

Supplementary Materials

1. Typical Treatment Schematic for Desalination of PW using Crystallization

Raw/untreated PW, either from a single well or a cluster of wells, is typically first sent to an aboveground storage tank (AST) for flow/composition equalization. Additionally, an oxidant (most typically chlorine) is added to PW at the inlet of the AST to oxidize soluble iron (from ferrous (Fe^{2+}) to ferric (Fe^{3+}) form) as well as for disinfection (bacteria control). Flow from the AST is then sent to a pretreatment unit/train. Typical technologies utilized for pretreatment include coagulation followed by settling and dissolved air flotation (DAF), followed by filtration, if necessary. In this study, the authors used a combination of microfiltration (MF) and ultrafiltration (UF) to treat PW straight from the AST. Filtrate from both the MF and UF were combined in equal proportion (as noted earlier) to provide feed for the steam stripping step (as shown in Figure SI-1 below). The quality of the MF/UF filtrate is noted below. Note that the TDS remains largely unchanged during pretreatment.

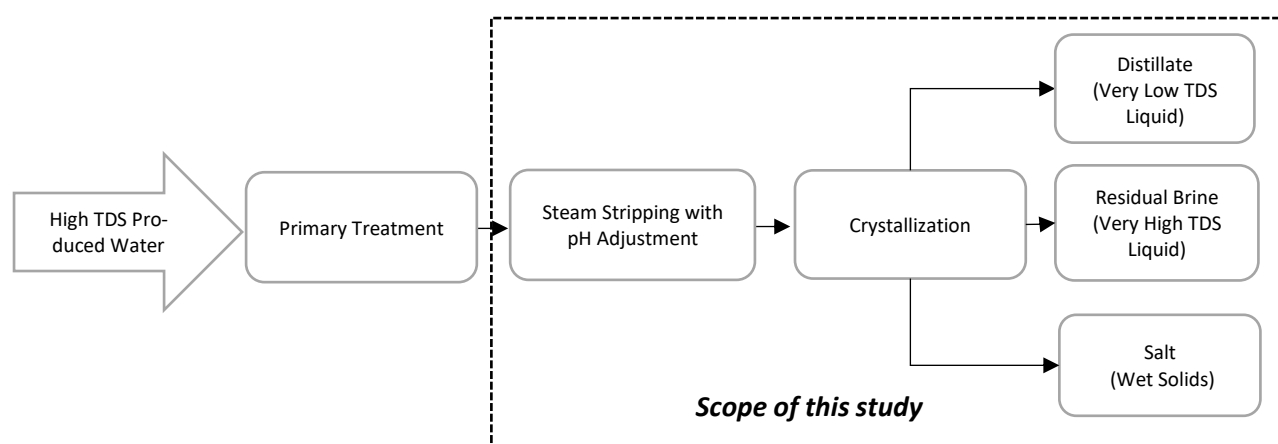


Figure S1. Block Flow Diagram of a typical thermal desalination process for high TDS produced water treatment.

Typical Pretreatment Specifications for Reuse in O&G Operations

Oil & Grease:	< 10 mg/L
pH:	6 – 8 su
Fe:	< 2 mg/L
Turbidity:	< 10 ntu (TSS was usually less than 10 mg/L)
ORP:	> 350 mv
FAC:	> 1 mg/L (free available chlorine)
H ₂ S:	No H ₂ S (oxidized to non-detect with chlorine)

Pretreated PW typically calcium and magnesium hardness that can combine with carbonates to produce mineral scale on equipment surfaces during thermal processing. Dissolved oxygen in raw produced water can also pose equipment corrosion issues, especially at elevated processing temperatures. Therefore, a common pre-treatment step before the thermal desalination of produced water is the reduction of sulfides (if present), bicarbonates (CO_2), and dissolved oxygen (DO) to very low levels. To achieve this, the pH of the produced water is reduced to change sulfides to H_2S and bicarbonates/carbonates to CO_2 , and the water is pumped through a steam stripper operated near the boiling point of the produced water. The stripping steam typically reduces H_2S , CO_2 , dissolved oxygen, and potentially VOCs contained in the raw produced water to very low levels.

2. OLI Flowsheet Simulation

Two OLI Systems, Inc., aqueous system modelling programs, Studio Analyzer and Flowsheet: ESP, were utilized for the desktop simulation (AQSim, 2017). The Flowsheet: ESP program employs a rigorous chemical thermodynamic framework for modelling solid-liquid-vapor systems that are primarily aqueous based. The chemistry within the calculation engine considers the non-ideality of aqueous solutions. In this study, a specific thermodynamic model called MSE-SRK was used to define behaviors of species in the produced water. The MSE-SRK model is based on the Mixed-Solvent Electrolyte (MSE) model for electrolyte systems and utilizes the Soave-Redlich-Kwong (SRK) equation of state for both the gas phase and the second liquid (or non-electrolyte) phase. This model is good for correlating electrolyte, non-electrolyte and organic interferences, especially in the high TDS produced water environment, and is designed to deliver the highest level of accuracy for process modelling and simulation of the behaviors of the species studied in produced water desalination applications (AQSim - OLI Electrolyte Solutions, 2017). Calculations are processed to steady state conditions and any kinetic effects are not considered in these simulations.

