Dewatering of High Salinity Brines by Osmotically Assisted Reverse Osmosis

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Motivation: Extracted CO_2 Storage Brines

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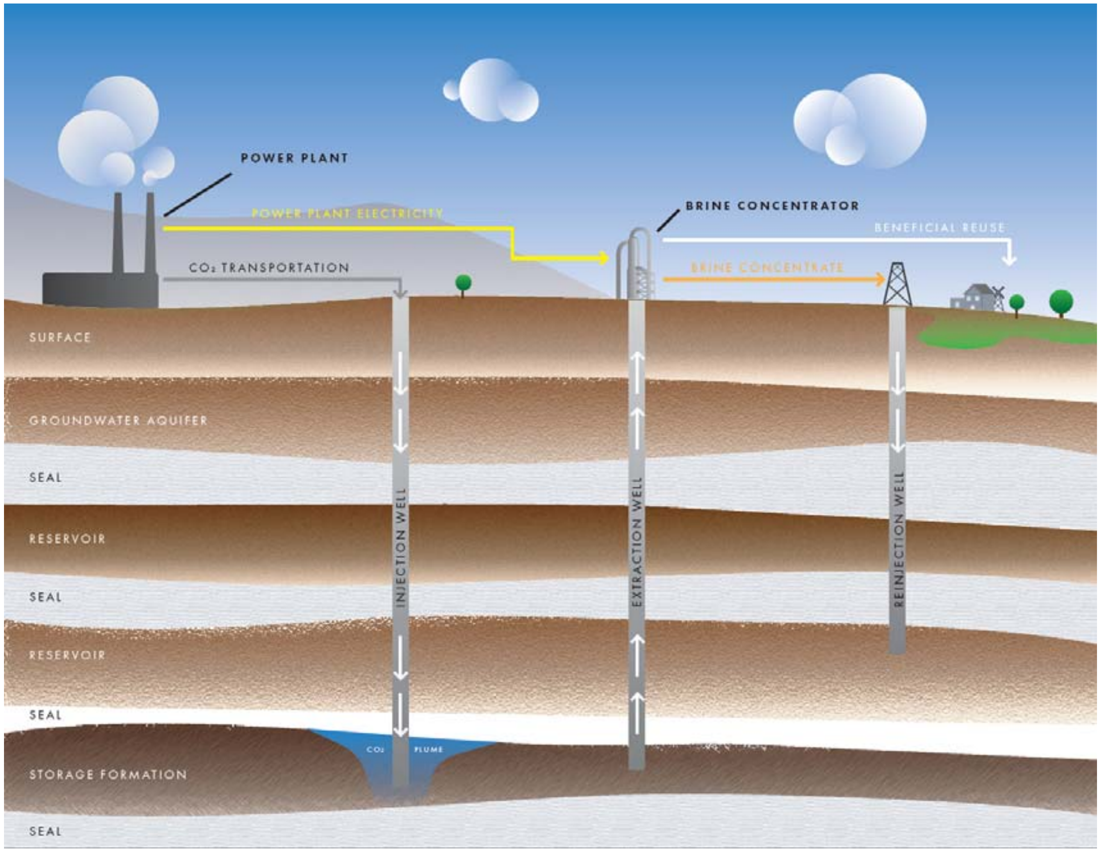
Capture CO_2 and prevent its release into the atmosphere

Store CO_2 by compression and injection into deep saline formations



Saline formation CO_2 storage scheme

- 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

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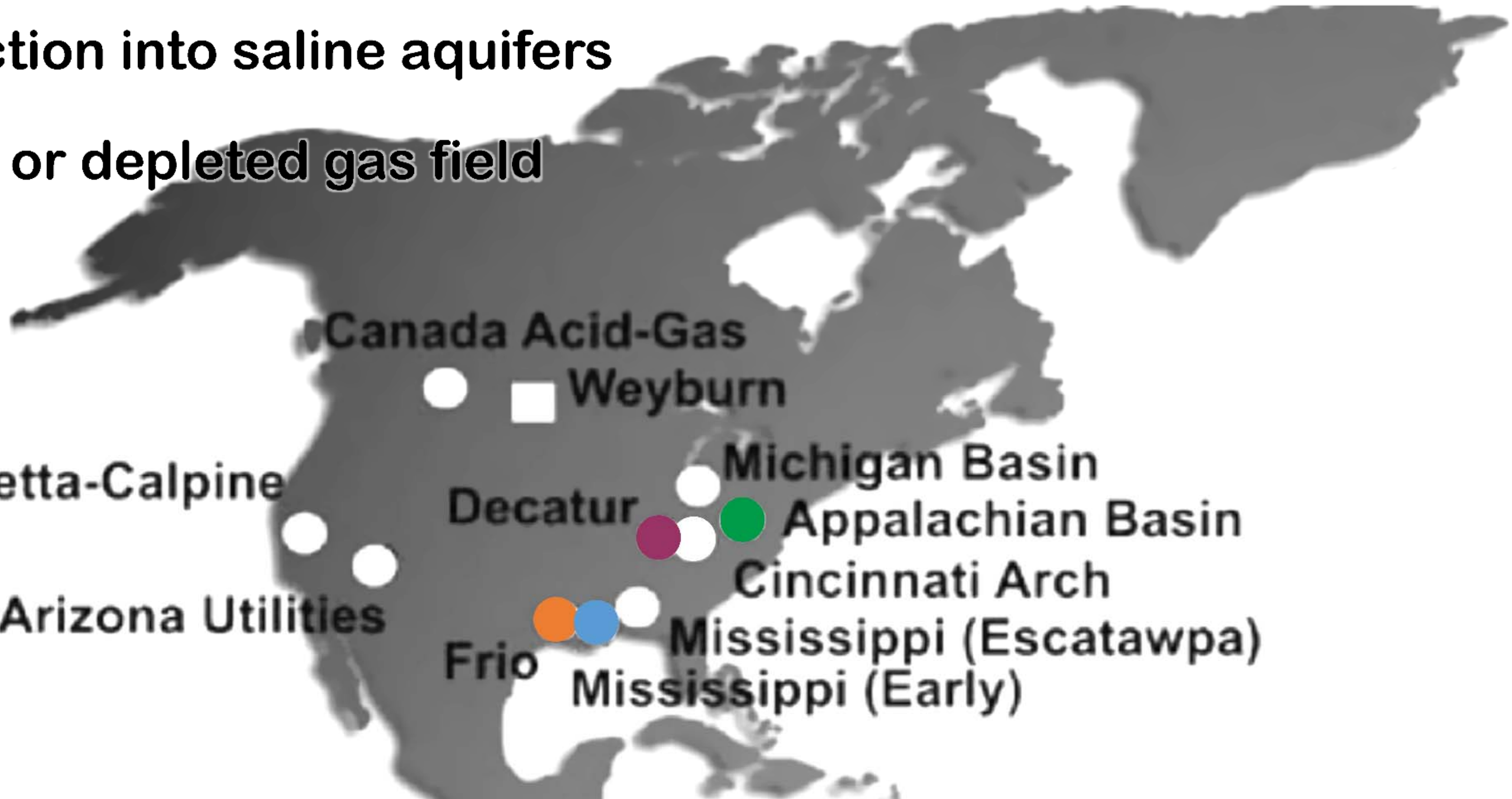
J.T. Arena et al. "Management and dewatering of brines extracted from geologic carbon storage sites," accepted to *Int. J. Greenhouse Gas Control*, in press.

Brine Composition

- ○ Injection into saline aquifers
- □ EOR or depleted gas field



Lower Tuscaloosa 149 g/L TDS	Mt. Simon 115 g/L TDS	Frio 109 g/L TDS	Oriskany 221 g/L TDS

Survey of subsurface brines

K. Michael et al. *Int. J. Greenhouse Gas Control* 4 (2010) 659-667.
J. Lu et al. *Chem. Geol.* 291 (2012) 269-277.
K.G. Knauss et al. *Chem. Geol.* 217 (2005) 339-350.
R. M. Dilmore *Environ. Sci. Technol.* 42 (2008) 2760-2766.
B. Sass et al. *Proceedings of the 4th Int. Conf. on Greenhouse Gas Control Technologies*, 1998, 1079-1088.

Eastern U.S. CO_2 Storage Brines

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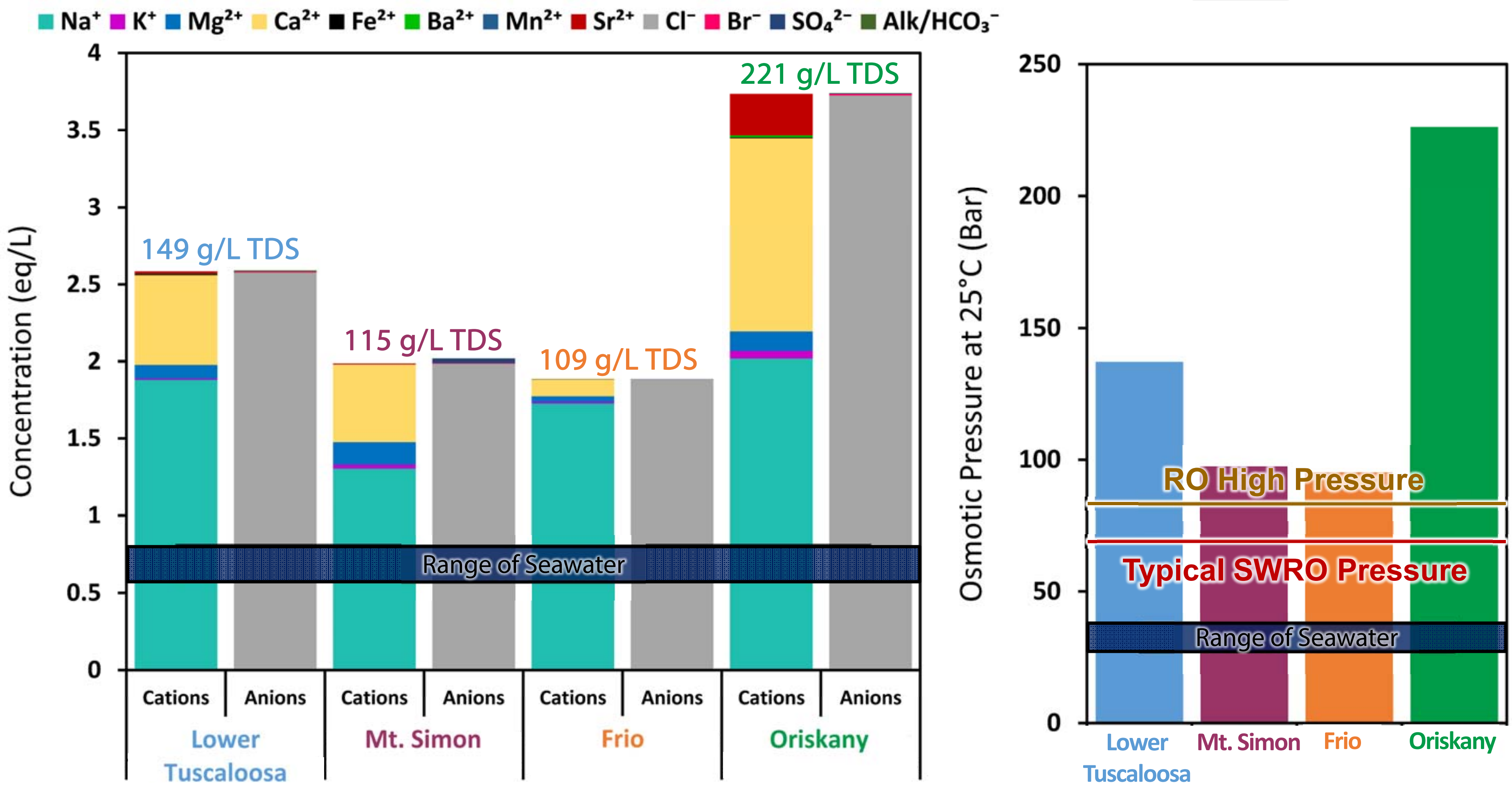

Composition (eq/ L) of four brines extracted from GCS-relevant formations in the eastern U.S. assuming complete dissociation. Osmotic pressure calculated from water activity determine using Geochemist's Workbench v9 with the thermo_phrqpitz database.

K. Michael et al. *Int. J. Greenhouse Gas Control* 4 (2010) 659-667.
J. Lu et al. *Chem. Geol.* 291 (2012) 269-277.
K.G. Knauss et al. *Chem. Geol.* 217 (2005) 339-350.
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Thermal / Evaporative Desalination

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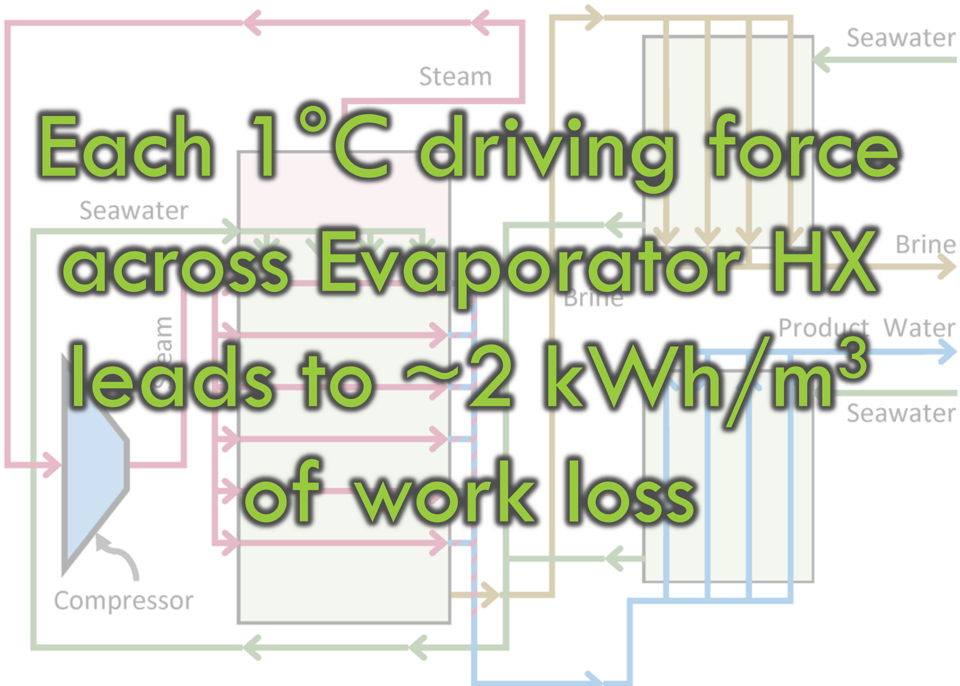
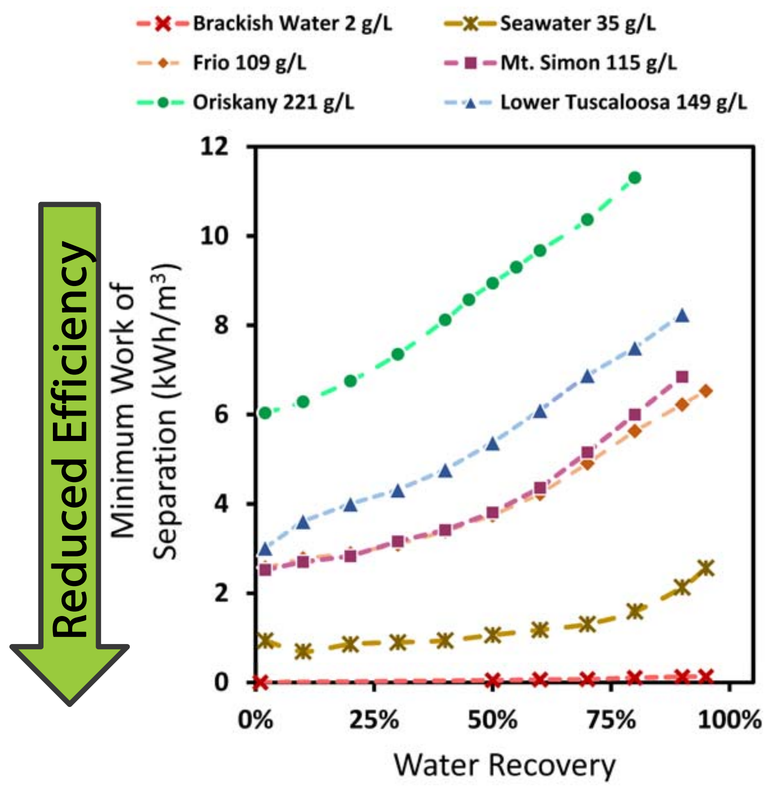
Current commercially available technologies

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





Minimum work required to produce a m³ of pure water. Calculations were done at 20°C using the ELECNRTL method within AspenPlus V8.4.

