An Integrated Supercritical System for Efficient Produced Water Treatment and Power Generation

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National Energy Technology Laboratory, U.S. Department of Energy

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Project Goals and Objectives

- Objective:
  - Evaluate feasibility of an integrated, supercritical (SC) cogeneration system for cost-effective treatment of produced water from CO_2 sequestration, oilfields, and CBM recovery

- Technical targets:
  - Evaluate techno-economic feasibility
  - Design, assemble, and test a system for SC salt precipitation
  - Design, assemble, and test a system for SC steam purification
  - Prepare, characterize, and test carbon membranes
  - Perform sampling and characterization of different produced water samples
  - Treat different produced waters to high quality water using fabricated supercritical salt precipitation and membrane distillation system

Milestone Title/Description	**Planned Completion Date**
Process simulation and techno-economic analysis completed	6/30/2015
Design, assembly, and baseline testing of the SC salt precipitation system completed	12/31/2015
Membrane preparation and characterization completed	2/29/2016
Produced water sampling, analysis, and pre-treatment completed	5/31/2016
Design, assembly, and baseline testing of the SC membrane distillation system completed	6/30/2016
Produced water SC salt precipitation and membrane distillation treatment completed	12/31/2016

Outline

- Background
- Description of the proposed technology
- Project results and update
  - Process simulation and techno-economic evaluation
  - Laboratory-scale supercritical desalination system
  - Development and characterization of carbon membranes
  - Produced water sampling and characterization
  - Produced water pretreatment
  - Desalination of produced water sample with supercritical desalination system
- Summary, conclusions, and future work

Produced Water Treatment

- Produced water from fossil fuel production (i.e., oil, gas, and coal) or CO_2 sequestration as a valuable nontraditional water resource
- Main challenge is desalination of concentrated brines (e.g., TDS > 100,000 mg/L) by energy efficient processes

Pre-treatment to remove:
- Residual oil
- Dissolved organics
- Suspended solids
- Scale-forming species

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Desalination or the main treatment:
- Reverse osmosis RO (TDS < 50,000 ppm)
- Thermal distillation systems
- Crystallization for zero-liquid discharge (ZLD)
- Others




Sources: Veil et al., 2004; Clark and Veil, 2009; Knutson, Dastgheib et al., 2012; NETL, 2015

High-TDS Water Desalination Challenge and Power/Water Cogeneration

- None of the existing established seawater desalination technologies can be used for producing freshwater from high salinity water (e.g., TDS ~ 100,000-300,000 ppm)
- Expensive and energy-intensive brine evaporator/crystallizer might be the only available commercial technology
- Near ZLD desalination of Mt. Simon brine (~220,000 ppm TDS) by multi-effect evaporators*
  - Thermal energy = 246 kWh/m^3 recovered water
  - Electrical energy = 2 kWh/m^3 recovered water
- A new approach for treatment of high salinity produced water is needed, preferably with electricity cogeneration

*Energy demand of water desalination by RO or existing cogeneration technologies for seawater desalination***

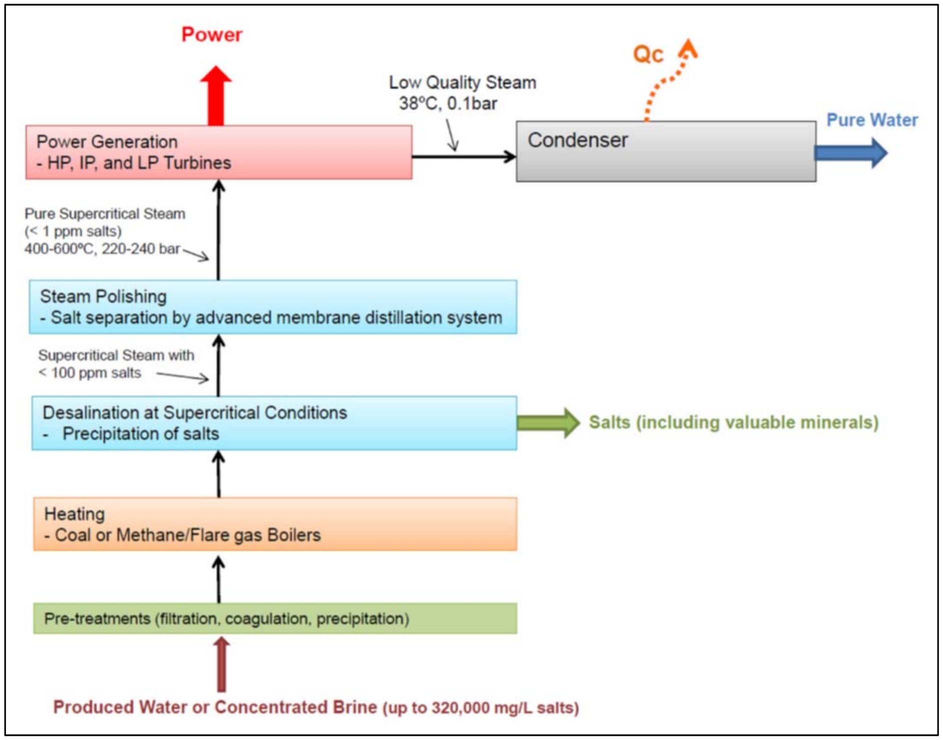
Seawater desalination by power-water cogeneration or stand alone RO	Electrical energy (kWh/m^3)	Thermal energy (kWh/m^3)
Case 1: Desalination by MED in a cogeneration plant	~2	~28
Case 2: Desalination by MSF in a cogeneration plant	~4.2	~45
Case 3: Desalination by stand alone RO	~up to 8	0

