Water Treatment and Low-Quality Waters

Ted Peltier
Department of Civil, Environmental and Architectural Engineering

Kansas Water Workshop
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## Water Withdrawals in the U.S. and Kansas

<table>
<thead>
<tr>
<th>Category</th>
<th>US</th>
<th>KS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Totals (mgd)</td>
<td>355,000</td>
<td>4,000</td>
</tr>
<tr>
<td>Groundwater</td>
<td>22%</td>
<td>80%</td>
</tr>
<tr>
<td>Surface Water</td>
<td>78%</td>
<td>20%</td>
</tr>
<tr>
<td>Freshwater</td>
<td>86%</td>
<td>100%</td>
</tr>
<tr>
<td>Irrigation</td>
<td>32%</td>
<td>76%</td>
</tr>
<tr>
<td>Public Supply</td>
<td>12%</td>
<td>10%</td>
</tr>
<tr>
<td>Power</td>
<td>45%</td>
<td>9%</td>
</tr>
<tr>
<td>Livestock</td>
<td>0.6%</td>
<td>3%</td>
</tr>
</tbody>
</table>

USGS Circular 1405 “Estimated Use of Water in the United States in 2010”

[Graph showing 2010 withdrawals by category, in million gallons per day]

Values do not sum to 355,000 Mgal/d because of independent rounding.
Water Stress and Scarcity

Population growth in the US is often concentrated in areas with low or declining water reserves.

Groundwater use rates are depleting existing aquifers.

Water Reuse and Recycling options:
- Gray water reuse
- Groundwater recharge
- Wastewater treatment for indirect or direct potable reuse
- Industrial WW Recovery

Projected water withdrawal ratios in 2050 (Roy et al. 2012)
Alternative Water Source Development

(Image from USGS, data and original map from Feith, 1965)
Challenges in Utilizing Low Quality Waters

• Lack of treatment standards

• Variable quality, including ‘uncommon’ pollutant compounds

• Higher treatment requirements and energy costs

• Compatibility with water storage and transmission system

• Ownership and other legal issues

• Public cooperation and acceptance
KU Strengths in Low Quality Water Treatment

• People

• Expanded research facilities and equipment

• Existing multi-disciplinary research groups addressing related topics

• State agency interest and related work

• History of successful collaboration with water and wastewater utilities and organizations at local and national level
Water Treatment Technologies

• Stephen Randtke (CEAE)- Drinking Water Treatment Processes and Infrastructure
• Belinda Sturm (CEAE)- Biological WW Treatment and Bioreactor Design
• John Devlin (Geology)- Groundwater remediation and contaminant transport
• Mark Shiflett (CPE)- Energy-efficient desalination
• Gibum Kwon (ME)- Membranes for Oil-Water Separation
Water and Energy Research

Algal Biofuels Research
Belinda Sturm (CEAE) and Susan Stagg-Williams (CPE)

Reduced Cooling Water Use at Power Plants
Ted Bergman and Ron Dougherty (ME)

Water use in Oil and Gas Production
Reza Barati (CPE)
Shahin Negahban, Karen Peltier and Stan McCool (TORP)

Produced Water Management and Treatment Group
An Overview of the Produced Water Management and Treatment Program
Produced Water Research Program

• NSF-Sponsored Program at KU and West Virginia University

• Goal: Develop management strategies to reduce the impact of oil and gas production on existing water resources and to increase use and reuse of produced water

• Specific Research Objectives
  1. Treatment of produced water and formation brines to encourage beneficial use and reuse
  2. Minimization of freshwater use in oil and gas production
  3. Assessment of impacts of produced water on aquatic ecosystems
## Participants

<table>
<thead>
<tr>
<th>University of Kansas</th>
<th>West Virginia University</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Collaborators</strong></td>
<td><strong>Collaborators</strong></td>
</tr>
<tr>
<td>Edward Peltier</td>
<td>Paul Ziemkiewicz</td>
</tr>
<tr>
<td>Stephen Randtke</td>
<td>Lian-Shin Lin</td>
</tr>
<tr>
<td>Karen Peltier</td>
<td>Joseph Donovan</td>
</tr>
<tr>
<td>Reza Barati</td>
<td>Harry Finklea</td>
</tr>
<tr>
<td>Belinda Sturm</td>
<td>J. Todd Petty</td>
</tr>
<tr>
<td>Jyun-Syung Tsau</td>
<td>Shawn Grushecky</td>
</tr>
<tr>
<td><strong>Staff</strong></td>
<td><strong>Staff</strong></td>
</tr>
<tr>
<td>Ray Carter Jr.</td>
<td>Jennifer Hause</td>
</tr>
<tr>
<td>Mark Ballard</td>
<td></td>
</tr>
<tr>
<td><strong>Post-Doctoral Researchers</strong></td>
<td><strong>Post-Doctoral Researchers</strong></td>
</tr>
<tr>
<td>Ming Chen, Karla Leslie, Masoumeh Veisi, Sheng-Xue Xie</td>
<td>Eric Merriam</td>
</tr>
</tbody>
</table>
What is Produced Water?

