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

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Principal Investigator: Seyed A. Dastgheib
Illinois State Geological Survey
University of Illinois at Urbana-Champaign

Team Members: Seyed A. Dastgheib, Hafiz Salih, Ali Ashraf, Hong Lu, SungWoo Nam

Project Manager: Barbara Carney

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Outline

- Introduction and background information
- Description of the proposed technology
- Objectives and technical targets
- Process simulation and techno-economic evaluation
- Laboratory-scale supercritical desalination system
- Development and characterization of carbon membranes
- Produced water treatment
- Summary and conclusions

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

→

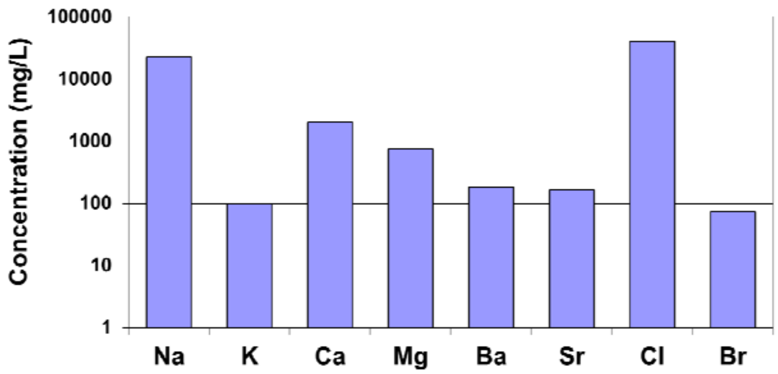
Desalination or the main treatment:
- Reverse osmosis RO (TDS < 50,000 ppm)
- Thermal distillation systems
- Crystallization for zero-liquid discharge (ZLD)
- Others

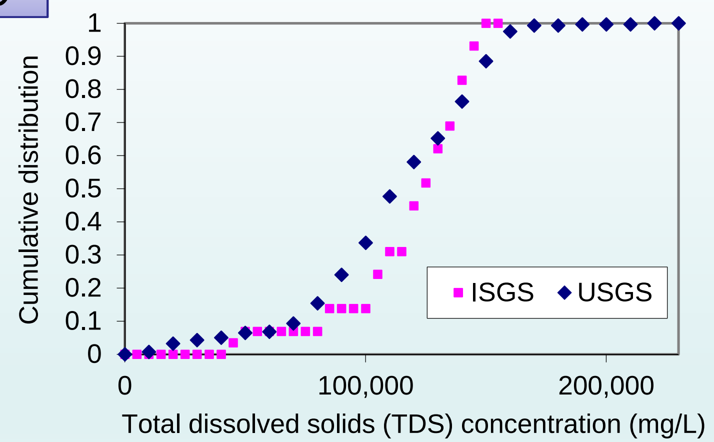
Sources: Veil et al., 2004; Clark and Veil, 2009; Knutson, Dastgheib et al., 2012; NETL, 2015

Produced Water Quality

- Total Dissolved Solids (TDS) in a wide range of < 1,000 ppm to > 200,000 ppm, depending on produced water source and type
- Water salinity mainly from NaCl but other major and trace cations and anions also exist
- Significant organic impurities (suspended, colloidal, and dissolved aromatic and aliphatic species) exist in oilfield brines
- Oilfield brines usually have high TDS values. In Illinois, more than 2/3 of samples had TDS values larger than 100,000 ppm
- Produced water from coal-bed methane usually has better quality than oilfield brines
- TDS of produced water from CO_2 sequestration varies in a large range, can be larger than 200,000 ppm