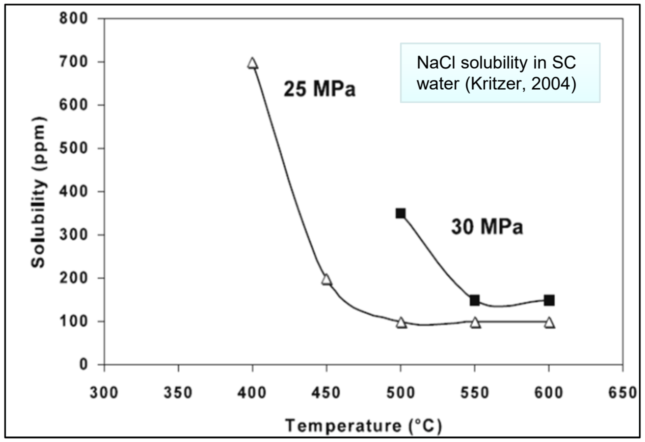
Kaplan et al., Desalination 404 (2017) 87-101.

***Mezher et al., Desalination 266 (2011) 263-273.*

Proposed Water-Power Cogeneration System

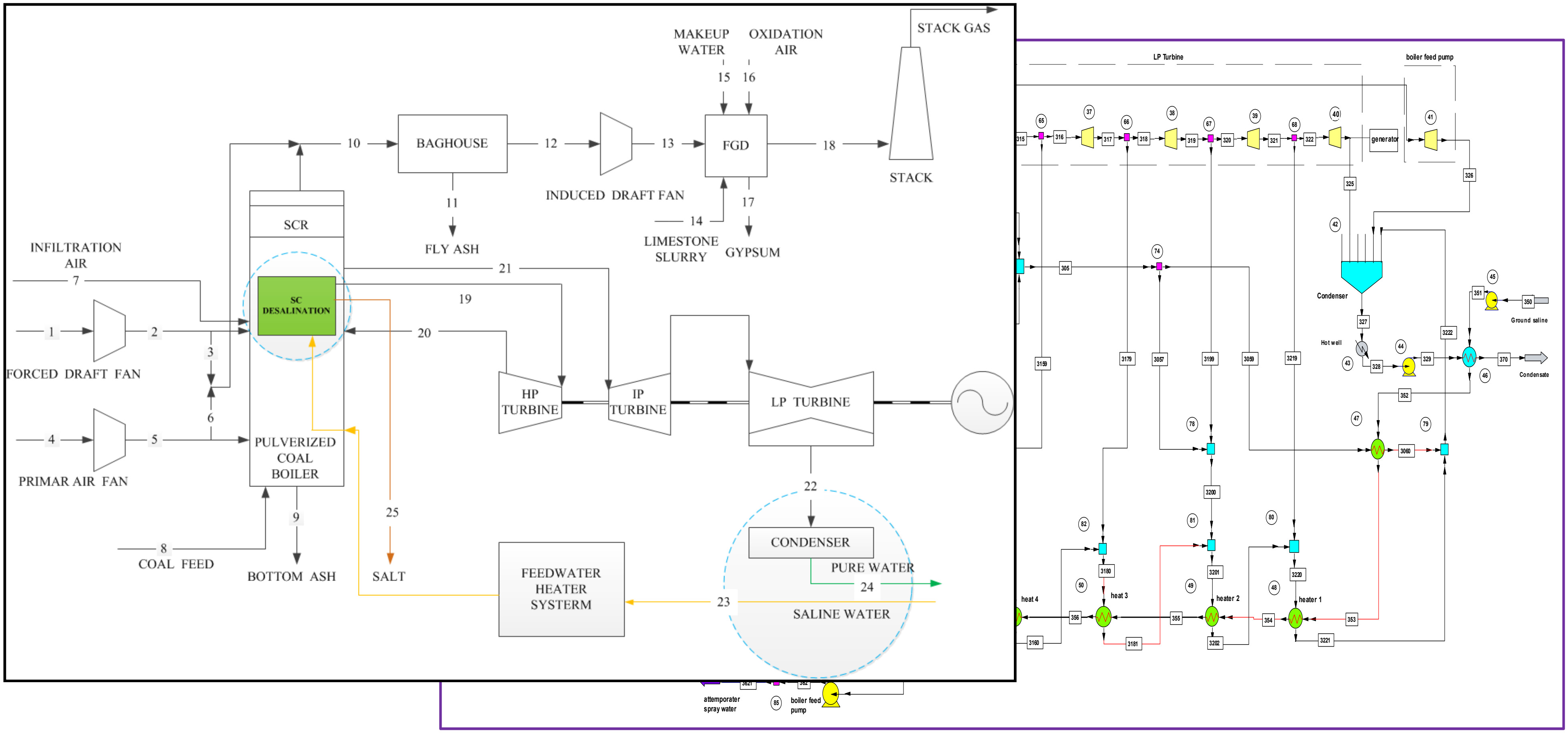
- Integration of water treatment and power generation
- Pretreatment → Salt Precipitation at Supercritical Conditions → Steam Polishing → Power Generation
- Utilization of supercritical steam for power generation might be possible with the proposed approach
- Steam polishing is the critical stage. TDS requirement for steam purity ranges from < 0.05 ppm to 1 ppm depending on drum pressure and boiler type [Ref. Table 16.1 of GE water handbook reprinted from American Boiler Manufacturers Association,1982]





Process Simulation and Thermodynamic Analysis

- Used Chemcad simulation to perform simulations and mass/energy balances
- Performed simulations for a 550 MW integrated SC system for coal-fired (Illinois # 6 coal) and NG-fired boilers
- Assumed saline water input at 3 levels: 30,000 ppm, 100,000 ppm, and 200,000 ppm TDS



Process Simulation and Thermodynamic Analysis

- Plant efficiency loss for coal and NG cases is estimated in the range of <1% to ~4 % -- NG and lower salinity cases have higher efficiencies
- Efficiency loss is for energy loss for additional water pumping, heat loss with the salt product, pressure drop across membranes, and required energy for salt/water separation