- **Flowback water**
  - Injected fracturing fluid returning to the wellhead
  - Occurs primarily in the first few weeks

- **Formation water**
  - Water from hydrocarbon-bearing formations, or injected for enhanced recovery purposes
  - Composition depends on formation chemistry
  - Returns throughout production
Produced Water Volumes

- Over 20 billion barrels (3.3 billion m³) generated in U.S. in 2012
- KS is 5th largest generator
  - 1.1 billion barrels (~45 billion gallons) in 2012
- KS volumes stable from 2007-2012
  - Oil production increased by ~20%
- KS wells average ~20 barrels of water per barrel of oil
  - National average ~10 bbl/bbl

Data from Veil (2015) and Clark & Veil (2009)
Produced Water Disposal in Kansas

- In Kansas, ~ 2/3 of KS disposed of by deep-well injection; ~ 1/3 reused by oil & gas producers
- Deep-well injection has been linked to increased seismic activity (induced seismicity)
- Area-based restrictions on deep well injection since 2015
- Incentives exist for increased water reuse and recovery, and for reducing volumes sent to disposal.

Source: Virginia Tech Seismological Observatory
# Inorganic Constituents

<table>
<thead>
<tr>
<th>Constituent (in mg/l)</th>
<th>Barnett (TX)</th>
<th>Haynesville (AK, LA, TX)</th>
<th>Marcellus (NY, PA WV)</th>
<th>Western U. S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>40,000-185,000</td>
<td>40,000-250,000</td>
<td>45,000-185,000</td>
<td>1,000-400,000</td>
</tr>
<tr>
<td>Chloride</td>
<td>25,000-110,000</td>
<td>20,000-150,000</td>
<td>25,000-105,000</td>
<td>ND-250,000</td>
</tr>
<tr>
<td>Sodium</td>
<td>10,000-47,000</td>
<td>15,000-55,000</td>
<td>10,000-45,000</td>
<td>ND-150,000</td>
</tr>
<tr>
<td>Calcium</td>
<td>2,200-20,000</td>
<td>3,100-34,000</td>
<td>5,000-25,000</td>
<td>ND-74,000</td>
</tr>
<tr>
<td>Strontium</td>
<td>350-3,000</td>
<td>100-3,000</td>
<td>500-3,000</td>
<td>ND-6,250</td>
</tr>
<tr>
<td>Magnesium</td>
<td>200-3,000</td>
<td>300-5,200</td>
<td>500-3,000</td>
<td>ND</td>
</tr>
<tr>
<td>Barium</td>
<td>30-500</td>
<td>100-2,200</td>
<td>50-6,000</td>
<td>ND-850</td>
</tr>
<tr>
<td>Iron</td>
<td>22-100</td>
<td>80-350</td>
<td>20-200</td>
<td>ND</td>
</tr>
<tr>
<td>Sulfate</td>
<td>15-200</td>
<td>100-400</td>
<td>10-400</td>
<td>ND-15,000</td>
</tr>
</tbody>
</table>
Reuse Barriers

- High salinities affect water and nutrient uptake and reduce crop yield.
- Presence of dispersed oil and dissolved hydrocarbon compounds
- Scale formation in treatment systems and producing formations from divalent cations precipitation with carbonates and/or sulfates
- Other constituents with water quality impacts or plant toxicity (e.g. B, Ra$^{2+}$, Ba$^{2+}$, Sr$^{2+}$)
- Corrosivity (CO$_2$, H$_2$S, salinity)
New & Improved Fracking Fluids

- Energized fluids, including supercritical CO2 foams stabilized with polyelectrolyte complex nanoparticles (PECNPs)
  - Reduced freshwater use
  - Better suspension of proppants
  - Improved oil recovery

- Using Produced Water to Prepare Fracking Fluids
  - Optimized formulations and salinity levels
  - Stabilization with PECNPs
  - Benefits include increased O&G production and reduced demand on freshwater supplies
PW Treatment: General Strategy

Initial TSS and oil separation occurs at the well site

Minimal treatment for direct reuse, to prevent scaling or clogging

Salinity reduction required for secondary uses

PRODUCED WATER

- Removal of particulate matter, oil droplets
- Removal of soluble organics
- TDS reduction/Desalination
- Removal of NORMs, scale-causing components

Secondary reuse (‘clean’ water)

Direct industry reuse (reusable water)
## Polyelectrolytes used as “scale inhibitors”

<table>
<thead>
<tr>
<th>Structure*</th>
<th>Abbreviation</th>
<th>Name</th>
<th>Average MW tested</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>PAA</td>
<td>Poly(acrylic acid) sodium salt</td>
<td>5.1, 100, 250 kD</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>PSSM</td>
<td>Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt</td>
<td>20 kD</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>PSS</td>
<td>Poly(4-styrenesulfonate) sodium salt</td>
<td>70, 200, 1,000 kD</td>
</tr>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>PVS</td>
<td>Poly(vinylsulfonic acid) sodium salt</td>
<td>4-6 kD</td>
</tr>
</tbody>
</table>