IL oilfields produced water quality



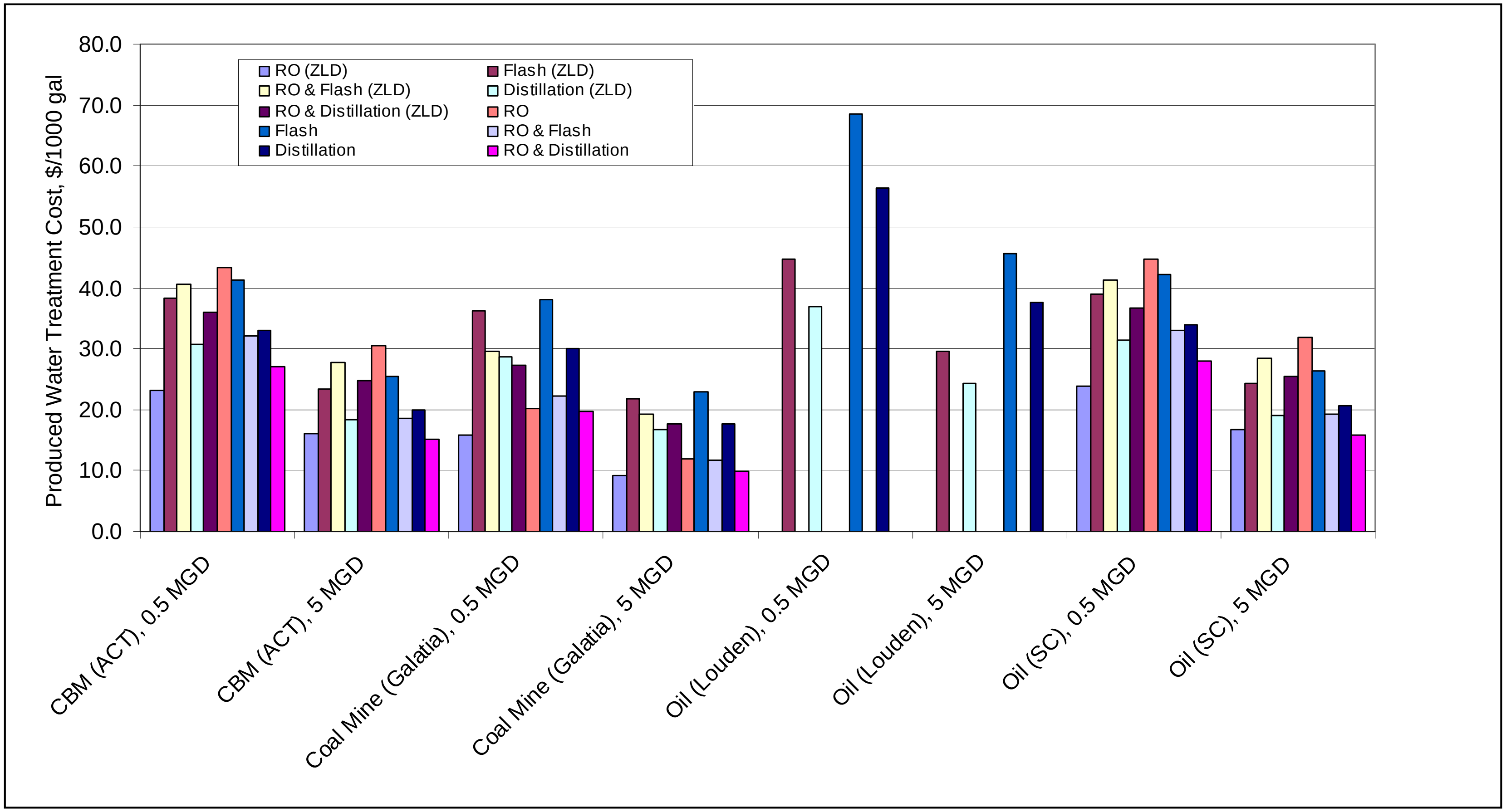


Source: Knutson, Dastgheib et al., 2012

Produced Water Treatment Cost

- For 5 mgd (million gallon per day) plant capacity estimated cost of treatment is: ~$10-$20/1,000 gal for brackish coal mine water to ~$25-$45/1,000 gal for high TDS (~100,000 ppm) oilfield brine

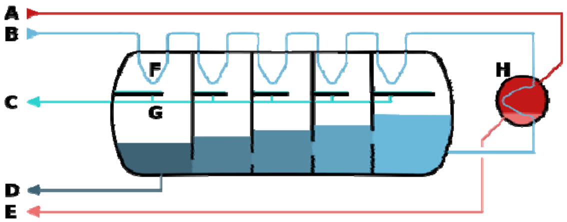
- *Treatment of highly saline produced water with the available technology is excessively costly – new innovative cost-effective technologies are needed*



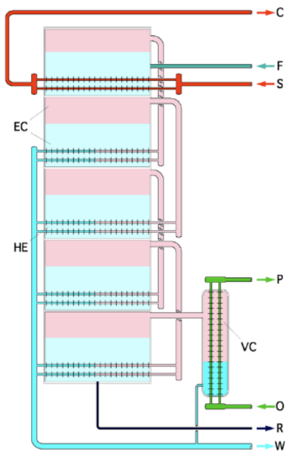
Source: Knutson, Dastgheib et al., 2012

Energy Analysis of Desalination Technologies

- Thermodynamic limit
  - Theoretical minimum energy (Gibbs free energy of mixing) to desalinate seawater (35,000 ppm salinity) is 0.76 kWh/m^3 with recovery rate approaching 0%
  - 1.06 kWh/m^3 is the minimum energy for 50% recovery for seawater
- Existing desalination technologies
  - RO: ~3-4 kWh/m^3
  - Thermal distillation systems: 28-83 kWh/m^3 (thermal) plus additional electrical energy
- Significant improvement for increasing energy efficiencies of desalination systems especially for thermal distillation systems is possible



Schematic of a multistage flash desalinator
A – steam in
B – seawater in
C – potable water out
D – waste out
E – steam out
F – heat exchange
G – condensation collection
H – brine heater



Schematic of a multiple effect desalination plant. F - feed water in. S - heating steam in. C - heating steam out. W - Fresh water (condensate) out. R - brine out. O - coolant in. P - coolant out. VC is the last-stage cooler

RO production train, North Cape Coral RO Plant

Sources: Elimelech and Phillip, 2011; Mezher et al., 2011; Wikipedia, 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
- A new approach for treatment of high salinity produced water is needed, preferably with electricity cogeneration

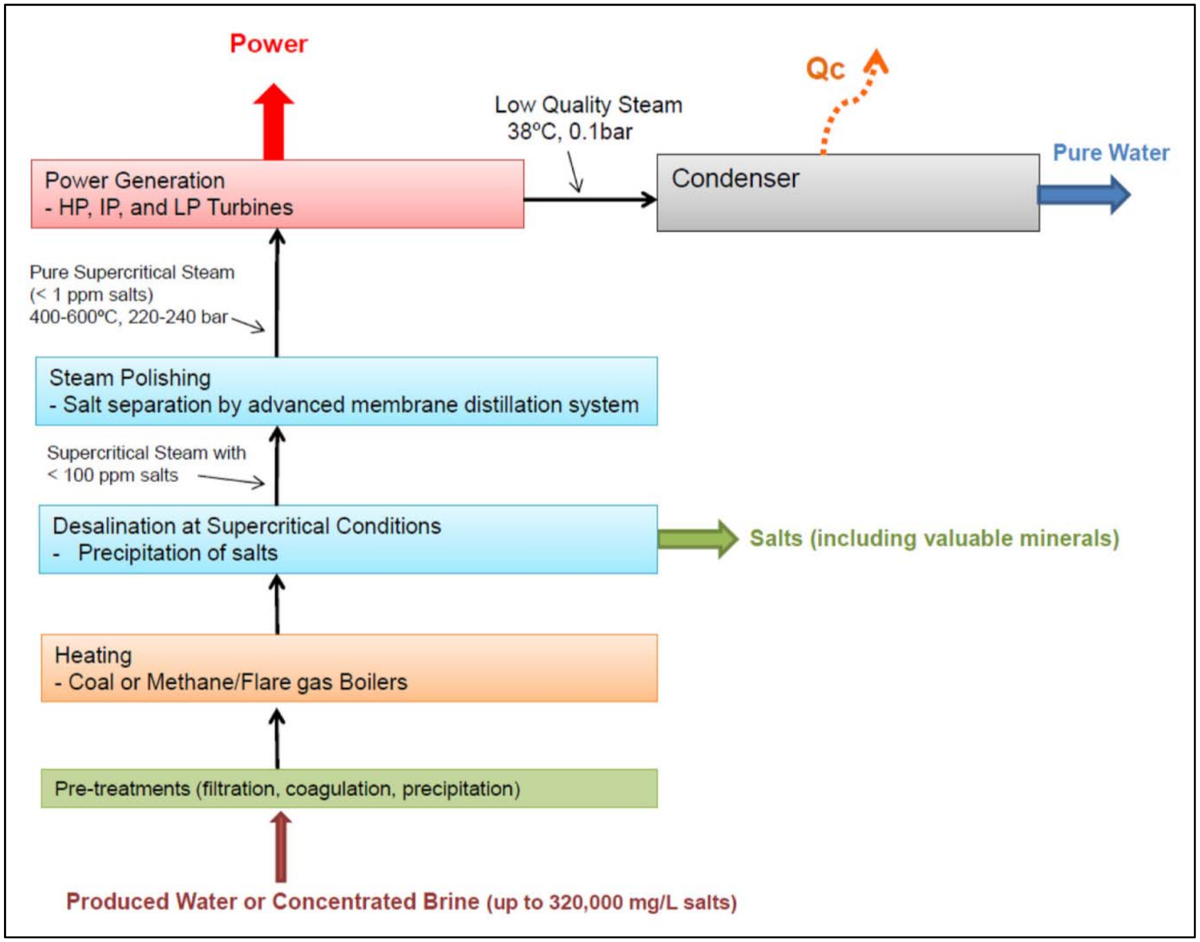
Energy demand of water desalination by RO or existing cogeneration technologies for seawater desalination*

