Water Treatment Technologies for Global Unconventional Gas Plays
U.S. – China Industry Oil and Gas Forum

Fort Worth, TX
September 16, 2010
Overview of CDM

- Company Background
  - Founded in 1947
  - 4,500+ Employees in Over 85 U.S. Offices and 24 International Offices
  - Over $1 Billion in Revenues in 2009
  - Employee Owned / Operated

- Proven Reliability – We stand behind our work

- Our Core Business
  - Water and Wastewater Treatment
  - Air Quality
  - Remediation
  - Management Consulting
  - Design Build Operate
Introduction and Purpose

- The United States has experienced a significant transformation of our energy sector in the last 5 to 10 years due to the development of unconventional gas.
- Development has posed significant challenges to engineering, consulting, construction, and operational professionals.
- CDM has the opportunity to support the development of these resources utilizing our core service area strengths.
- These value-added services are transferable throughout the world.
- CDM is well positioned to use our strong client relationships and reputation with public, political, and regulatory agencies to develop significant business opportunities in the U.S., Poland, the Middle East and throughout Central Europe.
Agenda

- Overview of Shale Gas Development
  - Overview
  - Development Information
- Development Process and Challenges
- Flow and Water Chemistry
- Water Management and Treatment Alternatives
Natural Gas – Important Energy Source for U.S. and Abroad

- Cleanest burning fossil fuel emitting the fewest pollutants into the air
- Produces less CO₂ emissions than oil and coal
- Ideal “bridge” fuel to support alternative energy development

- Recent increase in national reserves as a result of the economical development of unconventional gas sources:
  - Coalbed Methane
  - Tight gas
  - Shale gas
Gas Play Types

Schematic geology of natural gas resources

- Conventional non-associated gas
- Coalbed methane
- Conventional associated gas
- Seal
- Sandstone
- Gas-rich shale
- Tight sand gas
- Oil

U.S. Energy Information Administration
Natural Gas Production by Source

The chart shows the production of natural gas by source from 1990 to 2030. The data is represented in trillion cubic feet. Key sources include:

- **Onshore unconventional**
- **Onshore conventional**
- **Offshore**
- **Alaska**

From the chart, we can observe that:

1. **Onshore unconventional** production has been declining since 2005.
2. **Onshore conventional** production has seen an initial rise followed by a decline.
3. **Offshore** production has increased steadily over the years.
4. **Alaska** production remains relatively stable but shows a slight increase in recent years.
United States Unconventional Gas Outlook

![Graph showing production capacity of unconventional gas types from 1990 to 2018. The graph indicates a significant increase in production capacity, particularly for Shale Gas and Coalbed Natural Gas, with Tight Gas showing a more gradual increase. Source: Modified from American Clean Skies, Summer 2008.](image-url)
U.S. Shale and Tight Gas Basins
Horizontal Drilling

- 6 to 8 wells at a single site versus approximately 16 separate wells for typical vertical well spacing
- ~1/10 surface impact
- 2,000 – 6,000 feet of formation exposure per well versus only formation thickness (50 – 300 feet typical) for vertical wells
Hydraulic Fracturing Process – The Solution and the Controversy

- Frac Water Volume: 3 to 7 M gal
- Additional components include biocides, corrosion inhibitors, O₂ scavengers, proppant, etc.
- 20 -30% Frac “flowback” water recovery requires collection, handling, and disposal / treatment

Composition of a Fracturing Fluid

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>
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<tr>
<td>Calcium</td>
<td>22</td>
<td>22,200</td>
</tr>
<tr>
<td>Magnesium</td>
<td>6</td>
<td>1,940</td>
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<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>
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<tr>
<td>Strontium</td>
<td>0.45</td>
<td>4,030</td>
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<tr>
<td>Manganese</td>
<td>1</td>
<td>4</td>
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<tr>
<td>Sulfate</td>
<td>5</td>
<td>32</td>
</tr>
<tr>
<td>Chloride</td>
<td>20</td>
<td>121,000</td>
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<tr>
<td>Methanol</td>
<td>Negligible</td>
<td>2,280</td>
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<tr>
<td>TOC</td>
<td>Negligible</td>
<td>5,690</td>
</tr>
<tr>
<td>TSS</td>
<td>Negligible</td>
<td>1,211</td>
</tr>
</tbody>
</table>
TDS Profile Barnett Horizontal Well

30 day TDS Profile

0 10000 20000 30000 40000 50000 60000 70000 80000 90000

1 2 3 4 5 6 7 8

STW Resources, Inc.

