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# **Hanford Supplemental Low Activity Waste Simulant Evaporation Testing for Removal of Organics**

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## EXECUTIVE SUMMARY

The Hanford site has approximately 56 million gallons of radioactive waste stored in 177 underground storage tanks. The Hanford Waste Treatment and Immobilization Plant (WTP) is being built to treat and immobilize the tank waste. The baseline method for immobilization of Low Activity Waste (LAW) is vitrification, but additional immobilization capacity is likely needed to supplement the initial melters. An alternative cementitious waste form is being investigated for that future supplemental immobilization method. However, one impediment to a cementitious waste form is the presence of Land Disposal Restricted (LDR) organic chemicals in tank waste. [1] Developing a method to remove the organics would eliminate that impediment to permit possible use of a cementitious waste form. Savannah River National Laboratory (SRNL) performed testing to examine evaporation as a method to remove some prevalent organics from the Supplemental LAW (SLAW) stream. Samples of product streams from the evaporation were analyzed to determine partitioning of the organics. Modeling was also performed to determine if the experimental and modeling results matched. A description of the experimental details, equipment, and results of that testing are included in this report. The work is intended to inform future SLAW flowsheet development activities and gather useful data about the partitioning of constituents through a possible SLAW feed evaporator.

SRNL testing consisted of preparing the SLAW simulant, spiking that simulant with organic chemicals, and evaporating the mixture via a differential distillation. The apparatus was a laboratory-scale vacuum evaporator designed to operate at  $60 \pm 5$  torr absolute, which resulted in an initial boiling point of the liquid around  $44^\circ\text{C}$  under reduced pressure. The SLAW simulant preparation (without organics) was based on previous work [2] to develop a formulation that represented the LAW expected to be retrieved from the tank farms at approximately 4.0 M  $[\text{Na}^+]$  total sodium ion concentration. Five organic chemicals of concern in tank waste (e.g., acetone, acetophenone, butanol, methanol, and pyridine) were then added to the simulant. The concentration of the organics added was significantly higher than typically found in the samples so that the results would bound the expected evaporator performance on any possible future tank compositions.

While organic separation results depend on evaporator design, laboratory experiments verified that organic partitioning to the overhead condensate stream by evaporation is a practical process. Specific observations are:

- More than 98% of the organic chemicals investigated were removed via differential distillation.
- No significant reactions of organic species with the simulant were observed.
- Results were supported by thermodynamic equilibrium modeling using OLI Studio (OLI Systems, Inc.).
- Proton Nuclear Magnetic Resonance ( $^1\text{H}$ NMR) was a good method for analyzing all 5 organic chemicals in liquid samples. Detection limits for organic chemicals was 1.5 mg/L or better.
- Both higher temperature and salt molarity increase volatilization of organic compounds.

An auxiliary benefit to this work was the demonstration that methanol in tank waste can be quantified using  $^1\text{H}$  NMR analytical methods. Prior to this study, there was no existing method

for quantitative analysis of methanol in aqueous tank waste at Hanford and this work demonstrated this NMR spectroscopy technique could be a viable method.

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### LIST OF ABBREVIATIONS

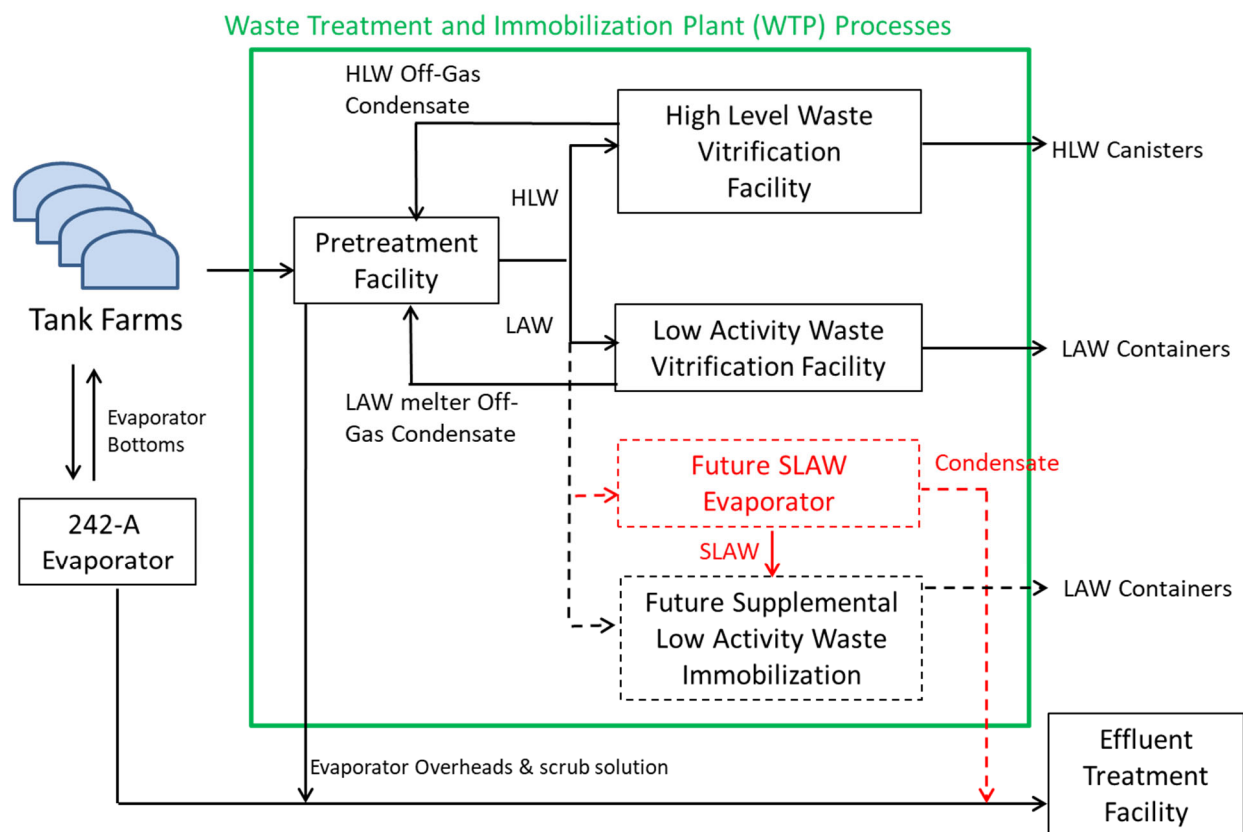
atm	atmospheres
C	Celsius
cm	centimeters
ETF	Effluent Treatment Facility
g	grams
H	Henry's Law coefficient, units atm-m <sup>3</sup> /mol
HLW	High Level Waste
<sup>1</sup> HNMR	Nuclear Magnetic Resonance, hydrogen
hr	hour
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
Inter	Intermediate evaporation point
KOP	Knock Out Pot
L	Liter
LAW	Low Activity Waste
LDR	Land Disposal Restricted
m	meter
M	Molar
M&TE	Measurement and Test Equipment
mol	mole
μ	micro
mg	milligram
mL	milliliter
mm	millimeter
mM	millimolar
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance
ppm	Parts per million
RCRA	Resource Conservation and Recovery Act
SLAW	Supplemental Low Activity Waste
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
Std. Dev.	Standard Deviation
TIC	Total Inorganic Carbon

TWINS	Tank Waste Information System
VOA	Volatile Organic Analysis
SVOA	Semi-volatile Organic Analysis
WRPS	Washington River Protection Solutions
wt %	Weight percent
WTP	Waste Treatment and Immobilization Plant
x	liquid phase mole fraction
y	gas phase mole fraction

## 1.0 Introduction

The U.S. Department of Energy's Hanford Site in southeastern Washington State has approximately 56 million gallons of radioactive waste stored in 177 underground storage tanks. The Hanford WTP is being built to treat all of the waste (including high-level waste (HLW) and low activity waste) and to immobilize the waste in glass waste forms. The aqueous tank waste, or LAW, will be decontaminated by removing key radionuclides, and then immobilized. This decontaminated LAW will initially be immobilized by vitrification in a glass melter in WTP, however the LAW vitrification facility is predicted to not have the capacity to solidify all of the LAW. A second facility will be needed to expand the immobilization capacity. This expansion will be the SLAW process. One option under investigation for immobilization is to solidify waste in a cementitious waste form that meets Resource Conservation and Recovery Act (RCRA) LDR requirements. One issue with the proposed use of a non-thermal immobilization method is that there may be small amounts of a variety of RCRA regulated organic chemicals in the aqueous waste. These regulated organics must be treated in order to permit disposal of the aqueous waste in a grout waste form. One treatment method that has been proposed is to remove the organics from the aqueous stream by co-evaporation with the waste so that the aqueous condensate containing the organics can be further treated in the Effluent Treatment Facility (ETF), and thereby enabling disposal of the LAW in a cementitious waste form.[1] This method is similar to the current evaporative volume reduction of tank waste performed by the 242-A evaporator, which results in an aqueous stream that also contains some organics. The ETF is an existing permitted facility that already treats the aqueous evaporator condensate from the 242-A evaporator, including some dissolved organics. The overall conceptual flow-sheet is shown in Figure 1-1, with the baseline shown in black, and the alternate evaporator and condensate pathway shown in red. The results of this initial testing can be used in future SLAW flowsheet development activities and to document useful data about the partitioning of constituents through a possible SLAW feed evaporator, but is not a comprehensive examination of all factors that would influence a decision on selecting a SLAW waste form.