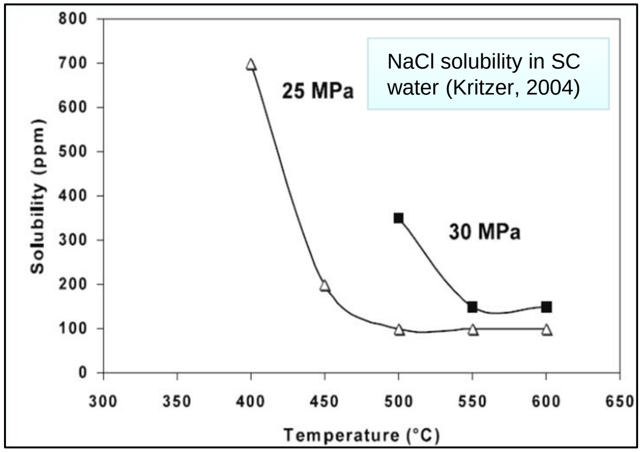
Seawater desalination by power-water cogeneration or stand alone RO	Electrical energy (kWh/m^3)	Thermal energy (kWh/m^3)	Total electrical energy equivalent *assuming* 40% power generation efficiency (kWh/m^3)
Case 1: Desalination by MED in a cogeneration plant	~2	~28	**~13.2**
Case 2: Desalination by MSF in a cogeneration plant	~4.2	~45	**~22.2**
Case 3: Desalination by stand alone RO	~4	0	**~4**

**Based on the data obtained from Mezher et al., 2011, Desalination*

Proposed Water-Power Cogeneration System

- Integration of water treatment and power generation
- Pretreatment → Salt Precipitation at Supercritical (SC) Conditions → Steam Polishing → Power Generation
- Utilization of supercritical steam for power generation might be possible with the proposed approach
- Steam polishing is a 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]





Significance and Potential Outcome

- Produced water treatment
  - A potential transformative concept for treatment of concentrated produced water, generated from fossil fuel production or CO_2 sequestration, with salt concentrations up to ~300,000 mg/L

- Power-water cogeneration
  - Simultaneous water purification and power generation by an innovative integrated supercritical system using coal or NG
  - Other fossil fuels and even renewables (e.g., solar, biomass) can also provide the heat source

- Higher energy efficiency
  - High salinity water treatment
  - Power/water cogeneration

- Environmental sustainability
  - Zero-liquid discharge
  - Lower carbon footprint

- Recovery of minerals
  - Valuable elements (e.g., Li, I, rare earth elements)
  - Salt for deicing application