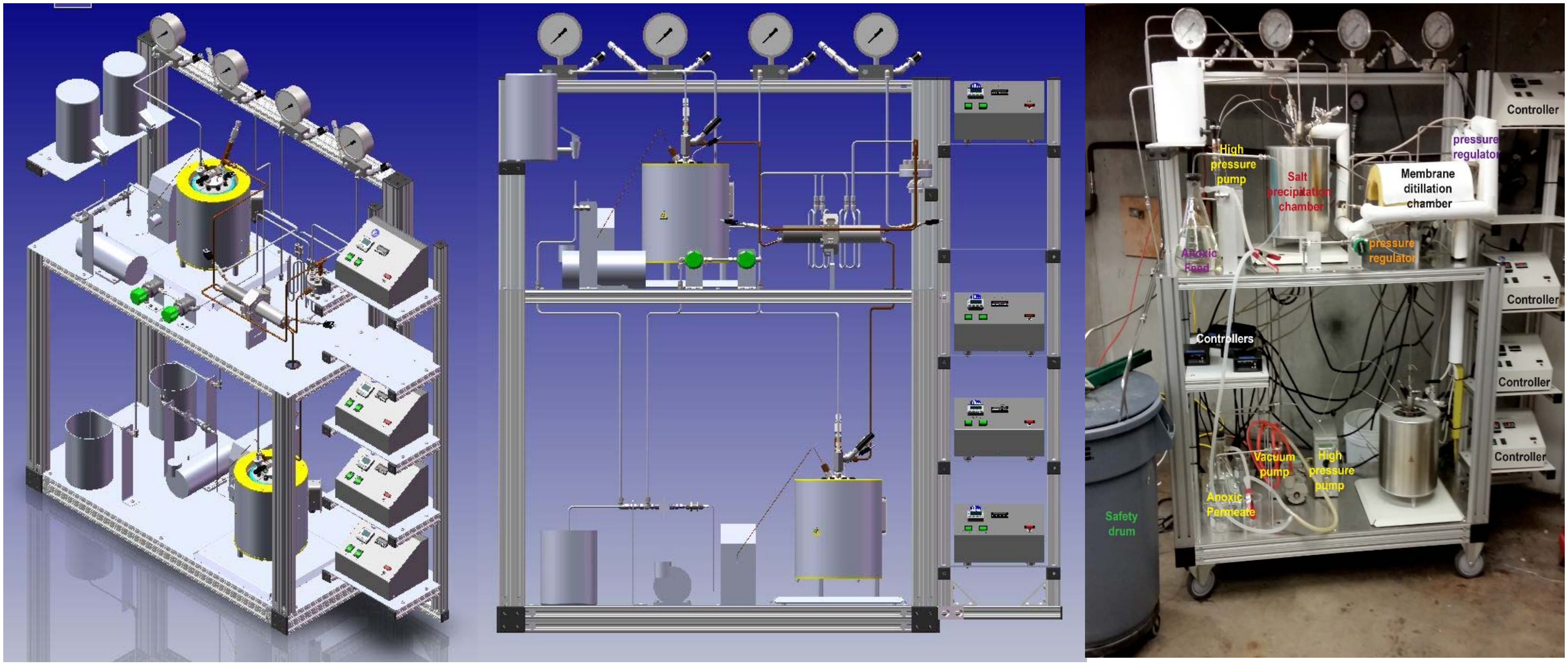
	Unit	NETL Case 11 Simulation # 1-0	Simulation # 1-3	Simulation # 1-10	Simulation # 1-20
Raw saline water salinity	mg-NaCl/L-solution	N/A	30,000	100,000	200,000
Raw saline water input	gpm	N/A	5,611	5,718	5,960
Total power generated (steam turbines)	MWe	580.5	578.3	578.3	578.3
Coal input	lb/hr	409,528	412,088	416,900	427,665
Thermal input	MWe	1,400	1,409	1,425	1,462
Total power loss (auxiliary+salt-water separation)	MWe	30.4	37.4	49.7	64.7
Net power generation	MWe	550.1	540.9	528.6	513.6
Net power generation normalized to the thermal input of the baseline case	MWe	550.1	536.4	522.5	500.7
Net power penalty compared to the baseline case	MWe	0.0	13.7	27.6	49.4
Power penalty cost	$/kgal treated water	N/A	2.4	4.8	8.6
Net plant efficiency (HHV)		39.30%	38.40%	37.10%	35.10%
Water production	gpm	0	5,554	5,554	5,554

Techno-Economic Evaluation

- For cost estimation both operating cost (power loss penalty) and capital cost for boiler and feed water modification are considered. Two cases are also considered: with or without assuming a credit for the salt and water products
- The cost of produced water treatment even with a 100% capital cost increase assumption for boiler and feed water systems is in the range of $8.6-$11.6 per kgal that is significantly lower than the treatment cost by conventional methods