Technology development and maturation activities were conducted by the Savannah River National Laboratory (SRNL) to investigate the efficacy of an evaporator to both reduce the aqueous waste volume and simultaneously remove organics from simulated Hanford tank waste. The experiment was performed using a differential distillation at  $60 \pm 5$  torr (absolute), which resulted in an initial boiling point of around  $44^\circ\text{C}$  under reduced pressure. These test conditions are in the range of those used to reduce salt waste volume in the 242-A evaporator. They are also comparable to the Feed Evaporator Process and the Treated LAW Evaporation systems within WTP, which were based on the 242-A evaporator system. The 242-A evaporator could be used for this process to both reduce aqueous volume and remove the organics but only before the aqueous waste is treated to remove cesium because that evaporator is highly contaminated. Similarly, the Feed Evaporator Process and/or the Treated Law Evaporation systems in WTP could be used to both reduce volume of the feed and remove the organics. The schematic in Figure 1-1 shows an auxiliary evaporator for this process instead of the 242-A or WTP evaporators, but this is just one possible approach and is meant to convey the concept. Either way, the test results will provide information on the expected distribution of organic species in those evaporators.



**Figure 1-1: Simplified Proposed WTP Flow-sheet**

### 1.1 Testing Basis and Objective

The scope of this task is to determine the potential for using evaporation of the SLAW stream to remove organic chemicals to enable a possible cementitious waste form. Test results will be used to determine if this is a plausible method to disposition the LDR organics and if further testing is warranted.

### 1.2 Computer Modeling Basis and Objective

OLI Systems, Inc. chemical thermodynamic software programs are used in calculating aqueous electrolyte chemistry. One of the components of this software system, the Studio, is used to reconcile chemical analyses, calculate thermodynamic parameters, and predict phase splits. Studio provides complete speciation of all phases that are in the databank for a given aqueous chemistry composition, along with the thermodynamic parameters (only the Studio 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 Studio) have been evaluated and used previously.[3] For this work, the Studio software was utilized by SRNL to calculate the expected speciation and behavior of organic chemicals during evaporation under various conditions. The results were then compared to the simulant testing. If the simulant behavior and the model agree, it is envisioned that the OLI model could be used in future flowsheet modeling efforts to predict partitioning of other organics for

process feasibility evaluations without having to perform extensive testing of all of the dozens of species that may be present in tank waste.

The OLI Studio 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 the 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. SRNL used this software and databanks without modification. OLI Studio version 10.0 was used for this work.

### 1.3 Simulant Formulation Basis

The inorganic and ionic composition of the simulant was based on that previously developed for Cast Stone testing.[2] Table 1-1 below (reproduced from Table 3.5 in the reference) shows the target composition for the “LAWPS 4.0M Na Simulant Initial Liquid Phase Composition” formulation after accounting for charge-balancing and solubility and eliminating the trace amount of Cs and adding chromate. The amount of chromate is based on the original “HTWOS<sup>1</sup> Overall Average” simulant formulation [4], adjusted for 4.0 M [Na<sup>+</sup>]. Nitrate ion is reduced to compensate for the ion balance. The removal of fluoride and cesium, and addition of chromate per the reference [4] concentration, were based on discussions with WRPS. Chromate is commonly found in Hanford nuclear waste and might be chemically active with organic species in important ways. Fluoride tends to precipitate with phosphate and thus does not add value to the current work.

**Table 1-1: SLAW evaporator simulant target composition  
(based on LAWPS 4.0M Na Simulant)**

Constituent	Concentration (M)
Na <sup>+</sup>	4.00E+00
K <sup>+</sup>	8.71E-02
Al <sup>+3</sup>	1.19E-01
Cl <sup>-</sup>	8.71E-02
SO <sub>4</sub> <sup>-2</sup>	4.72E-02
PO <sub>4</sub> <sup>-3</sup>	3.09E-02
NO <sub>2</sub> <sup>-</sup>	7.29E-01
NO <sub>3</sub> <sup>-</sup>	1.25E+00
CO <sub>3</sub> <sup>-2</sup>	3.34E-01
oxalate	9.07E-03
CrO <sub>4</sub> <sup>-2</sup>	1.16E-02
Free OH <sup>-</sup>	1.01E+00

<sup>1</sup> HTWOS (Hanford Tank Waste Operations Simulator) was the name of the software model used to calculate the composition of the tank waste until 2018 when it was replaced by TOPSim (Tank Operations Simulator).

It was necessary to select organic compounds that could be used for this test program. Table 1-2 shows data drawn from a prior report on the organic compounds in Hanford waste tanks.[5] Specifically, the list of compounds and some information in the table below is from Table 11 in the referenced report. The table shows the Tank Waste Information System (TWINS) data with measurable quantities of organic compounds that are identified as analytes required for regulatory analyses. It was not practical to include all of these compounds in a single test, so a few were selected for testing. Selection criteria included chemicals that were: (1) used or detected at Hanford and considered to be likely in the waste, (2) non-reactive with the simulant, (3) moderately soluble, and (4) measurable with existing techniques. Several of the compounds in Table 1-2 were culled from the list for various reasons. Several of the compounds had high Henry's Law coefficients ("high H"), so were believed to be easily stripped by evaporation. Several others were either not detected in any samples ("0 detected") or were detected at concentrations below the action limit ("<limit"). The two phthalates were excluded because they have very low solubility and are likely unstable in tank waste. Note that phthalates are also common plasticizers and their presence in samples may be due to collection and storage of tank samples. Another compound, 2-butanone, is present in many tank samples at concentrations above the action limit, but it was excluded here because it is very flammable and would complicate testing at the high concentrations needed for this experiment; further, its Henry's Law coefficient was easily bounded by other compounds that were included in testing.

**Table 1-2. TWINS data with measurable quantities of required organic compounds [5]**

Constituent	Detects w/Passing QC	Action limit (µg/ml)	Highest Concentration (µg/mL)	H (atm- m <sup>3</sup> /mol)*	Solubility in water (µg/mL)*	Included?; Reason
1,1,1-trichloroethane	1	0.054	0.4	2.0E-2	1.29E3	No; High H
2,4,5-Trichlorophenol	0	0.18	0.012	2.21E-6	1.20E3	No; No <limit
2-Butanone	70	0.28	8.1	5.69E-5	2.23E5	No; bounded H
4,6-Dinitro-o-cresol	0	0.28	0.553	1.40E-6	1.98E2	No; 0 detected
4-Methyl-2-pentanone	0	0.14	0.01	1.38E-4	1.90E4	No; 0 detected
Acetone	128	0.28	11	3.50E-5	miscible	Yes
All Aroclors	3	0.1	0.0074	NA	NA	No; <limit
Benzene	18	0.14	0.0282	5.56E-3	1.79E3	No; <limit
Butyl benzyl phthalate	2	0.017	0.564	1.26E-6	2.69	No; low solubility
Chloroform	1	0.046	0.0008	3.67E-3	7.95E3	No; high H
di-n-butylphthalate	4	0.057	0.4	1.81E-6	1.1E1	No; Low solubility
Methylene chloride	35	0.089	0.383	3.25E-3	1.30E4	No; high H
n-Butyl alcohol	105	5.6	79.655	8.81E-6	6.32E4	Yes
Nitrobenzene	1	0.068	0.021	2.40E-5	2.09E3	No; <limit
Pyridine	8	0.014	0.08	1.10E-5	miscible	Yes
Trichloroethylene	1	0.054	0.0477	9.02E-3	1.28E3	No; <limit

\*at 20-25 °C in water; from <https://pubchem.ncbi.nlm.nih.gov>

The five LDR organic constituents selected for study are provided in Table 1-3 below. Species were selected to cover a feasibly wide range of Henry's Law coefficients. Selection also includes practical considerations such as chemical availability and usability in a laboratory setting without significant safety or regulatory issues. Methanol and acetophenone were included in this evaporator testing simulant although they were not in the table above. Methanol was not in the table because there is no analysis method for it in Hanford tank samples. Acetophenone was

included in testing because it had a relatively low Henry's Law coefficient, is believed stable in the simulant, is highly soluble, and is an underlying hazardous constituent. Its inclusion in this testing does not imply that it is believed present in tank waste. While methanol was not measured in aqueous Hanford tank waste due to the lack of an analysis method, it was included here because it is known that it was used, has been observed in headspace samples, is regulated, and is suspected of being particularly challenging to remove by evaporation from an aqueous alkaline solution.

