Advanced Integrated Technologies for Treatment and Reutilization of Impaired Water in Fossil Fuel-Based Power Plant Systems

Jason Trembly

Tuesday April 10, 2018

2018 Annual Review Meeting for Crosscutting Research

RUSS COLLEGE OF ENGINEERING AND TECHNOLOGY
Create for Good.
OHIO UNIVERSITY 1804

Disclaimer

"This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

Presentation Overview

- Institute for Sustainable Energy and the Environment Overview
- Produced Water Management
- Supercritical separation via Joule-Heating
- Experimental Results
- Modelling
- Summary

ISEE Overview

Institute Facts

- Faculty: 3
- Staff: 4 (Engineers and scientists)
- Students: 16 GS; 14 UG
- Space: 14,000 ft^2
- Over $15M in external research since 2008

Research Capabilities

- Thermocatalytic Processes
- Process Engineering & Design
- Process Modeling & Simulation

Home to Ohio Third Frontier Innovation Platform Program & OHIO Shale Innovation Projects

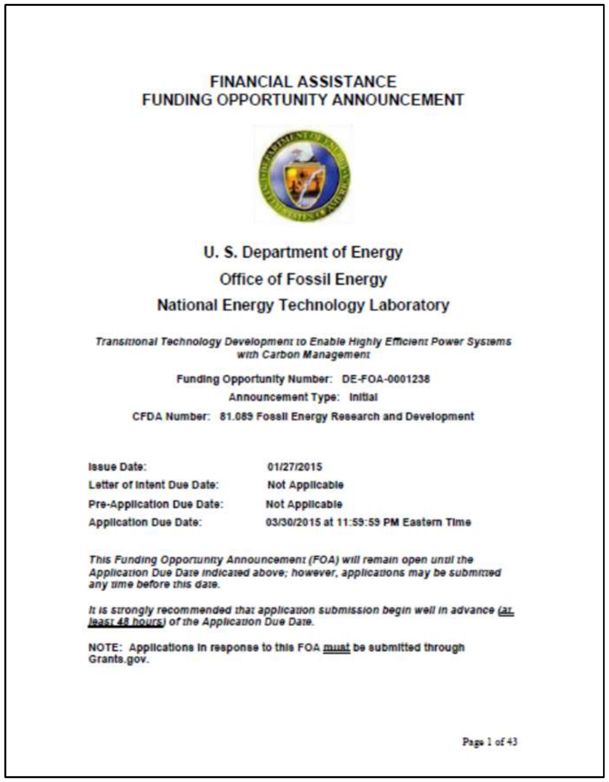
Water
- Brine treatment
- Nutrient recovery
- NORM capture

Coal
- Coal conversion (syngas & pyrolysis)
- Coal liquefaction
- Composite materials

Oil & Gas
- Reinjection & reservoir scaling studies
- Reservoir nanofracturing and modeling
- Modular alkanes separations

Biomass
- Algae growth & conversion
- Thermocatalytic conversion
- Biochemicals production

Project Specifics and Team



FINANCIAL ASSISTANCE
FUNDING OPPORTUNITY ANNOUNCEMENT

U. S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Transitional Technology Development to Enable Highly Efficient Power Systems with Carbon Management

Funding Opportunity Number: DE-FOA-0001238
Announcement Type: Initial
CFDA Number: 81.089 Fossil Energy Research and Development

Issue Date:	01/27/2015
Letter of Intent Due Date:	Not Applicable
Pre-Application Due Date:	Not Applicable
Application Due Date:	03/30/2015 at 11:59:59 PM Eastern Time

This Funding Opportunity Announcement (FOA) will remain open until the Application Due Date indicated above; however, applications may be submitted any time before this date.

It is strongly recommended that application submission begin well in advance (at least 48 hours) of the Application Due Date.

NOTE: Applications in response to this FOA must be submitted through Grants.gov.

Page 1 of 43

Project Specifics

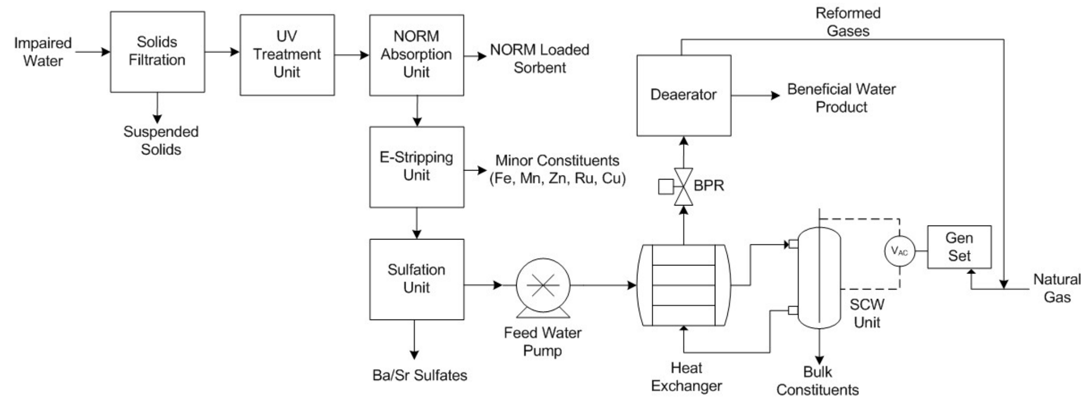
- DOE/NETL Cooperative Agreement No. DE-FE0026315
- DOE Project Manager: Barbara Carney
- Principal Investigator: Jason Trembly
- Collaborators: WVU and AEP

Period of Performance

- September 1, 2015 to August 30, 2018

Brine Treatment Process

- **Technologies**
  - UV Treatment
  - NORM Absorption (Produced water)
  - Electrochemical Removal
    - Minor constituent removal (Fe^{2+}/Fe^{3+}, Mn^{2+}, Ru^{2+}, Zn^{2+}, and Cu^{2+})
  - Selective precipitations
    - Minor constituents (Ba^{2+} and Sr^{2+})
  - SCW Treatment
    - Bulk constituents



Brine Treatment Process

OHIO UNIVERSITY 1804
Institute for Sustainable Energy and the Environment
RUSS COLLEGE OF ENGINEERING AND TECHNOLOGY

Project Objectives

Overall

- Develop a site deployable cost-effective technology for treating brine generated from CO_2 storage operations

Small Scale Testing

- Validate technical and commercial feasibility of new internally heated SCW treatment methodology for removal of major constituents from impaired water
- Determine effectiveness of electrochemical stripping to remove minor constituents from impaired water
- Determine effectiveness of corrosion resistant coatings to improve SS performance in high chloride content water

Process Engineering

- Identify process configurations which maximize constituent removal, optimize heat integration, and minimize water treatment costs

Methodologies

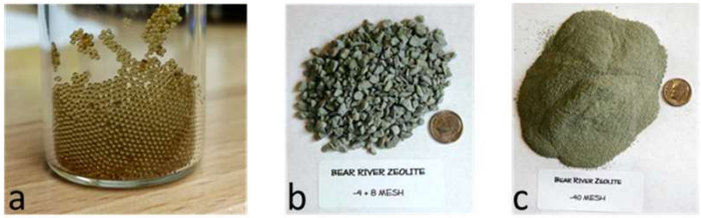


Figure 1. Solid sorbents evaluated in batch equilibrium studies. a) Dowex® G-26 resin (Dowex), b) granulated clinoptilolite (G-Clino), c) powdered clinoptilolite (P-Clino)

- Three sorbents tested in batch (Figure 1)
- DI and Simulated produced water

Ionic Strength (M)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Ba^{2+} (mg/L)	Mg^{2+} (mg/L)	Sr^{2+} (mg/L)	Ra-226 (nCi/L)
0.5	8,300	3,300	750	350	500	10

- Batch Testing (Equilibrium)
- 50 mL centrifuge tubes
- 0.01 g to 1 g of sorbents (P-Clino, G-Clino, and Dowex)
- 10 mL radioactive solution (10 nCi/L)
- Overnight agitation
- RadEye HEC testing on supernatant

- Column Testing (Dynamic)
- NORM sorption reactor (Figure 15)
- 1 g of sorbents (P-Clino, and Dowex)
- ~ 3 L radioactive solution (10 nCi/L)
- ¼" tubing bed
- 10 mL/min flow rate
- Sampling every 15 to 20 min
- RadyEye HEC testing

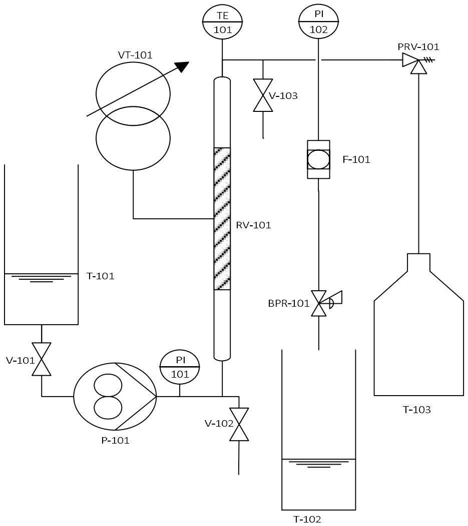


Figure 2. P&ID of the NORM Sorption column reactor

Clino Stability

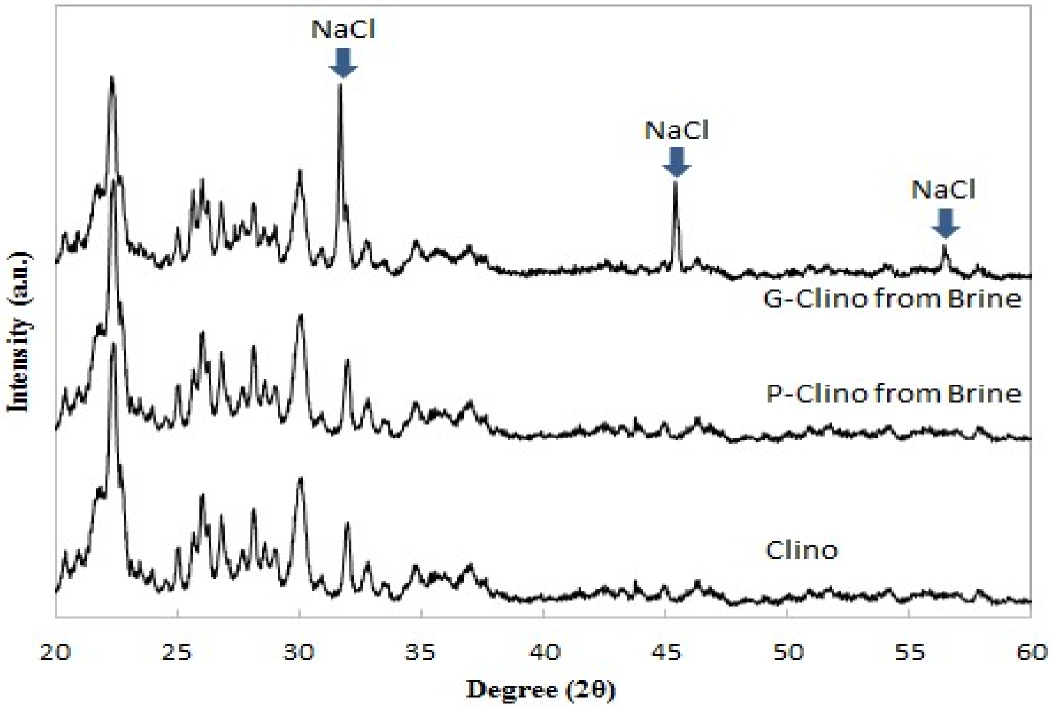


Figure 3. XRD pattern of clino before and after brine treatment containing 168,000 ppm Cl^- at 120 °C for 25 days

