Upstream Operating Practices Impact on Downstream Refining Processes

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Markets We Serve

- **UPSTREAM**
  - Oil and Gas Production Operations

- **MIDSTREAM**
  - Pipeline Inspection, Cleaning, and Field Services

- **DOWNSTREAM - INDUSTRIAL**
  - Petroleum Refining, Power Generation, and Petrochemical Processing

- **AQUANESS CHEMICAL**
  - Pumping Services Additives, Drilling Fluid Additives, and Production Chemical Intermediates

- **POLYMERS**
  - Specialty Polymers, Candles, Plastics, Imaging, Personal Care
A Typical Oil Production Site
The challenges - Upstream and Downstream

- Upstream has a significant amount of investment in each operation that they want to protect.

- Many of the challenges that the refinery segment sees is due to natural occurrences within the crude oil production operation.

- There are some issues induced through the operation of the oil well that may negatively impact the downstream operations.

- Communications between upstream and downstream are critical in order to minimize processing issues across the supply chain while maintaining high crude oil quality standards.
The Life Cycle of an Oil Well

- Exploration → Drilling → Production → Enhanced Recovery Methods → Capping
## The Life Cycle of an Oil Well (Following Exploration to Capping)

<table>
<thead>
<tr>
<th>Action/Programs</th>
<th>Drilling</th>
<th>Production</th>
<th>Enhanced Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mudding</td>
<td>√</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Acidizing</td>
<td>N/A</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Corrosion Control</td>
<td>N/A</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Paraffin/Asphaltene Dispersants</td>
<td>N/A</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Biocides</td>
<td>N/A</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>H2S Management</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Scale Inhibitors</td>
<td>N/A</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Demulsifiers</td>
<td>N/A</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Water/CO2 Flooding</td>
<td>N/A</td>
<td>N/A</td>
<td>√</td>
</tr>
</tbody>
</table>
Challenges in the Reservoir
Production Blockage

- Organic Damage
  - Paraffin
  - Asphaltenes

- Inorganic Damage
  - Calcium Carbonate
  - Iron Sulfide

- Other Damage
  - Emulsion
  - Acid Sludge
  - Oil-wet Solids
  - Water Blockage
Well Stimulation
Well Stimulation - Acidizing

- **Purpose** - To remove blockage in and around the wellbore to increase production by reducing backpressure constraints

- Requires a significant amount of pre-treatment engineering work in order to insure success. This includes selecting the type of acid to be used, the concentration of each acid constituent, and the pumping rates of the acid

- Acids commonly used include HCl, HF, and Acetic Acid. Others may be used dependent upon the minerals that require dissolution.

- Some evidence of Acetic Acids have been found in some crude slates

- Can impact low pH conditions in crude storage tanks and low lying areas of pipelines
Acid Number Analysis

- Typical parameter for crude oil analysis is TAN (Total Acid Number)

- TAN is exactly that……Total Acid Number

- In order to understand the acid profile of a crude oil better a TAN along with a CAN (Carboxylic Acid Number) should be run. If there is a significant difference, further research to determine the acid species present can be conducted.

- Take Away – Understand fully what information an analysis is providing.
Wellbore Stimulation and Maintenance – Paraffin and Asphaltene Plugging

- Old practice of using waste solvents such as drycleaner solvents (organic chlorides) for dissolving paraffins and asphaltenes in the wellbore. Feedback to producers from purchasers cut this practice in the oilfield.

- End of Organic Chloride issues?
Organic Chlorides

- There are low cost dispersants that are used in the oil field that may have residual organic chloride contamination remaining in them from their manufacturing process or the manufacturer that provides them with the chemistry.

- There are some dispersant products that will break down at the oil well elevated temperatures to produce organic chlorides.

