

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 CO₂ 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	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
 - 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 and conclusions

Produced Water Treatment

- ❑ Produced water from fossil fuel production (i.e., oil, gas, and coal) or CO₂ 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



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

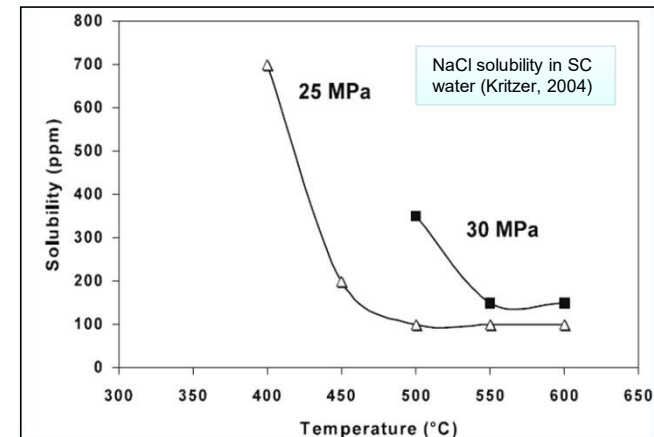
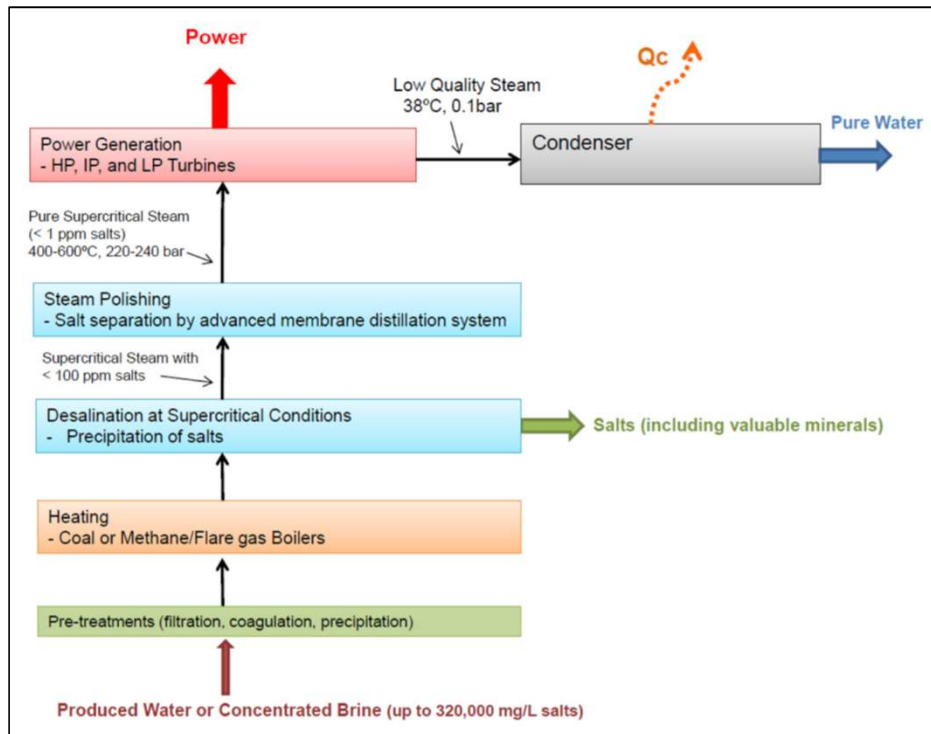
High-TDS Water Desalination Challenge and Power/Water Cogeneration

- ❑ 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/m³ recovered water
 - Electrical energy = 2 kWh/m³ recovered water
- ❑ A new approach for treatment of high salinity produced water is needed, preferably with electricity cogeneration
- ❑ Co-generation of power and freshwater can address our two major needs: electricity and water