Clino Properties

- Bear River Zeolite Company (Preston, ID)
- Chemical formula: $(Ca_{0.67}K_{1.44})(Al_{2.50}Si_{15.50}O_{36})$
- Density: ~950 kg/m^3

Table 1. Evalauted clino properties

Material	Surface Area (m^2/g)	Pore Volume (cm^3/g)
Granulated (G-Clino)	25.49	0.008
Powdered (P-Clino)	70.21	0.026

Selectivity Results

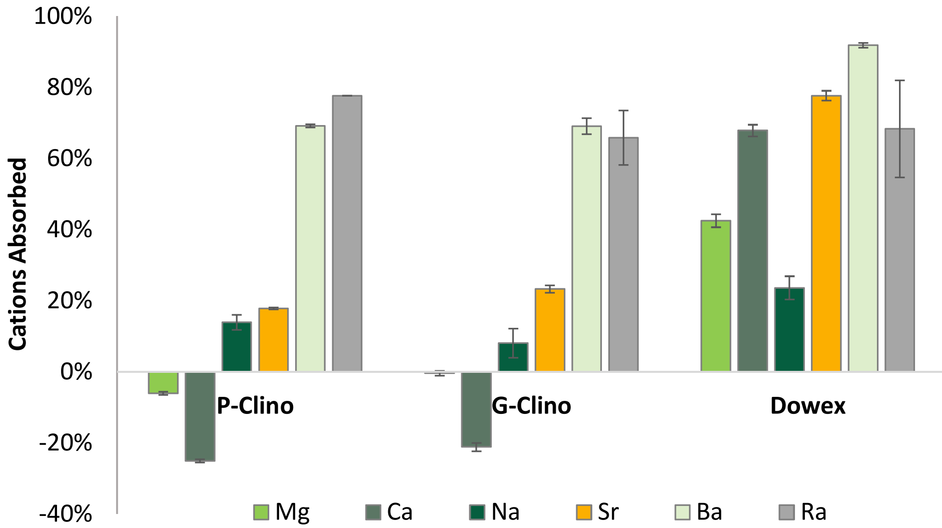
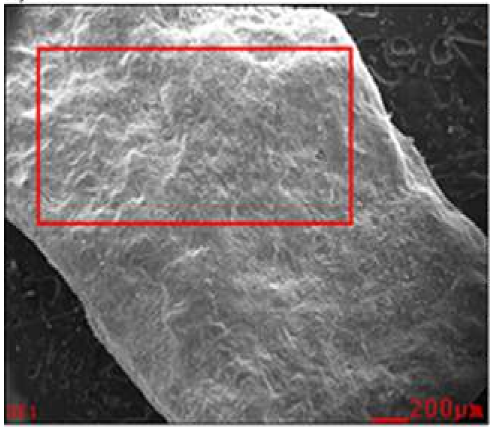


Figure 5. Percentage of cations absorbed on three different sorbents

a)



b)

Element	Pre-exposure		Post-exposure	
	Wt%	At%	Wt%	At%
C	13.59	23.22	9.66	17.71
O	29.61	38	26.09	35.9
Na	-	-	5.06	4.85
Al	6.26	4.76	6.12	5
Si	40.43	29.54	35.79	28.06
Cl	-	-	8.03	4.99
Pd	2.39	0.46	2.45	0.51
K	5.21	2.73	4.7	2.65
Ca	2.47	1.26	-	-
Ba	-	-	2.09	0.33

Figure 4. Clino pre- and post-exposure to simulated produced water a) representative SEM image and b) representative EDS analysis results ("-" indicated below limits of detection)

Table 2. Compiled batch capacity results for clino and Dowex® resin

Solution	Capacity (nCi/g)		
	G-Clino	P-Clino	Dowex® Resin
DI water	2.0 ± 0.15	19.3 ± 0.91	14.8 ± 0.73
Simulated produced water	0.08 ± 0.006	0.69 ± 0.06	0.48 ± 0.04

Joule-heating Desalination

H_2O/NaCl Phase Behavior

Characteristics

- Increased pseudocritical temperature
  - Vapor/solid phases
- Vapor-liquid equilibrium
  - Vapor: Low salt concentration
  - Liquid: High salt concentration

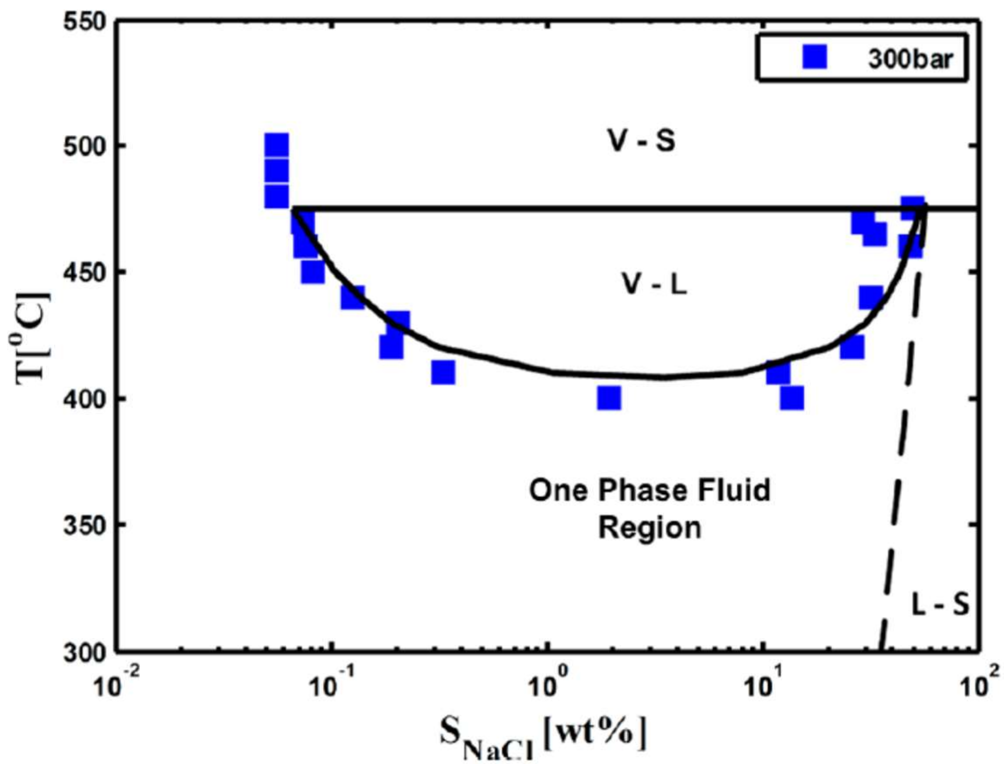


Figure 6. H_2O/NaCl phase diagram at 300 bar*

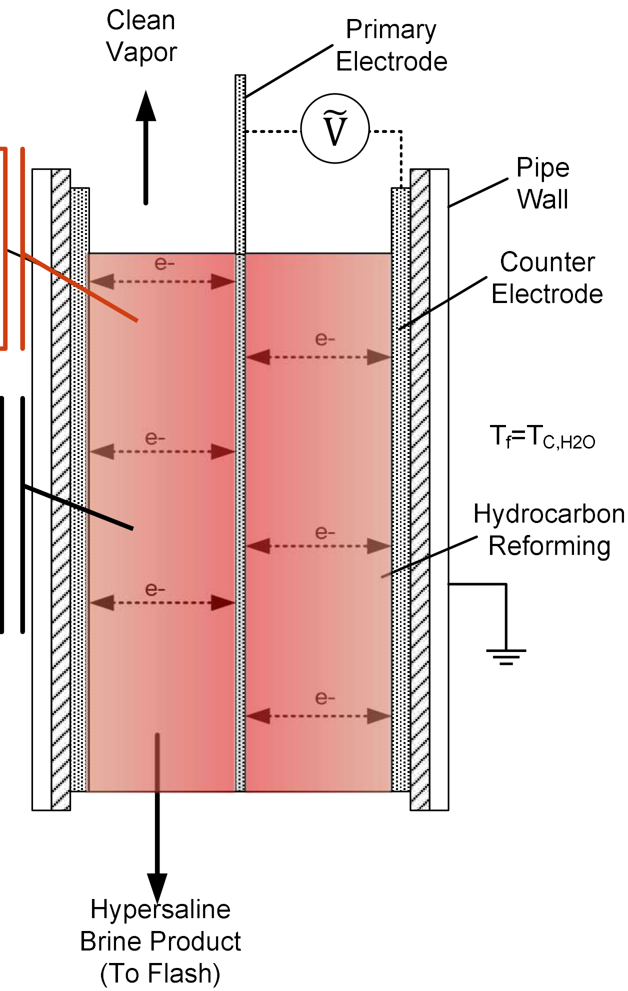
*Odu et al, 2015

Joule Heating Design

- Operating Fundamentals
  - Utilizes brine conductivity and AC electrical power to heat solution
  - Products include clean vapor and hypersaline brine streams
    - Product brine flashed to achieve further water recovery
- Advantages
  - Significantly lower reactor wall temperature
  - Small footprint with high throughput

- Conductivity of produced water allows for conduction of AC current
- Resistive heating causes homogeneous heating

- Internal heating significantly reduces wall temperature
- Allows for small footprint with high throughput



Experimental Setup

- Design Specs
  - Pressure: 32 MPa (4,641 psi)
  - Temperature: 450 °C
  - Material of Construction: Hastelloy C-276
  - Feed Rate: 0-300 mL/min
- Safety Measures
  - Pressure relief valves (3) and rupture discs (3)
  - Interlocked control system monitoring system temperature, pressure, and current

