COHO - Utilizing Waste Heat and Caron Dioxide at Power Plants for Water Treatment

DE-FE0024057

Porifera

(subcontract to Idaho National Laboratory)

INL: **Aaron D. Wilson,** Chris Orme

Porifera: Jen Klare, Ravindra Revaneur, Charlie Benton, Erik Desormeaux, Olgica Bakajin*

April, 2016

www.inl.gov

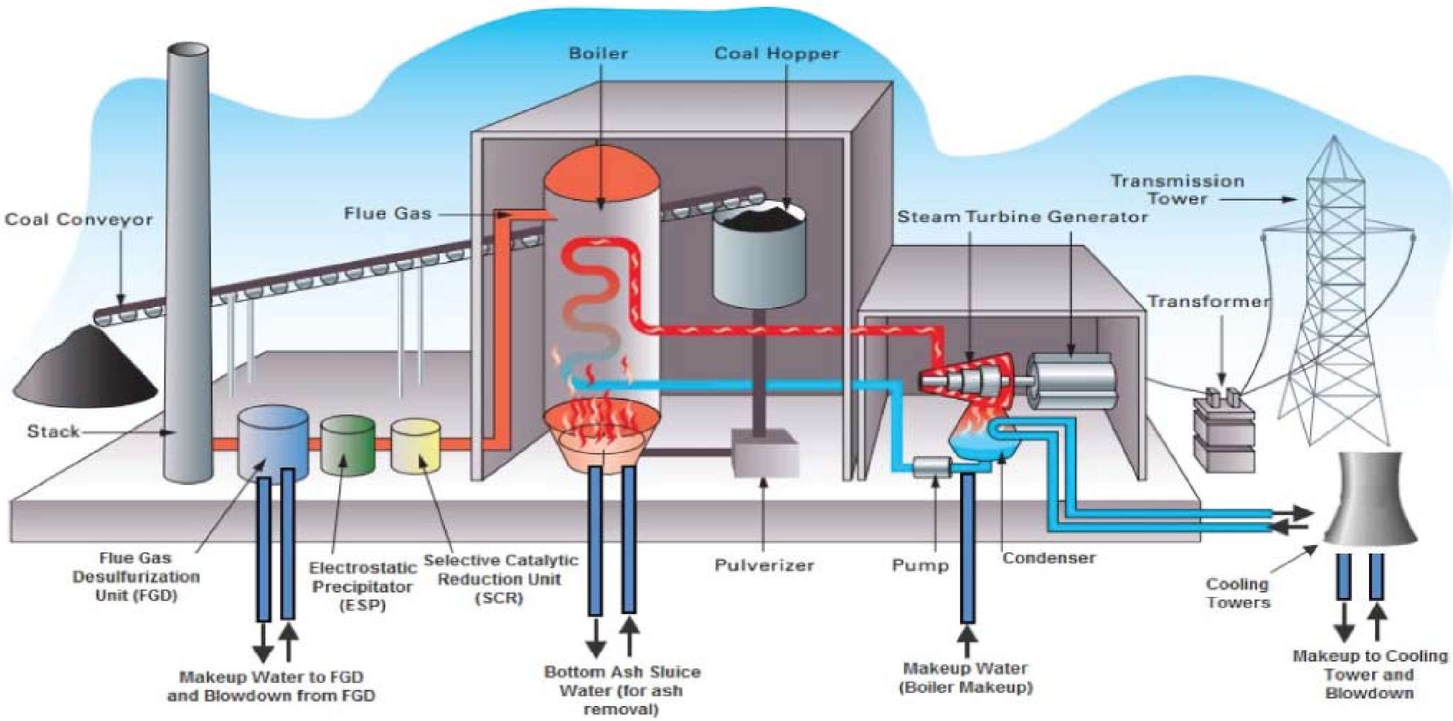
Idaho National Laboratory

Impact of Water on Energy Generation

Water-Smart Power (2013) Union of Concerned Scientists. Select events 2006-2012

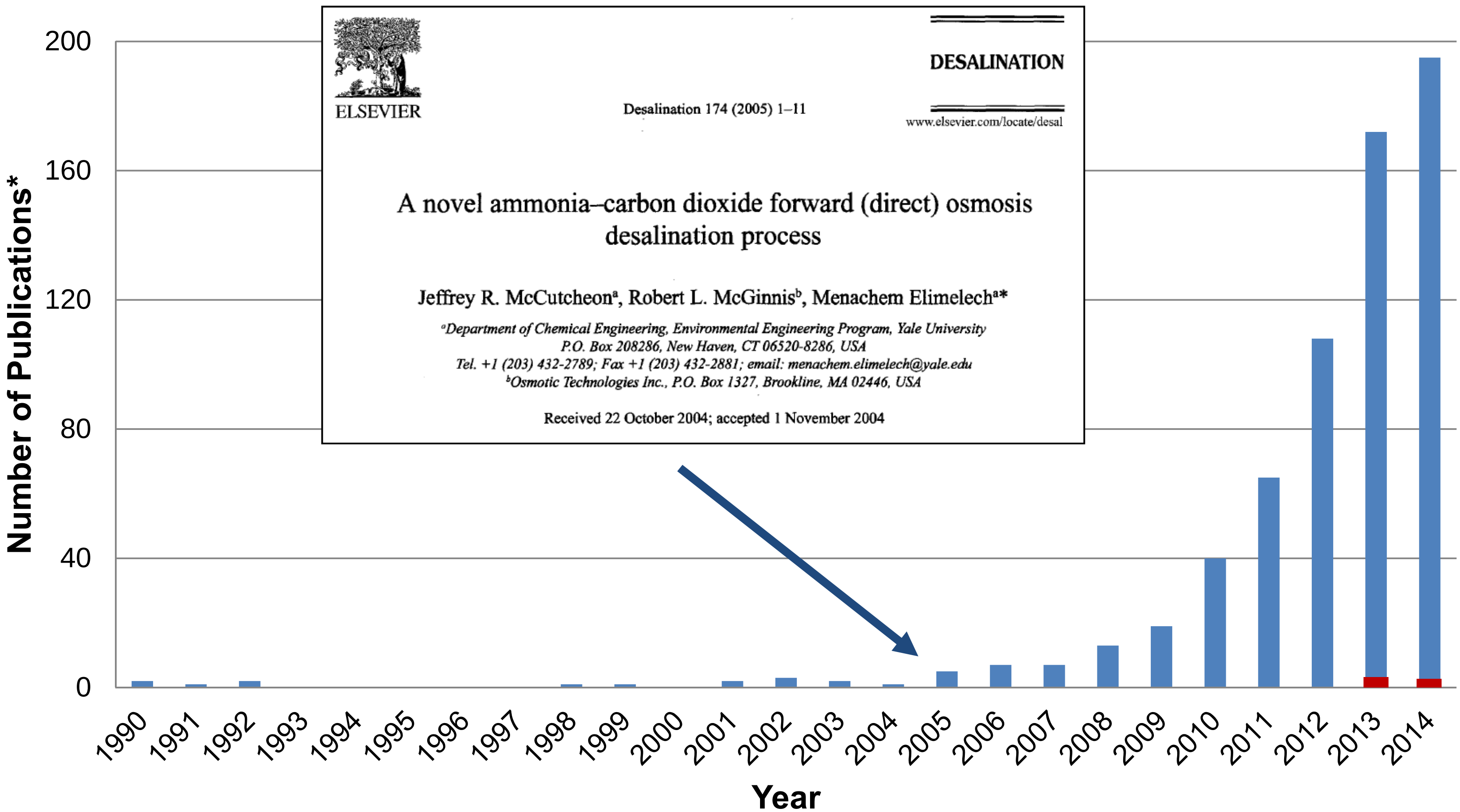
An Opportunity in the Water–Energy Nexus

Can we combine carbon capture with water reuse?



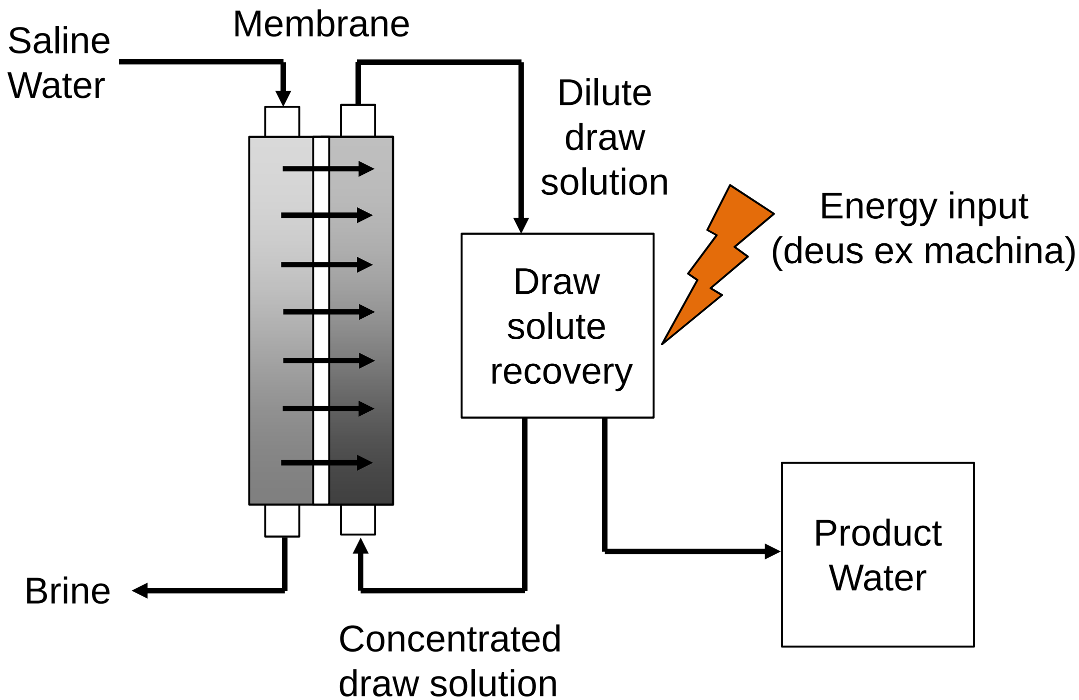
Benefits of COHO: Use flue gas to drive water purification, producing pure CO_2 stream and a new water stream for reuse, with waste heat.

