TO: Texas Hazardous Waste Research Center

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SUBJECT: Annual Progress Report

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PROJECT TITLE: Coupling of Produced Water Treatment and Flare Recovery in Unconventional Oil and Gas Production

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Project Description

Oil & gas industries are actively seeking solutions for cost effective treatment strategies as part of their business plan. Table 1 shows the comparison of several dominant treatment technologies for shale gas produced water.

Table 1 Comparison of produced water treatment technologies[5]

Technologies	MSF	MED	VCD	RO
Feed Requirement	TDS ≤200,000 ppm	TDS ≤200,000 ppm	TDS ≤200,000 ppm	TDS ≤50,000 ppm
Energy Consumption (Thermal)	3.35 kWh/bbl			
Energy Consumption (Power)		1.3-1.9 kWh/bbl	1.3 kWh/bbl	SWRO: 0.46-0.67 kWh/bbl BWRO: 0.02-0.13 kWh/bbl
Chemical Use	Scale Inhibitors: EDTA, acids etc.	Scale Inhibitors: EDTA, acids, etc	Scale inhibitors required	Scale Inhibitors required
Pre/post-treatment	Pre-treatment to remove large suspended solids	Pre-treatment to remove large suspended solids	Pre-treatment and post-treatment are required	Extensive pretreatment is required to prevent membrane fouling
Capital cost	$250-360 per bpd	$250-330 per bpd	$140-250 per bpd	SWRO:$125-295/bpd BWRO:$35-170/bpd
Operation cost	$0.12/bbl	0.11/bbl	$0.075/bbl	SWRO:$0.08/bbl BWRO:$0.03/bbl

In the past, the comparison between desalination technology deployment was mainly focused on technological and economical dimensions. For example, a six-step ranking system was proposed for comparisons among several water desalination technologies based on technological criteria such as removal efficiency, resource consumption, pre- or post-treatment requirement, durability, mobility and level of contaminants in feed. However, the results are subjective and changeable to different occasions.

Objective

We are trying to evaluate the performance of various shale gas produced water desalination technologies. Starting from process simulation, evaluation will be from the following dimensions: Technological, Economic, Environmental and Societal.

Methodology

Aspen Plus is used as the tool for process simulation. The property method in Aspen Plus was calibrated using published phase diagram.

Accomplishments/Problems

The produced water composition and flare gas composition used in our simulation is derived from typical ones at Marcellus shale with good approximation (Table 1). The produced water composition includes 20-30 different cations and anions, and it's rather inefficient to include all the ions in the simulation. Reasonably good results could be achieved by including only the dominant ions. We include sodium and calcium (Na^+, Ca^{2+}) as cations and chloride (Cl^-) as anions that can better represent the physical properties of produced water.

Table 2 Flare gas and produced water components in the simulation

Flare gas components	Mole fraction	Produced water components	Mass fraction
Methane	0.794	Water	0.894084
Ethane	0.161	NaCl	0.07848
Propane	0.04	$CaCl_2$	0.027436
CO_2	0.001		
Nitrogen	0.004		

The MSF and MED desalination processes are simulated and the results are optimized in Aspen Plus. (Figure 3 & 4)

Property Method

The ENRTL-RK property method in Aspen Plus is among the most versatile property method that can accurately describe aqueous electrolyte systems up to very high concentration[20]. To verify the accuracy of ENRTL-RK, a dedicated simulation case was created and corresponding results are checked on the phase diagram constructed from trusted experimental data. In the simulation case, the aqueous feed containing known concentrations of NaCl and $CaCl_2$ are flashed at 50°C with increasing vapor fractions (0-0.9). The brine stream components after flash operation are shown below (Table 2). The simulation results predicted that NaCl should start to precipitate at vapor fraction=0.7, and no other salts will precipitate at vapor fraction greater than 0.7. Next, a ternary phase diagram is constructed from reported experimental data21 as shown in Figure 1. Point A and B represent the solubility of sodium chloride and calcium chloride dehydrate, and point C is the eutectic point of sodium chloride and calcium chloride. Curve AC and BC are the saturation lines of single salt of NaCl and CaCl2 respectively. Beyond curve ACB, no salt should exist in the aqueous phase. In the region ACD and BCE, either NaCl or CaCl2 will precipitate and in the region CDFE, both salts should precipitate. To verify the simulation results on the phase diagram, the brine stream composition from simulation represented by triangle dot are plotted on the diagram. As shown on the diagram, dots with vapor fraction between 0-0.6 falls beyond curve ACB where no salt should exist. At vapor fraction=0.7, the dot falls in the region ACD, and all the dots with vapor fraction>0.7 fall in the same region, where only NaCl(s) precipitates. The simulation results using ENRTL-RK has exactly the same predictions with phase diagram prediction and therefore used in the following simulation cases.

