Advanced Membrane Materials & Processes for Desalination of High Salinity Brines

Nicholas S. Siefert,[1] Kathryn A. Berchtold,[2] Meagan S. Mauter,[3] Jason T. Arena,[1] Rajinder Singh,[2] Jinesh Jain,[1] Danylo B. Oryshchyn,[1] Arpita Idday,[3] Laura Mey[3]

[1] U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA 15236
[2] U.S. Department of Energy, Los Alamos National Laboratory, Los Alamos, NM 87545
[3] Carnegie Mellon University, Pittsburgh, PA 15213

Research & Innovation Center

Overarching Objective Development and demonstration of advanced membrane materials and processes that can achieve cost and energy reductions for brine/water separation from high salinity produced waters.

Energy Costs of Desalination

Use experimentally measured membrane performance data to design, model, and evaluate brine concentrator processes at process scale to compare with matured technologies.

Reverse osmosis (RO) is a dominant technology for the desalination of seawater due to is lower cost[1] and higher energy efficiency[2] compared to thermal processes. One primary drawback of reverse osmosis lies in the upper limit of solution salinity that can be concentrated by reverse osmosis because the osmotic pressure of a solution must be overcome to force water through a semi-permeable membrane. Energy consumption of these processes are large and energy recovery can help reduce the demands of these processes.

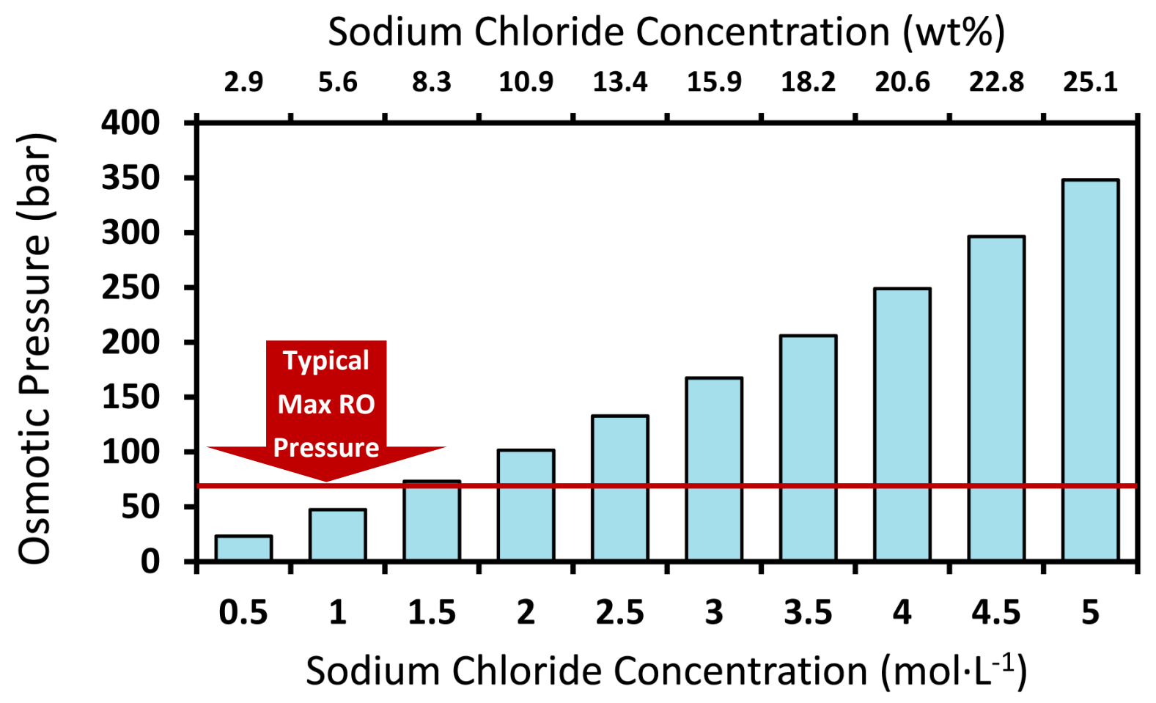

Figure 1. Osmotic pressure of a sodium chloride solution at 25°C as a function concentration.[3]
36 bar = 1 kW·h·m^{-3}