State of the Art
Publications in FO/PRO



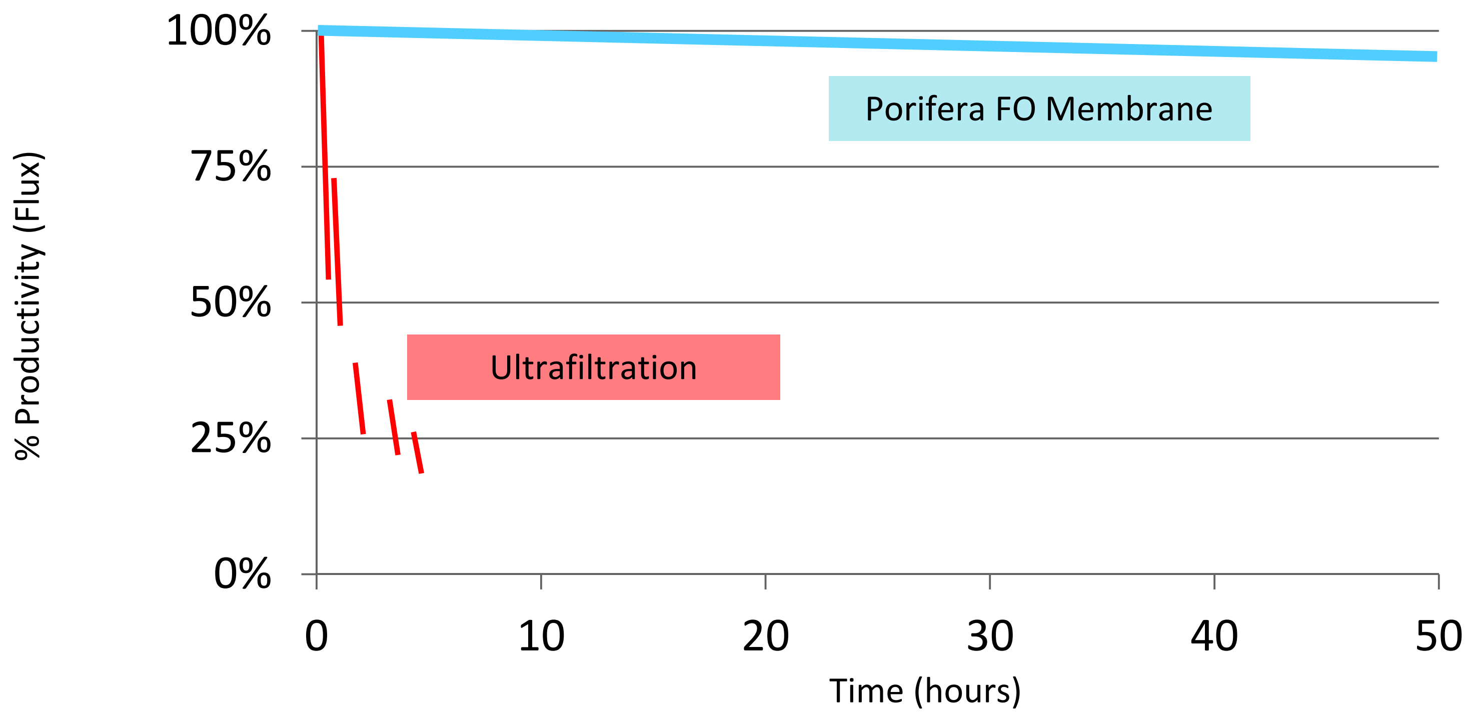
***Topic "forward osmosis" *or* "pressure retarded osmosis" in Web of Science**

State of the Art: Forward Osmosis Introduction



- Forward osmosis membrane flux spontaneous (No energy input)
- Primary process energy requirements delivered during **draw solute recovery**, which can include:
  - Reverse Osmosis,
  - Various Distillation including Membrane Distillation, and
  - Thermal solute separation such as thermolytic solutes (Switchable Polarity Solvents).

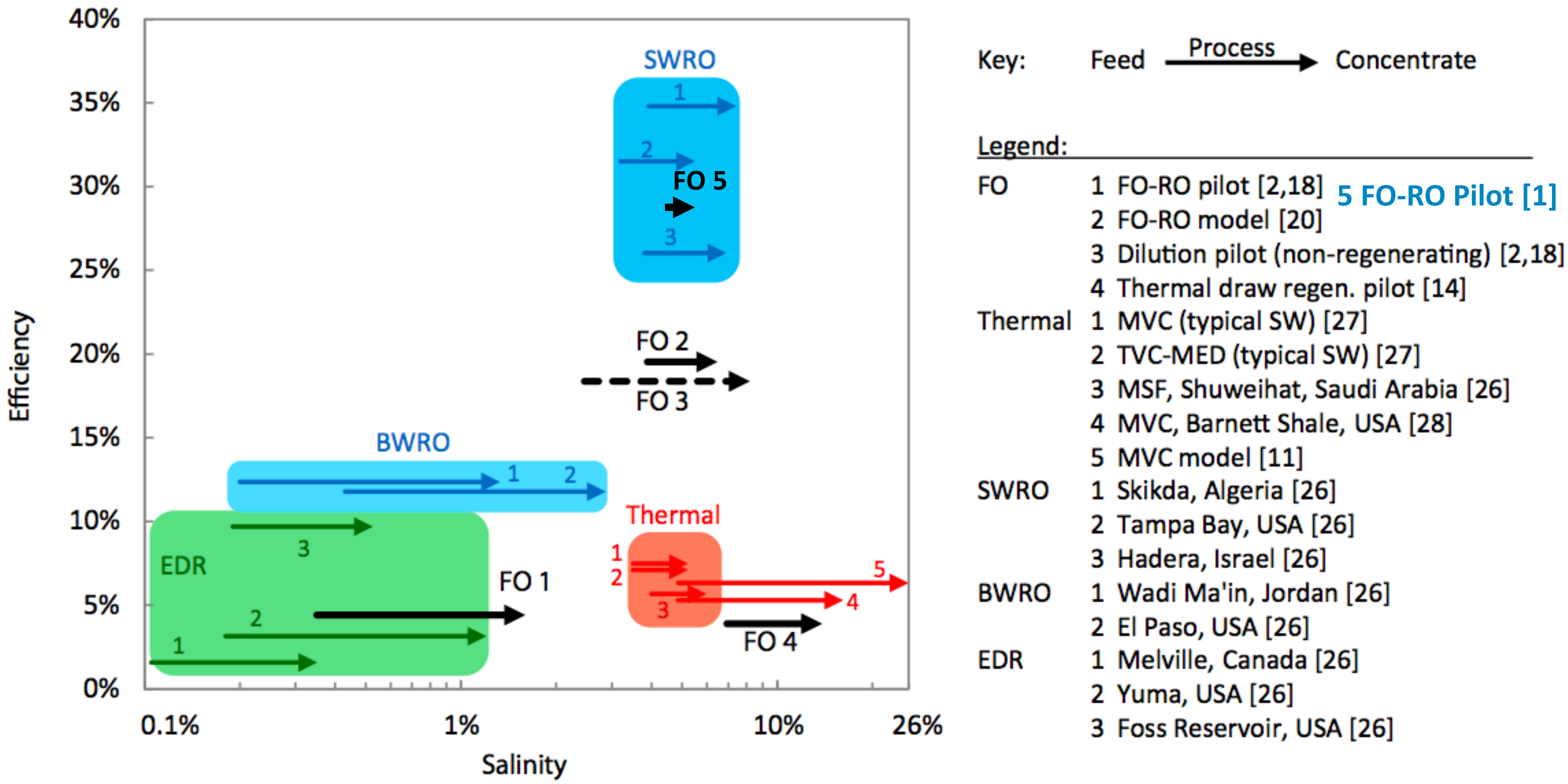
Fouling Resistance



- DARPA "Challenge" Solution: seawater mix contained inorganic salts, algae, humic acid, and arizona fine dust.
- More than 5x lower fouling rate than UF.

Data supplied by Porifera

FO Efficiency



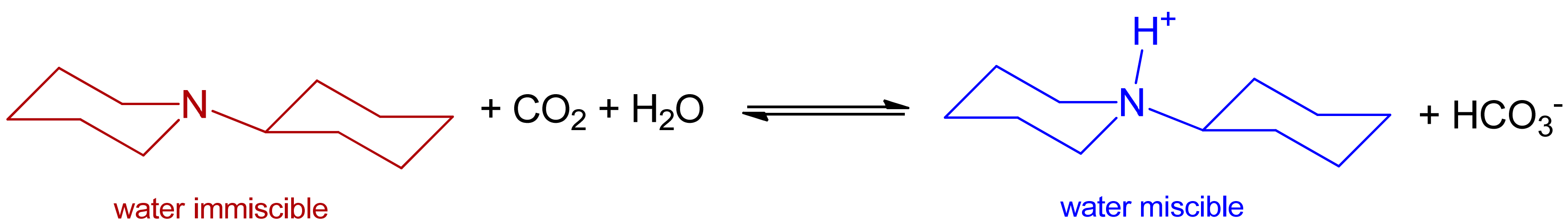
Efficiency = (0.91 kWh/m^3 [2] / 2.81 kWh/m^3)*100 = 33%

FO-RO does not increase energy consumption significantly if the desalination system is designed for energy efficiency!

[1] Lundin, C.D.; Benton, C.; Bakajin, O. AWWA Membrane Technology Conference 2014 Proceedings.
[2] Reimund, K.K.,; McCutcheon, J.R.; Wilson, A.D. Journal of Membrane Science 487 (2015) 240 – 248.
[3] Tow, E.W.; McGovern, R.K.; Leinard, J.H. Desalination 366 (2015) 71 – 79.