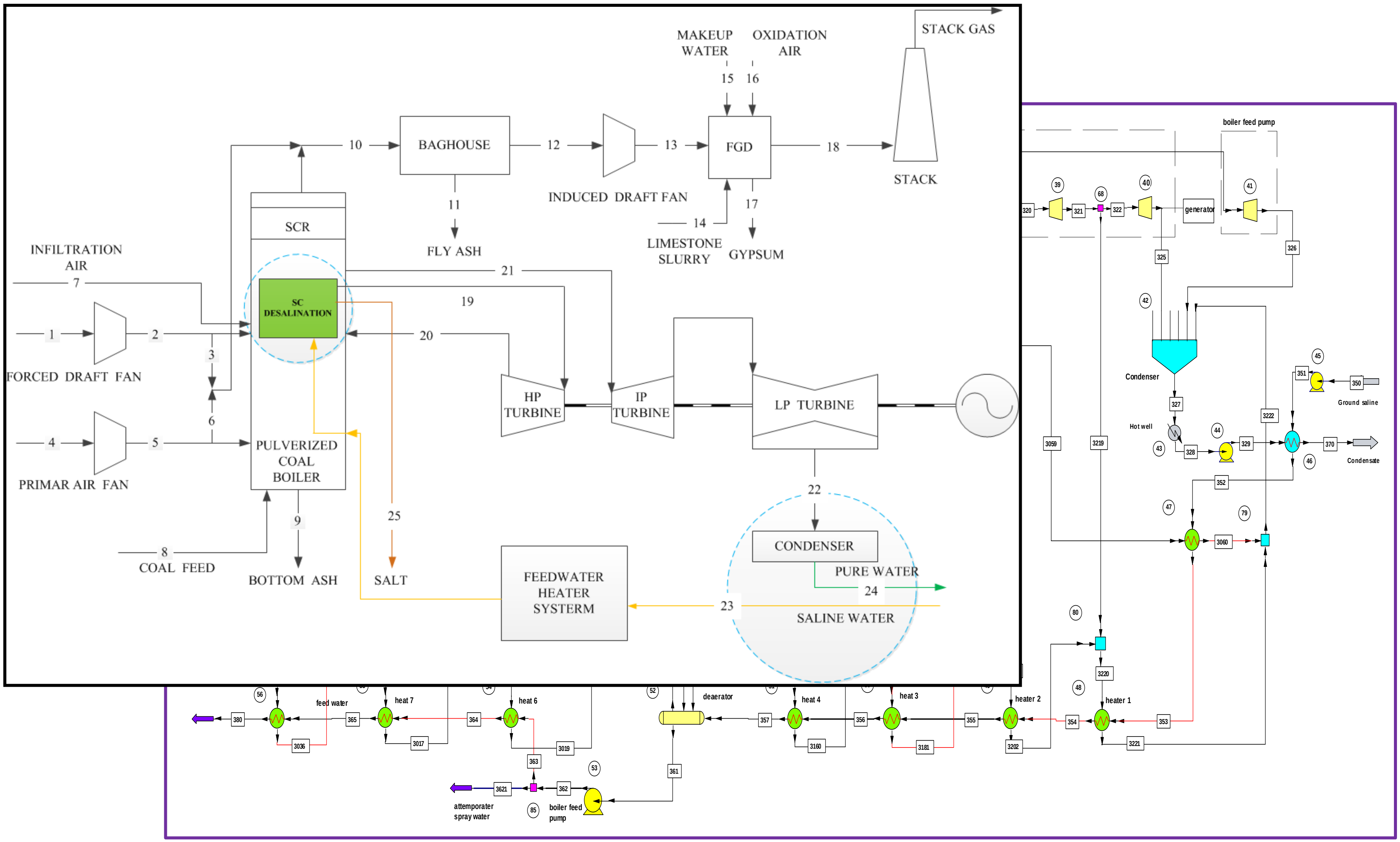
Objective and Technical Targets

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

- Technical targets:
  - Evaluate techno-economic feasibility of the proposed process through process simulation, thermodynamic analysis, and cost estimation studies
  - Design, assemble, and test a system for SC salt precipitation
  - Design, assemble, and test a system for SC steam purification by a membrane distillation system
  - Prepare, characterize, and test carbon membranes (e.g., graphene, carbon nanotubes)
  - Perform sampling, characterization, and pretreatment of different produced water samples
  - Treat different produced waters to high quality water using fabricated supercritical salt precipitation and membrane distillation system

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 1-4 %, 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

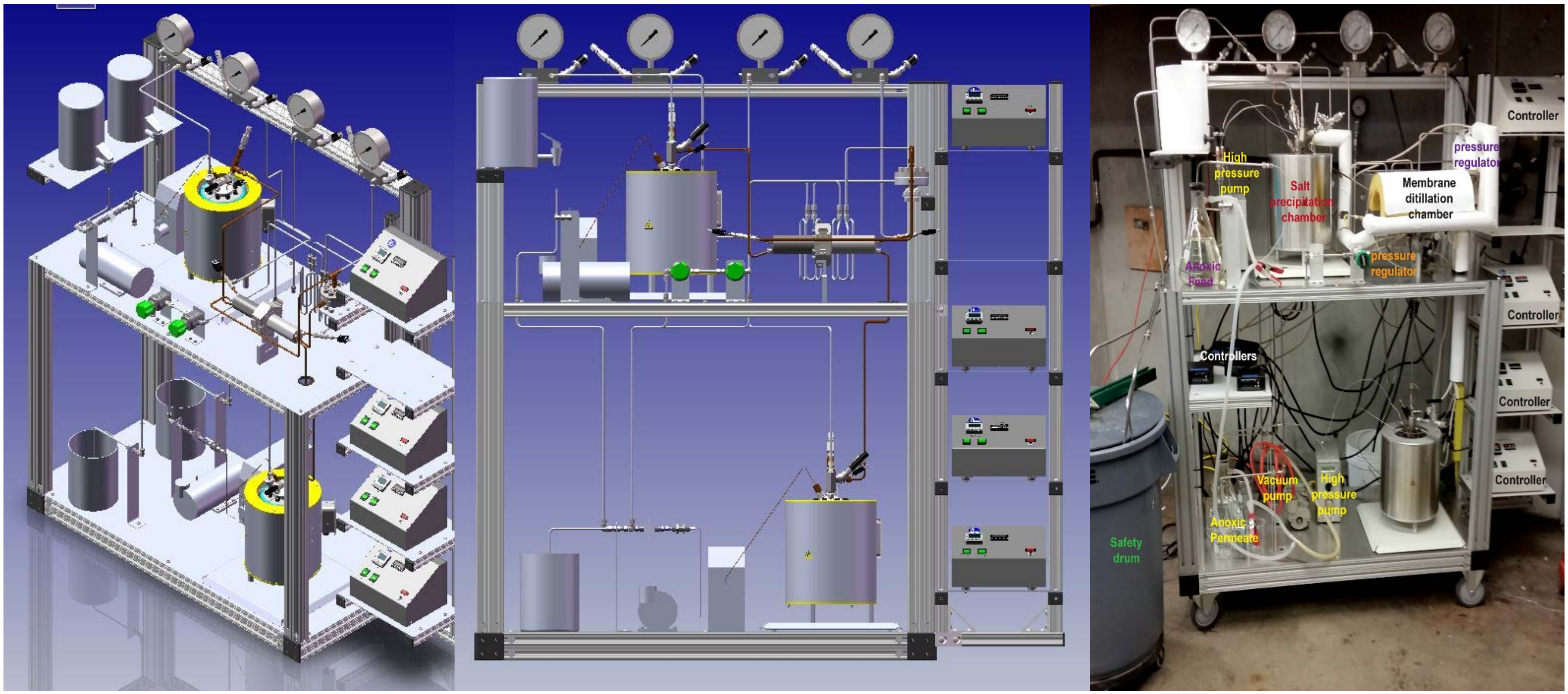
	Unit	NETL Case 11 Simulation # 1-0	Simulation # 1-3	Simulation # 1-10	Simulation # 1-20
Raw saline water salinity	mg-NaCl/L-solution	N/A	30,000	100,000	200,000
Raw saline water input	gpm	N/A	5,611	5,718	5,960
Total power generated (steam turbines)	MWe	580.5	578.3	578.3	578.3
Coal input	lb/hr	409,528	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