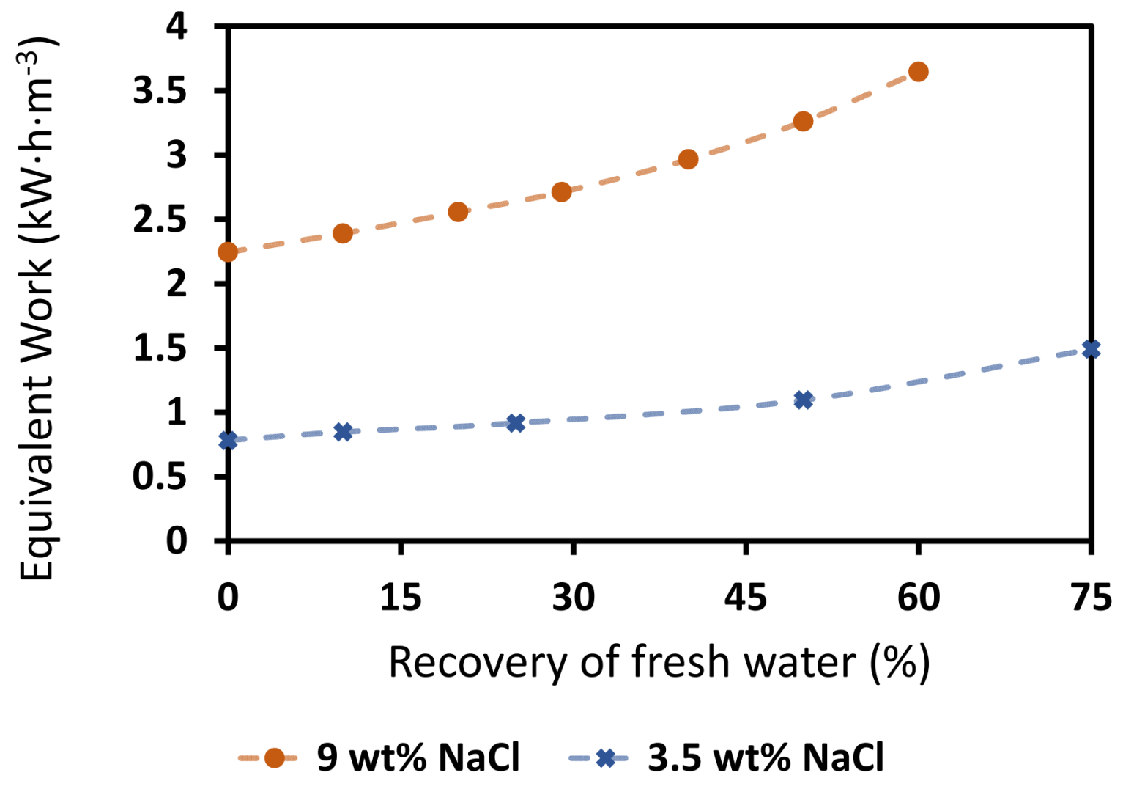

Figure 2. Minimum equivalent work required to desalinate a saline water source with increasing recovery at 20°C.