Tertiary Amine Switchable Polarity Solvents

- **High concentration in polar form.**
- **Can be mechanically separated once switched to non-polar form.**



1-cyclohexylpiperidine

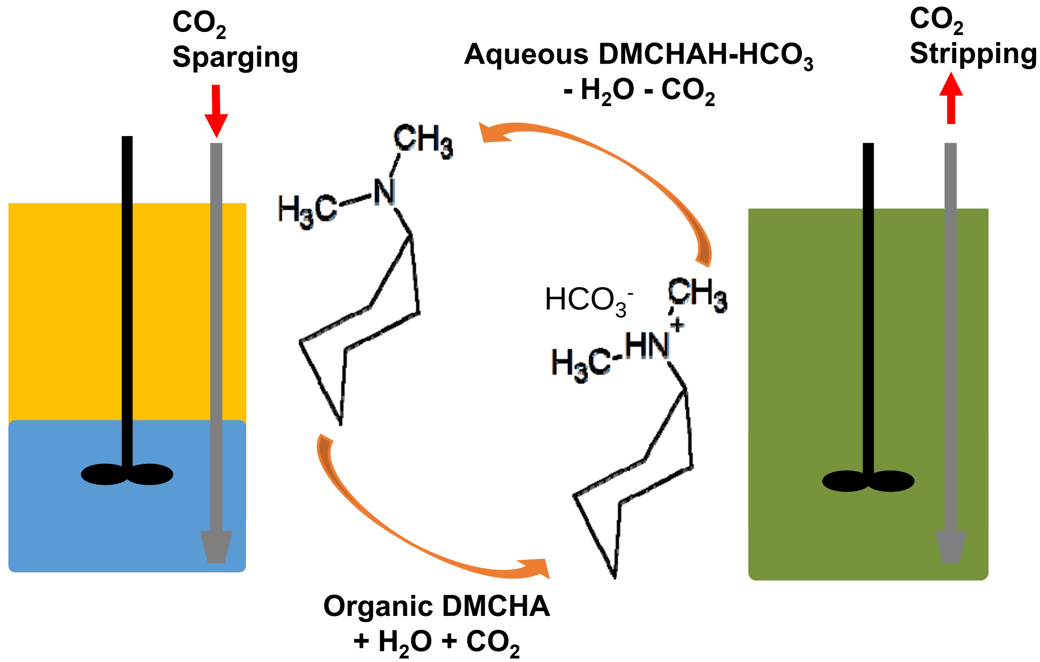
- 2nd Generation SPS Draw Solute.
- Identified with Quantitative Structural Activity Relationship (QSAR) model.
- Material balances non-orthogonal (interdependent) draw solute properties.

1-cyclohexylpiperidenium bicarbonate

- Maximum concentrations over 70 wt%.
- Has an osmotic pressure over 500 atm which should extract water from a fully saturated brine solution (6.14 mol/Kg ~370 atm), precipitating NaCl solid.

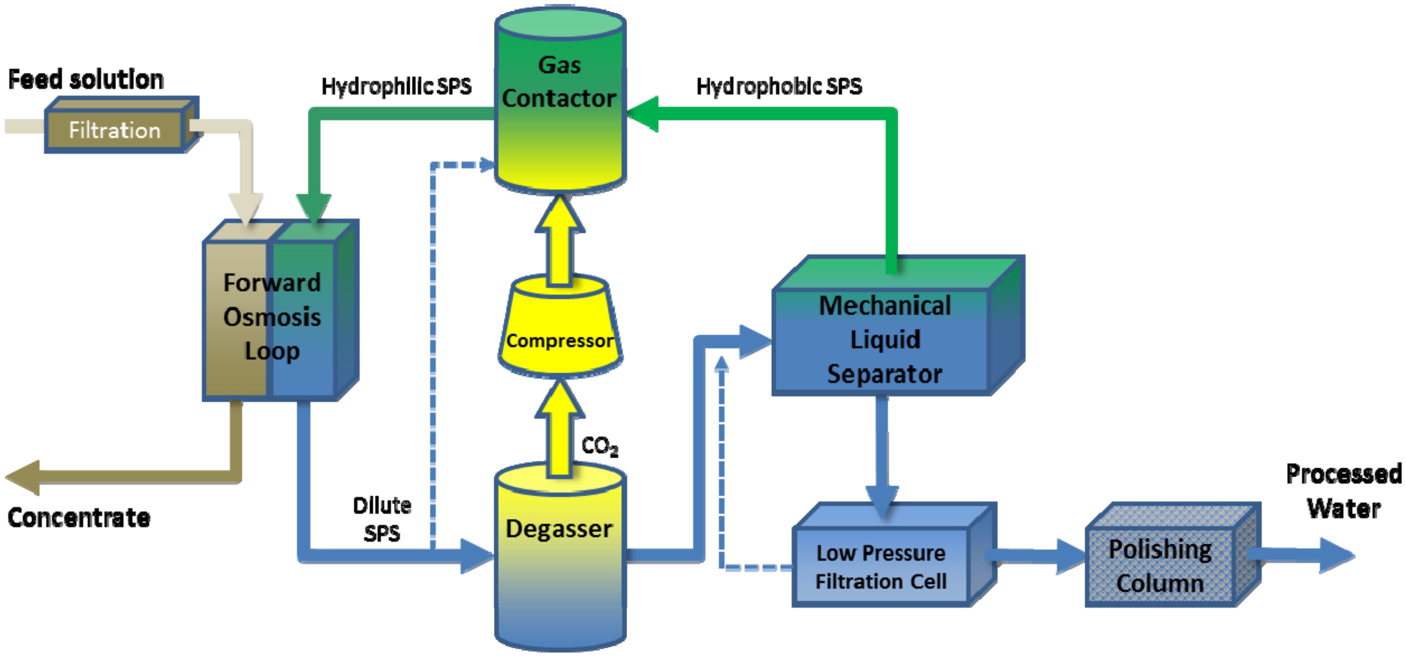
Orme, Wilson, 1-Cyclohexylpiperidine as a Thermolytic Draw Solute for Engineered Osmosis. *Desalination* 2015. *371*, 126-133
McNally, Wilson Density Functional Theory Analysis of Steric Impacts on Switchable Polarity Solvent (SPS) *Journal of Chemical Physics B* 2015, *119*, 6766-6775.
Wilson, Orme Concentration Dependent Speciation and Mass Transport Properties of Switchable Polarity Solvents *RCS Advances* 2015, *5*, 7740-7751
Wilson, A. D.*; Stewart, F. F. Structure-Function Study of Tertiary Amines as Switchable Polarity Solvents *RCS Advances* 2014, *4*, 11039-11049.

Tertiary Amine Switchable Polarity Solvents



- High concentration in polar form.
- Can be mechanically separated once switched to non-polar form.

Proposed Switchable Polarity Solvents Forward Osmosis System



Thermally driven process with the majority of energy input at the CO_2 degasser

Wilson; Stewart; Stone **Methods and Systems for Treating Liquids Using Switchable Solvents.** US20130048561 A1.
Wilson; Stewart; Stone **Methods and Systems for Treating Liquids Using Switchable Solvents.** WO2013032742 A1.

Stone; Rae; Stewart; Wilson **Switchable Polarity Solvents as Draw Solutes for Forward Osmosis** *Desalination* **2013**, *312*,124-129.

High Salinity, High Fouling, High Recovery

- Pre-treatment can be the bulk of the water treatment cost.
  - → FO requires little to no pre-treatment.
- Disposal of the waste brine can be the bulk of the water treatment cost.
  - → High recovery even from high salinity feeds.
- State of the art methods are reaching thermodynamic limits but the cost is still too high.
  - → Thermally driven processes uses lower cost energy than electrically driven processes.

SPS Used in Carbon Capture - Hu

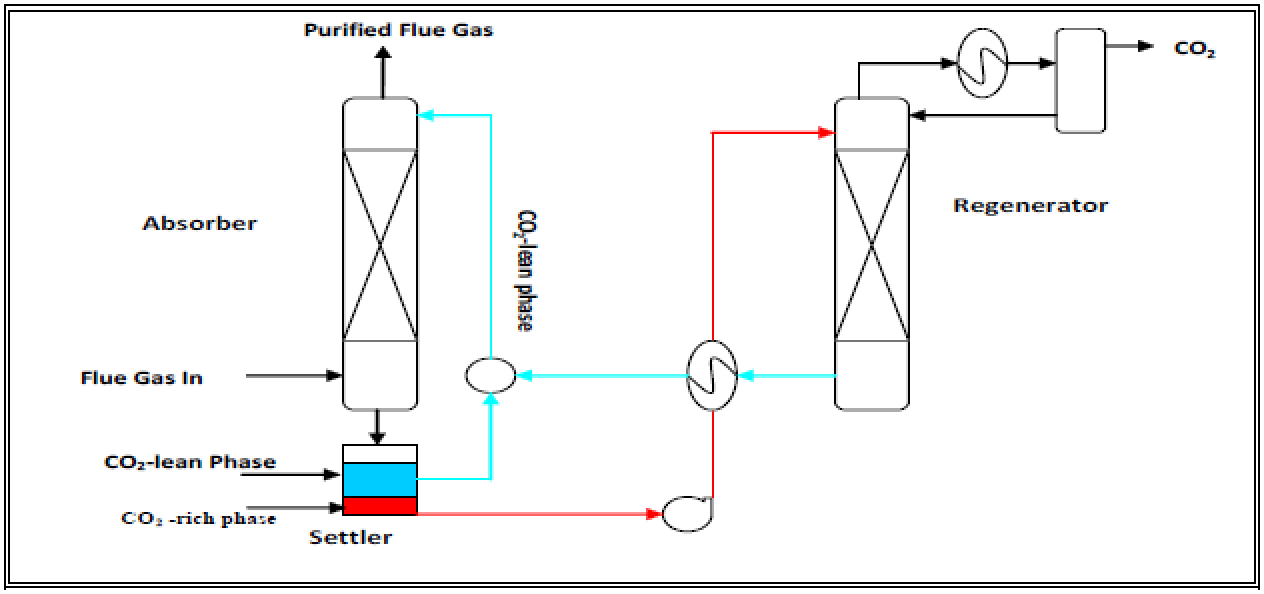


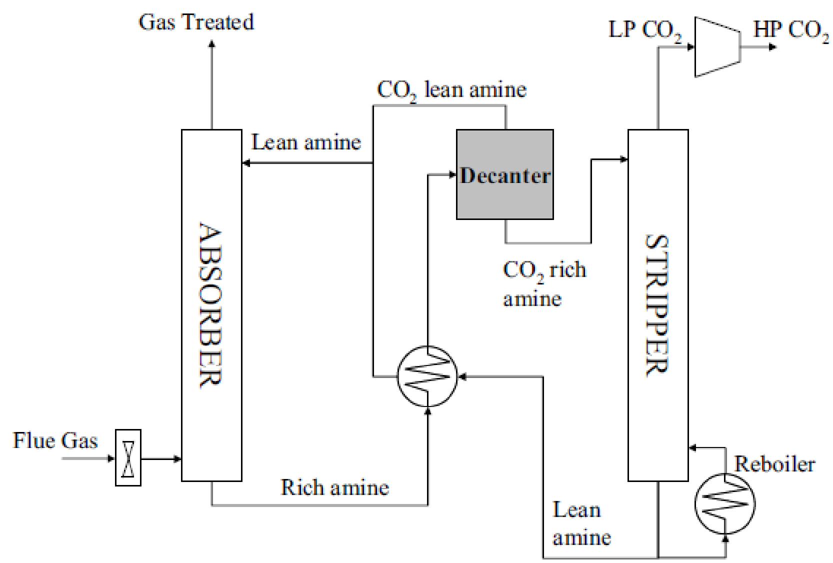
Figure 1: Concept Flow Diagram of Phase Transitional Absorption

- CO_2 Capture from Flue Gas by Phase Transitional Absorption - Liang Hu (Hampton University, 3H Company) DE-FG26-05NT42488 (PM Isaac Aurelio)
- Post-Combustion CO_2 Capture for Existing PC Boilers by Self-Concentrating Amine Absorbent - Liang Hu (3H Company) DE-FE0004274 (PM Morgan Mosser)

Hu, L. United States Patent: 7541011 - Phase Transitional Absorption Method. 7541011, June 2, 2009.