- The organic chlorides found in these streams are generally low molecular weight that will end up in the Naphtha streams and produce corrosion downstream at the hydrotreaters.
Biological Challenges

- Microbial activity occurs throughout the crude oil supply chain.
- Creates MIC (Microbiologically Induced Corrosion) and Biofilms
Biocide Applications are Utilized to Control MIC

- Biocides applied both at the Well site as well as the pipelines
- Predominant chemistries include Quaternary Ammonium Compounds and THPS (TetrakisHydroxymethylPhosphonium Sulfate)
- Removal of biomasses from Crude Oil Transmission lines via pigging and chemical treatment
Black Powder
Black Powder

- Formed in all oil producing wells
- Forms in sales gas, pipelines, and other transport systems
- Consists of various forms of iron oxides, iron sulfides an iron carbonates
- Formation attributed to low corrosion rates in piping, pipelines, and storage tanks

**SEM image of black powder**
Formation of Iron Sulfide

- Iron sulfides form from the reaction of dissolved iron in the produced brine and dissolved hydrogen sulfide in gas phase or arising from bacteria activity.
- Hydrogen sulfide which is a gas initially dissolves in the brine and then dissociates;

\[
\text{H}_2\text{S}_{(\text{gas})} \rightarrow \text{H}_2\text{S}_{(\text{aqueous})} \quad \text{Dissolution}
\]
\[
\text{H}_2\text{S}_{(\text{aqueous})} \rightarrow \text{H}^+ + \text{HS}^-_{(\text{aqueous})} \quad \text{Dissociation}
\]

At pH of 6.5 predominant form is HS

- FeS precipitates after dissolved H2S reacts with dissolved iron

\[
\text{Fe}^{2+} + 2\text{HS}^-_{(\text{aqueous})} \rightarrow \text{Fe(HS)}_2 \rightarrow \rightarrow \text{FeS}_{(\text{solid})} \quad \text{Precipitation}
\]
Formation of Iron Oxides

- Typically formed by direct oxidation of the pipeline wall in the presence of condensed water:

\[ 2Fe^0 + H_2O + 3/2O_2 \rightarrow 2\alpha, \beta, \gamma FeO(OH) \]

- \( \gamma \)-FeO(OH) is unstable and will rapidly change into the magnetite \( Fe_3O_4 \) via the following reaction

\[ 8\gamma FeO(OH) + Fe^0 \rightarrow 3Fe_3O_4 + 4H_2O \]

- Hematite form of iron \( Fe_2O_3 \) will form when water in the system is saturated with dissolved oxygen
Formation of Iron Carbonates

- Formed from carbonates in the process water at depressed pH’s (below 7 pH)
- Formed from CO2 flooding (enhanced oil recovery)
- Formed with “sweeping” operations on barges and ships in the attempts to remove H2S
- Not as much of a corrosion issue in oil field operations as the Iron Carbonate, although will create scale, actually serves to help protect the metallurgy from other contaminants

\[ \text{Fe}^{2+} + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3 \]
## Water Solubility of Different Scales

<table>
<thead>
<tr>
<th>SCALE</th>
<th>Common Name</th>
<th>SOLUBILITY (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSO₄</td>
<td>Barite</td>
<td>3</td>
</tr>
<tr>
<td>FeS</td>
<td>Mackinawite</td>
<td>5</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Calcite, Aragonite</td>
<td>18</td>
</tr>
<tr>
<td>MgCO₃</td>
<td></td>
<td>106</td>
</tr>
<tr>
<td>SrSO₄</td>
<td>Celestite</td>
<td>140</td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td>Gypsum</td>
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</tr>
<tr>
<td>CaSO₄</td>
<td>Anhydrite</td>
<td>3104</td>
</tr>
<tr>
<td>Na₂CO₃</td>
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<td>263,000</td>
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<tr>
<td>NaCl</td>
<td>Halite</td>
<td>370,000</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td></td>
<td>435,000</td>
</tr>
<tr>
<td>MgSO₄</td>
<td></td>
<td>500,000</td>
</tr>
</tbody>
</table>
Where do most Problems Occur?