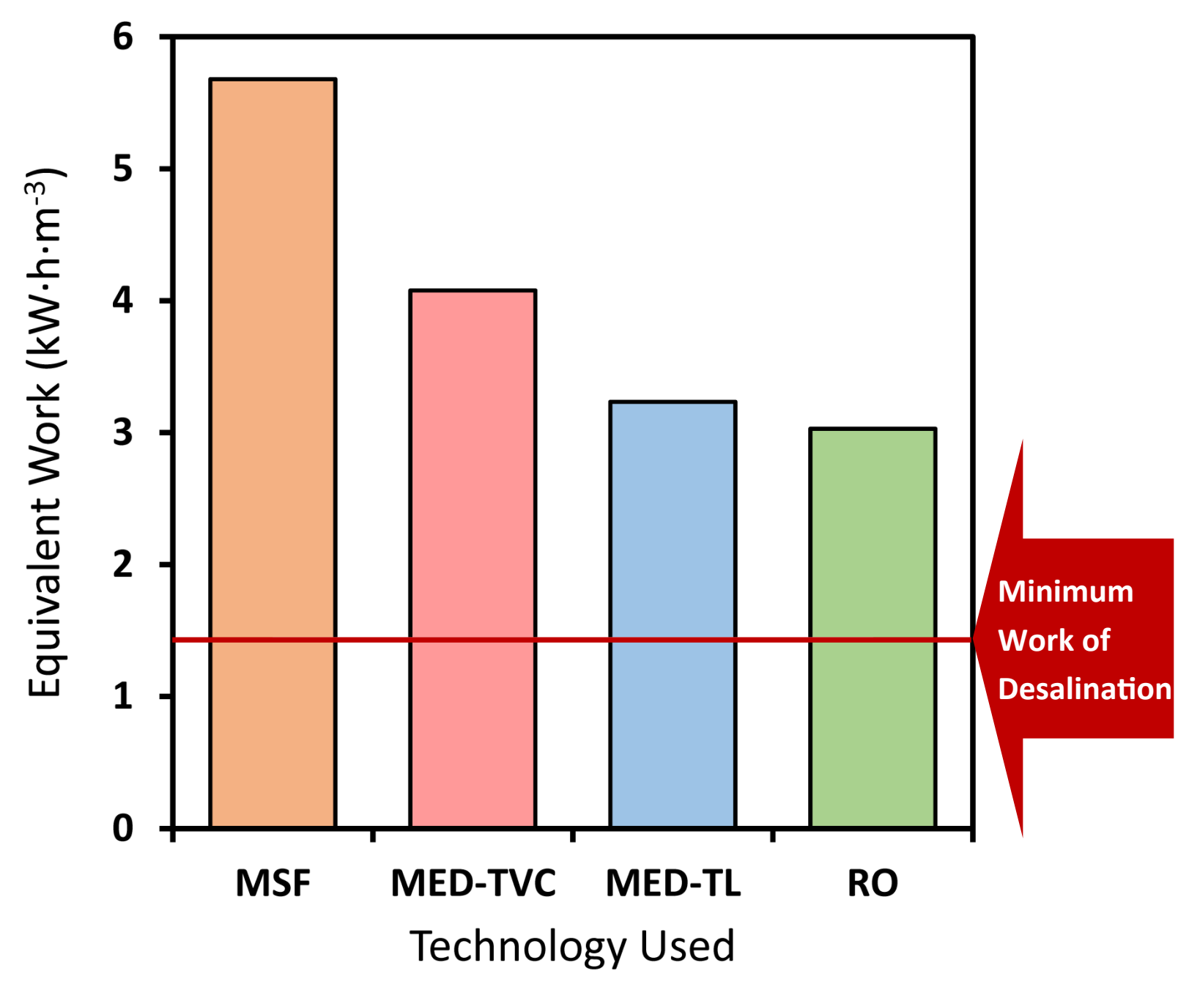

Figure 3. Equivalent work needed for various desalination technologies at 20°C assuming 75% recovery of seawater.[2]

To evaluate new technologies detailed process models are needed for a comparison of novel and emerging techniques for high salinity brine concentration.