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

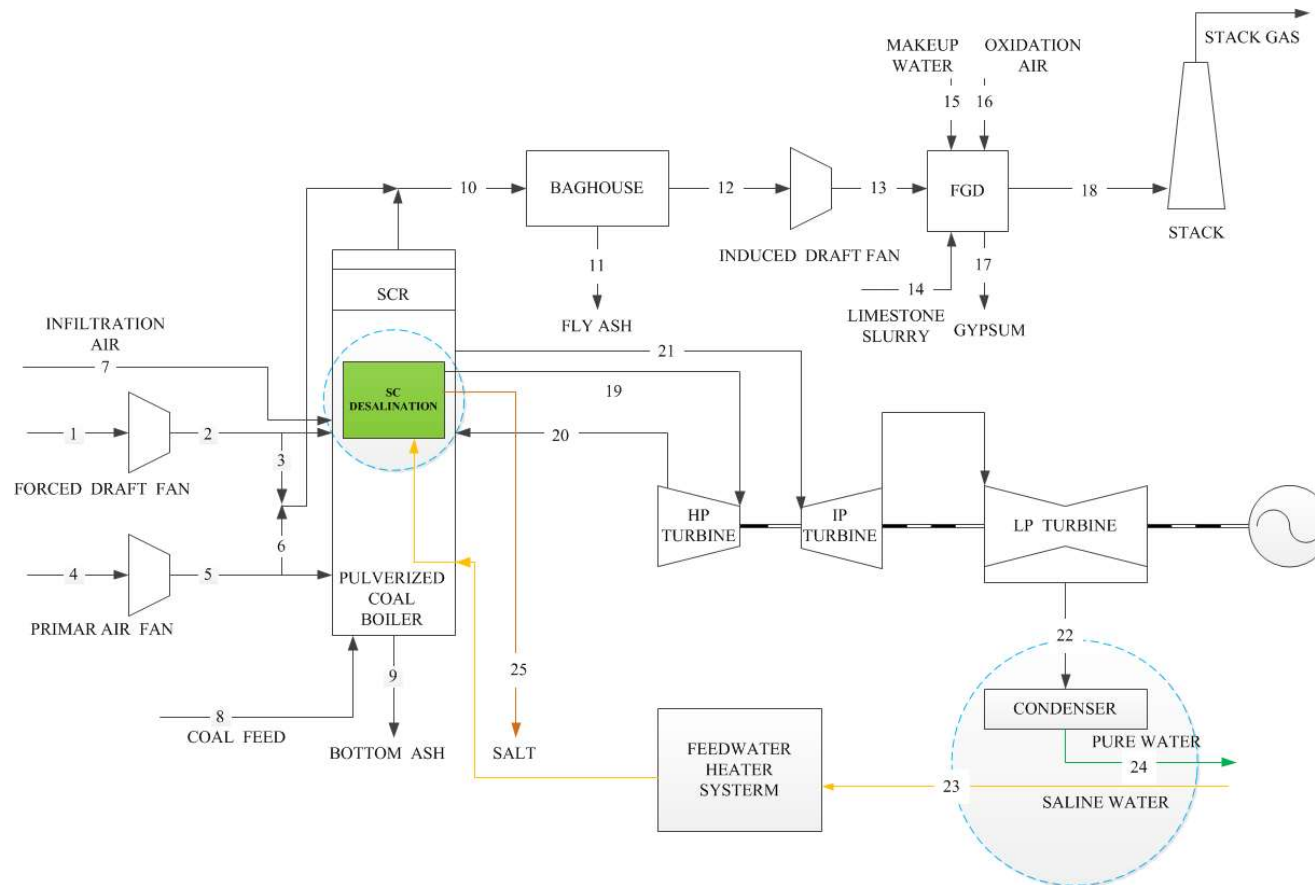
Proposed Water-Power Cogeneration System

- 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]