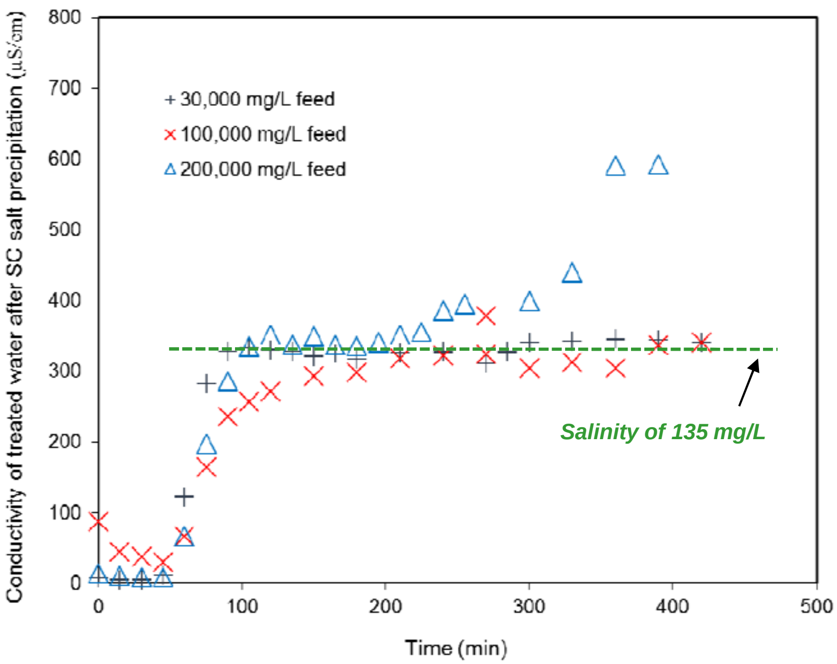
	CBM-SC PC (Simulation 1-3)	**oilfield-SC PC (Simulation 1-10)**	**CO2-seq-SC PC (Simulation 1-20)**	**CBM-SC NG (Simulation 2-3)**	**oilfield-SC NG (Simulation 2-10)**	**CO2-seq-SC NG (Simulation 2-20)**
Cost of produced water treatment by the co-generation process assuming 100% cost increase for boiler and feed water system (no credit for water and salt products), $/kgal treated water	9.5	10.4	11.6	8.7	8.9	8.6
Cost of produced water treatment by the co-generation process assuming 100% cost increase for boiler and feed water system (assuming credit for water and salt products), $/kgal treated water	2.7	-8.0	-25.3	1.9	-9.5	-28.3

Laboratory-Scale Supercritical Desalination System



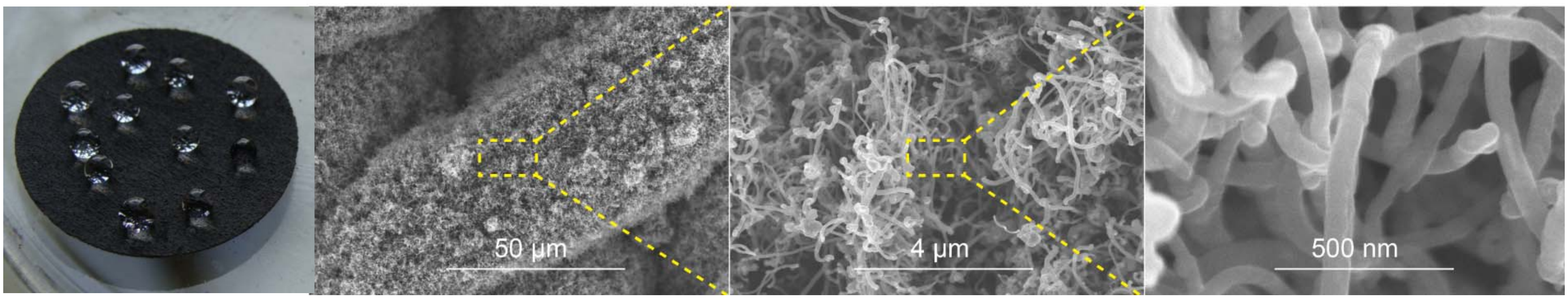
Rapid Salt Precipitation at Supercritical Conditions – Baseline NaCl Solutions

- Supercritical salt precipitation at 500 ºC and 3500 psia
- Feed salinity input of 30,000-200,000 mg/L
- Treated water conductivity of ~320 µS/cm equivalent to ~135 mg/L salinity
- 99.6-99.9% of dissolved salt quickly crystallized by shock crystallization and precipitated



Carbon Membrane Development and Characterization

Pure Carbon Nanotubes (CNT) or Carbon Nanofibers (CNF)	CNT on Below Substrates	Pyrolytic carbon (PC) on Below Substrates	Pure Graphite	Graphene on Below Substrates
- BP (pure CNT) - CNF paper	- Stainless Steel - Nickel (Ni)-coated SS - Hastelloy C - Ni-coated Hastelloy C - Catalyst-coated Hastelloy C - Ni mesh - Ni foam - Catalyst-coated tissue quartz filter	- Stainless Steel - Quartz frit - Carbon cloth - BP - CNF paper - Ceramic disk - Hastelloy C - Tissue quartz filter	- Porous graphite - Non-porous graphite	- Catalyst-coated quartz frit - Hastelloy C - Ni foam - Catalyst coated tissue quartz - Cu foam - Ni-coated SS mesh