**Table 1-3: Target Organic Chemical Concentrations in SLAW simulant**

Constituent	Formula	Concentration (mg/L)	Concentration (M)	Henry's Law Coefficient <sup>2</sup> (atm-m <sup>3</sup> /mol)
Methanol	CH <sub>3</sub> OH	1.58E+02	4.90E-03	4.55E-06
n-butyl alcohol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub> OH	1.62E+02	2.20E-03	8.81E-06
Pyridine	C <sub>5</sub> H <sub>5</sub> N	1.96E+02	2.50E-03	1.10E-05
Acetophenone	C <sub>6</sub> H <sub>5</sub> C(O)CH <sub>3</sub>	2.06E+02	1.70E-03	1.04E-05
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	1.57E+02	2.70E-03	3.50E-05

The molar amounts of each constituent listed in Table 1-3 corresponds to an addition of 200 µL/L of each pure organic liquid. Concentrations of the species were based on an examination of the measured concentrations in waste tanks, and consideration of the analytical detection limit such that a high Decontamination Factor could be measured. All of the chemicals were added at concentrations at least ten times higher than their highest measured concentration in tank waste, with the exception of n-butanol, which was two times higher.

#### 1.4 Simulant Evaporation Condition Basis

The evaporator was intended to operate under pressure and temperature conditions consistent with those anticipated in a vacuum evaporator comparable to the WTP and 242-A evaporators. These evaporators operate at approximately 60 torr and ~50 °C. The 242-A evaporator has a continuous feed of between 70 and 130 gallons/minute [HNF-14755]. The normal operating capacity including the recirculation loop and reboiler is 22,500 to 26,000 gallons [HNF-14755]. These ranges of volumes and flowrates equates to minimum and maximum residence times of 173 and 371 minutes, respectively. Testing at SRNL was performed with the lab scale glass vacuum evaporator used in previous testing.[3, 6, 7] Unlike the 242-A evaporator, the lab-scale evaporator is not a continuous feed system but is operated in batch mode. Samples from both the evaporator condensate and evaporator pot were periodically withdrawn from the apparatus and analyzed for the distribution of species. The typical duration between sampling times (1-2 hours) is shorter than the shortest residence times for the 242-A evaporator, so should yield a comparable result. Since the residence time, pressure, composition, and temperature are similar, the organic chemicals should be stripped in roughly the same proportion in the full-scale evaporator.

<sup>2</sup> <https://pubchem.ncbi.nlm.nih.gov>



## 2.0 Experimental Procedure

### 2.1 Simulant Preparation

A 1-Liter batch of the simulant was prepared from laboratory chemicals. The specific chemicals and target weights are shown in Table 2-1. The bright yellow solution did not have any visible solids. Subsamples were collected and analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), Ion Chromatography (IC), and Total Inorganic Carbon (TIC). A calibrated pipette was used to add 0.20 mL of each organic compound listed in Table 1-3 to the mixture. Subsamples were acquired and organic concentrations were confirmed using Volatile Organic Analysis (VOA), Semi-volatile Organic Analysis (SVOA), and proton Nuclear Magnetic Resonance ( $^1\text{H}$ NMR).

**Table 2-1: Simulant Preparation Target Composition.**

Chemical	Formula	Target Mass, g
Sodium hydroxide 50 wt% solution	NaOH	1.19E+02
Aluminum nitrate nonahydrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	4.45E+01
Potassium chloride	KCl	6.50E+00
Sodium nitrate	$\text{NaNO}_3$	7.78E+01
Sodium nitrite	$\text{NaNO}_2$	5.03E+01
Sodium phosphate dodecahydrate	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	1.17E+01
Sodium sulfate	$\text{Na}_2\text{SO}_4$	6.70E+00
Sodium carbonate	$\text{Na}_2\text{CO}_3$	3.54E+01
Sodium oxalate	$\text{Na}_2\text{C}_2\text{O}_4$	1.22E+00
Sodium dichromate dihydrate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	1.73E+00

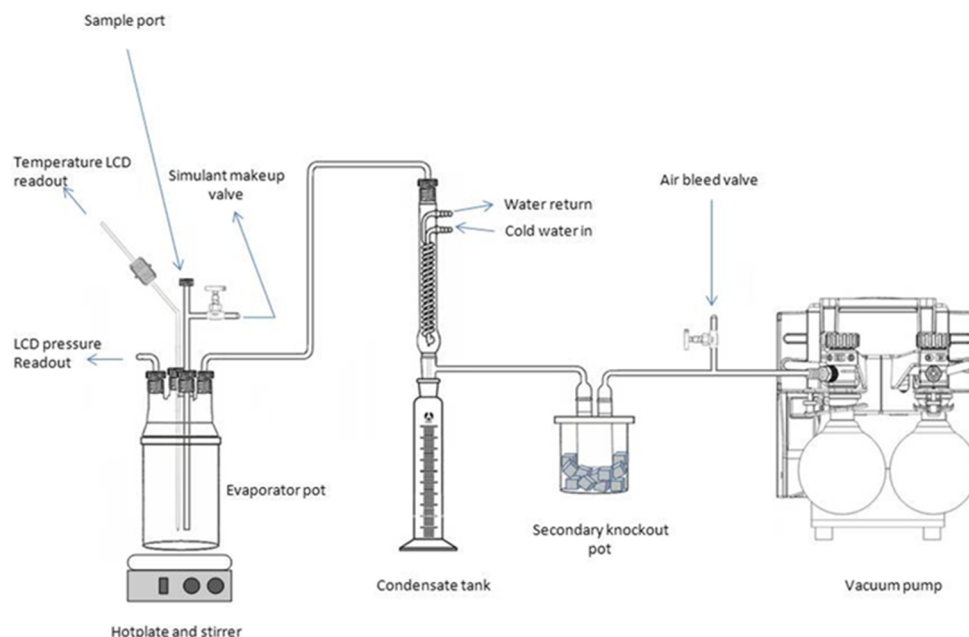
### 2.2 OLI Modeling

The composition of the aqueous phase was input into OLI Studio 10.0. The “public” or “AQ” aqueous databank was used and it contained all of the species of interest. Nitrogen gas was added (0.003 moles) to simulate a vapor phase. Initial absolute pressure was set to 0.079 atmospheres (60 torr) to examine the distribution of organics to the vapor phase in the evaporator. A survey was conducted at constant pressure, varying the temperature from 42° to 48° C. Note that 42° C was selected because it is approximately the beginning of boiling of the water, under reduced pressure.

### 2.3 Evaporator Apparatus

The major components of the vacuum evaporator consist of a glass evaporator pot, condenser, and dry ice trap and are shown in Figure 2-1, and an image is shown in Figure 2-2. Unlike the 242-A evaporator, the lab-scale evaporator is not a continuous feed system but is operated in batch mode.

Feed was added to the pot, and then boiled down to the target concentration ( $\sim 8 \text{ M } [\text{Na}^+]$ ). Samples from both the evaporator condensate and evaporator pot were taken approximately half-way through the evaporation, when the evaporator pot was  $\sim 5.6 \text{ M } [\text{Na}^+]$ , and again at the end. Conditions of the experiment were monitored and recorded, including evaporator pot temperature, pressure, and time. The system was maintained at the target operating pressure of  $60 \pm 5 \text{ torr}$ , which resulted in an initial boiling point of the liquid around  $44^\circ\text{C}$ .



