GROUND WATER PROTECTION COUNCIL

2016 UIC CONFERENCE – DENVER, COLORADO

TREATING PRODUCED WATER FOR BENEFICIAL USE – CURRENT CHALLENGES AND POTENTIAL FUTURE ADVANCES

RICK McCURDY

MANAGER – CHEMICALS AND WATER RECLAMATION
AGENDA

• Current Technologies for Treating Produced Water

• Issues With Current Technologies

• Potential Alternatives on the Horizon
CURRENT TECHNOLOGIES

• REVERSE OSMOSIS (RO)
• VACUUM DISTILLATION / MECHANICAL VAPOR RECOMPRESSION (VD/MVR)
• CRYSTALLIZATION (ZERO LIQUID DISCHARGE - ZLD)
CURRENT TECHNOLOGIES

• Reverse Osmosis
  – Uses pressure to push water molecules through a permeable membrane
  – Requires extensive pretreatment, but removes all minerals, salts and metals
  – Easy to foul media (hydrocarbons and bacteria are troublesome)
  – Inefficient with brines exceeding 50K total dissolved solids (TDS)

Photo courtesy of R. McCurdy

www.degremont-technologies.com
CURRENT TECHNOLOGIES

• Vacuum Distillation / Mechanical Vapor Recompression
  - Requires pretreatment to remove hydrocarbons, total suspended solids (TSS), iron and divalent cations
  - Energy intensive
  - High temperature systems require corrosion resistant alloys ($$)
  - Usually has a clean, concentrated brine stream that can be used as a “kill” fluid

Photo copyright 212 Resources

Diagram copyright Fountain Quail

Photo copyright GE Corporation
BRINE CONCENTRATOR AND CRYSTALLIZER

Brine Concentrator

Brine Crystallizer

www.veoliawaterstna.com
GENERATION OF USEABLE BY-PRODUCTS

**Uses**

**Barium Sulfate (BaSO\(_4\))**
- Preparation of drilling mud, glass manufacturing, rubber manufacturing, production of pigments

**Sodium Chloride (NaCl)**
- Feed stock for chlor-alkali industry, chemical industry, roadway deicing

**Calcium Chloride (CaCl\(_2\))**
- Preparation of drilling mud, completion fluid, workover fluid
ISSUES WITH CURRENT TECHNOLOGIES

- ECONOMICS
- POWER DEMAND
- WASTE / PRODUCT GENERATION
ECONOMICS

$/BBL

Total Dissolved Solids

RO

VD/MVR

Crystallization

50K  100K  150K  200K  250K  300K
POWER DEMAND

- VD/MVR & ZLD plants typically need 6-8 kwh / bbl water processed
- 50,000 bpd plant would use 109.5-146.0 gwh/year
- Avg household consumption is 10,932 kwh/year\(^1\)
- Avg household in Oklahoma has 2.55 people\(^2\)
- A single 50,000 bpd plant will have the energy demand of a city with a population of 25,000-34,000 people!

\(^1\) U.S. Energy Information Administration (2014)
\(^2\) U.S. Census 2010
### WASTE / PRODUCT GENERATION

<table>
<thead>
<tr>
<th>Capacity</th>
<th>Products and waste</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Filter Cake, (tons/day)</td>
</tr>
<tr>
<td>bbl/day</td>
<td>MGD</td>
</tr>
<tr>
<td>5,000</td>
<td>0.2</td>
</tr>
<tr>
<td>50,000</td>
<td>2.1</td>
</tr>
<tr>
<td>100,000</td>
<td>4.2</td>
</tr>
<tr>
<td>200,000</td>
<td>8.4</td>
</tr>
<tr>
<td>300,000</td>
<td>12.5</td>
</tr>
</tbody>
</table>

1 Numbers based off of typical composition of a produced water that is relatively high in salinity with a moderate level of hardness.
POTENTIAL ALTERNATIVES ON THE HORIZON

• ACID BASE GENERATION
• MEMBRANE DISTILLATION
• PLASMA ARC GENERATION
• CAPACITIVE DEIONIZATION
ACID BASE GENERATION PROCESS SCHEME

Produced water

Pretreatment

- Removal of hydrocarbons, suspended solids, hardness ions (Ca, Mg) and metals (Ba, Sr)