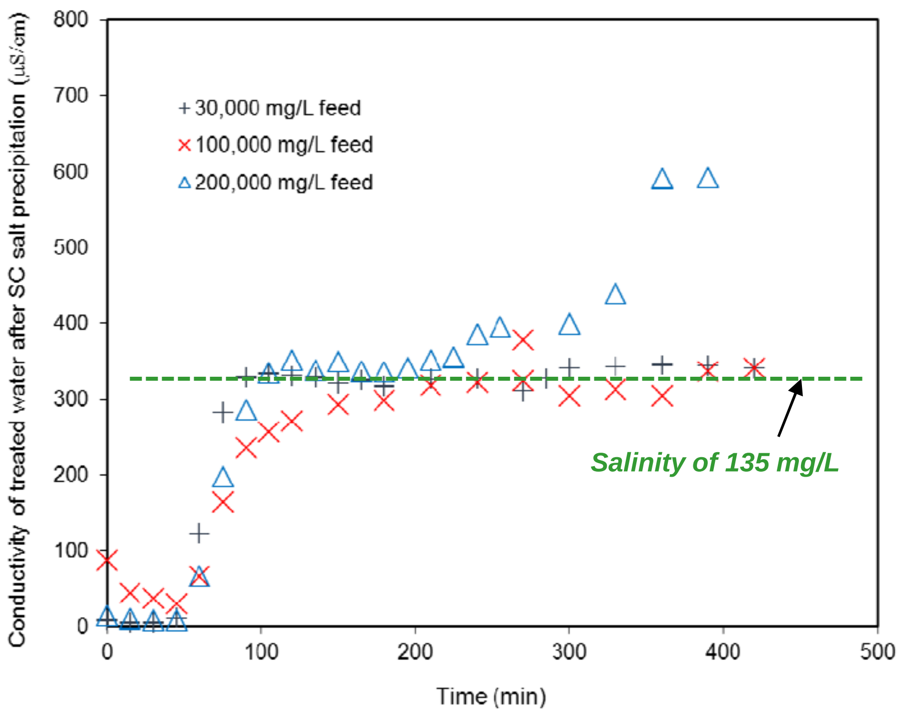
	CBM-SC PC (Simulation 1-3)	**oilfield-SC PC (Simulation 1-10)**	**CO2-seq-SC PC (Simulation 1-20)**	**CBM-SC NG (Simulation 2-3)**	**oilfield-SC NG (Simulation 2-10)**	**CO2-seq-SC NG (Simulation 2-20)**
Cost of produced water treatment by the co-generation process assuming 100% cost increase for boiler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



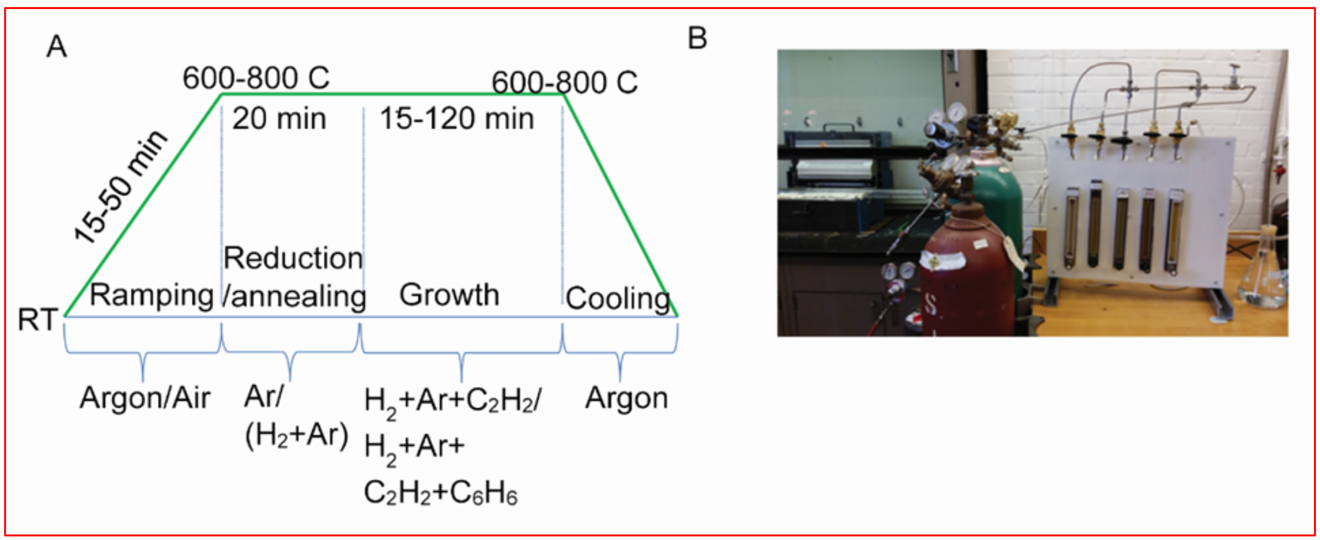
Rapid Salt Precipitation at Supercritical Conditions

- Supercritical salt precipitation at 500 ºC and 3500 psia
- Feed salinity input of 30,000-200,000 mg/L (conductivity of ~70,000-472,000 µS/cm)
- 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

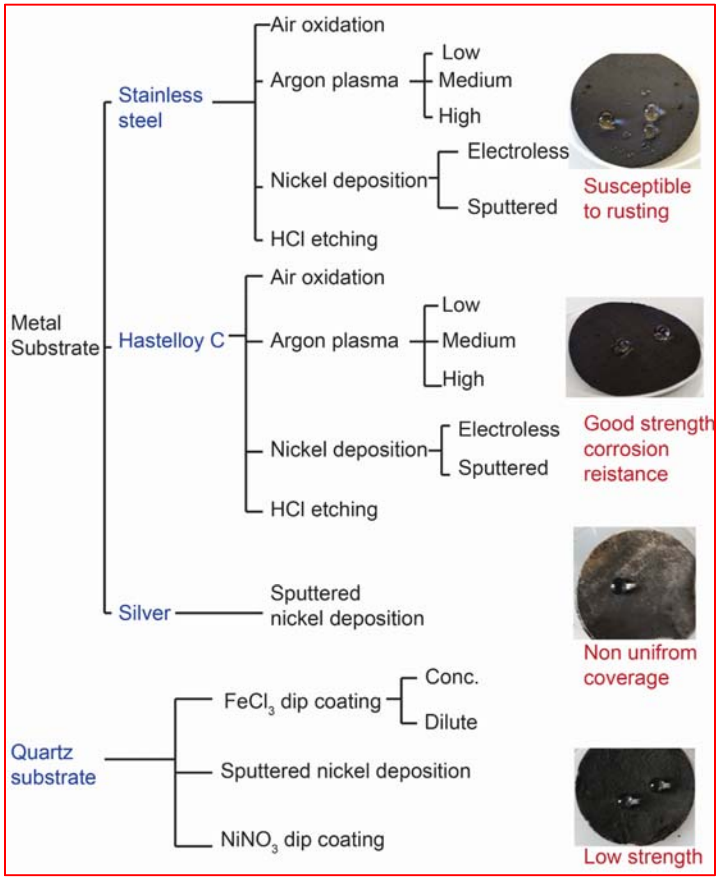
Pure Carbon Nanotubes (CNT) or Carbon Nanofibers (CNF)	**CNT on Below Substrates**	**Pyrolytic carbon (PC) on Below Substrates**	**Pure Graphite**	**Graphene on Below Substrates**
- BP (pure CNT) - CNF paper	- Stainless Steel - Nickel (Ni)-coated SS - Hastelloy C - Ni-coated Hastelloy C - Catalyst-coated 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 - Steam-treated porous graphite	- Catalyst-coated quartz frit - Hastelloy C - Ni foam - Catalyst coated tissue quartz - Cu foam - Ni-coated SS mesh

