Key Considerations for Frac Flowback / Produced Water Reuse and Treatment
NJWEA Annual Conference – Atlantic City, NJ

May 2012
Today’s Agenda

• Overview of Hydraulic Fracturing Process
• Water Quality
• 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 (95k to 142k bbl)
- Flowback: 15 – 35% return
Composition of a Fracturing Fluid

- Fracturing solution consists of sand and water
- Additives include biocides, corrosion inhibitors, O2 scavengers, friction reducers, surfactants, etc.

Reference: All Consulting 2009
### Frac Flowback Water Quality

All values in mg/L

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Typical Flowback Characteristics

The longer Frac water is in the formation, the higher the TDS levels may become.

Source: Siemens AG 2009
Wide Variation in Frac Flowback Chemistry

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All values in mg/L  
Total Dissolved Solids from the Produced Water Database in the United States

• Typical Produced Water TDS Levels – Selected Areas
  – Powder River CBM – 1,200 mg/l
  – San Juan CBM – 4,500 mg/l
  – Greater Green River – 8,000 mg/l
  – Eagle Ford Shale – 20,000 mg/l
  – Fayetteville Shale – 25,000 mg/l
  – Barnett Shale – 60,000 mg/l
  – Woodford Shale – 110,000 mg/l
  – Haynesville Shale – 120,000 mg/l
  – Permian Basin – 140,000 mg/l
  – **Marcellus Shale** – 180,000 mg/l

Source: USGS
Key Water Management Concerns

- Wasting water and general water resource concern
- Surface water quality impacts
- Shallow groundwater quality impacts
- Long-term soil damage from salinity
- Transportation – 100,000 bbl = 770 trucks

**BOTTOM LINE:**

- Huge unconventional gas resources are driving development; and water solutions are key
- Water quality concerns leading to more treatment and reuse
- Solutions can be simple to very complex – *Reduce, Reuse, Recycle* are key goals
Design Basis
Critical First Step

- Feed Water Volume
- Feed Water Quality
- Treated Effluent Requirements
- Site Specific Considerations
Flowback / Produced Water Treatment Solutions

- Treatment for Reuse Without TDS Removal
- Treat for Reuse / Discharge with TDS Removal
TREATMENT FOR REUSE
WITHOUT TDS REMOVAL
Range of Applicability vs. Cost

- **RO**
  - Total Dissolved Solids (mg/L TDS): 3,000
  - Costs per Barrel: 750
- **Evaporation**
  - Total Dissolved Solids (mg/L TDS): 40,000
  - Costs per Barrel: 3,000
- **Crystallization**
  - Total Dissolved Solids (mg/L TDS): 260,000
  - Costs per Barrel: 1,000,000
- **Treatment for Reuse**
  - No TDS Removal
  - Costs per Barrel: 13
  - Total Dissolved Solids (mg/L TDS): 260,000
Example Feed Water Quality

- Water May Also Contain:
  - Polymers
  - Other Organics
  - Radium
  - Other Inorganics (e.g., boron)

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Example Treatment Requirements

- pH: 6.5 to 7.5
- Iron: < 10 mg/L
- TSS: < 50 mg/L
- Bacteria: None
- Treatment Residuals: Non-hazardous
- Mobile system required (5,000 to 10,000 BWPD)
Keys Design Considerations

- **Water Chemistry**
  - Presence of organics, oxygen, and nutrients will result in bacteria growth!
  - Precipitation of barium sulfate will tend to adsorb radium, which may cause the sludge to become hazardous

- **Treatment Selection**
  - Efficient solids / liquid separate required (small footprint)
  - Sludge management
  - Chemical consumption / dosing

![Diagram]
## Treatment Technology Options

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Example of Reuse Treatment Solution Without TDS Removal

- **Frac Flowback Water**
- **Chemical Oxidation**
- **Free Oil and TSS Removal**
- **TSS and O/G Polish**
- **Disinfection**

- **Oil Byproduct**
- **Sludge for dewatering/disposal**
- **Treated Water**
- **Promotion of:**
  - Chlorine Dioxide
  - Air