Studio Analyzer was used to reconcile and define the input water streams for the Flowsheet: ESP simulation from the developed representative produced water analysis. Approximately 5% additional chloride was added to the selected representative produced water during the reconciliation step, which was required to produce a charge-neutral feed brine for the simulation. In actual operation, aqueous brines are electrically neutral, but water analysis tests are limited in their accuracy and rarely provide a complete ion balance. A total ionic imbalance of up to 10% is typical in water analysis results. The reconciled produced water stream was then used as the input to the Flowsheet: ESP model

3. Summary of Analytical Methods

Parameter.	Sample	Sampling Plan	Comments
Barium, Ba Boron, B Calcium, Ca Iron, Fe Lithium, Li Magnesium, Mg Manganese, Mn Potassium, K Sodium, Na Strontium, Sr Zinc, Zn	Brine Liquid & Distillate	Inductively Coupled Plasma (ICP)	The concentrations of barium, boron, calcium, iron, lithium, magnesium, manganese, potassium, sodium, strontium, and zinc in the each of the water samples were determined using Inductively Coupled Plasma Spectroscopy. It should be noted that the sample solution was diluted as required prior to analysis.
Bromide, Br Chloride, Cl Iodide, I Sulfate, SO ₄	Brine Liquid & Distillate	Ion Chromatography (IC)	The concentrations of bromide, chloride, iodide, and sulfate in each of the water samples were determined using a Dionex ICS 3000 Ion Chromatograph. It should be noted that the sample solution was diluted as required prior to analysis.
Total Alkalinity, Bicarbonate (HCO ₃), Carbonate (CO ₃), Hydroxide (OH)	Brine Liquid & Distillate	Ion Chromatography (IC)	The concentrations of carbonate and bicarbonate in each of the water samples were determined using Dionex ICS 3000 Ion chromatography. It should be noted that the sample solution was diluted as required prior to analysis.

Temperature		Digital Thermometer
pH		Digital pH meter by ASTM D1293
Density		Digital Densitometer by ASTM D4052
Conductivity	Brine Liquid & Distillate	Digital Conductivity meter by ASTM D1125
Resistivity		Calculation
Calculated TDS		Calculation
Gravimetric TDS		ASTM D5907
Hardness		Calculation
Salinity		Calculation
Ionic Balance		Calculation
Stiff Diagram		Calculation
Acetate	Brine Liquid & Distillate	Ion Chromatography (IC)
Butyrate		
Formate		
Propionate		
Glycolate		
Benzene	Brine Liquid & Distillate	GC-FID
Toluene		
Ethylbenzene		
Xylene		

The concentrations of acetic acid, butyric acid, formic acid, glycolic acid, and propionic acid in each of the water samples were determined using a Dionex ICS 3000 Ion Chromatograph. It should be noted that the sample solution was diluted as required prior to analysis.

The concentrations of benzene, toluene, ethylbenzene, and xylenes in each of the water samples were determined using a gas chromatograph equipped with a flame ionization detector.

4. Sodium and Chloride Concentration in Distillate

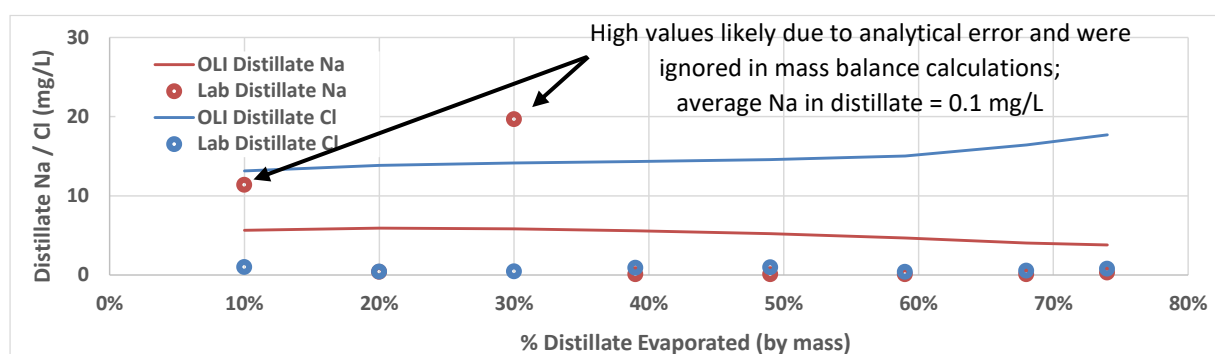


Figure S2. Variation in Na and Cl concentration in Distillate as a function of PW Evaporation.