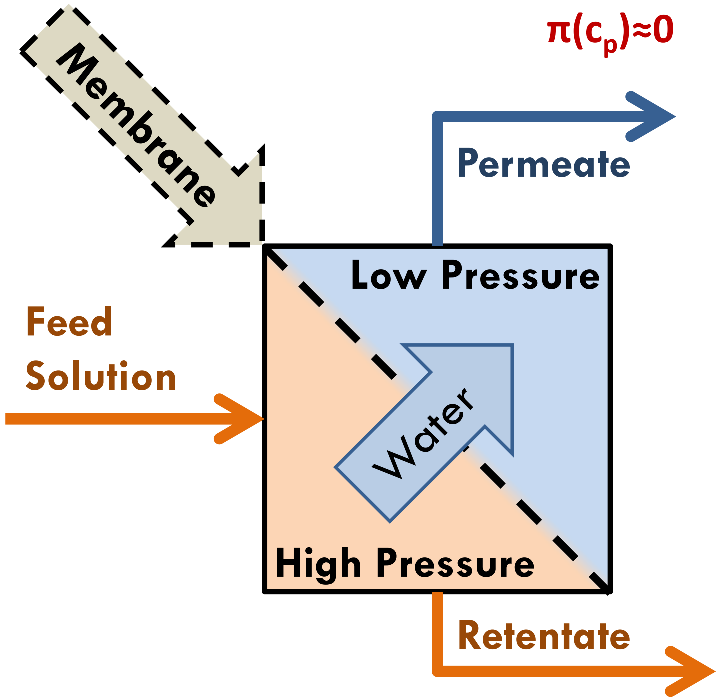
Osmotically Assisted Reverse Osmosis

Osmotically Assisted Reverse Osmosis (OARO) differs from conventional RO and FO

Reverse Osmosis

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

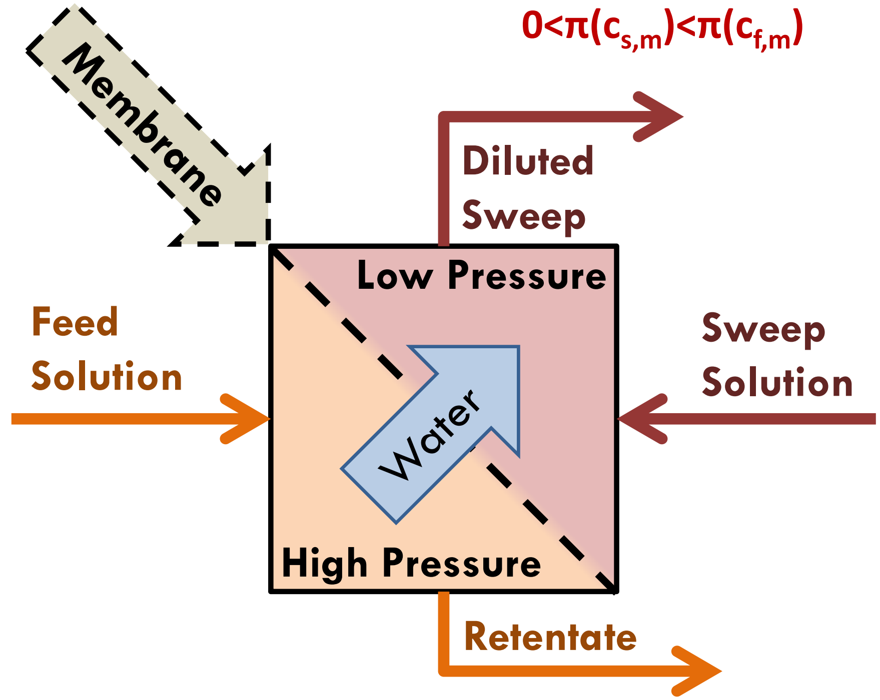
$\pi(c_p) \approx 0$



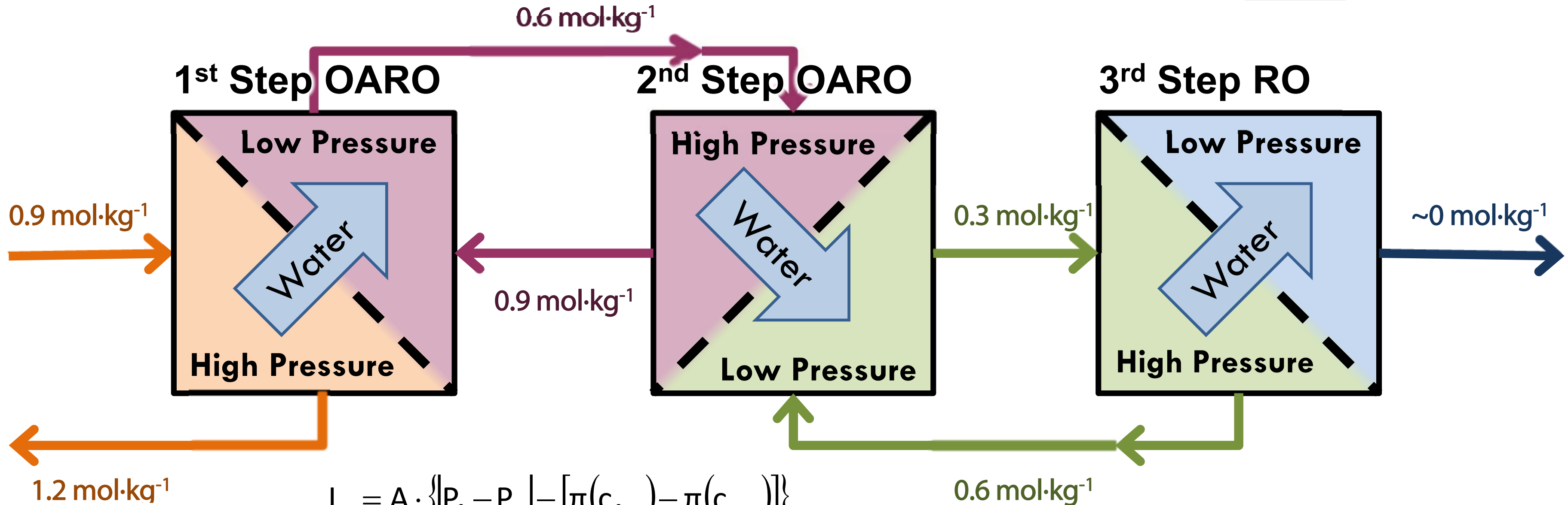
Osmotically Assisted Reverse Osmosis

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

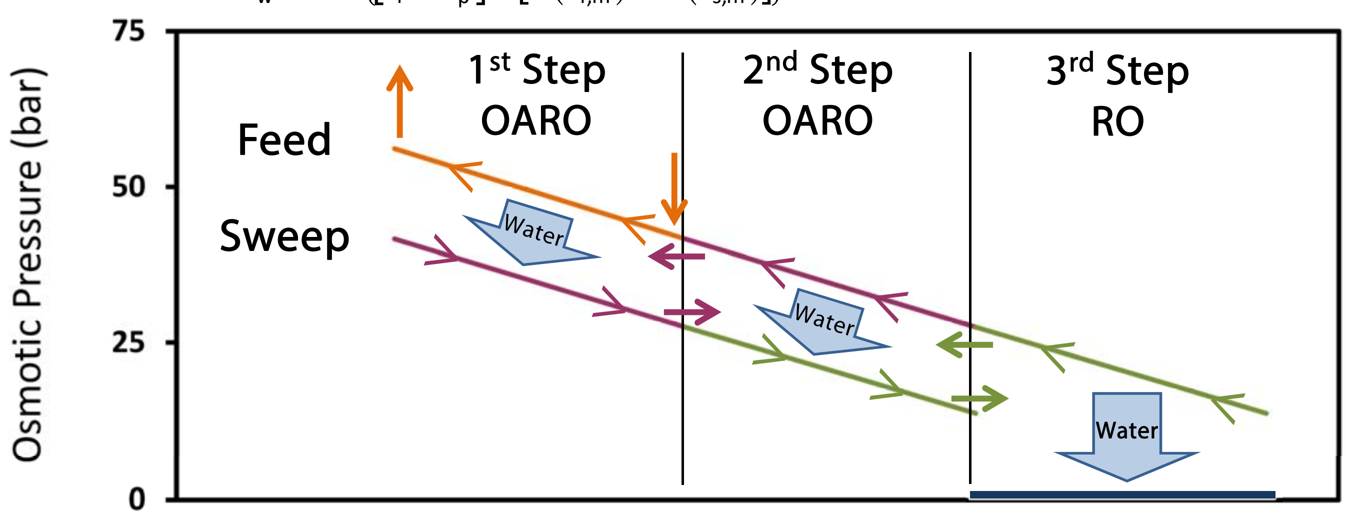
$0 < \pi(c_{s,m}) < \pi(c_{f,m})$



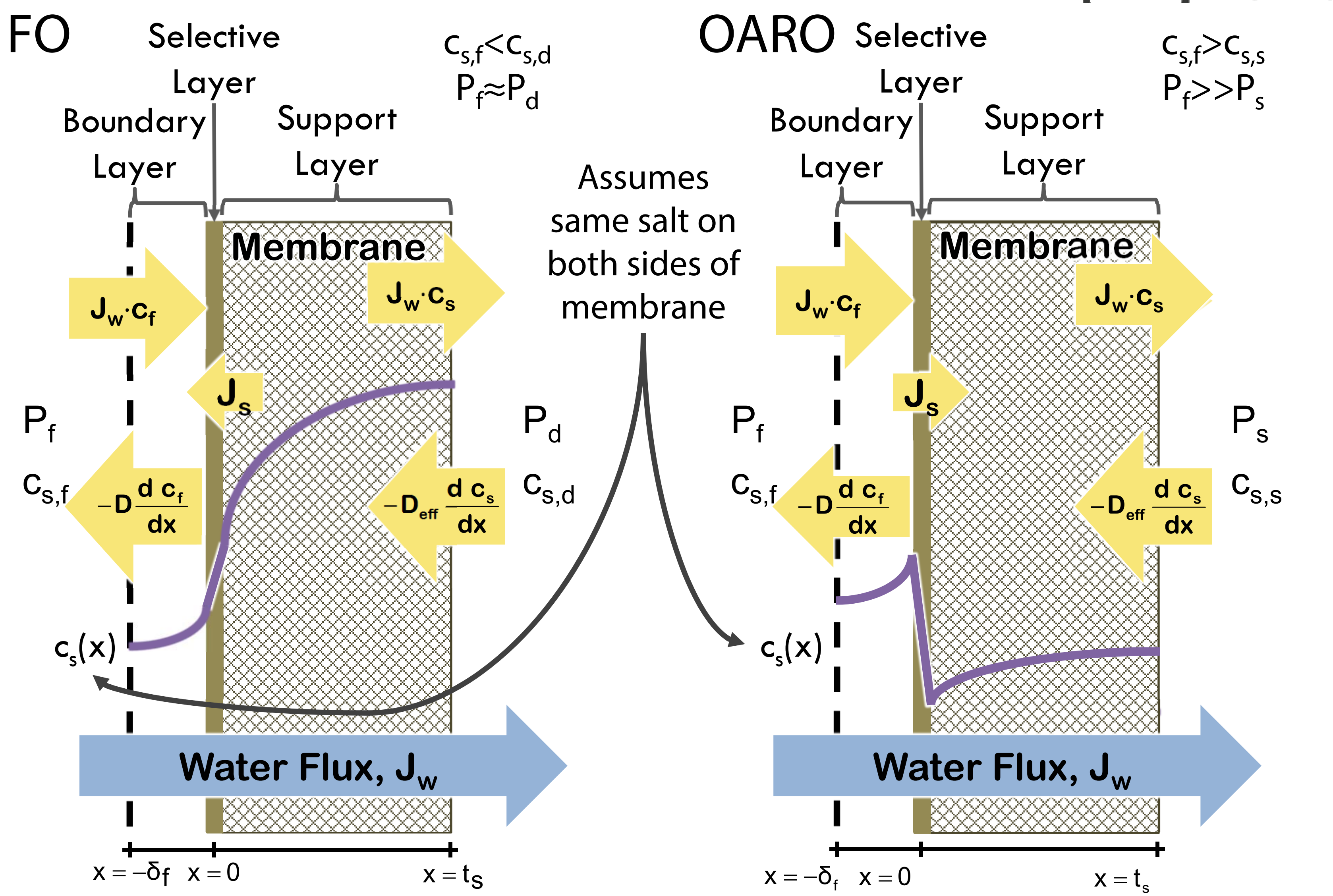
Process Configuration



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



Mass Transport in Membrane Support Layers



J.R. McCutcheon, M. Elimelech, *J. Membr. Sci.* 284 (2006) 237-247.
A. Tiraferri et al. *J. Membr. Sci.* 444 (2013) 523-538.