- **Sand Filter:**
  - TSS Removal
  - Chlorine Dioxide
Step 1. Chlorine Dioxide Oxidation

- 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, etc.
- More efficient than bleach – does not react with ammonia and many other organics

Ref: Sabre Technologies
Step 2. Dissolved Air Flotation

- 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

NOTE: Dissolved Gas or Induced Gas Flotation may also be considered

Ref: Pan America Environmental Website
Step 3. Multi-Media Sand Filtration

• 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.
• Chlorine dioxide disinfection of final product water
Summary of Reuse Treatment

*Without TDS Removal*

- Simplest and least expensive form of treatment
- Multiple technology and design options available
- Reduces fresh water makeup requirements and off-site disposal costs
- Applicable only if drilling operations that need frac flowback water are on-going
- Bench and pilot-scale testing recommended to select best treatment options and minimize cost
TREATMENT OPTIONS FOR TDS REMOVAL
Viable TDS Removal Alternatives

• Membrane Treatment
• Evaporation
• Crystallization
Range of Applicability vs. Cost

- **RO**
- **Evaporation**
- **Crystallization**

Total Dissolved Solids (mg/L TDS)

- Treatment for Reuse
- Evaporation
- Crystallization

$ Costs per Barrel

- RO: 750
- Evaporation: 3,000
- Crystallization: 40,000
- Treatment for Reuse: 260,000
- 1,000,000
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 (continued)

- 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
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
## Scale Forming Salts

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Key to Success: Efficient Pretreatment

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

Result: Better pretreatment leads to less membrane fouling, higher water recovery and a lower cost of brine disposal
Example Treatment Solution for TDS Removal

- Frac Flowback Water
- Chlorine Dioxide
- Air
- Sludge for dewatering/disposal
- RO: TDS Removal
- Treated Water
- Brine Conc.
- Sand Filter: TSS Removal
- Chlorine Dioxide
- Cartridge Filtration: TSS Polish
- Anti-scalant
- Sulfite
- Oil Byproduct
- Oil Byproduct
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
  - Chloride concentrations
  - Temperature
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
MVR Evaporator

Most Economical for this Application
Range of Applicability vs. Cost

- **RO**
- **Evaporation**
- **Crystallization**

**Total Dissolved Solids (mg/L TDS):**
- Treatment for Reuse: 260,000
- Evaporation: 40,000
- RO: 3,000
- Crystallization: 750

**Costs per Barrel:**
- Treatment for Reuse: $1,000,000
- Evaporation: $260,000
- RO: $260,000
- Crystallization: $40,000

$ Costs per Barrel
Crystallizer

- Complex system capable of producing purified salt **products** from impure solutions
- Multiple Types of Crystallizers available
- Principles of Crystallization include:
  - Evaporation to form supersaturated solution
  - Nucleation and growth of salt crystals
  - Harvesting, washing and drying of salt crystals
Application of a Crystallizer in the Marcellus

- Crystallizer Products:
  - Calcium Chloride Liquid
  - Sodium Chloride Dry Salt
  - Distilled Water

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<tr>
<th>Parameter</th>
<th>Feed Water</th>
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<tbody>
<tr>
<td>pH</td>
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<tr>
<td>Bicarbonate</td>
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<tr>
<td>Calcium</td>
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<tr>
<td>Magnesium</td>
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<td>Sodium</td>
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<td>Iron (diss)</td>
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<tr>
<td>Barium</td>
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<td>Strontium</td>
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<td>Chloride</td>
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<td>TSS</td>
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<td>TDS</td>
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Key Considerations

• Proper Design
• Feed Water Management
• Economics – Byproduct Chemical Sales (ASTM specifications)
TDS Treatment Options Summary

- RO membranes have found little use in the Marcellus
- Evaporation technology using Mechanical Vapor Recompression most common form of TDS Treatment
- Crystallization technology is complex but can be cost effective with sale of commodity chemical byproducts
- All technologies generally produce some amount of waste brine that requires disposal
Questions and Answers

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