Switchable Polarity Solvent Forward Osmosis Process Development

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April, 2016
Impact of Water on Energy Generation

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).
• 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 = \( \frac{0.8 \text{ kWh/m}^3 [2]}{2.8 \text{ kWh/m}^3} \) · 100 = 29%

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

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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
Wilson, Orme Concentration Dependent Speciation and Mass Transport Properties of Switchable Polarity Solvents RCS Advances 2015, 5, 7740-7751
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Proposed Switchable Polarity Solvents Forward Osmosis System

Thermally driven process with the majority of energy input at the CO$_2$ degasser


Stone; Rae; Stewart; Wilson *Switchable Polarity Solvents as Draw Solutes for Forward Osmosis Desalination 2013,* 312,124-129.
Heat added – bicarbonate decomposition reaction that liberates CO₂ which changes solvent to a non-polar form (hydrophobic)

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

NR₃(org) + CO₂(g) + H₂O → HNR₃⁺(aq) + HCO₃⁻(aq)

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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.
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

Orme, Wilson, 1-Cyclohexylpiperidine as a Thermolytic Draw Solute for Engineered Osmosis. Desalination 2015. 371, 126-133
Advantages of 2\textsuperscript{nd} Generation SPS Draw

\[ J_w \]
(Water Flux)

\[ \pi_{HI} \]
(Maximum Available Osmotic Pressure)

\[ \rho_{\pi}, \rho_{\pi c} \]
(Osmotic density and cost)

\[ \Delta V/V_{HI} \text{ or } K_{\Delta V} \]
(Carrying Capacity)

\[ J_s \]
(Reverse Solute Flux)

\[ \Delta\Pi/\Delta T \]
(Entropic Sensitivity)

\[ \pi_{SPO} \]
(Minimum Stimuli-Driven Osmotic Concentration)

Material/Membrane Compatibility

Molecular Mass

Low \hspace{2cm} High

GTO Effort: System Design and Testing

Initial scale (2011)


Lab scale (2014)

0.5 to 50 gallon per hour pilot system (2015)
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 (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

NF and RO performance Metrics

- Two staged NF/RO membrane system

<table>
<thead>
<tr>
<th></th>
<th>Permeance L⋅m²/(hr⋅bar)</th>
<th>Rejection</th>
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<tbody>
<tr>
<td>DOW NF90 module</td>
<td>5.5</td>
<td>99.4%</td>
</tr>
<tr>
<td>DOW TW30 module</td>
<td>12.0</td>
<td>97.0%</td>
</tr>
</tbody>
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Diagram:
- High pressure pump
- Nano-filtration membrane
  - Reject 1
  - Reject 2
- Reverse osmosis membrane
  - Permeate water
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**
- Frederick F. Stewart
- Mark L. Stone
- Christopher J. Orme
- Michael G. Jones
- Joshua S. McNally
- Catherine M. Hrbac
- Birendra Adhikari
- Daniel S. Wendt
- Gregory L. Mines
- Lucia M. Petkovic
- Luis A Diaz Aldana

**Funding**
- DOE Energy Efficiency and Renewable Energy (EERE) Geothermal Technology Office (GTO)
- DOE Office of Science - Small Business Innovation Research (SBIR) Program
- DOE Office of Fossil Energy (FE) - National Energy Technology Laboratory (NETL) Novel Crosscutting Research and Development to Support Advanced Energy Systems
- Battelle Energy Alliance (INL)
  - LDRD
  - Royalty Fund
Idaho National Laboratory