5. Calcium Concentration in Distillate and Brine

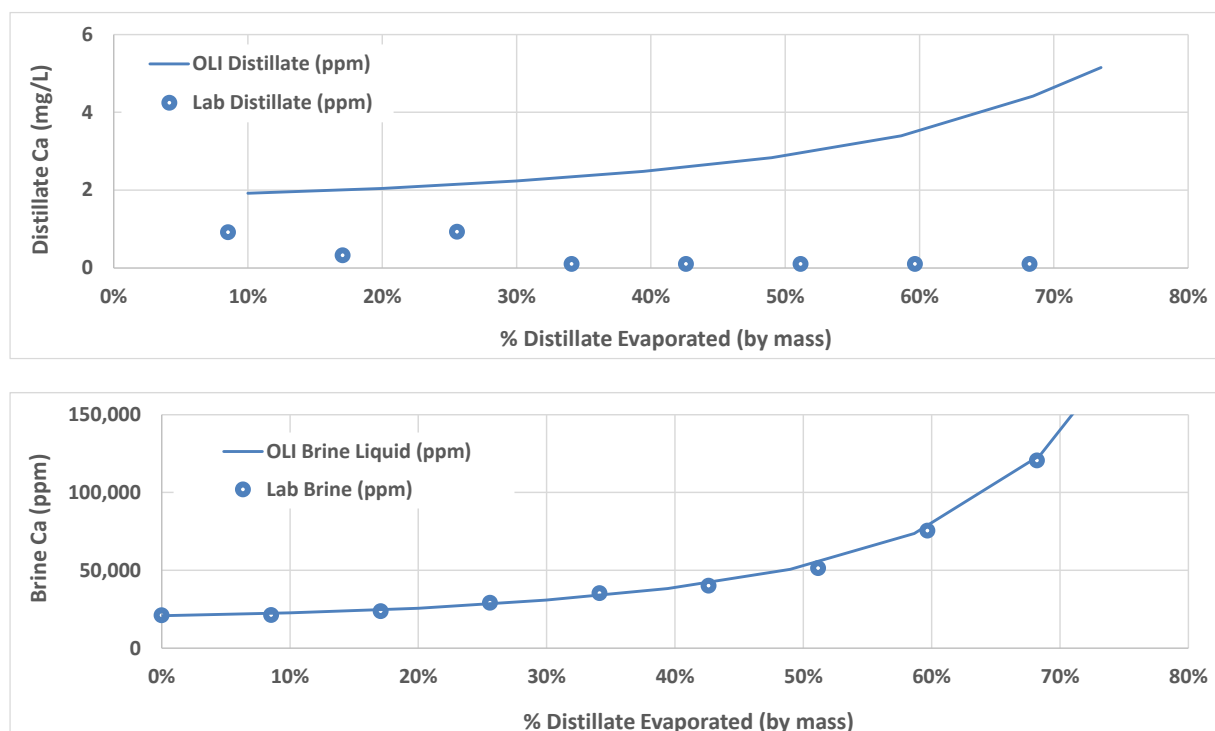


Figure S3. (a) Variation in Ca concentration in Distillate as a function of PW Evaporation, (b) variation in Ca concentration in Brine as a function of PW Evaporation.

6. Magnesium Concentration in Distillate and Brine

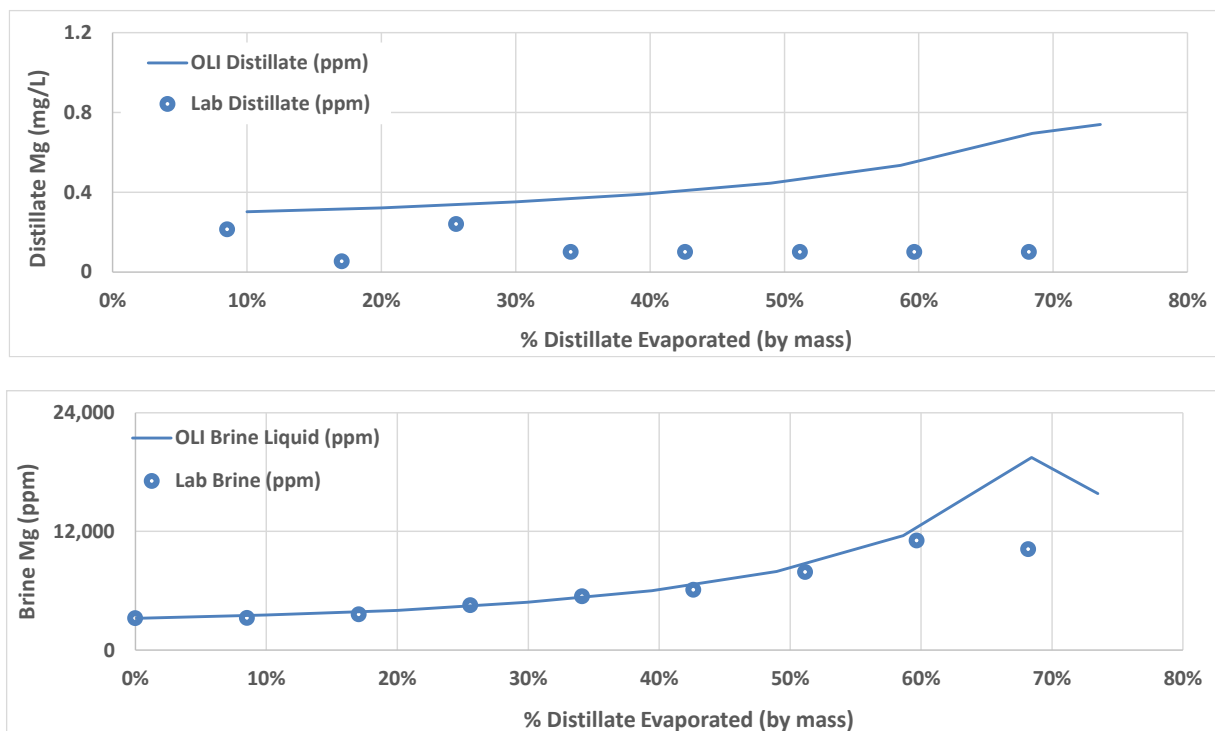


Figure S4. (a) Variation in Mg concentration in Distillate as a function of PW Evaporation, (b) variation in Mg concentration in Brine as a function of PW Evaporation.