**Figure 2-1: Evaporator Equipment Schematic**

Differences between a batch and continuous process include the effects of temperature and sodium molarity over time. Batch processing starts at  $4 \text{ M}$  sodium for the current work and rises to  $\sim 8 \text{ M}$  with time, while continuous evaporation starts and remains at the high value ( $8 \text{ M}$  sodium). Both the steady high temperature and steady high salt (salting out effect) for the continuous process favor organic chemical evaporation vs. batch distillation. However, the batch process is more efficient overall compared to the continuous process because of its initially higher organic concentration. Modeling and calculations are needed for a specific evaporator to help predict performance when Henry's Law coefficients are known. Other effects like refluxing in the headspace of plant evaporators may be present to enhance separation, as an example.



**Figure 2-2: Image of Evaporator Equipment<sup>3</sup>**

During the design and construction of the evaporator, 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 a precautionary measure to minimize loss of key components that might absorb (partition) 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.

The contents of the pot were kept under a vacuum, typically at an absolute pressure of 60 torr as measured by a pressure transducer. 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 3-4 °C. Any vapors that passed through the condenser were condensed in the glass trap used as a 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<sup>®</sup> diaphragm vacuum pump, Type: MZ 2C.

The contents collected inside the KOP were always frozen when it was disconnected and had to be thawed before they could be transferred to the sample collection bottle. Care was taken to

<sup>3</sup> This image is merged from two images and edited using Photoshop Elements

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 60 torr and a temperature of 42 °C. This compares well with CRC Steam Tables [8] that show a boiling point of water at 108.0 °F (42.2 °C) at 62.2 torr.

Two evaporator tests were performed sequentially (labeled: “Run 1” and “Run 2”). Both runs were performed under similar conditions using aliquots of the same feed simulant to generate duplicate results. A description of the tests follows. Approximately 400 mL of feed simulant was loaded into the evaporator pot. The pressure was adjusted to approximately 60 torr (absolute) and the simulant was heated using a hot plate and stirred continuously with a Teflon-coated magnetic stir-bar. The pressure in the system was maintained at  $60 \pm 5$  torr and the solution boiled at approximately 44 °C. The temperature of the simulant and the pressure in the system was measured in the evaporator pot. During the first “concentration phase”, the simulant was concentrated until ~100 mL of condensate was collected. At this point, boiling was paused and a ~30 mL sample was withdrawn from the evaporator pot and the accumulated condensate was collected as shown in Table 2-2. The system was sealed and boiling resumed until an additional 75 mL of condensate was collected. At this point, boiling was stopped and a final ~30 mL sample was withdrawn from the evaporator pot and the accumulated condensate was collected.

**Table 2-2: Pot Sample Target Concentrations.**

<b>Sample Name</b>	<b>Cumulative Total Simulant added to pot (mL)</b>	<b>Cumulative Condensate &amp; KOP collected (mL)</b>	<b>Calculated [Na<sup>+</sup>] (M)</b>
Feed	400	0	4
Intermediate Pot	400	100	5.33
Final Pot	400	175	7.4 <sup>a</sup>
<sup>a</sup> Concentration accounts for intermediate evaporator sample removal			

#### 2.4 Nuclear Magnetic Resonance Analysis Method

The five organic species spiked into the evaporator feed liquid were quantified by proton (<sup>1</sup>H) NMR. The original plan was just to use <sup>1</sup>HNMR to quantify methanol because SRNL has no other method for that chemical. However, the <sup>1</sup>HNMR method successfully quantified all five species, and is thus the primary source of organic composition data for this evaporator testing. The <sup>1</sup>HNMR experiment WATERGATE (Water Suppression by Gradient Tailored Excitation) was applied to suppress the large water signal at 5.1 ppm in the aqueous samples. This method relies on applying a gradient spin echo technique to separate the water magnetization (by diffusing it with two gradients) from other signals.[9] A hard 90-degree pulse is applied to magnetize the water followed by a 2 millisecond gradient pulse (a sine-shaped gradient of 50 millitesla/m was applied to diffuse it). Lastly, a train of pulses set at different angles acts as a 180-degree pulse for everything else in the sample except for water. The delay between the pulses was 355

microseconds, the spectral width was 72,000 hertz, and the time domain was 8000 data points (the acquisition time was 56 milliseconds). The method removes any signal that overlaps with the water signal which is the target of the attenuation. Usually the water signal occupies an approximately 1 to 1.5 ppm wide region (depending on the level of hydrogen bonding) near 4.9 ppm, but hydrogens characteristic of each species does not need such signal for quantification. In addition, the hydrogen bonding interaction of the organic -OH group with water, such as with methanol, suppresses the hydrogen signal from that group.

The samples were prepared by spiking them with known quantities of organic tracers. The first data set used hydroxyquinone ( $C_6H_6O_2$ ), providing 4 equivalent hydrogens. The second data set used benzoic acid,  $C_7H_6O_2$ , with 10 equivalent hydrogens. Organic concentrations were calculated considering specific peak areas, number of hydrogens at specific locations in the target molecule, standard spike data, and molecular weights.

### 2.5 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 #C8102-00273-03. This report documents completion tasks in the Task Technical and Quality Assurance Plan SRNL-RP-2020-00406, Rev. 0.[10] OLI modeling is controlled under Software Quality Assurance Plan X-SQP-A-00001, Rev. 0.[11]

## 3.0 Results and Discussion

### 3.1 Computer Modeling

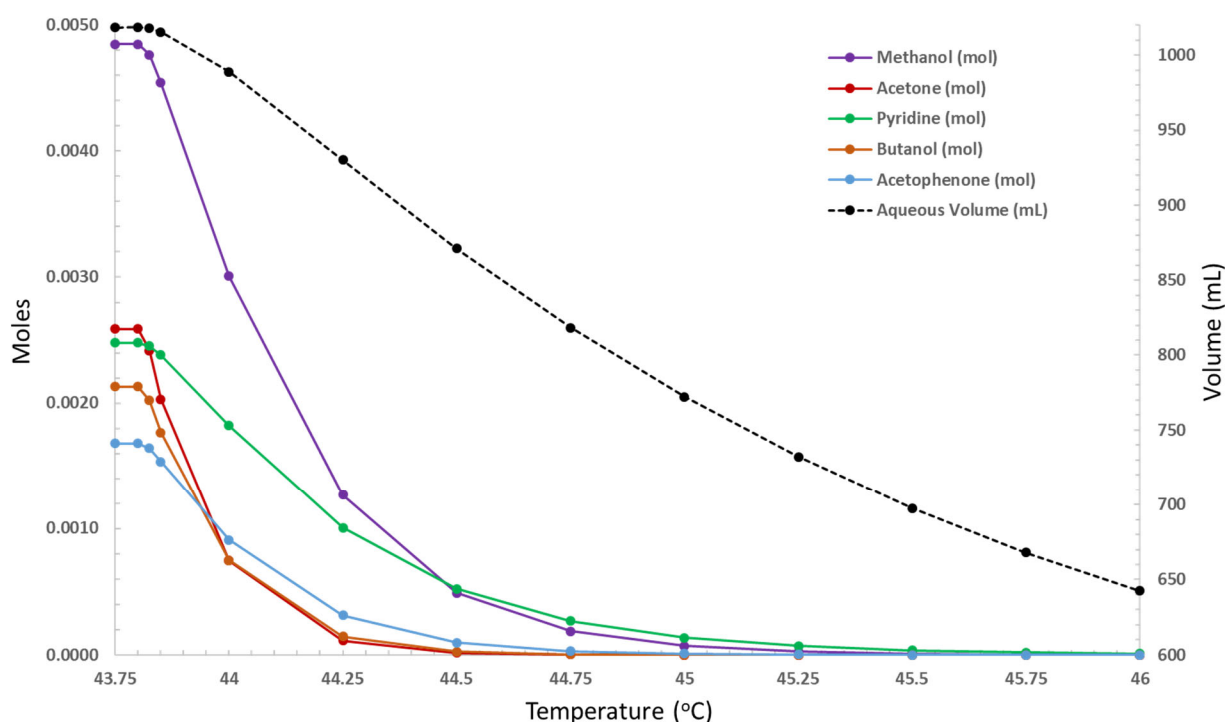
The primary test objective was to demonstrate separation of trace organic chemicals from a high salt aqueous feed to an evaporator. Evaporation is performed to reduce the volume of waste in the tanks. During evaporation, salts in the feed are concentrated in the bottoms, and it is also an opportunity to remove the organic species with the overhead (condensate) stream. At Hanford the low activity aqueous condensate containing the organic compounds would be directed to a permitted treatment facility.