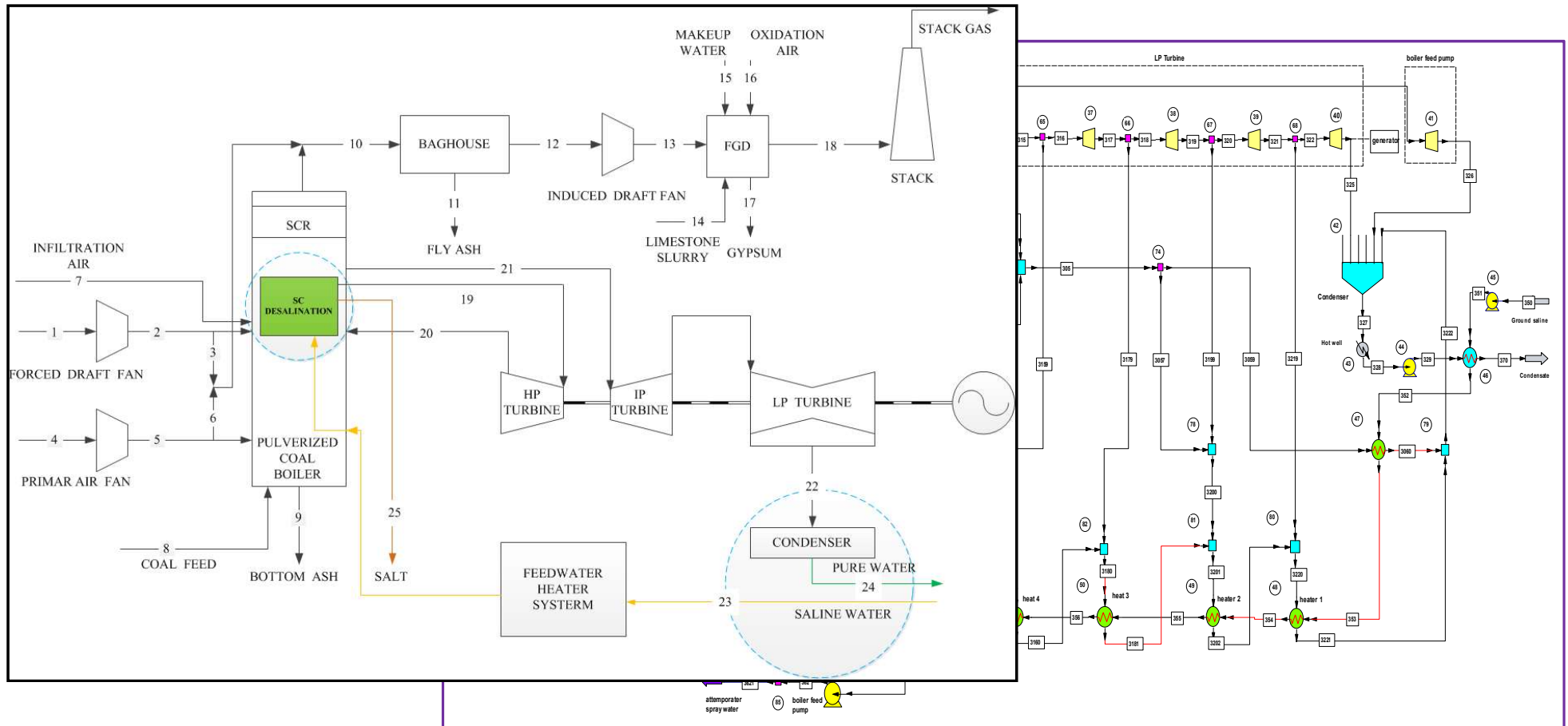
Process Description and Simulation

- ❑ Changed the closed-loop steam cycle to an open system (saline water in and condensed pure water out)
- ❑ Added supercritical salt desalination and steam polishing reactors to absorb heat from the boiler
- ❑ Highly pure SC steam is sent to turbines
- ❑ Corrosion-resistive alloys (e.g., Hast-C) should be used for FWHS and SC salt precipitation reactor