7. Barium Concentration in Distillate and Brine

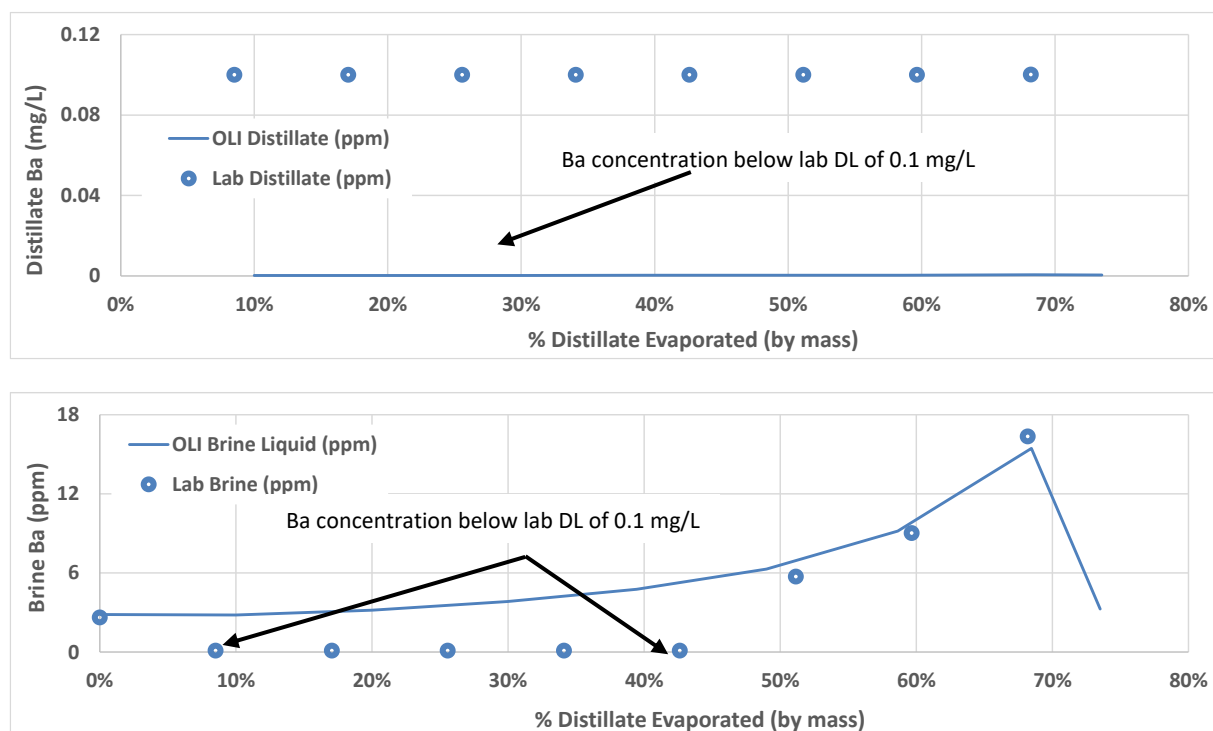


Figure S5. (a) Variation in Ba concentration in Distillate as a function of PW Evaporation, (b) variation in Ba concentration in Brine as a function of PW Evaporation.