- Down Hole
- Artificial Lift Systems
- Surface Equipment
  - Headers
  - Filters
  - Separators
- Injection and Disposal Wells
- Transmission lines
- Booster pumps
- Flow lines
- Refineries
Black Powder Prevention/Management

- Evaluate the respective H₂S, O₂, CO₂ and Fe²⁺ levels in the produced water

- Identify sources of precursors in system
  - Reservoir
  - Corrosion
  - Bacteria

- Identify the economies of treatment
  - Attacking limiting reagent (e.g. H₂S)
  - Addressing source of limiting reagent (e.g. bacteria)

- Prevention Strategies
  - Chelate Fe²⁺ in the produced water
  - Inhibit corrosion of pipelines
  - Biocide management in distribution systems
  - Scavenge H₂S in gas or liquid phase
  - Avoid sparging of marine vessels with CO₂ exhaust from the engines
Baker Hughes Patented Technology for Black Powder Monitoring

- Quartz crystal microbalance set-up developed to monitor black powder formation/corrosion rates.

- Sauerbrey equation convert changes in frequency to changes in mass

\[ \Delta f = -C_f \Delta m \]

where:

\( \Delta f = \) the observed frequency change, in Hz,
\( \Delta m = \) the change in mass per unit area, in g/cm², and
\( C_f = \) the sensitivity factor for the crystal used
Determine the total increase in mass from the drop in frequency.

Obtain the mass of iron oxide by subtracting the water film contribution to the total mass.

Calculate the resulting corrosion rate from the mass change due to iron oxide formation.
Scavengers for H2S

- Oilfield creativity for managing H2S is quite extensive. It is the management methodologies that render concerns for refineries. Among these are:
  - Use of MEA Triazines
  - Use of “Inhibited Hydroxyls” otherwise known as Potassium Hydroxide Blends
- MEA Triazines will contribute to overhead and tower corrosion issues

Exchanger tubes exposed to MEA Chlorides as a result of MEA Triazine treatment
Hydrogen Sulfide Scavenging with “Inhibited Hydroxyls”

- The use of Inhibited Hydroxyls will create very stable emulsions
Case History 1 – Black Powder in Refinery Feedstock

- Refiner was experiencing serious preheat train, furnace and tower fouling

- Feedstock analysis revealed an abundance of Black Powder in the condensate Feed

- Crude Oil Supplier and Refiner worked together with Baker Hughes to address the problem both upstream and downstream

- Upstream initiated a corrosion control program on their gathering system and eliminated sparging of the barges with CO2

- Result = Extended run length of Crude Unit from approximately 2 months to over 5 months now
Case History 2 – Tank Bottoms pH Controls

- Refiner was experiencing severe pH control issues in the incoming crude storage tank

- The crude oil had been treated with a Glyoxal chemistry for Hydrogen Sulfide management. First thought was that the H2S scavenger caused the issue

- Further investigation revealed high levels of acetic acid and not Glycolic Acids. The acetic acid is indicative of well acidizing operations.
Management of crude oil concerns at the Refinery Level

- It is impossible to capture all of the challenges that can be encountered through crude oil quality management upstream from the refinery

- Understanding some of the culprits of refinery issues from upstream operations and practices can aide the refinery in better preparing for the opportunity crudes as those opportunities arise

- Communicate with your crude suppliers as issues arise such that upstream can implement changes if deemed necessary or possible…..but the key is communication first

- Implementation of the proper programs within the refinery to address such things as fouling, corrosion, emulsion breaking and wastewater management

- We may change some things in our communications back upstream to the oil field, but production work is a never ending challenge with changes that we must learn to effectively work with. An understanding of upstream activities will improve our ability to manage downstream issues.
Conclusion

- Upstream Production Wells have a significant investment (even before the first drop of oil is received from a well) that production companies want to protect.

- Many of the problems that impact crude quality are natural occurring but some are induced by upstream operation and management of those operations.

- Understanding the upstream challenges and methods of management is the first step in the crude oil quality management in the supply chain for the refiner.