Table 3 The brine composition after flash at 50°C under various vapor fractions

	Mass Fraction			
Vapor Fraction	NaCl	CaCl2	H2O	NaCl (s)
0	0.0785	0.0274	0.8941	0
0.2	0.0970	0.0339	0.8691	0
0.4	0.1271	0.0444	0.8285	0
0.6	0.1840	0.0643	0.7517	0
0.7	0.1861	0.0813	0.6863	0.0463
0.8	0.1336	0.1067	0.5881	0.1716
0.9	0.0487	0.1537	0.4066	0.3910

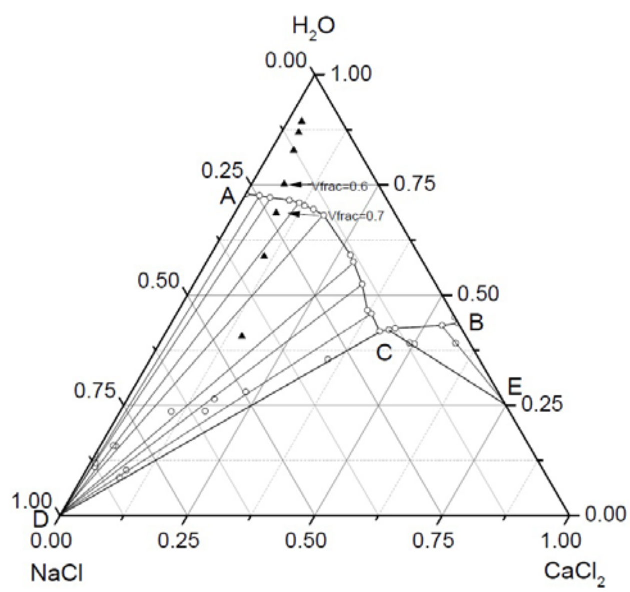

Figure 1. Confirm the Aspen plus solubility data with the phase diagram

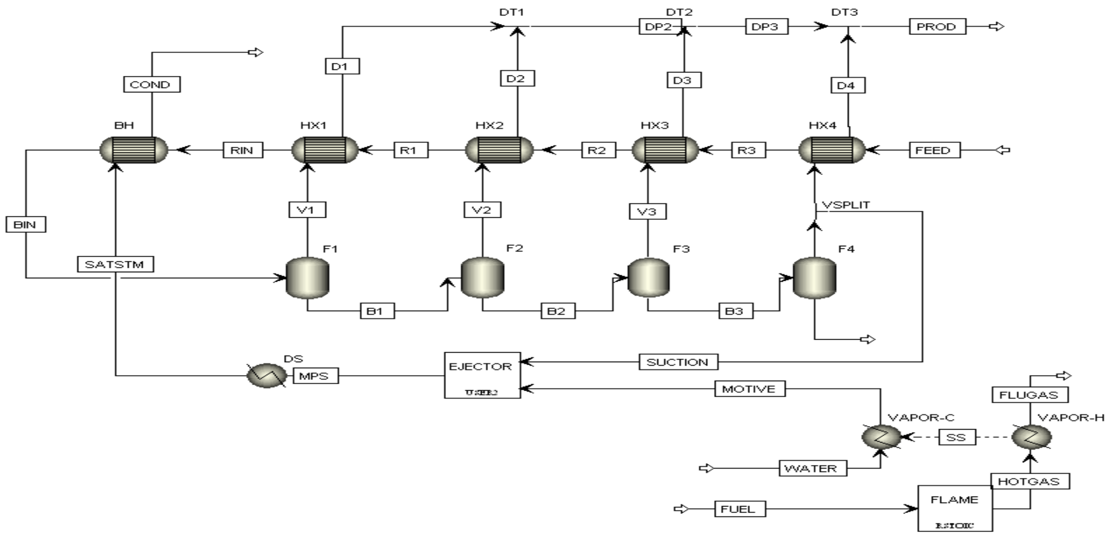

Figure 2. MSF desalination process

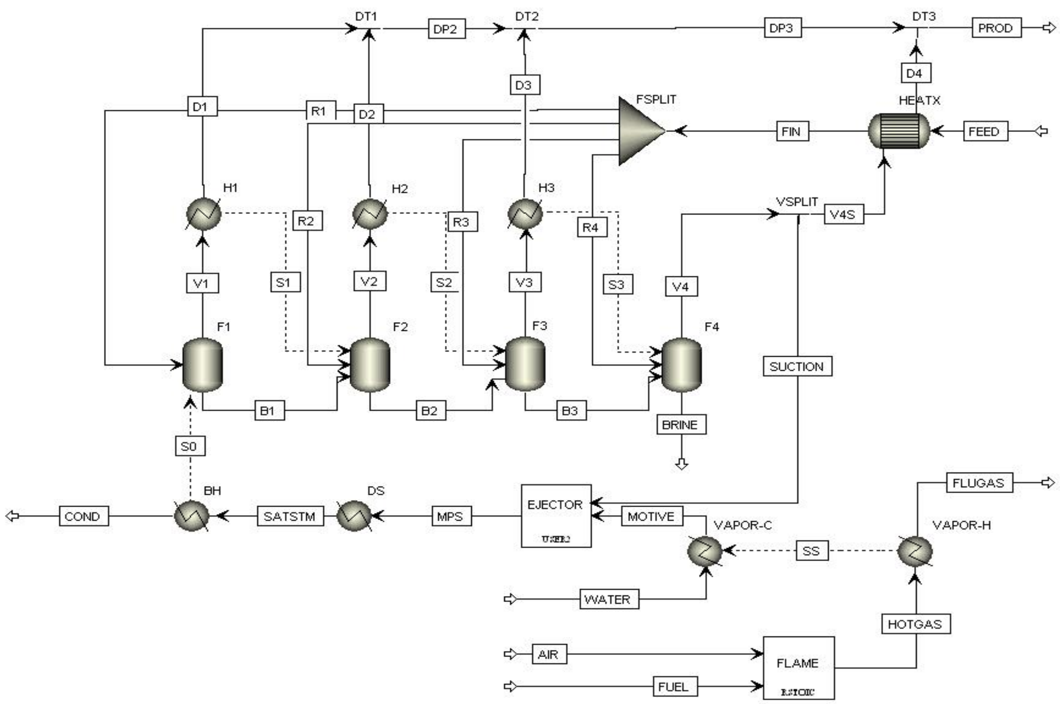

Figure 3. MED desalination process

The sustainability analysis for MSF and MED are performed and Table 2 shows the brief summary of the preliminary results.

Table 4 brief summary of sustainability analysis of MSF and MED

	Technologies	MSF	MED
Technological Dimension	GOR	6.45	7.28
	Recovery	28.4	36.4
Economic Dimension	Unit Product Cost ($/ton prod.)	1.45	1.29
Environmental Dimension	PEI/ton prod.	5.92E-03	5.29E-03

Future Work

The team will collect more data on the aforementioned aspects from various resources, including direct contact with the technology developers and users, literature review and process simulation when necessary. Process flowsheet will be constructed and optimized. The sustainability analysis of the four dimensions mentioned earlier will also be performed.

List of Publications and Presentations

1. Chen, L. W., Z. X. Tian, H. H. Lou, "Sustainable Manufacturing and Water Sustainability," Sustainable Water Management and Technologies, D. H. Chen (eds.), CRC Press/Taylor & Francis Group, Boca Raton, FL, accepted, 2013.
2. Chen, L. W. and Helen H. Lou, "Simulation and Sustainability Analysis for Produced Water Thermal Desalination Technologies," AIChE Annual Meeting, November 3-8, 2013, San Francisco, CA.
3. Chen, L. W., P. Saxena, H. H. Lou, Lily Xu and Danny Reible, Simulation and Sustainability Analysis for Produced Water Treatment driven by on-site waste heat, AIChE Spring Meeting, March 30- April 4, 2014, New Orleans, LA.