Produced Water Management – Solving “Scale /Solids” Accumulation- Case Study
Acknowledgement

We appreciate the help from Freese and Nichols, Inc. on the overall testing program.
Problem Statement

• Solids Build Up in Produced Water Pipeline
• Solids and Emulsion Build Up in Oil Water Separators, Storage Tanks, and Other Production Equipment at SWD Battery
• Increase SWD LOE, Reduced Pipeline Capacity, Potential to Curtail Production
Typical Response

• **Scaling Problem?**
  - Add more scale inhibitors
  - Switch scale inhibitors

• **Biomass Problem?**
  - Inject biocides
  - Switch biocides

• **Iron Problem?**
  - Inject iron control reagent
  - Include iron treatment process
Our Approach

• Analyze the Solid / Scale
  o Obtain samples from representative locations
  o Find out what are the major components

• Analyze the Water
  o Track the source of the solid / scale
  o Track the change of water quality throughout the system

• Bench Scale Test & Field Trial
  o Bench scale treatability test to determine treatment methods
  o Field trial to confirm the treatment methods
Case Study – System Overview

Barstow Water Gathering System
- 6 permitted SWDs (4 active)
- 30 miles of gathering pipe
- 45 delivery points across multiple productive intervals
- First flow in 3Q 2015
- 100% operational in 1Q 2016
- 35,000 - 40,000 BWPD gross system throughput
Case Study – Impacts to Operations

- Decreased hydraulic performance due to scale accumulation
  - Mechanical or chemical remediation

- Sub-optimal oil/water separation at SWDs
  - Design is <50 ppm TPH in injection stream

- Increased operator intervention at SWDs
  - Decreased mean-volume between filter changes
  - Inaccurate level readings
  - Equipment and labor-intensive skim oil recovery processes
Case Study – Solid / Scale Analysis

- Visually, the sludge is with high moisture and oil content.
- Sample was tested for moisture (Dean Stark), oil (toluene extraction) and inorganic species analysis (XRD + XRF).
- High oil contain.
- 5.7% is inorganic solid.
- Presence of NaCl crystal could be due to high TDS.
- Calcite, Magnetite, Pyrite are commonly seen.
### Tank Sludge / Solid Composition Analysis - XRF

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>20.3</td>
</tr>
<tr>
<td>Fe</td>
<td>14.0</td>
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<tr>
<td>S</td>
<td>10.5</td>
</tr>
<tr>
<td>Ca</td>
<td>4.8</td>
</tr>
<tr>
<td>Si</td>
<td>0.4</td>
</tr>
<tr>
<td>P</td>
<td>0.3</td>
</tr>
<tr>
<td>Sr</td>
<td>0.2</td>
</tr>
<tr>
<td>Al</td>
<td>0.2</td>
</tr>
<tr>
<td>K</td>
<td>0.2</td>
</tr>
<tr>
<td>Ba</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.1</td>
</tr>
<tr>
<td>V</td>
<td>0.0</td>
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<tr>
<td>Cr</td>
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<tr>
<td>Au</td>
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<tr>
<td>Rb</td>
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<tr>
<td>Bi</td>
<td>0.0</td>
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<tr>
<td>Pd</td>
<td>0.0</td>
</tr>
<tr>
<td>Se</td>
<td>0.0</td>
</tr>
<tr>
<td>As</td>
<td>0.0</td>
</tr>
<tr>
<td>Mo</td>
<td>0.0</td>
</tr>
<tr>
<td>Bal</td>
<td>48.7</td>
</tr>
</tbody>
</table>

- XRF Results confirm the finding through XRD
- Fe, S, Ca, Na and Cl should be the major elements
55.1% of the scale sample was oil (organic matter). Could be paraffin, asphaltenes or broken gels?

The majority of the solid was iron, silica and salt.
Elemental Analysis of Scale Sample 3

- 49.1% of the scale sample was solid.
- The majority of the solid was iron, silica, Ca and Mg scale, clay minerals, sulfur and salt.
Is this still a solid / scale problem?
Water Quality Analysis

• Samples were taken at 45 tank batteries and 3 SWDs

• Produced Water Qualities at Tank Batteries and SWDs
  ✓ Basic Water Quality
  ✓ Cations / Anions
  ✓ Scaling Species
  ✓ Bacteria

• Water Qualities at Different Locations of the SWDs
The water quality have wide ranges.

On Average:
- Low DO, neutral pH, high sulfide, high TDS
- Mid range TSS and Turbidity
- Low TDS, high bacteria at Delaware Mountain Group; High TDS, low bacteria at Deeper Targets

