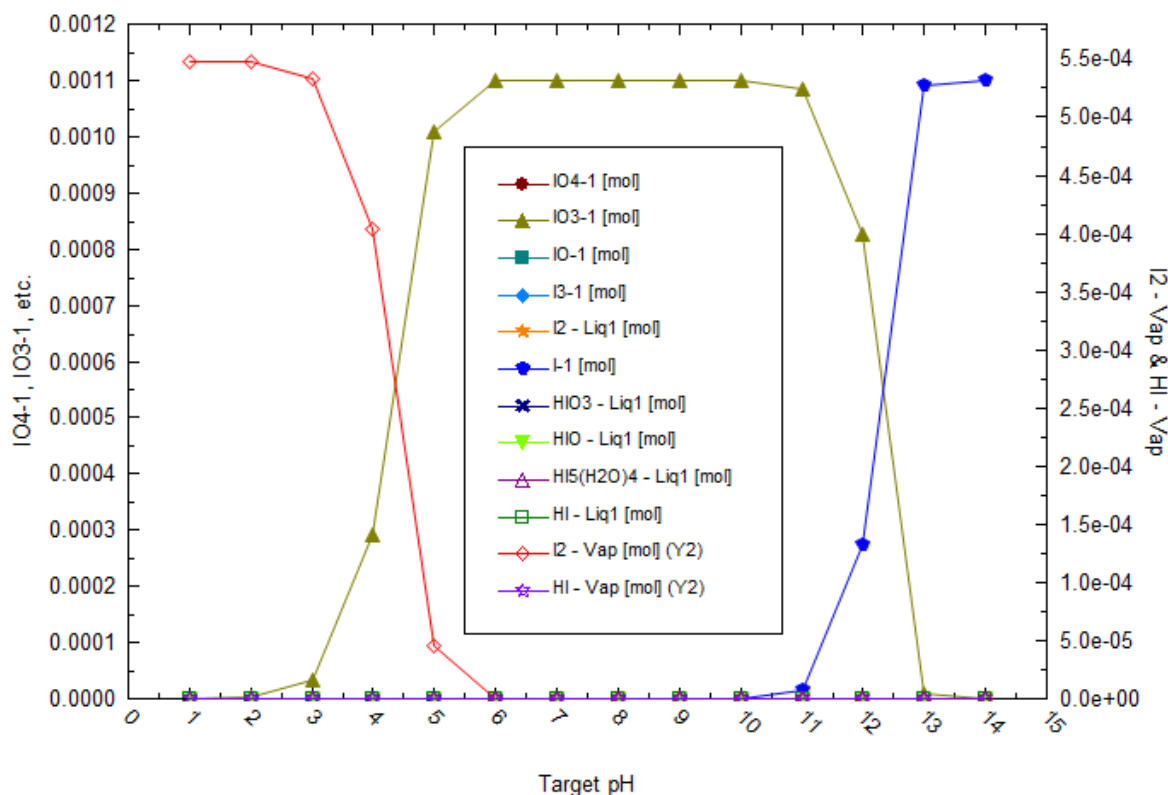
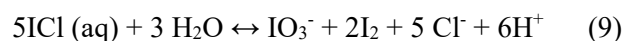


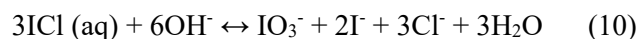
Figure 3-4. OLI Modeling output of SBS-WESP stream with Redox for Iodine and Nitrogen.

One objective of this work was also to determine which form of iodine to use in testing. Although molecular iodine could be used, it also may cause unintended consequences. Molecular iodine is a powerful oxidizer (Potential = 1.45 V), nearly as strong as molecular chlorine (1.63 V). It is expected that molecular iodine would oxidize other species in the aqueous solution, producing secondary byproducts. The presence of these secondary byproducts in the effluent streams from the evaporator may cause inaccurate conclusions that these secondary products will form in the WTP EMF. Note that the concentration of iodine used in testing greatly exceeds the amount actually present in Hanford tanks because the simulant testing relies on traditional analysis methods (Ion Chromatography) which require tens-of-mg/L concentrations to detect versus ^{129}I analysis by radiometric techniques in the waste at miniscule molar concentrations. Testing at SRNL began with iodine added to the simulant as potassium iodide in order to avoid these secondary byproduct reactions, since the OLI calculations indicate that the identical composition would be expected, and the VSL analysis method indicated that the final aqueous species is iodide.