SPS Used in Carbon Capture – DMX^{TM} Process

a)



b)

Solvent	DMX-1
Energy consumption	2.3 GJ/t CO_2
CO_2 output	110 bar (a)
Absorber packing	Mellapak 250X
Stripper packing	IMTP 50
Reboiler type	Kettle
Heat exchanger type	Gasketed Plates

Figure 6 : a) Simplified process flow diagram of the IFP Energies nouvelles DMX^{TM} process and b) corresponding main process characteristics.

- Process Developed at IFP Energies nouvelles (French public-sector research)

Raynal, L.; Alix, P.; Bouillon, P.-A.; Gomez, A.; de Nailly, M. le F.; Jacquin, M.; Kittel, J.; di Lella, A.; Mougin, P.; Trapy, J. The DMX^{TM} Process: An Original Solution for Lowering the Cost of Post-Combustion Carbon Capture. *Energy Procedia* **2011**, *4*, 779–786.

SPS Used in Carbon Capture – Zhang

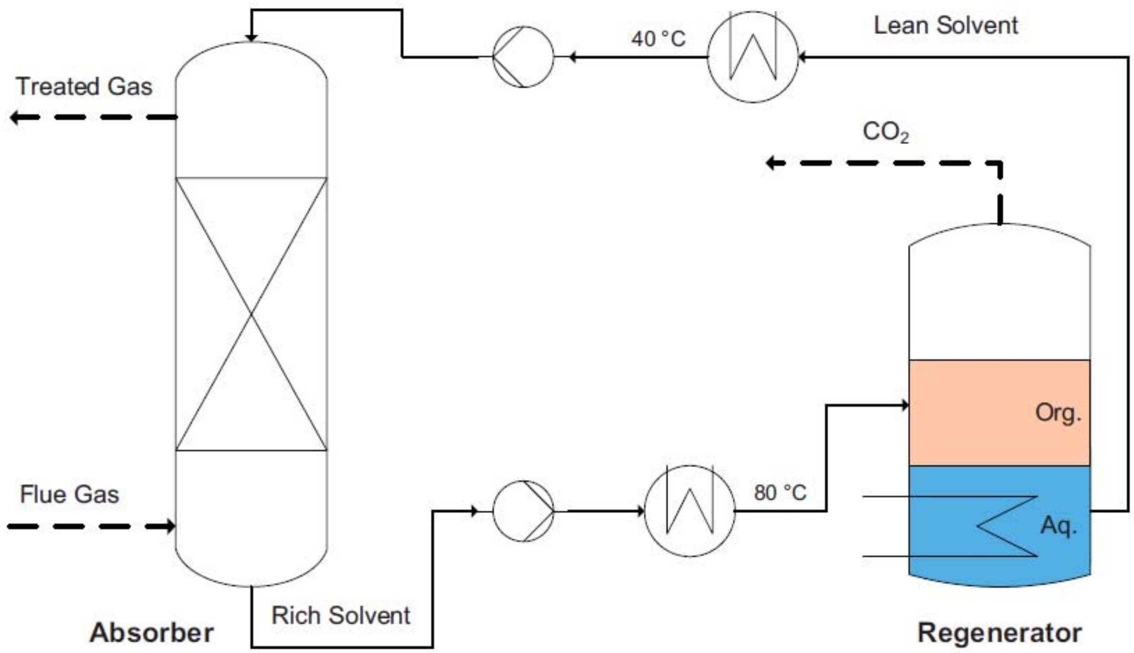


Fig. 1 – Basic process flow diagram of TBS system.

- Developed at the Technical University of Dortmund, Germany

Zhang, J.; Qiao, Y.; Agar, D. W. Intensification of Low Temperature Thermomorphic Biphasic Amine Solvent Regeneration for CO2 Capture. *Chemical Engineering Research and Design* **2012**, *90*, 743–749.

Proposed COHO System

The draw solution purifies wastewater (**1**) using osmotic potential to drive water across a selective membrane. (**2**) The draw solution is generated using carbon dioxide from flue gas to switch the draw solute to the miscible aqueous phase. Carbon dioxide (**3**) is released and clean water is produced (**4**) by using low-grade heat, switching the draw solute (**5**) back to its original immiscible phase for mechanical separation.

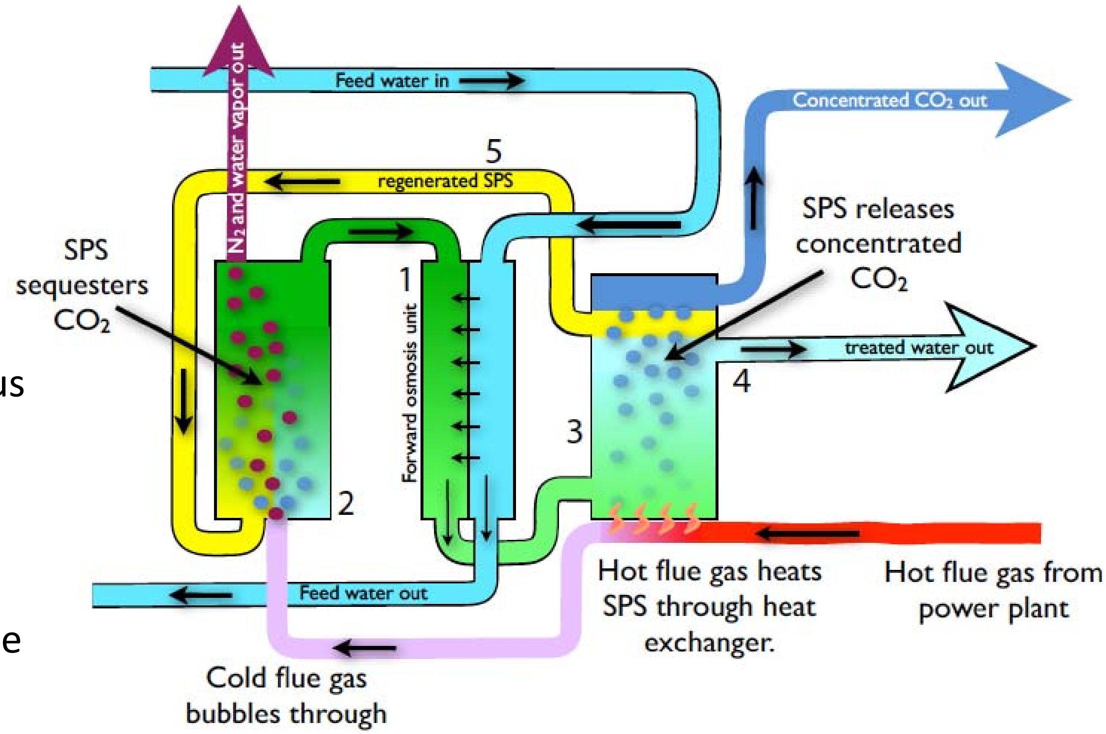
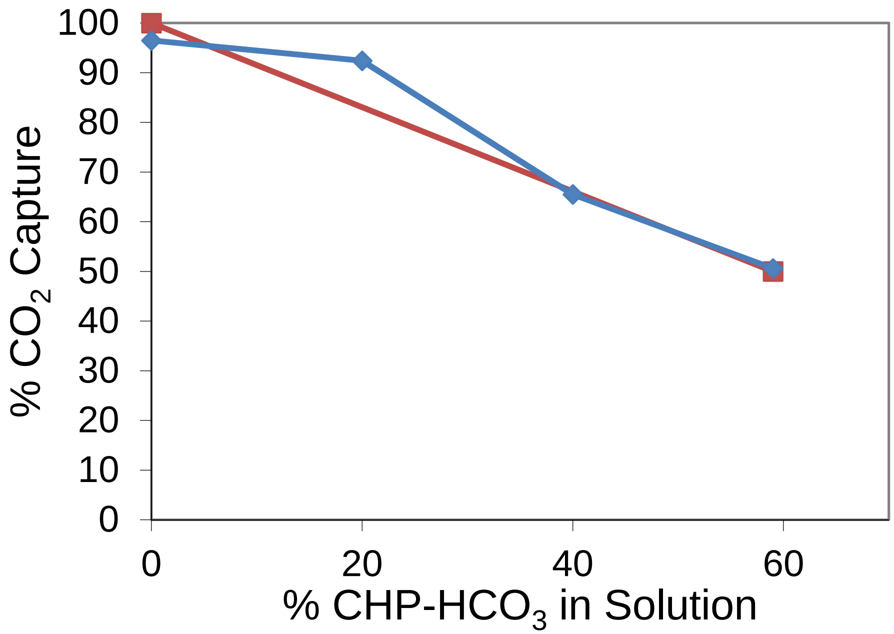


Figure 1. Schematic of COHO draw phase switching.

CO_2 Capture form simulated flue gas



- CO_2 capture from a simulant flue gas (10% CO_2 90% N_2).
- Need to capture 75% of the CO_2 feed the solution while generating a 60 wt% solution (osmotic pressure ~325 atm).
- Simplest system possible; gas bubbled through a stirred solution.