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

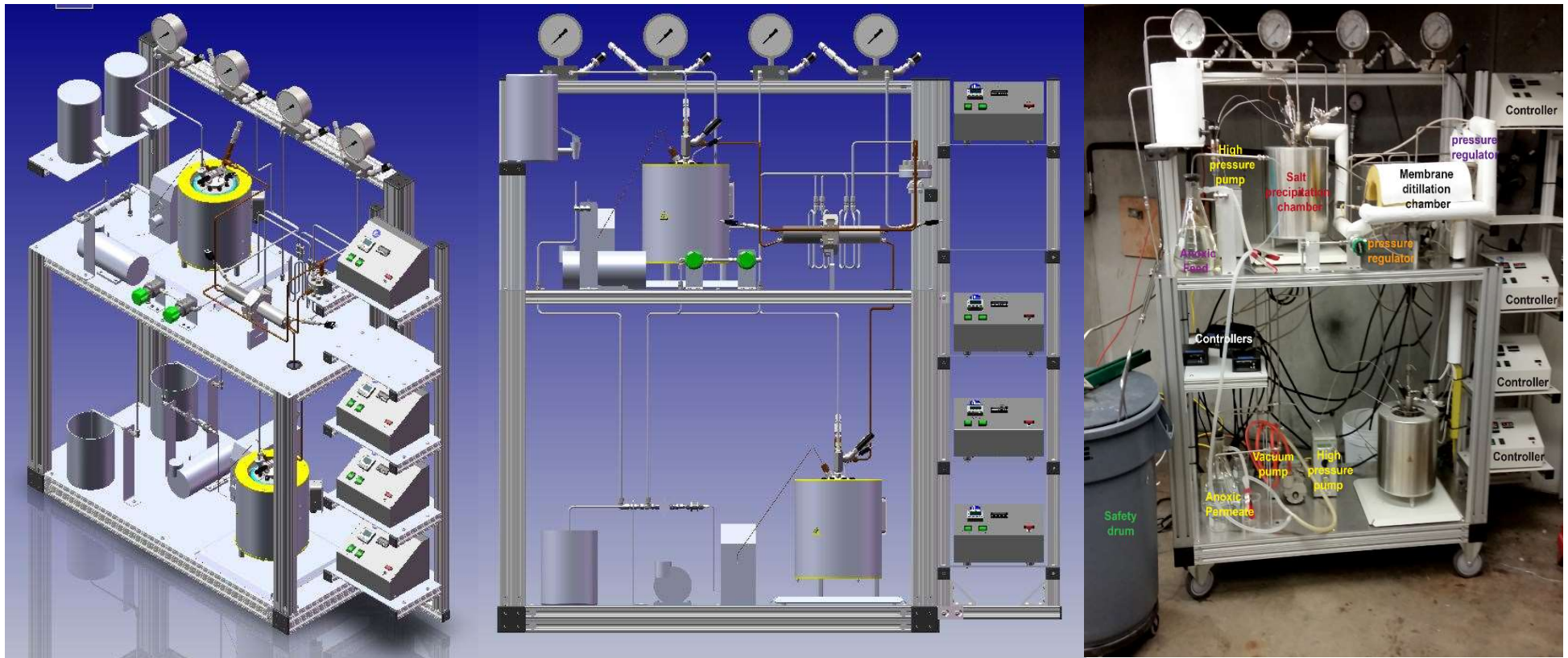
	Unit	NETL Case 11	Simulation # 1-3	Simulation # 1-10	Simulation # 1-20
		Simulation # 1-0			
Raw saline water salinity	mg-NaCl/L-solution	N/A	30,000	100,000	200,000
Raw saline water input	gpm	N/A	5,611	5,718	5,960
Total power generated (steam turbines)	MWe	580.5	578.3	578.3	578.3
Coal input	lb/hr	409,528	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
- ❑ Our other cost estimation results showed that the cost of high-TDS produced water treatment by conventional brine evaporators and crystallizers is ~\$30 per kgal

