# Desalination of high salinity produced waters and brines

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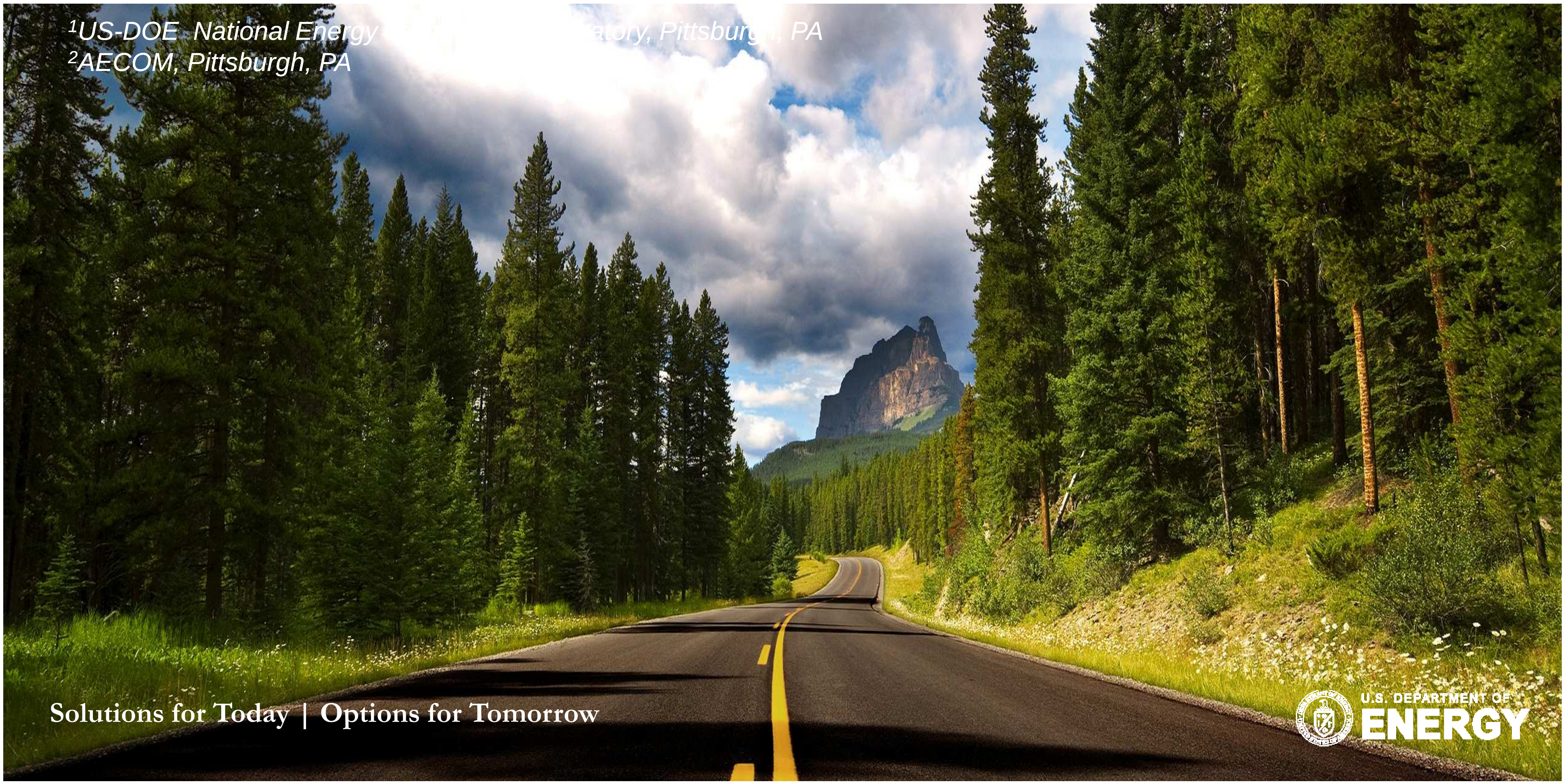
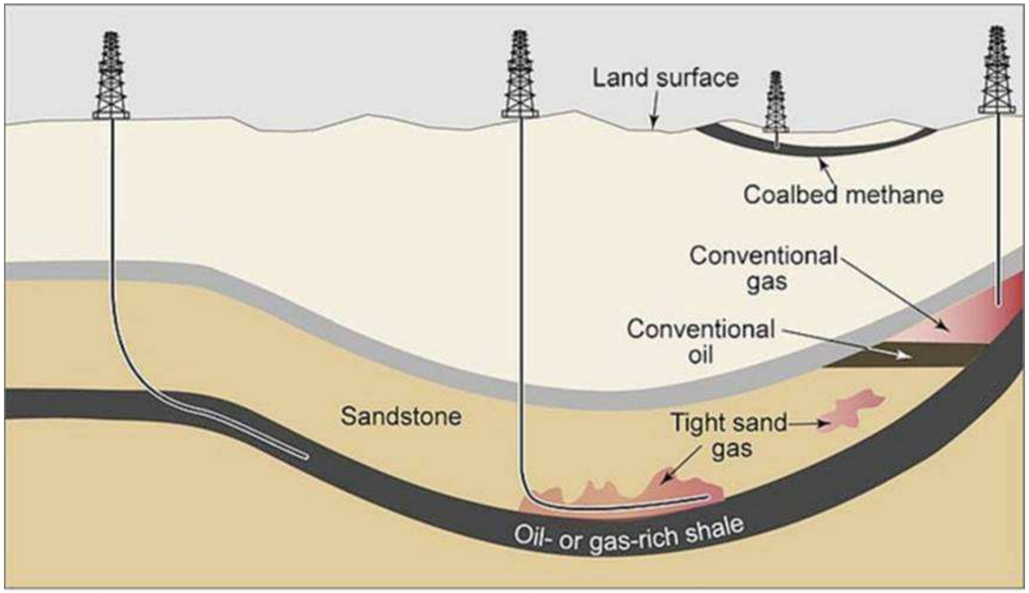


# Outline

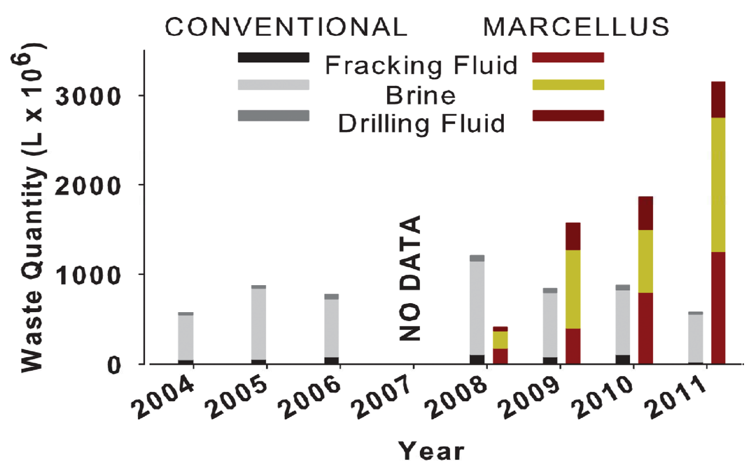
- Produced oil/gas water
- Extracted brines from CO2 storage
- Geological Overview
- Desalination
- Membrane Technologies
- Conclusions