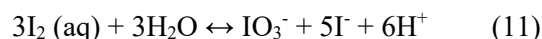
Based on the results of the FactSage modeling, Iodine Monochloride (ICl) would be expected to be the predominant species at the temperature in the SBS (50 °C). According to the literature, in aqueous solution, this disproportionates, depending on the condition [27]. In acidic solution, it forms iodate and iodine according to reaction 9.



In alkaline solution, the final products are iodate and iodide, according to equation 10.

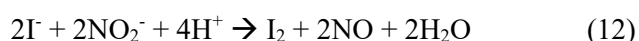


If some portion of the iodine species in the vapor is instead present as molecular iodine (I_2) or if it converts in aqueous solution, the literature reports [28, 29] indicate that it would be expected to disproportionate to mostly iodide, according to the overall reaction 11.



In all cases, the literature indicates that either iodine or iodine monochloride will disproportionate to predominantly iodide in solution. The small portion of iodate that forms is still a strong oxidizer and would be expected to react with a reductant in this solution, such as ammonia, and so would likely also convert to iodide.

The conclusion from the OLI modeling is that the reason that iodide was observed in the condensate in VSL testing was because of formation of molecular iodine (I_2) in the evaporator, which vaporized and condensed^a. In the condensate, it then converted to iodide, and a fraction of iodate, by disproportionation in the slightly alkaline solution by the reaction shown above (equation 10), or by redox reaction with a reductant. Because the redox was turned “off” for nitrogen species in the modeling (to prevent the reaction of nitrate/nitrite and ammonia), the model did not predict the reaction shown in equation 12. The oxidation by nitrite ion [29], instead of oxygen, could have occurred in the evaporator. There was ample nitrite present in the evaporator at VSL to react, and it could have been the oxidizer, although the solution was only slightly acidic. It seems plausible that nitrite was involved, since the evaporator was under vacuum and little dissolved oxygen would have been present compared to the abundant nitrite.



The literature and modeling agree that the iodine or iodine monochloride species would both be converted mostly or completely to iodide in the SBS and WESP. So these oxidation reactions of iodide by oxygen or nitrite in the evaporator would also be expected to occur regardless of whether the species used in formulating the simulant for evaporator testing was iodine or iodide.

The OLI modeling also indicates that the iodine would have remained in the evaporator pot as iodide and iodate ion if the pH was raised to 11.5-12, which is the condition planned for the EMF. Testing was performed to confirm this modeling result.

3.3 Simulant Analysis

Analytical results of the simulant used for this test are shown in Table 3-5. The results represent analysis of duplicate samples. All of the analytes are near the target values except the organics. The organics were added at 10 μ L/L, and the targets shown in the table are adjusted for density. The organics either evaporated or, more likely, decomposed prior to analysis. The density of the filtered simulant was 1.017 g/mL.

^a It is also possible that the volatile iodine species observed in the VSL testing was due to organic chemicals reacting with the molecular iodine to form organoiodides; however, this is exceedingly unlikely because the analytical analysis method used by VSL (IC) would not have identified these species in the offgas condensate since they are not ionic forms of iodine.

Table 3-5. EMF Core Simulant Filtrate Analysis Results.