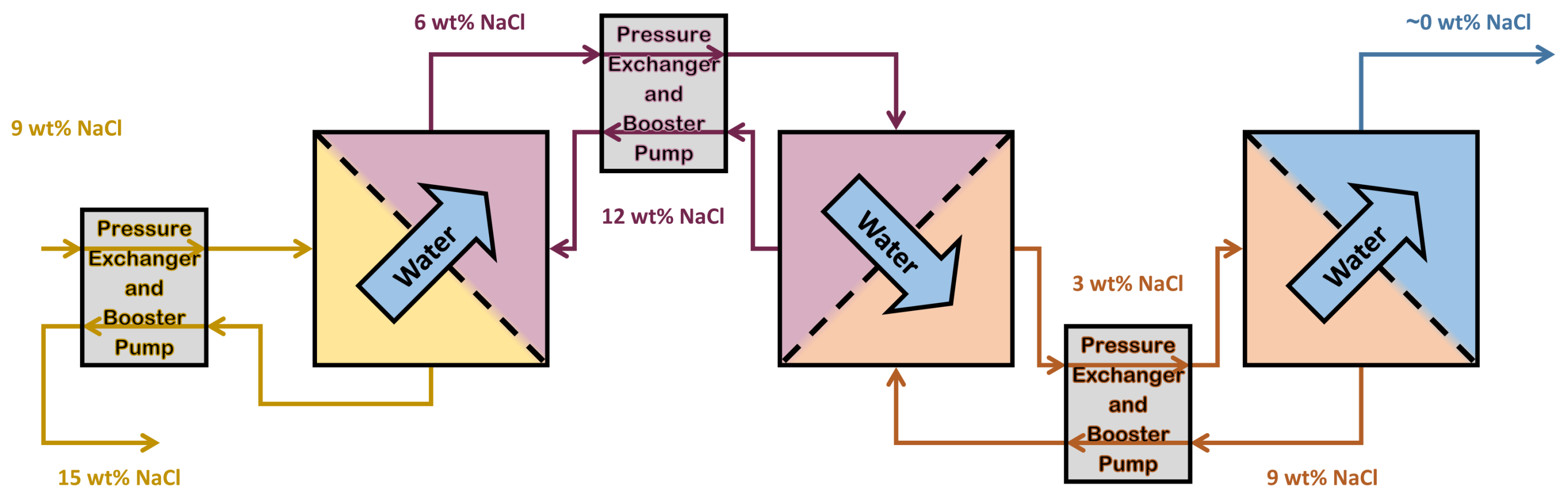

Figure 4. Staged osmotically assisted reverse osmosis process to concentrate a 9 wt% brine to 15 wt%.

Carnegie Mellon University

---

[1] I.C. Karagiannis, P.G. Soldatos, *Desalination* 223 (2008) 448-456.

[2] R.L. McGinnis, M. Elimelech, *Desalination* 207 (2007) 370-382.

Osmotically Assisted Reverse Osmosis

Study the significance of membrane properties and validate governing equations for the use of osmotically assisted reverse osmosis (OARO) to concentrate high salinity brines.

Water flux in RO is driven by exceeding the osmotic pressure difference across a semi-permeable membrane with an applied hydrostatic pressure. As a solute concentration increases so does its osmotic pressure requiring increased hydrostatic pressures to maintain water flow. The osmotic pressure difference across a membrane can be reduced by circulating a lower salinity sweep solution along the backside of the membrane to osmotically assist the reverse osmosis. This then requires small reductions in the sweep concentration to finally extract permeated water with RO.

