Water / Fluid Treatment Technologies and the Art of Applying Technology to Address Reuse and Recycling Challenges in the Oil and Gas Field

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The Issues

- Source of fluid to be reused / recycled
- End use of reuse / recycle
- Water chemistry / biology
- People chemistry
- Treatment options
- Waste generation and disposal
- Regulations
- Costs
Universe of Fluid Treatment Processes

- Pre-Treatment – solids removal, oil removal
- Chemical or Biological Clarification
- Filtration
- Solids Dewatering
- Selective Ion Removal
- TDS Removal
- Evaporation
- Crystallization
Complete Fluid / Water Treatment System
What is needed to meet the requirements?

Pre – Treated or Raw Water

Chemical Addition

30 – 50% Solids to Landfill

Dewatering

Clarifier

Chemical Addition

Mix Tank

Clarifier

Landfill

Recycle/Disposal

Bag Filter System

Reverse Osmosis, Ion Exchange, Electro dialysis

Disinfection

Crystallization

Recycle/Disposal

Landfill

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## Waste Discharges from Water Treatment

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Wastestream make-up</th>
<th>Disposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarification</td>
<td>Water / Solids mixture</td>
<td>Dewatering required before disposal</td>
</tr>
<tr>
<td>Filtration</td>
<td>Water / Solids mixture</td>
<td>Dewatering required before disposal Bags disposed directly</td>
</tr>
<tr>
<td></td>
<td>Filter bags</td>
<td></td>
</tr>
<tr>
<td>Selective Ion Removal</td>
<td>Water / Solids mixture</td>
<td>Dewatering required before disposal Disposal Wells or Crystallization</td>
</tr>
<tr>
<td></td>
<td>Concentrated Brine</td>
<td></td>
</tr>
<tr>
<td>Total Dissolved Solids Removal</td>
<td>Concentrated Brine</td>
<td>Disposal Wells or Crystallization</td>
</tr>
<tr>
<td>Evaporation / Crystallization</td>
<td>Steam Plumes Crystallized Salts</td>
<td>Specialty disposal to prevent resolubilizing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Budget Costs

• Typically the least expensive options includes bag filtration only, budget price $1.50 / Barrel.

• The most expensive option is to use evaporation / crystallization at $25.00 to $30.00 / Barrel.
Steps to a Successful Project

- Identify objectives of treatment
- Identify water qualities to be treated (when available)
- Collect and test water samples (when available)
- Identify equipment and methods to meet requirements
- Design the complete system
- Mobilize equipment and personnel
Project Summary from North America

- Treatment Objectives
- Low total dissolved solids
- No oil content
- Removal of total suspended solids
- Removal of dissolved metals
- Solids handling for landfill

Source Water: Produced water – oilfield
Purpose: Beneficial reuse in the community
Treatment of a Low Concentration Brine Stream, Low Oil Content

15 m³/hr < 35,000 mg/L TDS → CHEMICAL ADDITION → CLARIFICATION & FILTRATION

~0.8 m³/hr 0.3% SOLIDS → SOLIDS HANDLING

30% TO 50% SOLIDS TO LANDFILL

LOW TDS PRODUCT WATER

CRYSTALLIZATION

CRISTALLIZED SALT

REVERSE OSMOSIS

CONCENTRATED BRINE STREAM

EVAPORATOR

CONCENTRATED BRINE STREAM

UNTREATED FLUID

PRODUCT WATER

WASTE STREAM
Project Summary from Central America

• Treatment Objectives
• Replace existing system, unable to recover oil
• Recover oil 30 to 50 barrels
• Recover contaminated brine 500 m$^3$/day
• Operate 24 hours per day
• Decrease labor costs of existing system

Source Water: Produced water – oilfield
Purpose: Sell oil, sell clean brine
Process flow design
Project Photos from Central America
Achieved Treatment Objectives – Central America

- Plant is operating at 500 to 800 BPD
- Oil is being recovered
- Clean brine is being recovered
- Labor to operate has been reduced to one man per 12 hour shift. Operating at 24 hours / day
- Chemical cost has been reduced by 50 %
Project Summary from Marcellus - Barium

The Challenge

• Barium is being precipitated out of solution during the fluid treatment of frac flow back water

• A TCLP is showing elevated leaching levels of Barium (as high as 366mg/L)

• The reduction of Barium to 100 mg/L or less in the leachate is a must to maintain customer satisfaction

Hypothesis

By adding a combination of 9000 Series Performance Chemical and a precisely balanced chemical additives to the fluid, barium will be precipitated out in a insoluble form. As a result of the proper chemistry, operations and processes, the filter cake will meet acceptable landfill standards below 100mg/L drawn off a TCLP using a similar method to EPA 1311-TCLP.
Demonstration of Theory

- Barium Precipitation from frac flow back in the insoluble form with 9000 Series Performance Chemical
Comparison of Results

Barium Levels in Past TCLP Leachate Analysis Compared to Lab Test using EPA Test Method 1311/TCLP (mg/L)

- 11.2.2010: 211 mg/L
- 11.30.2010: 366 mg/L
- 12.14.2010: 239 mg/L
- Lab Test 3.22.2011: 5.3 mg/L
Marcellus Shale Barium Conclusions

- Near complete removal of barium was shown from the flow back fluid
- Elimination of the soluble barium to acceptable levels from the TCLP testing of waste solids was demonstrated
- Demonstration of a single solution for all operators was shown to be difficult, as site requirements, operator requirements, regulations influence final solutions
Project Summary from Marcellus Shale

- Treatment Objectives
- Fe removal
- Mn removal
- Total Suspended Solids Removal
- Solids handling for landfill

Source Water: Flowback and produced water

Purpose: Reuse for flowback
Site Preparation and Layout – Marcellus Shale
Photos of Site Layout – Marcellus Shale
Photos of Pilot Site Layout – Marcellus Shale
Turbidity (TSS) of Grab Samples from Treatment System. Marcellus Shale: Influent vs Effluent
Iron Concentration in mg/L of Composite Samples from Treatment Systems.
Marcellus Shale: Influent v. Effluent

Iron Concentration mg/L

<table>
<thead>
<tr>
<th>Composite Sample</th>
<th>Influent Iron (mg/L)</th>
<th>Effluent Iron (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>86.6 mg/L</td>
<td>0 mg/L</td>
</tr>
<tr>
<td>2</td>
<td>209.7 mg/L</td>
<td>0.6 mg/L 99.71% Removal</td>
</tr>
<tr>
<td>3</td>
<td>90.3 mg/L</td>
<td>0 mg/L 100% Removal</td>
</tr>
<tr>
<td>4</td>
<td>55.1 mg/L</td>
<td>0.3 mg/L 99.46% Removal</td>
</tr>
</tbody>
</table>
Manganese Concentration in mg/L of Composite Samples from Treatment System
Marcellus Shale: Influent v. Effluent

<table>
<thead>
<tr>
<th>Composite Samples</th>
<th>Influent Manganese (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6 mg/L 100% Removal</td>
</tr>
<tr>
<td>2</td>
<td>1.7 mg/L 100% Removal</td>
</tr>
<tr>
<td>3</td>
<td>3.8 mg/L 100% Removal</td>
</tr>
<tr>
<td>4</td>
<td>1.3 mg/L 100% Removal</td>
</tr>
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</table>
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