

Switchable Polarity Solvent Forward Osmosis Process Development

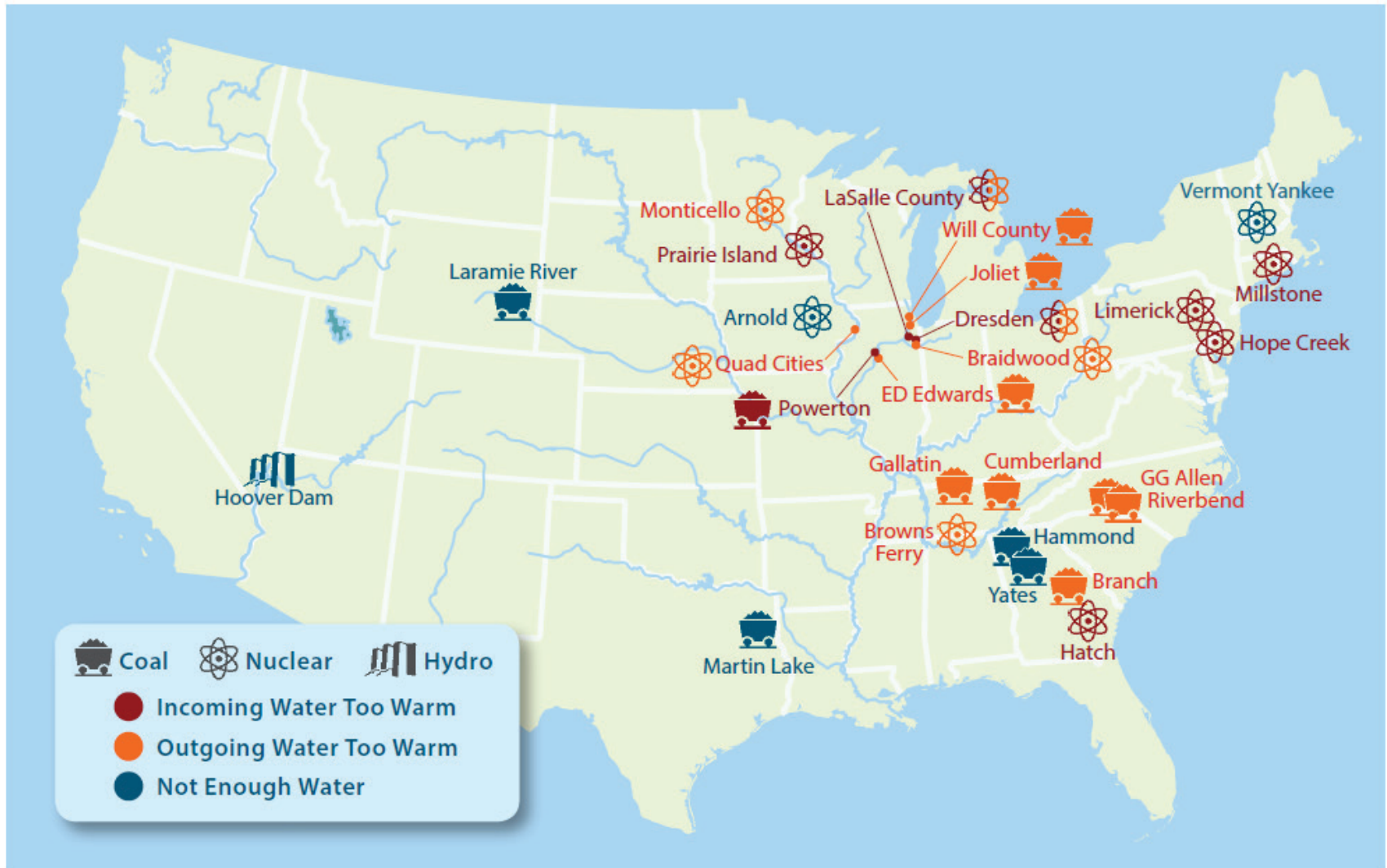
Aaron D. Wilson, Christopher J. Orme,
Michael G. Jones, Catherine M. Hrbac,
Birendra Adhikari, Daniel S. Wendt, and
Gregory L. Mines

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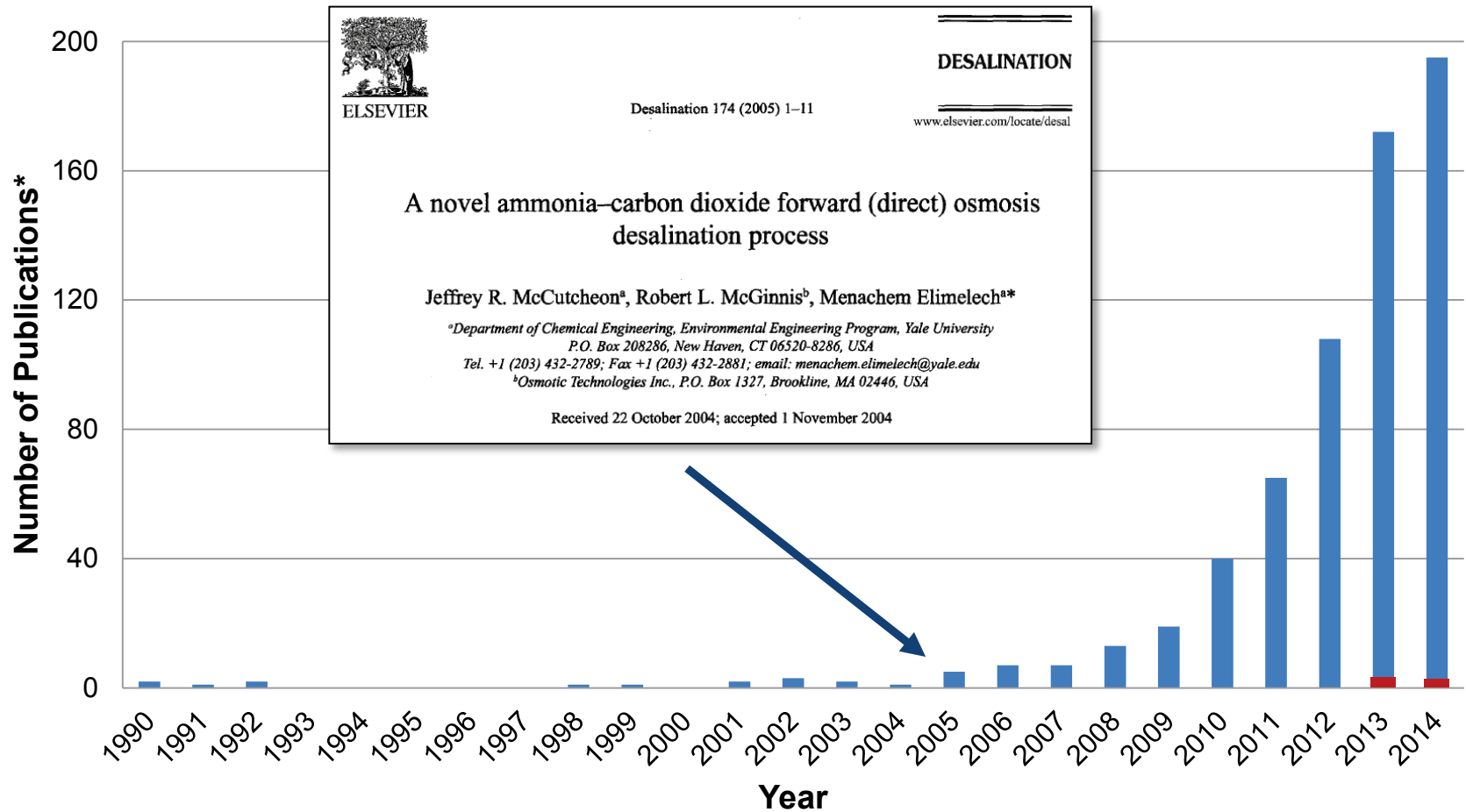