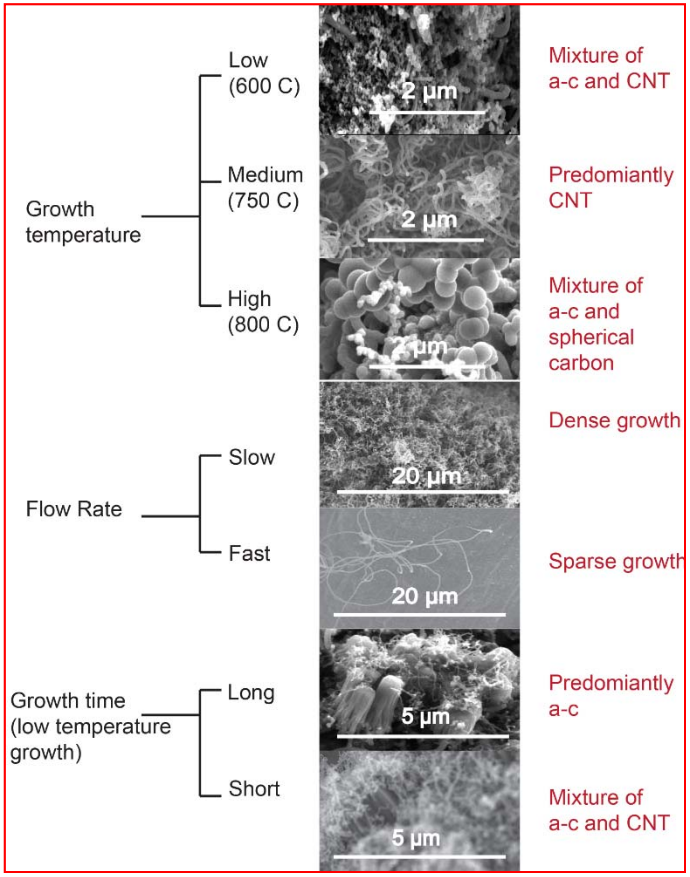


A: Graphical diagram of the developed chemical vapor deposition (CVD) method used for the growth of CNT on different pretreated substrates. B: Photograph of the CVD system used for sample preparation.

Carbon Membrane Development and Characterization

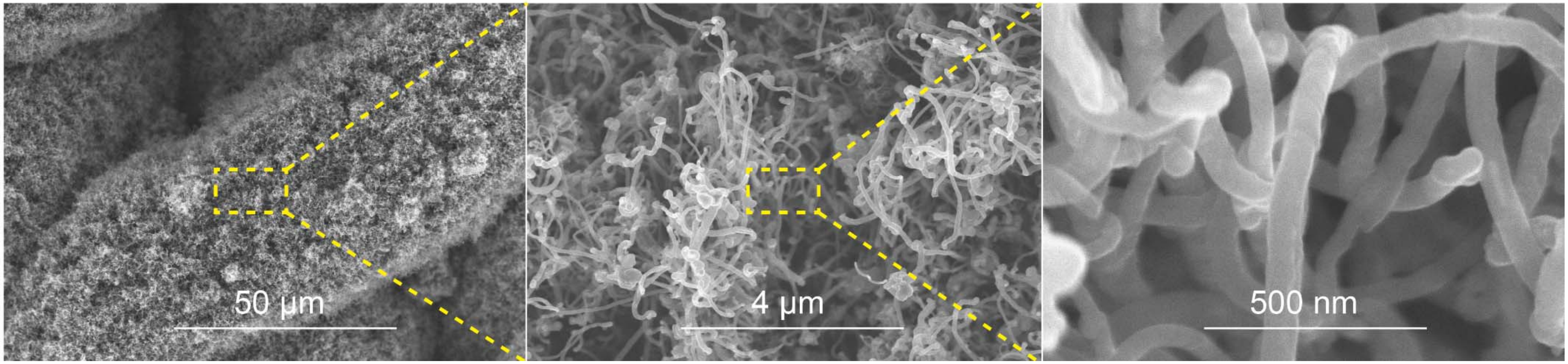
- Development of CNT membranes
  - Different support materials are subjected to various pretreatments to prepare catalytic sites for the growth of CNT
  - CNT is grown on substrates by CVD at different conditions
  - Process conditions including temperature, flow rate, and gas composition are optimized

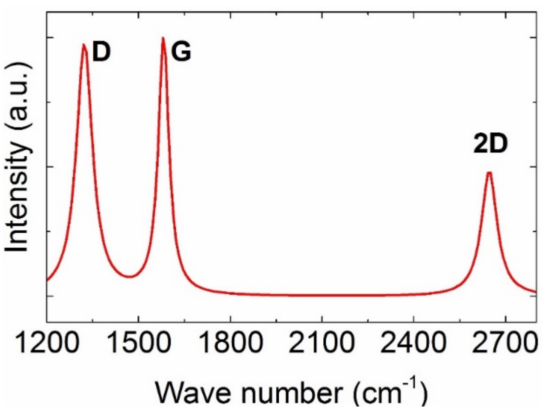


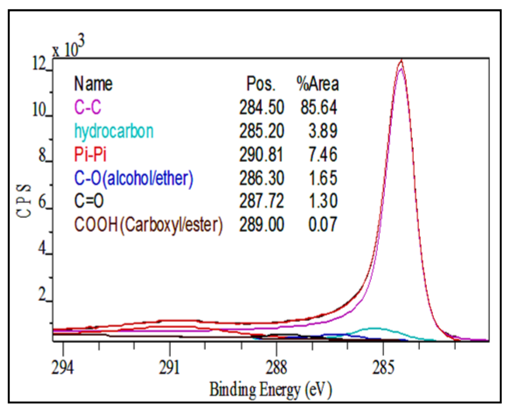


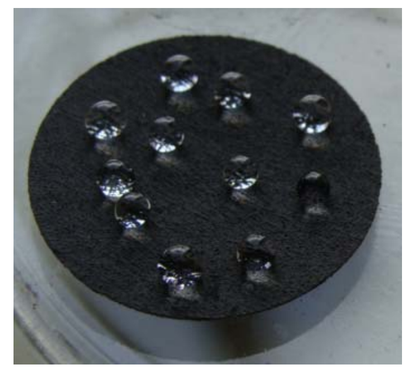
Carbon Membrane Development and Characterization