Gas Contactor Investigations

Prior Work (not funded by GTO) – Batch process, long time to full conversion

Glass Gas Wash Bottle

- Pressure: ~ambient
- Volume: ~0.5 L
- Full Conversion
  - Batch
  - ~2 weeks

Analytical System

- Pressure: ~ambient
- Volume: ~0.015 L
- Full Conversion
  - Batch
  - ~3 days

FY15 Work (funded by GTO) – Moved to continuous process with markedly reduced time to full conversion

Pressure system

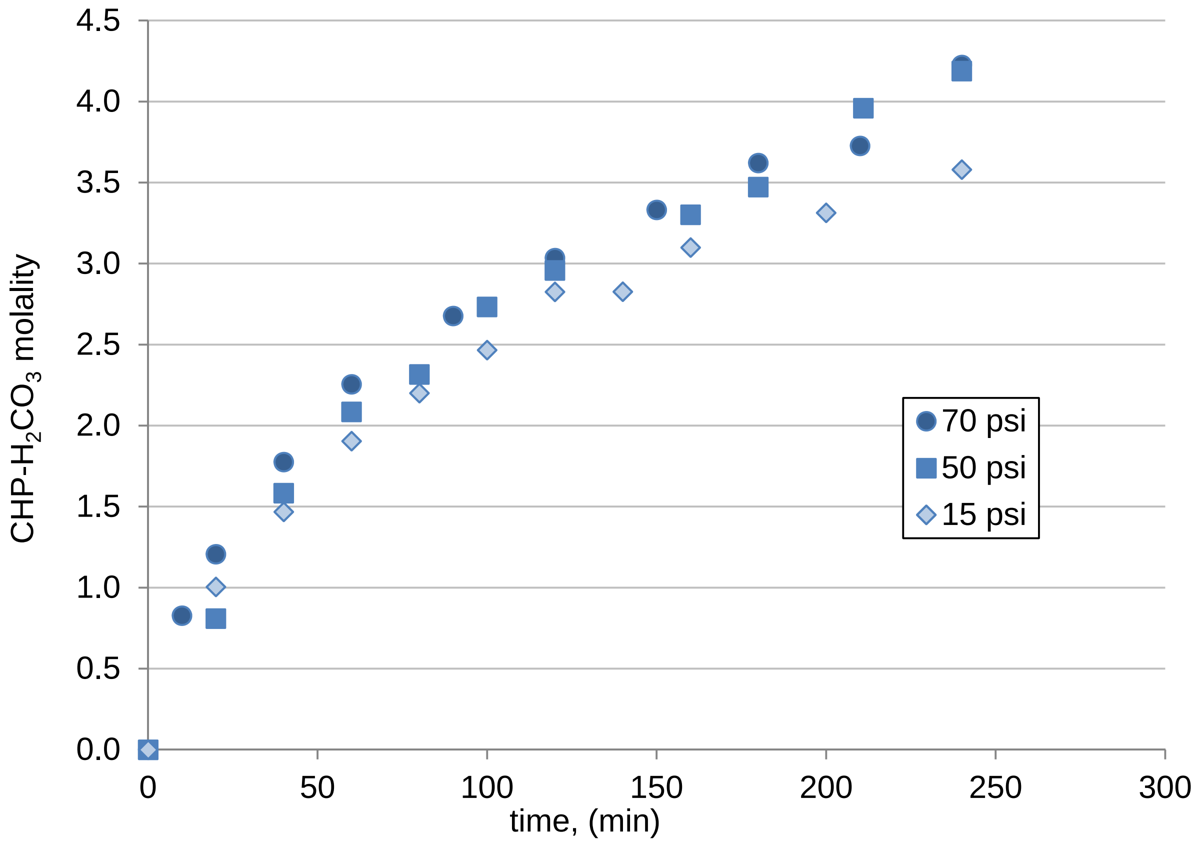
- Pressure: ~40 psi
- Volume: ~0.5 L
- Full Conversion
  - Batch
  - ~3 hours

2nd Gen Gas Contactor

- Pressure: ~ambient
- Volume: any
- Full Conversion
  - Continuous
  - ~0.5 L/hour
  - Easily scalable

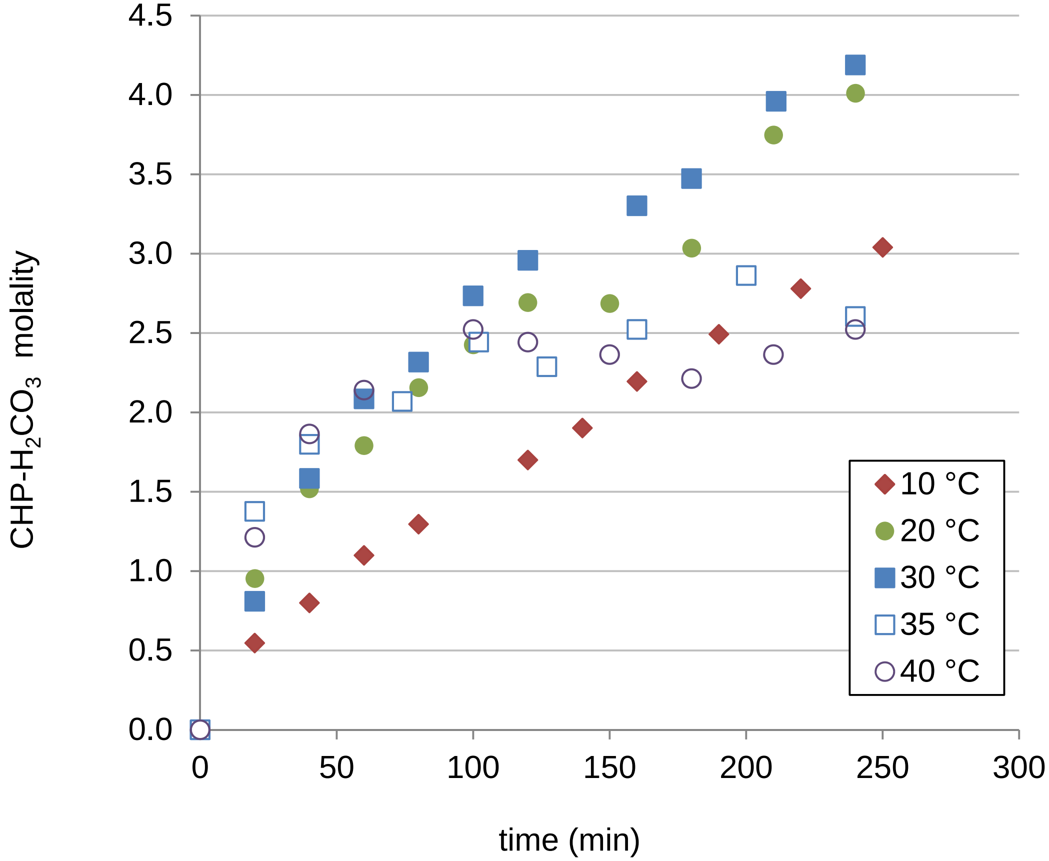
Module Scale Gas Contactor

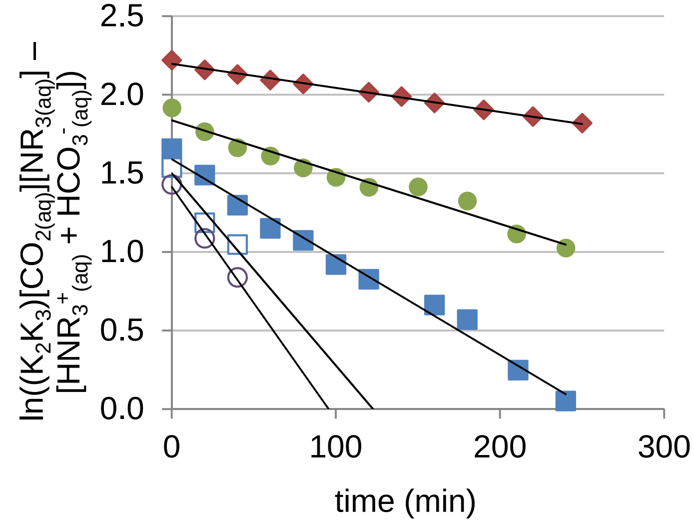
Gas Contactor Pressure/Mixing Study

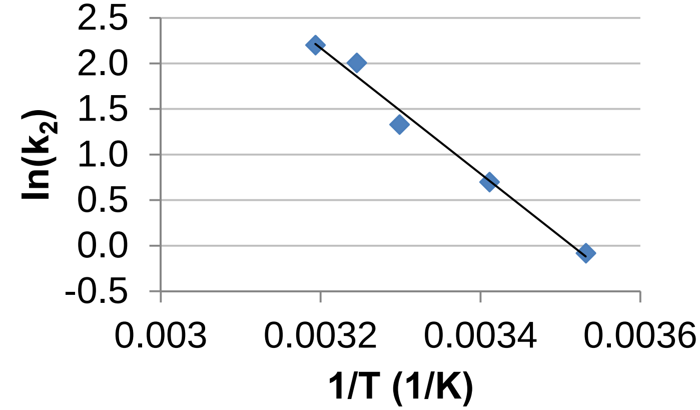


- Multiple forms of mass transfer.
  - Gas pressure and flow rate appear to play limited roles.
  - Surface area/module design influences reaction rate.

Gas Contactor Temperature Study



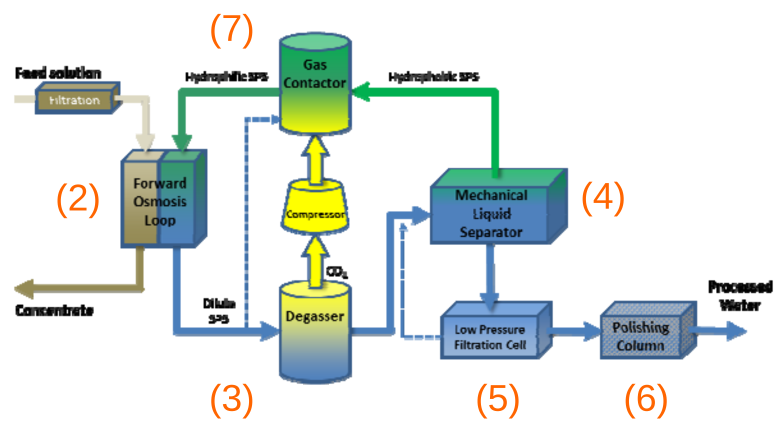




- Process in part chemical reaction rate limited
  - Sensitive to temperature and solution pressure.

