Technologies for High Salinity Water Desalination

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The Ohio State University
Water Management Workshop – Utica and Marcellus Shale
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• Total water withdrawn per year 123.9 trillion gallons, which is ~ yearly outflow of Mississippi river
• Direct energy demands (TE power generation) currently accounts for ~ 39% of all water withdrawal
• Existing ‘data’ needs to include unconventional oil and gas development → need for better accounting

Water and Energy are Interdependent

*Energy and power production require* **water**

- Thermoelectric cooling
- Hydropower
- Energy minerals extraction/mining
- Fuel Production (fossil fuels, H\(_2\), biofuels, *shale*)
- Emission control

*Water production, processing, distribution, & end-use require* **energy**

- Pumping
- Conveyance and Transport
- Treatment and disposal
- Use conditioning
- Surface and Ground water

Information Courtesy: Michael Hightower, Sandia National Labs, 2010
Energy accounts for the largest water withdrawal including mining, UOG, refining, and generation

- Significant opportunity for reuse and reducing consumptive loss
- New sources of energy (biomass, syngas, hydrogen, etc.) will more than double current use per gallon or kWhr (4-6 gal. H₂O/gal ethanol)
- Water withdrawals expected to be TWO orders magnitude larger with increased ‘new’ energy

We’re the Saudi Arabia of Shale Oil and Gas, but we can’t utilize it without proper water use and disposal
Pressures on Water Sources: Energy Impact

- Population Growth (>1% per year) and Population Shifts to Urban Areas: Changes and increases demand in water, food, and energy
  - Local problems growing
  - Logistics for distribution, management, maintenance will only get harder
  - Concern for WWTPs, ground injections → need for new technology development

- Over-pumping of Ground Water Aquifers: Unsustainable
  - Ogallala aquifer is considered ‘depleted’ → already impacts Bakken shale
  - Bakken shale uses Fox hill and Kildeer aquifers → water is high salinity, large amount of bicarbonates accounts for complex water chemistry
    - Pressure head declining at 1-2 feet/year as per 2012 estimates

- Source Waters Matter! Cross-talk between surface and aquifers is growing, reducing dilution solutions – more treatment is needed → new technology is imperative as current membranes do not work for these new salinities
  - Finite (and increasing) energy costs

- Current centralized WWTPs are capital, energy, and chemically intensive. No viable on-site treatment system to permit reuse

Prakash et al. (2014) Chapters 27 and 28 in Aquananotechnology, CRC Press
Shannon, MA (2011), U. Illinois, Personal Communication
Water Impact on UOG Development

- Unconventional oil and gas generates significant produced water
  - Estimated at 570 million m³ (~ 4800 million barrels)
  - Trucking cost for water estimated to be ~ $4/bbl
  - Salinity can reach 3-7X of seawater

- Emerging (and some existing) regulatory concerns
  - WWTPs in Pennsylvania cannot treat flowback/produced water due to elevated TSS and salinity
    - Limit on volume content
    - Restrictions on holding/evaporation ponds and storage
  - EPA draft report out for comment
    - “Insufficient” pre- and post- hydraulic fracturing data on impact of UOG on surface and ground water impact especially towards drinking water
    - Accidents and spill data for two states (Colorado and Texas) only estimated at ≤ 12 wells/100 wells generate water-related impacts
    - Difficult to track ‘rapidly’ changing industrial development
    - Radionuclides found in inadequately treated water from Marcellus shale
      - 10-1000 pCi/L including gross α and β emissions in effluents

Thiel et al. (2015), Desalination;  EPA/600/R-15/047c (June 2015)
Why Desalinate Produced Water?

- Global implications for water resource management with UOG development
  - Estimates are that China has ~ 36 trillion m$^3$ in shale gas reserves with aim to develop > 6 billion m$^3$ by 2015
  - China estimates use of 171 million m$^3$ water in Sichuan province, ~ 10.5% of province’s total water demand

- Significant costs involved in treatment and disposal with emerging regulatory landscape on water reuse
  - Average cost of trucking ~ $4/bbl; can reach $7/bbl
  - Reports of > $20,000/day for water removal, disposal, handling of ‘low volume’ wastewater
  - Regulators paying attention to new reports suggesting water contamination possibilities → reuse makes economic and resource management sense

- Fundamental science still lags in sub-surface transport
  - Pore size (throats) in shale formations at similar length scales as gas molecule mean free paths
  - Standard fluid mechanics and porous material theories are inadequate at these length scales, even more so with complex fluid mixtures