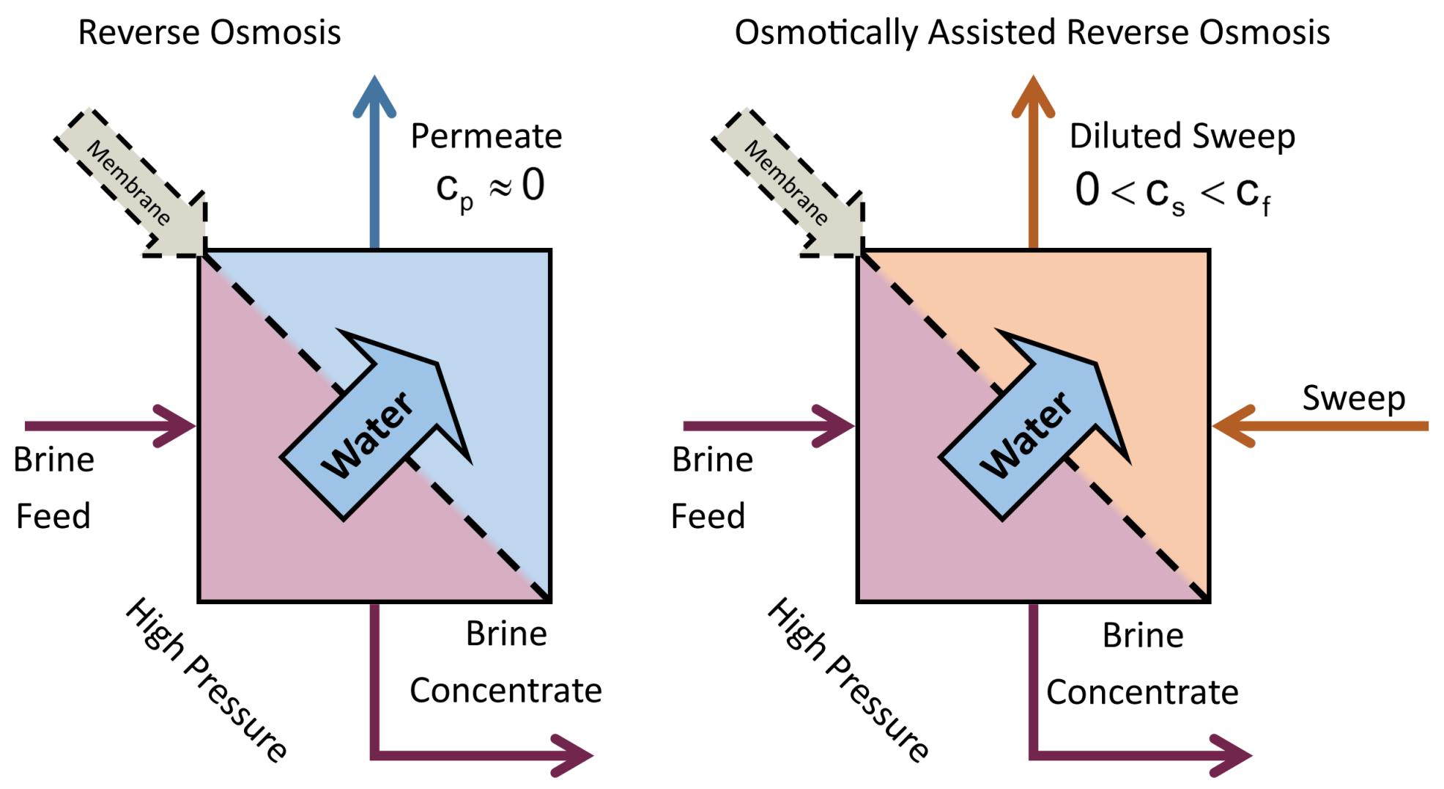

Figure 5. Comparison of a conventional reverse osmosis with osmotically assisted reverse osmosis.

Governing Equations for OARO

A	Membrane Water permeance	P_s	Sweep hydrostatic pressure
B	Membrane solute permeability	$c_{f,m}$	Feed salt concentration
S	Membrane structural parameter	$c_{s,m}$	Sweep salt concentration
		D	Salt diffusion coefficient
J_w	Water flux	δ_f	Feed boundary layer thickness
J_s	Salt flux	$\pi(c)$	Osmotic pressure a function of concentration
P_f	Feed hydrostatic pressure		