Cellulose Acetate Membranes

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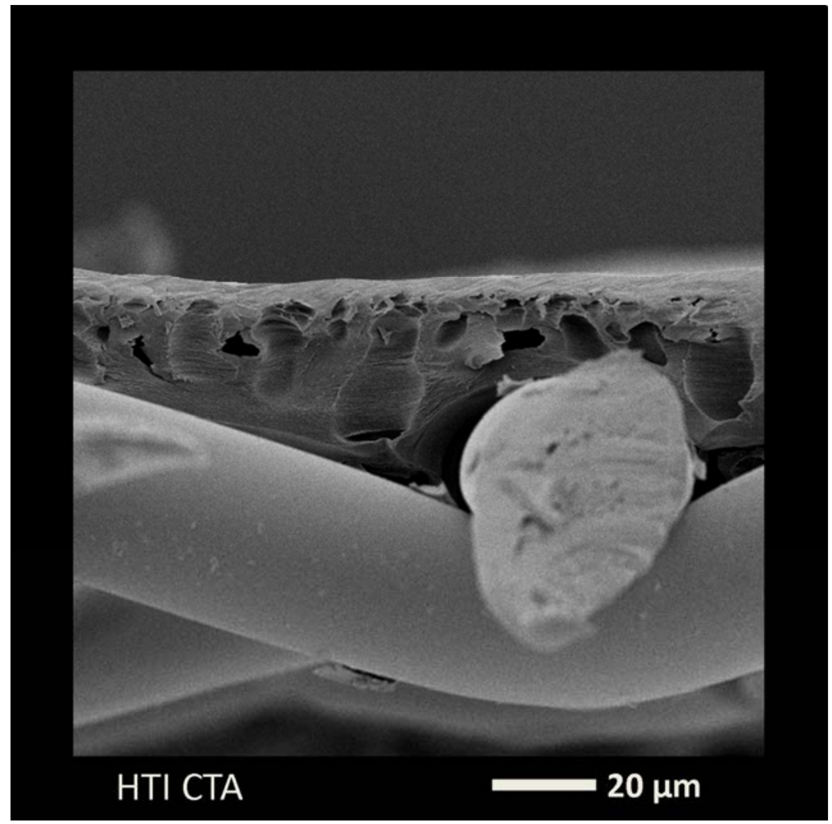
Cellulose Triacetate FO membrane developed by Hydration Technology Innovations (HTI)

Subsequent iteration manufactured by Fluid Technology Solutions (FTSH_2O)

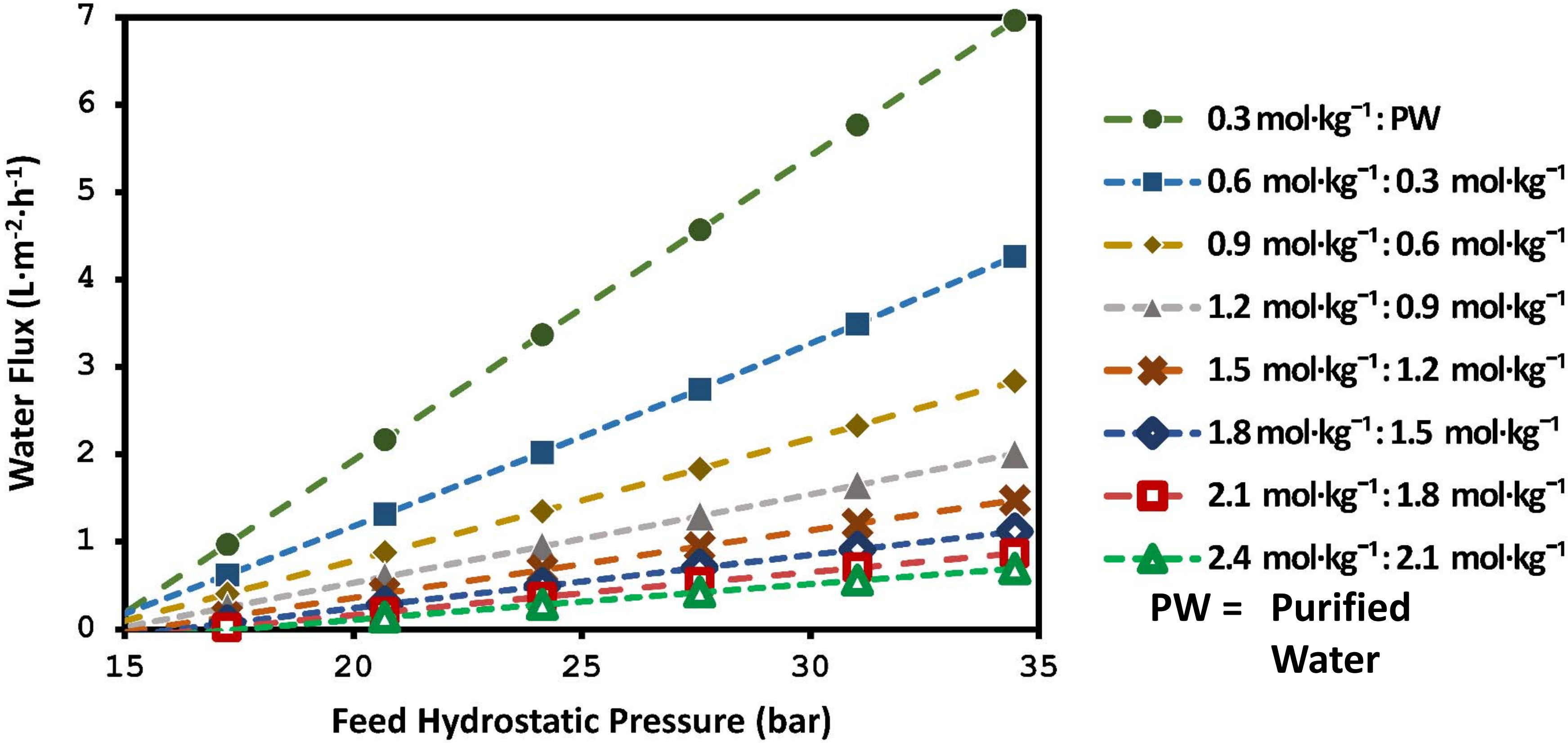
CTA selective layer
And support layer

Embedded
hydrophilic mesh



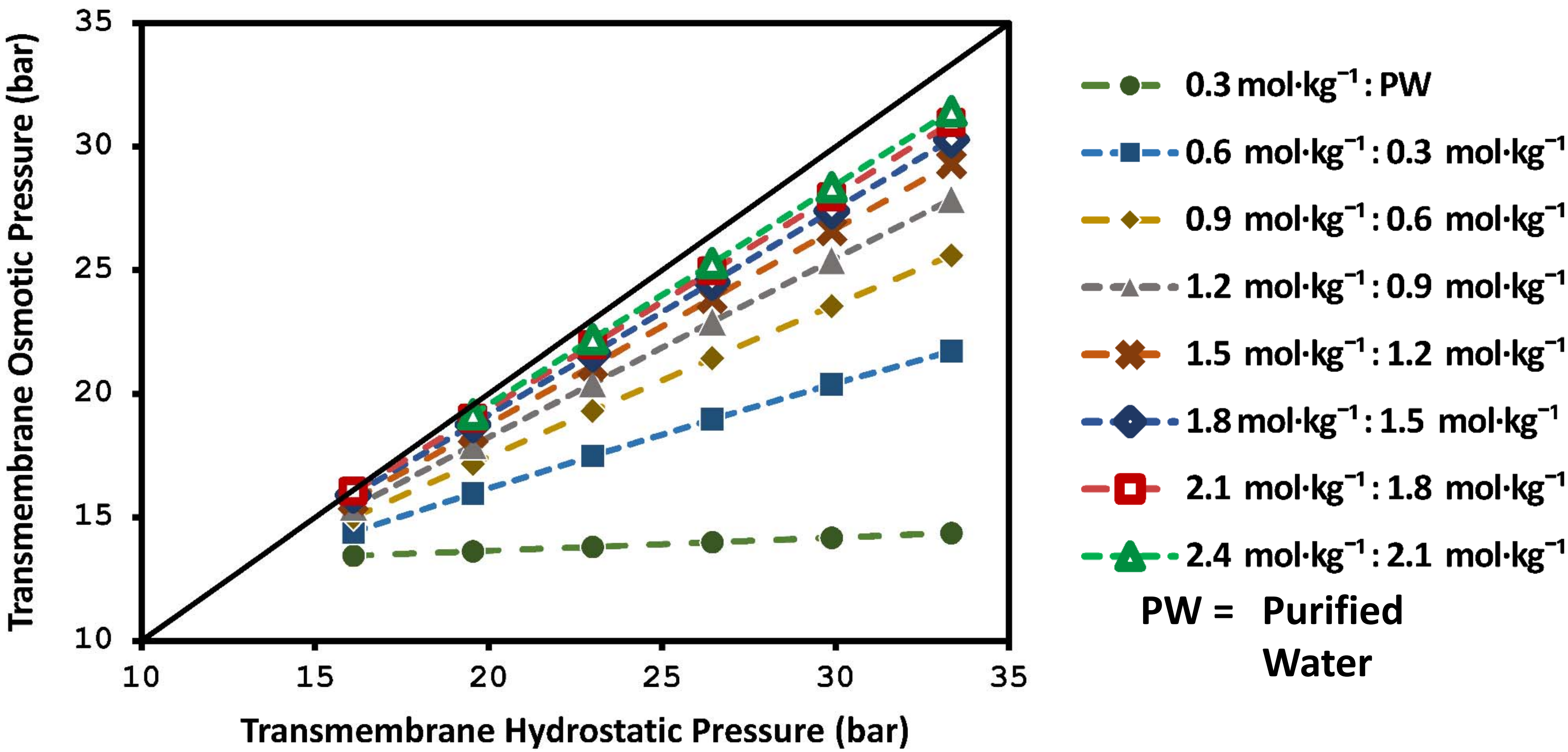
J.T. Arena, *Polydopamine Modified Thin Film Composite Membranes for Engineered Osmosis*, Ph.D. Dissertation 2015.

Simulated Water Flux



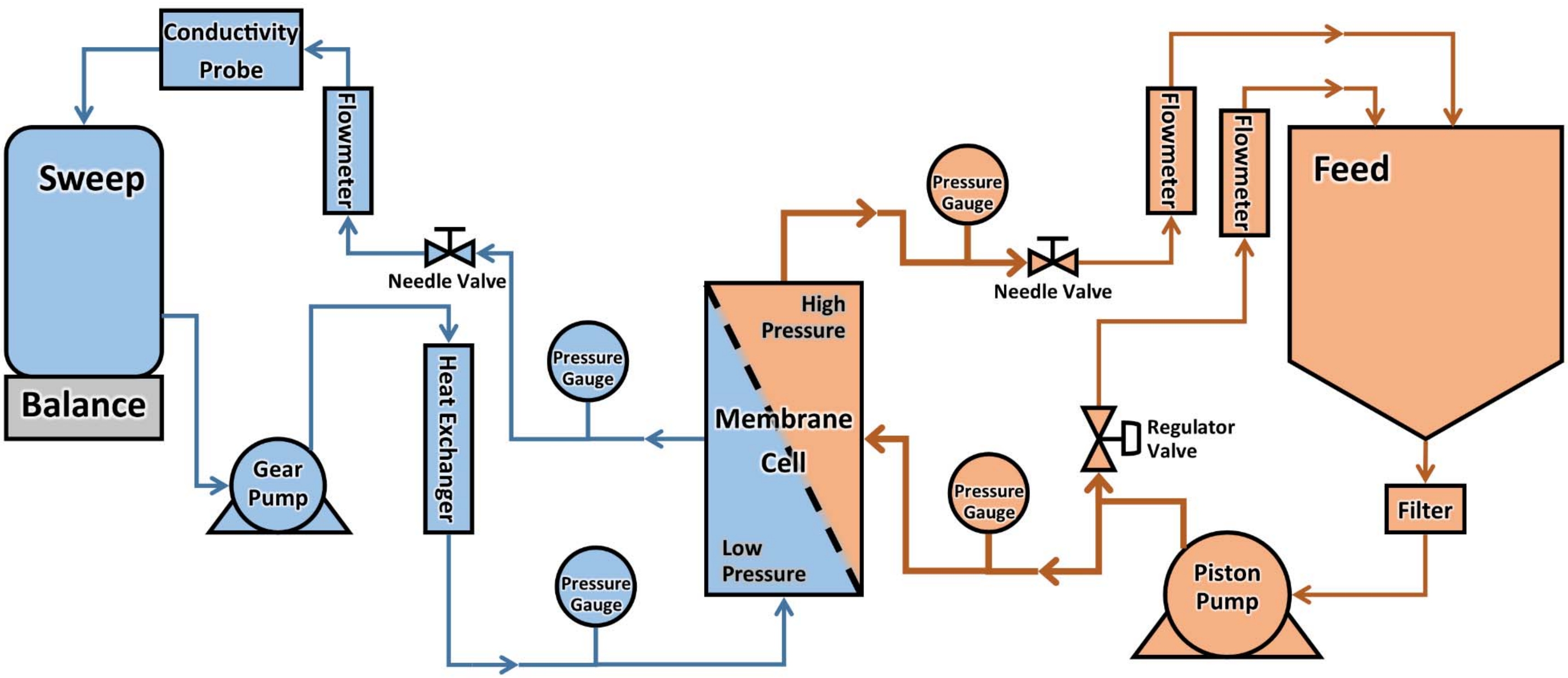
Simulated water flux for HTI's woven support CTA membrane in OARO. Assumes constant A and B of 0.3672 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$ and 0.2768 $L{\cdot}m^{-2}{\cdot}h^{-1}$ respectively, structural parameter increases linearly with applied feed hydrostatic pressure, external boundary layer thickness of 50 µm, sweep pressure of 1 bar, and a temperature of 25°C.

Transmembrane Osmotic Pressure



Simulated transmembrane osmotic pressure for HTI's woven support CTA membrane in OARO. Assumes constant A and B of 0.3672 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$ and 0.2768 $L \cdot m^{-2} \cdot h^{-1}$ 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



J.T. Arena et al. "Dewatering of High Salinity Brines by Osmotically Assisted Reverse Osmosis," in *Proceedings of the 2017 AWWA-AMTA Membrane Technology Conference and Exposition*, February 13-17, 2017.