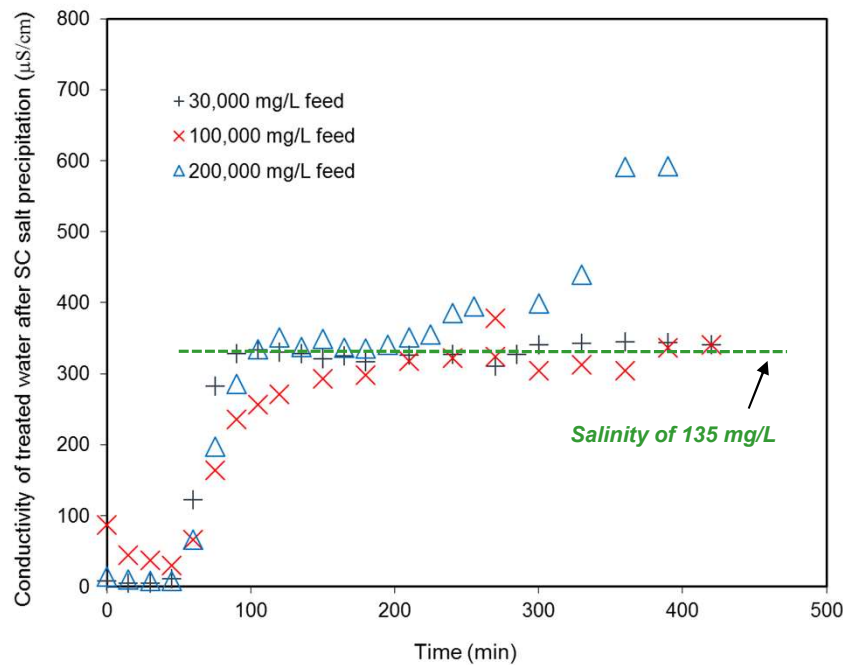
	CBM-SC PC (Simulation 1-3)	oilfield-SC PC (Simulation 1-10)	CO2-seq-SC PC (Simulation 1-20)	CBM-SC NG (Simulation 2-3)	oilfield-SC NG (Simulation 2-10)	CO2-seq-SC NG (Simulation 2-20)
Cost of produced water treatment by the co-generation process assuming 100% cost increase for boiler and feed water system (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



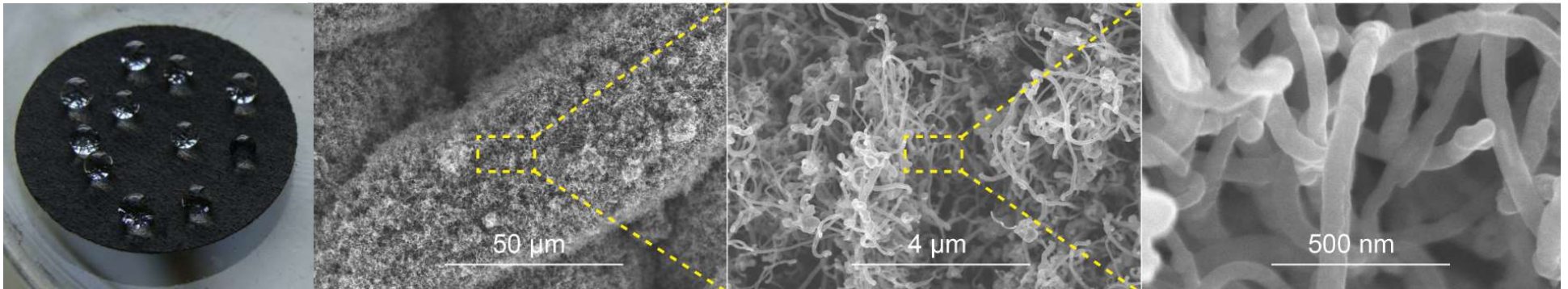
Rapid Salt Precipitation at Supercritical Conditions – Baseline NaCl Solutions

- ❑ Supercritical salt precipitation at 500 °C and 3500 psia
- ❑ Feed salinity input of 30,000-200,000 mg/L
- ❑ Treated water conductivity of $\sim 320 \mu\text{S}/\text{cm}$ equivalent to $\sim 135 \text{ mg/L}$ 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
<ul style="list-style-type: none"> - BP (pure CNT) - CNF paper 	<ul style="list-style-type: none"> - 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 	<ul style="list-style-type: none"> - Stainless Steel - Quartz frit - Carbon cloth - BP - CNF paper - Ceramic disk - Hastelloy C - Tissue quartz filter 	<ul style="list-style-type: none"> - Porous graphite - Non-porous graphite 	<ul style="list-style-type: none"> - Catalyst-coated quartz frit - Hastelloy C - Ni foam - Catalyst coated tissue quartz - Cu foam - Ni-coated SS mesh