Impact of Water on Energy Generation



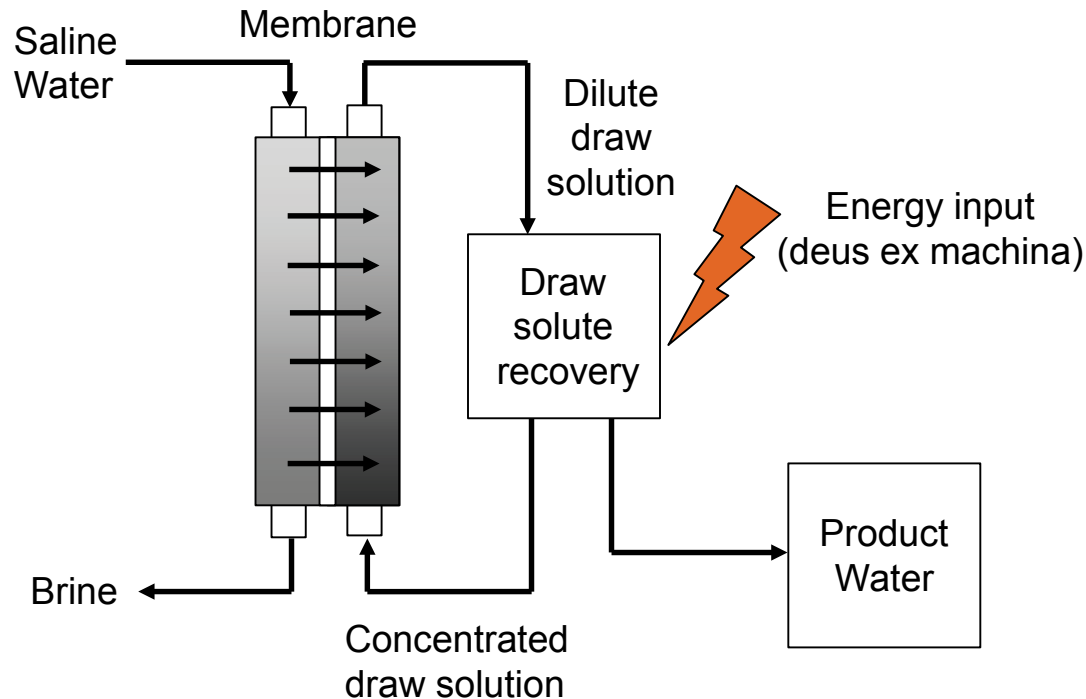
Water-Smart Power (2013) Union of Concerned Scientists. Select events 2006-2012

State of the Art Publications in FO/PRO



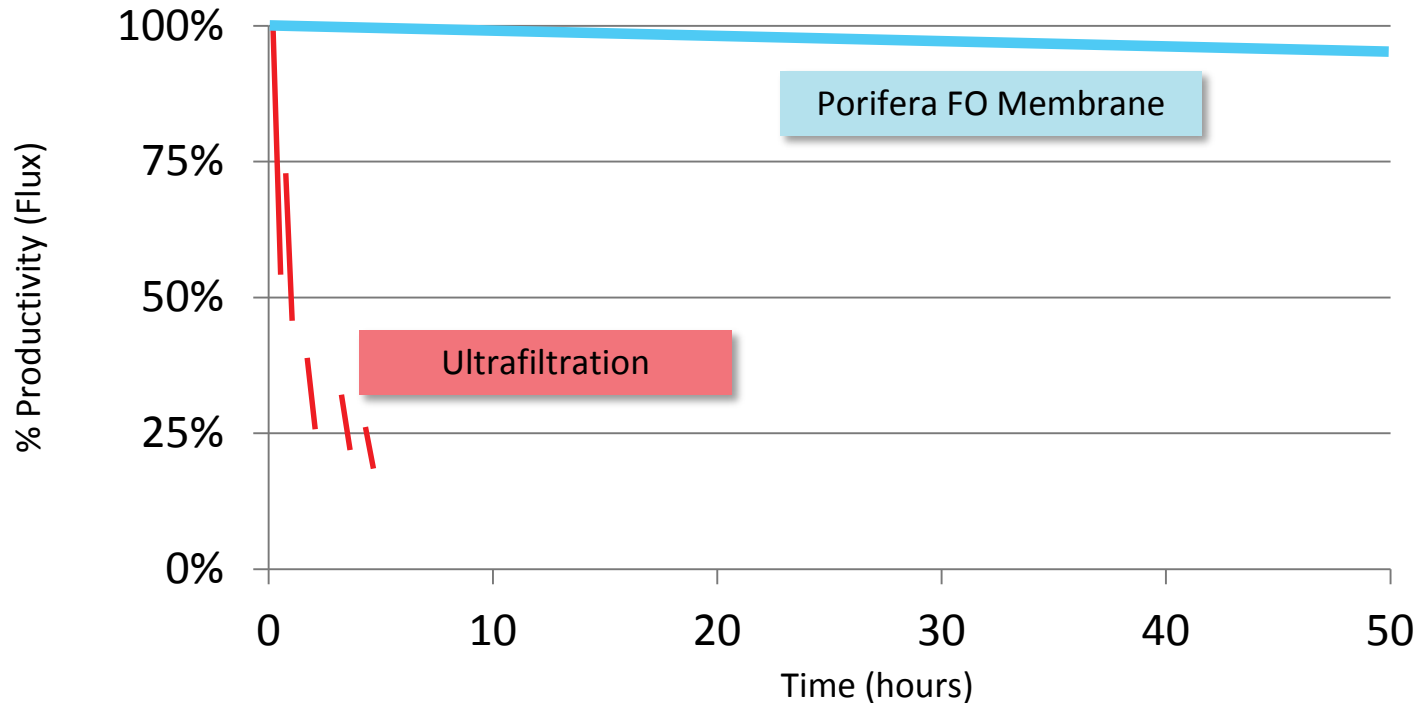
***Topic “forward osmosis” or “pressure retarded osmosis” in Web of Science**

State of the Art: Forward Osmosis Introduction



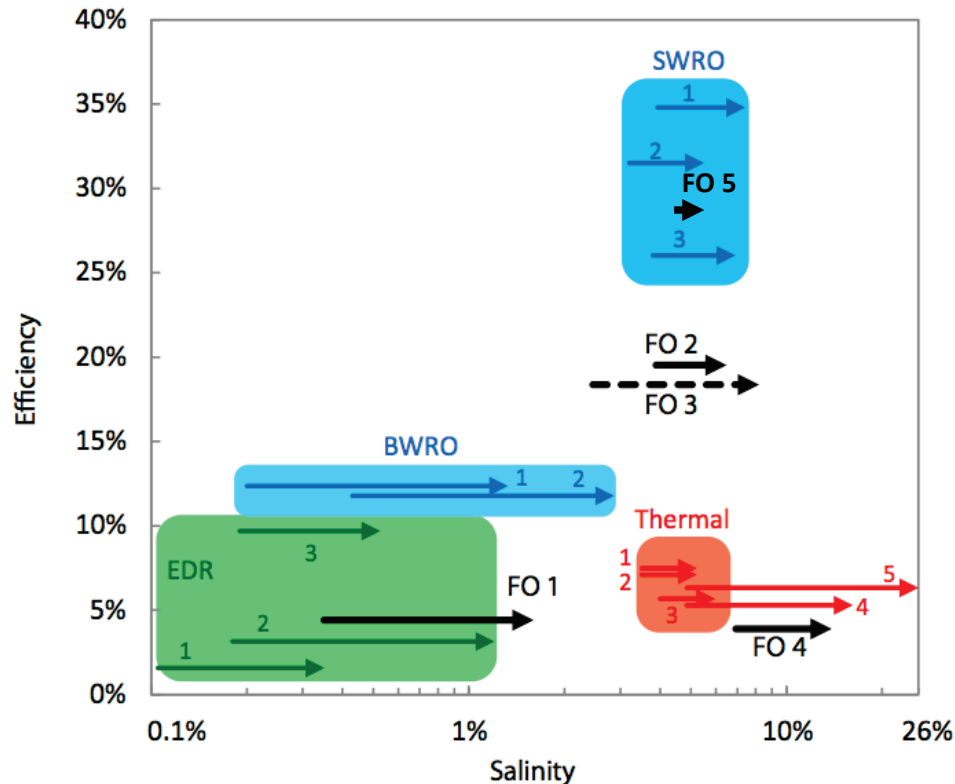
- Forward osmosis membrane flux spontaneous (No energy input)
- Primary process energy requirements delivered during **draw solute recovery**, which can include:
 - Reverse Osmosis,
 - Various Distillation including Membrane Distillation, and
 - Thermal solute separation such as thermolytic solutes (Switchable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

FO Efficiency



Key: Feed $\xrightarrow{\text{Process}}$ Concentrate

Legend:

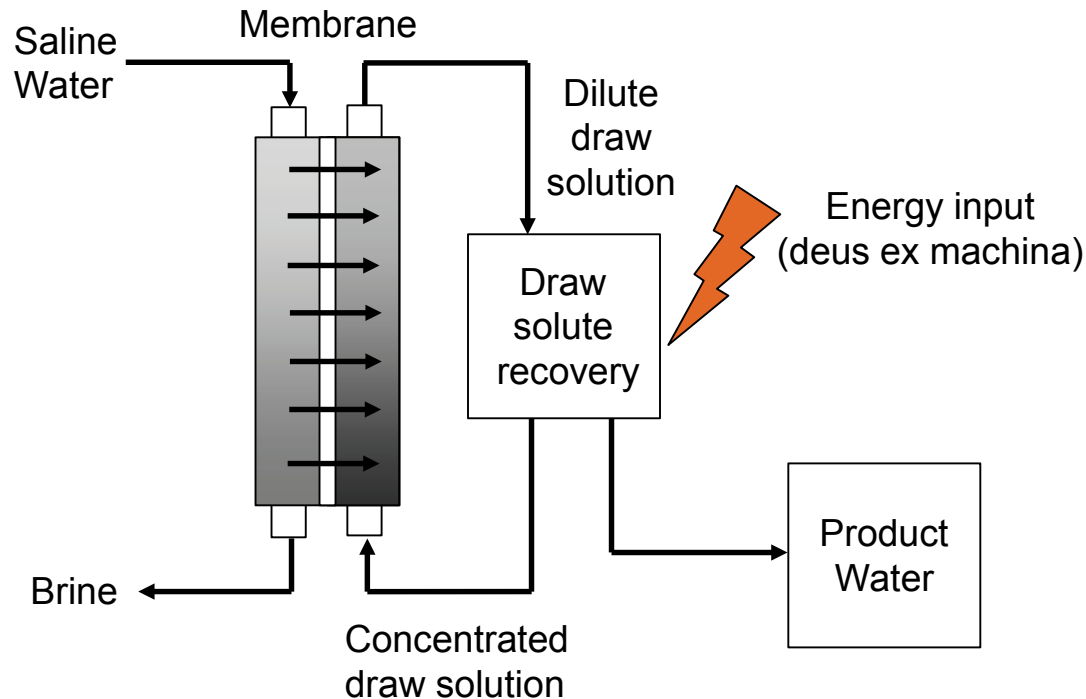
- | | | |
|---------|--|-------------------|
| FO | 1 FO-RO pilot [2,18] | 5 FO-RO Pilot [1] |
| | 2 FO-RO model [20] | |
| | 3 Dilution pilot (non-regenerating) [2,18] | |
| Thermal | 1 MVC (typical SW) [27] | |
| | 2 TVC-MED (typical SW) [27] | |
| | 3 MSF, Shuweihat, Saudi Arabia [26] | |
| | 4 MVC, Barnett Shale, USA [28] | |
| | 5 MVC model [11] | |
| SWRO | 1 Skikda, Algeria [26] | |
| | 2 Tampa Bay, USA [26] | |
| | 3 Hadera, Israel [26] | |
| BWRO | 1 Wadi Ma'in, Jordan [26] | |
| | 2 El Paso, USA [26] | |
| EDR | 1 Melville, Canada [26] | |
| | 2 Yuma, USA [26] | |
| | 3 Foss Reservoir, USA [26] | |

$$\text{Efficiency} = (0.8 \text{ kWh/m}^3 [2] / 2.8 \text{ kWh/m}^3) \cdot 100 = 29\%$$

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.

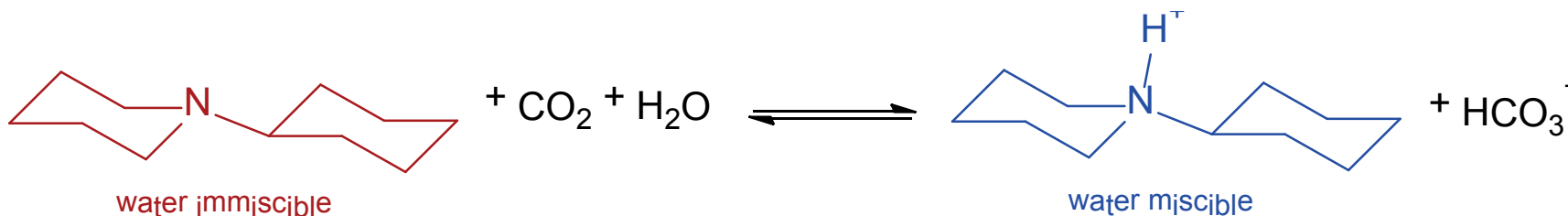
State of the Art: Forward Osmosis Introduction



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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-cyclohexylpiperidinium 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.

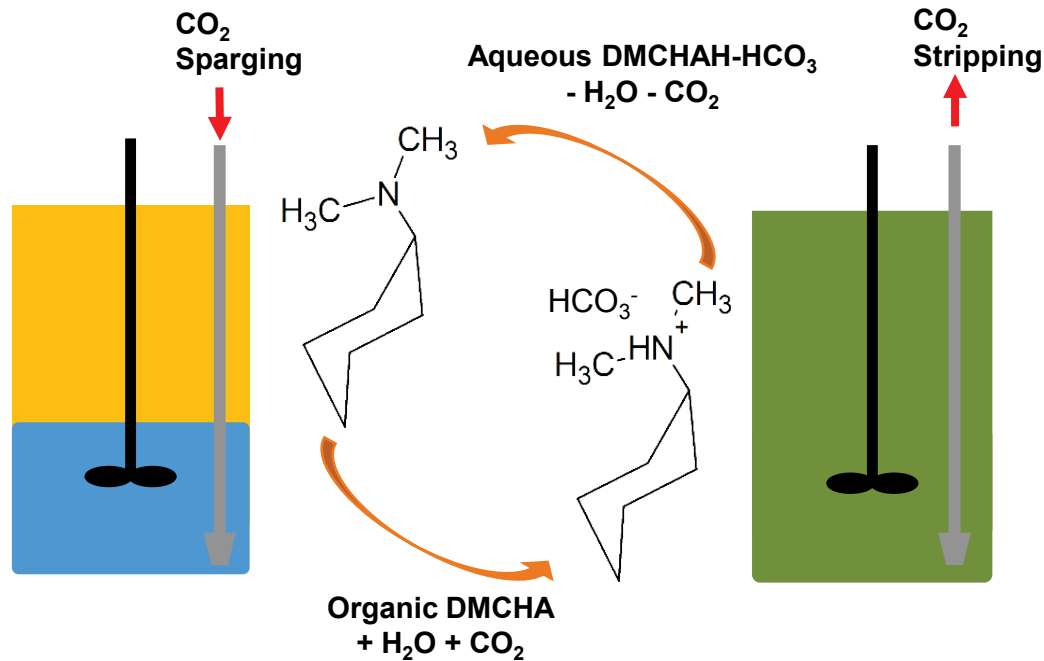
Orme, Wilson, 1-Cyclohexylpiperidine as a Thermolytic Draw Solute for Engineered Osmosis. *Desalination* **2015**, 371, 126-133

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

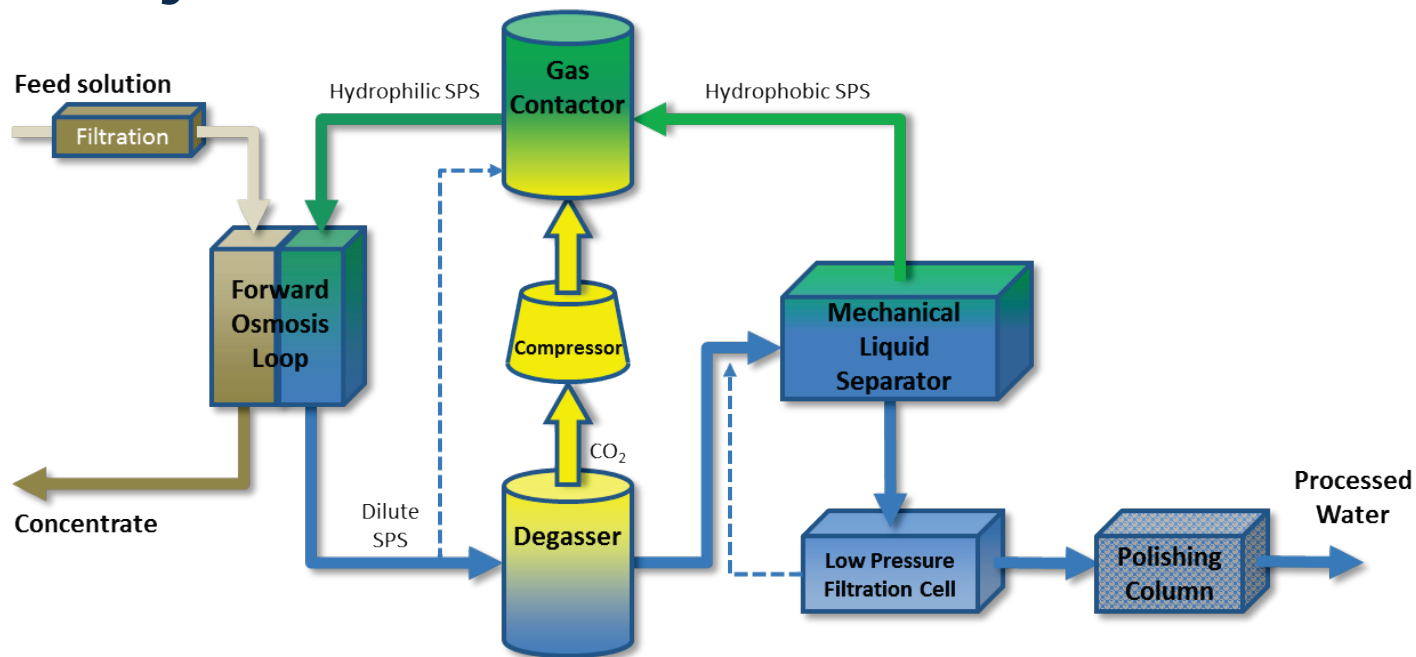
Wilson, A. D.*; Stewart, F. F. Structure-Function Study of Tertiary Amines as Switchable Polarity Solvents *RCS Advances* **2014**, 4, 11039-11049.