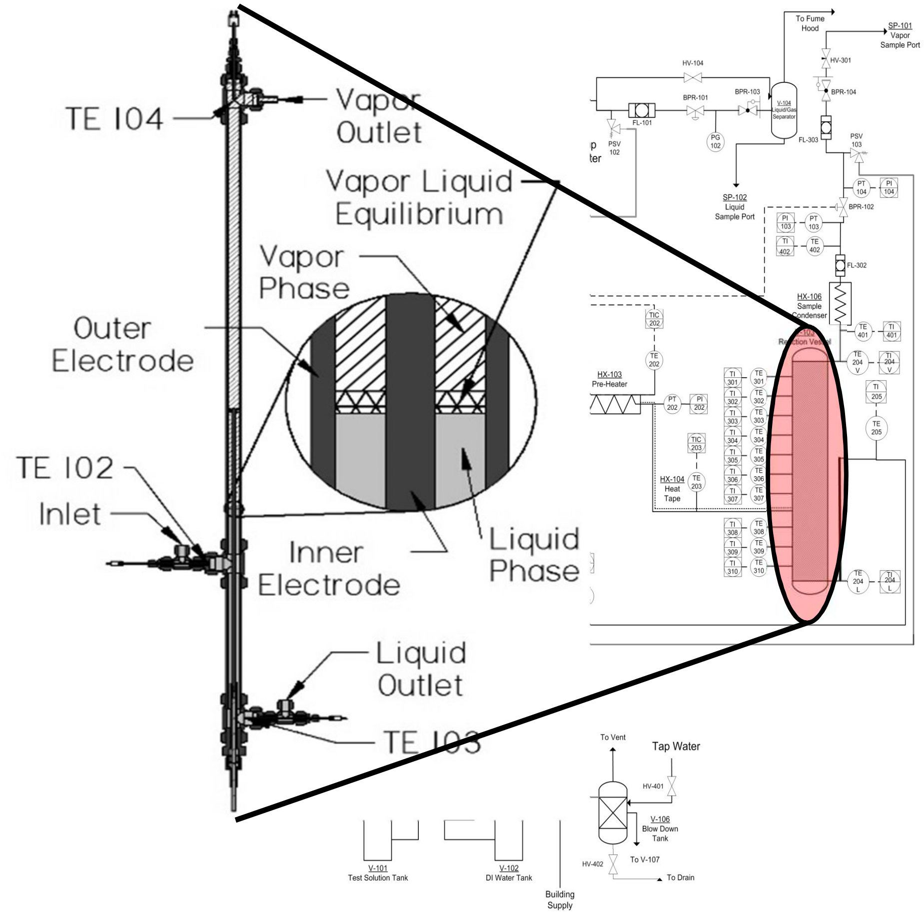


Figure 7. Reverse flow system P&ID

System Operation

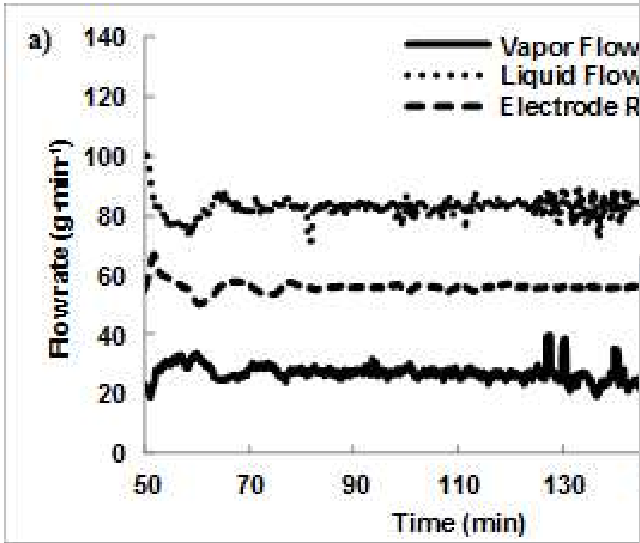


Figure 8. Reverse flow system P&ID

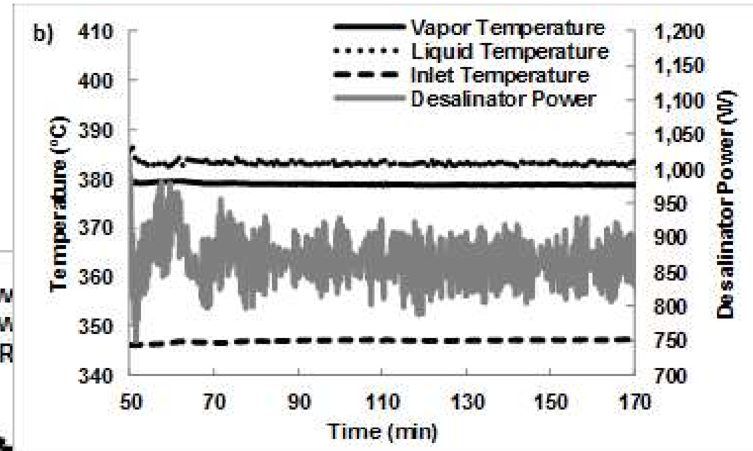


Figure 9. Reverse flow system P&ID

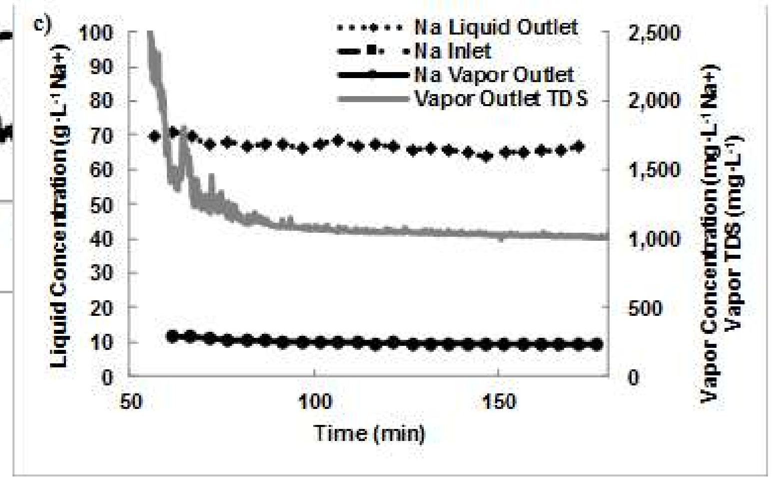


Figure 10. Reverse flow system P&ID

Desalination Results

- Calibration trials
  - Pressure: 250 bar
  - Solutions: 50 and 180 g·L^{-1} NaCl
- Multicomponent Trials
  - Pressure: 230-280 bar
  - Solutions: 50 and 180 g·L^{-1} multicomponent

Component	Concentration
K^+ (mg·L^{-1})	54-194
Ca^{2+} (mg·L^{-1})	4,261-15,222
Na^+ (mg·L^{-1})	14,956-53,429
Sr^{2+} (mg·L^{-1})	109-389
Ba^{2+} (mg·L^{-1})	27-97
Total (g·L^{-1})	50-180

Ogden and Trembly, Desalination 424, 149-158

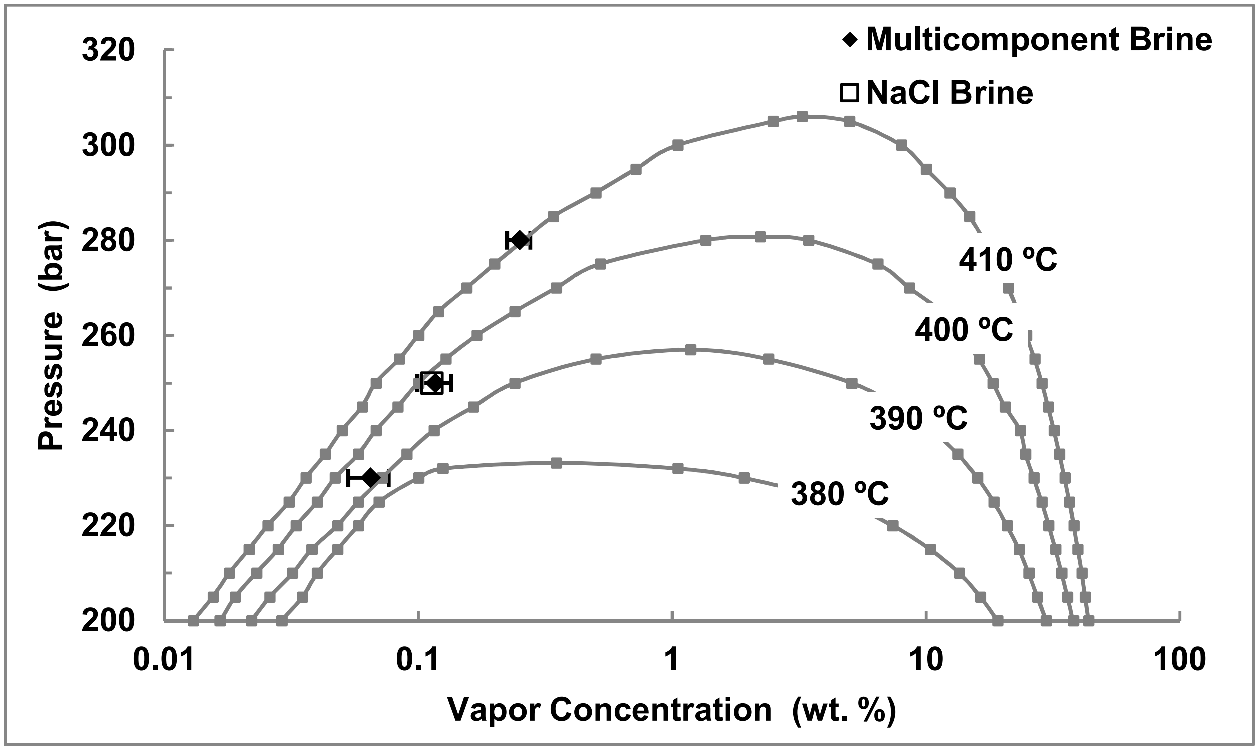


Figure 11. Comparison of vapor TDS concentrations from 50 and 180 g·L^{-1} NaCl brine and 50 and 180 g·L^{-1} multicomponent brine study results with Bischoff and Pitzer data*

*Bischoff and Pitzer, 1989.