Species	Target (mg/L)	Result average (mg/L)	Std. Dev. ^a	Percent of Target
B	918	907	0.707	99
Cr	35	33.5	0	97
K	2511	2280	7.07	91
Li	40	39.0	0.0707	97
Na	6765 ^b	6460	28.3	-
Si	2.8	< 0.357	-	< 13
NH ₄ ⁺	1171	1010	7.07	86
Cl ⁻	1720	1750	21.2	101
F ⁻	409	375	3.54	91
NO ₃ ⁻	705	712	14.1	101
NO ₂ ⁻	5568	5960	42.4	107
SO ₄ ⁻²	2331	2660	14.1	114
CO ₃ ⁻²	173	NA	-	-
I ⁻	74	71.7	2.33	96
PO ₄ ⁻²	*	48.4	0.919	-
oxalate	50	65.6	0.354	130
Acetone	7.9	0.21	0.0	3
Acetonitrile	7.9	<0.1	NA	<1
Acrylonitrile	8.1	<0.1	NA	<1
Methylene chloride	13.3	2.34	2.07	18
pH	11.5-12	11.74	-	-
a Standard deviation of the average of 2 measured values b Since NaOH is used to adjust pH, Na concentration is an estimate, not a target * phosphate was not added; assumed to be contaminant in lab chemicals or artifact of analytical method NA = not analyzed; - = not applicable or because of single measurement or less than detection limit				

3.4 Evaporator Operation

The evaporator was operated under vacuum at approximately 60 torr and boiling at approximately 42 °C for the entire test campaign. The temperature of the simulant and the pressure in the system was measured in the evaporator pot. The boil-off rate of the condensate was approximately 5 mL/min during the simulant test. As shown in Figure 3-5 the variance in pressure was minor over the entire test campaign, ranging from 56.8-61.5 torr. Likewise, only minor fluctuations in the temperature were observed. After initial heating, temperature readings ranged from 42.5 °C to 43.9 °C.

During boiling of the first 600 mL of condensate, the flow rate of cooling water through the condenser was too slow to chill it sufficiently to collect all of the water vapor, and approximately 15% of it passed to the KOP and the collection bulbs on the vacuum pump. As a result, the first set of condensate and KOP samples

may be non-typical of the remainder of the testing. This situation was corrected after the first condensate and KOP samples were collected.

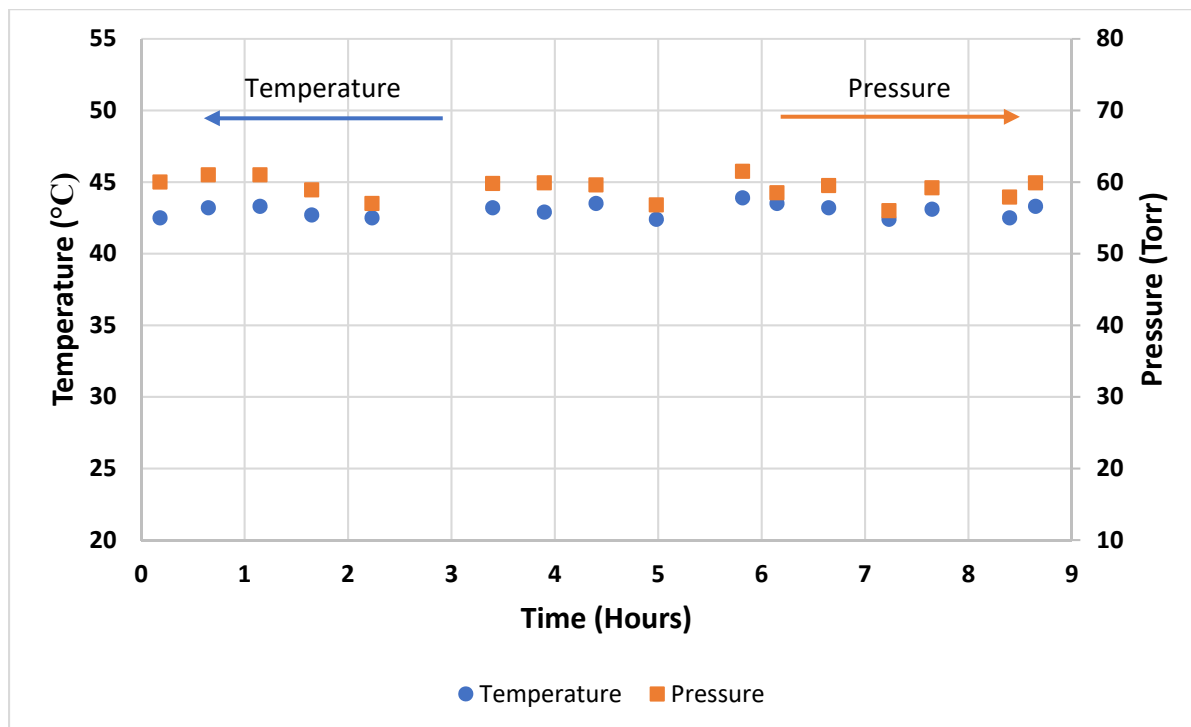


Figure 3-5. Test Conditions, Temperature and Pressure.