The experimental apparatus used in this work performs as what is called a *batch* or *differential* still. Ideally there is no reflux operation above the pot. Vapor generated in the pot pushes forward previously evaporated material. That material would be richer in light components which have a high relative volatility compared to the water in the pot. The vapor travels forward to the condenser, containing water recirculating at  $\sim 4^\circ\text{C}$ , where, ideally, all vaporized components are liquefied and condense. The pot liquid, which is mostly distilled water and trace organics, is assumed to be well mixed and in local equilibrium with the vapor that is immediately above the liquid.

OLI Studio was used to approximate this operation in steps. This software models solution chemistry and includes a simulation of the increase of Henry's Law coefficients for organic volatiles with both increasing temperature and salt concentration. Modeling of batch distillation must include a mass balance of all volatile components and must remove the initial richer gas phase from the pot so that further stripping is realistic. In each step, a vapor phase volume of water

and organic components is created from the pot liquid, subtracting those amounts from the liquid batch. The new liquid batch composition is used to form the next vapor volume. Liquid and vapor phases are in equilibrium in each step. Pressure is held constant, so the liquid boiling point increases because of increased sodium molarity.

Results of the OLI Studio calculation for the evaporator pot liquid from 43.75 to 46.0 °C (the temperature range where the majority of organics are removed) are shown in Figure 3-1. Note that for convenience of visualizing the partitioning, this calculation shows an initial 1 L of liquid, not the experimental volume of ~400 mL. Once the evaporation has reached its target of ~0.54 L of remaining liquid in the pot, virtually all of the organics have partitioned to the vapor phase. This indicates that evaporating the waste should be highly effective at removing the organics from the aqueous phase.



**Figure 3-1: OLI Calculation Results of the Evaporator Pot during Vacuum Evaporation**

### 3.2 Simulant Composition

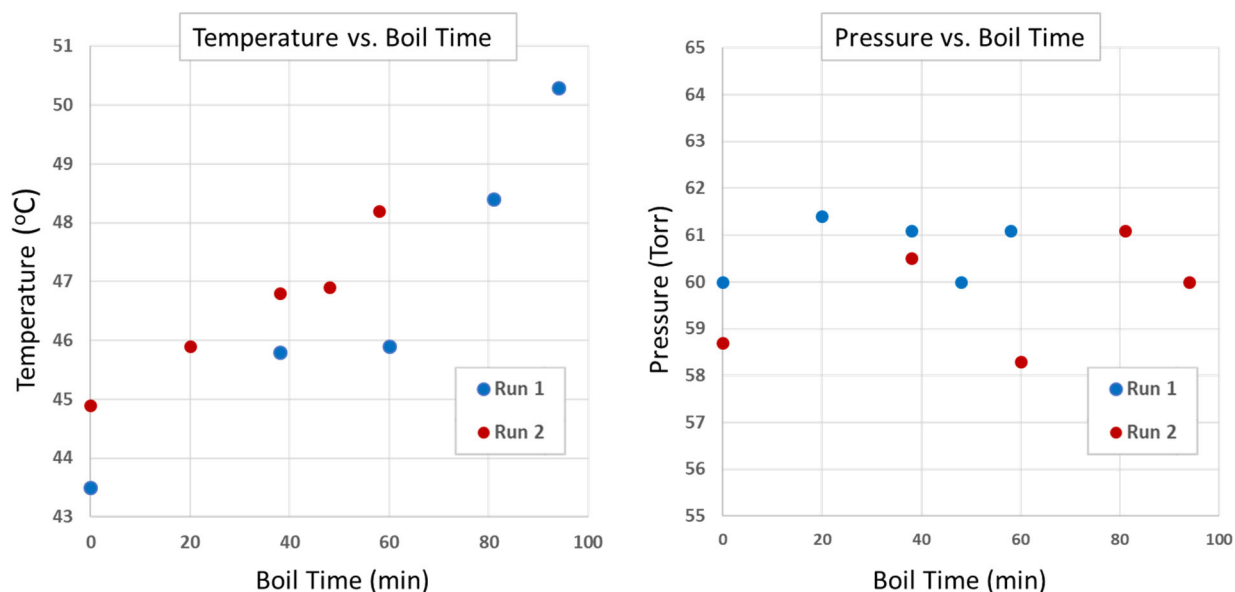
Analytical results of the evaporator feed simulant are shown in Table 3-1. The measured mass of sodium nitrite was 15% higher than the target, as a result the sodium concentration was 4.12 M as opposed to the target molarity of 4.02. In general, analytical results of the inorganic species are in agreement with measured masses; with deviations presumed to primarily be an artifact of the 10% measurement uncertainty of ICP-OES and IC-Anions. Some of the results for the anions are outside this range, but the reasons for this are not known.

**Table 3-1: Core Feed Analysis Results**

Species	Target (mg/L)	Mass Added (mg/L)	Percent of Target	Analytical Results (mg/L) <sup>a</sup>	Std. Dev. <sup>b</sup>	Percent of Target
Al	3.20E+03	3.20E+03	100%	3.17E+03	5.60E+01	99.0%
Cr	6.04E+02	6.05E+02	100%	5.96E+02	9.90E+00	98.7%
K	3.41E+03	3.41E+03	100%	3.54E+03	6.40E+01	104%
Na	9.23E+04	9.48E+04	103%	9.23E+04	7.80E+02	100%
Cl <sup>-</sup>	3.09E+03	3.09E+03	100%	3.56E+03	3.50E+01	115%
NO <sub>3</sub> <sup>-</sup>	7.88E+04	7.89E+04	100%	9.23E+04	1.50E+03	117%
NO <sub>2</sub> <sup>-</sup>	3.35E+04	3.85E+04	115%	3.67E+04	5.70E+02	109%
SO <sub>4</sub> <sup>-2</sup>	4.53E+03	4.53E+03	100%	4.89E+03	6.40E+01	108%
CO <sub>3</sub> <sup>-2</sup>	2.00E+04	2.00E+04	100%	3.41E+04	1.50E+03	170%
PO <sub>4</sub> <sup>-3</sup>	3.11E+03	3.11E+03	100%	3.62E+03	4.20E+01	116%
Oxalate	8.01E+02	8.02E+02	100%	7.72E+02	1.00E+01	96.3%
Methanol	1.58E+02	1.58E+02	100%	1.94E+02	7.60E+00	122%
Acetone	1.57E+02	1.57E+02	100%	1.30E+02	3.10E+00	82.8%
Butanol	1.62E+02	1.62E+02	100%	1.39E+02	5.50E+00	85.8%
Pyridine	1.96E+02	1.96E+02	100%	1.51E+02	8.70E+00	77.0%
Acetophenone	2.06E+02	2.06E+02	100%	1.79E+02	1.52E+01	86.7%
<sup>a</sup> Measured by ICPEs, IC-Anions, TIC, or <sup>1</sup> HNMR						
<sup>b</sup> Standard deviation of the average of 2 measured values						

### 3.3 Evaporation Processing

Plots of temperature and pressure for both runs can be found in Figure 3-2. A temperature rise caused by an increase in salt concentration was measurable in both runs. The system was operated under vacuum at approximately 60 torr and only minor fluctuations in pressure were observed. Boiling was stopped after 18 minutes of Run 1 due to an errant reading on the pressure sensor by turning off the heat and allowing pressure to return to atmospheric. After a 152-minute delay, operability was restored to the pressure transducer and boiling was resumed. Outside of the delay, the run shows the same temperature trend as Run 2. Data reported in Figure 3-2 only considers reaction conditions while boiling and does not include conditions during sampling or the 152-minute delay in Run 1 where the system was cooled and brought to atmospheric pressure.