8. Strontium Concentration in Distillate and Brine

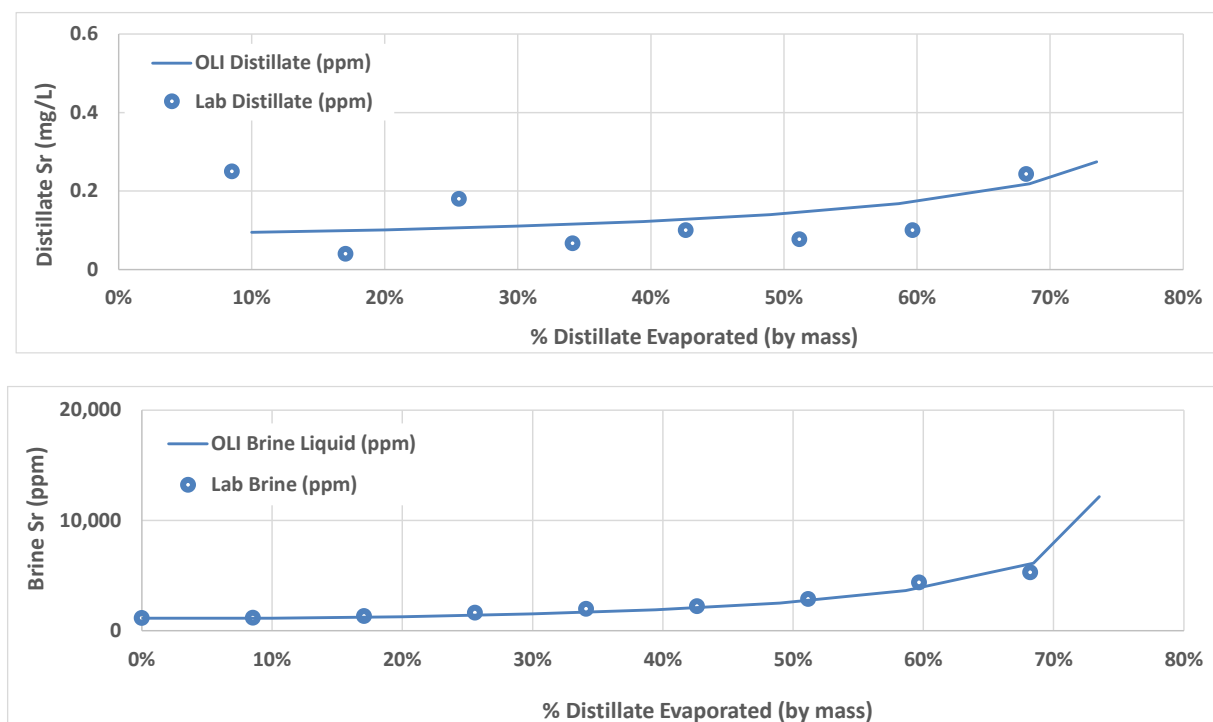
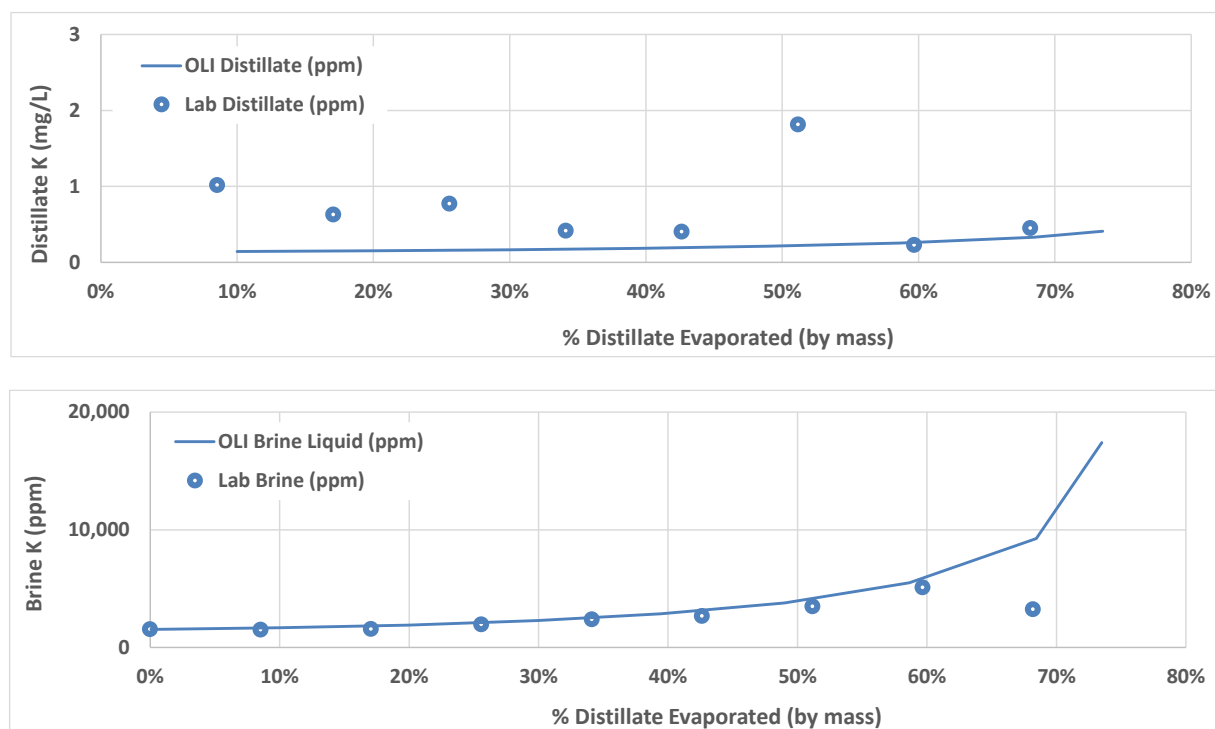


Figure S6. (a) Variation in Sr concentration in Distillate as a function of PW Evaporation, (b) variation in Sr concentration in Brine as a function of PW Evaporation.

9. Potassium Concentration in Distillate and Brine



Note: Triplicate analysis of K concentration in brine at the 68.4% evaporation by mass point showed a concentration of 3233 mg/L (values of 3395, 3351 and 2954 mg/L), indicating precipitation of from solution, and represents a significant deviation from OLI model prediction. A possible reason for this deviation may be a decrease in accuracy of activity coefficients assumed in the OLI model for K at high ionic strengths.

Figure S7. (a) Variation in K concentration in Distillate as a function of PW Evaporation, (b) variation in K concentration in Brine as a function of PW Evaporation.

