A New Process for Removing Calcium from Crude Oils Containing Calcium Naphthenates

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Agenda

- Problems caused by high calcium crude oils
- Overview of the EXCALIBUR process
- Benefits of EXCALIBUR technology
- Field performance data
- Conclusions
What are some of the crude oils that contain calcium naphthenates?

- West Africa (Doba, Kuito)
- North Sea (Heidrun, Captain)
- China (Bohai Bay, Shengli)
- Indonesia (Serang)
Problems Caused by High Ca Crude Oils

Tank Farm problems

• Calcium naphthenates are natural emulsion stabilizers
  ➢ High BS&Ws in oil charged to crude unit

Desalting problems, when metals are present as naphthenate salts or fine particulates

• High conductivity causes voltage loss
• Emulsion stabilization
• Water carryover
• Poor effluent water quality (high O&G can impact waste water treatment plant)

Desalter effluent water exchanger scaling

• Calcium deposits
Problems Caused by High Ca Crude Oils

Crude unit corrosion

- Most high Ca crudes also high in total acid number (TAN)
  - Atmospheric tower overhead corrosion control
    - High organic acid loading in overhead system can increase neutralizer demand
  - Increased probability of high temperature naphthenic acid corrosion
Problems Caused by High Ca Crude Oils

High Ca levels in residual streams

- FCCU catalyst deactivation, if resids are fed to the FCCU or RFCCU
- Higher coke Ca content
  - May not be able to make anode grade coke
- Higher heavy fuel oil Ca content
  - New ISO-8217 specs will include maximum Ca levels in HFO; some fuel oil traders and end users already measure Ca
  - Increased slagging in furnaces burning refinery fuel oil
**EXCALIBURSM Metals Removal Technology**

**EXCALIBUR**: A Process for Removing Calcium from Crude Oil in Crude Unit Desalting Operations

- Developed by Baker Petrolite for a major oil company
- Designed for crude oils high in calcium naphthenates (> 100 ppm as Ca)
- May also remove inorganic iron compounds, or iron present as naphthenate salts
- Does not remove nickel or vanadium
- Proven, industry-leading technology already used in Europe, US and Asia
Process Overview

- Inject metals complexing agent into desalter wash water
- Maintain high mixing energy to promote good contact of water/complexing agent and oil
- Complexing agent converts metallic species such as Ca, Fe naphthenates into water soluble compounds
- Solubilized metals partition into the aqueous phase and are removed with desalter effluent water
- Naphthenic acids stay in the crude oil
Benefits of Using **EXCALIBUR** Metals Removal Technology

- Up to 85% calcium removal efficiency achieved in field applications
  - Allows processing of higher rates of high Ca crude oils
  - Increased refinery margins when crudes are purchased at a discount
  - Reduces calcium levels in atmospheric, vacuum resids
    - Minimizes FCCU catalyst degradation
    - Reduced Ca levels in coke and heavy fuel oils
    - Reduced boiler, heater tube slagging
European Location

• 30 - 120 ppm Ca in crude blend (15% Doba), 62 ppm average
• Program target is < 20 ppm Ca in desalted crude
• Average Ca removal efficiency 70%
• 85% Ca removal achieved when desalter effluent pH < 6
• Reduced Ca levels allows refinery to feed atmospheric resid to FCC
USA Location

- Up to 50 ppm Ca in crude blend (15% Doba typical)
- < 10 ppm average Ca in desalted crude
- Ca removal efficiency averages 70%
- Reduced Ca levels allows refinery to feed atmospheric resid to FCC
EXCALIBUR Iron Removal

EXCALIBUR Metals Removal Technology can also remove iron from certain crudes
  • Iron naphthenates
  • Inorganic iron oxides, sulfides

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron, ppm</th>
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<tbody>
<tr>
<td>Heavy Canadian Crude Oil</td>
<td>19.9</td>
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<tr>
<td>+ 30 ppm Additive in Crude Oil</td>
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(5% wash water rate, with 6 ppm emulsion breaking chemical)
Conclusions

- A laboratory-tested, field proven process to remove calcium from high Ca crude oils
- Industry-leading EXCALIBUR Metals Removal Technology has been used to remove up to 85% of crude oil calcium present as calcium naphthenates
  - Significant economic benefits to the refiner
  - Good desalter performance is maintained
  - Desalter water injection and removal system corrosion and scaling can be controlled
  - Minimal impact on waste water treatment plant
- Laboratory screening tests can be used to predict EXCALIBUR performance on specific crude oil blends