Figure 3-6 is an image of the simulant boiling in the evaporator pot. The evaporator pot was typically insulated during operation, but the black insulation on the side of the evaporator pot was periodically moved to allow for visual observation. The liquid continued to boil during these brief evolutions and did not interrupt the experiment.

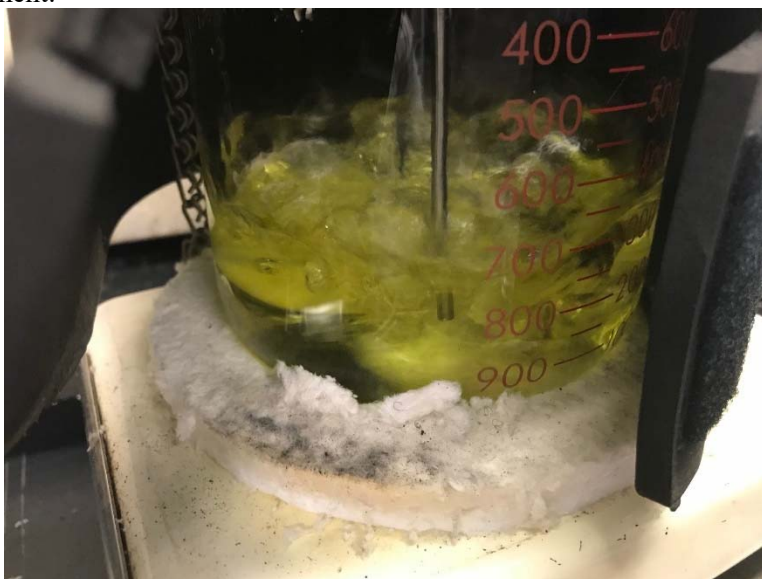


Figure 3-6. Simulant Boiling in the Evaporator Pot.

The first 50 mL concentrate sample was pulled from the evaporator pot after boiling down (concentrating) to 5X. This concentration was reached after the addition of approximately 1,250 mL of simulant and the collection of almost 1000 mL of condensate and KOP liquid. All six of the 50 mL concentrate samples were taken from the pot at consecutive points when the concentration factor was re-established to ~5.5X. Each 50 mL sample was removed from the evaporator pot using a large syringe to draw the liquid through stainless steel tubing into a glass bottle.

The evaporator was shut down seven times to collect the condensate from the Condensate Tank. Other than Condensate sample #1, all the condensate was collected when the concentrate in the evaporator pot was calculated to be at 5.3-5.6X. Condensate sample #1 was collected midway through the initial concentration phase, so the pot was not yet at 5.5X. All of the condensate samples were clear and colorless.

At the end of the test campaign, the sum total of the KOP samples was 92.802 grams of liquid; although almost all of this was from the first sample (75.037 g). The condensate collected in the KOP was collected each time the Condensate Tank was emptied. Other than the first sample, typically, 2 to 4 mL were collected from the thawed KOP each time. The KOP condensate was clear and colorless.

Figure 3-7 is an image of the concentrated bottoms in the EMF evaporator pot at the end of the test campaign.