Tertiary Amine Switchable Polarity Solvents



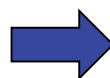
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Proposed Switchable Polarity Solvents Forward Osmosis System



Thermally driven process with the majority of energy input at the CO₂ degasser

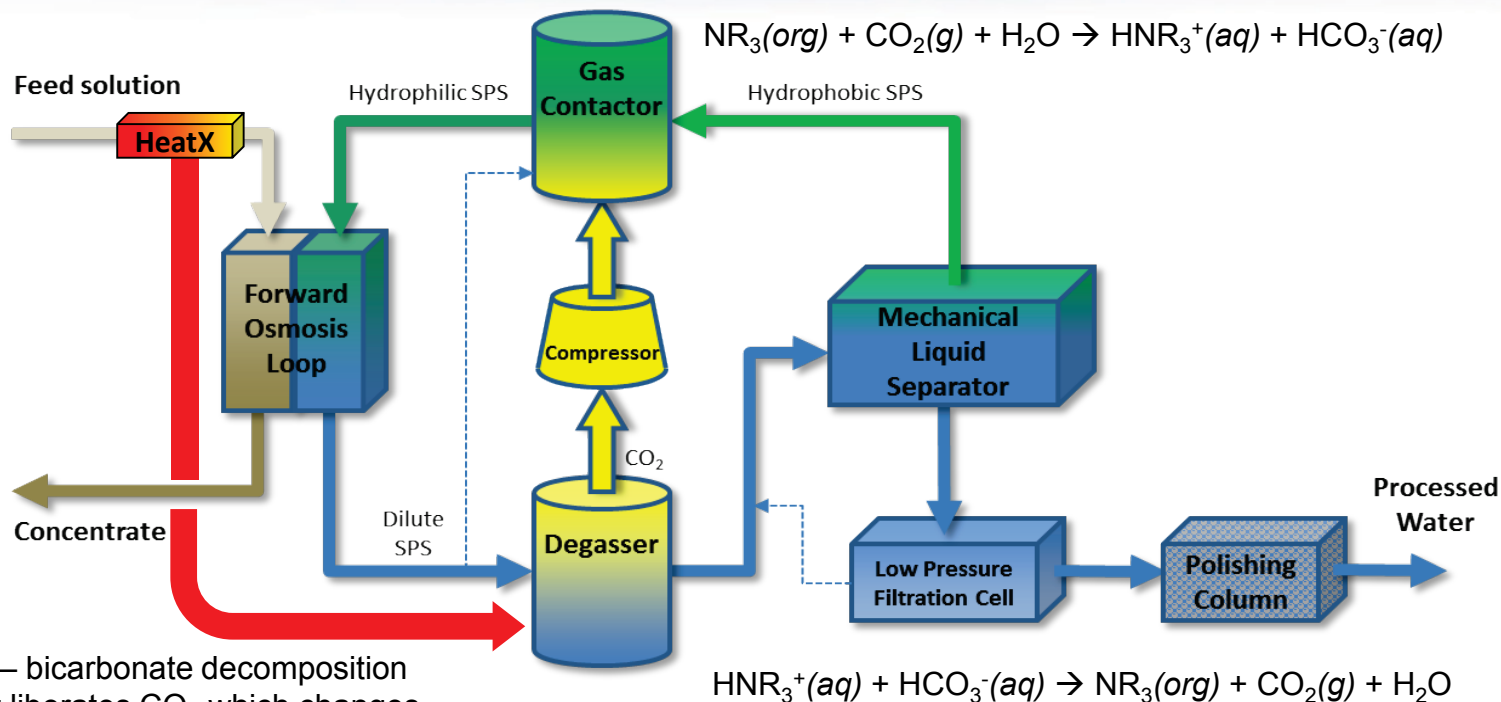
Wilson; Stewart; Stone **Methods and Systems for Treating Liquids Using Switchable Solvents**. US20130048561 A1.
 Wilson; Stewart; Stone **Methods and Systems for Treating Liquids Using Switchable Solvents**. WO2013032742 A1.



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



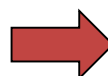
SPS-FO Process Configuration



Heat added – bicarbonate decomposition reaction that liberates CO_2 which changes solvent to a non-polar form (hydrophobic)

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.
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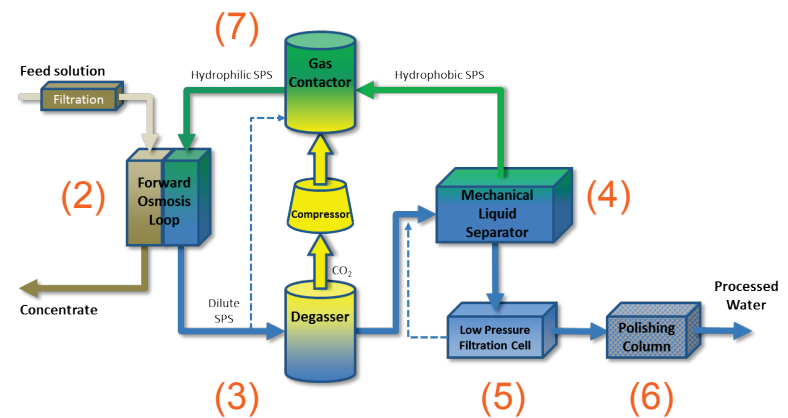