10. Boron Concentration in Distillate and Brine

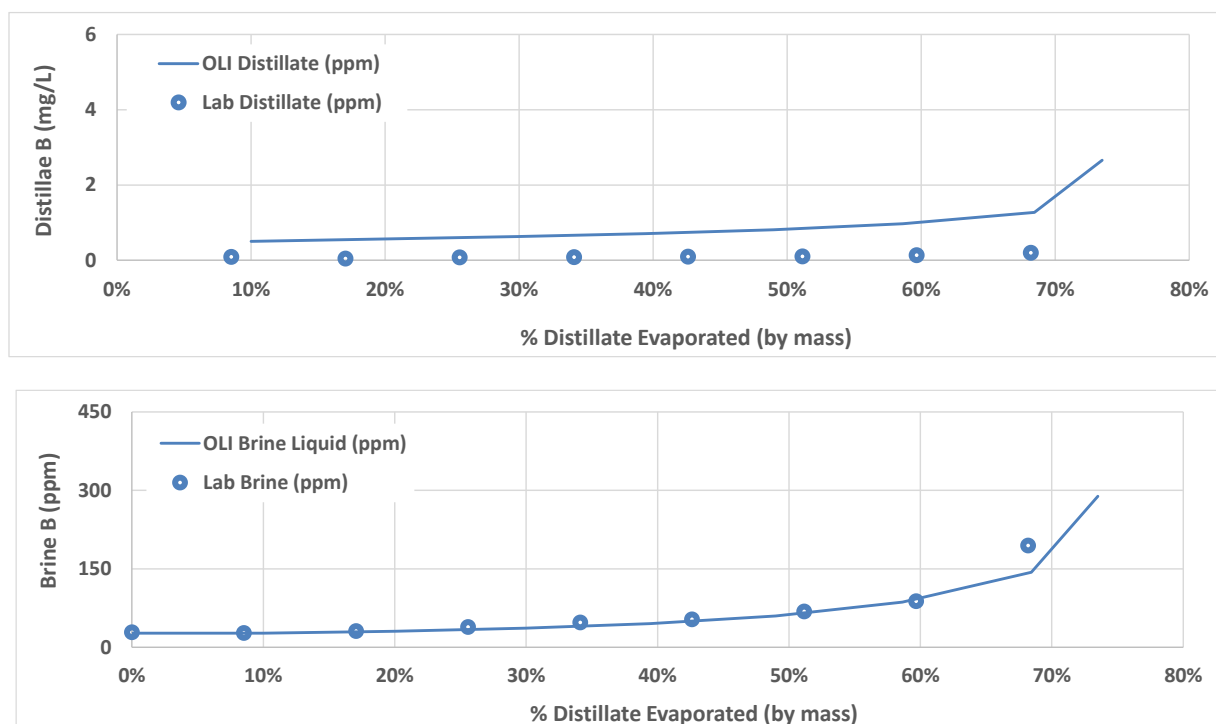


Figure S8. (a) Variation in B concentration in Distillate as a function of PW Evaporation, (b) variation in B concentration in Brine as a function of PW Evaporation.

11. Sulfate Concentration in Distillate and Brine

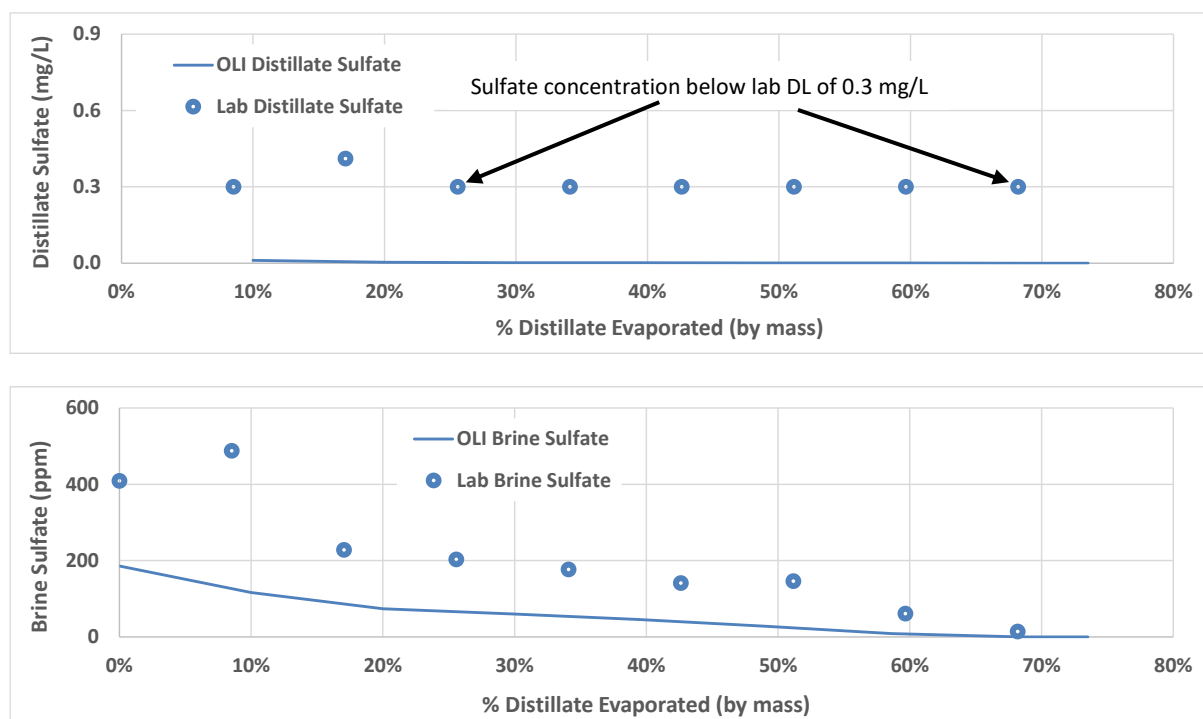


Figure S9. (a) Variation in Sulfate concentration in Distillate as a function of PW Evaporation, (b) variation in Sulfate concentration in Brine as a function of PW Evaporation.

