Key Considerations for Frac Flowback/Produced Water Reuse and Treatment

NJWEA Annual Conference

May 9 – 13, 2011
Atlantic City, NJ
Today’s Agenda

- Hydraulic Fracturing Process
- Flow and Water Chemistry
- Treatment Alternatives
Hydraulic Fracturing

- Frac Method: Typically slick water frac
- Wells: 4 to 8 wells per pad
- Frac Water Volume: 4 to 6 million gallons per well
- Flowback: 15 - 35% Frac “flowback” water recovery requiring collection, handling, and disposal / treatment

Composition of a Fracturing Fluid

- Fracturing solution consists of sand and water
- Additives include biocides, corrosion inhibitors, O\textsubscript{2} scavengers, friction reducers, surfactants, etc.

Reference: All Consulting 2009
# Frac Flowback Water Quality (mg/L)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feed Water</th>
<th>Flowback</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.5</td>
<td>4.5 to 6.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>22</td>
<td>22,200</td>
</tr>
<tr>
<td>Magnesium</td>
<td>6</td>
<td>1,940</td>
</tr>
<tr>
<td>Sodium</td>
<td>57</td>
<td>32,300</td>
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<tr>
<td>Iron</td>
<td>4</td>
<td>539</td>
</tr>
<tr>
<td>Barium</td>
<td>0.22</td>
<td>228</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.45</td>
<td>4,030</td>
</tr>
<tr>
<td>Manganese</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Sulfate</td>
<td>5</td>
<td>32</td>
</tr>
<tr>
<td>Chloride</td>
<td>20</td>
<td>121,000</td>
</tr>
<tr>
<td>Methanol</td>
<td>Neglible</td>
<td>2,280</td>
</tr>
<tr>
<td>TOC</td>
<td>Neglible</td>
<td>5,690</td>
</tr>
<tr>
<td>TSS</td>
<td>Neglible</td>
<td>1,211</td>
</tr>
</tbody>
</table>
Wide Variation in Frac Flowback Chemistry (mg/L)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Frac 1</th>
<th>Frac 2</th>
<th>Frac 3</th>
<th>Frac 4</th>
</tr>
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<tbody>
<tr>
<td>Barium</td>
<td>7.75</td>
<td>2,300</td>
<td>3,310</td>
<td>4,300</td>
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<tr>
<td>Calcium</td>
<td>683</td>
<td>5,140</td>
<td>14,100</td>
<td>31,300</td>
</tr>
<tr>
<td>Iron</td>
<td>211</td>
<td>11.2</td>
<td>52.5</td>
<td>134.1</td>
</tr>
<tr>
<td>Magnesium</td>
<td>31.2</td>
<td>438</td>
<td>938</td>
<td>1,630</td>
</tr>
<tr>
<td>Manganese</td>
<td>16.2</td>
<td>1.9</td>
<td>5.17</td>
<td>7.0</td>
</tr>
<tr>
<td>Strontium</td>
<td>4.96</td>
<td>1,390</td>
<td>6,830</td>
<td>2,000</td>
</tr>
<tr>
<td>TDS</td>
<td>6,220</td>
<td>69,640</td>
<td>175,268</td>
<td>248,428</td>
</tr>
<tr>
<td>TSS</td>
<td>490</td>
<td>48</td>
<td>416</td>
<td>330</td>
</tr>
<tr>
<td>COD</td>
<td>1,814</td>
<td>567</td>
<td>600</td>
<td>2,272</td>
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</tbody>
</table>

Flowback Water Management Issues

- Limited disposal capacity
- Long haul distances
- Limited freshwater supplies for fracturing
- Water volumes and chemistry presents treatment challenges
- Increased regulatory scrutiny
Flowback Water Management Solutions

- Treatment for Reuse
  - Oil/Grease
  - Hardness
  - Bacteria

- Treat for Discharge
  - Same as Reuse, Plus:
    - TDS
Treatment for Reuse
Range of Applicability vs. Cost

$ Costs per Barrel

Total Dissolved Solids (mg/L TDS)

- IX
- RO
- Evaporation
- Crystallization

Treatment for Reuse
Treatment for Reuse

Objectives

- Remove petroleum hydrocarbons
- Remove friction reducers and other polymer additives
- Remove inorganic scale forming compounds
- Kill bacteria
- Cost-effective
Re-use Technologies

Organic Removal
- API Separators
- Dissolved Air Flotation
- Chemical Oxidation
- Biological Processes
- Activated Carbon
- Walnut Shell Filters
- Organo-Clay Adsorbants
- Air Stripper (VOC)