- Seyed A. Dastgheib, Ali Ashraf, Hafiz Salih, SungWoo Nam. "ROBUST CARBON NANOTUBE MEMBRANES AND METHODS OF MAKING THE SAME", U.S. Patent Application US2017/0165612 A1, June 15, 2017.
- 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 robust carbon membranes (graphitic, CNT, or composite membranes)
- ❑ Tested membranes showed salt rejections of 53% to >99% with flux values up to 300 Kg/m².h
- ❑ A newly developed carbon membrane showed extremely high flux of 200-300 kg/m².h that is one order of magnitude higher than the flux of conventional membranes. This membrane also showed 90-93% salt rejection

Membrane	Flux (kg/m ² .h)	Salt Rejection (%)
A	119	53
B	16	99
C	200-300	90-93

Produced Water Sampling, Characterization, and Pretreatment

- ❑ Collected samples from CBM, oilfield, and CO₂ 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

* Air-equilibrated samples.



Produced Water Treatment

- ❑ Produced water pretreatment
 - Removal of oil/organics, suspended solids, and scale-forming species

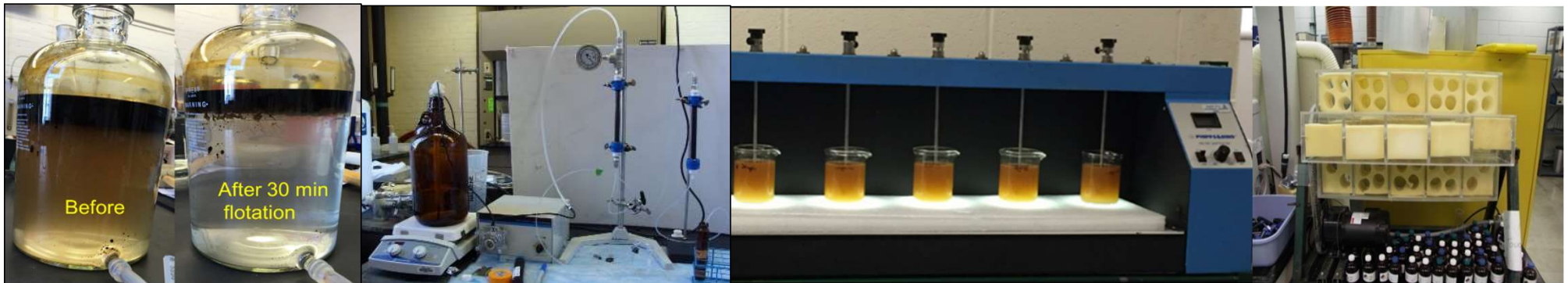
- ❑ Supercritical salt precipitation
 - Pretreated produced water samples (TDS up to 200,000 ppm) → ~ 100 ppm TDS water

- ❑ Supercritical membrane distillation
 - ~ 100 ppm TDS water → ~ 1 ppm TDS water in one stage and ~ 10 ppb in 2-3 stages



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 °C and 3,500 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