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

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

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

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

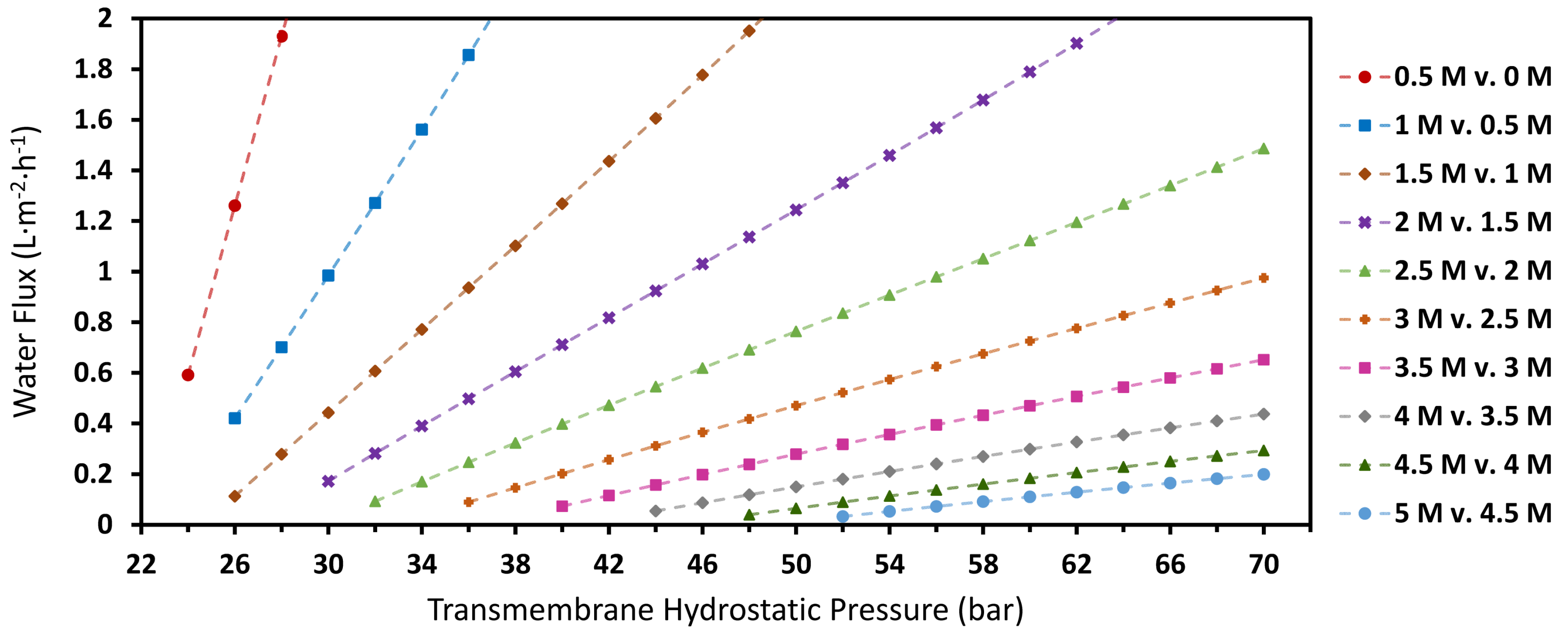

Figure 6. Simulated flux from an osmotically assisted reverse osmosis process using Hydration Technology Innovations woven supported cellulose triacetate forward osmosis membrane. Assumes constant water permeance (A) and salt permeability (B). Effective structural parameter is assumed to be linearly responsive with applied transmembrane pressure. Operating temperature 25°C. Membrane data from She et al.[4]

Research & Innovation Center

---

[3] G. Scatchard, W.J. Hamer, S.E. Wood, *J. Am. Chem. Soc.* 60 (1938) 3061-3070.

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

Advanced Thermally Robust Membranes

Characterize membrane performance and durability/stability in chemically challenging process environments having high salinity and high temperature.

Managing and extracting value from the large quantities of produced waters, either from CO_2 storage, oil/gas development, or geothermal reservoirs, poses major technical, economic, and environmental challenges. The temperatures and salinity of these produced waters span broad ranges that pose significantly more challenges than encountered in traditional desalination applications. The focus of this effort is the development of a polymeric membrane technology that can withstand high temperature, high salt concentration, and the presence of oxygen. These conditions are found when using a hot, waste gas stream as a membrane sweep within the proposed "hot gas sweep membrane brine separation" (HGSMBS) process. This process requires a membrane made from a thermo-chemically robust polymer, such as polybenzimidazoles (PBI).