- Seyed Dastgheib, Ali Ashraf, Hafiz Salih, SungWoo Nam. "Robust Carbon Nanotube Membranes and Methods of Making the Same", U.S. Patent Application # 15/344,697.
- Ali Ashraf, Hafiz Salih, SungWoo Nam, Seyed A. Dastgheib. "Robust Carbon Nanotube Membranes Directly Grown on Hastelloy Substrates and Their Potential Application for Membrane Distillation." *Carbon* 106 (2016) 243-251.

Steam Purification using Supercritical Membrane Distillation System - Baseline

- Designed and fabricated a high pressure/temperature membrane distillation system to purify supercritical water
- Supercritical steam containing ~100 ppm dissolved NaCl was treated by membranes
- Tested membranes showed salt rejections of 53% to >99% with flux values up to 119 $Kg/m^2.h$

Membrane	**Flux ($Kg/m^2.h$)**	**Salt Rejection (%)**
A	119	53
B (1st test)	16.5	99
B (2nd test)	15.4	99

Produced Water Sampling, Characterization, and Pretreatment

- Collected samples from CBM, oilfield, and CO_2 sequestration sites
- Characterized samples for pH, turbidity, total suspended solids (TSS), total dissolved solids (TDS), conductivity, alkalinity, dissolved organic carbon (DOC), and various cations and anions

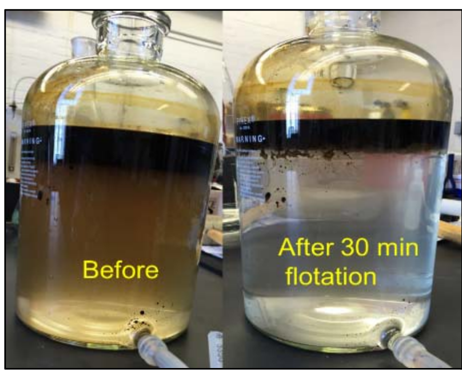
Produced Water	pH	Alkalinity (mg/L $CaCO_3$)	Conductivity (mS/cm)	Turbidity (NTU)	DOC (mg/L)	TDS (mg/L)	TSS (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)
CBM	7.5	422	57	66	<1	37,000	60	13,000	50	400	200
Oilfield	7.0	95	153	6	13	120,000	30	38,000	600	5,000	1,500
CO_2 seq. (Mt. Simon brine)	5.0*	21	191	633	58	220,000	2,800	45,000	2,000	20,000	2,000

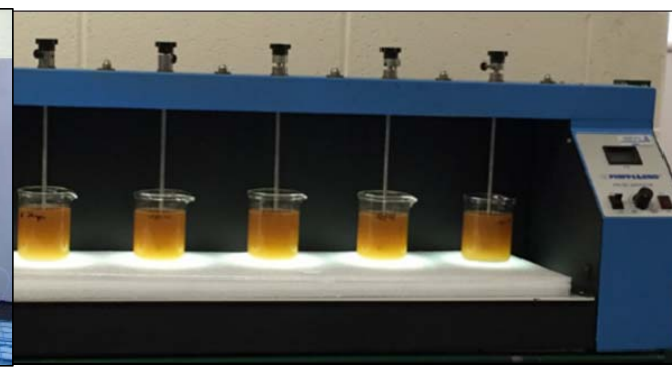
***Note: Listed number are approximate values*.**
**** Air-equilibrated samples.***




Produced Water Pretreatment

- Pretreated samples by coagulation/sedimentation, filtration, activated carbon adsorption, and ion-exchange adsorption
- Coagulation:
  - Lime addition (dose ~ 150 mg/L) for Mt. Simon brine is needed to increase the pH to ~8; other produced waters required no pH adjustment
  - Alum coagulation/sedimentation at a dose of 40-100 mg/L can reduce the turbidity to less than 1 NTU
- Filtration through a sand filter or 0.45 µm filter lowers the turbidity to < 0.01 NTU
- A mesoporous/macroporous activated carbon at a relatively large dose can be used to remove organics from produced waters
- Ion-exchange:
  - Cation exchange resins, even in unrealistic high doses (> 100 g/L), are inefficient for removing Ca and Mg from high-TDS Mt. Simon and oilfield produced water samples
  - For CBM produced water doses higher than 20 g/L can be effective