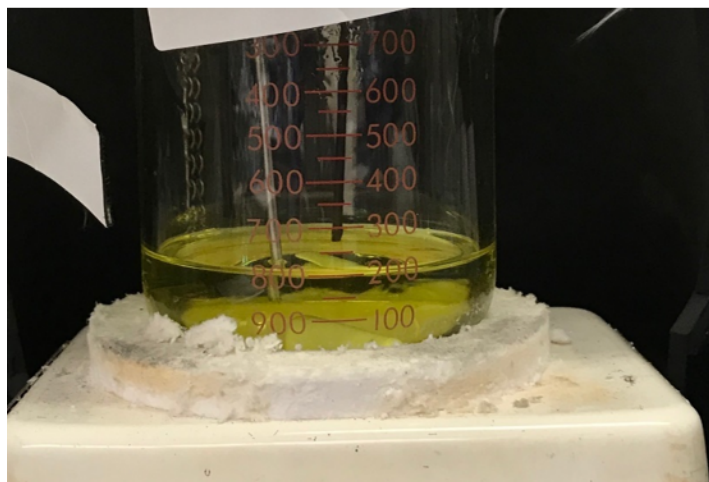


Figure 3-7. Evaporator Concentrate (~5.6X) at the End of Boil-down.

3.5 Sample Analysis Results

Evaporator Concentrate samples #1, #4, and #6 were analyzed for the same chemical species as the original EMF simulant. The concentrations of the individual species (metals, cations, and anions) are mainly uniform across the three concentrate samples, as seen in Table 3-6. The pH of the concentrate samples was also consistent. The average concentrations calculated from the three concentrate samples are also shown in Table 3-6 with the expected analytical results (based on the measured EMF simulant composition multiplied by a concentration factor of 5.5X). The average concentrations generally align with the expected results. The expected concentrations for the organics are not shown because they would be expected to either vaporize or decompose. Most of the anions were slightly high, with the exception of oxalate. This is assumed to be due to analytical analysis variability. In general, these results help confirm that the concentration in the evaporator pot was consistently about 5.5X.

Table 3-6. Evaporator Concentrate Analytical Results.

Species	EMF Conc. #1 (mg/L)	EMF Conc. #4 (mg/L)	EMF Conc. #6 (mg/L)	EMF Conc. Avg. (mg/L)	Std. Dev. (mg/L)	Expected Result 5.5X Conc. Factor (mg/L)	Percent of Expected
B	5460	5240	5120	5.27E+03	1.7E+02	4.99E+03	106%
Cr	200	184	173	1.86E+02	1.4E+01	1.84E+02	101%
K	13800	13100	12800	1.32E+04	5.1E+02	1.25E+04	106%
Li	254	234	219	2.36E+02	1.8E+01	2.14E+02	110%
Na	39600	39500	37200	3.88E+04	1.4E+03	3.55E+04	109%
S	5790	5330	5040	5.39E+03	3.8E+02	4.72E+03	114%
Si	< 10.3	< 10.3	< 10.3	< 10.3	-	< 1.96E+00	NA
NH ₄ ⁺	<10	<10	<10	<10	-	5.53E+03	< 0.2%
I ⁻	392	359	336	3.63E+02	2.8E+01	3.94E+02	92%
Cl ⁻	11200	10400	9920	1.05E+04	6.5E+02	9.60E+03	109%
F ⁻	2240	2080	1980	2.10E+03	1.3E+02	2.06E+03	102%
NO ₃ ⁻	4540	4290	4070	4.30E+03	2.4E+02	3.92E+03	110%
NO ₂ ⁻	37100	34600	32900	3.49E+04	2.1E+03	3.28E+04	106%
SO ₄ ⁻²	17300	16100	15300	1.62E+04	1.0E+03	1.46E+04	111%
oxalate	286	262	242	2.63E+02	2.2E+01	3.61E+02	73%
Density	1.12	1.11	1.11	1.11	5.8E-03	NA	NA
pH	13.3	13.3	13.2	13.3	5.8E-02	NA	NA
Acetone	<0.1	<0.1	<0.1	<0.1	NA	NA	NA
Acetonitrile	<0.1	<0.1	<0.1	<0.1	NA	NA	NA
Acrylonitrile	<0.1	<0.1	<0.1	<0.1	NA	NA	NA
Methylene chloride	<0.1	<0.1	<0.1	<0.1	NA	NA	NA
NA = not applicable							

As discussed above, the contents of the Condensate Tank were emptied seven times during the run and stored in separate bottles. These storage bottles were subsampled and ~25 mL of four of these was submitted for analysis. Table 3-7 gives the summary of results from the condensate analysis. The only analyte detected by ICP-OES was sodium ion at 3.70 mg/L. All other analytes were below detection other than ammonium. The ammonium concentration in the first condensate sample is lower than the others, consistent with the observed bypassing of some condensate to the KOP. Overall, the average ammonium concentration in the condensate is 90% of the measured feed concentration. Since the ammonium was absent from the pot samples, it partitioned entirely to the condensate and so it should have been ~120% of the feed concentration. This loss indicates that some ammonia partitioned to the KOP and perhaps some was lost by evaporation during handling or processing.

