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

DE-FE0024057

Porifera
(subcontract to Idaho National Laboratory)

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Impact of Water on Energy Generation

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 CO₂ stream and a new water stream for reuse, with waste heat.
A novel ammonia–carbon dioxide forward (direct) osmosis desalination process

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*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
Efficiency = (0.91 kWh/m³ [2] / 2.81 kWh/m³)*100 = 33%

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

**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
**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


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.
- 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.
SPS Used in Carbon Capture - Hu

- CO₂ Capture from Flue Gas by Phase Transitional Absorption - Liang Hu (Hampton University, 3H Company) DE-FG26-05NT42488 (PM Isaac Aurelio)

- Post-Combustion CO₂ Capture for Existing PC Boilers by Self-Concentrating Amine Absorbent - Liang Hu (3H Company) DE-FE0004274 (PM Morgan Mosser)

SPS Used in Carbon Capture – DMX™ Process

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

• Developed at the Technical University of Dortmund, Germany

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.
**CO₂ Capture form simulated flue gas**

- CO₂ capture from a simulant flue gas (10% CO₂ 90% N₂).
- Need to capture 75% of the CO₂ 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

- **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

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

Lab scale (2014)


10 gallon per hour pilot system (2015)
White House Water Summit 2016
INL FO Module Demonstration
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
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
NF/RO Coupon tests

**Nanofiltration membranes**

- GE Osmonics DL (1R)
- GE Osmonics DL (2R)
- DOW FILMTEC NF90 (1R)
- DOW FILMTEC NF90 (2R)
- DOW FILMTEC NF90 (3R)

**Permeance, Lm⁻²h⁻¹bar⁻¹**

- Feed concentration, %
- Rejection, %

**Reverse osmosis membranes**

- DOW FILMTEC BW30 (1R)
- DOW FILMTEC BW30 (2R)
- Toray 73-AC (1R)
- Toray 73-AC (2R)
- TriSep ACM1 (1R)
- TriSep ACM1 (2R)

**Permeance, Lm⁻²h⁻¹bar⁻¹**

- Feed concentration, %
- Rejection, %
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

<table>
<thead>
<tr>
<th></th>
<th>Permeance L·m²/(hr·bar)</th>
<th>Rejection</th>
</tr>
</thead>
<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>
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</tbody>
</table>
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

Up to 93% Savings over Existing Technologies

Cost per 1,000 gallons ($)
Assumes 20 year project cost, based on future PFO pricing

- **Porifera PFO**
  - Thermal: 24.30
  - PFO concentrator: 6.90
  - PFO+RO for high fouling, medium TDS: 3.61
  - 71% Savings
  - 93% Savings
  - 30% Savings
  - 55% Savings

- **Competing Technology**
  - UF/RO+pre/post treatment for high TDS: 1.64

33
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