Vapor Composition/T_{VLE}

Inlet Composition

Component	Concentration
K^+ (mg·L^{-1})	54-194
Ca^{2+} (mg·L^{-1})	4,261-15,222
Na^+ (mg·L^{-1})	14,956-53,429
Sr^{2+} (mg·L^{-1})	109-389
Ba^{2+} (mg·L^{-1})	27-97
Total (g·L^{-1})	50-180

Product Water Quality

- 230 bar: 655±41 mg·L^{-1}
- 250 bar: 1,240 ±75.2 mg · L^{-1}
- 280 bar: 2,608 ±263 mg · L^{-1}

Ogden and Trembly, Desalination 424, 149-158

T_{VLE} Determination / Product Water Composition

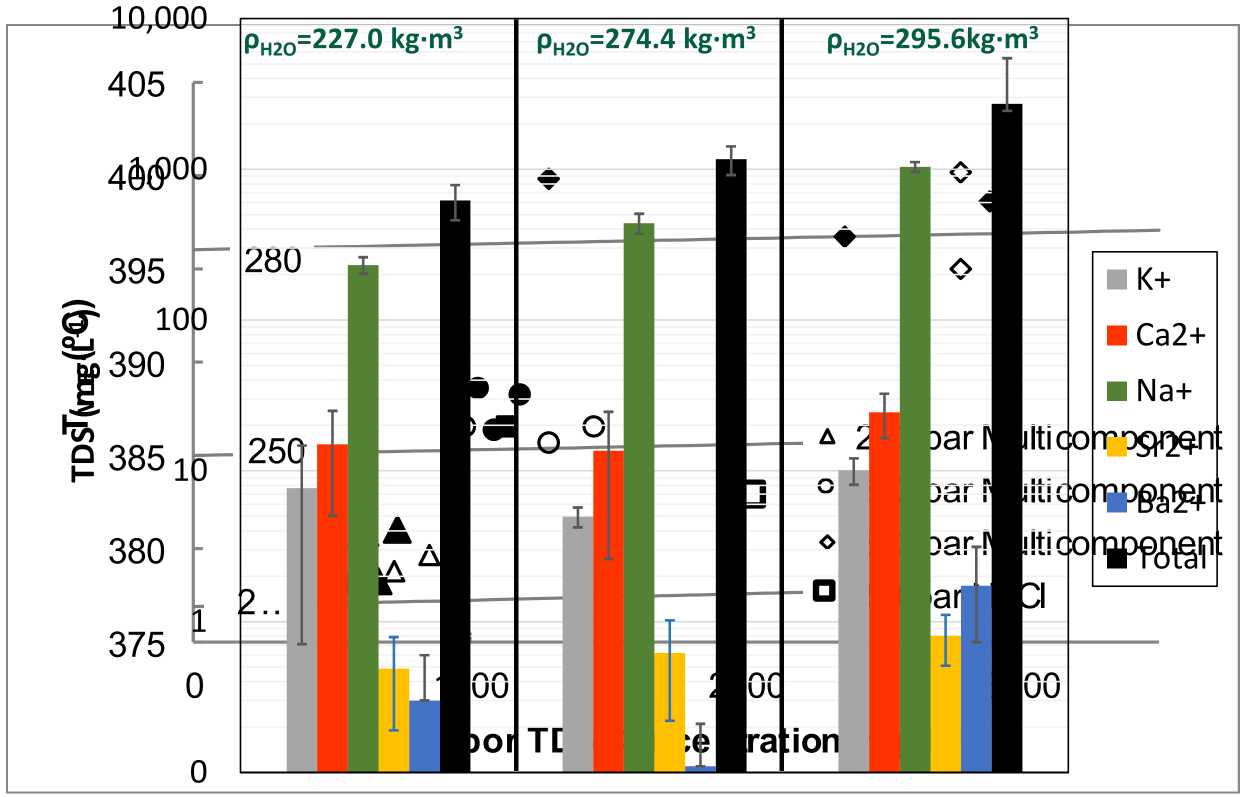


Figure 13. Experimental T_{VLE} results with vapor concentration for 230, 250 and 280 bar. Provided lines of pseudocritical temperature derived from Driesner model

Figure 12. Vapor product compositions

*Driesner and Heinrich, 2007.

OHIO UNIVERSITY 1804
Institute for Sustainable Energy and the Environment
RUSS COLLEGE OF ENGINEERING AND TECHNOLOGY

Voltage/Current Relationship

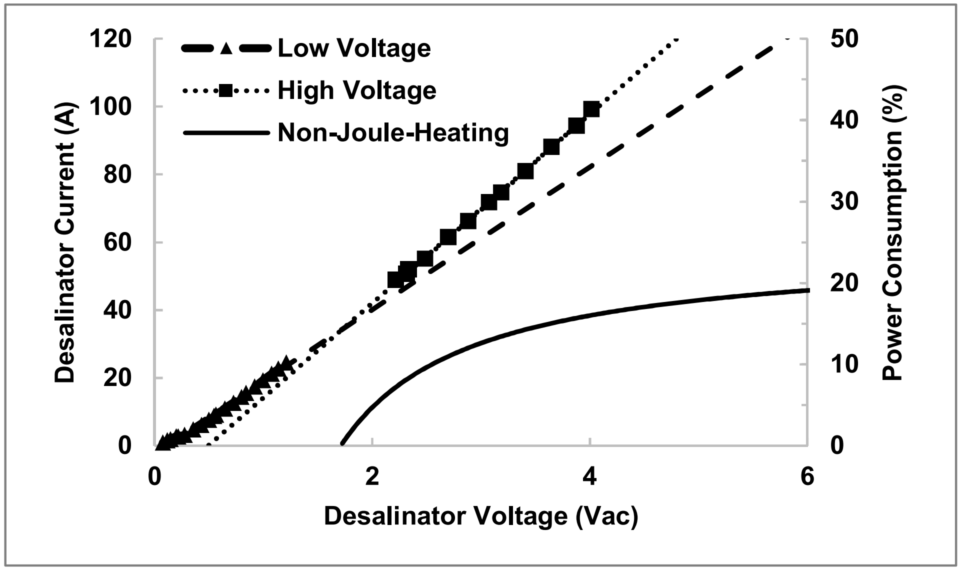


Figure 14. Desalinator voltage/current relationship and electrochemical reaction power consumption.

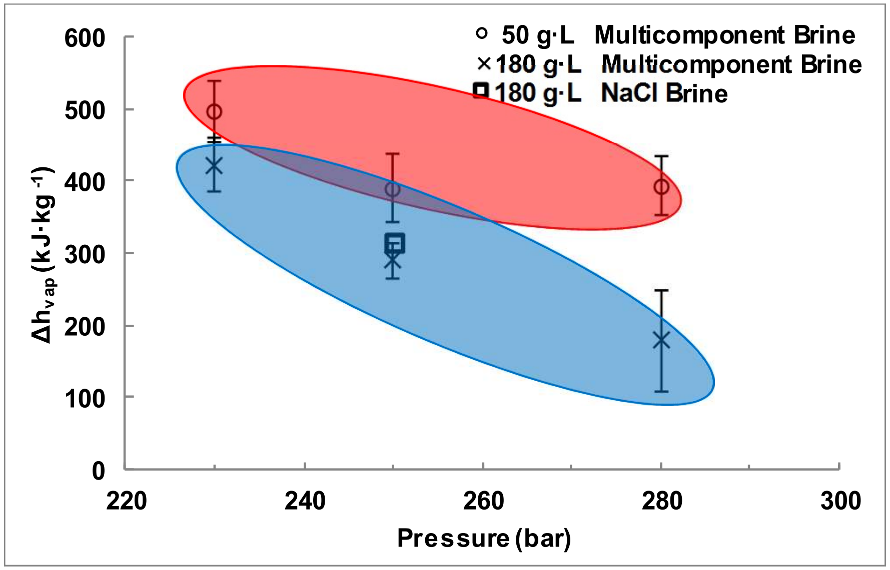


Figure 15. Enthalpy of vaporization for 180 g·L^{-1} NaCl brine and 50 and 180 g·L^{-1} multicomponent brines at evaluated pressures.

Ogden and Trembly, Desalination 424, 149-158

Water Recovery

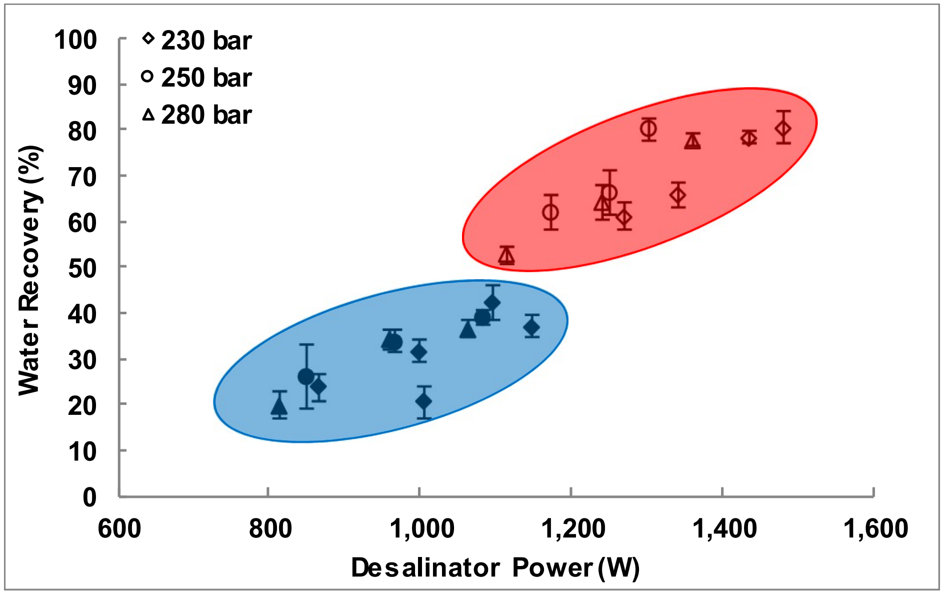


Figure 16. Water recovery from experimental trials based upon desalinator power. Corrected for reactor heat loss. Filled data: 180 g·L^{-1}; Hollow data: 50 g·L^{-1}.

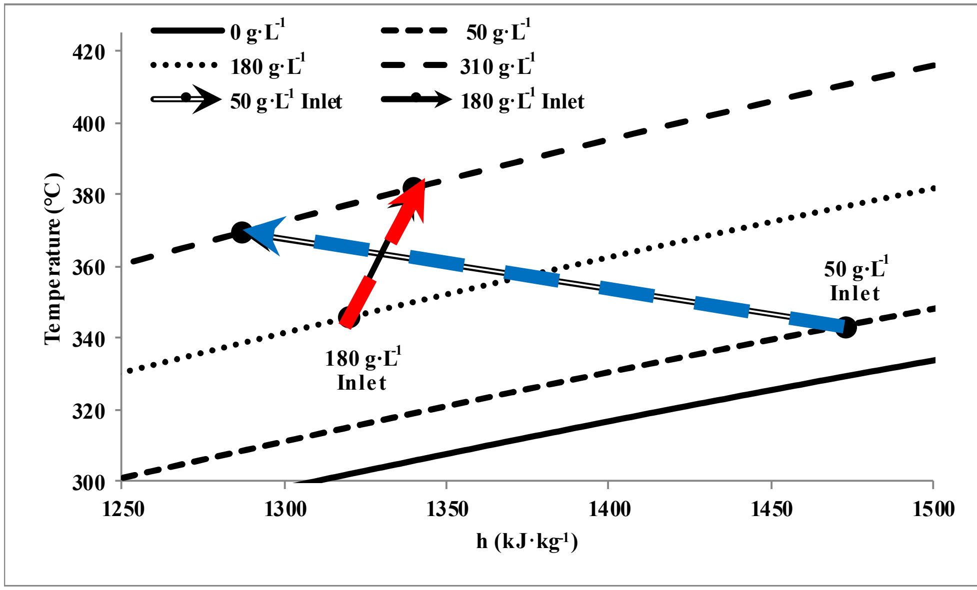


Figure 17. T-h diagram for H_2O/NaCl system.