12. Cation-Anion Balance in Distillate and Brine

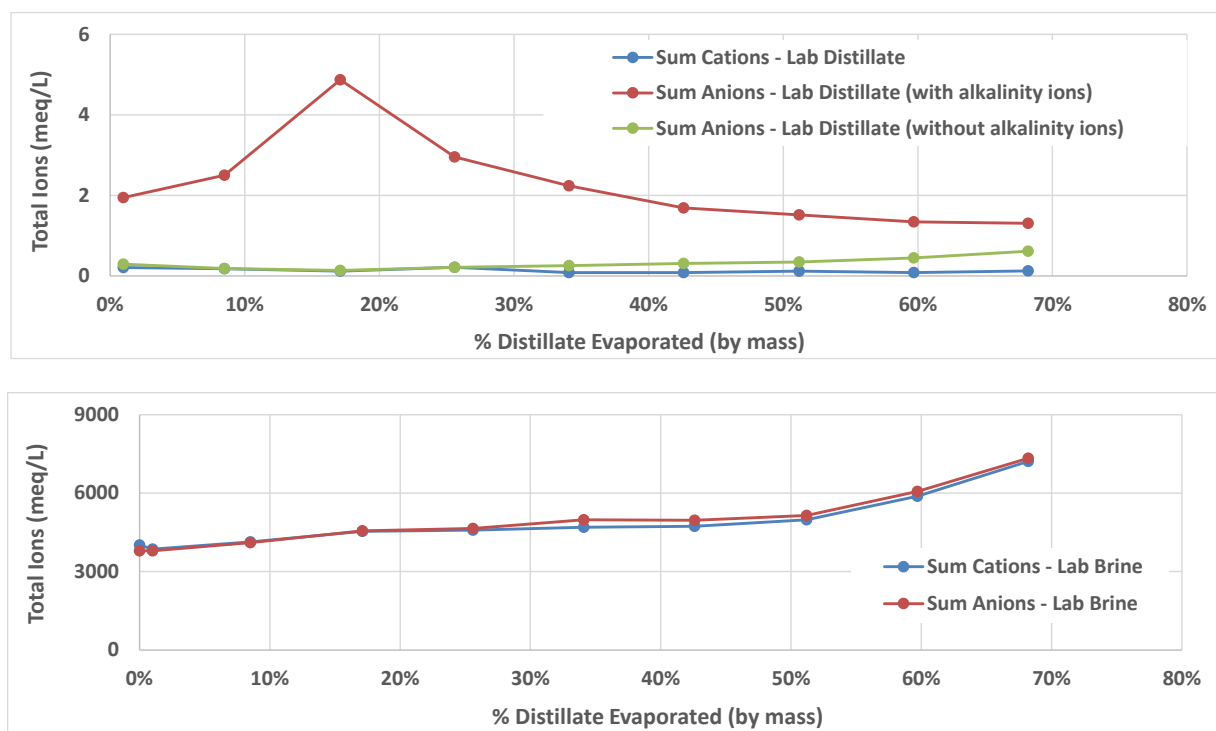


Figure S10. (a) Cation-Anion Balance in Distillate as a function of PW Evaporation, (b) Cation-Anion Balance in Brine as a function of PW Evaporation.

13. Acetate Partitioning – Residual Brine and Simplified Brine

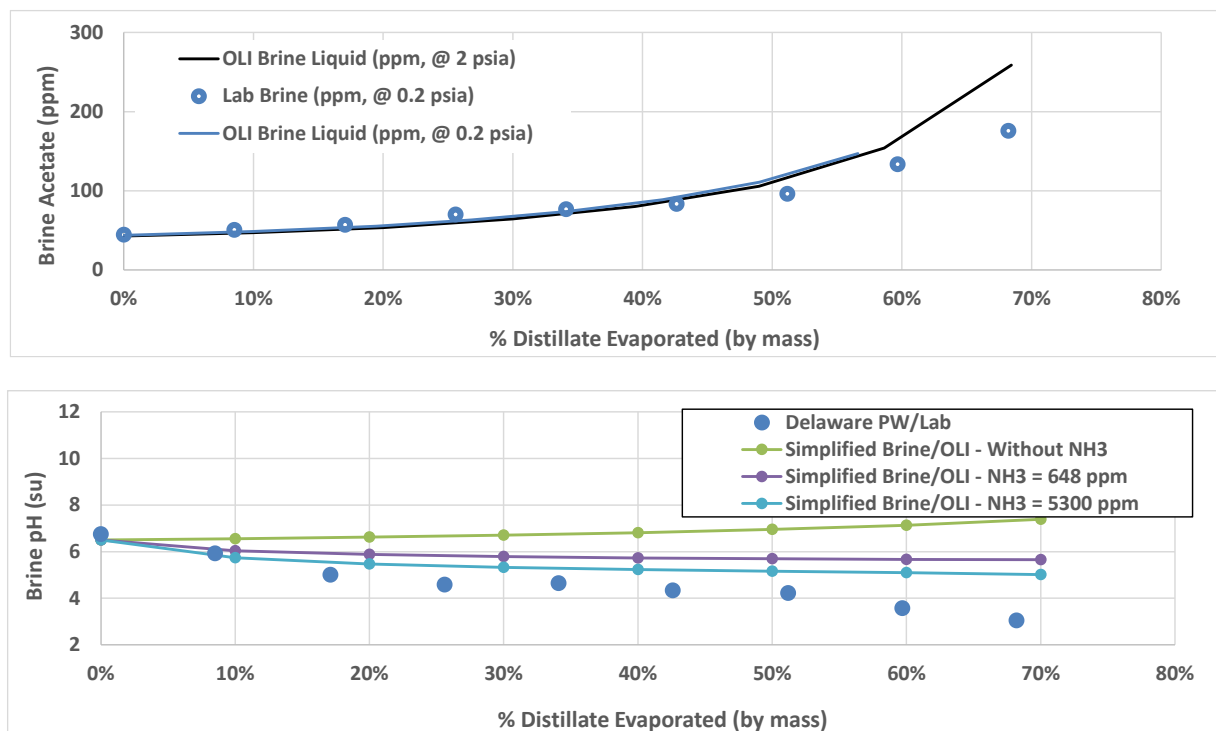


Figure S11. (a) Concentration of Acetate in residual brine as a function of PW Evaporation, (b) pH of simplified test brine as a function of ammonia and PW Evaporation.