Table 3-7. Condensate Analytical Results.

Species	Condensate #1 (mg/L)	Condensate #3 (mg/L)	Condensate #5 (mg/L)	Condensate #7 (mg/L)	Average (mg/L)	Std. Dev. (mg/L)
B	< 2.09	< 2.09	< 2.09	< 2.09	< 2.09	NA
Cr	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07	NA
K	< 0.13	< 0.13	< 0.13	< 0.13	< 0.125	NA
Li	< 0.02	< 0.02	< 0.02	< 0.02	< 0.015	NA
Na	5.75	2.44	3.86	2.75	3.70	1.5
S	< 1.72	< 1.72	< 1.72	< 1.72	< 1.72	NA
Si	< 1.99	< 1.99	< 1.99	< 1.99	< 1.99	NA
NH ₄ ⁺	808	896	977	941	906	73
I ⁻	< 5	< 5	< 5	< 5	< 5	NA
Cl ⁻	< 10	< 10	< 10	< 10	< 10	NA
F ⁻	< 10	< 10	< 10	< 10	< 10	NA
NO ₃ ⁻	< 10	< 10	< 10	< 10	< 10	NA
NO ₂ ⁻	< 10	< 10	< 10	< 10	< 10	NA
SO ₄ ⁻²	< 10	< 10	< 10	< 10	< 10	NA
oxalate	< 10	< 10	< 10	< 10	< 10	NA
Density	1.00	1.00	1.00	1.01	1.00	5.0E-03
pH	12.1	12.1	12.2	12.2	12.2	5.8E-02
Acetone	0.17	0.2	0.23	0.23	0.21	0.03
Acetonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	NA
Acrylonitrile	<0.1	<0.1	<0.1	<0.1	<0.1	NA
Methylene chloride	<0.1	<0.1	<0.1	<0.1	<0.1	NA
NA = not applicable						

Since sodium is the dominant species, any entrainment would be most easily quantified by analyzing sodium. Other non-volatile components would be expected to have comparable entrainment behavior, and thus have comparable decontamination factors, but are beneath the analysis detection limits so cannot be calculated. The average sodium concentration in the condensate is 3.70 mg/L, and the evaporator concentrate samples are over 38,000 mg/L. Therefore, the decontamination factor (i.e., evaporator concentrate concentration divided by condensate concentration) for sodium exceeds 10,000.

The condensate in the KOP samples were collected individually during the test campaign. Some samples were combined so that enough was available for analyses, although the small sample size (other than sample #1), still limited the analyses that could be performed. Samples #2 and #3 were combined, and #6 and #7 for GC analysis for organics. Samples #4 and #5 were combined for ICP-OES and IC analysis and those results are shown in Table 3-8. The sodium concentration result is higher than the condensate samples above because the small amount of sample available was insufficient to get the ideal dilution ratio for analysis, so those results should be considered tentative. The ammonium concentration in the KOP exceeded the concentration in the feed, indicating that it was not all captured by the condenser. All of the anion results were below the method detection limits.

Table 3-8. Knock-Out Pot Analytical Results.

Species	KOP #4+5 Concentration (mg/L)
B	< 18.8
Cr	< 0.73
K	< 2.5
Li	< 0.09
Na	27.7
S	< 30.4
Si	< 7.44
NH ₄ ⁺	2050
I ⁻	< 5
Cl ⁻	< 10
F ⁻	< 10
NO ₃ ⁻	< 10
NO ₂ ⁻	< 10
SO ₄ ⁻²	< 10
oxalate	< 10

Table 3-9 depicts a total liquid volume and iodide mass balance. A total of 2629 mL of simulant, containing 189 mg of iodide, was fed to the evaporator over the course of testing. From the condensate, KOP, and concentrate, 2630 mL of liquid was recovered. This liquid volume corresponds to a percent recovery of 100.0%.