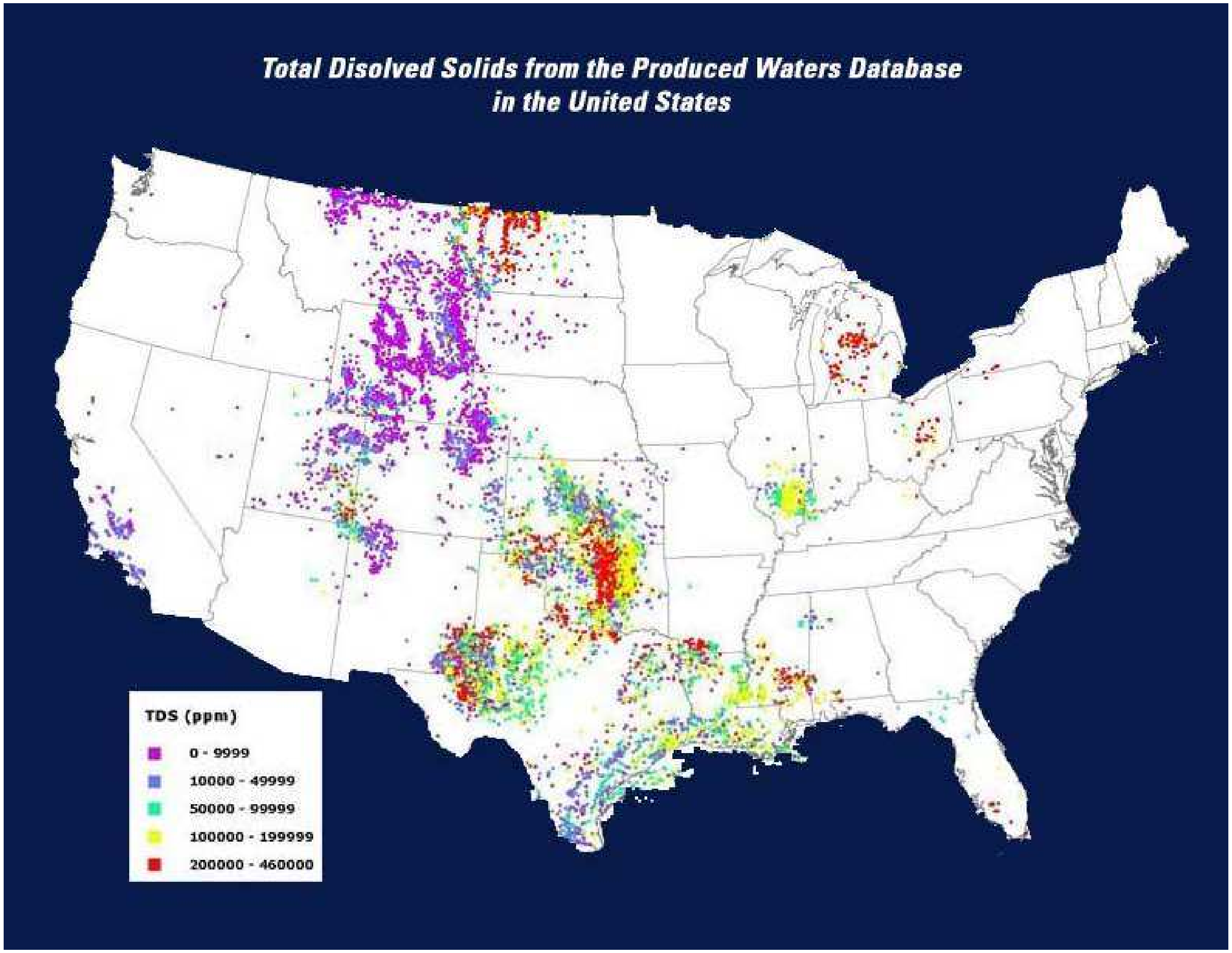

Sources: U.S. Energy Information Administration and U.S. Geological Survey.

# Produced water

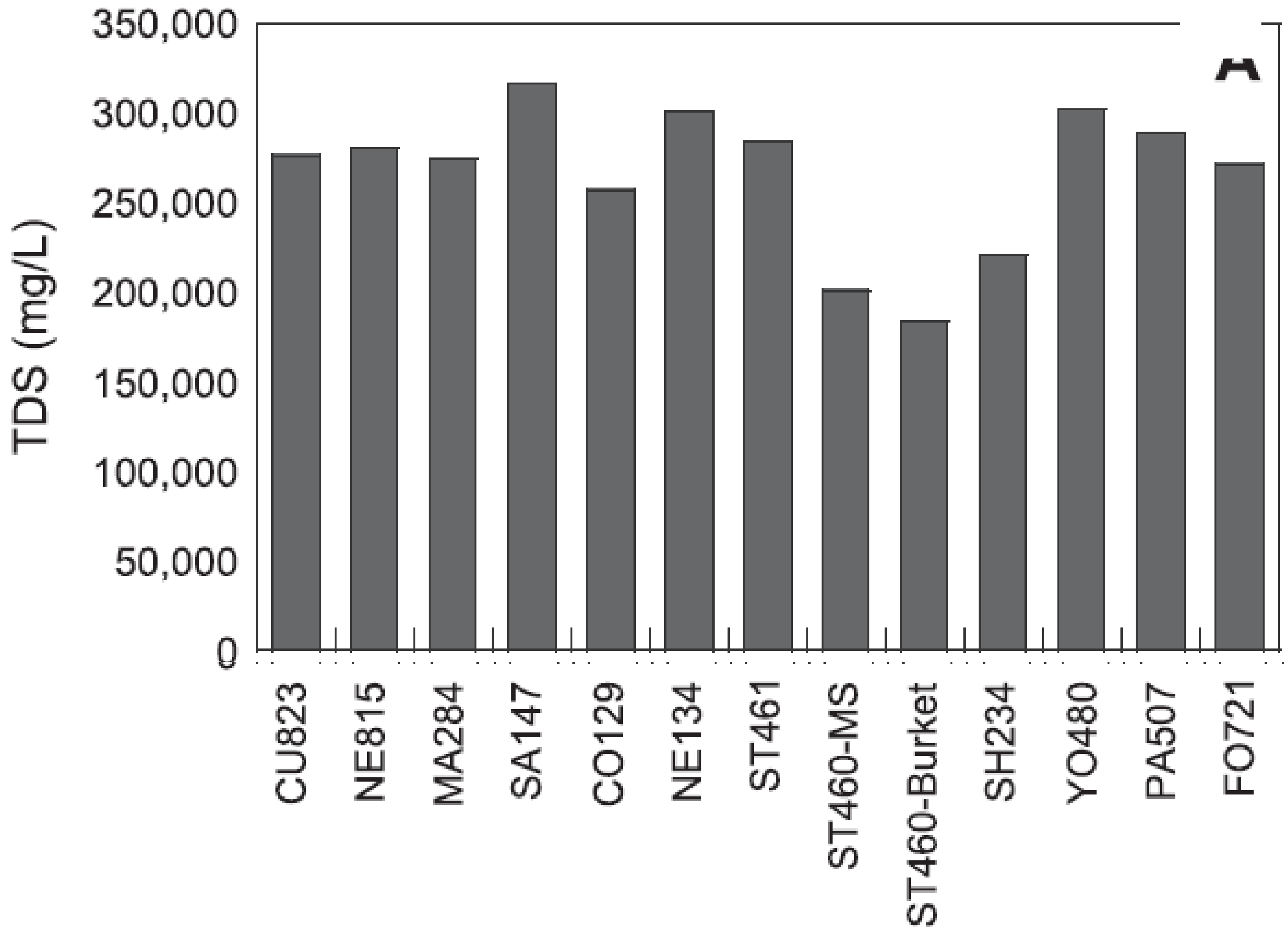
- Water from underground formations brought to the surface during  oil and gas production
- About 15-20 billion barrels per year or 1.7-2.3 billion Gallons per day (ANL Report 2009)
- Water from conventional and Marcellus wells is given in the figure (Lutz et al., Water Resour. Res., 49, 2013)
- It contains dissolved and dispersed oil compounds, formation minerals, production chemicals, production solids, and dissolved gases
- Water Management is a significant factor in the profitability of oil and gas production