14. Li, Br and I Enrichment in Produced Water

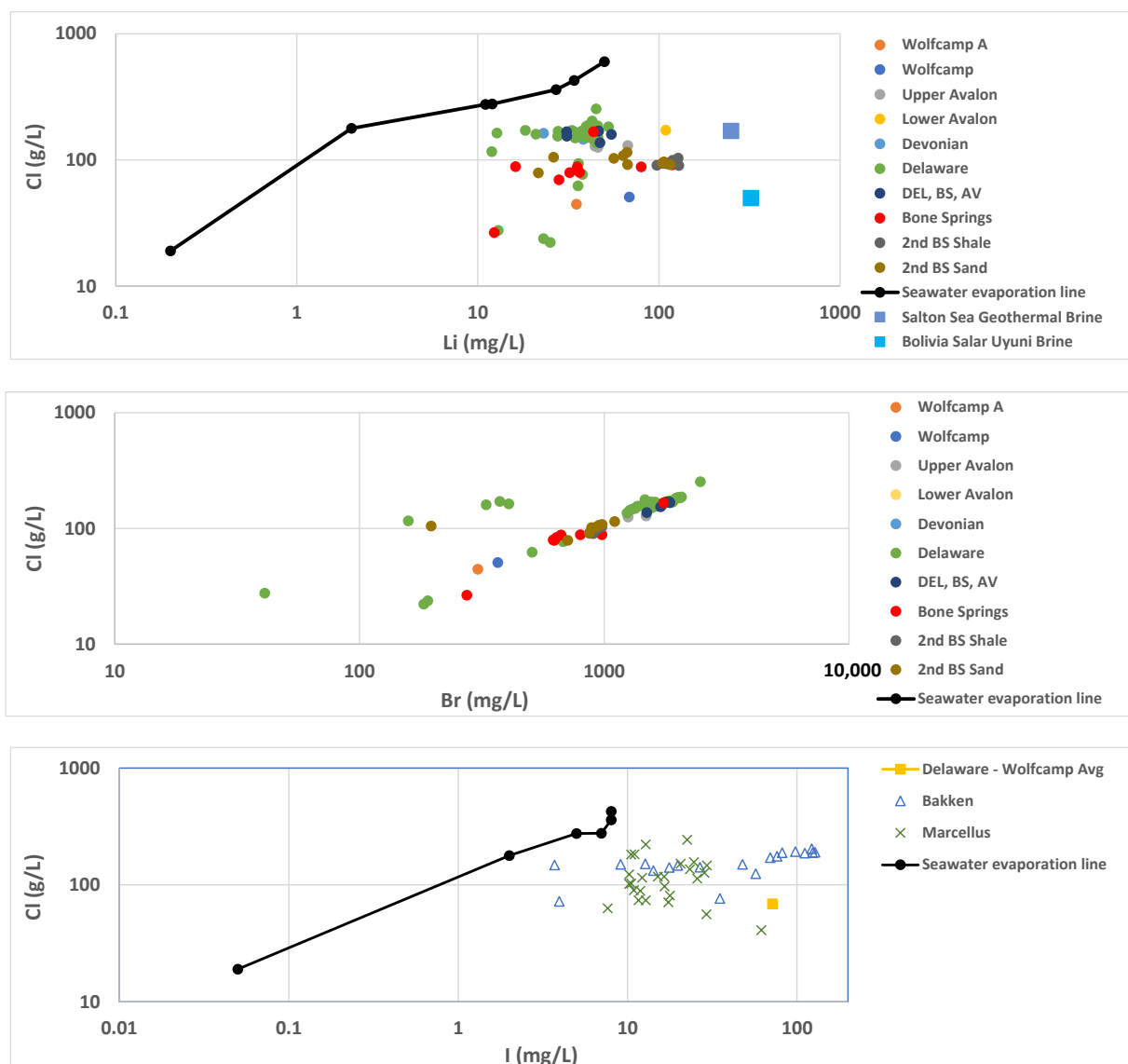


Figure S12. (a) Preferential enrichment of Lithium in PW compared with seawater for Delaware Basin formations, (b) Preferential enrichment of Bromide in PW compared with seawater for Delaware Basin formations, (c) Preferential enrichment of Iodide in PW compared with seawater for formations from the Delaware, Marcellus and Bakken Basins.

15. Elemental Composition of Precipitated Solids (XRF)

Table S1. Elemental composition of solids at three evaporation cuts (by mass).

Element	% Distillate Evaporation by Mass (Lab Solids by XRF)		
	25.6%	59.7%	68.2%
	Elements wt%		
Na	77.2	70.7	60.2
Cl	20.2	24.4	29.6
Mg	1.2	2.3	5.1
Ca	0.8	2.0	4.1
Al	0.3	0.5	0.7
S	0.4	0.1	0.1
Br	0.1	0.3	0.5
Si	0.03	0.1	0.2
Sr	0.03	0.1	0.2