Ogden and Trembly, Desalination 424, 149-158

Utica Shale Brine Results

Inlet Composition

Component	Concentration
K^+ ($mg \cdot L^{-1}$)	430.7±20.3
Ca^{2+} ($mg \cdot L^{-1}$)	25,767±910
Na^+ ($mg \cdot L^{-1}$)	35,406±853
Sr^{2+} ($mg \cdot L^{-1}$)	2,093±61
Total ($g \cdot L^{-1}$)	178,961±4,110

Product Water Quality

- 230 bar: 655±41 $mg \cdot L^{-1}$
- 250 bar: 1,240 ±75 $mg \cdot L^{-1}$
- Flash: 618 ±34 $mg \cdot L^{-1}$

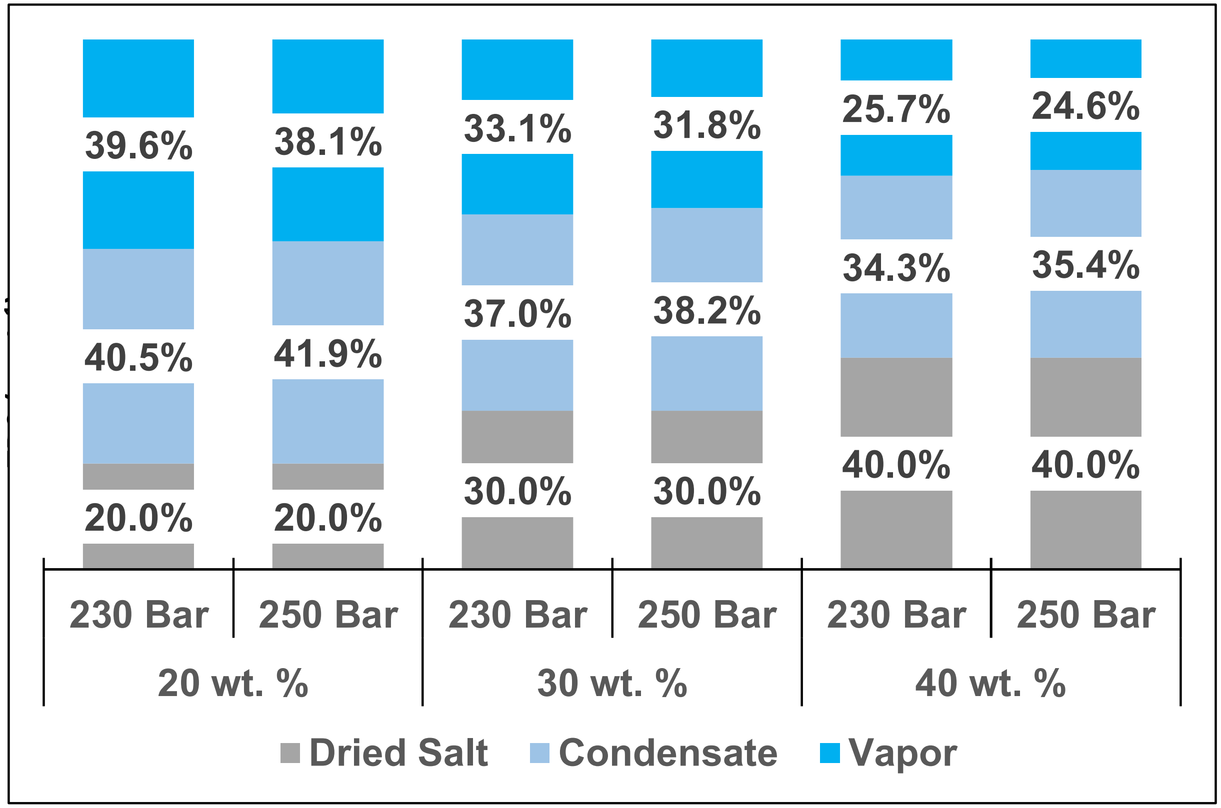


Figure 18. Flash recovery results

Figure 19. Vapor product compositions

OHIO UNIVERSITY 1804
Institute for Sustainable Energy and the Environment
RUSS COLLEGE OF ENGINEERING AND TECHNOLOGY

Process Modeling & Techno-economics

Water Recovery

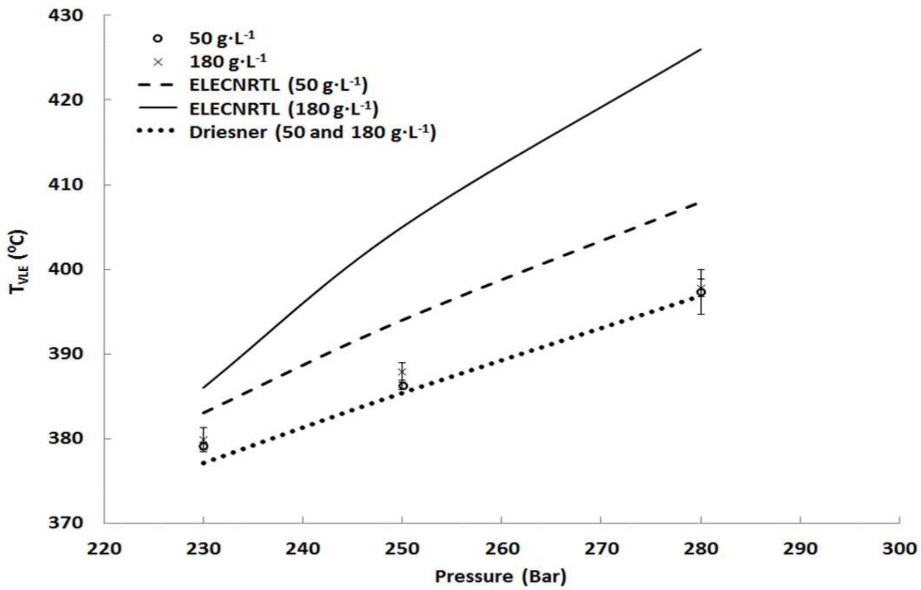


Figure 20. T_{VLE} comparison of 50 and 180 $g{\cdot}L^{-1}$ experimental values with Aspen Plus® ELECNRTL model results.

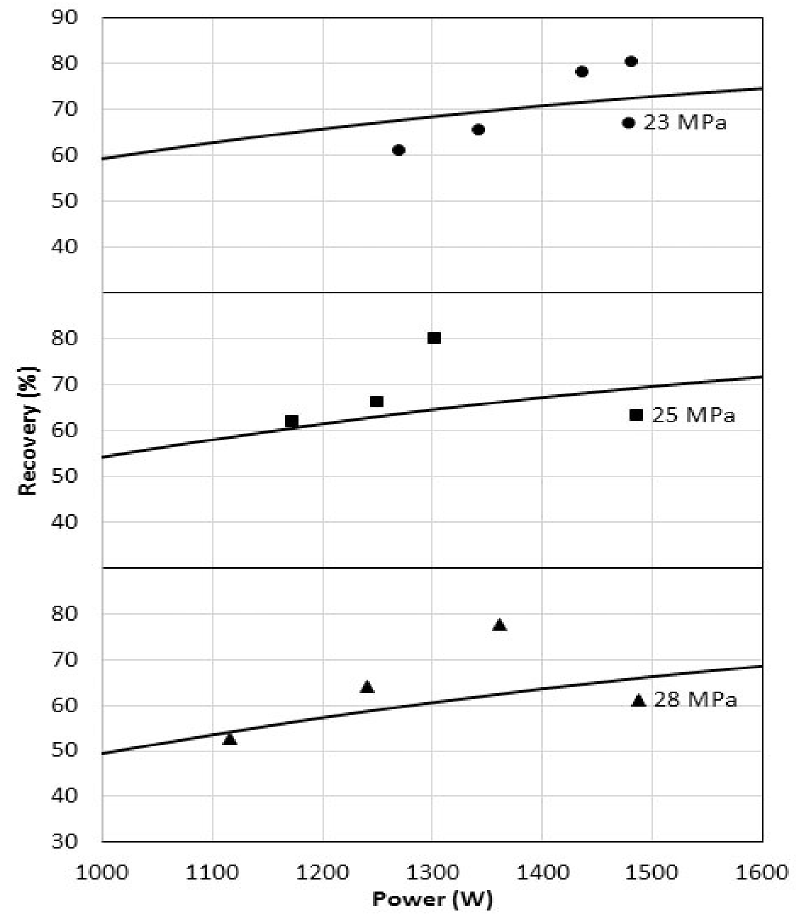


Figure 21. Water recovery based with desalinator duty for 50 $g{\cdot}L^{-1}$.

Ogden and Trembly, Desalination 424, 149-158

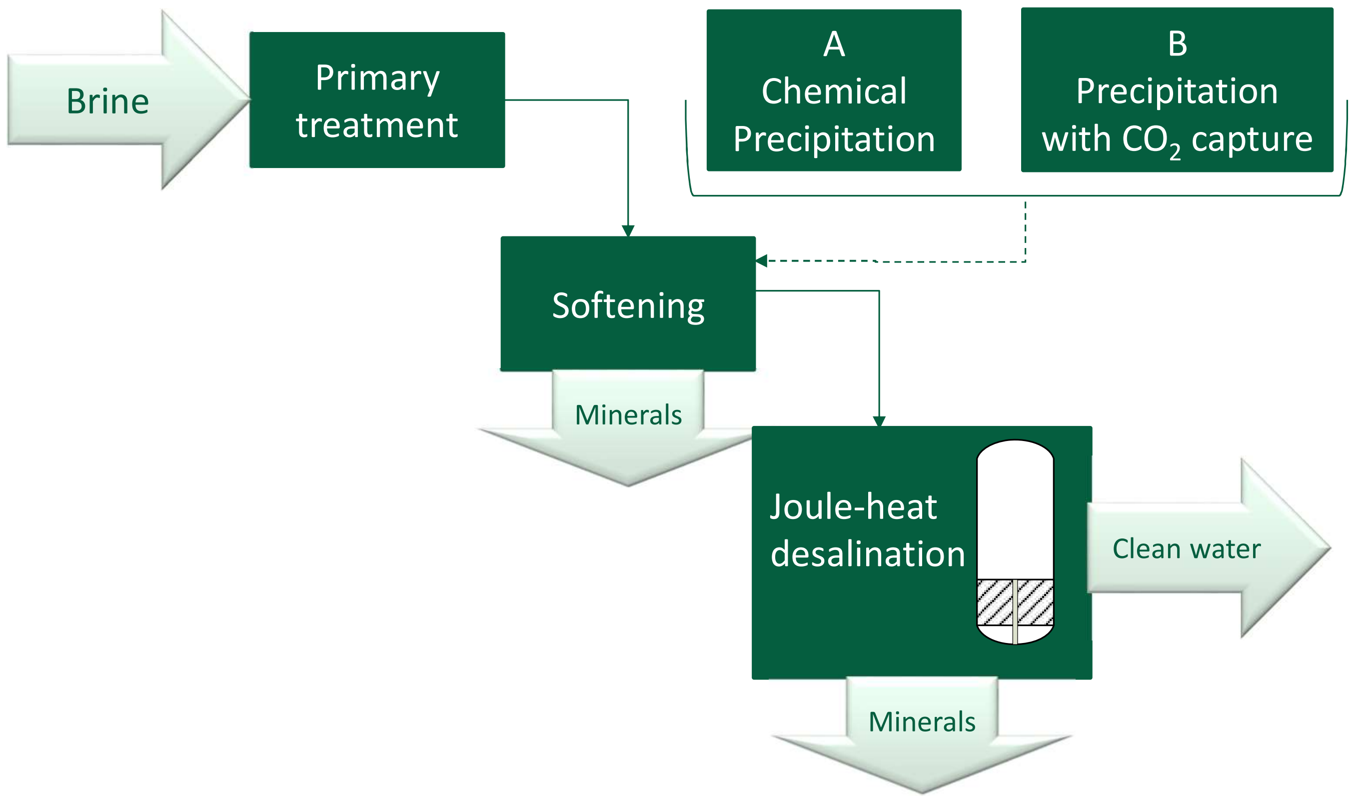
Model Overview

Aspen Plus® desalination simulation	
Software	Aspen Plus® V9
Thermodynamic property method	ELECNRTL
Water chemistry	Produced water
Nameplate plant capacity	500 GPM of brine (> 15 wt. %)
Feed conditions	25 °C and 1 bar
Economic Assessment	
Capital Expense	• APEA (Aspen Process Economic Analyzer) • AED&R (Aspen Exchanger Design & Rating) • Cost charts • Vendor quotes
Year basis	2015
Capacity factor	0.85
Interest rate (capital charge factor)	10 %
Cost Units	U.S. dollars