Components of Process Development

1. Working Fluid Selection
2. Forward Osmosis Membrane and Module Selection
3. Degasser Optimization
4. Mechanical Liquid Separator
5. Low Pressure Filtration Cell
6. Polishing Column Material Selection and Design
7. Gas Contactor Design
8. System Design and Testing
9. Process monitoring mythology



System Design and Testing

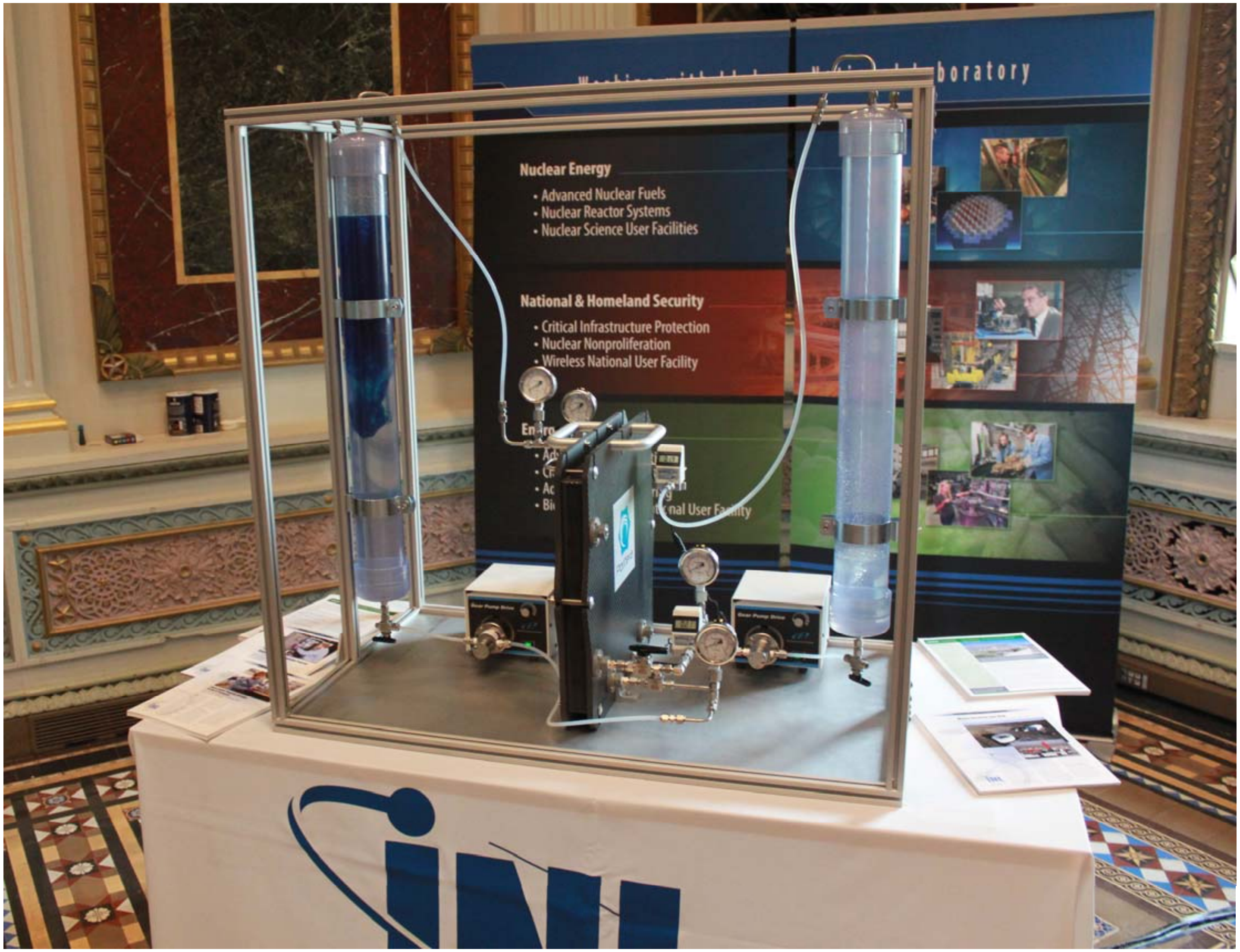
Initial scale (2011)

Long Term Module Testing (2015)

Lab scale (2014)

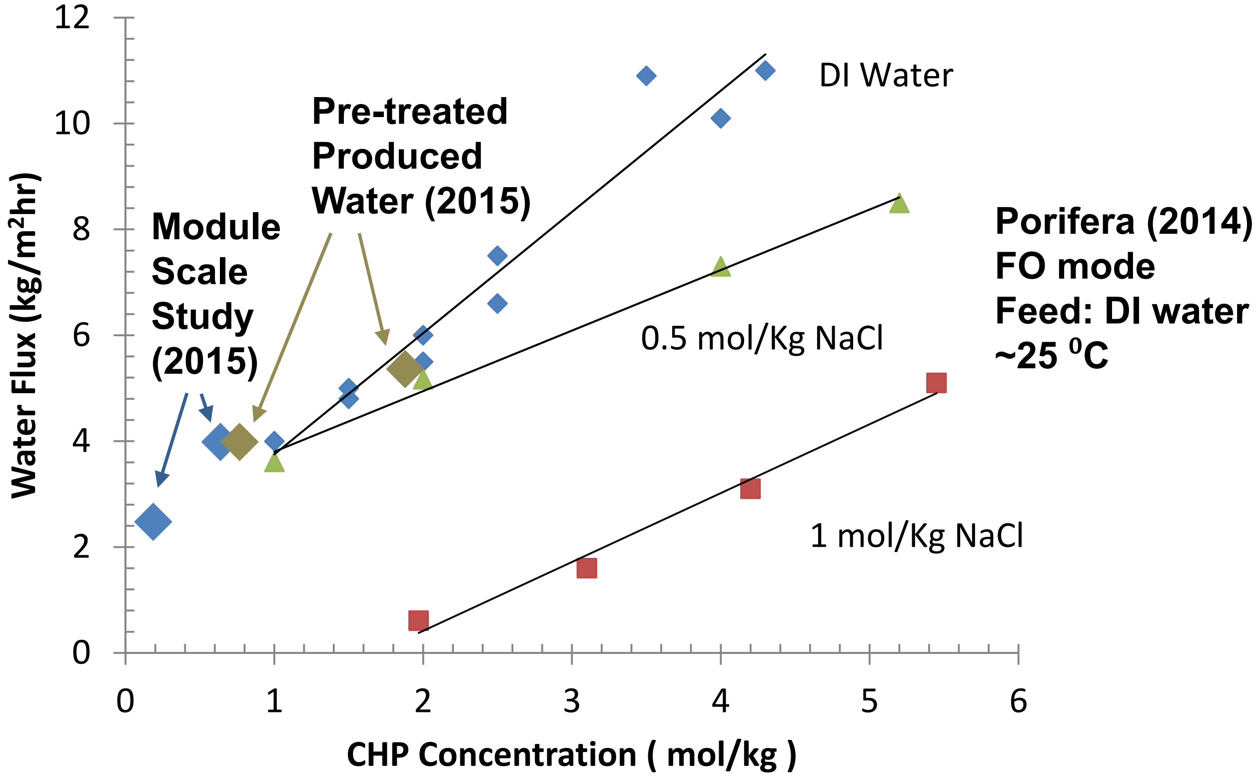
10 gallon per hour pilot system (2015)

White House Water Summit 2016
INL FO Module Demonstration



CHP flux over a range of concentration feeds

Christopher Orme

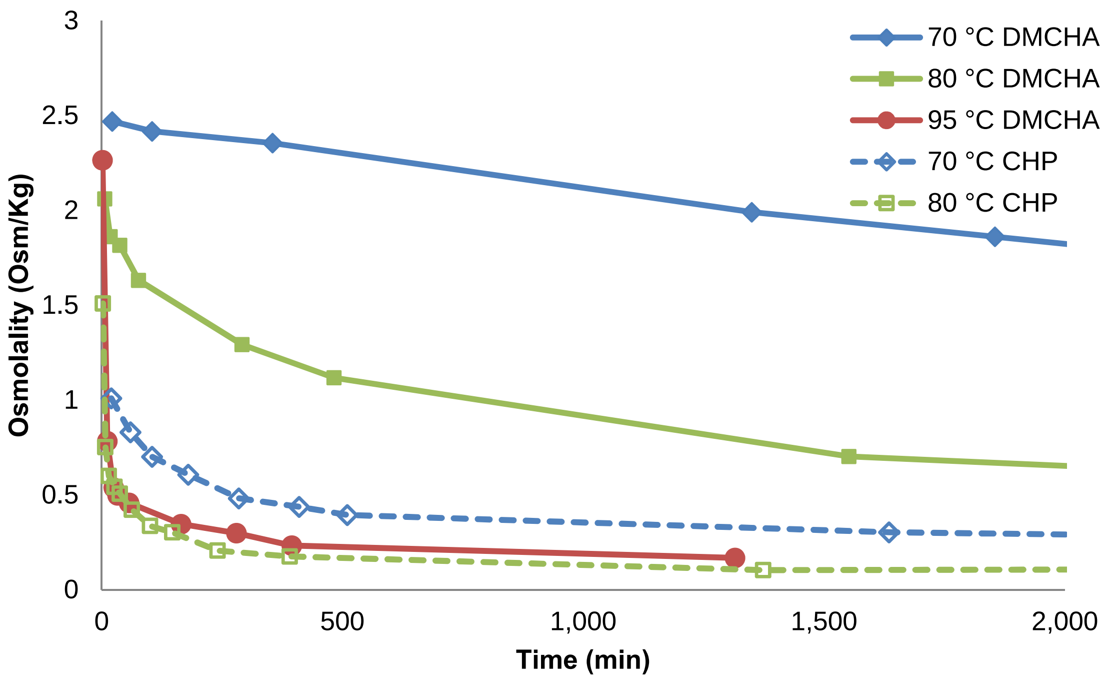


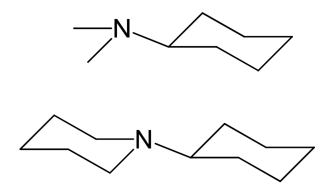
- FO flux tests against DI water can have limited implications on FO performance against a feed with real world osmotic pressures. Thus tests against 0.5 and 1.0 mol/Kg NaCl feed solutions.
- There is a modest flux attenuation for CHP vs DMCHA attributed to a shift is rheological properties associated with moving from a 8 to an 11 carbon amine.

Degassing Experiments

water miscible → water immiscible

$$HNR_3^+ + HCO_3^- \xrightarrow{\Delta} NR_3 + CO_2 + H_2O$$





- N,N-Dimethylcyclohexylamines (DMCA) requires 95 °C to achieve a good degassing and phase separation at ambient atmospheric pressures.
- Gen 2 can be degassed at 70 °C under ambient atmospheric pressures or less with limited amount of vacuum.
- Gen 2 CHP draw solution to <2wt% with 80 °C and <2 psi vacuum.

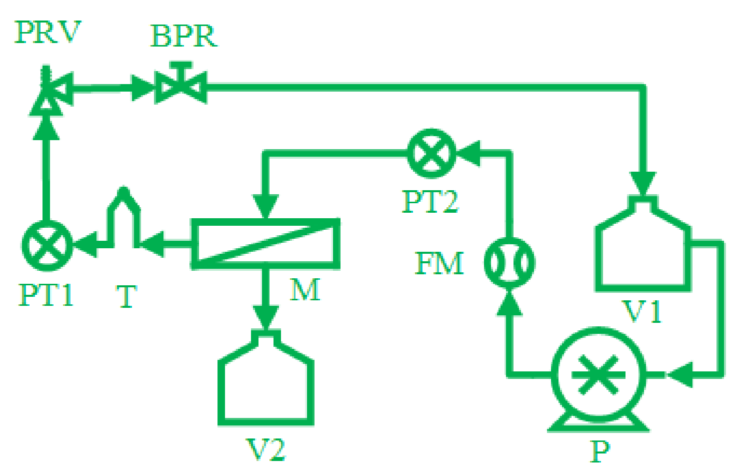
CHP = 1-Cyclohexylpiperidine

Orme; Wilson **1-Cyclohexylpiperidine as a Thermolytic Draw Solute for Osmotically Driven Membrane Processes**. *Desalination* **2015**, *371*, 126–133.