- Membrane characterization by various methods including water contact angle measurement, scanning and transmission electron microscopy (SEM and TEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, thermogravimetric analysis, corrosion test, low temperature membrane distillation tests

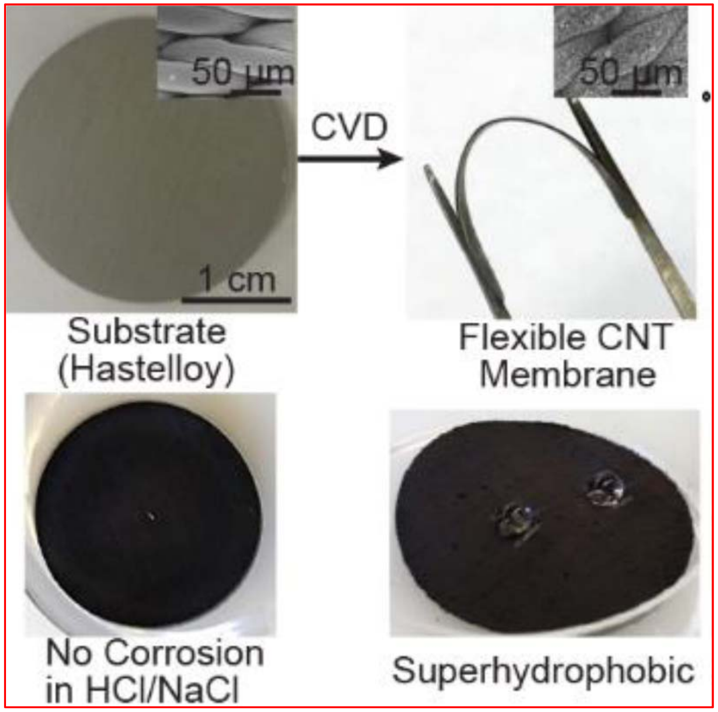


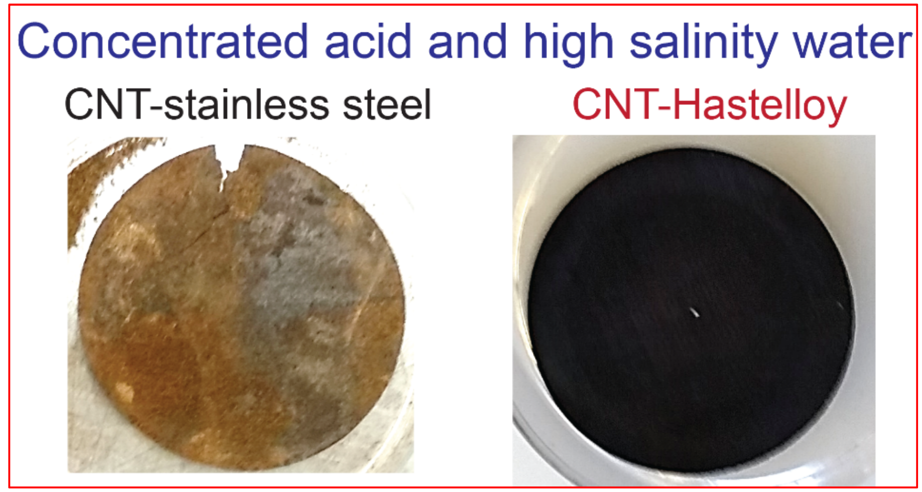




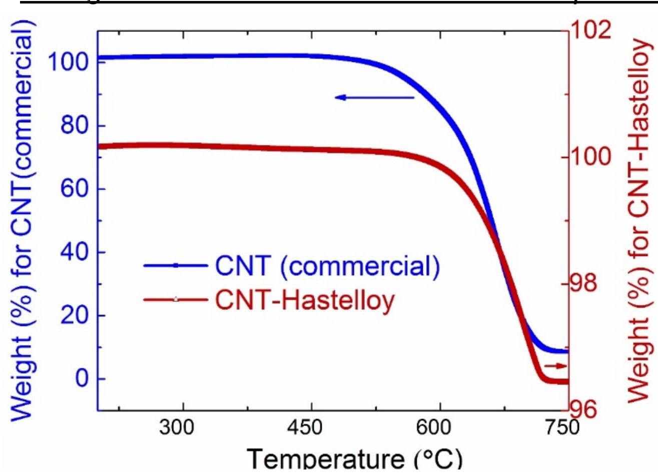


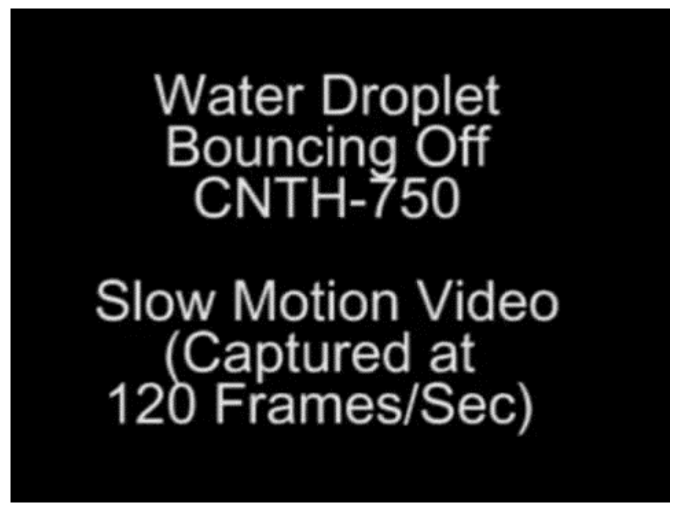
Robust CNT-Hastelloy Membranes





<u>*No significant wt. loss when heated in air up to 500 °C*</u>





Steam Purification using Supercritical Membrane Distillation System

- Designed and fabricated a high pressure/temperature membrane distillation system to purify supercritical water
- Supercritical water containing ~100 ppm dissolved salt was treated by membranes
- Tested membranes showed salt rejections of 53% to >99% with flux values up to 119 $Kg/m^2.h$
- With high salt rejection membranes it is possible to reduce salt content of SC steam to < 1 ppm in a single polishing stage. It is also possible to achieve < 10 ppb level in two polishing stages