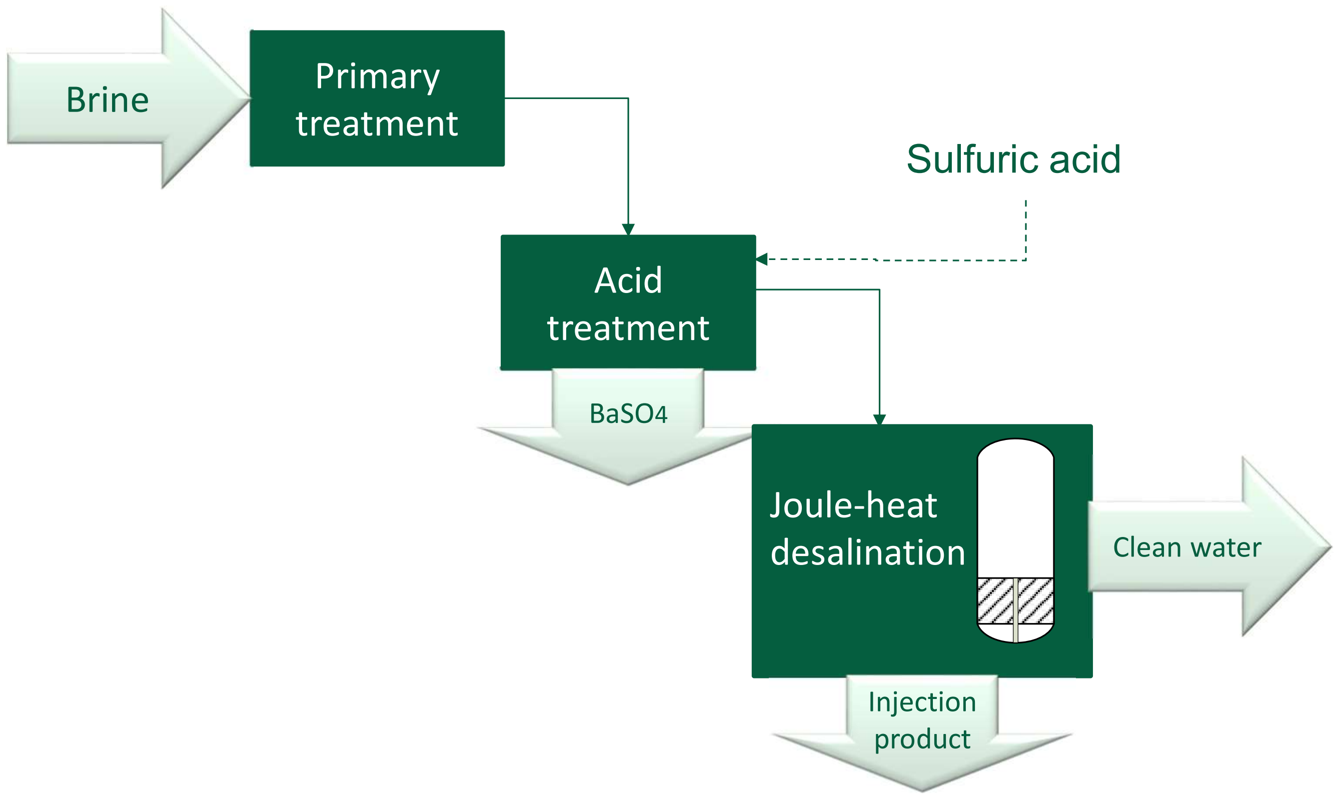
Table 1. Model Brine Composition

Constituent	Concentration (mg/L)	Molarity (mol/L)
Na^{+}	37,939.0	1.650
Ca^{2+}	12,575.0	0.314
Ba^{2+}	7,944.6	0.058
Sr^{2+}	4,153.8	0.047
Mg^{2+}	1,106.4	0.046
Cl^{-}	90,869.3	2.563
SO_4^{2-}	779.0	0.008
TDS	155,336.1	

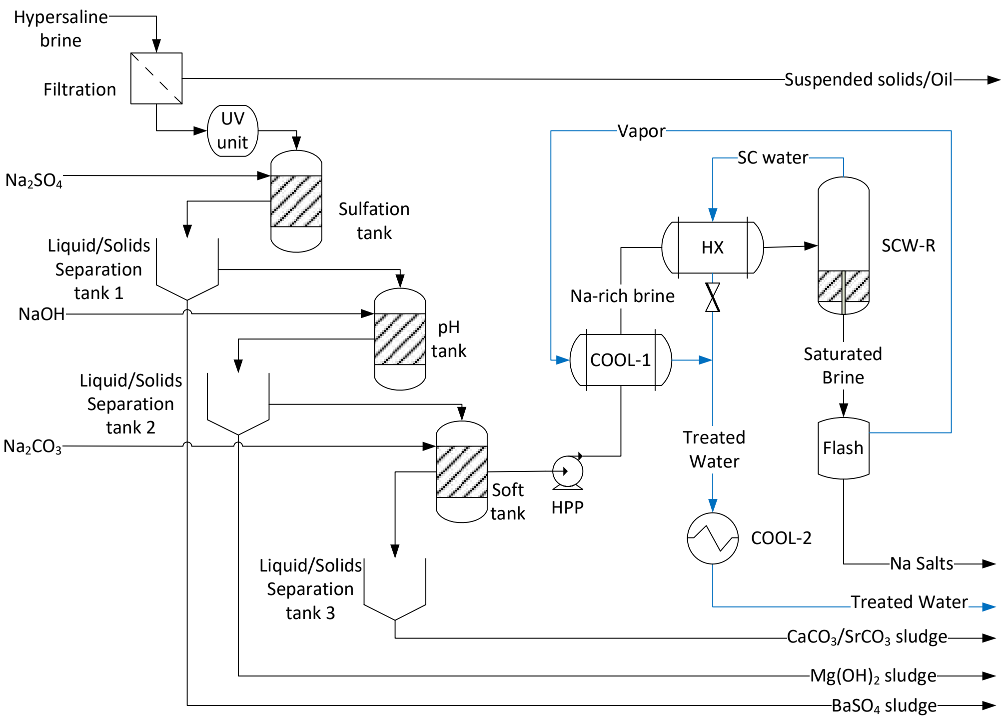
Model Scenarios (A & B)



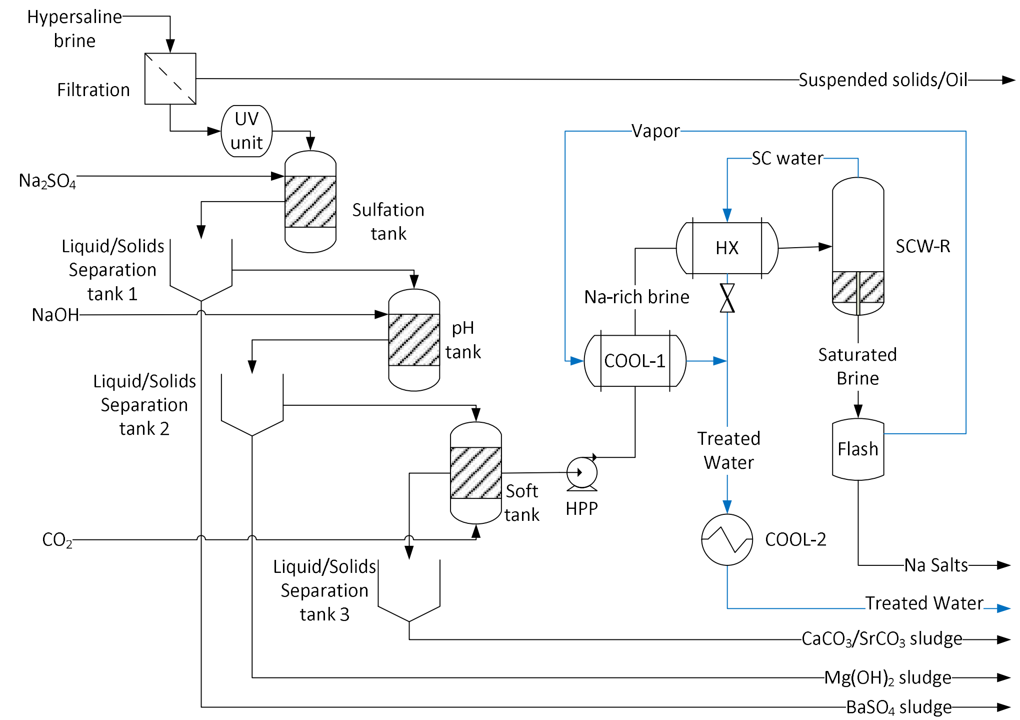
Model Scenarios (C)