Mechanical Liquid Separator – Vertical Decanter

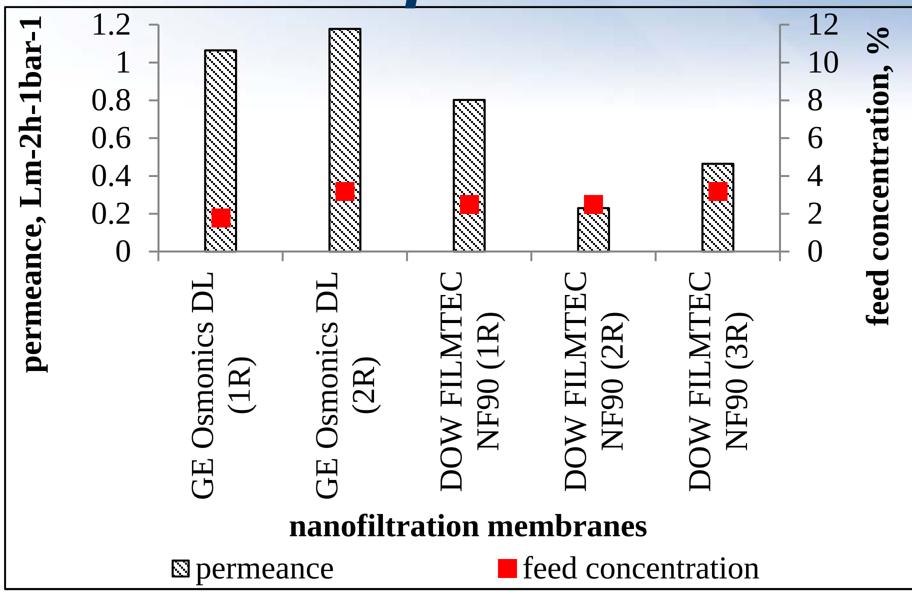
Low pressure osmotic filtration

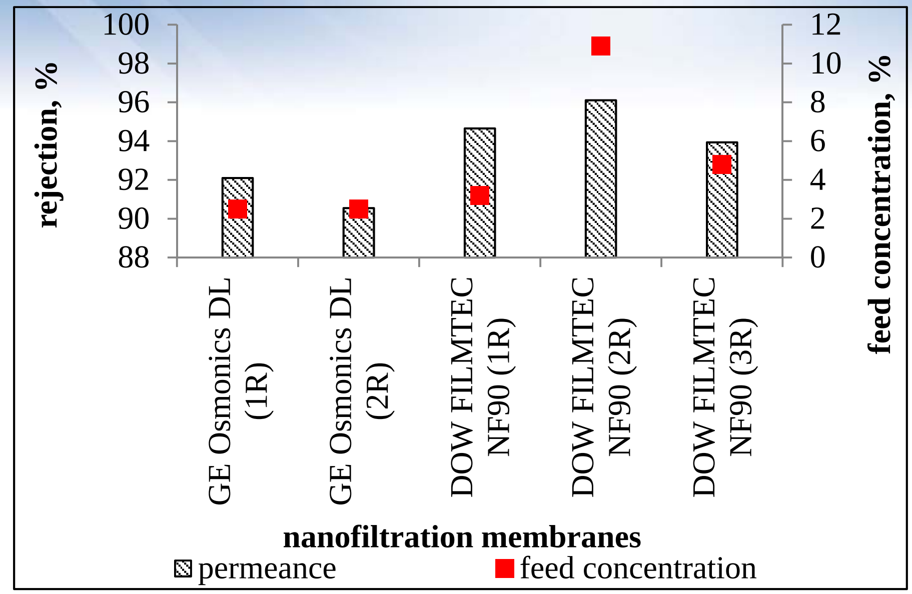
- This is required to remove and recycle trace bicarbonates from degassed SPS solution.
- Tested commercially available NF/RO membranes for chemical compatibility and selectivity

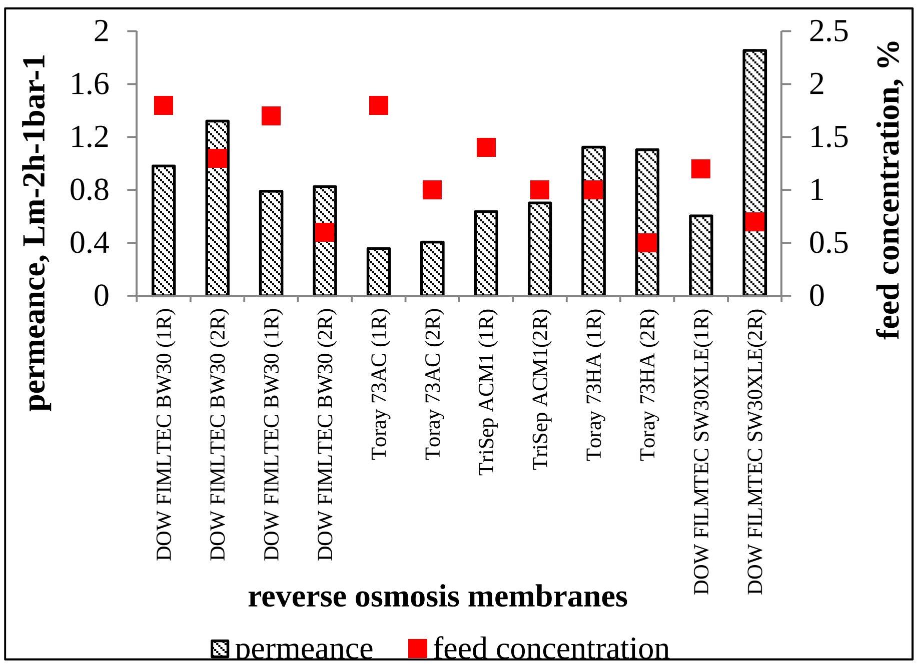


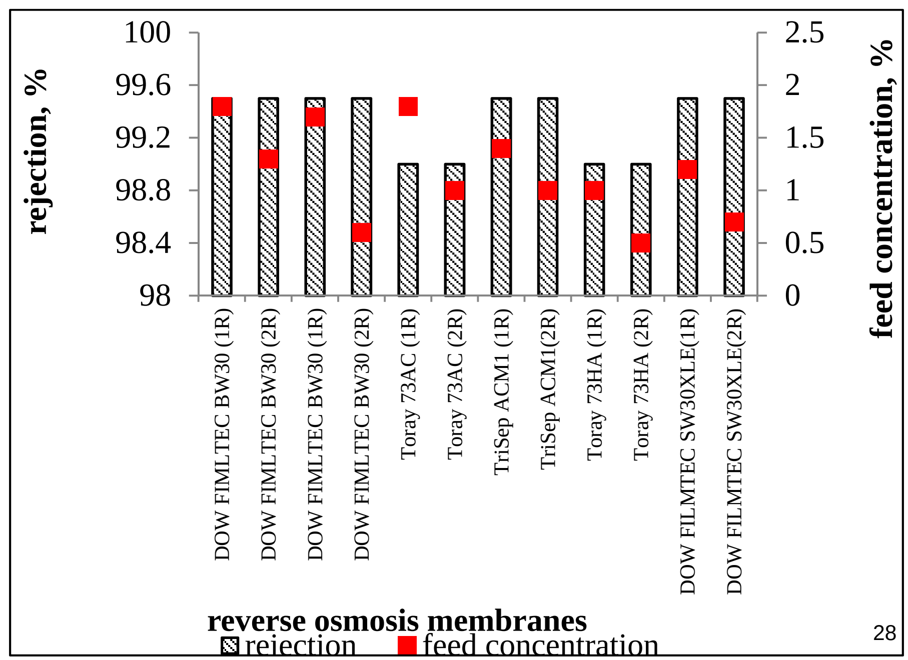
BPR1	Back pressure regulator	FM	Flow meter	M	Membrane P Pump
PRV	Pressure relief valve	PT1	Pressure transducer 1	PT2	Pressure transducer 2
T	Thermocouple	V1	Feed vessel	V2	Permeate vessel

NF/RO Coupon tests









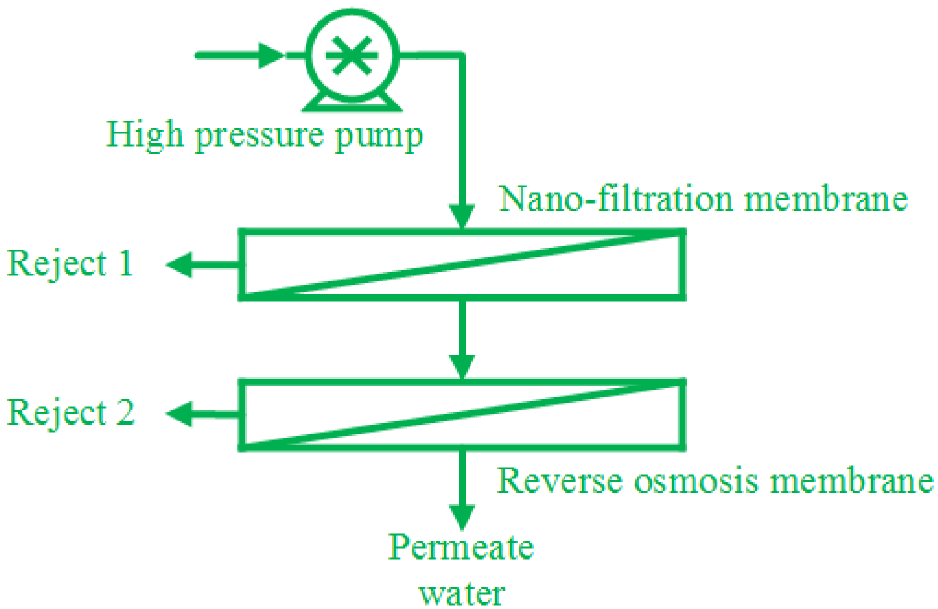
NF Module & TW30 Module Test System

- Less than 100 psi is expected to remove greater than 5 nines of CHP draw.