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

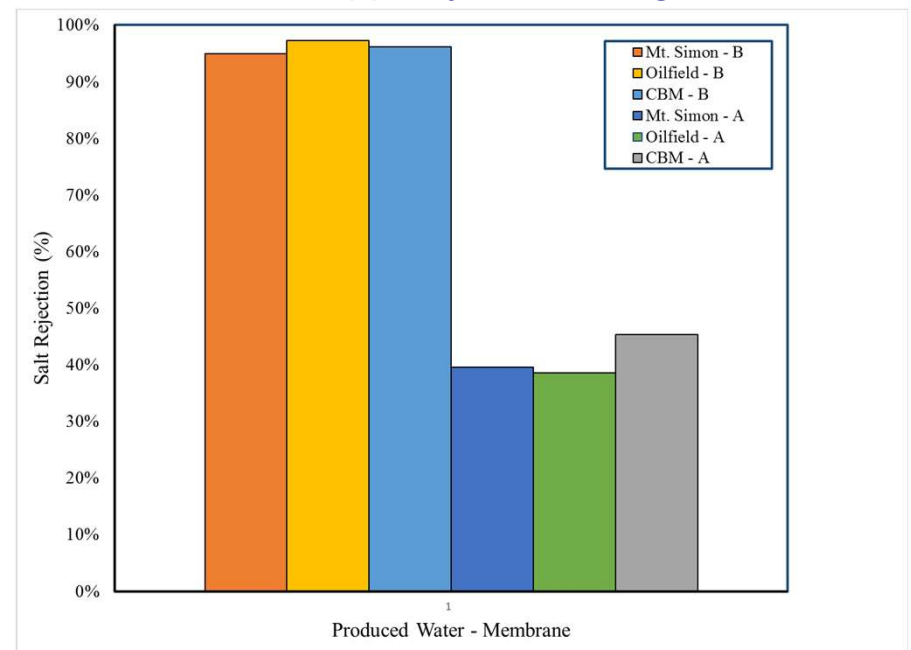
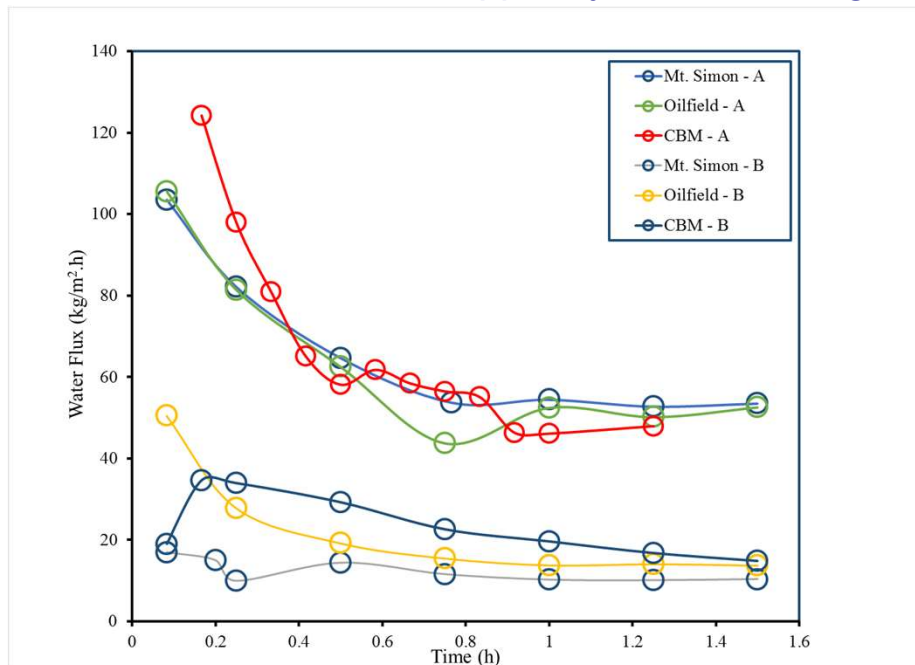
Precipitation of Salts at SC conditions of 500 °C and 3,500 psia