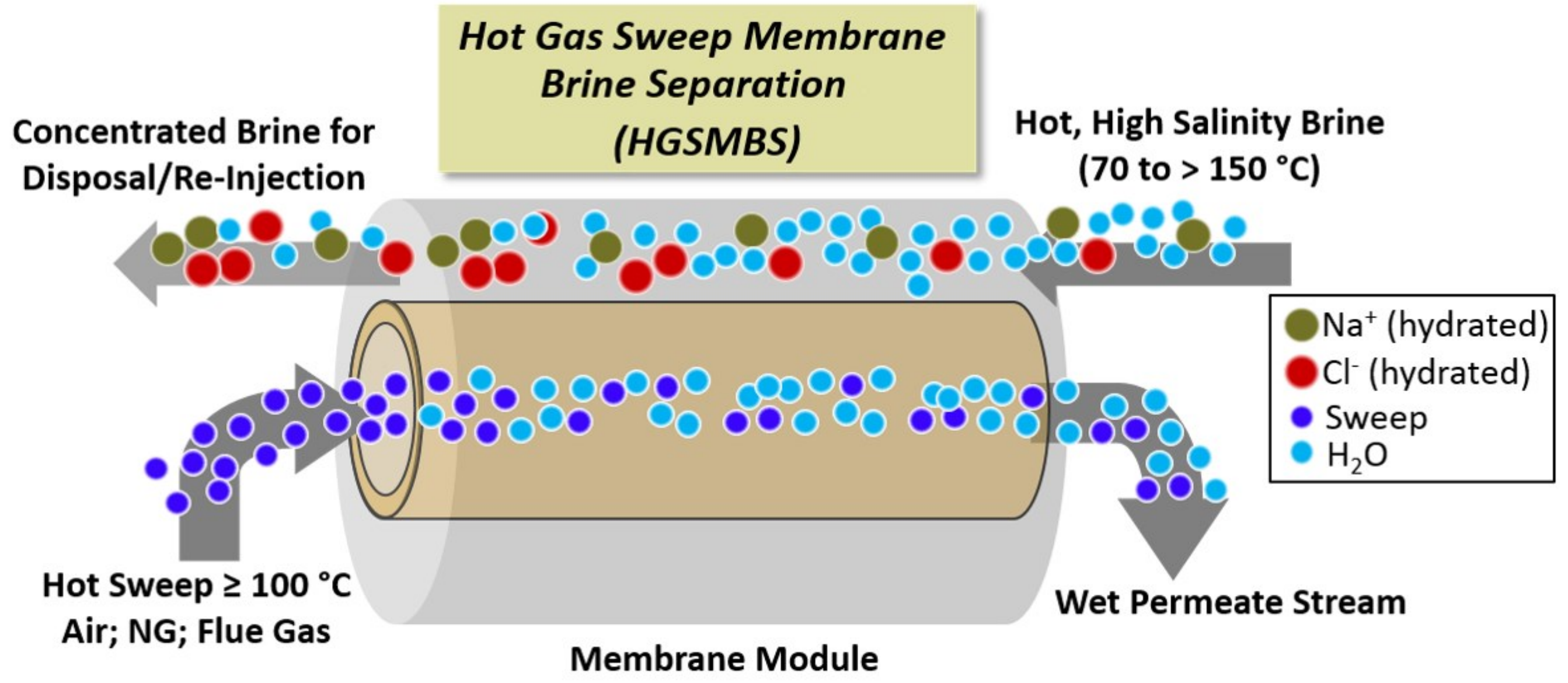

Figure 7. Conceptual depiction of the HGSMBS process for high salinity brine treatment.

Table 1. Sample flow streams in HGSMBS assisted power production process.[5]

	A3	A3H	L1	L2
T (°C)	332	111	120	110
P (bar)	9.6	9.5	10.0	9.6
ṅ (mol/s)	489	571	168	86
Mol Comp.				
N_2	78%	67%	0%	0%
O_2	21%	18%	0%	0%
H_2O	1%	15%	99%	98%
NaCl	0%	0%	1%	2%