0.3 mol · kg⁻¹ Bulk Concentration Difference

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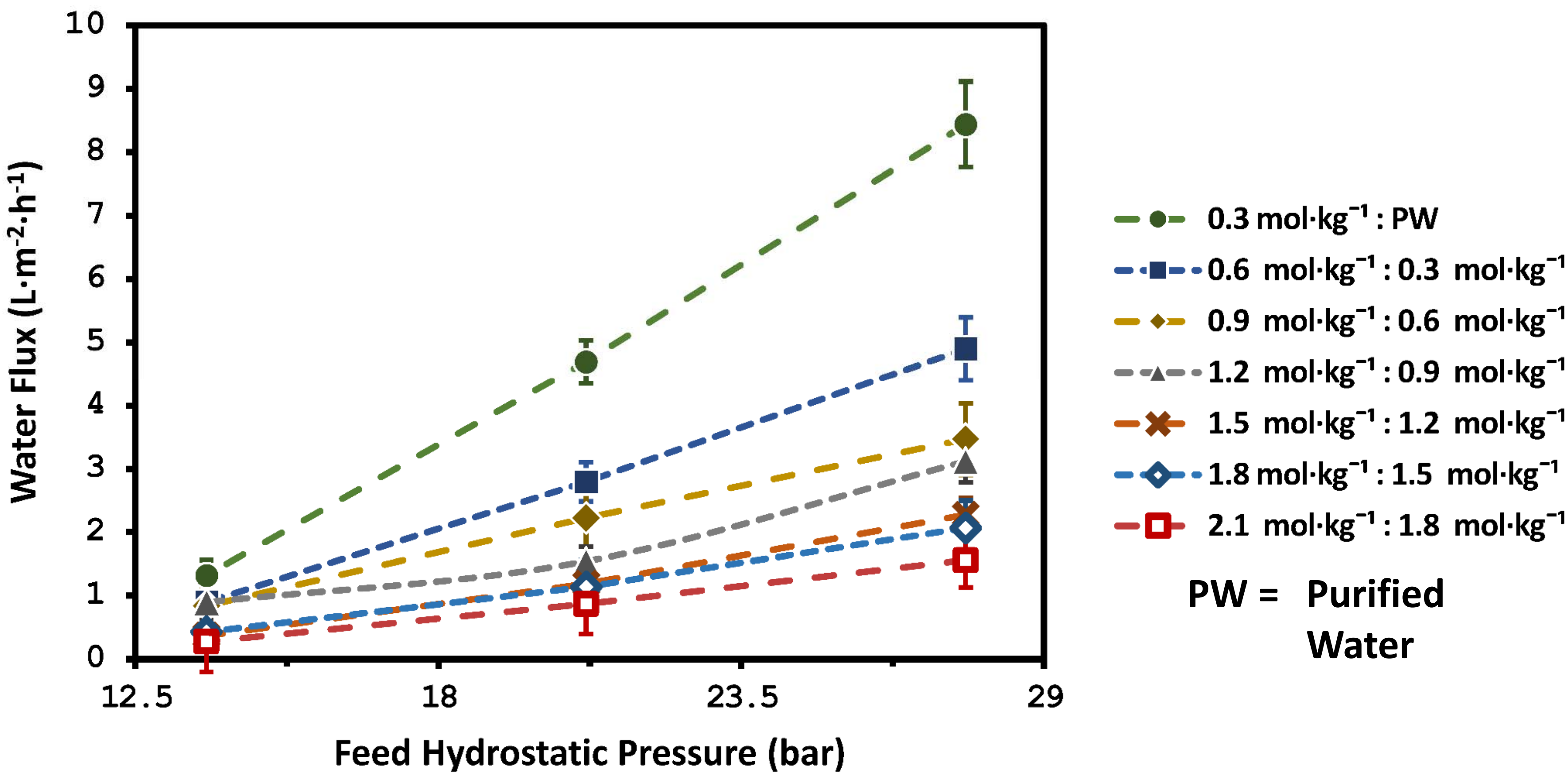
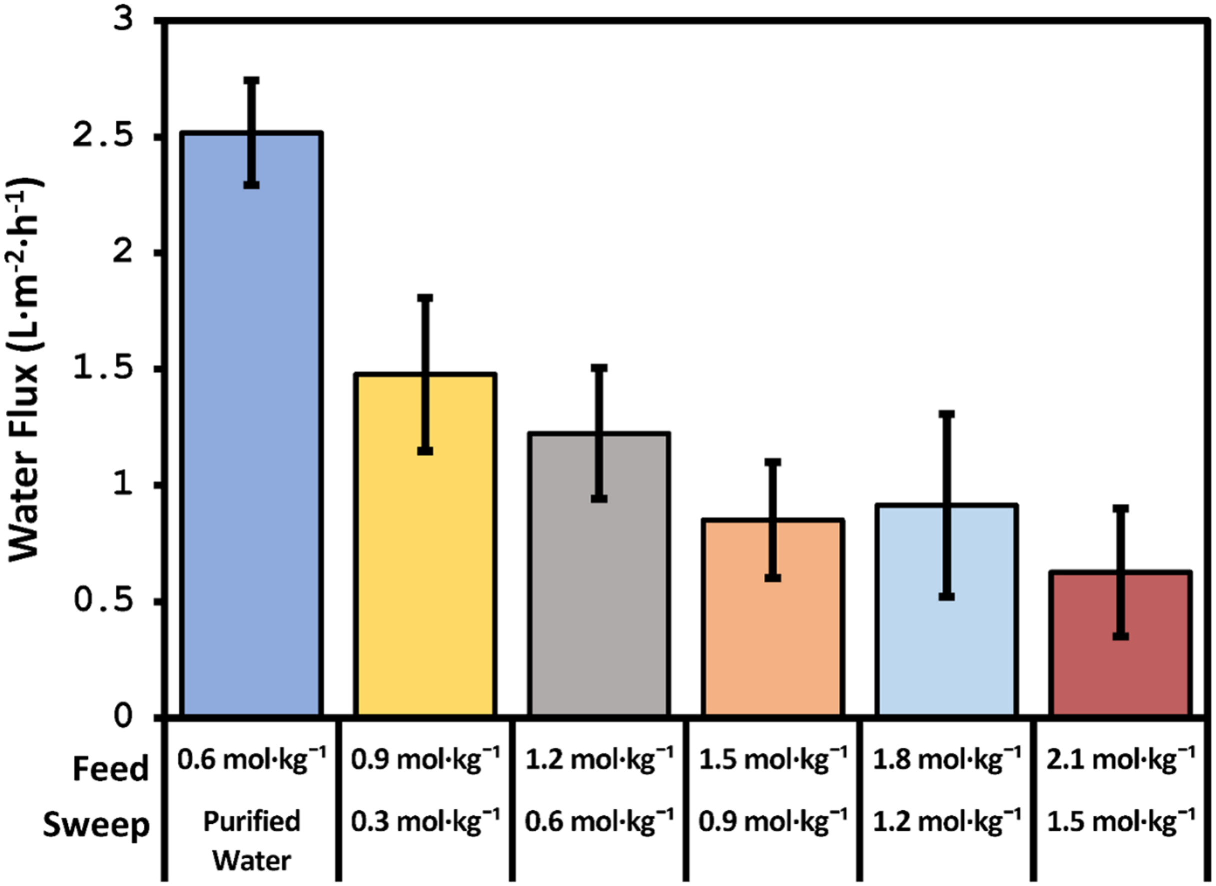


Water flux observed for FTS's woven supported CTA membrane using constant concentration difference of 0.3 mol·$kg_{H_2O}^{-1}$ between feed and sweep solutions of sodium chloride at 25°C with a feed flowrate 1.0 L·min^{-1}, sweep flowrate of 0.5 L·min^{-1}, and average sweep pressure ~1 bar.

0.6 mol · kg^{-1} Bulk Concentration Difference



Water flux observed for FTS's woven supported CTA membrane using constant concentration difference of 0.6 mol·kg$_{H_2O}^{-1}$ 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 – Purified Water Sweep

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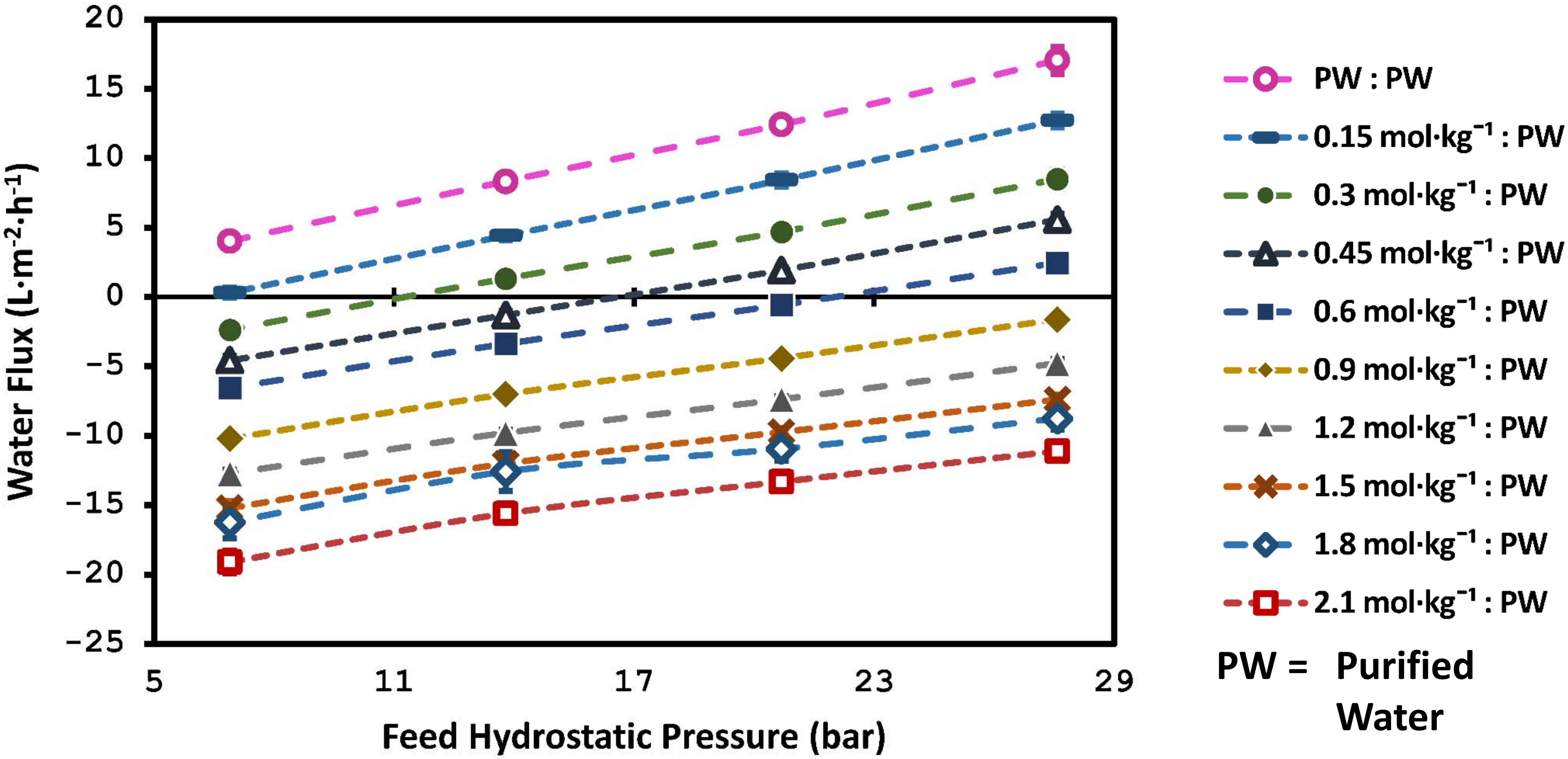
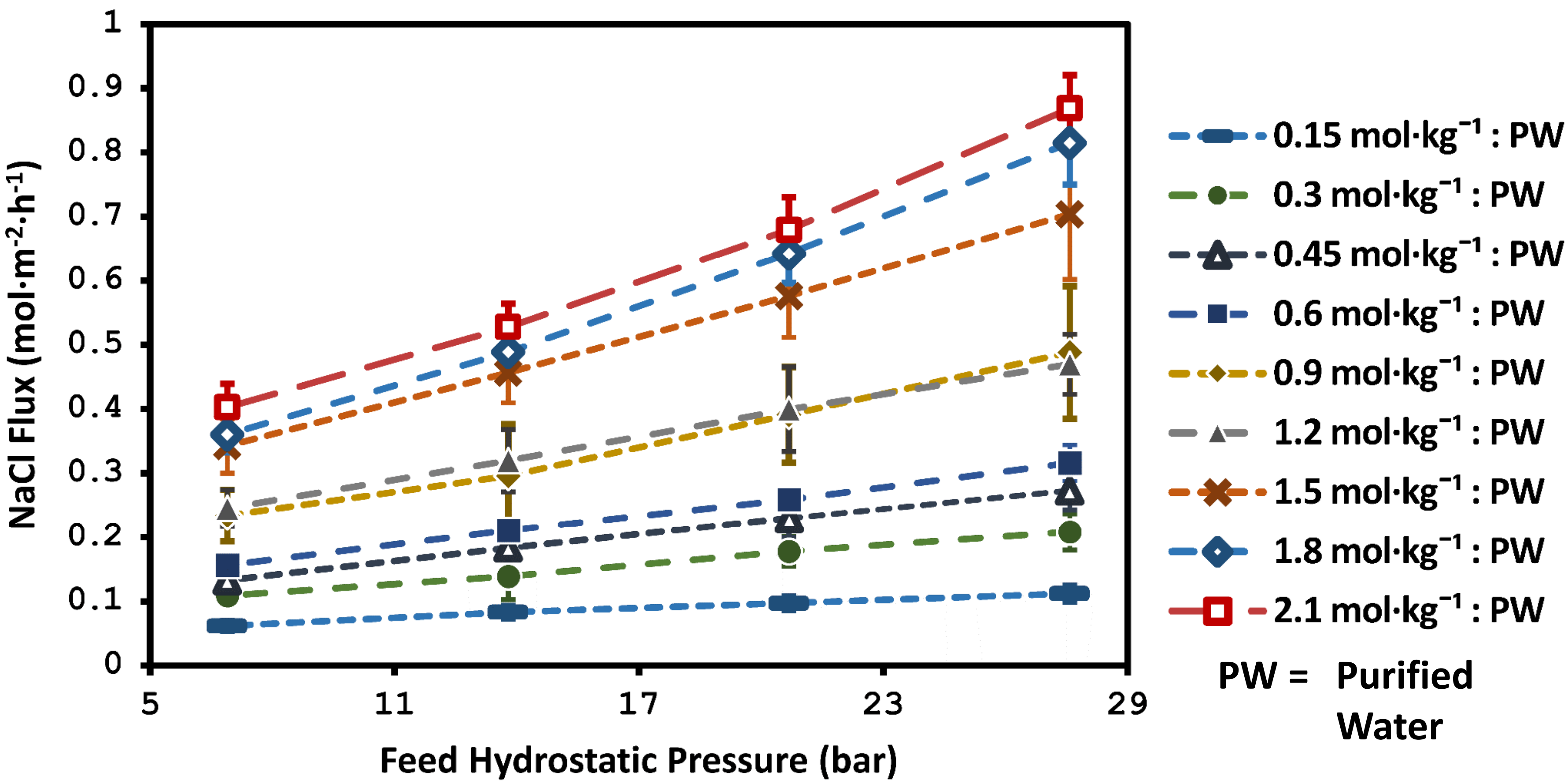


Water flux observed for FTS's woven supported CTA membrane using feed (selective layer) solutions of sodium chloride with a purified water sweep (support layer) at 25°C with a feed flowrate 1.0 L·min^{-1}, sweep flowrate of 0.5 L·min^{-1}, and average sweep pressure ~1 bar.

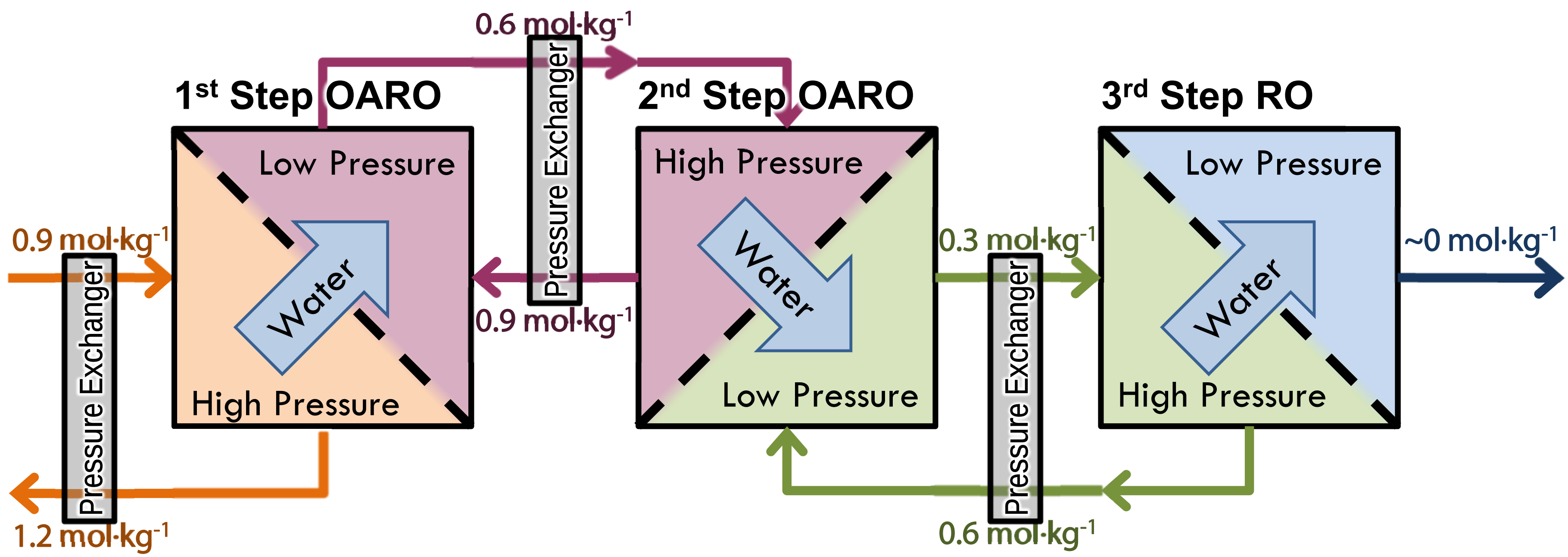
Salt Flux – Purified Water Sweep



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.

J.T. Arena et al. "Dewatering of High Salinity Brines by Osmotically Assisted Reverse Osmosis," in *Proceedings of the 2017 AWWA-AMTA Membrane Technology Conference and Exposition*, February 13-17, 2017.