Bipolar membrane electrodialysis (BMED) or similar process

- Generation of acid (HCl), base (NaOH) and biocide
EXAMPLE OF ACID BASE GENERATION PROCESS

<table>
<thead>
<tr>
<th><strong>Uses</strong></th>
<th><strong>Hydrochloric Acid (HCl)</strong></th>
<th><strong>Sodium Hydroxide (NaOH)</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>New well stimulation,</td>
<td>• New well stimulation, restore permeability of existing wells, removing scale, corrosion by-products and cement debris</td>
<td>• Drilling fluids, petroleum production, refineries, chemical industry</td>
</tr>
<tr>
<td>restore permeability of</td>
<td>from wellbores, chemical industry</td>
<td></td>
</tr>
<tr>
<td>existing wells, removing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>scale, corrosion by-products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>and cement debris from</td>
<td></td>
<td></td>
</tr>
<tr>
<td>wellbores, chemical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>industry</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
BY-PRODUCTS GENERATED

By-products generated for a 5,000 bbl/day plant

<table>
<thead>
<tr>
<th>Products</th>
<th>bbl/day</th>
<th>Gal/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% HCl</td>
<td>1,800</td>
<td>75,600</td>
</tr>
<tr>
<td>25% NaOH</td>
<td>960</td>
<td>40,320</td>
</tr>
<tr>
<td>Anolyte biocide</td>
<td>250</td>
<td>10,500</td>
</tr>
<tr>
<td>Degreaser</td>
<td>50</td>
<td>2,100</td>
</tr>
</tbody>
</table>


- One business model would allow an operator to provide brine free of charge and then take back generated products at a discount to current market pricing. Products not utilized by local oil and gas industry would be marketed to other commodity users.

- Approximately, 15 tons of solids/day will be generated in the pretreatment process.
ACID BASE GENERATION

• Pros
  > Generate products regularly used by Oil and Gas industry
    - HCl, NaOH, biocide
  > Plant easily expandable from 5,000-50,000 bpd
  > Can co-operate with other brine-mining operations such as iodine extraction

• Cons
  > Energy intensive (2-4 kwh per bbl treated)
  > Market for generated products?
    - A small 5,000 bpd plant will produce:
      - 75,000 gal 15% HCl
      - 40,000 gal 25% NaOH
      - 10,000 gal oxidizing biocide EACH DAY!
MEMBRANE DISTILLATION


http://www.memsys.eu/products.html
MEMBRANE DISTILLATION

• Pros
  > Membrane is resistant to fouling
    - only pretreatment is oil removal
    - Hardness and bacteria have not shown to be troublesome
  > Low energy demand
  > Can handle high TDS brines
  > Can utilize waste heat sources
  > Potential to provide recovery of a distillation unit at the cost of an RO

• Cons
  > Oil can foul membranes
  > While more economical than a VD/MVR process and much less energy intensive – still cannot compete with majority of Class II SWD options; however, waste heat can swing the pendulum
PLASMA ARC

Plasma spark in water

http://www.plasmawhirl.com/index.php

http://drexel.edu/plasma/plasmagallery/plasma-photos/

US Patent 7,422,695
PLASMA ARC

• Pros

> Can handle any TDS water with minimal pretreatment requirements.

> Mobile treatment units that can be installed at well pads.

> Planned designs for systems from 1,500 – 10,000 bbl/day capacity

• Cons

> Insufficient data on air emissions

> Mineral scale deposition potential has not been fully vetted during through field pilots

> Cyclonic nature will require upstream removal of abrasive solids (e.g. proppant, sand, iron)

> Energy demand not vetted through field scale pilots
CAPACITIVE DEIONIZATION

http://pubs.rsc.org/en/content/articlelanding/2013/cp/c3cp50514f#!divAbstract

http://netl.doe.gov
CAPACITIVE DEIONIZATION

• **Pros**
  > Can handle high TDS water (~250k) with minimal pretreatment requirements.
  > Minimal pressure treatment system
  > No fouling
    - polarity reversal allows for self-cleaning

• **Cons**
  > Current systems inefficient at salt removal requiring multiple passes
  > Current systems are relatively micro-scale and not sized for oilfield volumes
  > High TDS brine from self-cleaning process will still require disposal
Thank You!

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