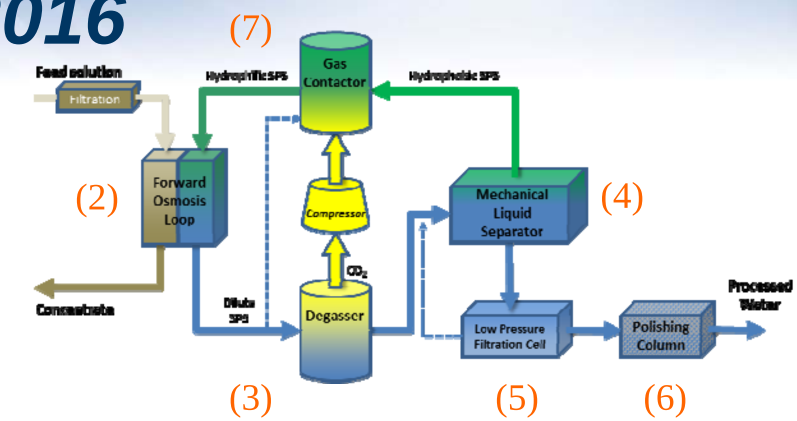
NF and RO performance Metrics

- Two staged NF/RO membrane system

	Permeance L·m²/(hr·bar)	Rejection
DOW NF90 module	5.5	99.4%
DOW TW30 module	12.0	97.0%

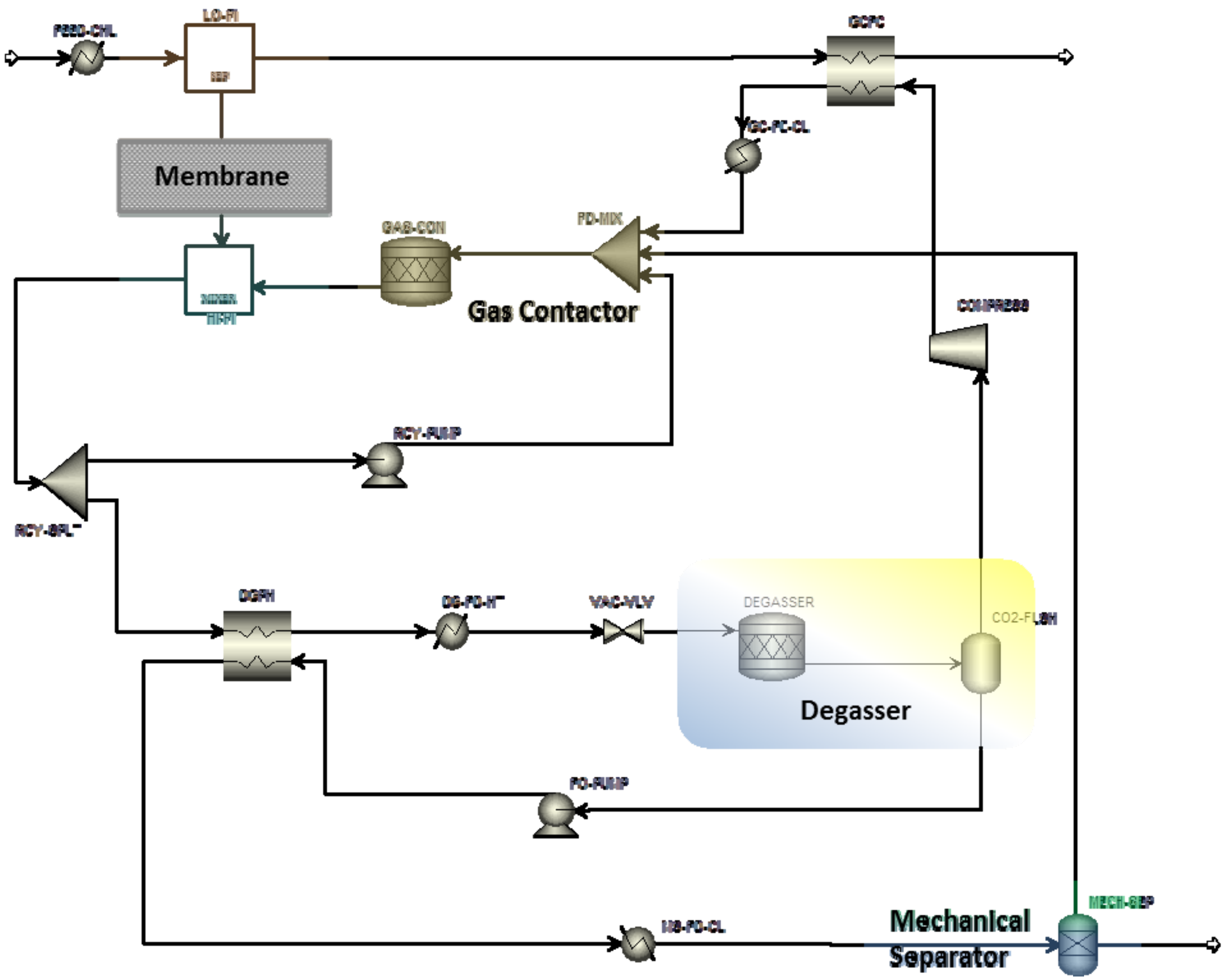


SPS FO Project Status Mar 2016



1) **Working Fluid Selection**
   - Cyclohexylpiperidine (CHP) selected.
2) **Forward Osmosis Membrane and Module Selection**
   - Porifera modules are compatible.
   - Long term studies underway.
3) **Degasser Optimization**
   - Functional for the reduction of CHP draw solution to <2wt% with 80 °C and <2 psi vacuum.
4) **Mechanical Liquid Separator**
   - Model decanter to be tested with CHP solutions.
5) **Low Pressure Filtration Cell**
   - NF90 and TW30 appear to be optimal membranes for CHP draw solution <3wt%. At module scale <100 psi is expected to be required for >5 nines removal of CHP draw.
6) **Polishing Column Material Selection and Design**
   - Useful activated carbons identified.
7) **Gas Contactor**
   - Requires <15 psi for very rapid industrial relevant gas contactor.
8) **System Design and Testing**
   - Purchased FO/RO system.
   - Testing with industrial water.
9) **Process monitoring methodology**
   - Not ideal but between osmometry, conductivity, gas chromatography, and FTIR the effort is workable.

ASPEN Evidence for SPS FO cost competitiveness

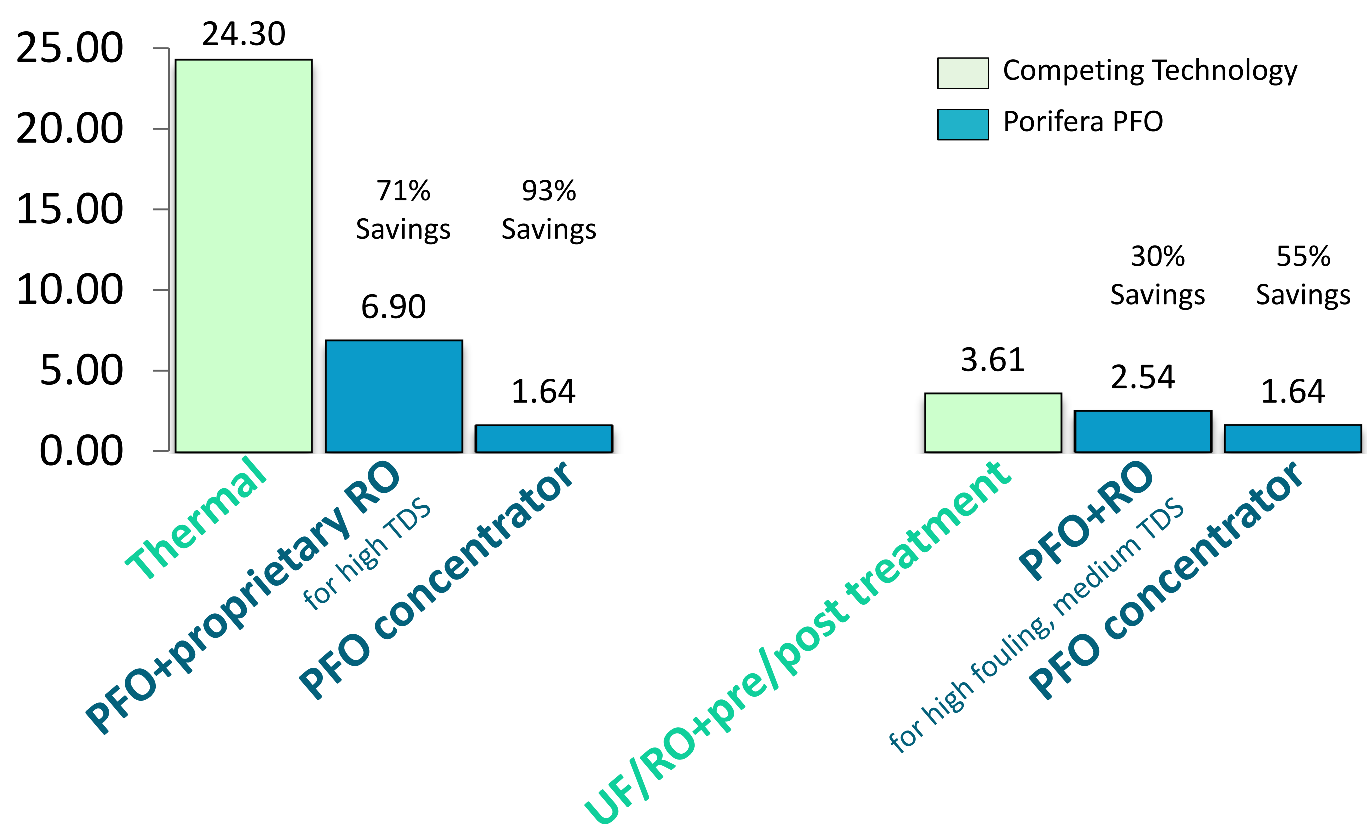


Wendt, D. S.; Orme, C. J.; Mines, G. L.; Wilson, A. D.* Energy requirements of the switchable polarity solvent forward osmosis (SPS-FO) water purification process. *Desalination* 2015, 374, 81-91, DOI:10.1016/j.desal.2015.07.012

Up to 93% Savings over Existing Technologies

Cost per 1,000 gallons ($)

Assumes 20 year project cost, based on future PFO pricing



High Salinity, High Fouling, High Recovery

- Pre-treatment can be the bulk of the water treatment cost.
- Disposal of the waste brine can be the bulk of the water treatment cost.
- State of the art methods are reaching thermodynamic limits but the cost is still too high.

→

- FO requires little to no pre-treatment.
- High recovery even from high salinity feeds.
- Thermally driven processes uses lower cost energy than electrically driven processes.

Acknowledgements

INL Team

- Frederick F. Stewart
- Mark L. Stone
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  - LDRD
  - Royalty Fund


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