OARO Process Simulations



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 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$
- Membrane structural parameter of 1000 μm
- Temperature 25°C

System Model Recovery Rates

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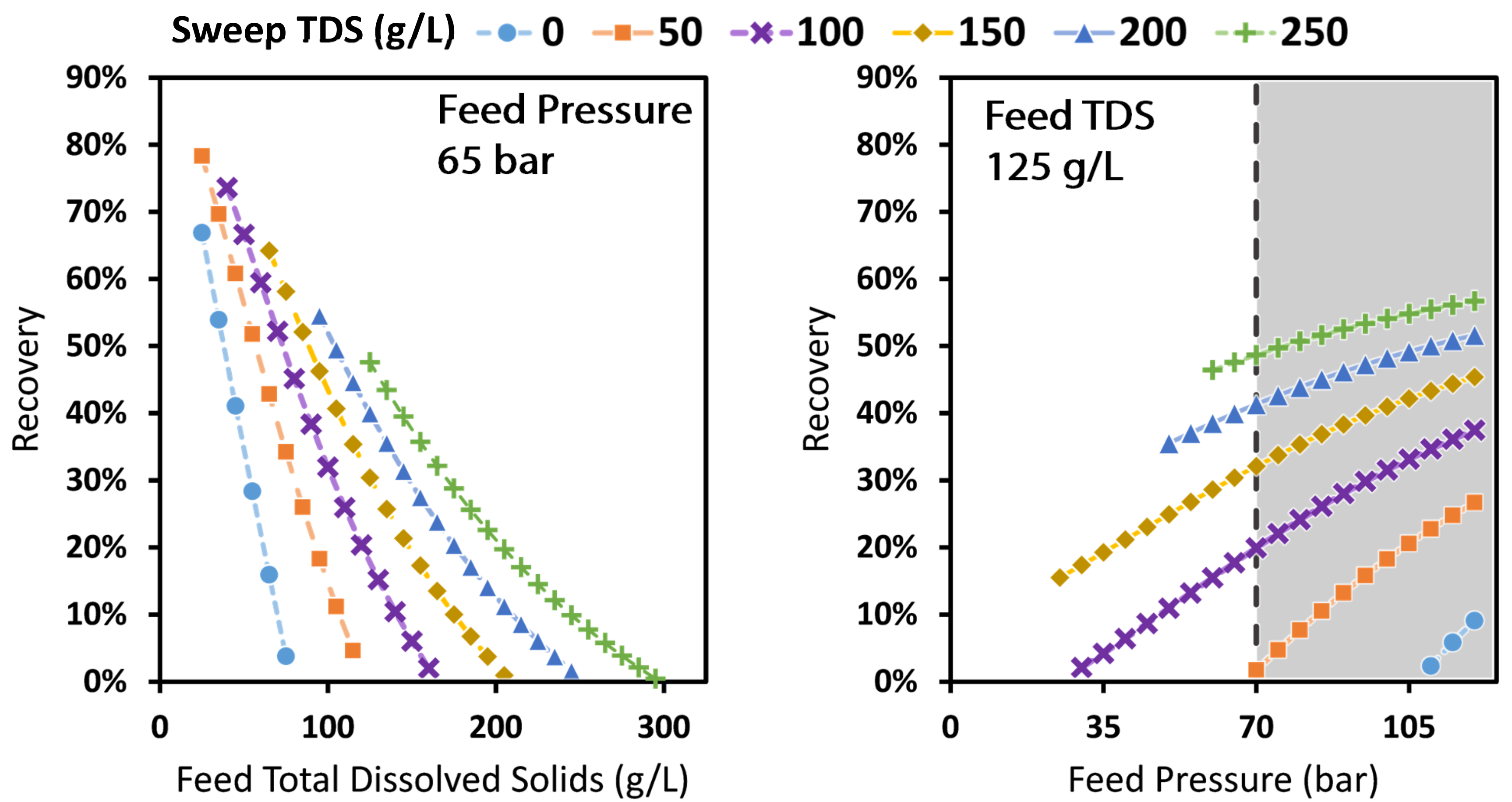
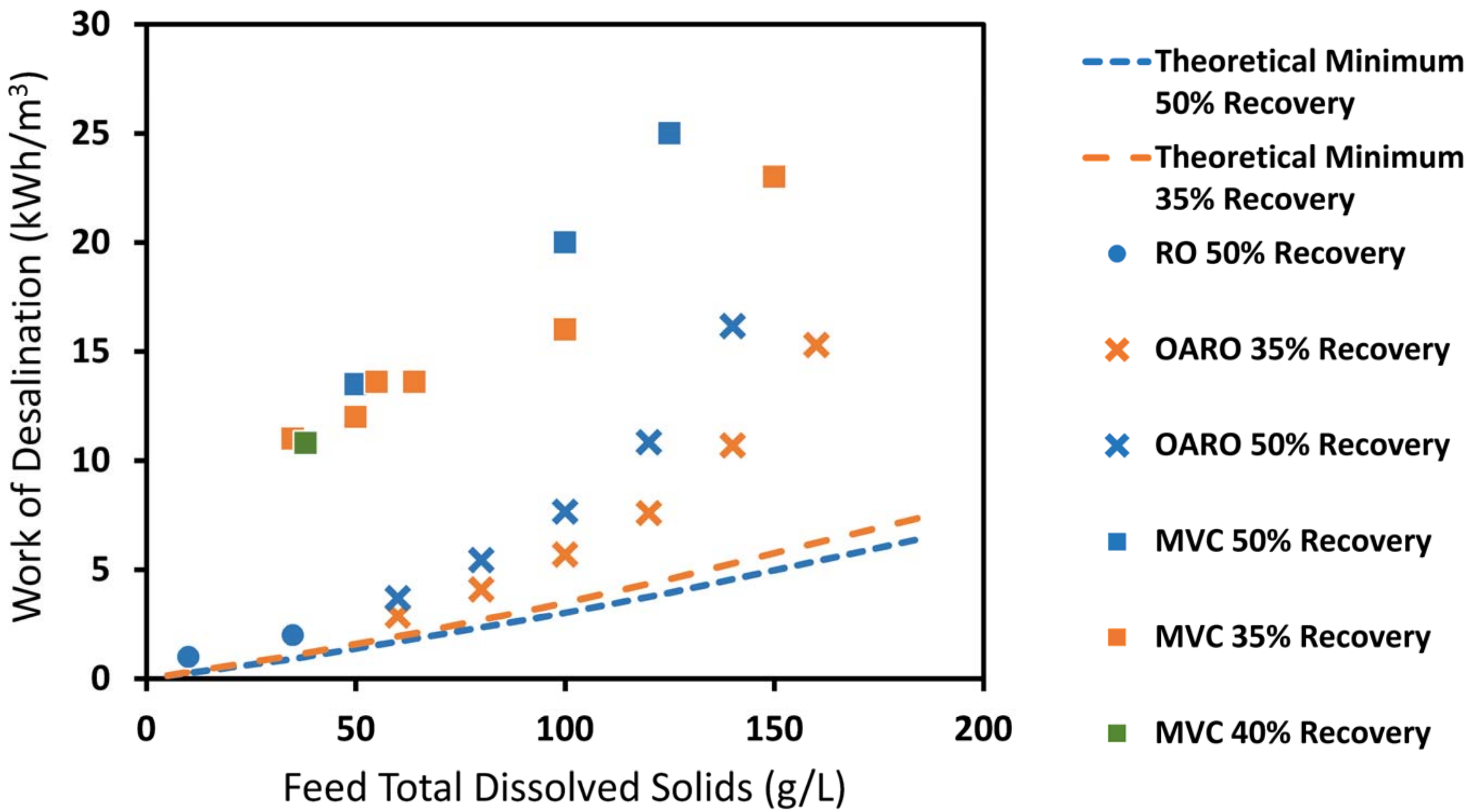


Maximum water recovery for a constant feed pressure of 65 bar with variable feed concentration and sweep concentration.

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

T.V. Bartholomew *et al.*, "Osmotically Assisted Reverse Osmosis for High Salinity Brine Treatment," submitted to *Desalination, Under review* (2017.)

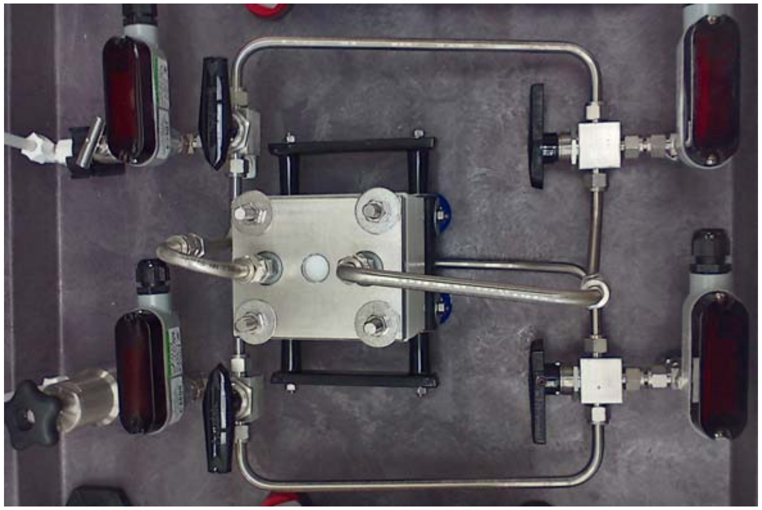
Comparison of OARO Simulations vs. MVC

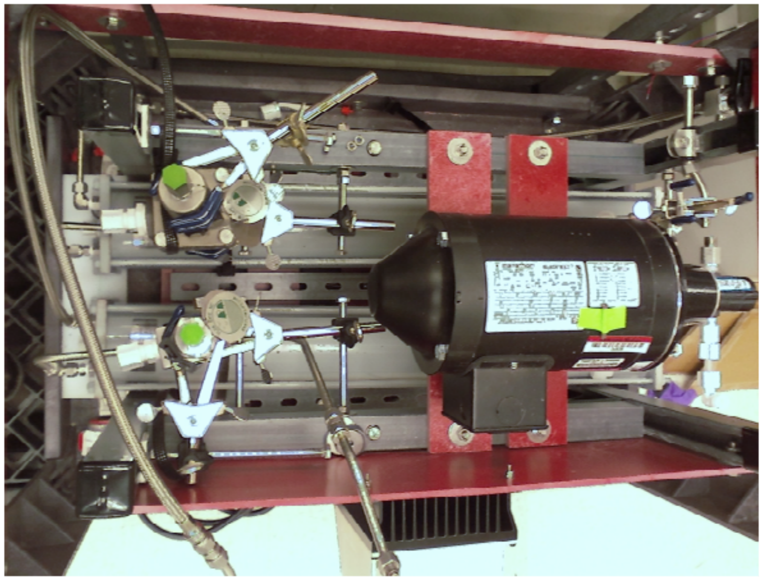


Energy consumption of RO, MVC, OARO water treatment and theoretical minimum work with respect to feed TDS concentration and recovery

T.V. Bartholomew *et al.*, "Osmotically Assisted Reverse Osmosis for High Salinity Brine Treatment," submitted to *Desalination*, under review.
G.P. Thiel et al. *Desalination* 366 (2015), 94-112.
J. Veza, *Desalination* 101 (1995) 1-10.
A. Koren, et al. *Desalination* 98 (1994), 41-48.

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

Acknowledgements

- NETL Technical Support Staff
  - Rich Valdisera
  - John Midla
  - Bill Stile
  - Rocky Stoneking
  - John O'Connor
  - Mike Ciocco
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- IE&WP Team Lead
  - Randy Gemmen
- CMU Staff
  - Larry Hayhurst
  - Cornelia Moore
- 3d Printing
  - Don Ferguson
  - Ed Robey
- NETL Project Management
  - Jessica Mullen
  - Barbara Carney
  - Karol Schrems
  - Bob Romanosky

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Questions?

Thank you for your attention.

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Governing Equations for OARO

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

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

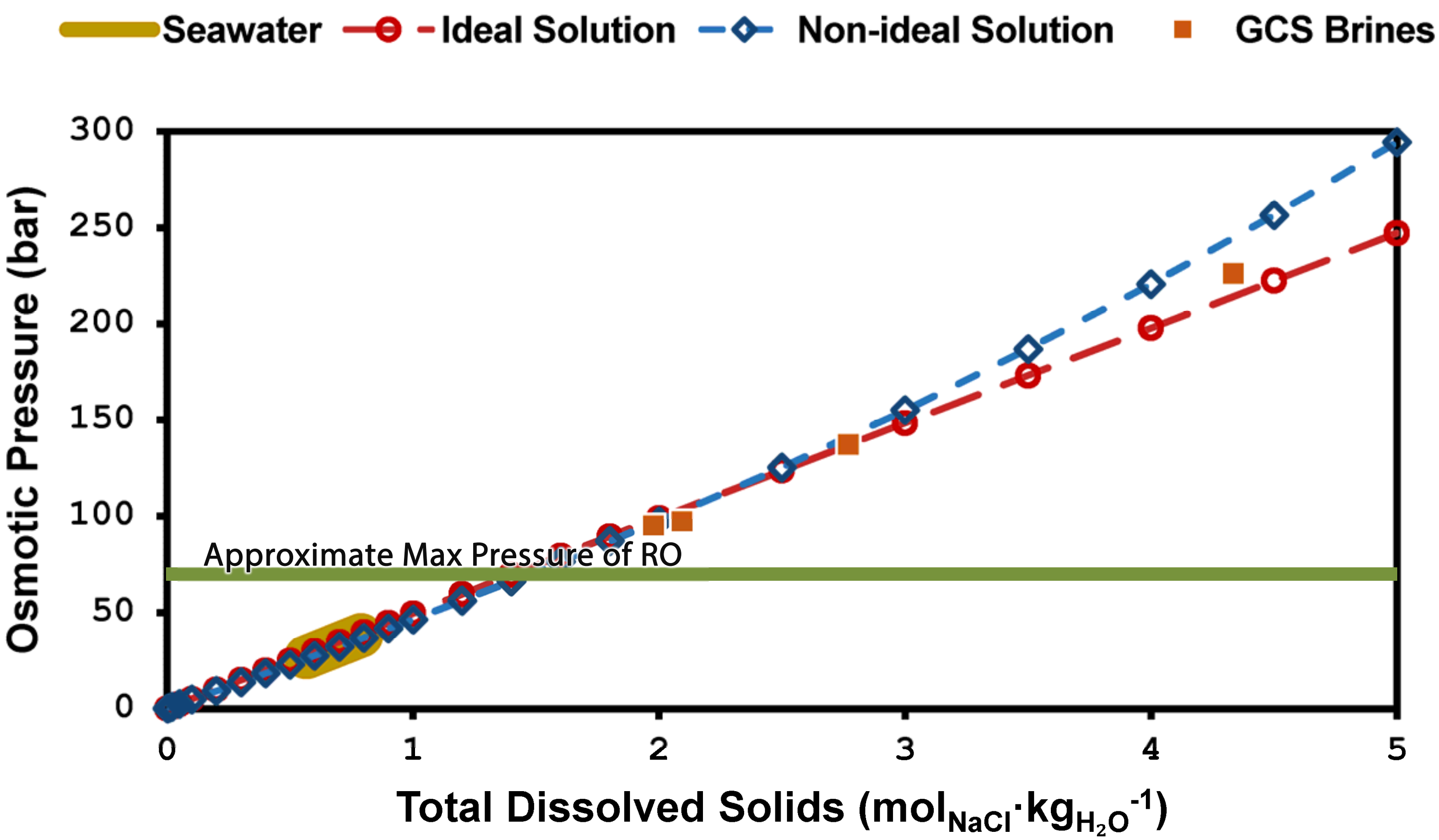
$$c_{f,m} = c_{f,b} \cdot \exp\left(\frac{J_w \delta_f}{D}\right) + \frac{B}{J_w} \cdot \left[\frac{c_{f,b} \cdot \exp\left(\frac{J_w \delta_f}{D}\right) - c_{s,b} \cdot \exp\left(-\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \cdot \left\{ \exp\left(\frac{J_w \delta_f}{D}\right) - \exp\left(-\frac{J_w S}{D}\right)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