# Produced waters from oilfields



# Marcellus Shale produced water Composition




Akob et al., Applied Geochemistry, 2015

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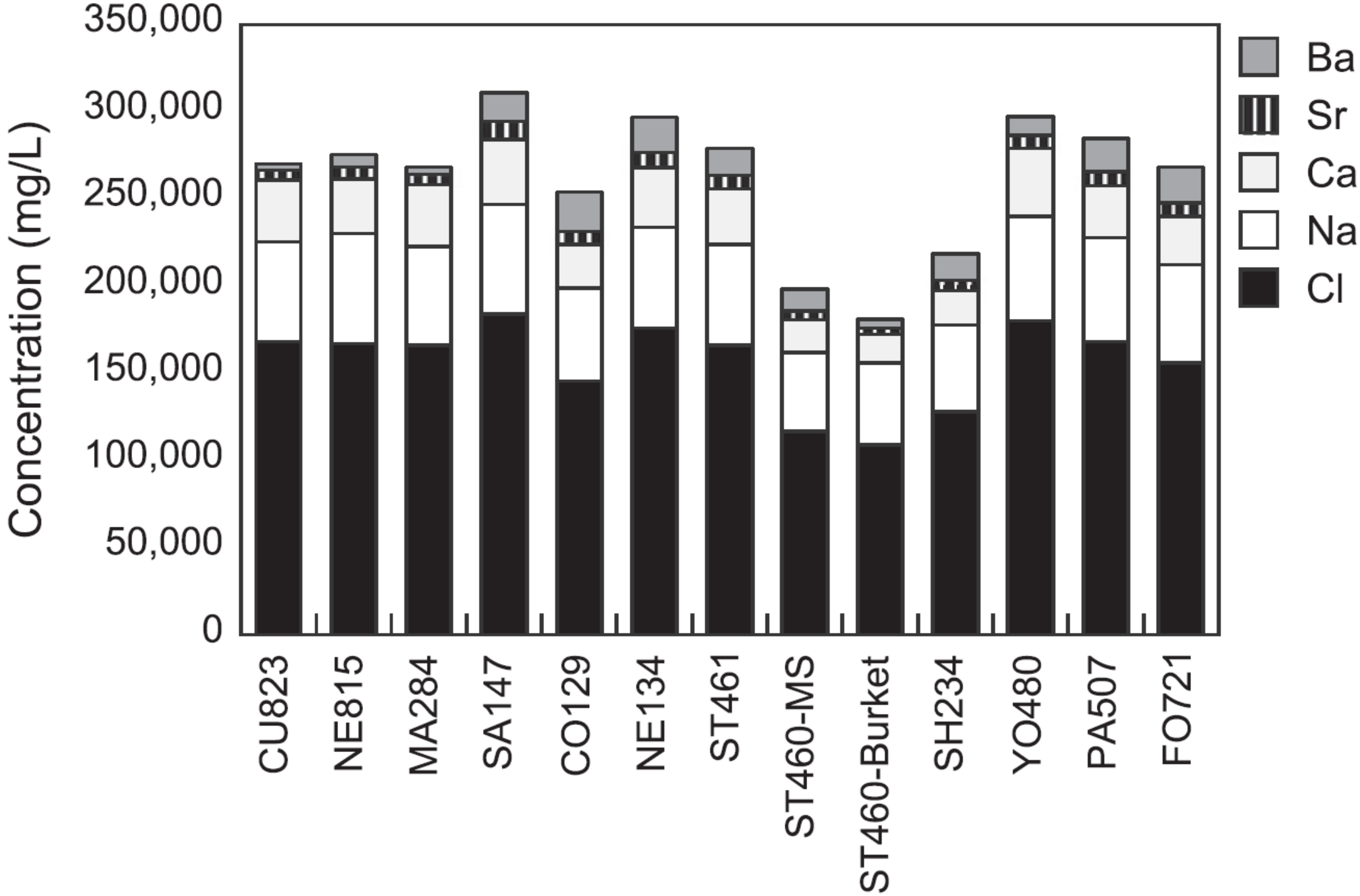
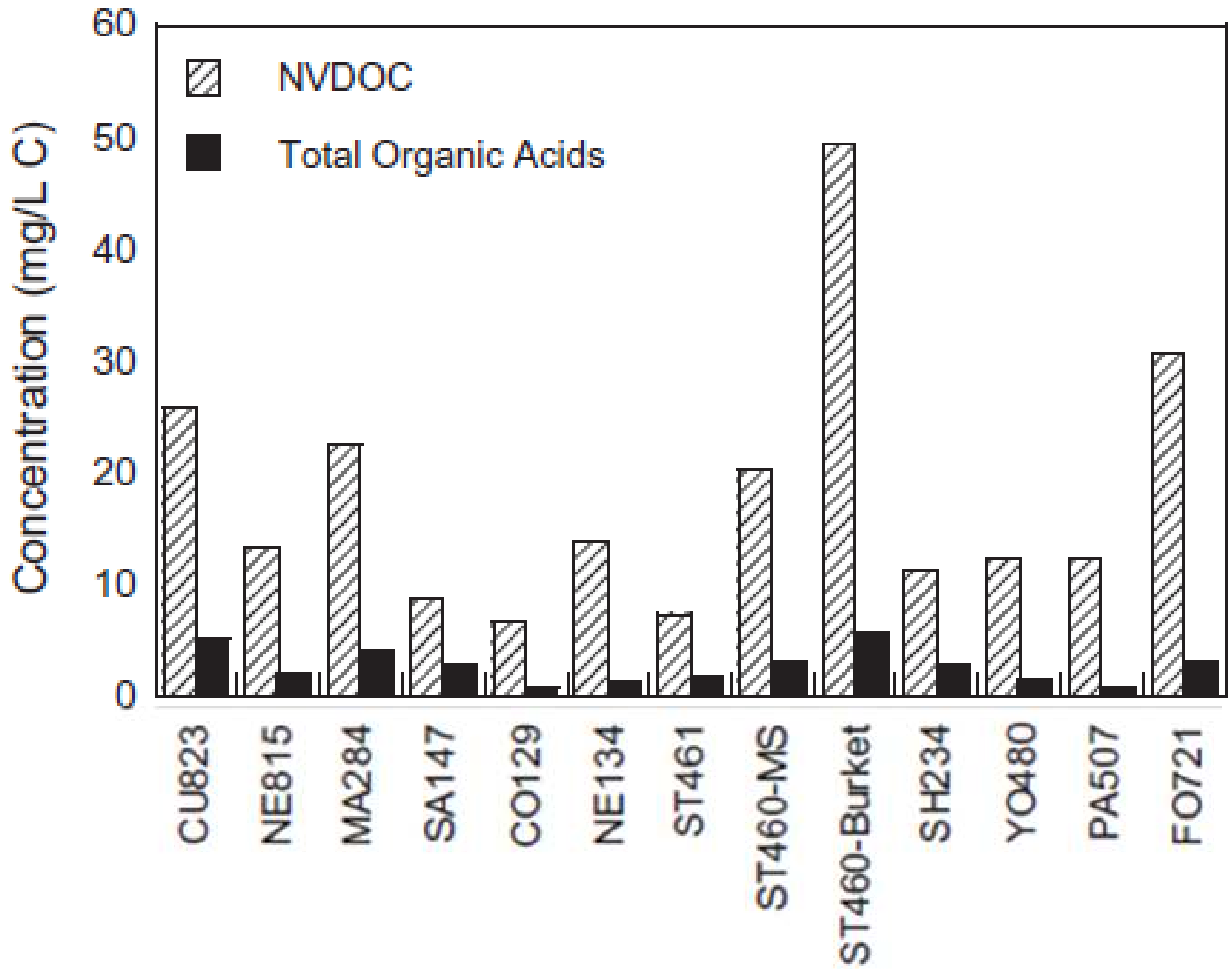



