Dewatering of High Salinity Brines by Osmotically Assisted Reverse Osmosis

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Motivation: Extracted CO$_2$ Storage Brines

Capture CO$_2$ and prevent its release into the atmosphere
Store CO$_2$ by compression and injection into deep saline formations

- Manage subsurface pressure and increase storage capacity
- **Treatment and disposition**
  - Cannot discharge to surface waters
  - Concentrate brine and reinject into alternate formation
    - Fresh water production
    - Crystallize salt for its commercial value at select locations

Saline formation CO$_2$ storage scheme
Brine Composition

- Injection into saline aquifers
- EOR or depleted gas field

Survey of subsurface brines

- Lower Tuscaloosa: 149 g/L TDS
- Mt. Simon: 115 g/L TDS
- Frio: 109 g/L TDS
- Oriskany: 221 g/L TDS
Eastern U.S. CO₂ Storage Brines

Composition (eq/L) of four brines extracted from GCS-relevant formations in the eastern U.S. assuming complete dissociation. Osmotic pressure calculated from water activity determine using Geochemist’s Workbench v9 with the thermo_phrqszt database.
Current commercially available technologies

- Mechanical Vapor Compression (MVC) or MVC-MED hybridization

Each 1°C driving force across Evaporator HX leads to ~2 kWh/m³ of work loss

Minimum work required to produce a m³ of pure water. Calculations were done at 20°C using the ELECNRTL method within AspenPlus V8.4.
Osmotically Assisted Reverse Osmosis (OARO) differs from conventional RO and FO.

Reverse Osmosis:

\[ J_w = A \cdot \left[ P_f - P_p \right] - \left[ \pi(c_{f,m}) - \pi(c_p) \right] \]

\[ \pi(c_p) \approx 0 \]

Osmotically Assisted Reverse Osmosis:

\[ J_w = A \cdot \left[ P_f - P_p \right] - \left[ \pi(c_{f,m}) - \pi(c_{s,m}) \right] \]

\[ 0 < \pi(c_{s,m}) < \pi(c_{f,m}) \]
Process Configuration

1st Step OARO
- Low Pressure
- Water

2nd Step OARO
- High Pressure
- Water

3rd Step RO
- Low Pressure
- Water

Mathematical Expression:

\[ J_w = A \left( \left[ P_f - P_p \right] - \left[ \pi(c_{f,m}) - \pi(c_{s,m}) \right] \right) \]

Feed

Sweep

Osmotic Pressure (bar)

0 25 50 75

1st Step OARO

2nd Step OARO

3rd Step RO

Water

0.6 mol·kg\(^{-1}\)

0.3 mol·kg\(^{-1}\)

~0 mol·kg\(^{-1}\)

0.9 mol·kg\(^{-1}\)

0.9 mol·kg\(^{-1}\)

1.2 mol·kg\(^{-1}\)
Mass Transport in Membrane Support Layers

FO

Selective Layer

Support Layer

Membrane

Boundary Layer

Water Flux, \( J_w \)

Support Layer

Assumes same salt on both sides of membrane

OARO

Selective Layer

Support Layer

Membrane

Boundary Layer

Water Flux, \( J_w \)

\[ x = -\delta_f \quad x = 0 \quad x = t_s \]

\[ J_s \]

\[ J_w \cdot c_f \]

\[ J_w \cdot c_s \]

\[ P_f \approx P_d \]

\[ c_{s,f} < c_{s,d} \]

\[ -D \frac{d c_f}{dx} \]

\[ -D_{eff} \frac{d c_s}{dx} \]

\[ c_s(x) \]

\[ x = -\delta_f \quad x = 0 \quad x = t_s \]

\[ c_{s,f} > c_{s,s} \approx 0 \]

\[ P_f >> P_s \]

\[ c_{s,f} > c_{s,s} \]

\[ P_f \gg P_s \]
Cellulose Acetate Membranes

Cellulose Triacetate FO membrane developed by Hydration Technology Innovations (HTI)

Subsequent iteration manufactured by Fluid Technology Solutions (FTSH2O)