Rapid Salt Precipitation at Supercritical Conditions – Pretreated Produced Water Samples

- Supercritical salt precipitation at 500 ºC and 3500 psia
- Salinity of feed input: 37,000 mg/L, 120,000 mg/L, and 220,000 mg/L
- About 99.9% of dissolved salt quickly crystallized by shock crystallization and precipitated
- Texture and porosity of precipitated salts are different than the NaCl baseline case

<u>Oilfield brine feed (TDS = 120,000 mg/L)</u>
Na = 38,400 mg/L
Ca = 5,120 mg/L
K = 563 mg/L
Mg = 1,660 mg/L
Ba = 16 mg/L

↓

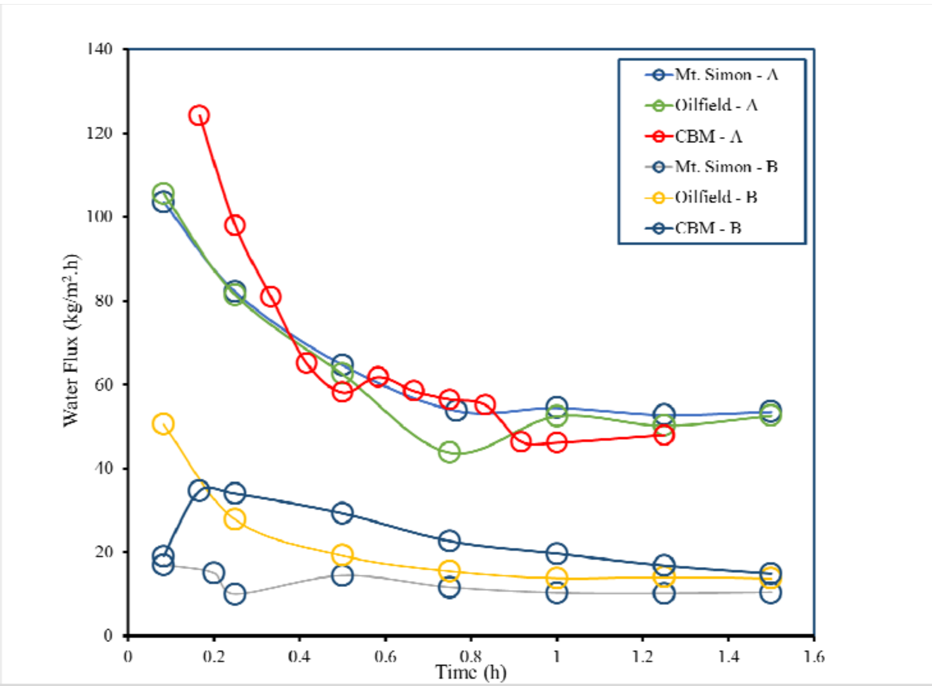
Precipitation of Salts at SC conditions of 500 ºC and 3500 psia