Technologies for Desalination: Seawater

- Current (sea)water desalination methods are energy intensive

<table>
<thead>
<tr>
<th>Process</th>
<th>MSF</th>
<th>MED/TVC</th>
<th>RO</th>
<th>ED*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Consumption (kJ/l)</td>
<td>290</td>
<td>145-390</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Electricity Consumption (kJ/l)</td>
<td>10.8-18</td>
<td>5.4-9</td>
<td>9-25.2</td>
<td>4.32-9</td>
</tr>
<tr>
<td>Total Energy Consumption (kJ/l)</td>
<td><strong>300.8-308.8</strong></td>
<td><strong>150.9-399</strong></td>
<td><strong>9-25.2</strong></td>
<td><strong>4.32-9</strong></td>
</tr>
<tr>
<td>Typical Production Capacity (m³/day)</td>
<td>~ 76,000</td>
<td>~ 36,000</td>
<td>~ 20,000</td>
<td>~ 19,000</td>
</tr>
<tr>
<td>Conversion to Freshwater</td>
<td>10-25%</td>
<td>23-33%</td>
<td>20-50%</td>
<td>80-90%</td>
</tr>
<tr>
<td>Pretreatment required</td>
<td>little</td>
<td>little</td>
<td>demanding</td>
<td>moderate</td>
</tr>
</tbody>
</table>

* For brackish water

- We are far from the natural law limits for separating salts and solids from water:
  - Currently at 4-100X times higher for nearly all methods
  - RO is most energy efficient, but requires stringent pre-treatment
  - Due to produced water salinity → RO energy increases by ~ 9X over seawater

- All membrane methods suffer from capital and membrane replacement costs due to fouling
  - Significant technology development in membrane materials

Prakash et al. (2014) Chapters 27 and 28 in Aquananotechnology, CRC Press
Both Fracking fluids and produced water represent a complex chemical system, which are not uniform geographically.

Minimal data on foulants and scalants like silica, even for ‘well documented’ Barnett and Marcellus shales.

Salty stuff

The mix of fracking fluid and groundwater known as produced water contains wide variations in water chemistry.

<table>
<thead>
<tr>
<th>Content (mg/l)</th>
<th>Barnett (TX)</th>
<th>Haynesville (AR, LA, TX)</th>
<th>Marcellus (NY, PA, WV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>40,000–185,000</td>
<td>40,000–205,000</td>
<td>45,000–185,000</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>25,000–110,000</td>
<td>20,000–105,000</td>
<td>25,000–105,000</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>10,000–47,000</td>
<td>15,000–55,000</td>
<td>10,000–45,000</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>2200–20,000</td>
<td>3100–34,000</td>
<td>5000–25,000</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>350–3000</td>
<td>100–3000</td>
<td>500–3000</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>200–3000</td>
<td>600–5200</td>
<td>500–3000</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>30–500</td>
<td>100–2200</td>
<td>50–6000</td>
</tr>
<tr>
<td>Fe(^{2+}/Fe(^{3+})</td>
<td>22–100</td>
<td>80–3500</td>
<td>20–200</td>
</tr>
<tr>
<td>SO(_4)(^2-)</td>
<td>15–200</td>
<td>100–400</td>
<td>10–400</td>
</tr>
</tbody>
</table>

TDS = total dissolved solids. Source: GE Power and Water.

No existing (publicly available, peer-reviewed) data for Utica shales

What Technologies are Available?

- Water desalination (and filtration for TSS) are old ideas
  - First recorded desalination attempt \( \rightarrow \) evaporation in 4\(^{th}\) century by Greek sailors
  - Membrane-based methods developed around WWII

**Thermal (distillation) methods:**
- Multi-effect, multi-stage, solar,…

Energy intensive but high product water recovery possible for high salinity waters

**Membrane-based methods:**
- Forward osmosis, reverse osmosis, electrodialysis,…

Low energy cost but membranes foul.
Product water recovery limited with increasing salinity

**Hybrid methods:** Combine thermal and membrane or multiple membrane methods

**Key challenge:** Provide enough energy for desalination away from ‘grid’ infrastructure at economically viable conditions

**Possible solutions:** use geothermal, solar, or even heat from flaring methane

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Prakash et al. (2014) Chapters 27 and 28 in Aquananotechnology, CRC Press; Shaffer et al., (2013) ES&T
Pie-in-Sky Ideas: Nanotechnology Solutions for New Desalination Systems

- Biological systems are close to the natural law energy limits and operate at the nanoscale

- New water purification technologies using point-of-source supply, point-of-discharge, and point-of-use systems: The new (oldest) paradigm in infrastructure

- New technologies can greatly improve how clean water is supplied – Can change everything!

First generation lab device at OSU inspired by biology for desalination at thermodynamic limits

Chip-scale system at MIT to deliver de-salted water from seawater at a fraction of the energy cost

Kim, S. J. et al. Nature Nanotechnology 2010
Prakash et al., Patent Pending (2013)
Water and Energy is a coupled problem and must be addressed by bringing in ‘stakeholders’ at all levels (local to federal government, private enterprises, utilities, consumers, technology development, and market transition).
Acknowledgements

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Questions?