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Delaware Mountain Group</th>
<th>Deeper Targets</th>
<th>SWDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>37.3</td>
<td>35.5</td>
<td>34.1</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>mg/L</td>
<td>1.4</td>
<td>2.3</td>
<td>1.5</td>
</tr>
<tr>
<td>pH</td>
<td>s.u.</td>
<td>7.2</td>
<td>6.2</td>
<td>6.6</td>
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<tr>
<td>Sulfide</td>
<td>mg/L</td>
<td>39.6</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/m</td>
<td>7842</td>
<td>36052</td>
<td>21364</td>
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<tr>
<td>Total Dissolved Solids</td>
<td>mg/L</td>
<td>51388</td>
<td>292048</td>
<td>158767</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg-CaCO3/L</td>
<td>865</td>
<td>34</td>
<td>399</td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>mg/L</td>
<td>68</td>
<td>317</td>
<td>181</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>67</td>
<td>96</td>
<td>114</td>
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<tr>
<td>Specific Gravity</td>
<td>[-]</td>
<td>1.040</td>
<td>1.156</td>
<td>1.113</td>
</tr>
<tr>
<td>ATP</td>
<td>pg/ml</td>
<td>9955</td>
<td>19</td>
<td>1578</td>
</tr>
</tbody>
</table>
Most of the parameters are with wide ranges
Na, Ca, Mg are the major cations, there are certain levels of K and NH$_4^+$
Water from Deeper Targets is with higher Na and Ca Levels
Cations Level for the Water at Tank Batteries and SWDs -2

- Iron levels are lower at Delaware Mountain Group.
- Manganese presents at Deeper Targets and the SWDs
- Barium level is higher at Deeper Targets and SWDs.
Most of the parameters are with wide ranges

- Cl\(^-\) is the predominant anion.
- SO\(_4^{2-}\) and Br\(^-\) are normally in the 500 to 1,000 mg/L range.
- Sulfate level is higher at Delaware Mountain Group.
Boron presents in the water samples, mostly under 50 mg/L. Higher level at Delaware Mountain Group.

The levels of nitrate, Fluoride and Phosphate are low and negligible.
• TDS readings are generally higher than the sum of all the ions.
• Need to pay attention to the testing methods for the TDS testing.
Anions charge appears to be higher than the cations charge.

Filtration of samples prior to cations testing could have contributed to the difference.

Always double check the testing methods.
 Scaling Species for the Water at Tank Batteries and SWDs

- Ca and Mg are the major scaling species, Ba level is low.
- Bicarbonate level is mostly under 500 mg/L and averaged around 300 mg/L.
- Ca level is high at Deeper Targets, while the Sulfate level is higher at Delaware Mountain Group.
Scaling Index for the CaSO₄ and BaSO₄ for the Water at Tank Batteries and SWDs (25°C)

- Positive SI indicates the potential to form scale
- Out of the 50 samples, 46 sampling had positive SI for both BaSO₄ and CaSO₄; 1 sample had positive SI for BaSO₄ while negative SI for CaSO₄; only 3 samples are with negative SI for both BaSO₄ and CaSO₄.
- The scaling tendency of the water at the SWDs is higher due to the mixing of water from different sources.
Out of the 50 samples, 27 of the samples were with low ATP (bacteria) level (< 500 pg/ml). 9 samples were with relatively high ATP level (1,000-5,000 pg/ml) while 23 samples were with extremely high ATP level (> 5,000 pg/ml).

Bacteria growth appears to be an issue for a good portion of the tank batteries and SWDs, especially at Delaware Mountain Group.
Bacteria Growth at the SWDs

- Bacteria is detected at Ballpark 20D and Barstow 26-20D, while it is not detected for the sample from Arco State.
- At Ballpark 20D, most of the bacteria is SRB
- At Barstow 26-20D, only APB is detected, but the level is high
Water Qualities at Different Locations of the SWDs

- Samples were taken at the Inlet, right after the ClO₂ injection, after the Oil/Water Separators and right before the well heads.
- Iron level fluctuates as the water flows through the facility. The level at Barstow is higher than at Arco State and Ballpark.
- Sulfide level is low at all three SWDs, while it fluctuates throughout the facility.
- The ATP level at Arco State and Barstow is relatively low, while it is high throughout the whole facility of Ballpark.
Case Study – Bench Scale Analysis

• How can we break the solid?
• How can we prevent the forming of the solid?
Tank Sludge / Solid Break Test – Acetone Dissolution

- Little amount of the sludge dissolved into the acetone solution.

Sludge Sample in Acetone Solution

Substance Captured by Filter after Dissolution
Little amount of the sludge dissolved into the hexane solution.

- Sludge Sample in Hexane Solution
- Substance Captured by Filter after Dissolution
Tank Sludge / Solid Break Test – Diesel Dissolution

- Fast dissolving of the majority of the sludge.
Tank Sludge / Solid Break Test – $\text{H}_2\text{SO}_4$ Digestion

- Small percentage of sludge dissolved in the acid solution.

Sludge Sample in $\text{H}_2\text{SO}_4$ Solution

Sludge Sample after $\text{H}_2\text{SO}_4$ Digestion Solution
Two tank sludge/solid samples were collected, one from Barstow 26-20D, the other one from Ballpark 20D.
With the suspicion that most of the sludge is paraffin, tests were conducted by dissolving the sludge with paraffin solvent at room temperature to check the solid/water/paraffin separation.
Dissolution of Tank Sludge / Solid Sample from Barstow 26-20D

- Good oil/water/solid separation was observed
- The paraffin solvent we chose appears to be effective
Dissolution of Tank Sludge / Solid Sample from Ballpark 20D

- As it is shown in the centrifuge tube, there is good separation of oil/water/solid after the dissolution
Summary

• Start the approach from Solid / Scale analysis
• Paraffin is the major issue other than inorganic scales in this case
• Water qualities need to be investigated with a holistic program
• Testing methods need to be verified.
• Bench scale test treatability test can be an important step in the approach.
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Thank You