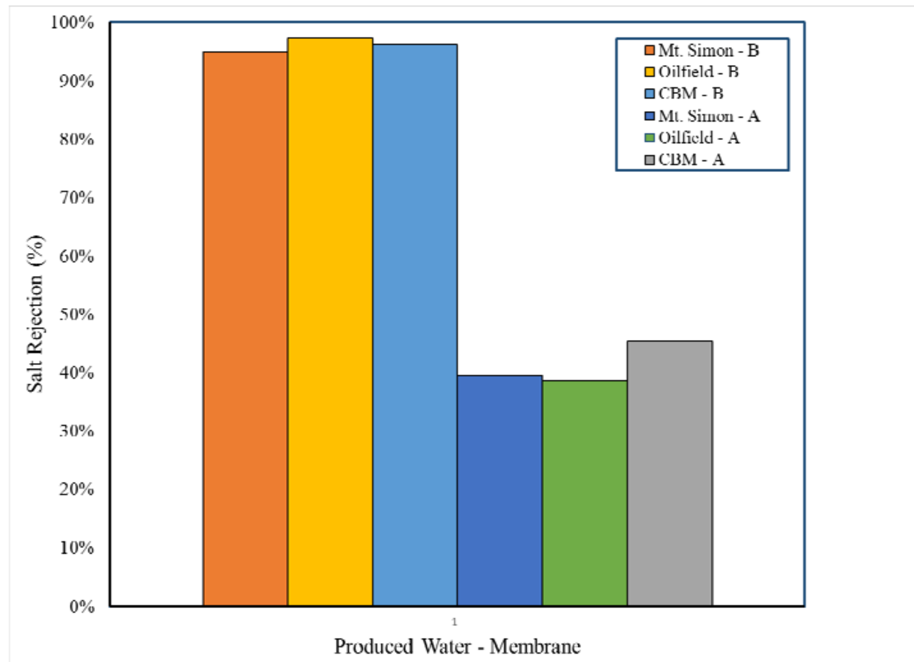
↓

<u>Treated water</u>
Na = 29.2 mg/L
Ca = 0.6 mg/L
K = 0.4 mg/L
Mg = 0.9 mg/L
Ba = <0.1 mg/L

Purification of SC steam using Supercritical Membrane Distillation System

- Polishing treatment of three types of produced waters (Mt. Simon, oilfield, and CBM) from ~150-300 ppm level that can be obtained from the SC precipitation stage
- Tested membranes showed salt rejections of up to ~98% with stable flux values up to ~60 kg/m^2.h
- With high salt rejection membranes it is possible to reduce salt content of SC steam to ~5 ppm, that might be further reduced to ~0.1 ppm by a second-stage treatment, and even to ~2 ppb by a third stage treatment





Summary, Conclusions, and Future Work

- Treatment of highly saline produced water with the available technology is challenging and costly – new innovative cost-effective technologies are needed
- Proposed integrated SC water-power cogeneration system can be a potential transformative solution for treating high-TDS produced water
- Laboratory-scale SC desalination system is designed, fabricated, and tested
- Various carbon membranes for SC desalination are prepared
- Using the lab-scale SC desalination system, we demonstrated rapid salt precipitation at SC conditions by reducing TDS of three produced water samples from 37,000-220,000 ppm to 150-300 ppm
- Steam polishing from 150-300 ppm to ~5 ppm is demonstrated by single stage treatment. It is also possible to achieve ~0.1 ppm in two polishing stages or even ~2 ppb in three stages
- Work is progress to test additional membranes and develop a continuous system for removal of salts from the SC precipitation stage

Publications, Presentations, and Patent Application

- Peer-Reviewed Publication: Ali Ashraf, Hafiz Salih, SungWoo Nam, Seyed A. Dastgheib. "Robust Carbon Nanotube Membranes Directly Grown on Hastelloy Substrates and Their Potential Application for Membrane Distillation." Carbon 106 (2016) 243-251.
- Patent Application: Seyed Dastgheib, Ali Ashraf, Hafiz Salih, SungWoo Nam. "Robust Carbon Nanotube Membranes and Methods of Making the Same", U.S. Patent Application # 15/344,697, November 7, 2016.
- NETL Treatment/BEST meeting in Pittsburgh, PA, December 1, 2016.
- EPRI Workshop: A presentation about the goals and achievements of the project at the EPRI's Workshop on Produced Water Quality, Treatment, and End Uses in Scottsdale, AZ, February 25, 2016.
- AICHE Meeting: Ali Ashraf, Hafiz Salih, SungWoo Nam, Seyed A. Dastgheib. "Development and Characterization of Carbon Nanotube Membranes for Membrane Distillation", American Institute of Chemical Engineers Annual Meeting, Salt Lake City, UT, November 8-13, 2015.
- Website Information: A brief description of the project was prepared and posted on the ISGS website: http://isgs.illinois.edu/achievements/june/applied-research-laboratory-begins-innovative-project-develop-integrated
- NETL Kick-off Presentation: A detailed presentation about the project was prepared for a meeting with the NETL project manager and other NETL staff in Morgan town, WV, on February 5, 2015.
- ICCI Kick-off Presentation: A detailed presentation about the project was prepared for a meeting with the ICCI project manager in Champaign, IL, on March 24, 2015.

Acknowledgements and Contact Information

- Funding organizations
  - U.S. Department of Energy, National Energy Technology Laboratory (Cooperative Agreement DE-FE0024015)
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- Project contact information

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