CTA selective layer
And support layer

Embedded hydrophilic mesh
Simulated water flux for HTI’s woven support CTA membrane in OARO. Assumes constant A and B of 0.3672 L·m⁻²·h⁻¹·bar⁻¹ and 0.2768 L·m⁻²·h⁻¹ respectively, structural parameter increases linearly with applied feed hydrostatic pressure, external boundary layer thickness of 50 μm, sweep pressure of 1 bar, and a temperature of 25°C.
Simulated transmembrane osmotic pressure for HTI’s woven support CTA membrane in OARO. Assumes constant A and B of $0.3672 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and $0.2768 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ respectively, structural parameter increases linearly with applied hydrostatic pressure, external boundary layer thickness of 50 μm, and a temperature of 25°C.
Test System at Carnegie Mellon
Water flux observed for FTS’s woven supported CTA membrane using constant concentration difference of 0.3 mol·kg⁻¹ between feed and sweep solutions of sodium chloride at 25°C with a feed flowrate 1.0 L·min⁻¹, sweep flowrate of 0.5 L·min⁻¹, and average sweep pressure ~1 bar.
Water flux observed for FTS's woven supported CTA membrane using constant concentration difference of 0.6 mol·kg⁻¹ between feed and sweep solutions of sodium chloride at 25°C with a feed flowrate 1.0 L·min⁻¹, feed pressure of 31.0 bar, sweep flowrate of 0.5 L·min⁻¹, and average sweep pressure ~1 bar.
Water flux observed for FTS’s woven supported CTA membrane using feed (selective layer) solutions of sodium chloride with a purified water sweep (support layer) at 25°C with a feed flowrate 1.0 L·min⁻¹, sweep flowrate of 0.5 L·min⁻¹, and average sweep pressure ~1 bar.
Salt flux observed for FTS’s woven supported CTA membrane using feed (selective layer) solutions of sodium chloride with a purified water sweep (support layer) at 25°C with a feed flowrate 1.0 L·min⁻¹, sweep flowrate of 0.5 L·min⁻¹, and average sweep pressure ~1 bar.
Assumes
- Steady state
- Perfectly selective membrane
- Reynolds number of 1000 for sweep and feed
- 5 kPa pressure drop per meter of module

- 1 m wide by 10 m long module
- Membrane water permeance of 0.36 L·m⁻²·h⁻¹·bar⁻¹
- Membrane structural parameter of 1000 μm
- Temperature 25°C
System Model Recovery Rates

Maximum water recovery for a constant feed pressure of 65 bar with variable feed concentration and sweep concentration.

Maximum water recovery for a constant feed concentration of 125 g/L with variable feed pressure and sweep concentration.

Comparison of OARO Simulations vs. MVC

Energy consumption of RO, MVC, OARO water treatment and theoretical minimum work with respect to feed TDS concentration and recovery
NETL’s Test System
Conclusions & Future Work

• OARO appears to be fundamentally feasible in for single bench tests and with simple models
  – Able to dewater other high salinity brines
• Characterize flat sheet and hollow fiber membrane on NETL system to better capture salt transport in OARO
• Determine mass transport properties both external and internal of membrane
• Work with CMU collaborators for refined process simulations for technoeconomic analysis for comparison with MVC
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Thank you for your attention.

Questions?

Thank you for your attention.
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Governing Equations for OARO

\[ J_w = A \cdot \{[P_f - P_s] - \pi(c_{f,m}) - \pi(c_{s,m})\} \]  
Water Flux

\[ J_s = B \cdot [c_{f,m} - c_{s,m}] \]  
Salt Flux

\[ c_{f,m} = c_{f,b} \cdot \exp\left(\frac{J_w \delta_f}{D}\right) + \frac{B}{J_w} \cdot \frac{c_{f,b} \cdot \exp\left(\frac{J_w \delta_f}{D}\right) - c_{s,b} \cdot \exp\left(-\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \cdot \exp\left(\frac{J_w \delta_f}{D}\right) - \exp\left(-\frac{J_w S}{D}\right)} \cdot \left[1 - \exp\left(\frac{J_w \delta_f}{D}\right)\right] \]

\[ c_{s,m} = c_{s,b} \cdot \exp\left(-\frac{J_w S}{D}\right) + \frac{B}{J_w} \cdot \frac{c_{f,b} \cdot \exp\left(\frac{J_w \delta_f}{D}\right) - c_{s,b} \cdot \exp\left(-\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \cdot \exp\left(\frac{J_w \delta_f}{D}\right) - \exp\left(-\frac{J_w S}{D}\right)} \cdot \left[1 - \exp\left(-\frac{J_w S}{D}\right)\right] \]