High Salinity, High Fouling, High Recovery

- 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.**

Components of Process Development

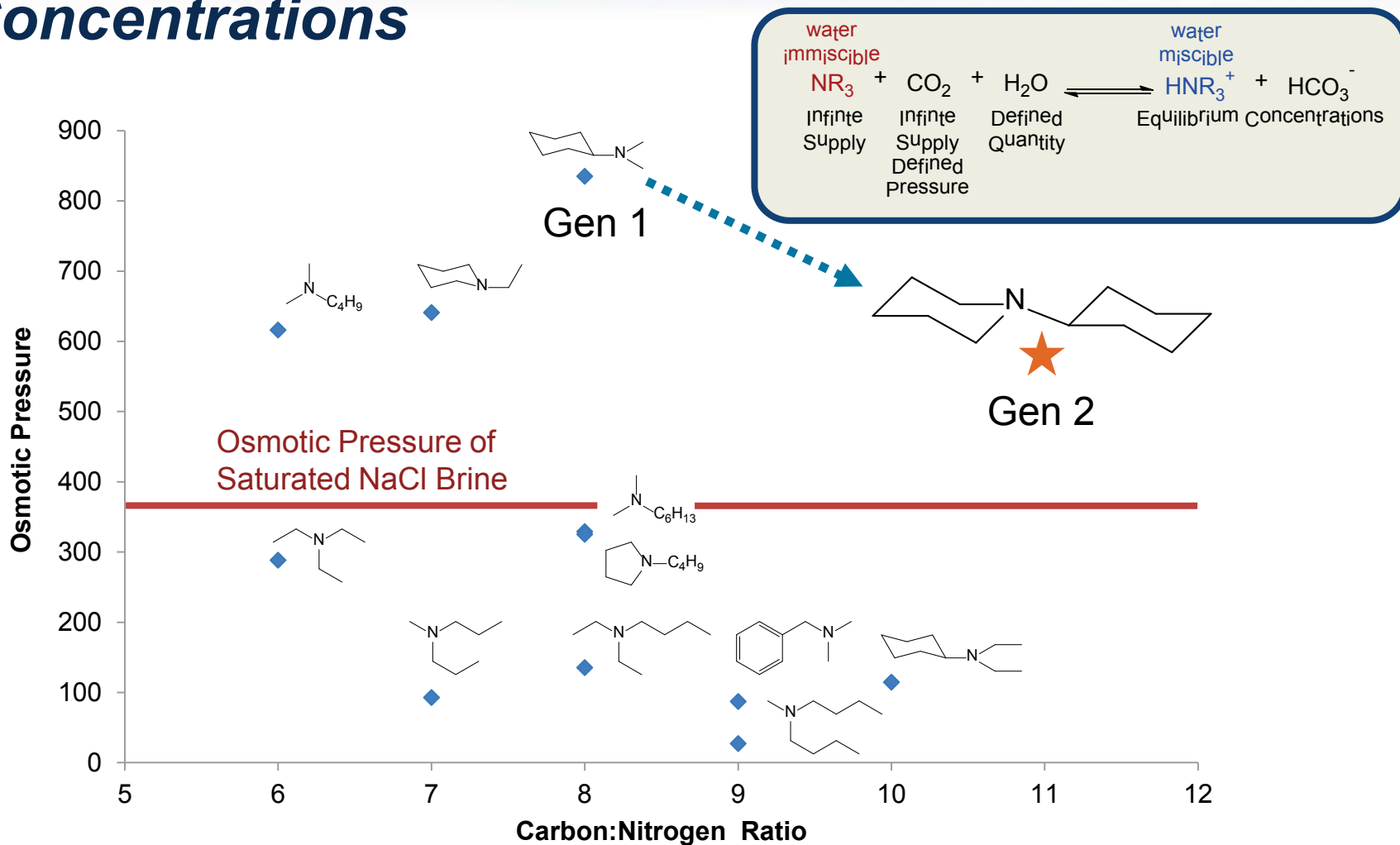
1. Working Fluid Selection
2. Forward Osmosis Membrane and Module Selection
3. Degasser Optimization
4. Mechanical Liquid Separator
5. Low Pressure Filtration Cell
6. Polishing Column Material Selection and Design
7. Gas Contactor Design
8. System Design and Testing
9. Process monitoring mythology



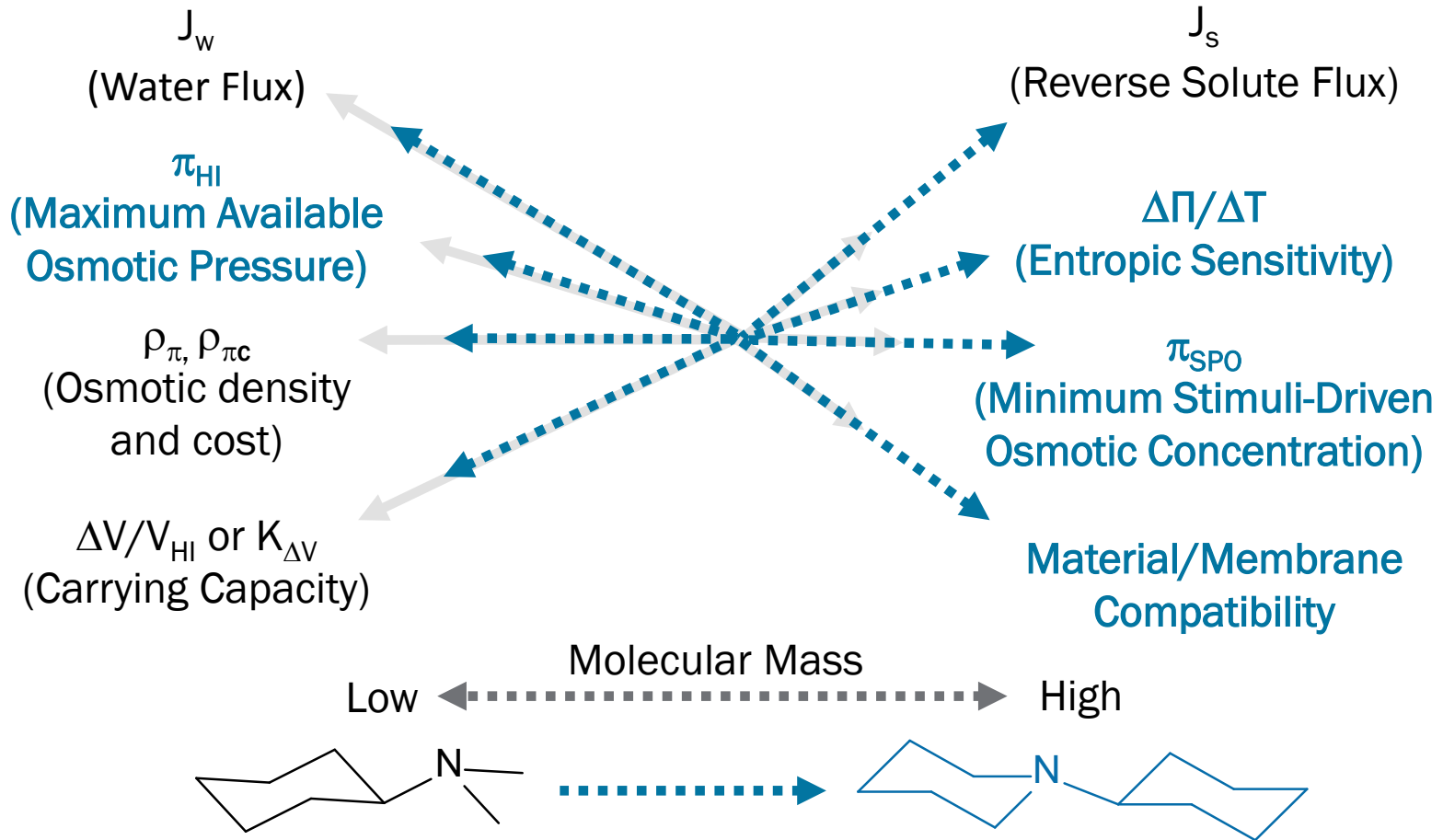
Pre GTO Effort Work: Selecting an amine SPS for osmotically driven membrane processes

- **Desired properties for SPS draw solute**
 - Effective polar to non-polar phase transition
 - Rapid transition kinetics
 - Low temperature/energy requirements
 - Completeness of transition
 - Low SPS water solubility of the non-polar form
 - Low SPS membrane permeability
 - High osmotic pressure in the polar form
 - Effective mass transport (High flux, Low viscosity)
 - Compatibility with a wide range of materials

Projected Osmotic Pressures of Equilibrium Concentrations



Advantages of 2nd Generation SPS Draw

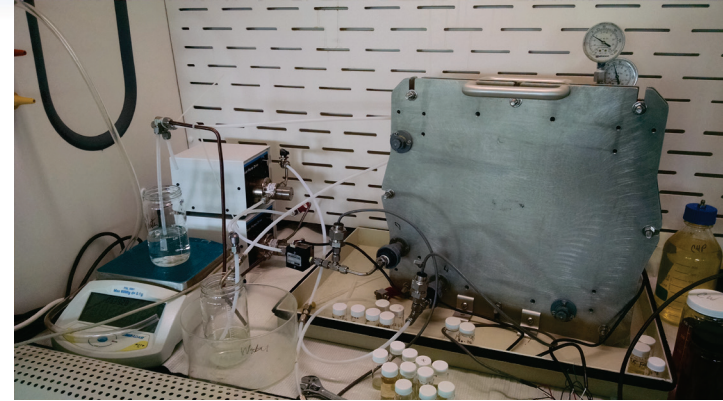


Orme; Wilson 1-Cyclohexylpiperidine as a Thermolytic Draw Solute for Osmotically Driven Membrane Processes. *Desalination* 2015, 371, 126–133.