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

Interface Concentrations

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
δ_f	Feed boundary layer thickness
$\pi(c)$	Osmotic pressure as a function of concentration

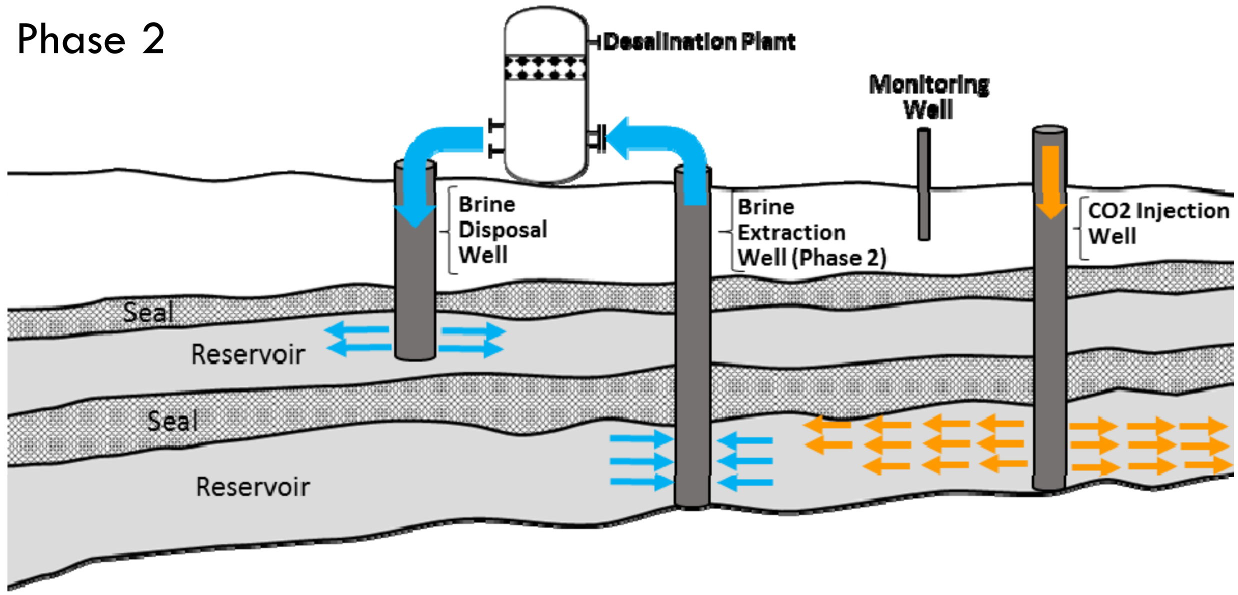
Osmotic Pressure of Brines



Osmotic pressure of sodium chloride solutions and produced brines at 25°C
Brine osmotic pressures calculated using Geochemist's Workbench v9 with thermo_phrqpitz

K. Michael et al. *Int. J. Greenhouse Gas Control* 4 (2010) 659-667.
K.G. Knauss et al. *Chem. Geol.* 217 (2005) 339-350.
B. Sass et al. *Proc. 4th Int. Conf. on Greenhouse Gas Control Technologies*, 1998, 1079-1088.
R. M. Dilmore et al. *Environ. Sci. Technol.* 42 (2008) 2760-2766.
W.J. Hamer and Y.C. Wu, *J. Phys. Chem. Ref. Data* 1 (1972) 1047-1100.
J. Lu et al. *Chem. Geol.* 291 (2012) 269-277.

Dual-mode Extraction/Injection Wells

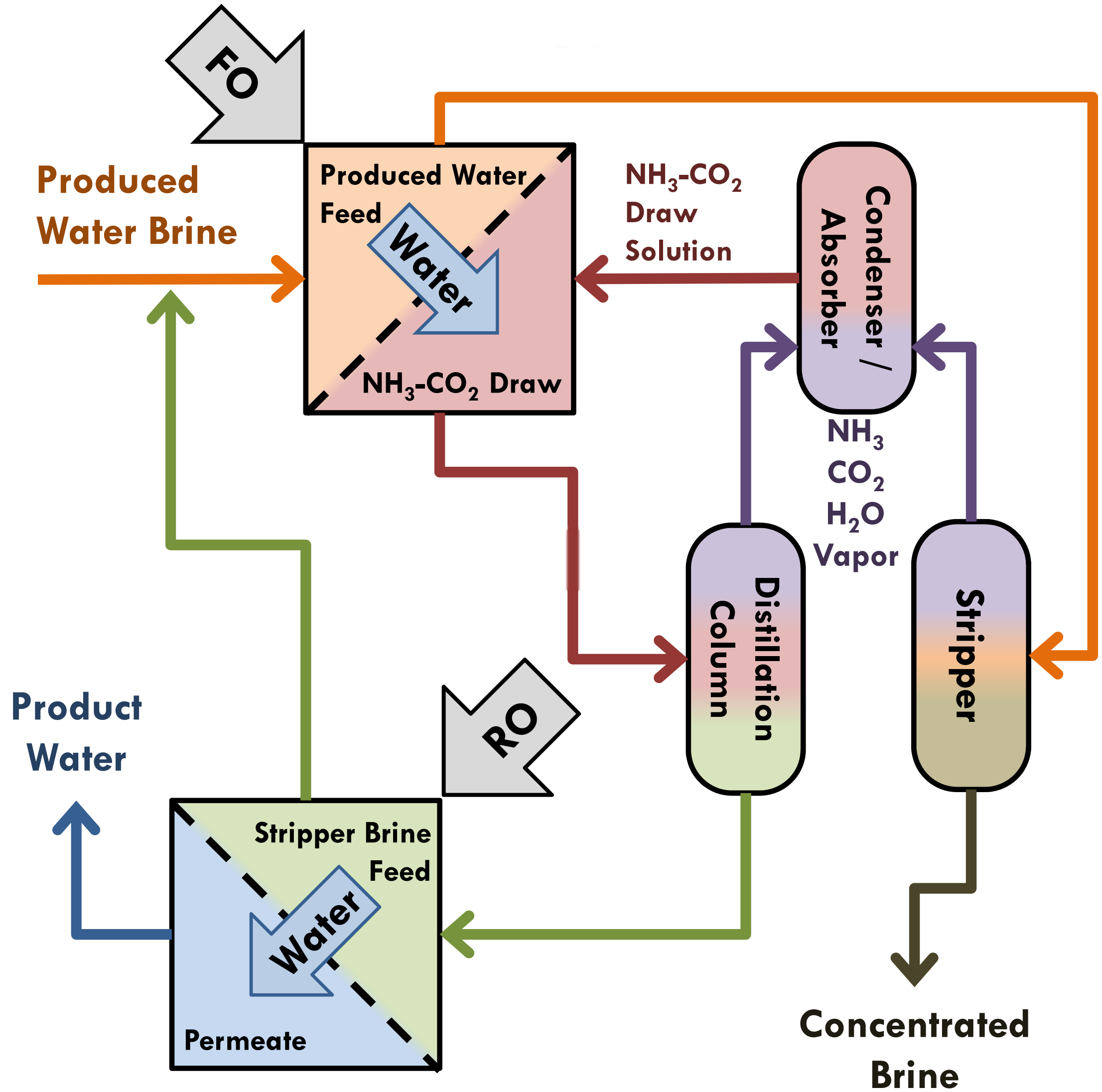


Phase 2-CO_2 Storage

- Pre-injection brine extraction well is converted to a CO_2 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

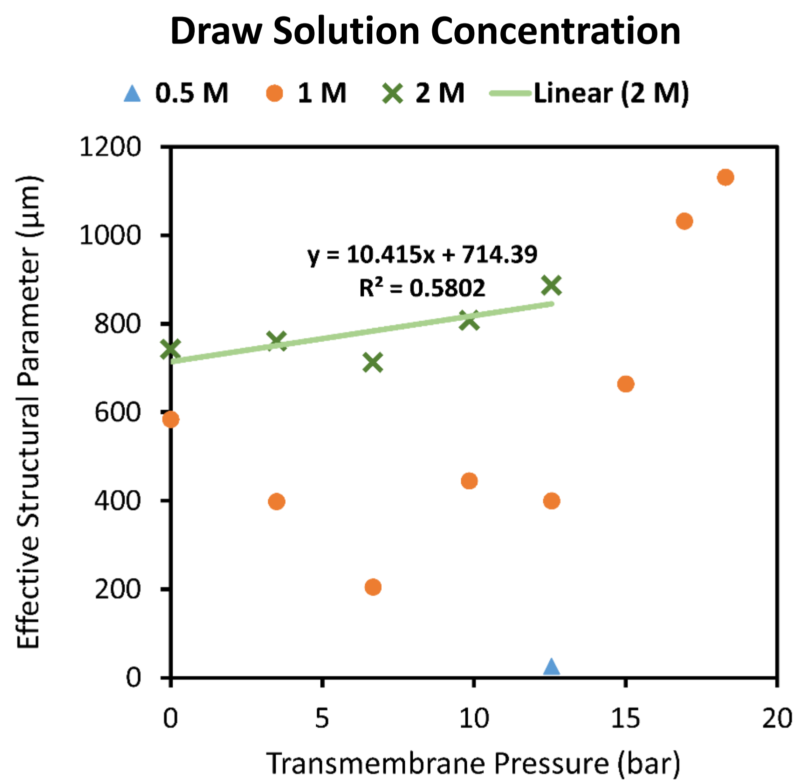
High Salinity Brine Dewatering with FO

- 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



CA Membranes in PRO

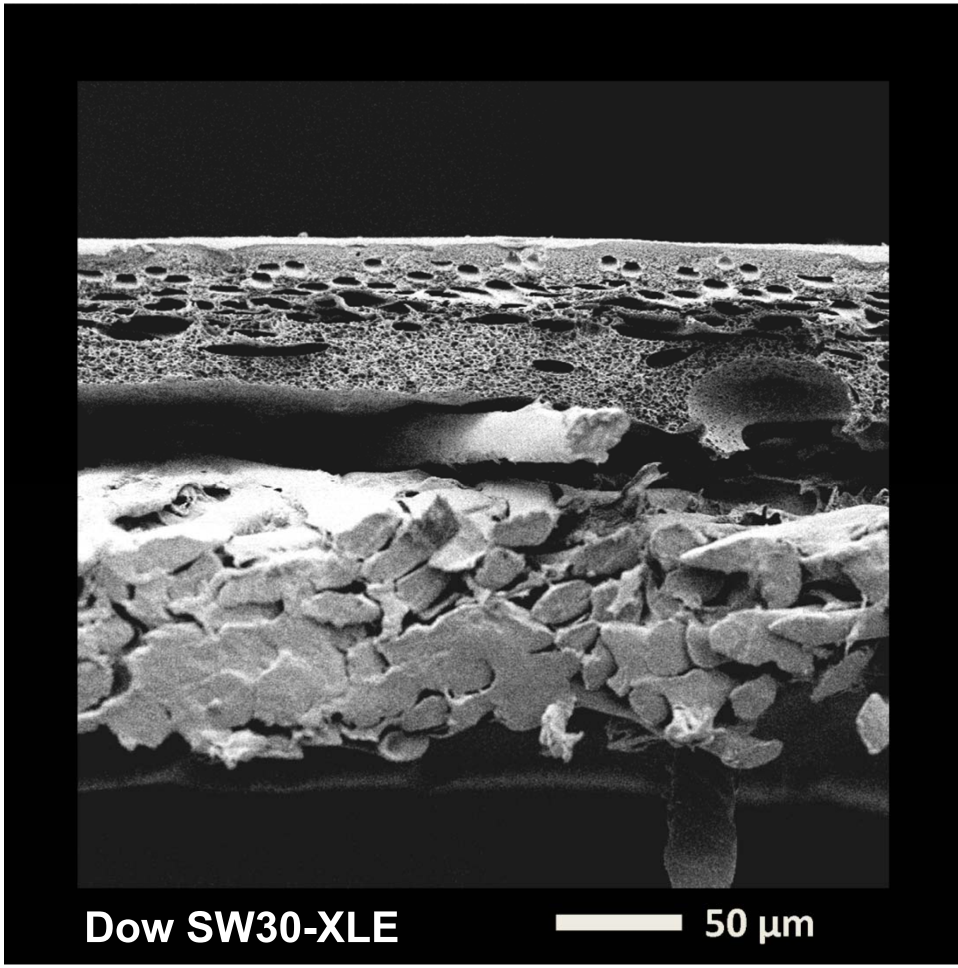
- Structural parameters are often calculated in studies that develop and/or characterize membranes for forward osmosis
- Structural parameters may change as a membrane is compacted by applied hydrostatic pressure
- Accurate simulation of OARO should measure membrane properties at conditions which reflect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



Effective structural parameter of Hydration Technology Innovations' (HTI) woven supported cellulose triacetate membrane calculate from pressure retarded osmosis using a 0.01 M sodium chloride feed at 25°C

Q. She, X. Jin, C.Y. Tang, *J. Membr. Sci.* 401-402 (2012) 262-273.

Issues with TFC Chemistry



Hydrophobic support layer

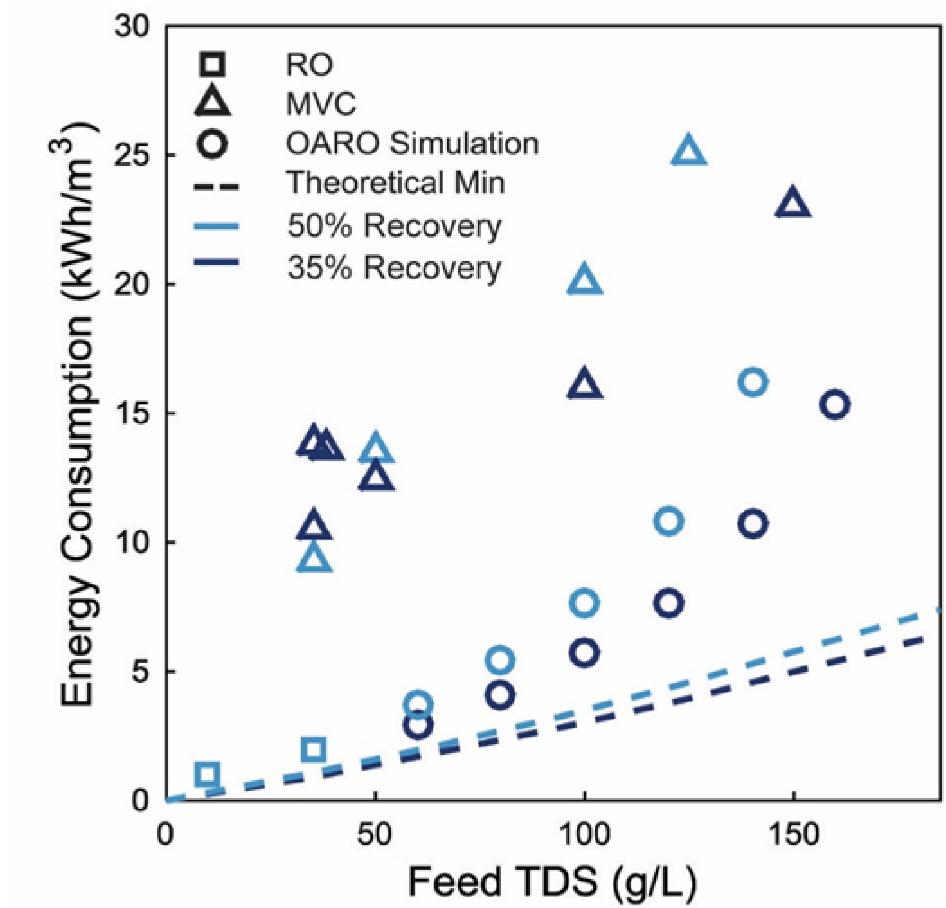
Polyamide (PA) Selective Layer

Polysulfone (PSu)
Polymer Layer

Polyethylene terephthalate (PET)
Fabric Layer

J.R. McCutcheon, M. Elimelech, *J. Membr. Sci.* 318 (2008) 458-466.
J.T. Arena, *Polydopamine Modified Thin Film Composite Membranes for Engineered Osmosis*, Ph.D. Dissertation 2015.