**Figure 3-2: Plots of Temperature (*Left*) and Pressure (*Right*) as a Function of Boil Time**

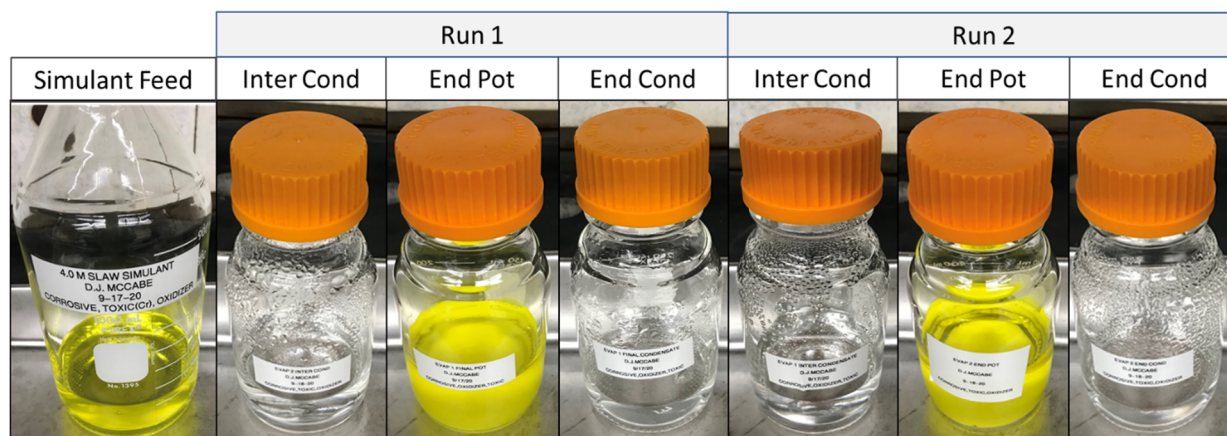
The masses and volumes of each subsample and the initial feed, intermediate (“Inter”), and end pots are reported in Table 3-2 for both runs. The “Inter Pot” is the calculated amount of liquid that remained in the evaporator pot before the sample was withdrawn from the pot at the intermediate evaporation point. The “Inter Pot Sample” was the liquid withdrawn from the evaporator pot at the intermediate evaporation point. The “KOP” and “Condensate” were the liquids in the knockout pot and condensate collection container, respectively. Masses were measured directly using an analytical balance and volumes were determined using measured or assumed densities. The density of the initial and final pot samples was measured to be 1.19 and 1.35 g/mL respectively. The density of the intermediate pot was assumed to be 1.28 g/mL and used to estimate the volume loss from sampling. All condensate samples were assumed to have a density of 1.0 g/mL.

**Table 3-2: Masses and Volumes from Runs 1 and 2**

Stage	Run 1		Run 2	
	Mass (g)	Volume (mL)	Mass (g)	Volume (mL)
Feed	4.17E+02	3.51E+02	4.36E+02	3.66E+02
Inter Pot	3.16E+02	2.49E+02	3.33E+02	2.64E+02
Inter Pot Sample <sup>a</sup>	4.09E+01	3.20E+01	3.77E+01	2.95E+01
Inter Condensate	9.99E+01	9.99E+01	1.02E+02	1.02E+02
Inter KOP	1.57E+00	1.57E+00	5.94E-01	5.94E-01
End Pot	1.88E+02	1.39E+02	2.13E+02	1.58E+02
End Condensate	7.77E+01	7.77E+01	7.59E+01	7.59E+01
End KOP	7.18E-01	7.18E-01	4.11E-01	4.11E-01
<sup>a</sup> assumed density of 1.28 g/mL				



At the end of the test campaign, the concentrated simulant density was 1.35 g/mL at room temperature. As seen in Figure 3-3, pot samples retained the yellow chromate color for the duration of the experiment. No insoluble solids were visible in any samples initially, but small amounts of white solids were visible after the final pot samples had cooled to room temperature. All condensate samples were clear, colorless, and free of solids or second liquid phases.



**Figure 3-3: Photographs of the SLAW Simulant Feed (*far left*) and Intermediate Condensate, Final Pot, and Final Condensate Samples From Runs 1 and 2.**

### 3.4 Evaporator Sample Analysis

Evaporator condensate and pot samples were analyzed for the organic chemical species added to the feed simulant listed in Table 1-3. The  $^1\text{H}$ NMR results for Runs 1 and 2 are found in Table 3-3, including the mass balance between the initial feed and the sum of the final pot and all condensate samples. Values preceded with a “<” symbol denote the result is below the listed method detection limit. The feed sample results for both runs are shown as the average of two measurements, but all other values are results of a single analysis. Insufficient volumes of KOP samples remained for  $^1\text{H}$ NMR analysis, but these values are assumed to minimally effect the mass balance due to the small volume collected.

KOP results were measured using VOA/SVOA and are reported in Appendix A. The results of the VOA/SVOA analysis do not appear reliable and are not used for interpretation of the test results. The results of analysis of the feed samples, which contained a known amount of each organic chemical, did not match the known amounts; and the results from all other samples appears scattered and inconsistent. The reason for the mismatch between expected and measured results was investigated but is not known.

**Table 3-3: NMR Analytical Results and Mass Balance**

<b>Run 1</b>					
<b>Sample</b>	<b>Methanol (mg/L)</b>	<b>Acetone (mg/L)</b>	<b>Butanol (mg/L)</b>	<b>Pyridine (mg/L)</b>	<b>Acetophenone (mg/L)</b>
<b>Feed</b>	1.94E+02	1.30E+02	1.39E+02	1.52E+02	1.79E+02
<b>Inter Pot</b>	< 5.0E-01	1.80E+00	< 5.0E-01	< 5.0E-01	< 5.0E-01
<b>Inter Cond</b>	4.58E+02	2.20E+02	5.22E+02	5.42E+02	6.95E+02
<b>End Pot</b>	< 3.0E-01	3.00E-01	< 3.0E-01	< 3.0E-01	< 3.0E-01
<b>End Cond</b>	2.60E+00	6.00E-01	2.40E+00	1.51E+00	5.60E+00
<b>Mass Balance<sup>a</sup></b>	67.7%	48.8%	107%	102%	111%
<b>Run 2</b>					
<b>Sample</b>	<b>Methanol (mg/L)</b>	<b>Acetone (mg/L)</b>	<b>Butanol (mg/L)</b>	<b>Pyridine (mg/L)</b>	<b>Acetophenone (mg/L)</b>
<b>Feed</b>	1.94E+02	1.30E+02	1.39E+02	1.52E+02	1.79E+02
<b>Inter Pot</b>	< 1.4E+00	2.45E+01	< 1.4E+00	< 1.4E+00	< 1.4E+00
<b>Inter Cond</b>	3.06E+02	2.30E+02	3.74E+02	3.65E+02	4.97E+02
<b>End Pot</b>	< 1.3E+00	7.00E-01	< 1.3E+00	< 1.3E+00	< 1.3E+00
<b>End Cond</b>	4.80E+00	2.60E+00	5.40E+00	4.80E+00	1.13E+01
<b>Mass Balance<sup>a</sup></b>	44.4%	52.9%	75.6%	67.5%	78.7%
<sup>a</sup> Percentage of organics in all measured condensate, KOP, and final pot samples verses the organics measured in the initial feed.					

<sup>1</sup>HNMR results also included examination of spectra for organic species other than the expected five spike chemicals in the pot samples, such as from decomposition products or contaminants. No more than 1.5 mg/L of any unknown/unexpected organic carbon signal was found. Since samples tended to have hundreds of mg/L of the added species, any appreciable decomposition products would be identified if present. The <sup>1</sup>HNMR data thus indicated that the five selected organic chemicals used in this work were stable in the caustic simulant.

The key takeaway from Table 3-3 is the vast majority of organics were removed during the first concentration step and, with the exception of acetone, no detectable organics remained in the pot. Comparison of the organic species concentrations in the intermediate versus end condensate samples suggest that less than 2% of organics in the first phase of differential distillation remained to be removed in the second (end) phase. The final Condensate samples contained < 6 mg/L of all organics excluding acetophenone (11.3 mg/L) in Run 2. The poor mass balance is presumably because the organics did not completely condense and were lost to the KOP and/or out through the pump ventilation. Another possibility is that these chemicals decomposed in the pot, but this is

unlikely since these are generally stable in caustic and the temperature of the liquid was only ~43 °C. The key observation, however, is the near complete removal of the organics from the evaporated simulant.

Measurements of elements detectable by ICP-OES in the initial feed, intermediate, and final pot samples are shown in Table 3-4. For comparison, Table 3-5 lists the predicted elemental concentrations assuming no carryover into the condensate and Figure 3-4 presents the average results for Runs 1 and 2 graphically. Based on these results, 92% to 100% of all measured elements remained in the pot after 100 mL of condensate was collected in the initial concentration phase. After 175 mL of condensate was collected, < 50% of phosphorus remained in the pot with 89% to 93% of other detectable elements remaining. Phosphates are likely to precipitate and form solids when the pot solution is concentrated and evidently did not get subsampled in the liquid taken for analysis. Relative to the organics in the initial feed, the majority of inorganic salts remained in the pot solution.