Akob et al., Applied Geochemistry, 2015

# Marcellus Shale produced water Composition




Akob et al., Applied Geochemistry, 2015

# Brines from CO2 Sequestration

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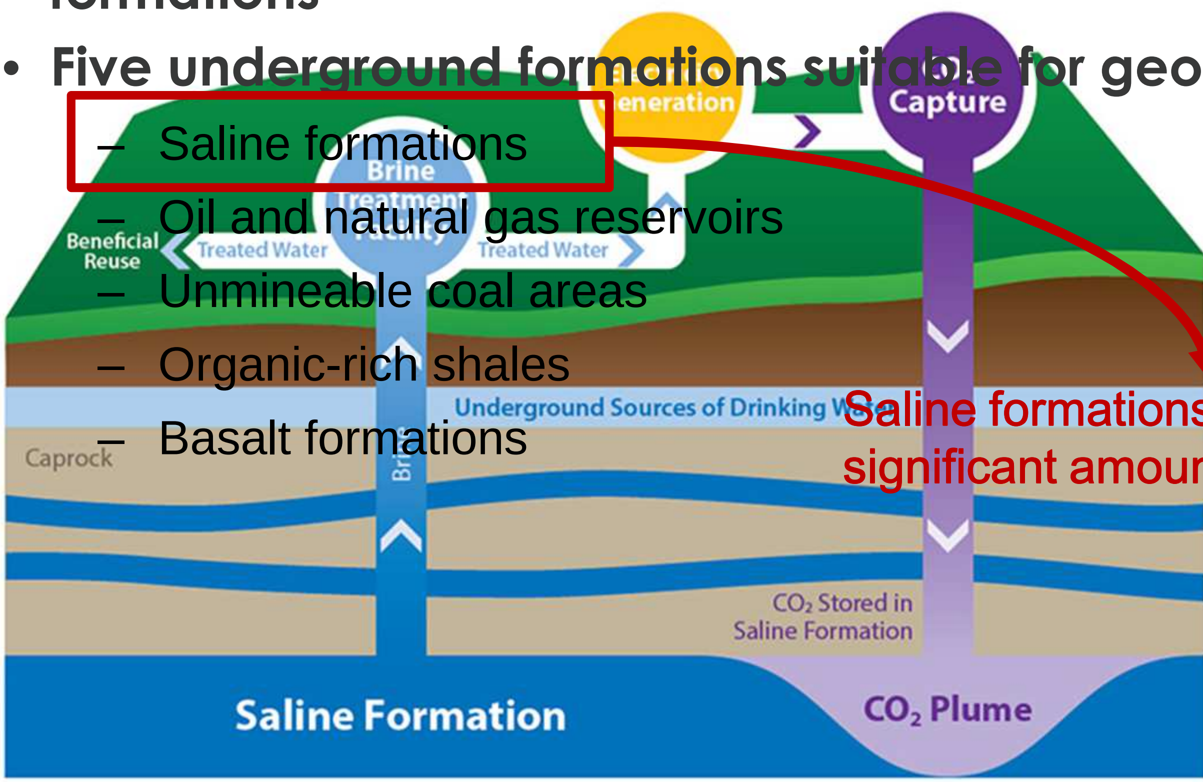
- Capture CO2 and prevent its release into the atmosphere
- Store CO2 by compression and injection into deep geological formations
- Five underground formations suitable for geologic storage
  - Saline formations
  - Oil and natural gas reservoirs
  - Unmineable coal areas
  - Organic-rich shales
  - Basalt formations

Saline formations can store a significant amount of $CO_2$

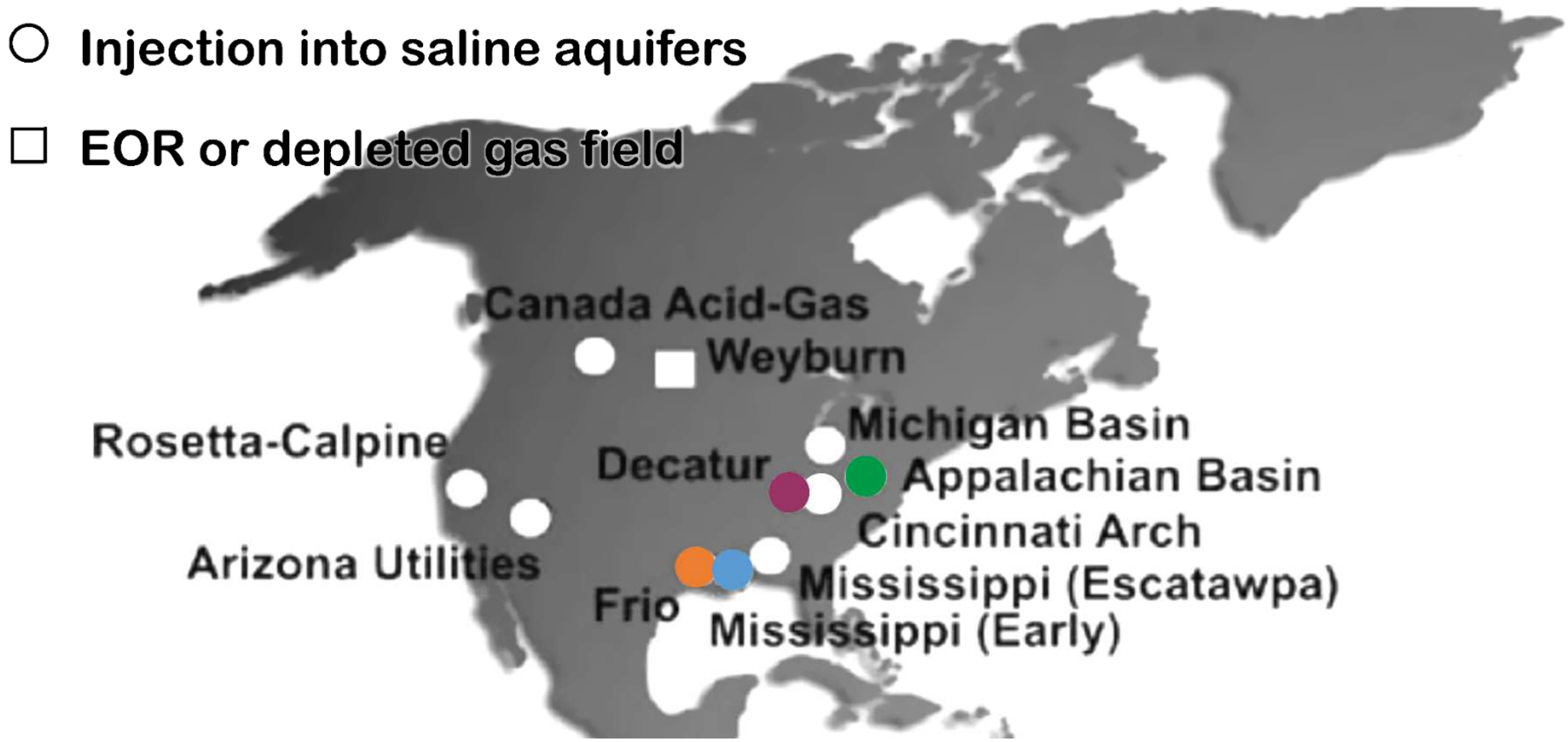



Saline formation $CO_2$ storage scheme

## Associated Risks

- Pressure build-up
- Seismic problems
- CO2 leakage
- Brine extraction
  - High salinity
  - Transportation and disposition

# Brine Composition




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.