Inorganic Removal
- Chemical Precipitation
- Lime/Soda Softening
- Clarifiers
- Settling Ponds
- Ion Exchange
- Multi-Media Sand Filtration
- Greensand Filters
- Cartridge Filtration
Example of Reuse Treatment Solution

- Frac Flowback Water
  - Oxidation: Chlorine Dioxide
  - Air

- Sand Filter:
  - TSS Removal

- GAC:
  - Organics Polish

- Lime or Caustic
- Sodium Sulfate
- Soda Ash

- Precip/Clarifier:
  - Hardness Removal

- Sand Filter:
  - TSS Removal

- Oil Byproduct

- Treated Water

- Acid

Byproduct
Step 1. Chlorine Dioxide Oxidation Oxidation/Disinfection

- Chlorine dioxide is a strong oxidant that provides selective chemical oxidation
- Breaks oil/grease emulsions
- Destroys friction reducers and other chemical additives
- Kills Bacteria
- Oxidizes reduced compounds, such as Fe, Mn, Sulfide, ammonia, etc.
- More efficient than bleach

Ref: Sabre Technologies
Step 2. Dissolved Air Flotation
Hydrocarbon Removal

- Fine bubble diffusion floats oil/grease and TSS to top
- Skimmer potentially recovers saleable oil
- Covered designs also available for VOC emission control
- Skid-mounted design

Ref: Pan America Environmental Website
Step 3. Granular Activated Carbon
Organics Polish

- Liquid phase activated carbon removes most hydrocarbons and other organics
- Spent carbon is disposed of in approved facility
- Simple design and operation
- Skid-mounted design
- Periodically backwashed to remove TSS.
Step 4. Chemical Precipitation/Clarification
Metals/Hardness Removal

- Chemical precipitation system removes inorganic scale-forming compounds (barium, strontium, metals, hardness, etc.)
- Custom design mobile frac tank design includes multiple mix tanks and built-in clarifier
- Sludge is removed and dewatered in separate system prior to off-site disposal
- High pH operation (9.5 to 11)
- Elevated pH prevents bacteria from growing

Ref: Rain-for-Rent Website
Step 5. Multi-Media Sand Filtration  
TSS Polish

- Conventional sand filter removes TSS before reuse
- Acid or carbon dioxide addition ahead of filter to reduce pH and eliminate calcium carbonate scaling
- Periodically backwashed with filtered water. BW returned to front of system.
Summary of Reuse Treatment System

- Treatment systems are available to remove organic and scale-forming compounds, allowing reuse without TDS removal.
- Treatment reduces fresh water makeup requirements and off-site disposal costs.
- Multiple design options are available.
- Bench and pilot-scale testing recommended to select best treatment options and minimize cost.
Removal of TDS
Viable TDS Removal Alternatives

- Membrane Treatment
  - Reverse Osmosis
  - Nanofiltration
- Evaporation
  - Thermal Evaporators
  - Crystallization
Range of Applicability vs. Cost

- **Evaporation**
- **Crystallization**
- **Treatment for Reuse**
- **RO**
- **IX**

$ Costs per Barrel vs. Total Dissolved Solids (mg/L TDS)
Reverse Osmosis

- Membrane separation technology that removes dissolved solids (TDS) from water
- Membrane is semi-impermeable - allowing only water to pass; 99%+ of all ionized species are rejected
- Non-selective treatment process
- Degree of all ion rejection is dictated by size and charge
- NF is a loose RO membrane
Reverse Osmosis (cont)

- Maximum concentrate TDS is approx. 80,000 mg/L
- Energy costs are $1/10^{th}$ to $1/15^{th}$ the cost of mechanical evaporation
- Skid-mounted, compact design
- Operating pressures up to 1200 psig
- Multiple membranes and manufacturers available
Salt Concentration vs. Recovery

% RO Water Recovery

Salt Concentration Factor vs. Max Feed TDS (mg/L)

- Conc Factor
- Max Feed TDS

<table>
<thead>
<tr>
<th>% RO Water Recovery</th>
<th>Max Feed TDS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>8,000</td>
</tr>
<tr>
<td>20%</td>
<td>16,000</td>
</tr>
<tr>
<td>40%</td>
<td>32,000</td>
</tr>
<tr>
<td>60%</td>
<td>48,000</td>
</tr>
<tr>
<td>80%</td>
<td>64,000</td>
</tr>
<tr>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Historical Problems with RO Treatment for Produced Water

Limited success due to inadequate pretreatment, resulting in fouling and scaling from:

- Calcium Hardness
- Iron
- Barium and Strontium
- Silica
- Microbiological Growth
- Organics
- Silt and Suspended Solids
Key to Success: Efficient Pretreatment