**Table 3-4: Measured Elemental Concentrations in Pot Samples**

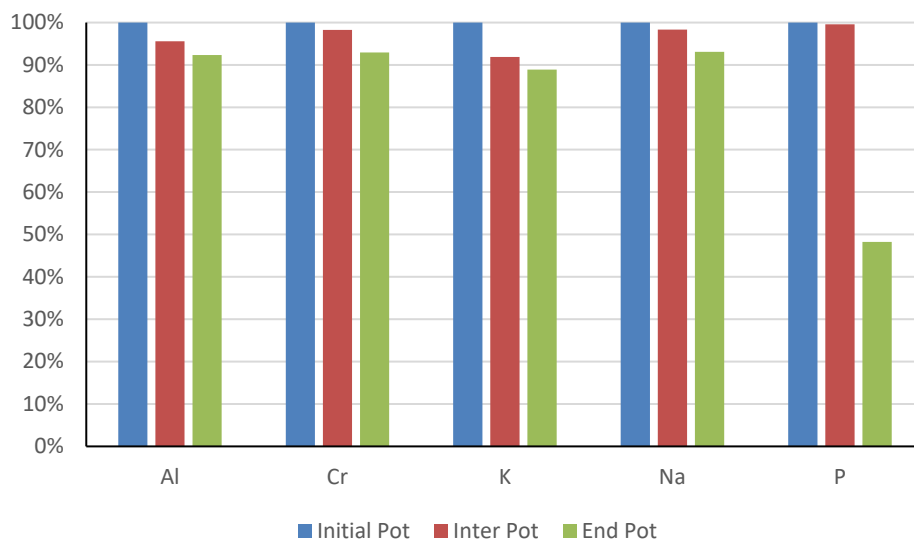
	<b>Initial Feed - Runs 1 &amp; 2</b>			<b>Run 1 - ICP-OES</b>		<b>Run 2 - ICP-OES</b>	
<b>Metal</b>	<b>Target (mg/L)</b>	<b>Mass Added (mg/L)</b>	<b>ICP-OES (mg/L)</b>	<b>Inter Pot (mg/L)</b>	<b>End Pot (mg/L)</b>	<b>Inter Pot (mg/L)</b>	<b>End Pot (mg/L)</b>
<b>Al</b>	3.20E+03	3.20E+03	3.17E+03	4.27E+03	6.35E+03	4.20E+03	6.12E+03
<b>Cr</b>	6.04E+02	6.05E+02	5.96E+02	8.31E+02	1.20E+03	8.06E+02	1.16E+03
<b>K</b>	3.41E+03	3.41E+03	3.54E+03	4.57E+03	6.84E+03	4.51E+03	6.55E+03
<b>Na</b>	9.23E+04	9.48E+04	9.46E+04	1.32E+05	1.92E+05	1.28E+05	1.83E+05
<b>P</b>	1.01E+03	1.01E+03	1.16E+03	1.62E+03	1.14E+03	1.61E+03	1.24E+03

<sup>a</sup> ICP-OES uncertainty is 10 %RSD for all measurements

**Table 3-5: Expected Elemental Concentrations in Pot Samples with no Carryover**

	<b>Initial Feed - Runs 1 &amp; 2</b>			<b>Run 1</b>		<b>Run 2</b>	
<b>Metal</b>	<b>Initial Target (mg/L)</b>	<b>Mass Added (mg/L)</b>	<b>ICP-OES (mg/L)</b>	<b>Inter Pot (mg/L)</b>	<b>End Pot (mg/L)</b>	<b>Inter Pot (mg/L)</b>	<b>End Pot (mg/L)</b>
<b>Al</b>	3.20E+03	3.20E+03	3.17E+03	4.41E+03	6.90E+03	4.46E+03	6.61E+03
<b>Cr</b>	6.04E+02	6.05E+02	5.96E+02	8.29E+02	1.30E+03	8.37E+02	1.24E+03
<b>K</b>	3.41E+03	3.41E+03	3.54E+03	4.91E+03	7.69E+03	4.97E+03	7.37E+03
<b>Na</b>	9.23E+04	9.48E+04	9.46E+04	1.34E+05	2.10E+05	1.31E+05	1.94E+05
<b>P</b>	1.01E+03	1.01E+03	1.16E+03	1.62E+03	2.53E+03	1.62E+03	2.41E+03

<sup>a</sup> ICP-OES uncertainty is 10 %RSD for all measurements



**Figure 3-4: The Percentage of Metals Measured in the Initial, Intermediate, and Final Pot Samples.**

### 3.5 Discussion of Henry's Law Coefficients

Henry's Law coefficients are commonly published for environmental work as shown in references [12] and [13]. The coefficients are often referred to as "constants" in research literature when they are actually strong functions of both temperature and salt content in the liquid phase. Furthermore, they are published in a wide range of units, including [pressure], [dimensionless] and [pressure/molarity]. Given the complex chemistry of nuclear waste and simulants, the use of Henry's Law coefficients is to be taken in approximate and relative ways.

A common temperature correction for the coefficients takes the form of a Van't Hoff equation [14]

$$\ln(H) = a - b/T \quad (1)$$

where T is absolute temperature and b is the enthalpy of vaporization of the volatile organic compound. National Institute of Standards and Technology (NIST) reference [12] provides such a coefficient for many organic chemicals so that H can be corrected for temperature. Note that when the correction is from one temperature to another, the "a" constant is not required.

Use of this equation and NIST data provide a means to compare the temperature adjustment from literature with that output by OLI. Table 3-6 below gives the results for a pure water solvent, the 5 organic species, and a temperature correction between 25 to 40 °C. The multipliers shown would be applied to the 25 °C value of H to provide the 40 °C value. It is seen that the OLI software does provide a correction, but it is often slightly weaker than the literature correction.

**Table 3-6: Comparison of OLI and NIST Temperature Adjustments for Henry's Law Coefficients**

Chemical	H*[12]	H* (OLI, 25 °C)	H* (OLI, 40 °C)	Ratio**	Ratio (NIST)***
<b>Butanol</b>	8.81E-6	1.24E-05	3.14E-05	2.54	3.18
<b>Acetone</b>	3.50E-5	1.96E-05	4.37E-05	2.23	2.11
<b>Methanol</b>	4.55E-6	4.22E-06	9.94E-06	2.36	2.38
<b>Acetophenone</b>	1.04E-5	5.75E-06	1.45E-05	2.53	2.62
<b>Pyridine</b>	1.10E-5	3.65E-06	6.48E-06	1.78	2.58

\* Units of Henry's Law coefficients in this table are atm-m<sup>3</sup>/mol.

\*\* Ratio of 4M sodium simulant Henry's Law coefficient at 40 °C divided by the coefficient at 25 °C using OLI modeling.

\*\*\* Ratio of Henry's Law coefficient at 40 °C divided by the coefficient at 25 °C using the NIST temperature correction equation and data.

Concerning the salting out effect, results from OLI are given in Table 3-7 below. Note that the multipliers to the Henry's Law coefficients are significant. Falabella et al. [15] discussed the effect further, and provided quantitative data showing the significance, including data for n-butanol in sodium sulfate solution. Dissolved sodium salts in the molar range significantly boost Henry's Law coefficients as shown and should be considered in modeling. It appears that OLI models the effect independent of specific organic species in most cases, but methanol was found to be an exception.

**Table 3-7: Salt Effect on Henry's Law Coefficient by OLI Modeling**

Chemical	H* (OLI, 25 °C, water solvent)	H* (OLI, 25 °C, Simulant, 4M sodium)	RATIO**
<b>Butanol</b>	1.24E-05	2.65E-05	2.14
<b>Acetone</b>	1.96E-05	4.19E-05	2.14
<b>Methanol</b>	4.22E-06	1.11E-05	2.63
<b>Acetophenone</b>	5.75E-06	1.23E-05	2.14
<b>Pyridine</b>	3.65E-06	7.82E-06	2.14

\* Units of Henry's Law coefficients in this table are atm-m<sup>3</sup>/mol.

\*\* Ratio of 4M sodium simulant Henry's Law coefficient divided by pure water Henry's Law coefficient

For batch distillation, Rayleigh's equation describes the amount of depletion of the more volatile of two components assuming relative volatility of that component is constant over the composition range.[16] Relative volatility  $\alpha$  is the ratio of the "K values" of the volatile and less volatile components, and is provided in Equation (2),

$$\alpha = \frac{\left(\frac{y}{x} \text{ more volatile component}\right)}{\left(\frac{y}{x} \text{ heavier component}\right)} \quad (2)$$

where “y” is gas phase mole fraction and “x” is liquid phase mole fraction. “a” is the Henry’s Law coefficient in proper units when concentration of the volatile chemical in the system is very low. This is because the denominator of the equation above is unity in that case.