# Produced water v/s Extracted Brines

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## Produced Water

- Presence of hydrocarbons
- Variable production flow and salinity with aging of wells
- Variable concentrations of dissolved solids and minor species
- Not a major concern

## Extracted Brines

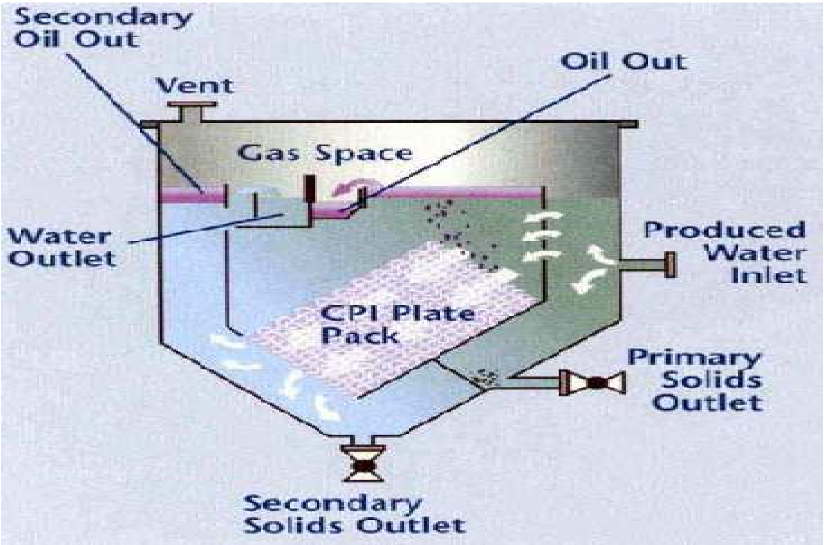
- Little or no hydrocarbons
- Little or no variation in salinity
- Little or no variation in TDS and minor species
- Minimizing CO2 emission

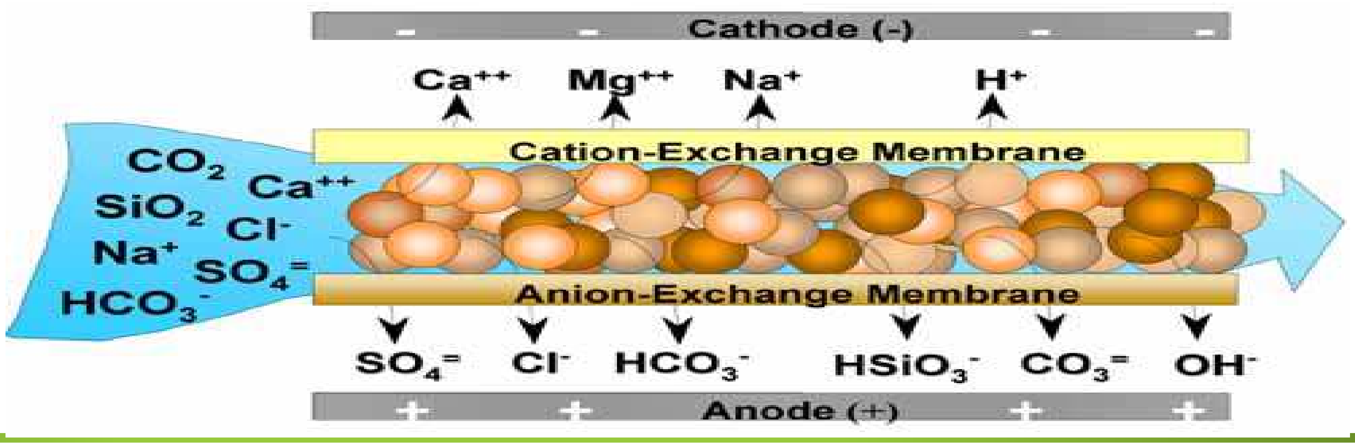
# Quandary of Produced water/Brine Disposal

- **Produced water/brines cannot be discharged to surface waters**
- **These could be crystallized (ZLD) and crystallized salt can have commercial value**
  - Salt purification and production is energy intensive
  - Cannot contain heavy metals
  - Production of crystal could quickly overwhelm markets
- **Reinjection in a different reservoir after concentration to reduce volume being reinjected**
  - Minimizes the environmental contamination
  - Allows production of fresh water

# Water Treatment

- De-oiling
- Removal of suspended particles and sand
- Removal of soluble organics
- Removal of dissolved gases
- Removal of NORM
- Disinfection
- Softening
- Desalination

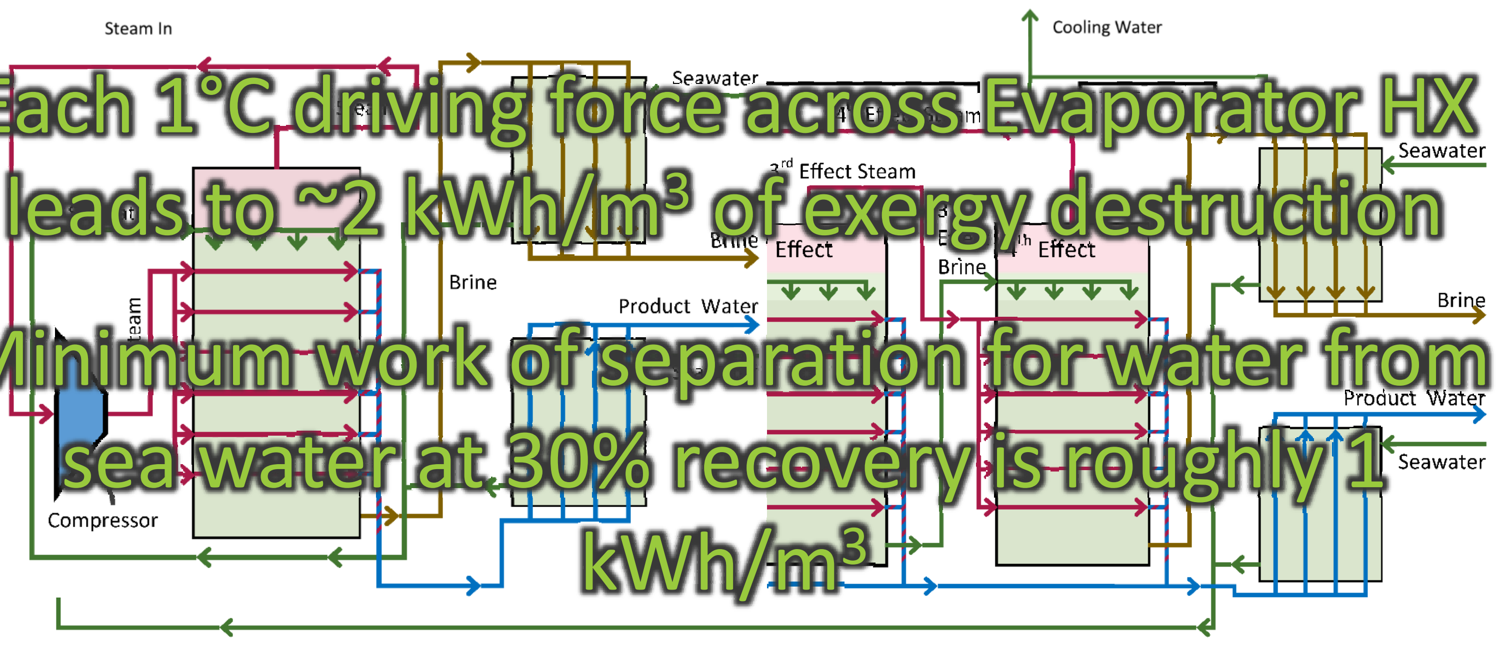



Arthur et.al., All Consulting, LLC Report, 2005

# Thermal / Evaporative Desalination

- **Current commercially available technologies**
  – Multistage Flash (MSF) (typically <10% efficient)
    - Steam from power plant is most likely not available
    - Electricity from power plant is likely available
  – Mechanical Vapor Compression (MVC) or MVC-MED hybridization

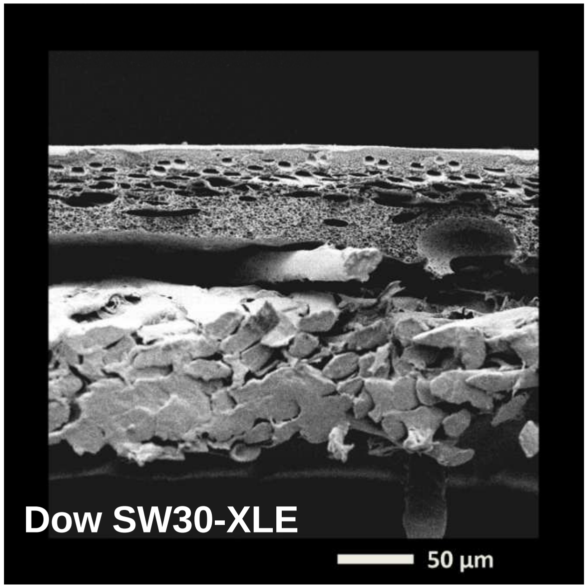



**Each 1°C driving force across Evaporator HX leads to ~2 kWh/m³ of exergy destruction**

**Minimum work of separation for water from sea water at 30% recovery is roughly 1 kWh/m³**

# Membrane Technologies

- **Hydraulic Pressure**
  - Micro-filtration (MF)
  - Ultra-filtration (UF)
  - Nano-filtration (NF) (Divalent ion removal)
  - Reverse Osmosis (RO)
    - Can be >30% efficient
- **Electrochemical**
  - Electrodialysis
    - Not suitable for high salinity brines
- **Vapor Pressure**
  - Membrane Distillation
  - Pervaporation
- **Osmotic Pressure**
  - Forward Osmosis