Since not all samples were analyzed, the concentration of iodide and density of the concentrate samples was averaged to calculate the material balance. Due to its volatility at alkaline pH as predicted by the modeling, virtually all iodide would be expected to remain in the evaporator and none expected present in the condensate. The condensate and concentrate contained < 10 mg and 171 mg of iodide, respectively. This corresponds to a percent recovery of 91% and is within the analysis uncertainty of the measurements. Furthermore, unlike the VSL test result which indicated 14-70 mg/L, there is no measurable iodide in the condensate, indicating that it is not sufficiently volatile under these conditions to be detectable.

Table 3-9. Total Volume and Ammonium and Iodide Balance.

Sample	Total Liquid Volume (mL)	NH ₄ ⁺ (mg/L)	NH ₄ ⁺ (mg)	I ⁻ (mg/L)	I ⁻ (mg)
Simulant	2629	1005	2643	72	188
Concentrate Recovered	471	<10	<10	363 ¹	171
Condensate recovered	2051	906 ¹	1885	<5	<10
Knock-out Pot + residues	108	2050	190	< 5	< 1
SUM (Condensate, Knock-out, Concentrate)	2630	NA	2075	NA	171
Percent Recovery	100.0	NA	79%	NA	91%

1. Average value used for calculations

As mentioned above, the condensate in the KOP samples were collected individually during the test campaign. Samples #2 and #3 were combined, and #6 and #7 for GC analysis for organics and results are shown in Table 3-10. A Gas Chromatography-Mass Spectroscopy (GC-MS) of the KOP samples assigned the volatile organic species based on the fragmentation pattern of the molecules in the ionizer. A small amount of the acetone was captured in the KOP samples, and the last sample had a trace amount of methylene chloride. The acetonitrile and acrylonitrile were below the detection limit, presumably because they had decomposed due to hydrolysis in the caustic solution. Since both of these have higher boiling points than acetone and methylene chloride, but both were present at lower concentrations even though they were added in similar quantities, it indicates that they decomposed rather than evaporated. Caustic solutions can decompose all of these organic species. Hydrolysis of nitriles in alkaline solution is a well known reaction [30, 31], although it typically occurs at higher temperatures than in this testing. If this occurred, the products of this hydrolysis would have been sodium salts of acetate and acrylate (see equations 13 and 14 below). These compounds would not have been detected in the GC-MS analysis due to low volatility of the salts at high pH, which would explain why no other products were observed. The traces of methyl isocyanate and methyl alcohol are probably decomposition products from the organics, but are in too low of concentration to be the dominant compounds. Other possible mechanisms for loss of the organics could be absorption into the poly bottle when they were initially added to the simulant, although this was only for a short period. Note that the decomposition would not have been observed in VSL testing because the pH was near neutral.

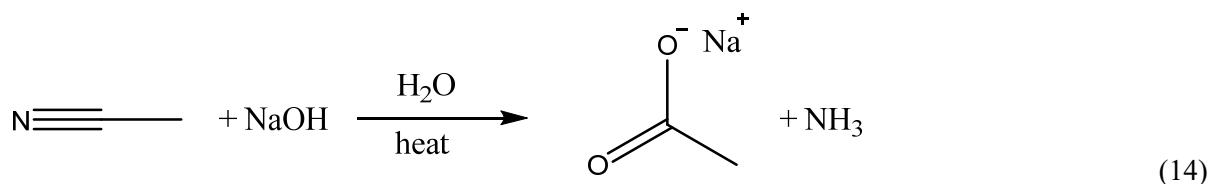
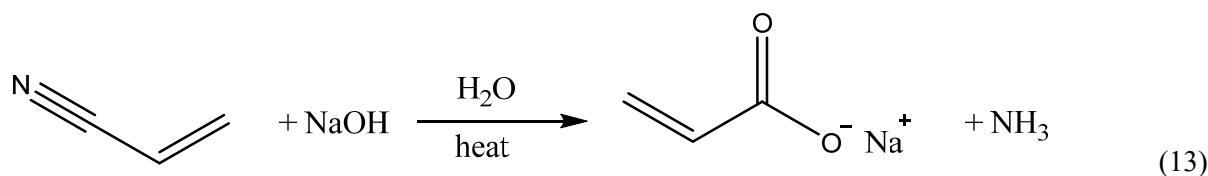


Table 3-10. Knock-Out Pot Organic Analysis Results.