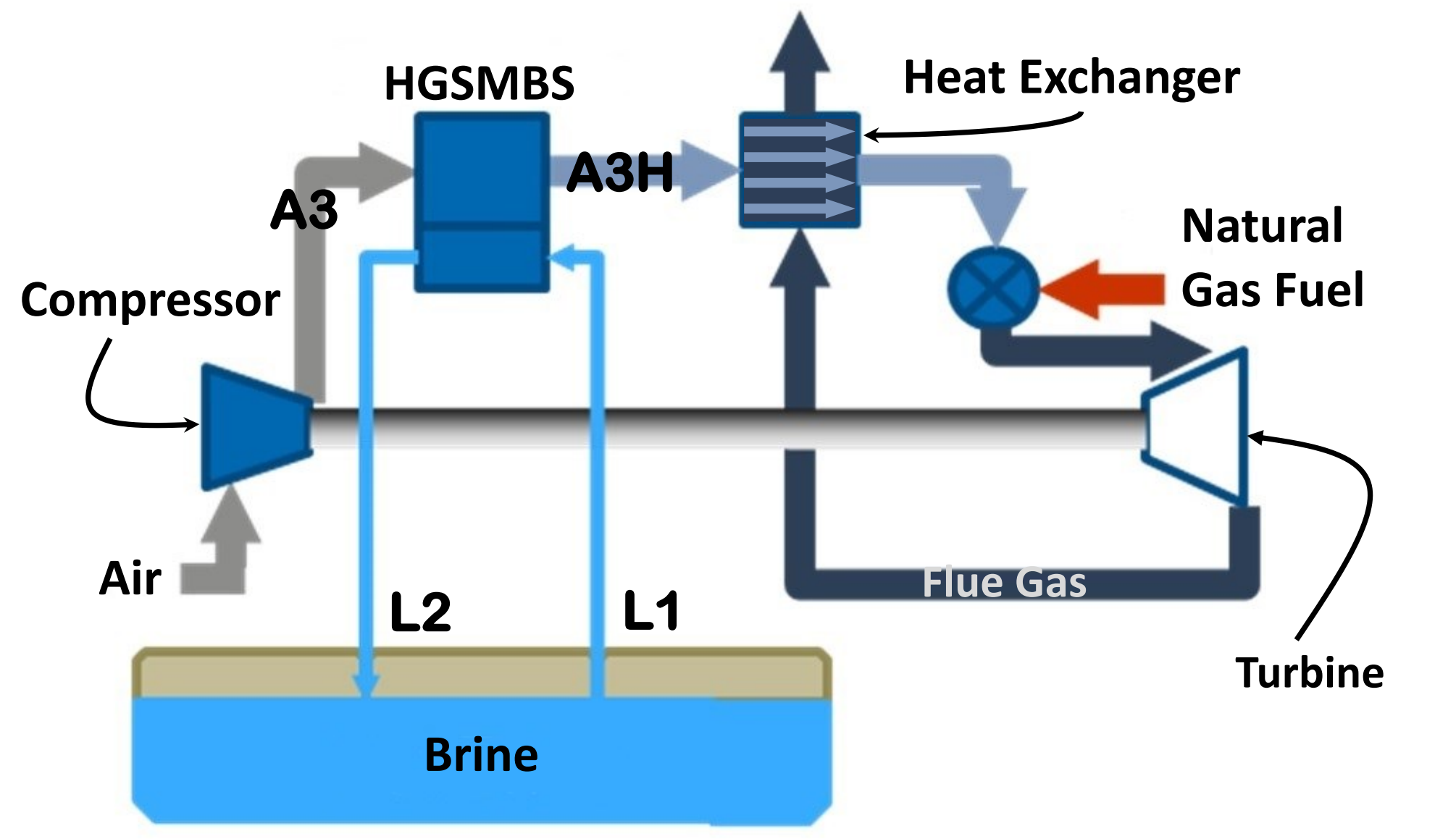

Figure 8. Conceptual HGSMBS assisted power production process.[5]

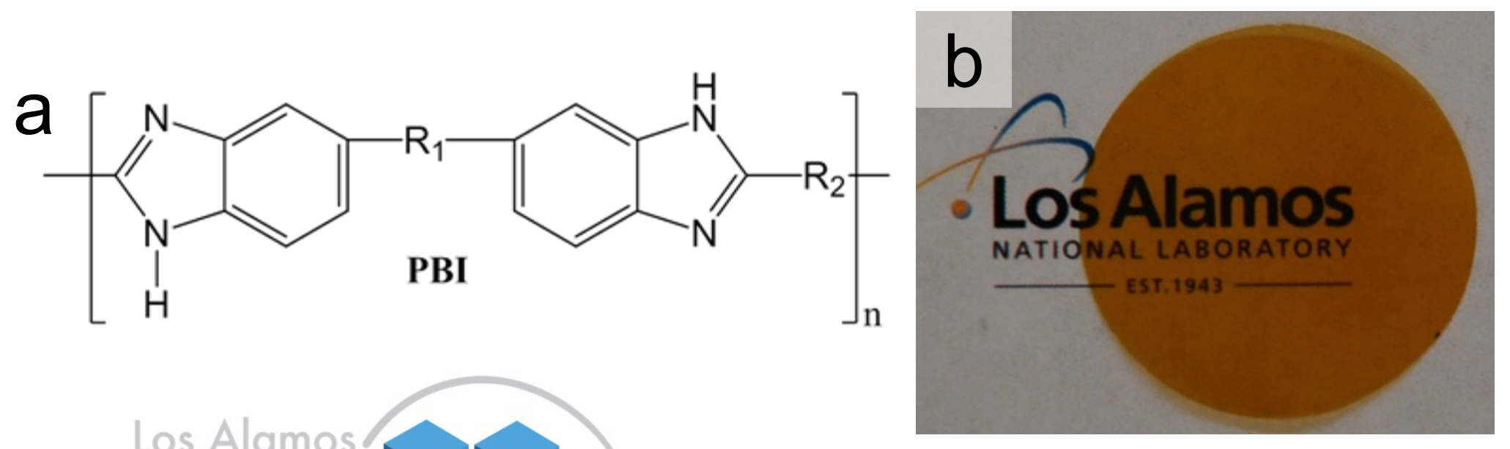

Figure 9. PBI based class of thermo-chemically robust materials under evaluation chemical structure (a) and representative film sample (b).

Los Alamos NATIONAL LABORATORY

---

[5] D. Oryshchyn et al. http://energy.gov/sites/prod/files/2015/06/f23/6-Geo%20Gas%20Turbine%20Hybrid%20Generator%20GGT_Hybrid_NETL.pdf

U.S. DEPARTMENT OF ENERGY | the ENERGY lab National Energy Technology Laboratory

Science & Engineering To Power Our Future