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

# Osmotic Pressure

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**What is osmotic pressure?**

**"When a solution, e.g. of sugar in water, is separated from the pure solvent - in this case water - by a membrane which allows water but not sugar to pass through it, then water forces its way through the membrane into the solution. This process naturally results in greater pressure on that side of the membrane to which the water is penetrating, i.e. to the solution side.**

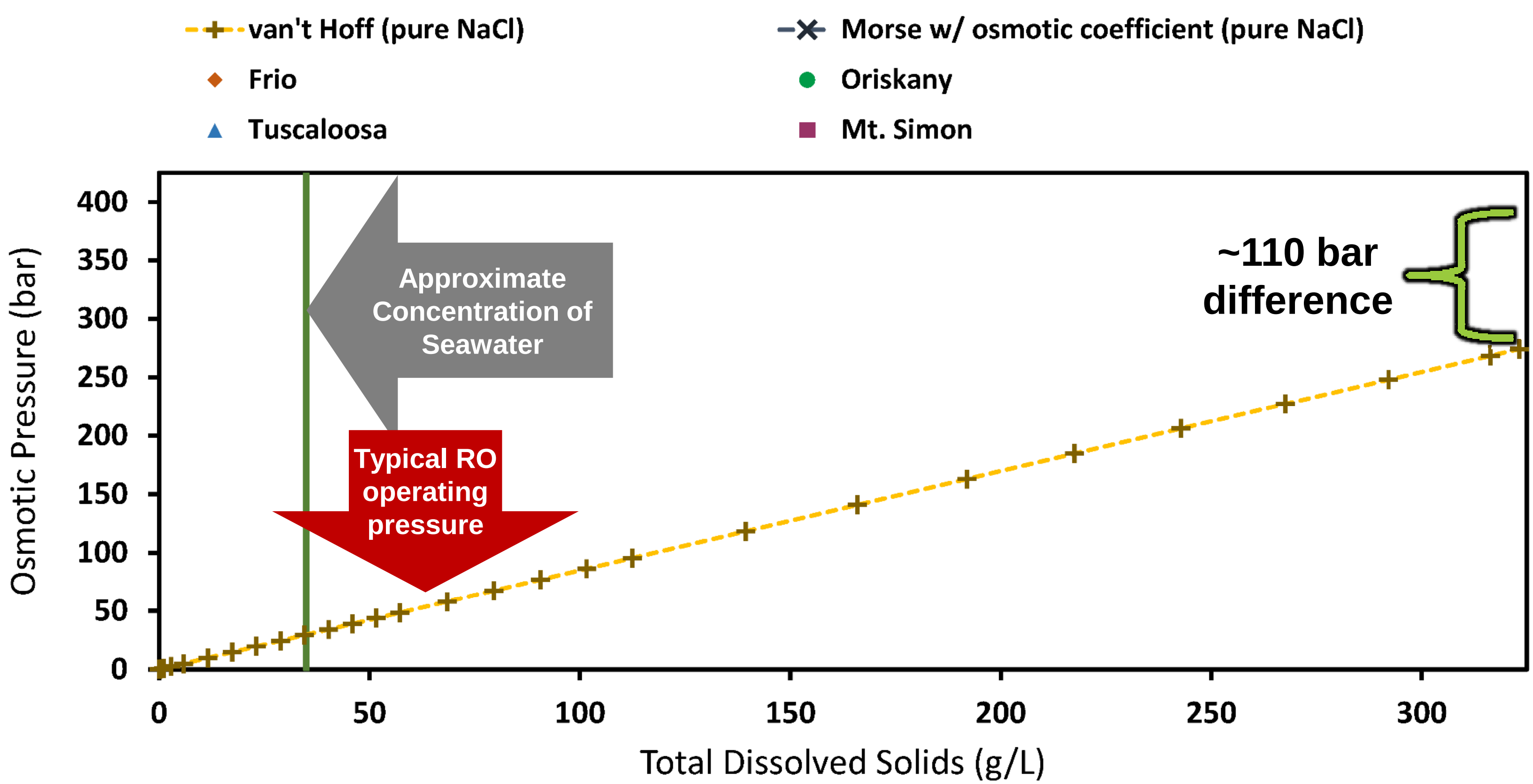
**This pressure is osmotic pressure."**

– Jacobus H. van't Hoff, 1901

$$\pi = -\frac{RT}{v_w}\ln(a_w) \approx RT\sum_{i\neq w} m_i\rho_w \approx RT\sum_{i\neq w} c_i$$

J.H. van't Hoff, Nobel Lecture, December 13, 1901.

# High-salinity brines are non-ideal solutions and can be treated as NaCl equivalent




Osmotic pressure of sodium chloride solutions and produced brines at 25°C

Brine osmotic pressures calculated using Geochemist's Workbench v9 with thermo_phrqpitz


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.