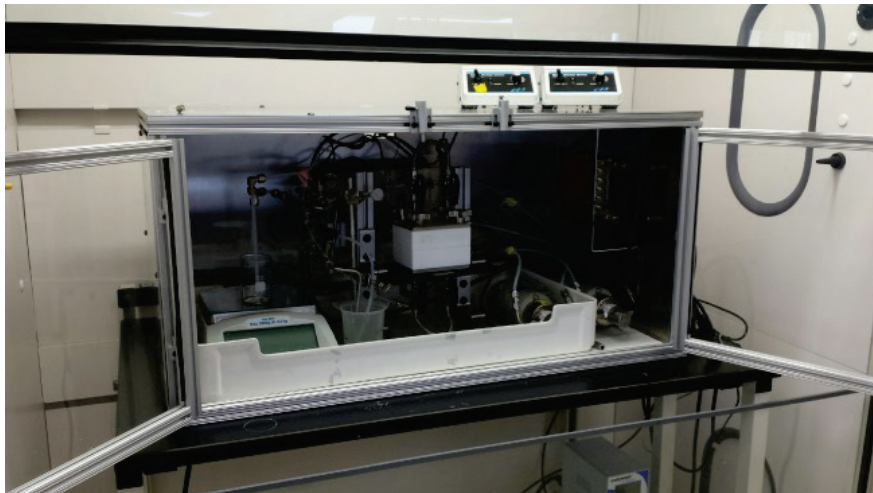
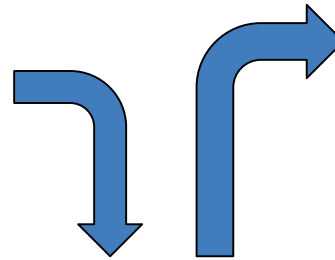
GTO Effort : System Design and Testing



Initial scale
(2011)



Long Term Module Testing (2015)

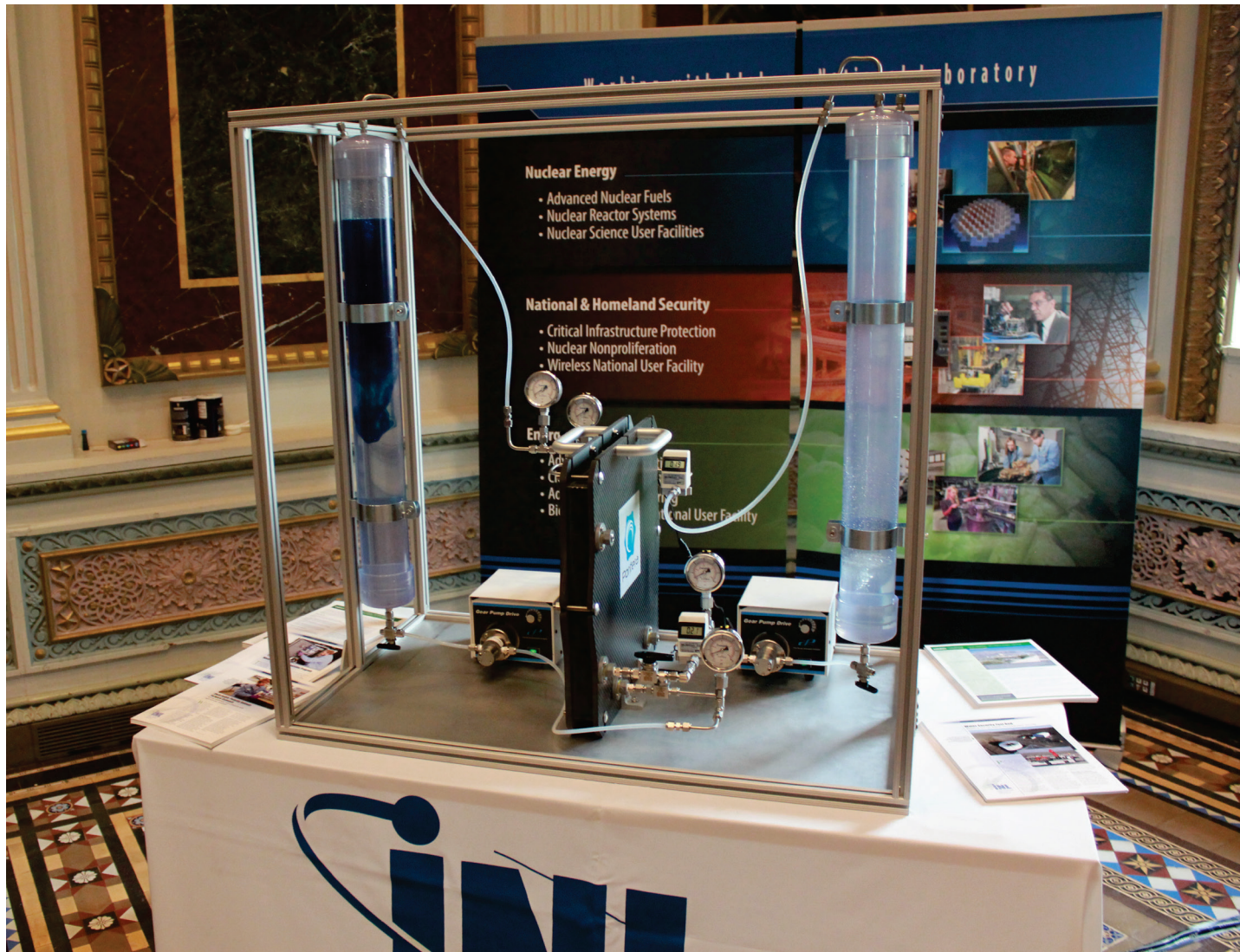


Lab scale (2014)



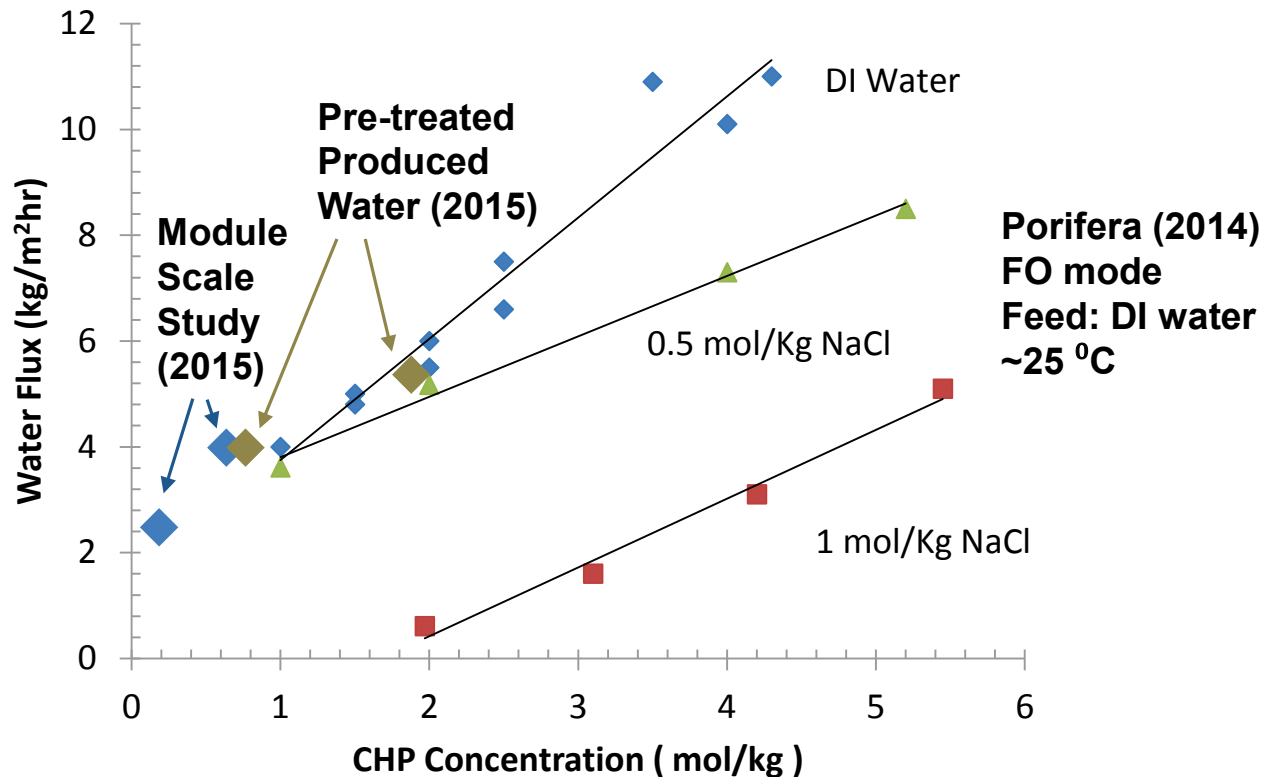
0.5 to 50 gallon per hour pilot system (2015)