Water Reclamation using GE Innovation
Wide Variation in Frac Flowback Chemistry

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Frac 3</th>
<th>Frac 2</th>
<th>Frac 1</th>
<th>Frac 4</th>
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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>
</tr>
<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>
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<tr>
<td>TSS</td>
<td>490</td>
<td>48</td>
<td>416</td>
<td>330</td>
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<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 Removal
Treatment for Reuse
Treatment for Reuse
Objectives

- Remove petroleum hydrocarbons
- Remove friction reducers and other polymer additives
- Remove inorganic scale forming compounds
- Kill bacteria
- Utilize mobile, on-site treatment technologies
- 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 → Oil Byproduct

Oxidation: Chlorine Dioxide → Air


Lime or Caustic → Sodium Sulfate → Soda Ash

Acid → Treated Water

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
- Mobile 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
- Mobile 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 helps minimize bacteria growth

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

- Mobile treatment systems are available to remove organic and scale-forming compounds, allowing reuse without TDS removal.
- On-site 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

- **Treatment for Reuse**: 750 - 3,000 TDS, $ Costs per Barrel up to $1,000,000
- **Evaporation**: 40,000 TDS, $ Costs per Barrel up to $260,000
- **RO**: 3,000 TDS, $ Costs per Barrel up to $40,000
- **Crystallization**: Above 260,000 TDS, $ Costs per Barrel above $1,000,000

Total Dissolved Solids (TDS) vs. Cost per Barrel
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 80,000 mg/L
- Energy costs are 1/10th to 1/15th the cost of mechanical evaporation
- Skid-mounted, compact design suitable for trailer mounting
- Operating pressures up to 1200 psig
- Multiple membranes and manufacturers available
Salt Concentration vs. Recovery

![Graph showing the relationship between Salt Concentration Factor and Max Feed TDS, with % RO Water Recovery as the x-axis. The graph includes data points such as 1.25 at 0%, 1.7 at 20%, 2.5 at 40%, 5 at 60%, 8,000 at 80%, and 16,000 at 100%.]
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 (coal fines, clay, etc.)
- Bacteria control

**Result:** High recoveries with much less fouling potential, resulting in a lower cost of operation and 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>
## Recommended RO Design Limits for Scale Forming Salts in the Concentrate

<table>
<thead>
<tr>
<th>Index</th>
<th>Typical</th>
<th>Aggressive</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSI</td>
<td>&lt;1.8</td>
<td>&lt;2.5</td>
</tr>
<tr>
<td>CaSO₄ (% Sat)</td>
<td>230</td>
<td>N/A</td>
</tr>
<tr>
<td>BaSO₄ (% Sat)</td>
<td>6,000</td>
<td>N/A</td>
</tr>
<tr>
<td>SrSO₄ (% Sat)</td>
<td>800</td>
<td>N/A</td>
</tr>
<tr>
<td>SiO₂ (% Sat)</td>
<td>100</td>
<td>150</td>
</tr>
</tbody>
</table>
Example Treatment Solution for TDS Removal Using RO Technology

Frac Flowback Water

- Oxidation: Chlorine Dioxide
- Air

Treated Water

Brine Conc.

Oil Byproduct

- Lime or Caustic
- Sodium Sulfate
- Soda Ash

Lime or Caustic

- Acid

RO Technology

- Sand Filter: TSS Removal
- Cartridge Filtration: TSS Polish
- Anti-scalant

Cartridge Filtration: TSS Polish

- RO: TDS Removal

Precip/Clarifier: Hardness Removal

GAC: Organics Polish

Example oxidation: Chlorine Dioxide

- Air

Lime or Caustic

- Acid

Sodium Sulfate

- Anti-scalant

Soda Ash

- Anti-scalant

Acid
Range of Applicability vs. Cost

- **Evaporation**
  - Costs per Barrel: 750
  - Total Dissolved Solids (TDS): 40,000

- **RO**
  - Costs per Barrel: 3,000
  - Total Dissolved Solids (TDS): 3,000

- **Crystallization**
  - Costs per Barrel: 260,000
  - Total Dissolved Solids (TDS): 1,000,000

- **Treatment for Reuse**
  - Costs per Barrel: 1,000,000
  - Total Dissolved Solids (TDS): 1,000,000
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 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
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
Questions and Answers

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