# Osmotic and Hydrostatic Pressure

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

$$J_w = A(\Delta \quad - \Delta \quad)$$

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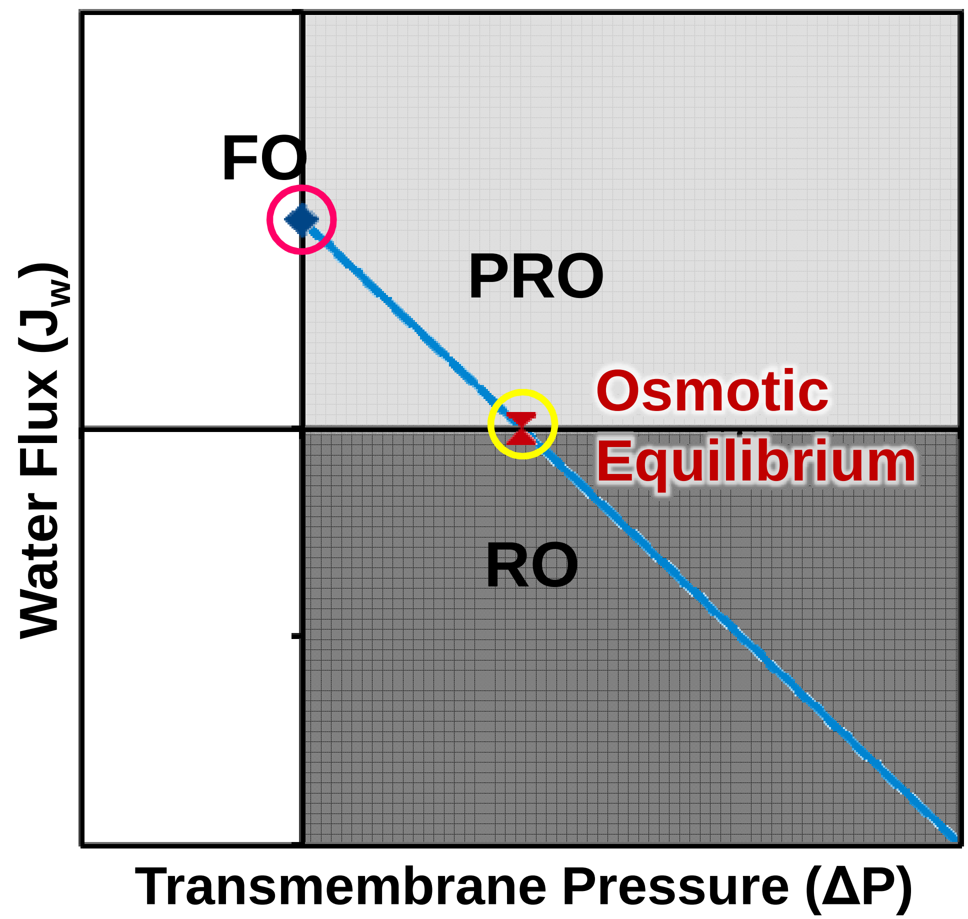
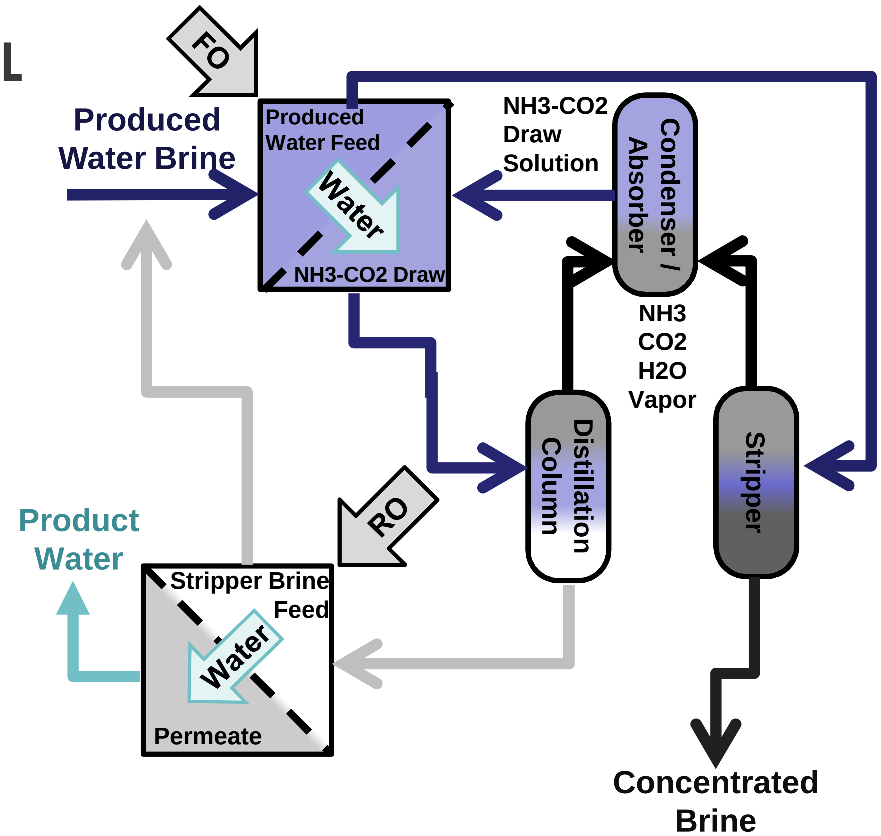



$$\Delta \quad = P_{concentrated} - P_{dilute}$$

# High Salinity Brine Dewatering with FO

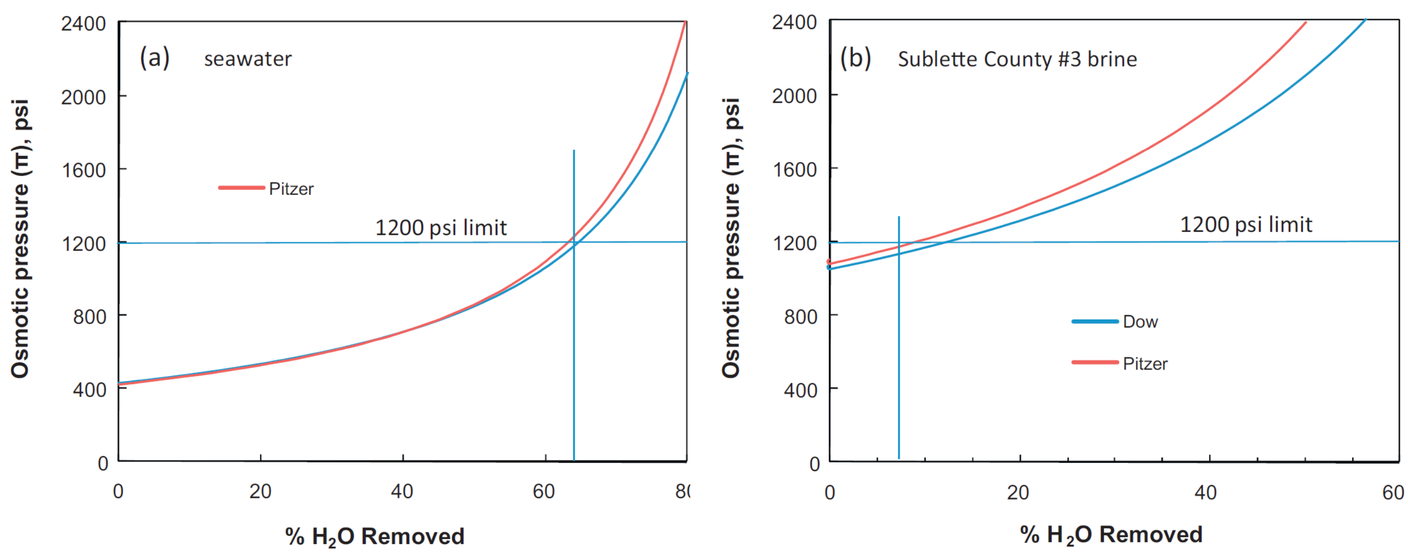
- NH3-CO2 osmotic brine concentrator pilot that was operated in the Marcellus Shale
- Concentrate brines up to 180 g/L TDS
- Process consists of:
  - FO stage @ low TMP
  - Draw solute stripper
  - RO stage @ high TMP




R.L. McGinnis et al. *Desalination* (2013).

# Conventional Reverse Osmosis

- 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.