White House Water Summit 2016 INL FO Module Demonstration



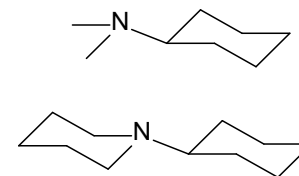
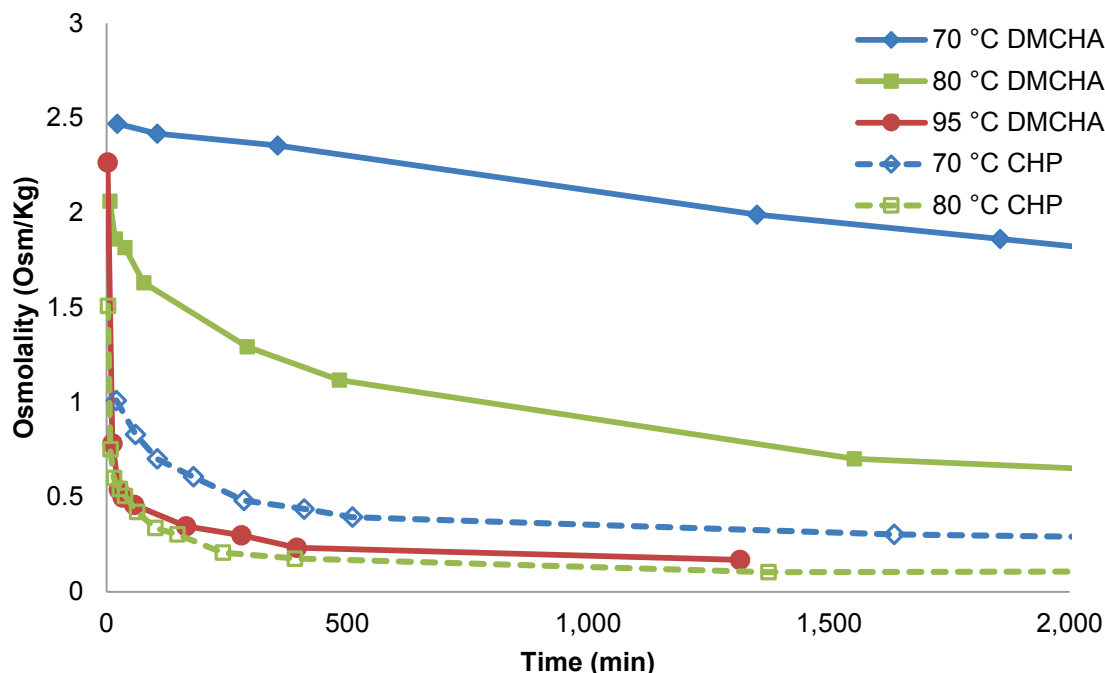
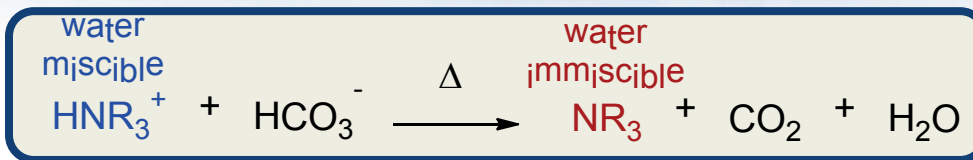
CHP flux over a range of concentration feeds

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 in rheological properties associated with moving from a 8 to an 11 carbon amine.

Degassing Experiments

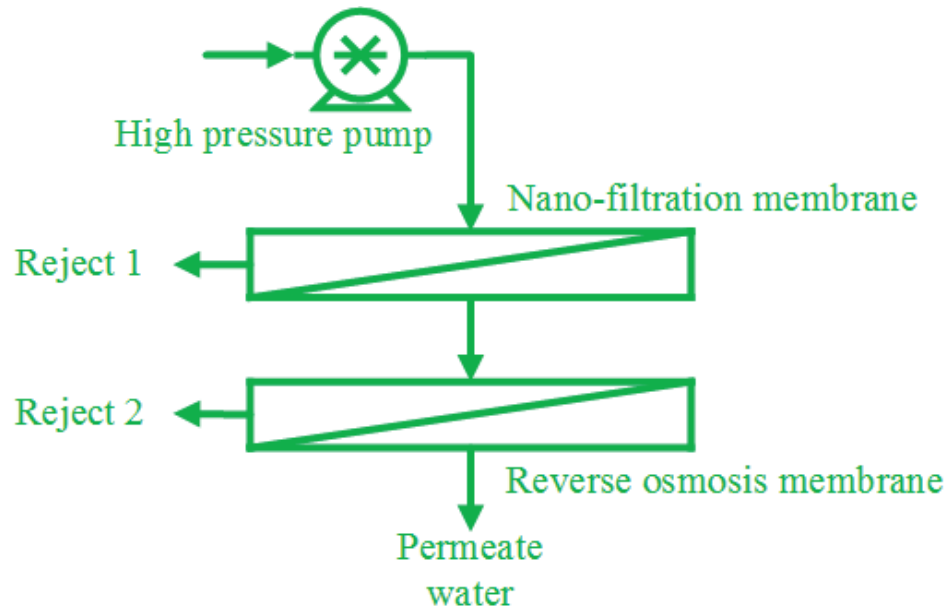


- N,N-Dimethylcyclohexylamines (DMCHA) requires 95 °C to achieve a good degassing and phase separation at ambient atmospheric pressures.
- Gen 2 can be degassed at 70 °C under ambient atmospheric pressures or less with limited amount of vacuum.
- Gen 2 CHP draw solution to <2wt% with 80 °C and <2 psi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

NF and RO performance Metrics

- Two staged NF/RO membrane system

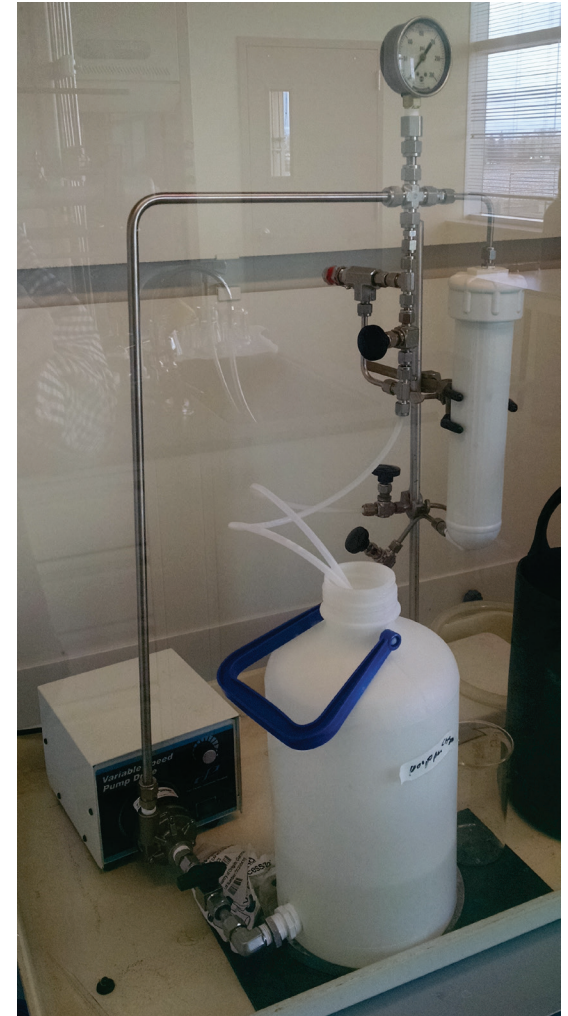
	Permeance $L \cdot m^2 / (hr \cdot bar)$	Rejection
DOW NF90 module	5.5	99.4%
DOW TW30 module	12.0	97.0%