For the volatile chemical, x and y in a binary system are given by

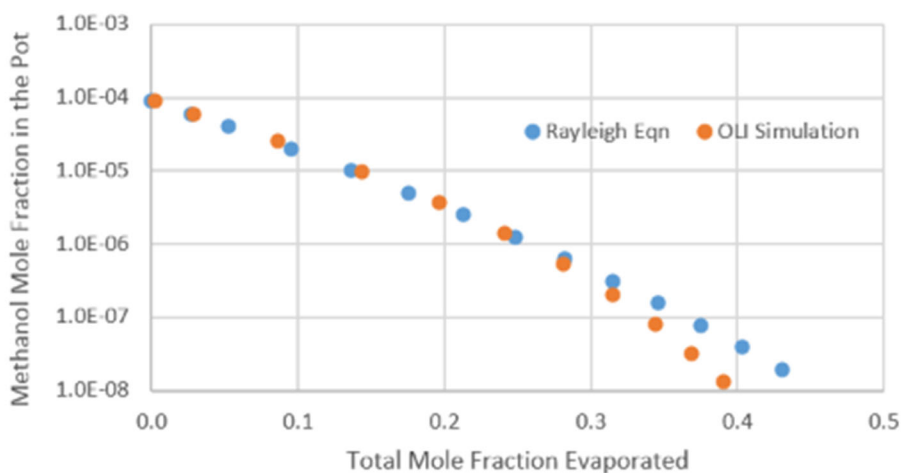
$$y = \frac{a \cdot x}{(1 + (a - 1) \cdot x)} \quad (3)$$

Rayleigh’s equation is

$$\ln \left( \frac{M}{M_0} \right) = \left( \frac{1}{a - 1} \right) \cdot \ln \left( \frac{x \cdot (1 - x_0)}{x_0 \cdot (1 - x)} \right) + \ln \left( \frac{1 - x_0}{1 - x} \right) \quad (4)$$

where “M’s” are total moles in the pot, subscript zeroes are initial values, and “M” and “x” are values after removal of some moles by batch distillation.

Conversion of the Henry’s Law coefficient for methanol in 4 M sodium simulant solution at 40 °C, 2.3E-05 atm·m<sup>3</sup>/mol, yields a relative volatility of 16 at 0.079 atm. Use of this input provides Figure 3-5 below. The methanol initial liquid mole fraction was 9.0E-05 as in the experiment, assuming that the liquid is about 55,000 millimoles of water per liter.



**Figure 3-5: Use of Rayleigh’s Equation for Modeling Batch Distillation of Methanol**

The result agrees reasonably well with the OLI simulation for methanol in section 3.1 above, though OLI predicts better separation of methanol than the Rayleigh equation at the longer extents of evaporation. This is likely due to OLI adjusting its effective Henry’s Law coefficient for higher salt concentration and temperature, while the Rayleigh equation uses a constant separation factor throughout. These predict that about 1.5% of the original methanol remains in the pot after pot volume is 75% of the starting value.

## 4.0 Conclusions

The work overall makes it clear that evaporation is an effective and successful process for stripping the five organic chemicals tested from a salt solution simulant. While organic chemical separation is a function of evaporator design, this work indicates that evaporation is a good practical separation process for chemicals with comparable Henry's Law coefficients to the species tested. Specific observations are:

- Differential distillation in two steps, removing about a quarter of the water from the initial or subsequent liquid simulant, removed more than 98% of each of the organic chemicals spiked into the feed.
- There was no indication of significant reaction of the chosen organic species with the caustic simulant. NMR spectra of pot and condensate samples showed organic chemicals other than those added to be less than 1.5 mg/L.
- Despite variations in modeling of Henry's Law coefficients, OLI modeling reproduced the effective removal.
- <sup>1</sup>HNMR was a good method for analyzing the 5 organic chemicals in liquid samples. VOA and SVOA in contrast were not found to provide useful data in this work.
- Henry's Law coefficients are very sensitive to both temperature and salt molarity in the aqueous phase. Both higher temperature and salt molarity favor more effective volatilization of organic compounds. The effects are significant enough in the operating range of interest that they need to be considered in analyses.
- The work provided liquid concentration data for major salt species. Data on dissolved salt species followed the volume balance around the evaporator, except for phosphate. It is likely that phosphate formed solids because Russell [2] found sodium aluminum phosphate, nahpoite, and trisodium phosphate solids in simulant preparations using X-ray diffraction. The solids were not characterized in the current work.

## 5.0 Recommendations, Path Forward or Future Work

Given the good effectiveness of evaporation as a process for mitigating the regulated trace organic compounds tested here, it would be good to revisit the list of organic chemicals of concern for wider effectiveness. Organic chemicals with Henry's Law coefficients exceeding the values of the five species tested here can be evaporated/separated more easily than what was observed with these five. (A convenient list of regulated chemicals with their water-based Henry's Law coefficients is found on the official website of the state of New Jersey.[17])

OLI software is a useful estimator of Henry's Law coefficients because it combines both temperature and salting out effects. These two effects are both significant as shown in this current work and cannot be neglected in flowsheet design. This capability would be useful for the assessment of other organic chemicals for separation by evaporation.

Past work on the degradation of the heaviest regulated organics indicated likely chemical instability of 181 organic chemicals out of 269 regulated organic chemicals considered [18]. In addition, past laboratory scale evaporation work examined organic vaporization.[3,19] Both

works observed degradation of some species that were spiked into the feed. These two works used OLI software as a guide, and this is recommended for the continuation of future work.

At some low value of Henry's Law coefficients, heavier compounds may not be separated well from the liquid phase by evaporation. As an estimate for water saturated at 42 °C (0.079 atm absolute), a Henry's Law coefficient of  $1.4\text{E-}06 \text{ atm-m}^3/\text{mol}$  would provide a separation factor of unity, and thus no separation by evaporation would be expected. If such compounds are found to be stable with respect to caustic degradation, they may separate slightly or not at all as evaporator pot contents are concentrated. Removal efficiency should still be checked with a laboratory evaporator.

Testing to observe degradation of selected heavy organic compounds, such as by hydrolysis, would help provide support for implementing process evaporation. Phthalate esters would be an example of compounds with measurable hydrolysis kinetics.



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## Appendix A. VOA/SVOA Analysis Results

Evaporator condensate and pot samples were analyzed for the organic chemical species added to the feed simulant. VOA was used to determine the concentration of Methanol, Acetone, Butanol, and Pyridine. SVOA was used to determine the concentration of Acetophenone. The results for Runs 1 and 2 are found in Table 6-1, including the mass balance between the initial feed and the sum of the final pot and all condensate samples. Values preceded with a “<” symbol denote the result is below the listed method detection limit. KOP results for Acetophenone are listed as “N/A” due to insufficient samples volumes remaining for analysis.

**Table 6-1: VOA/SVOA Analytical Results and Mass Balance**

<b>Run 1</b>					
<b>Sample</b>	<b>Methanol (mg/L)</b>	<b>Acetone (mg/L)</b>	<b>Butanol (mg/L)</b>	<b>Pyridine (mg/L)</b>	<b>Acetophenone (mg/L)</b>
<b>Feed</b>	< 0.25	265	32	< 0.25	223.5
<b>Inter Pot</b>	< 0.25	100	< 0.25	< 0.25	< 0.25
<b>Inter Cond</b>	< 0.25	380	140	38	579
<b>Inter KOP</b>	< 0.25	83	120	320	< 0.25
<b>End Pot</b>	< 0.25	94	< 0.25	0.25	< 0.25
<b>End Cond</b>	< 0.25	54	< 0.25	< 0.25	16.7
<b>End KOP</b>	< 0.38	< 0.38	< 0.38	< 0.38	< 0.38
<b>Mass Balance</b>	N/A	66%	126%	308%	75%
<b>Run 2</b>					
<b>Sample</b>	<b>Methanol (mg/L)</b>	<b>Acetone (mg/L)</b>	<b>Butanol (mg/L)</b>	<b>Pyridine (mg/L)</b>	<b>Acetophenone (mg/L)</b>
<b>Feed</b>	< 0.25	265	32	< 0.25	223.5
<b>Inter Pot</b>	< 0.25	29	< 0.25	< 0.25	< 0.25
<b>Inter Cond</b>	< 0.25	390	110	36	521
<b>Inter KOP</b>	< 0.45	< 0.25	< 0.25	140	N/A
<b>End Pot</b>	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
<b>End Cond</b>	< 0.25	< 0.25	< 0.25	< 0.25	34.6
<b>End KOP</b>	< 0.78	< 0.78	< 0.78	< 0.78	N/A
<b>Mass Balance</b>	N/A	43%	96%	257%	68%

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