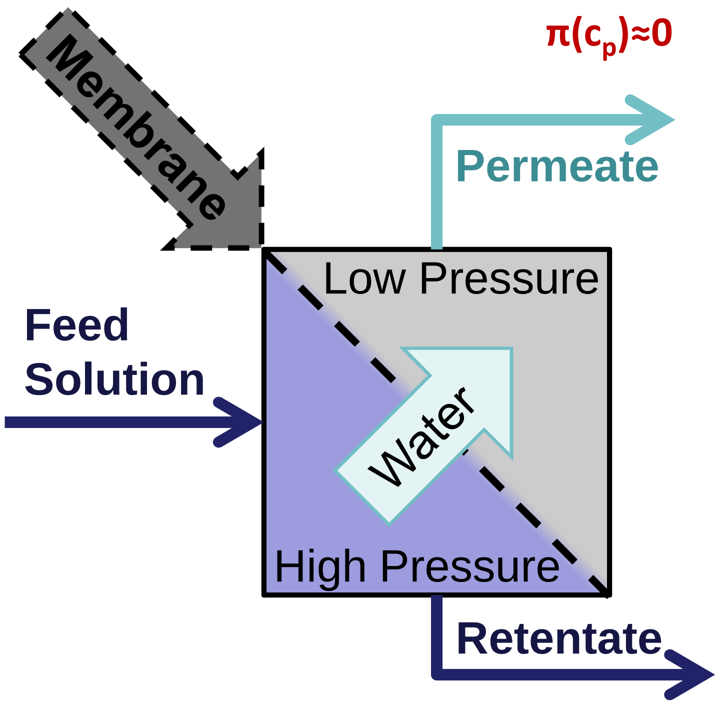
# Osmotically Assisted Reverse Osmosis

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

Reverse Osmosis

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

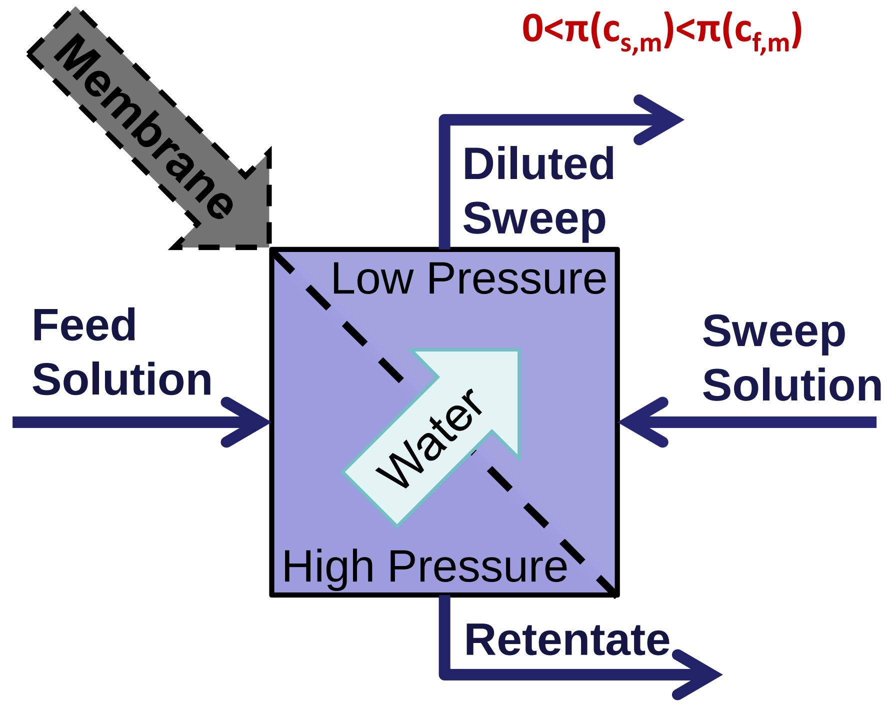
$\pi(c_p) \approx 0$




Osmotically Assisted Reverse Osmosis

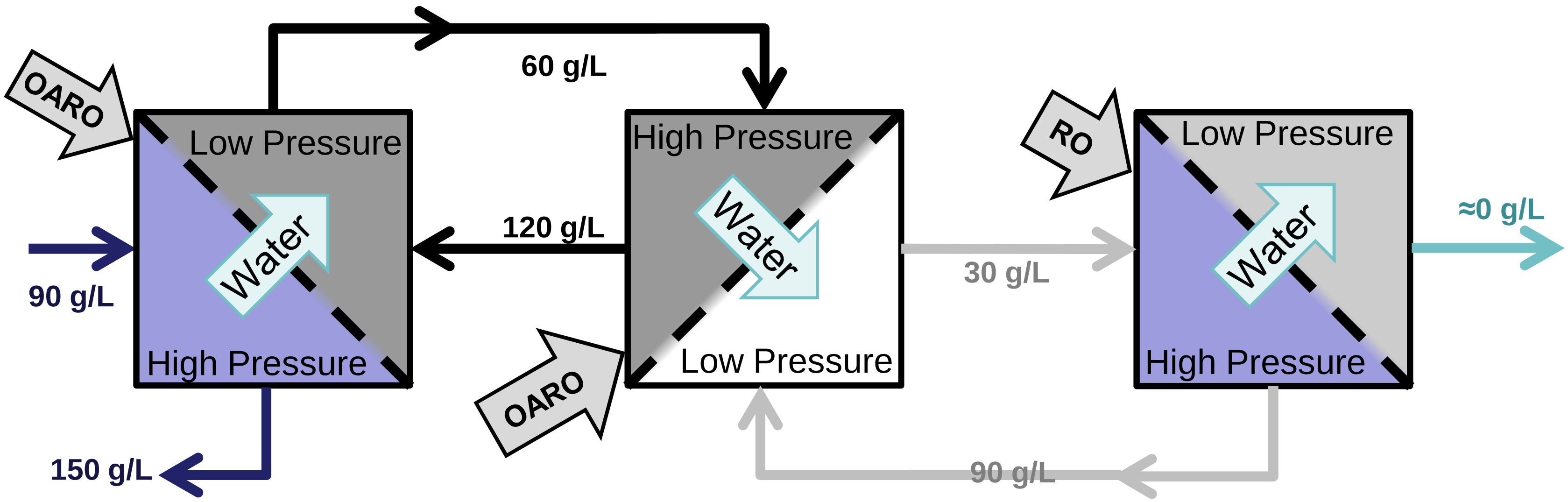
$$J_w = A \cdot \{[P_f - P_p] - [\pi(c_{f,m}) - \pi(c_{s,m})]\}$$

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



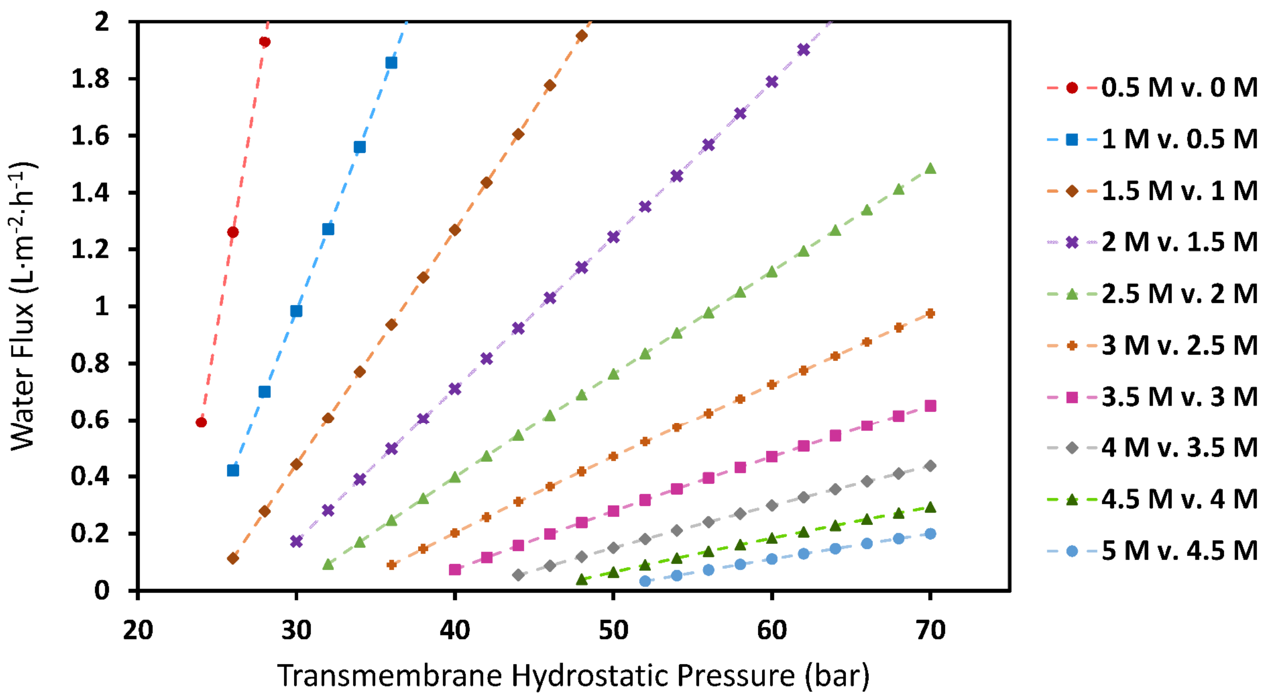
# Process Configuration

- **The OARO process**
  - Seeks to concentrate a brine in steps




  - Pressure limitations will affect concentration difference between the feed and sweep solutions

# Prediction of OARO Performance




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

# Conclusions & Future Work

- OARO appears to be fundamentally feasible with experimental data closely reflecting numerical predictions
- Continue preliminary OARO evaluation and determine mass transport properties both external and internal of membrane
- Construction of  a test system to perform laboratory experiments is in progress
- Demonstrate OARO process for desalination of high TDS produced water and GCS brines

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NATIONAL ENERGY TECHNOLOGY LABORATORY

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