Process Flow Diagrams

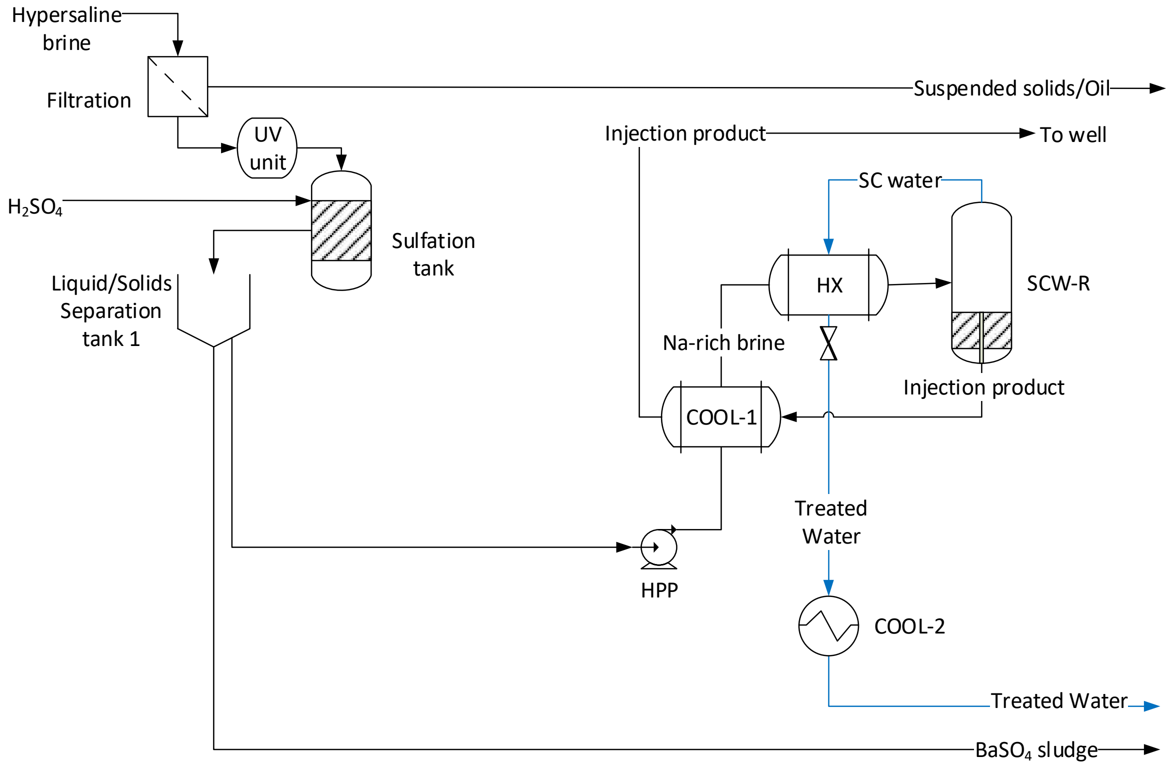


Scenario A



Scenario B

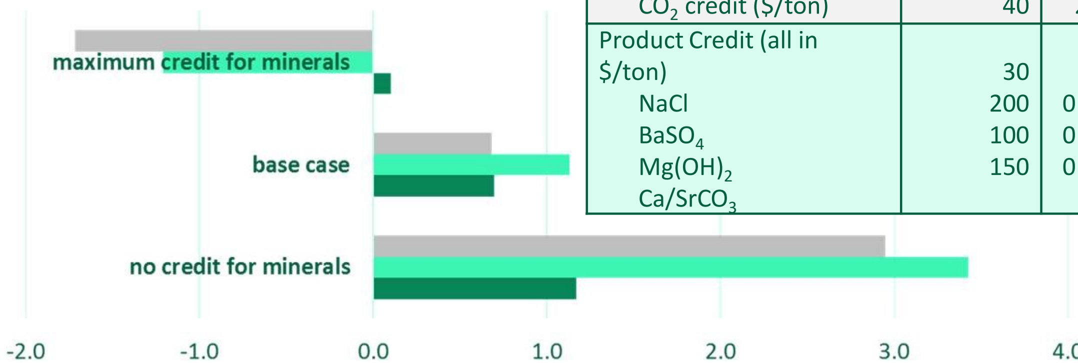
Process Flow Diagrams



Scenario C

Process Costing

	Base case	Range
CO_2 credit ($/ton)	40	20-60
Product Credit (all in $/ton)	30	0-60
NaCl	200	0 - 450
$BaSO_4$	100	0 - 250
$Mg(OH)_2$	150	0 - 300
$Ca/SrCO_3$		



	no credit for minerals	base case	maximum credit for minerals
A	2.9	0.7	-1.7
B	3.4	1.1	-1.2
C	1.2	0.7	0.1

Cost of Water Treatment ($/bbl)

A B C

Table 3. Scenario Cost Comparison

	Scenario A	Scenario B	Scenario C
Brine flow (GPM)	500	500	500
Capital cost ($M)*	7.8	8.6	7.5
Mineral product (tons/day)	597	594	40
Treatment cost ($/bbl)	0.7	1.2	0.7

* uncertainty +40%/-25 %

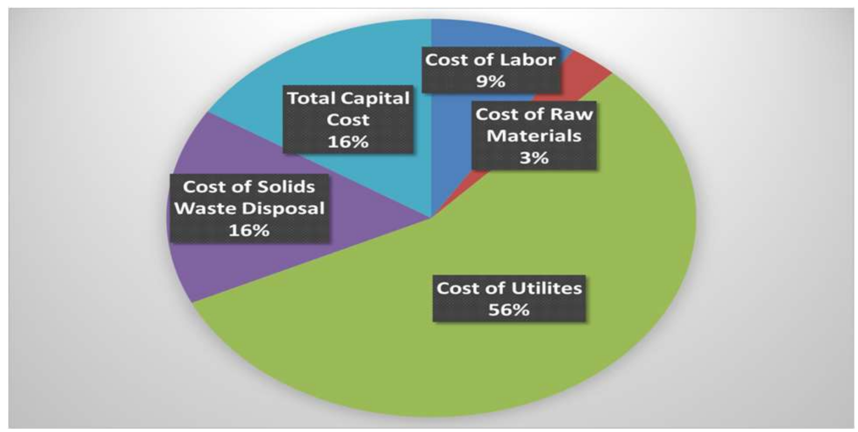


Figure 22. Produced Water Treatment Cost Categories

López and Trembly, Desalination 415, 49-57 and Dong et al., Energy, 133, 777-783

Summary

- Joule heating system
  - Wide range of brine solutions containing 50 to 180 $g \cdot L^{-1}$ tested
  - Ability to produce clean water product containing 600-2,800 $mg \cdot L^{-1}$ TDS demonstrated
  - Zero liquid discharge capability
  - Fundamental brine properties assessed
  - Over 2,200 hours of operational experience gained
- Process modeling & techno-economics
  - Existing ELECNRTL model insufficient in predicting brine properties at near critical conditions
  - Three process scenarios modeled ranging from zero liquid discharge to concentration with injection
  - Promising estimated brine treatment costs ranging from 0.7-1.2 $/bbl

Acknowledgements

- Project manager Barbara Carney for her input/feedback and National Energy Technology Laboratory (DE-FE-0026315) for their financial support
- Dr. Xingbo Liu (WVU), Tom Hart and Matt Usher (AEP), Mr. David Ogden and Dr. Dora E. Lopez for their experimental and process simulation efforts and Dr. Wen Fan, Mr. Eli Fox, Ms. Rachel Schack and Mr. Dominick Steinberg for their help in water analysis and system fabrication/operation.

Create for Good.

Questions: Jason Trembly

Website: https://www.ohio.edu/engineering/isee/

E-mail: trembly@ohio.edu

Phone: (740) 566-7046

OHIO UNIVERSITY 1804

Energy Consumption of Electro-Coagulation for Zn-ion Removal

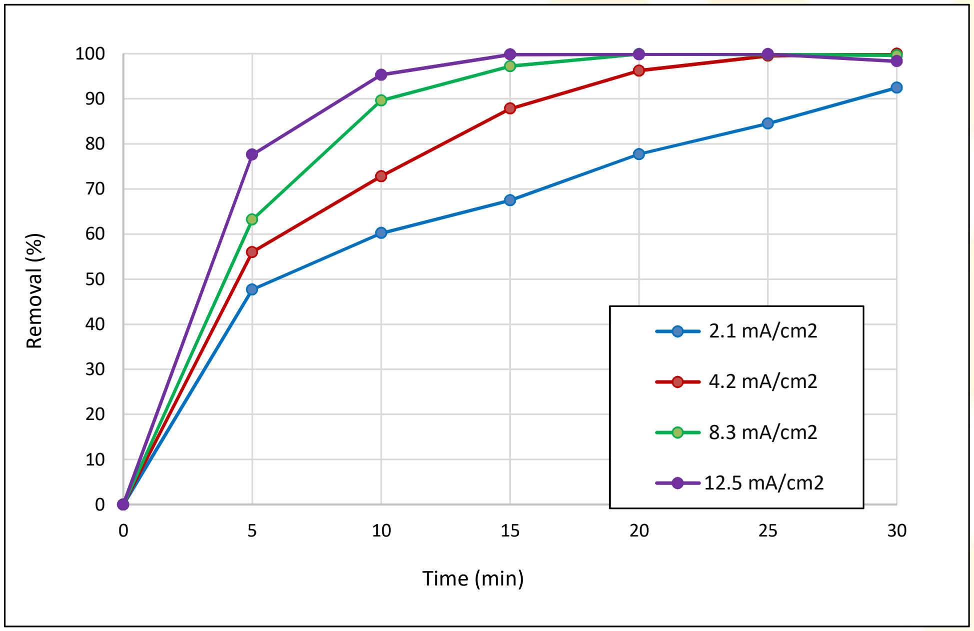


Fig. 1 Evolution of zinc removal efficiency versus EC time at different current densities. $C_0 = 50$ mg/L.

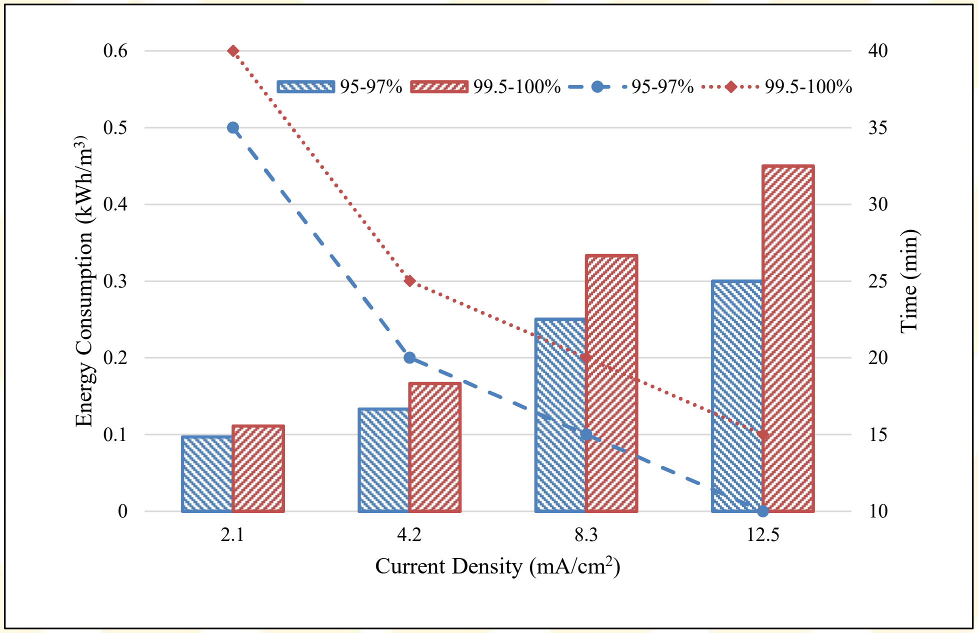


Fig. 2 Variation of energy consumption (bar) and required EC time (line) as a function of current densities for removal efficiency of 96% and 99%.