A  Membrane Water permeance
B  Membrane solute permeability
S  Membrane structural parameter
J_w  Water flux
J_s  Salt flux
P_f  Feed hydrostatic pressure
P_s  Sweep hydrostatic pressure
c_{f,m}  Feed salt concentration
c_{s,m}  Sweep salt concentration
D  Salt diffusion coefficient
\delta_f  Feed boundary layer thickness
\pi(c)  Osmotic pressure as a function of concentration
Osmotic pressure of sodium chloride solutions and produced brines at 25°C
Brine osmotic pressures calculated using Geochemist’s Workbench v9 with thermo_phrqpitz
Dual-mode Extraction/Injection Wells

Phase 2

Phase 2 - CO₂ Storage

- Pre-injection brine extraction well is converted to a CO₂ injection well
- New brine extraction well is put into operation with processing facility and new brine injection well
- A monitoring well may be completed in an overlying formation to assess possible seal leakage
NH$_3$-CO$_2$ osmotic brine concentrator pilot that was operated in the Marcellus Shale

Concentrate brines up to 180 g/L TDS

Process consists of:
- FO stage @ low TMP
- Draw solute recovery
- RO stage @ high TMP

Distillation

Column

Stripper

Condenser / Absorber

Produced Water

Brine

Feed

NH$_3$-CO$_2$ Draw

Stripper Brine

Feed

Water

Permeate

Produced Water Feed

Water
CA Membranes in PRO

- Structural parameters are often calculated in studies that develop and/or characterize membranes for forward osmosis.
- Structural parameters may change as a membrane is compacted by applied hydrostatic pressure.
- Accurate simulation of OARO should measure membrane properties at conditions which reflect process conditions.

Effective structural parameter of Hydration Technology Innovations’ (HTI) woven supported cellulose triacetate membrane calculated from pressure retarded osmosis using a 0.01 M sodium chloride feed at 25°C.
Issues with TFC Chemistry

- Hydrophobic support layer
- Polyamide (PA) Selective Layer
- Polysulfone (PSu) Polymer Layer
- Polyethylene terephthalate (PET) Fabric Layer

Dow SW30-XLE 50 μm
Comparison of OARO Simulations vs. MVC

Significantly less electricity consumption using OARO than from MVC

Assumes
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Osmotic and Hydrostatic Pressure

- Fixed osmotic pressure gradient
- Water flux into concentrated solution is positive

\[ J_w = A(\Delta \pi - \Delta P) \]

\[ J_w = A(\Delta P - \Delta \pi) \]

\[ \Delta P = P_{\text{concentrated}} - P_{\text{dilute}} \]
Prior Study of RO on GCS Brines

- Brine Concentration > Sea water (TDS ~ 35 g/L)
- Limited by mechanical stability of membrane
- Water recovery of brines > 85 g/L TDS is negligible for a 1200 psi membrane

Comparison of maximum water recovery using RO comparing seawater (a) and a 86 g/L brine (b) from a CO₂ sequestration site in Wyoming
The OARO process

- Seeks to concentrate a brine in steps

- Pressure limitations will affect concentration difference between the feed and sweep solutions
Minimum Work of Dewatering

2 mol/L (117 g/L) sodium chloride solution at 20°C using the NRTL electrolyte equation of state with AspenPlus V8.4

The minimum work of dewatering doubles for ZLD v. 65% recovery

~3.1 kWh/m³

~6.6 kWh/m³
# General Experimental Plan

<table>
<thead>
<tr>
<th>Test Regime</th>
<th>Test Pressures</th>
<th>Feed</th>
<th>Sweep</th>
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<tbody>
<tr>
<td><strong>Compaction</strong></td>
<td>31.0 bar</td>
<td>Purified Water</td>
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<tr>
<td><strong>RO/PRO Water and Salt Flux</strong></td>
<td>27.6–6.9 bar in 6.9 bar increments</td>
<td>Purified Water</td>
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<td>0.15 mol·kg^{-1} H₂O</td>
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<td>2.1 mol·kg^{-1} H₂O</td>
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<td>27.6–6.9 bar in 6.9 bar increments</td>
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