Comparison of OARO Simulations vs. MVC



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 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$
- Membrane structural parameter of 1000 μm

Significantly less electricity consumption using OARO than from MVC

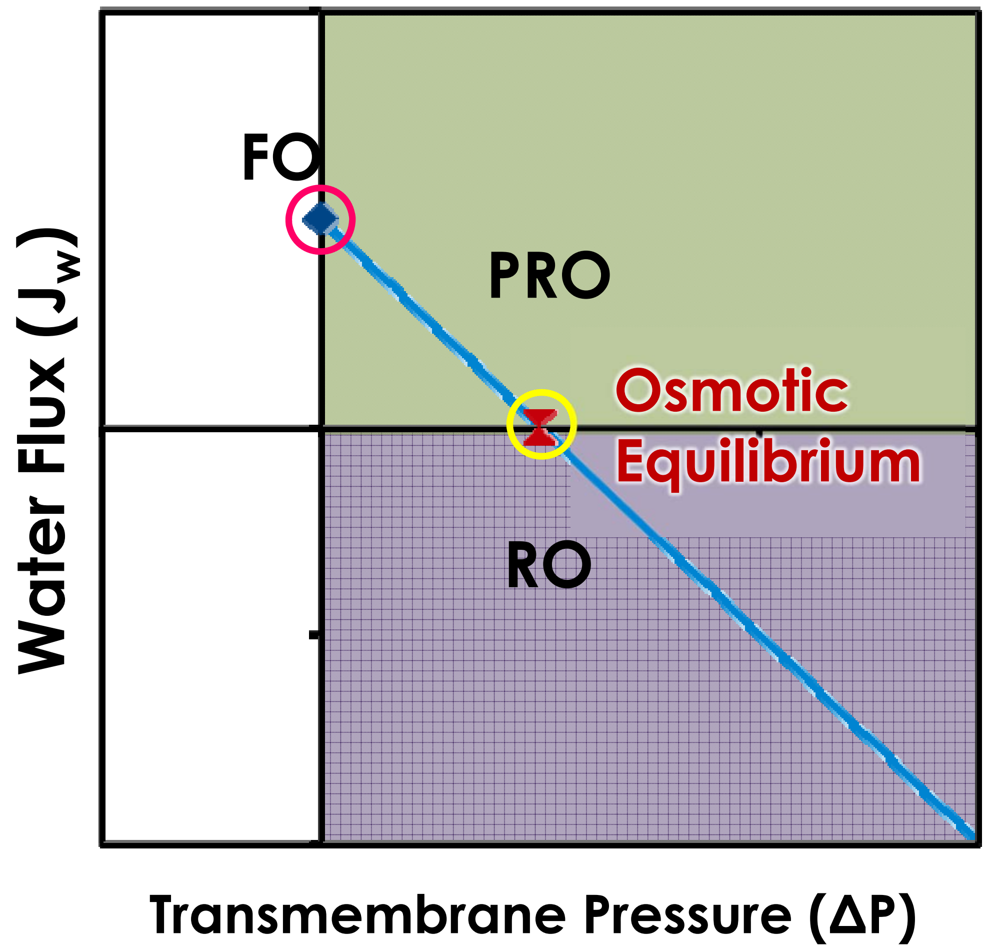
T.V. Bartholomew *et al.*, "Osmotically Assisted Reverse Osmosis for High Salinity Brine Treatment," submitted to *Desalination*, under review.
G.P. Thiel et al. *Desalination* 366 (2015), 94-112.
J. Veza, *Desalination* 101 (1995) 1-10.
A. Koren, et al. *Desalination* 98 (1994), 41-48.

Osmotic and Hydrostatic Pressure

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

$$J_w = A(\Delta\pi - \Delta P)$$

$$J_w = A(\Delta P - \Delta\pi)$$



$$\Delta P = P_{concentrated} - P_{dilute}$$

Prior Study of RO on GCS Brines

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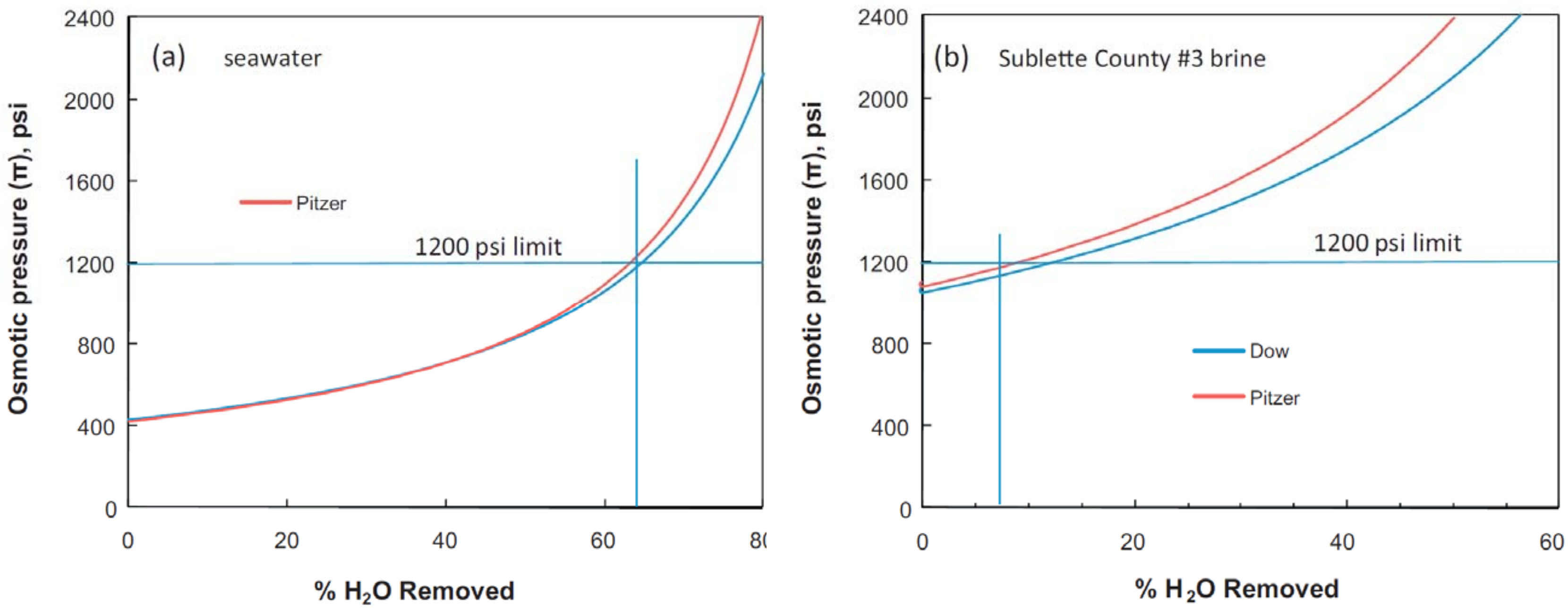
- Brine Concentration > Sea water (TDS ~ 35 g/L)
- Limited by mechanical stability of membrane
- Water recovery of brines > 85 g/L TDS is negligible for a 1200 psi membrane



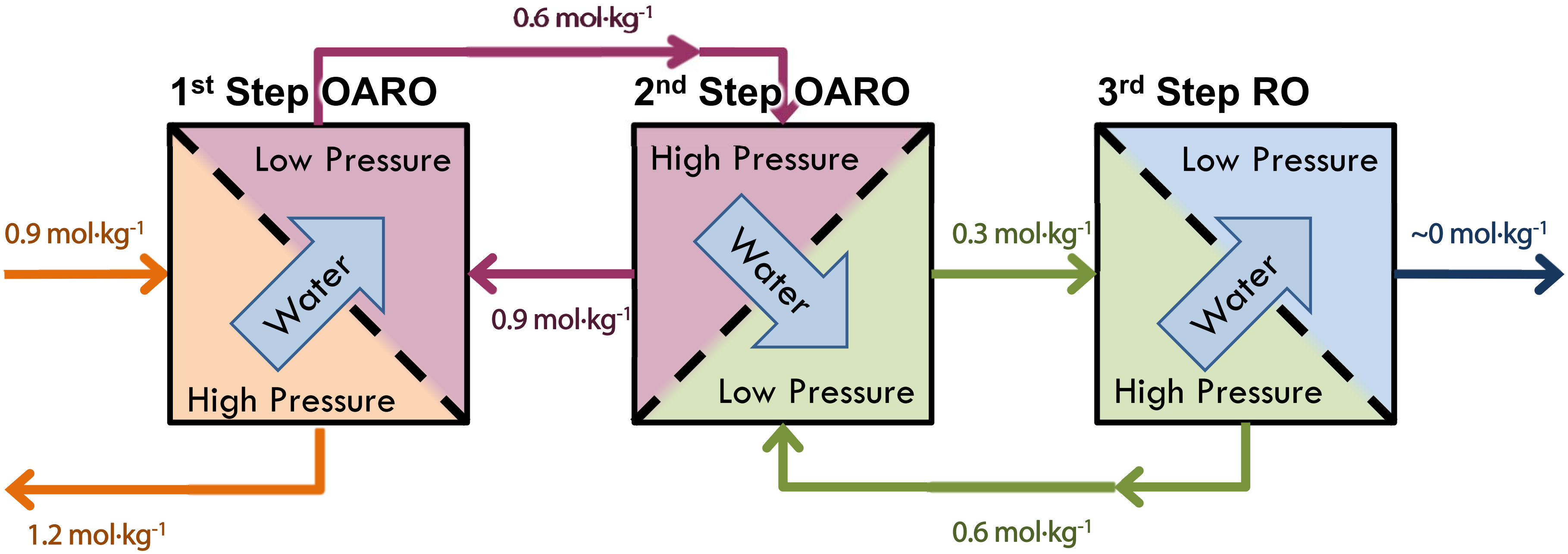
Comparison of maximum water recovery using RO comparing seawater (a) and a 86 g/L brine (b) from a CO_2 sequestration site in Wyoming

R.D. Aines et al. *Energy Procedia* 4 (2011) 2269-2276.
W.L. Bourcier et al. *Int. J. Greenhouse Gas Control* 5 (2011) 1319-1328.