NF Module & TW30 Module Test System



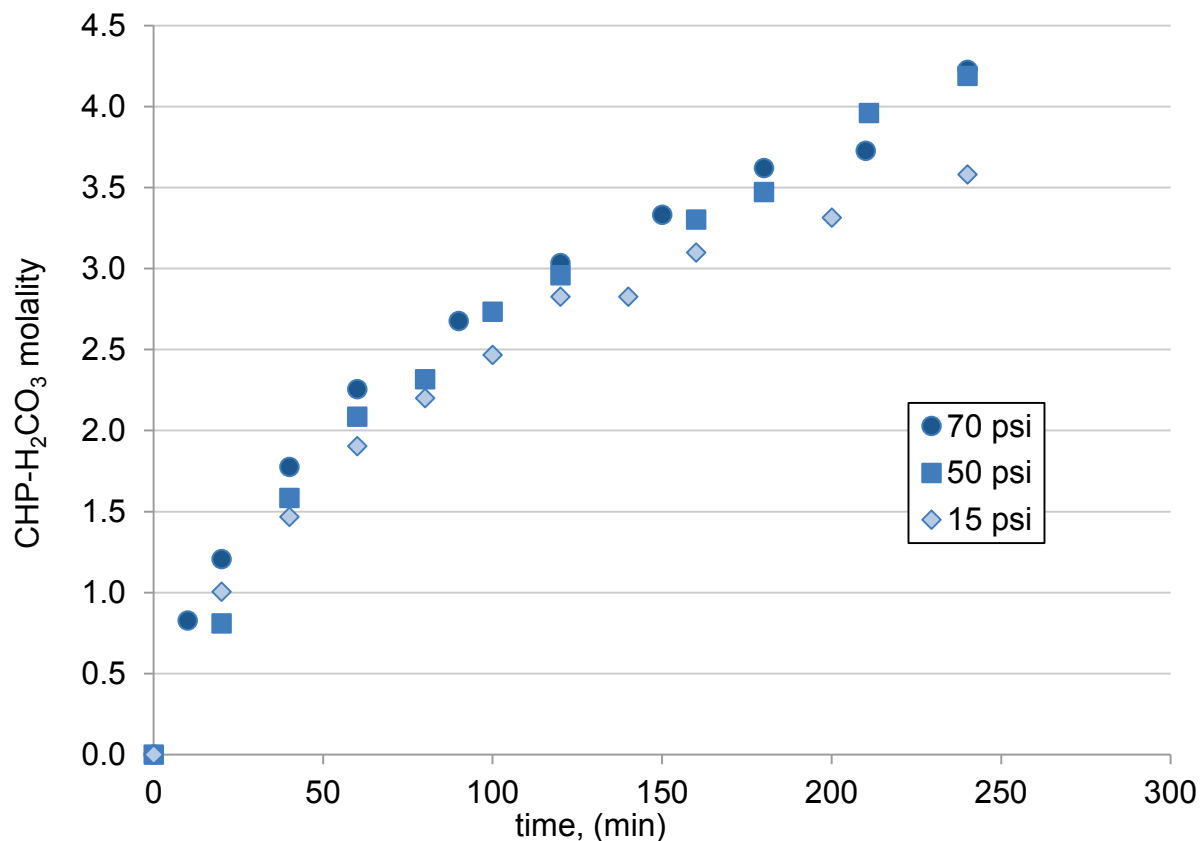
- Less than 100 psi is expected to remove greater than 5 nines of CHP draw.



Module Scale Gas Contactor

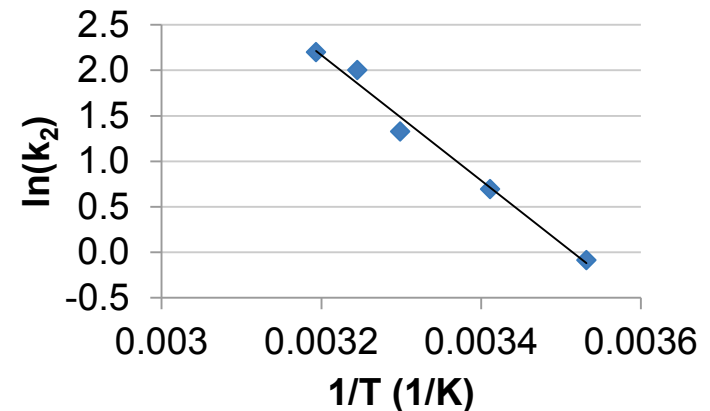
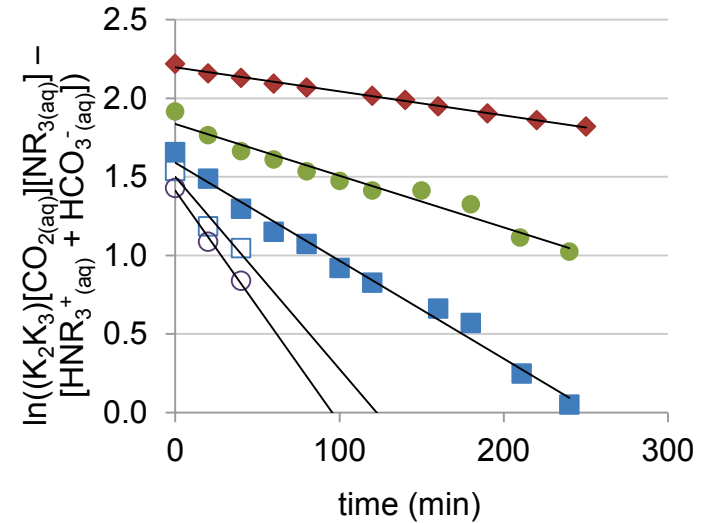
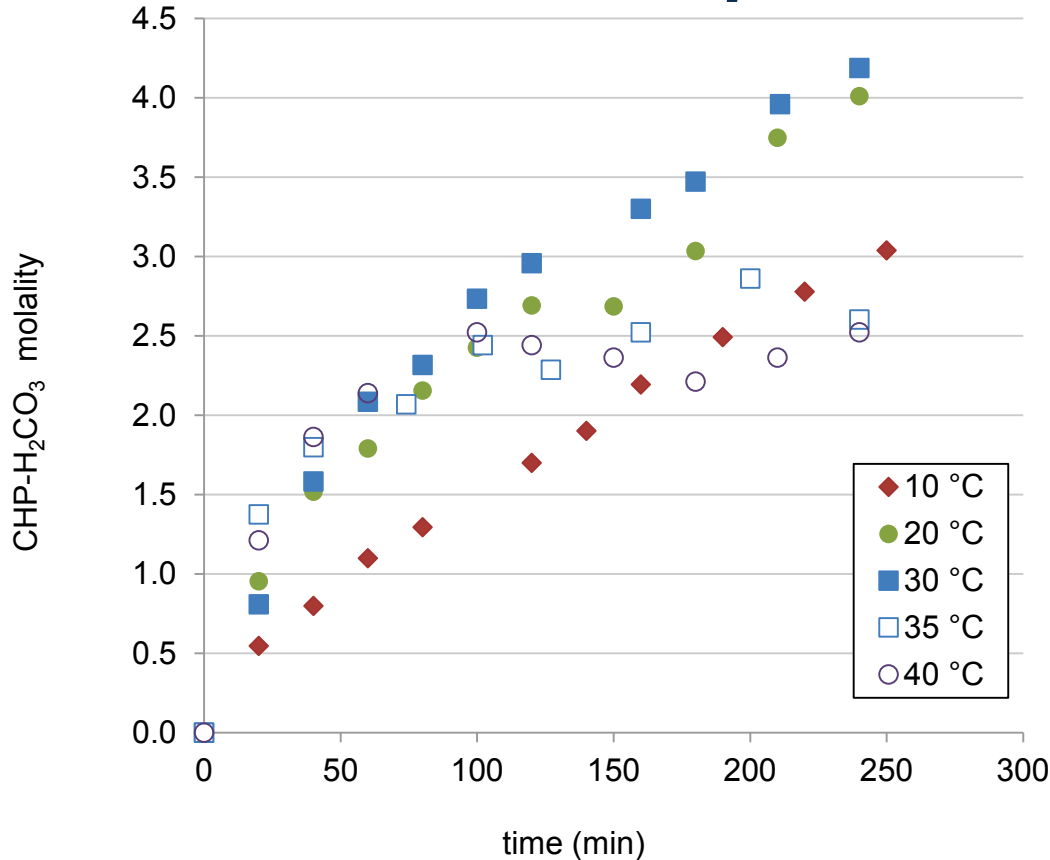


Gas Contactor Pressure/Mixing Study



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

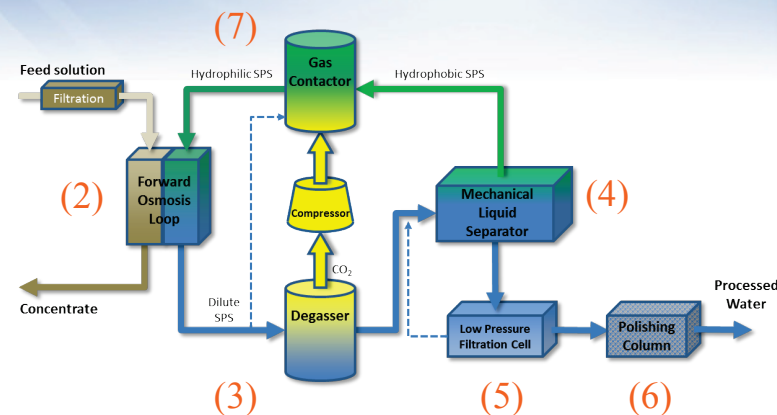
Gas Contactor Temperature Study



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

SPS FO Project Status

- 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.

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Acknowledgements

INL Team

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- Joshua S. McNally
- **Catherine M. Hrbac**
- **Birendra Adhikari**
- **Daniel S. Wendt**
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