*Chemicals (as well as structure information and MW data) were obtained directly from Sigma-Aldrich (www.sigmaaldrich.com).
Ba\(^{+2}\) Removal vs Polymer Type/Concentration

- **Barium Removed (µmoles)**
- **Polymer Concentration (percent weight)**

Polymer Types and Concentrations:
- PAA 100kD
- PAA 250kD
- PSS 70kD
- PSS 200kD
- PSSM(1:1) 20kD
- PSSM(3:1) 20kD
- PVS 4-6kD
- Total Present

The graph shows the relationship between the concentration of barium removed and the polymer concentration for different polymer types.
Best case for Sr+2: Combining pH with UF

![Graph showing strontium removal vs pH with different conditions: PSSM(1:1), PSSM(1:1) w/3kD UF, PSSM(3:1), PSSM(3:1) w/3kD UF.](image-url)
AEROBIC GRANULAR SLUDGE FORMATION IN HYPERSALINE SYNTHETIC PRODUCED WATER

- Inoculated with a mixed culture of combined irregular aerobic granules and flocs
- Inoculated with halophilic microorganisms (*Sporosarcina halophile*)
### Halophilic Microorganisms: Image Analysis*

<table>
<thead>
<tr>
<th></th>
<th>Granule formation</th>
<th>Granule maturation</th>
<th>Degranulation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NaCl, %</strong></td>
<td>1%</td>
<td>4%</td>
<td>7.5%</td>
</tr>
<tr>
<td>Avg. Dia., mm</td>
<td>0.24 ± 0.08</td>
<td>1.12 ± 0.18</td>
<td>0.9 ± 0.57</td>
</tr>
<tr>
<td>SVI, mL/g</td>
<td>62 ± 27</td>
<td>12 ± 5</td>
<td>22 ± 0.6</td>
</tr>
<tr>
<td>VSS/SS</td>
<td>0.76</td>
<td>0.82</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* Ibrahim et al., WEFTEC 2017
Desalination

• Reverse Osmosis (RO), Multi-stage Flash (MSF) distillation and Multi-Effect Distillation (MED) account for 94% of global desalination capacity

• Energy requirements rise quickly as inlet feeds become more saline

• At TDS 150,000-250,000 mg/L evaporative crystallizers can treat brines with zero-liquid discharge (ZLD) or near-ZLD

<table>
<thead>
<tr>
<th>Treatment Type</th>
<th>Energy Cost (kWh/m³)</th>
<th>Treatable TDS Limit (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO</td>
<td>3.5-6.0</td>
<td>~70,000</td>
</tr>
<tr>
<td>MSF</td>
<td>10-28</td>
<td>~150,000</td>
</tr>
<tr>
<td>MED</td>
<td>7-25</td>
<td>~150,000</td>
</tr>
<tr>
<td>Brine Concentrator</td>
<td>18-26</td>
<td>N/A</td>
</tr>
<tr>
<td>Brine Crystallizer</td>
<td>52-66</td>
<td>N/A</td>
</tr>
<tr>
<td>Brine Concentrator/Crystallizer</td>
<td>70-92</td>
<td>~250,000</td>
</tr>
</tbody>
</table>
Emerging Desalination Methods

• Multiple approaches being developed to reduce energy use and costs, or increase range of treatable waters.
  – Phase change-based separations (gas hydrate freeze-melting, supercritical desalination, humidification-dehumidification),
  – Advanced membrane processes (forward osmosis, membrane distillation)
  – Voltage-driven processes (electrodialysis, microbial desalination cells)

• Electrodialysis (ED) and membrane distillation (MD) systems have already been tested on a pilot-scale.

• Freeze-melting and supercritical desalination have the potential to significantly reduce energy requirements.
Salinity Exchange for High Salinity Produced Water

- High TDS Produced Water
- Low Salinity Water Flooding OR Treatment and Recovery
- “Salinity Exchange” - Dispose High TDS Water - Produce Low TDS Water - Pressure Management
Future Research Areas

• Produced and saline waters are potential resources in KS and elsewhere; improved treatment processes are needed

• Matching treated-water quality to desired uses can help optimize treatment requirements

• Identify availability of new/water reuse sources and how they can fit specific needs

• Cost-benefit of water recovery and management will be important, and will differ across applications

• Examine the impacts of water reuse or new source development on existing freshwater systems
Acknowledgements

• **Produced Water Research Group**

• **Research Partners & Collaborators**
  – Kansas Water Office
  – Kansas Geological Survey
  – Kansas Biological Survey

• **Funding Sources**
  – National Science Foundation, EPSCoR Research Infrastructure Improvement Program: Track-2, Focused EPSCoR Collaboration Award(OIA-1632892)
  – KU Strategic Initiative Grant
  – Tertiary Oil Recovery Program
  – KU Dept. of Civil, Environmental & Architectural Engineering

• **Many Graduate & Undergraduate Student Researchers**