Process Configuration

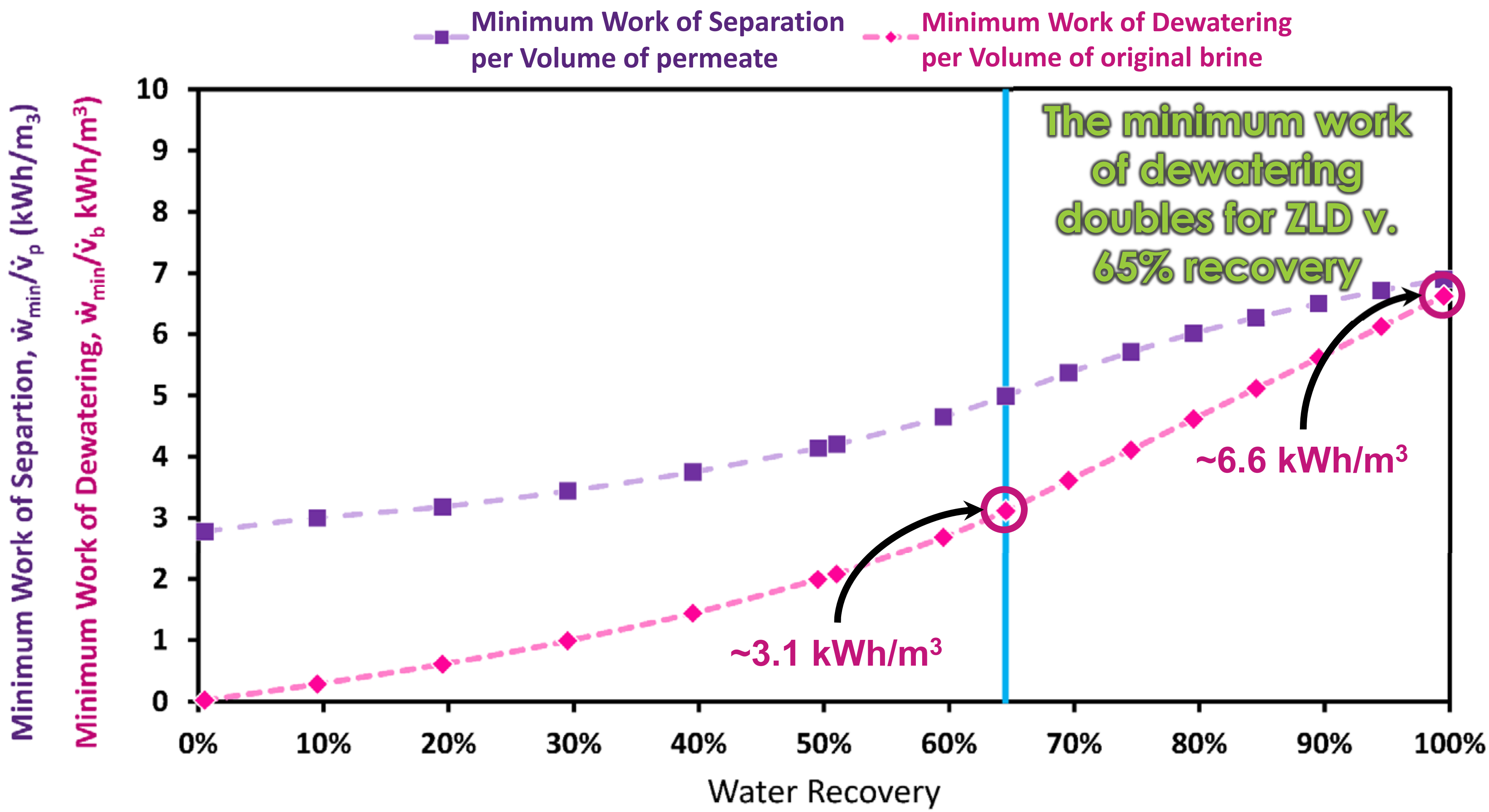
The OARO process

- 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

General Experimental Plan

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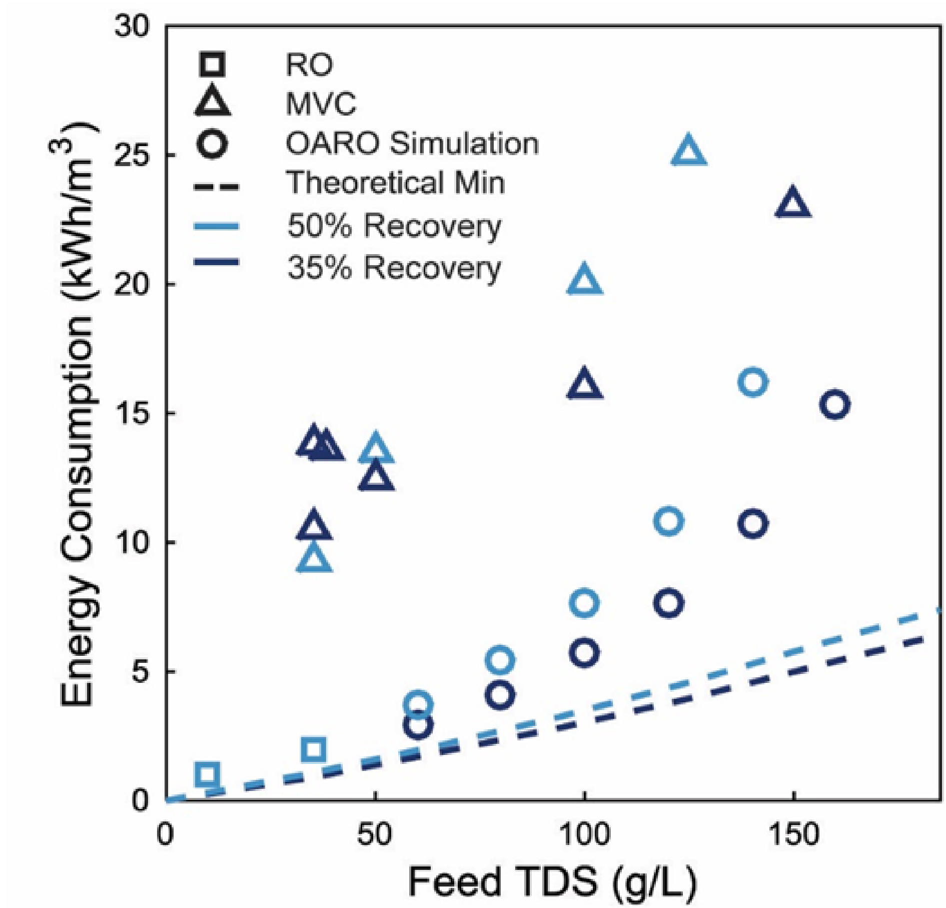
Test Regime	Test Pressures	Feed	Sweep
Compaction	31.0 bar	Purified Water	Purified Water
RO/PRO Water and Salt Flux	27.6–6.9 bar in 6.9 bar increments	Purified Water	Purified Water
		0.15 $mol \cdot kg_{H_2O}^{-1}$	" "
		0.3 $mol \cdot kg_{H_2O}^{-1}$	" "
		0.45 $mol \cdot kg_{H_2O}^{-1}$	" "
		0.6 $mol \cdot kg_{H_2O}^{-1}$	" "
		0.9 $mol \cdot kg_{H_2O}^{-1}$	" "
		1.2 $mol \cdot kg_{H_2O}^{-1}$	" "
		1.5 $mol \cdot kg_{H_2O}^{-1}$	" "
		1.8 $mol \cdot kg_{H_2O}^{-1}$	" "
		2.1 $mol \cdot kg_{H_2O}^{-1}$	" "
OARO Water Flux	27.6–6.9 bar in 6.9 bar increments	0.9 $mol \cdot kg_{H_2O}^{-1}$	0.3 & 0.6 $mol \cdot kg_{H_2O}^{-1}$
		1.2 $mol \cdot kg_{H_2O}^{-1}$	0.6 & 0.9 $mol \cdot kg_{H_2O}^{-1}$
		1.5 $mol \cdot kg_{H_2O}^{-1}$	0.9 & 1.2 $mol \cdot kg_{H_2O}^{-1}$
		1.8 $mol \cdot kg_{H_2O}^{-1}$	1.2 & 1.5 $mol \cdot kg_{H_2O}^{-1}$
		2.1 $mol \cdot kg_{H_2O}^{-1}$	1.5 & 1.8 $mol \cdot kg_{H_2O}^{-1}$

Comparison of OARO Simulations vs. MVC



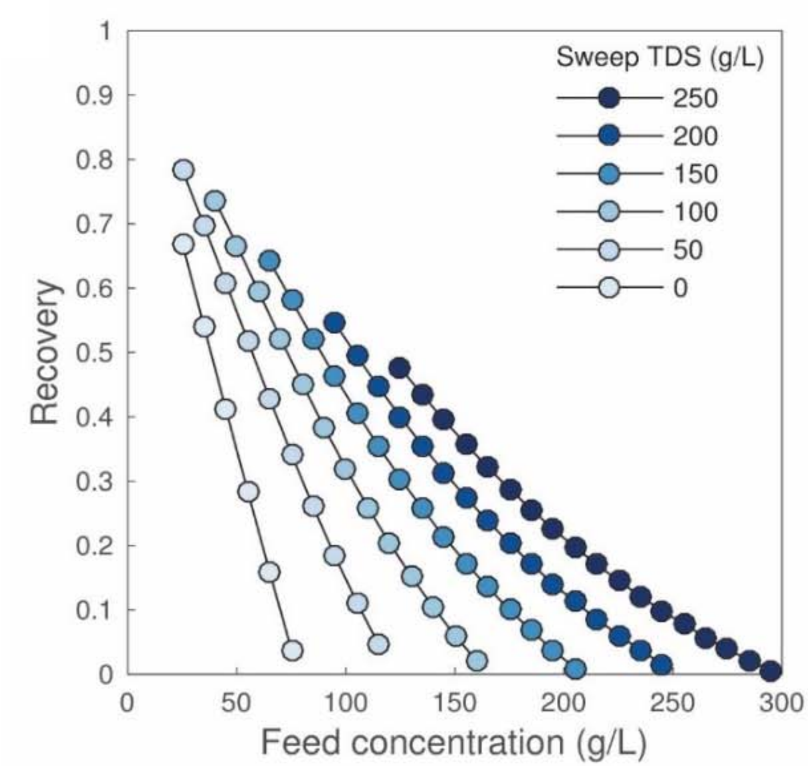
Assumes

- 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 $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$
- Membrane structural parameter of 1000 µm

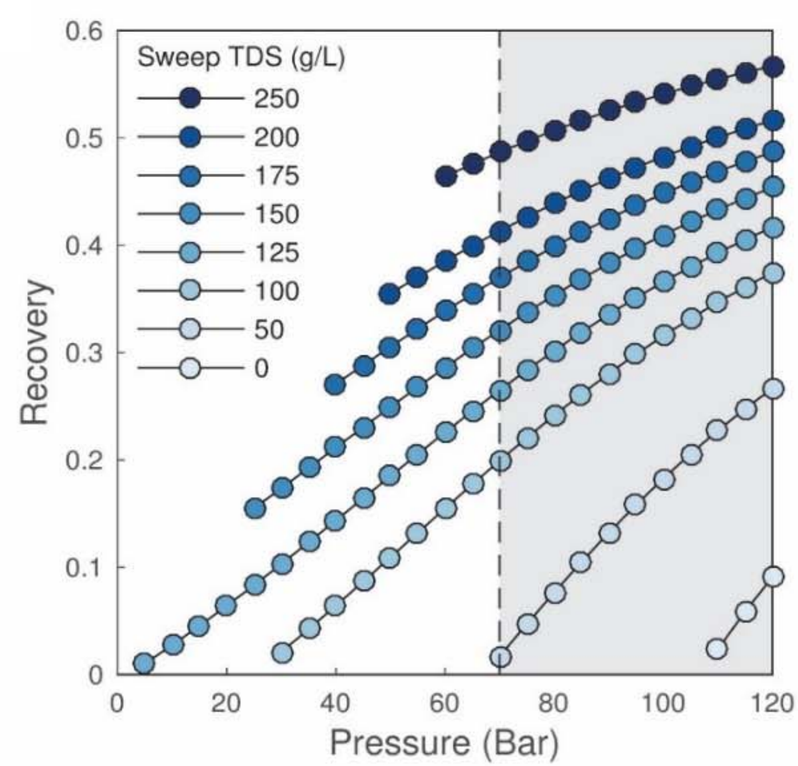
Significantly less electricity consumption using OARO than from MVC

T.V. Bartholomew *et al.*, "Osmotically Assisted Reverse Osmosis for High Salinity Brine Treatment," submitted to *Desalination*, under review.
G.P. Thiel et al. *Desalination* 366 (2015), 94-112.
J. Veza, *Desalination* 101 (1995) 1-10.
A. Koren, et al. *Desalination* 98 (1994), 41-48.

System Model Recovery Rates



OARO recovery for a constant feed pressure of 65 bar and variable feed concentration and sweep concentration.



OARO recovery for a feed with a TDS concentration of 125 g/L and variable feed pressure and sweep concentration.

Water Flux – Purified Water Sweep

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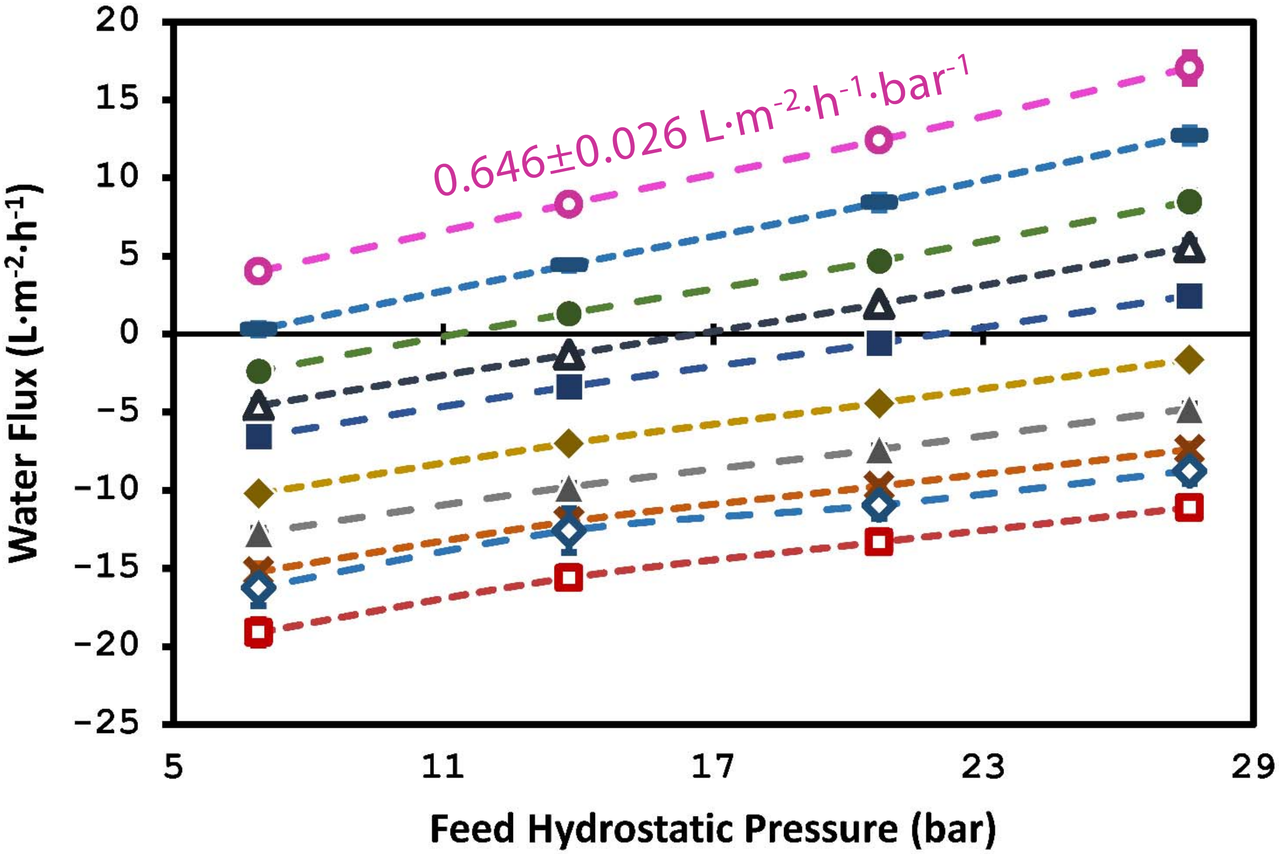
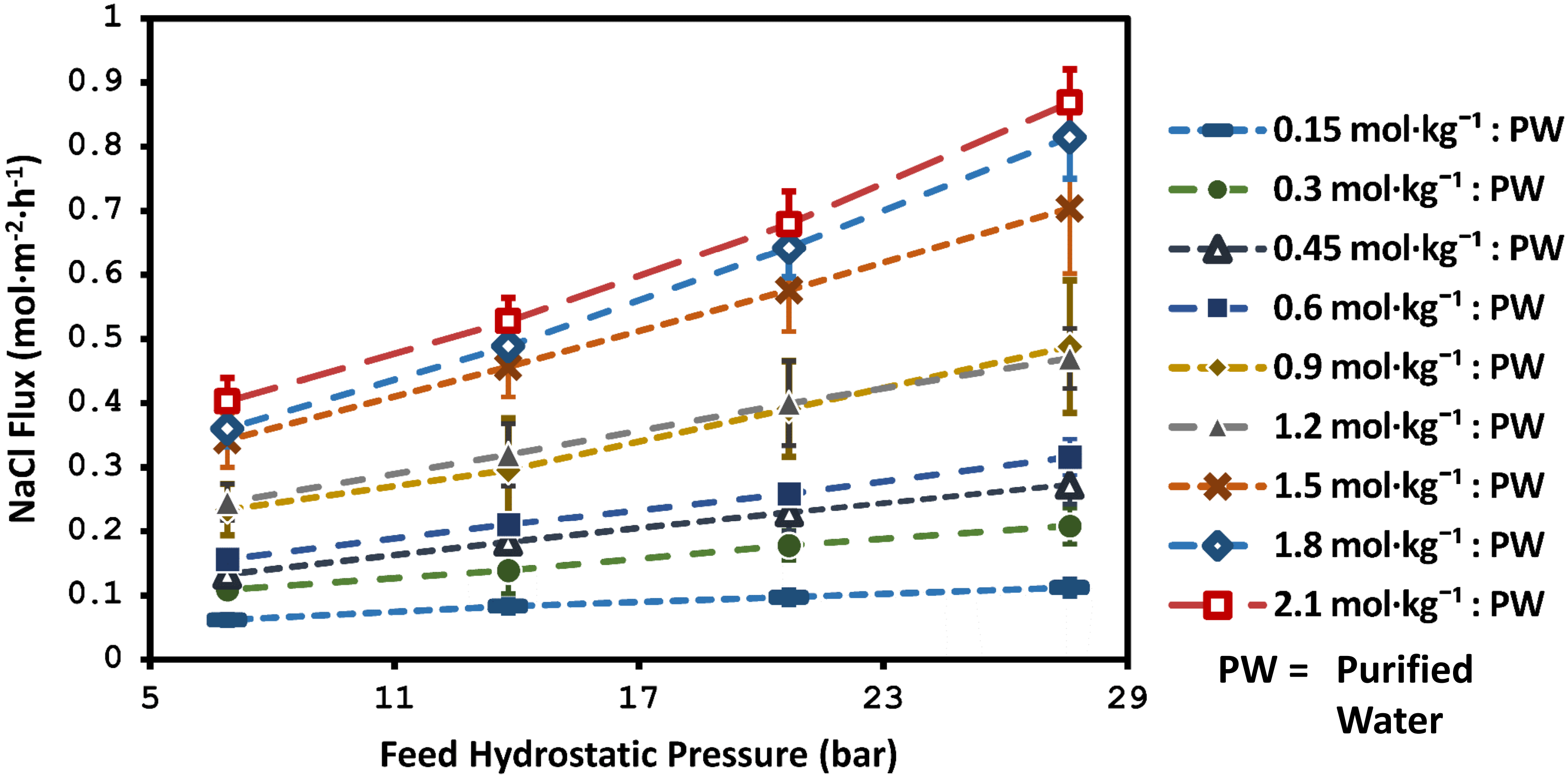


PW = Purified Water

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} and a sweep flowrate of 0.5 L·min^{-1}.

Salt Flux – Purified Water Sweep



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 $L{\cdot}min^{-1}$ and a sweep flowrate of 0.5 $L{\cdot}min^{-1}$.

J.T. Arena et al. "Dewatering of High Salinity Brines by Osmotically Assisted Reverse Osmosis," in *Proceedings of the 2017 AWWA-AMTA Membrane Technology Conference and Exposition*, February 13-17, 2017.

NETL's Test System