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 and Characterization

- Collected samples from CBM, oilfield, and CO_2 sequestration sites
- Samples are being characterized for pH, turbidity, total suspended solids (TSS), total petroleum hydrocarbons (TPH), total dissolved solids (TDS), conductivity, alkalinity, dissolved organic carbon (DOC), and various cations and anions

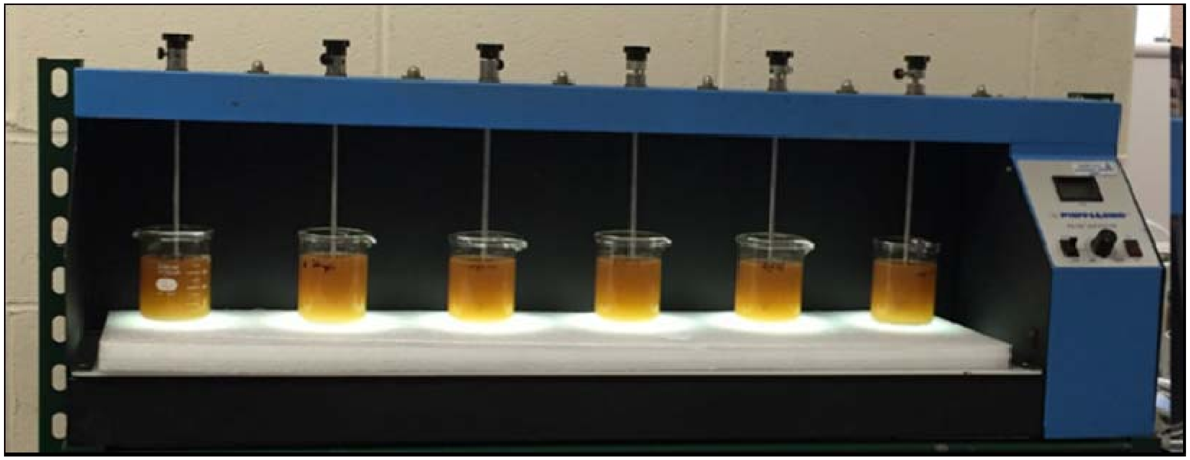
Produced Water	TDS (mg/L)	Na (mg/L)	Ca (mg/L)	Cl (mg/L)
CBM	37,000	13,000	400	25,000
Oilfield	120,000	38,000	5,000	75,000
CO_2 seq. (saline reservoir)	210,000	40,000	20,000	120,000

Note: Listed number are approximate values based on preliminary tests.




Produced Water Pretreatment

- Produced water pretreatment by coagulation/sedimentation, lime softening, filtration, activated carbon adsorption, and ion exchange treatment

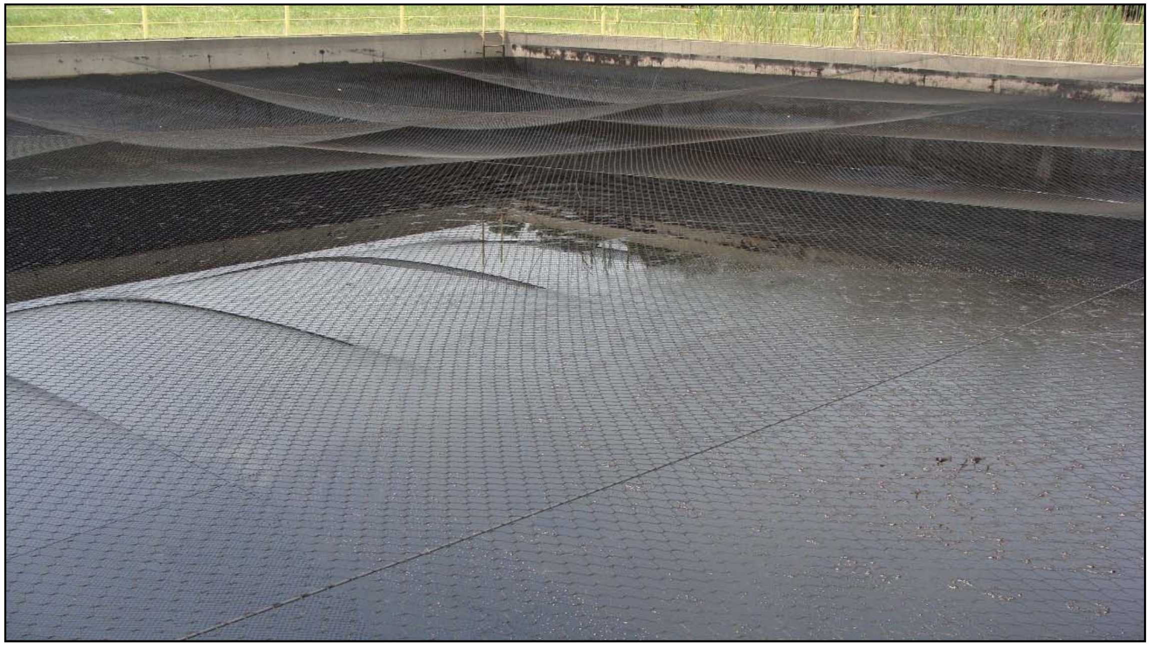


Produced Water Treatment

- 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 two stages



Summary and Conclusions

- 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
- Using the lab-scale SC desalination system, we demonstrated rapid salt precipitation at SC conditions by reducing TDS from 200,000 ppm to ~ 100 ppm
- Various carbon membranes for SC desalination are developed
- Steam polishing from ~100 ppm to < 1 ppm is demonstrated by single stage treatment. It is also possible to achieve < 10 ppb level in two polishing stages
- Work is progress to treat different produced water samples to high purity level

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 Application for Membrane Distillation." Carbon 2016 (under revision).
- Provisional Patent Application: Seyed Dastgheib, Ali Ashraf, Hafiz Salih, SungWoo Nam. "Robust Carbon Nanotube Membranes and Methods of Making the Same", December 11, 2015, Serial number: 62/266,171.
- 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.
- 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, on February 25, 2016.
- 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

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  - U.S. Department of Energy, National Energy Technology Laboratory (Cooperative Agreement DE-FE0024015)
  - Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute (Grant 15-US-5)
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- Project contact information

  - Seyed A. Dastgheib (Principal Investigator, ISGS/UIUC): seyed@Illinois.edu