Treated water
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



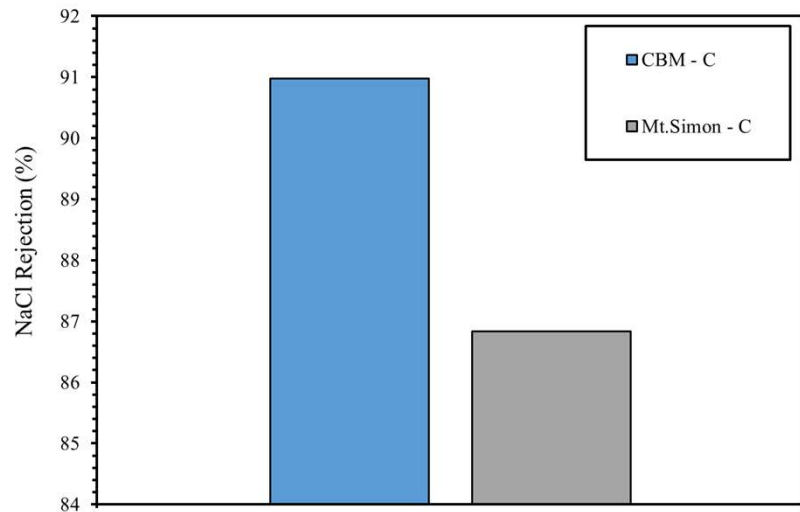
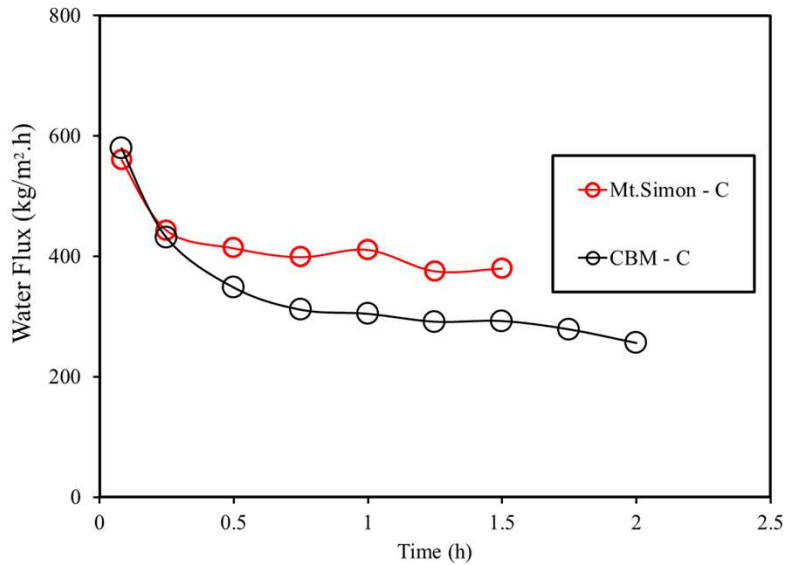
Purification of SC steam using Supercritical Membrane Distillation System

- 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
- Two types of membranes showed salt rejections of up to ~98% with stable flux values up to ~60 kg/m².h at SC conditions
- 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



Purification of SC steam using Supercritical Membrane Distillation System

- Polishing treatment of produced waters (Mt. Simon and CBM) from ~150-300 ppm initial concentration at SC conditions
- A newly developed membrane showed 87-91% salt rejection with extremely high flux values of ~300-400 kg/m².h at SC conditions



Summary and Conclusions

- ❑ 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 at SC conditions. It is also possible to achieve ~0.1 ppm in two polishing stages or even ~2 ppb in three stages
- ❑ A newly developed carbon membrane showed extremely high flux of 200-400 kg/m².h that is one order of magnitude higher than the flux of conventional membranes. This membrane also showed 87-93% salt rejection

Publications, Presentations, and Patent Applications

- 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 A. Dastgheib, Ali Ashraf, Hafiz Salih, SungWoo Nam. "ROBUST CARBON NANOTUBE MEMBRANES AND METHODS OF MAKING THE SAME", U.S. Patent Application US2017/0165612 A1, June 15, 2017.
- Invention Disclosure: Seyed A. Dastgheib, Hafiz Salih. "Continuous Supercritical System for Zero-Liquid Discharge Water Treatment and Salt Crystallization", Invention Disclosure Ref. Code 2017-110, University of Illinois, Office of Technology Management, June 12, 2017.
- ASME Meeting: Seyed A. Dastgheib, Hafiz Salih, Ali Ashraf, Hong Lu, and SungWoo Nam. "Water Desalination and Power Generation by an Integrated Supercritical System", American Society of Mechanical Engineers Annual Meeting, Power and Energy Conference, Charlotte, NC, June 26-30, 2017.
- 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>

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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