WestVirginiaUniversity
BENJAMIN M. STATLER COLLEGE OF ENGINEERING AND MINERAL RESOURCES

Removal of Metal Ions from Multi-Ion Solution

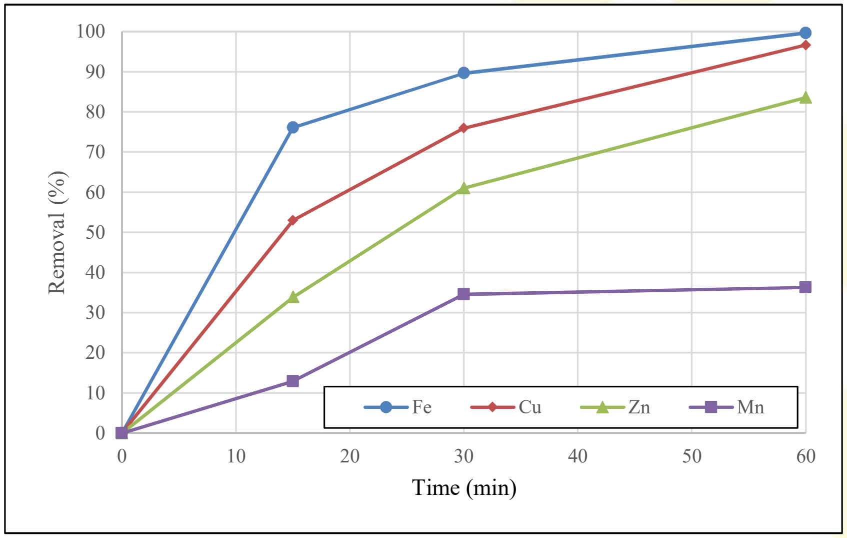


Fig. 3 Evolution of heavy metal ions removal efficiency versus EC time. Initial concentration of Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} = 25 mg/L in mixed solution.

- Competitive removal of Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} in the mixed solution.
- Removal rate of Zn^{2+} is almost two times slower than of Fe^{3+}, and half times slower than Cu^{2+} during a short EC time, but it tends to similar removal efficiency as increasing of duration time.

Typically, previous work focused on the zinc removal by EC.

What makes the different removal behavior of Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} ?

Removal of Metal Ions from Multi-Ion Solution

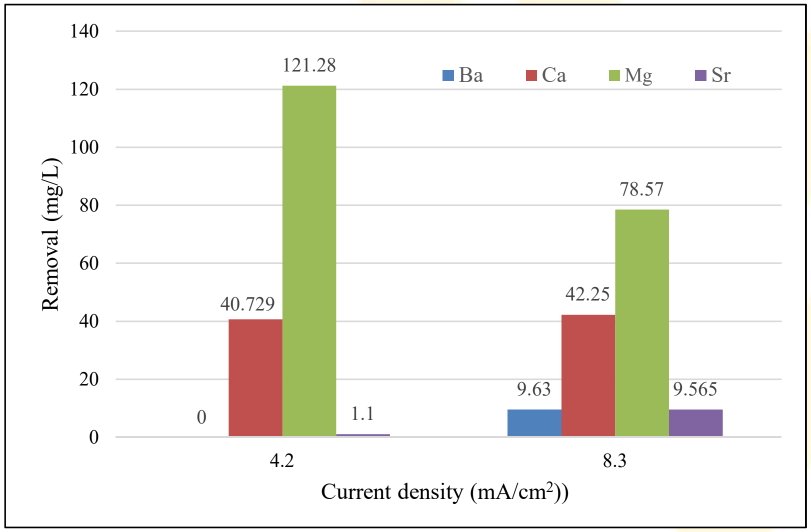


Fig. 4 Evolution of metal ions removal versus EC time at different current densities. mixed solution: t = 30 min
C_{Ba} = 249.15 mg/L, C_{Ca} = 729.73 mg/L
C_{Mg} = 316.07 mg/L, C_{Sr} = 1760.22 mg/L

Remove rate: Mg > Ca > Sr > Ba

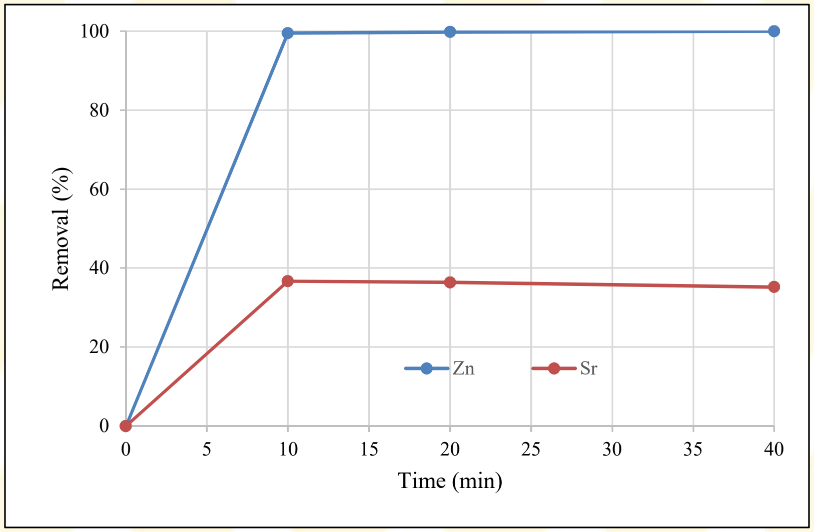
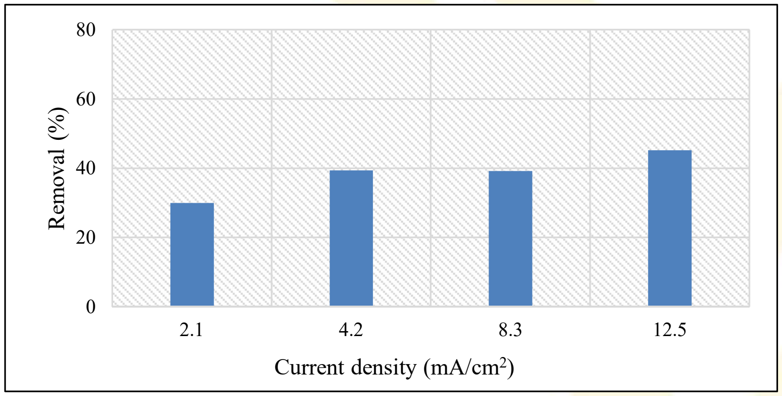


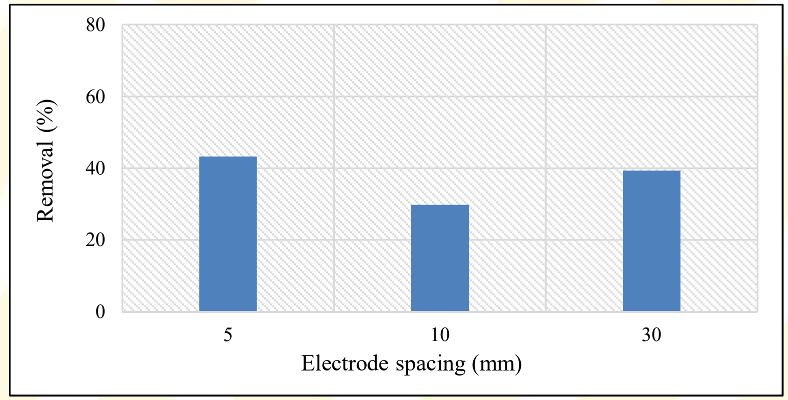
Fig. 5 Evolution of heavy metal ions removal efficiency versus EC time. Initial concentration of Zn^{2+} and Sr^{2+} = 10 mg/L in mixed solution, current density is 4.2 mA/cm^2.

Remove rate: Zn >> Sr

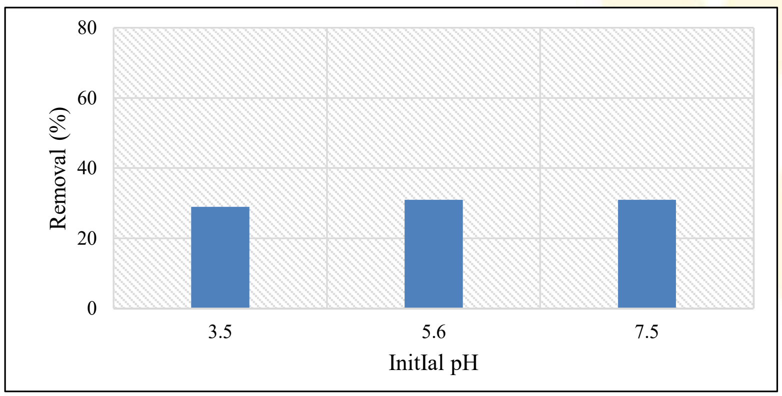
Removal of Strontium Ions



C_0 = 10 mg/L, t = 60 min, d = 10 mm, pH = 5.6



C_0 = 10 mg/L, d = 10 mm, CD = 2.1 mA/cm^2, pH = 5.6



C_0 = 10 mg/L, t = 30 min, d = 10 mm, CD = 2.1 mA/cm^2

The slower removal of Sr^{2+} compared to Fe^{3+}, Cu^{2+} and Zn^{2+} is attributed to a difference in the removal mechanisms

West Virginia University.
BENJAMIN M. STATLER COLLEGE OF
ENGINEERING AND MINERAL RESOURCES

Possible Removal Mechanisms: co-precipitation, precipitation as hydroxide forms

Ionic solid	K_{sp} (at 25°C)
$Fe(OH)_3$	4.0×10^{-38}
$Al(OH)_3$	2.0×10^{-32}
$Cu(OH)_2$	1.6×10^{-19}
$Zn(OH)_2$	4.5×10^{-17}
$Mn(OH)_2$	2.0×10^{-13}
$Mg(OH)_2$	8.9×10^{-12}
$Ca(OH)_2$	1.3×10^{-6}
$Sr(OH)_2$	3.2×10^{-4}
$Ba(OH)_2$	5.0×10^{-3}

- The differences of removal behavior between Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} could be attributed to the co-presence of different removal mechanisms.

- Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} compete for hydroxide ions produced at the cathode. → Precipitation as hydroxide forms

- Fe^{3+}, Cu^{2+}, Zn^{2+} and Mn^{2+} compete for sorption sites at the aluminum hydroxide surface → Coprecipitation: adsorbed by $Al(OH)_3$ coagulant

- Co-precipitation of Cu^{2+}, Zn^{2+} and Mn^{2+} at iron hydroxide surface, or $Cu(OH)_2$ and $Zn(OH)_2$ surface → Attributed to increase of removal efficiency