Species	KOP #1 (mg/L)	KOP #2+3 (mg/L)	KOP #6+7 (mg/L)
Acetone	0.6	3.1	3.7
Acetonitrile	<0.1	<0.1	<0.1
Acrylonitrile	<0.1	<0.1	<0.1
Methylene chloride	<0.1	<0.1	0.12
Methyl isocyanate	<0.1	0.18	0.29
Methyl alcohol	<0.1	<0.1	0.12

4.0 Conclusions

- A simulant of the projected feed to the EMF evaporator at Hanford's WTP was successfully evaporated in a bench-scale EMF Evaporator.
- At the end of the test campaign, the simulant had been concentrated to 5.5X with a density of 1.11 g/mL.
- No insoluble solids were visible in the concentrate at the end of the test campaign.
- The evaporation caused most of the ammonia to strip and partition to the condensate stream.
- Decontamination factor for this experiment exceeded 1.0E+04, based on sodium concentrations in the pot versus the condensate.
- The iodide remained in the evaporator concentrate and was below detection limits in all condensate and KOP samples, indicating it was not volatile.
- The behavior of iodide in the evaporator matched the computer modeling.
- The organic nitrile compounds were absent from the feed solution, either lost through evaporation or decomposition.
- The acetone and methylene chloride were below the target values in the feed and condensate samples, and were presumably lost to evaporation or decomposition.

5.0 Future Work

Further testing would be needed to verify that the organics were lost due to decomposition and to determine the decomposition rate. A separate test apparatus would need to be set up that specifically examines the behavior of the organics in this simulant.

The fate of iodine/iodide is consistent with the computer modeling. Further, although the FactSage modeling indicated that iodine is present as I_2 and ICl in the gas phase in the off-gas system, OLI modeling indicated that it would quickly decompose to iodide in the aqueous solution. The iodine in the simulant was added as potassium iodide, and this was consistent with the observed speciation in VSL testing, since they only used ion chromatography for iodide as the analysis method which would not measure other species. Future testing of the evaporation of the off-gas condensate obtained from a melter test should include adjustment of the pH to alkaline conditions to further support the modeling and observations in this report. Additional analysis methods to quantify total iodine in the scrubber solution, such as neutron activation analysis, would also help to confirm that other species are absent from that stream. Overall partitioning of iodine in the melter and other off-gas components was not examined in this work, and additional testing would be needed to address any technology gaps that are identified.

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7.0 Appendices

Appendix A. Detailed Analytical Development Results

Appendix B. M&TE used for this testing

7.1 Appendix A. Analysis Results

Table A-1. Analytical Results for Simulant Samples.

Analyte	Sample 1 (mg/L)	Sample 2 (mg/L)
B	906	907
Cr	33.5	33.5
K	2280	2270
Li	38.9	39
Na	6480	6440
S	855	860
I ⁻	73.3	70.0
F ⁻	377	372
Cl ⁻	1760	1730
NO ₂ ⁻	5930	5990
NO ₃ ⁻	722	702
SO ₄ ²⁻	2650	2670
oxalate	65.8	65.3
NH ₄ ⁺	1010	1000

7.2 Appendix B. M&TE used for this testing.

Table B-1 is a list of Measurement and Test Equipment (M&TE) equipment used in the test apparatus during the EMF evaporator testing. (The numbers are unique identifiers that can be traced to calibration records.) The temperature of the simulant and the pressure in the system was monitored in the evaporator pot using a thermocouple and pressure transducer, respectively.

Table B-2. M&TE Equipment used during the EMF Evaporator Testing

Equipment	M&TE
Pressure Transducer	41016
Thermocouple, K type	41055
Balance/scale	WP-941
Balance/scale	WP-944

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