Pretreatment Steps:
- Organics removal (oil/grease, polymers, etc.)
- Efficient hardness and metals removal
- Particulate removal
- Bacteria control

**Result:** Better pretreatment leads to less membrane fouling, higher water recovery and a lower cost of brine disposal
## Scale Forming Salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>Saturation Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Carbonate (CaCO$_3$)</td>
<td>8</td>
</tr>
<tr>
<td>Calcium Fluoride (CaF$_2$)</td>
<td>29</td>
</tr>
<tr>
<td>Calcium Orthophosphate (CaHPO$_4$)</td>
<td>68</td>
</tr>
<tr>
<td>Calcium Sulfate (CaSO$_4$)</td>
<td>680</td>
</tr>
<tr>
<td>Strontium Sulfate (SrSO$_4$)</td>
<td>146</td>
</tr>
<tr>
<td>Barium Sulfate (BaSO$_4$)</td>
<td>3</td>
</tr>
<tr>
<td>Silica, amorphous (SiO$_2$)</td>
<td>120</td>
</tr>
</tbody>
</table>
Example Treatment Solution for TDS Removal

- **Frac Flowback Water**
  - Oxidation: Chlorine Dioxide
  - Air

- **Oil Byproduct**

- **GAC:**
  - Organics Polish

- **Lime or Caustic**
  - Sodium Sulfate
  - Soda Ash
  - Acid

- **Precip/Clarifier:**
  - Hardness Removal

- **Sand Filter:**
  - TSS Removal

- **RO:**
  - TDS Removal

- **Cartridge Filtration:**
  - TSS Polish

- **Anti-oxidant**
  - Sulfite

- **Treated Water**

- **Brine Conc.**
Range of Applicability vs. Cost

- RO
- Evaporation
- Crystallization
- Treatment for Reuse
- IX

Costs per Barrel

Total Dissolved Solids (mg/L TDS)
Evaporation

- Ideal TDS Range of Feed Water is 40,000 to 120,000 mg/L
- Produces high quality distillate and liquid brine concentrate
- Brine concentrate requires further treatment or disposal (max TDS concentration is approx. 260,000 mg/L)
- Evaporation systems more energy intensive than RO
- Most evaporation systems cannot handle any solids
Types of Evaporation Systems

- Forced Circulation
- Falling Film
- Rising Film
- Agitated Thin Film
- Plate and Frame
Selection Considerations

- Chemical Composition of Feed Stream
- Scaling/Fouling Potential
- Foaming Potential
- Materials of Construction
  - Based on Corrosion Potential of Feed Stream
Economization

- **Multiple Effects**
  - Vapor From Each Effect is used in the Next/Previous Effect Depending on Set-up to Reduce Steam Use

- **Vacuum**
  - Reduces Boiling Point
  - Maximizes Efficiency When Used in Concert With Multiple Effects

- **Mechanical Vapor Recompression**
  - Recompresses the Vapor to Reduce Steam Use
  - Usually Uses Just One Effect
Pretreatment Equipment and Controls

- Particulate Removal via Filtration
- pH Control
- Scale Prevention
- Organic Removal
- Defoamer Addition
- Preheating via Heat Exchangers
MVR Evaporator
Most Economical for this Application
Range of Applicability vs. Cost

- RO
- Evaporation
- Crystallization
- IX
- Treatment for Reuse

Costs per Barrel

Total Dissolved Solids (mg/L TDS)
Brine Concentrate Treatment Options

- Crystallizer
- Drum Dryer
- Spray Dryer
- Haul to Disposal Well
Crystallizer

- Complex system designed to produced purified salt products
- Very large systems requiring central location
- Multiple Types of Crystallizers available
- For Marcellus flowback water, two products can be produced with proper pretreatment:
  - Sodium Chloride dry salt
  - Calcium Chloride liquid
Drum Dryer

- Capable of converting mixed salt liquids into dry solids
- Typically steam driven systems operating at atm or under vacuum
- Relatively compact footprint
- Multiple types of dryers available
- Results in dry product

Ref: Buflovak website
Spray Dryers

- Hot air produced from burning natural gas used to evaporate liquid sprayed in top of tall cylindrical vessel
- Dries solids quickly in a single pass
- Baghouse is used to collect salts and vent off gas
- Very tall systems require central treatment location
- In general, very effective for mixed salt streams

Ref: Swenson Technology Website
Evaporation Summary

- Most economical for high TDS/low volume sources
- Pretreatment necessary to keep heat transfer surfaces clean
- Variety of manufacturers and designs available
- Most efficient design is Mechanical Vapor Recompression
- Evaporators are generally very large; some skid mounted units available
- Produced brine stream requires further treatment