Opportunity Crude Processing

New Desalting Chemistry for Heavy/High Solids Crudes

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Essential Expertise for Water, Energy and Air
Opportunity Crude Availability Changing

• New pipeline cutting across Panama will bring South American crudes to West Coast
Why Focus On Canadian and South American Crudes?

• Combined now make up 50% of crude oil imports to the US
• Significant pipeline expansions under construction to increase distribution of heavy Canadian crudes
  – At least 11 refineries have current capacity improvement projects to process the projected 4 MBPD of Canadian crudes by 2020
• Refineries situated away from these pipelines are looking to South America, for example, Venezuela, Mexico, Brazil, etc., to obtain opportunity crudes.
Ramifications of Crude Diet Shift

• New crudes typically are challenge crudes
  – High Water / High Salt
  – High Solids
  – Asphaltene Incompatibility
  – High H₂S
  – High Pour Point
  – High TAN

• Impacts
  – Desalting
  – Wastewater Units
  – Crude Processing
    • Crude Unit
    • Downstream Units
Impact on Desalting

• Deterioration in desalting performance can manifest itself in numerous areas. The typical problems are:
  – Oil undercarry and higher levels of oil coated solids in desalter effluent
  – Stressed waste water treatment plant operations
  – Solids or asphaltene stabilized emulsion layer
  – Water and/or solids carryover in desalted crude
  – Desalting and dehydration performance decay
  – Increase corrosion potential in crude tower overhead systems
  – Higher fouling rates in hot preheat exchanger network
  – Increased energy consumption (excess water and preheat fouling)
  – Negative impacts to FCC catalyst life, Coker unit operation, etc.
Approach

• Phase I
  – Crude Oil Characterization
  – Solids Characterization
  – Develop test protocols

• Phase III
  – Identify additive(s) that show enhanced solids removal
  – Bottle and PED testing

• Phase III
  – Field test
Phase I
Solids Characterization

• Filtered and analyzed solids (Cold Lake)

• Primarily salt and clay
Solid Attributes
Emulsion Stability

Usually, solids capable of stabilizing emulsions are in the submicrometer to micrometer range [15, 26, 27]. The solids associated with oilfield emulsions are generally less than 1 μm in diameter [13]. Bensebaa et al. [28] and Kotlyar et al. [10, 11] have identified these oilfield emulsion solids as aluminosilicate clays with diameters of 100 to 200 nm and thicknesses of approximately 10 nm. Sztukowski and Yarranton [29] found that oil-sands clays from coker-feed bitumen varied from 50 to 500 nm with thicknesses of 8 nm.

Generally, emulsion stability increases with decreasing particle size and increasing particle concentration [7, 12, 15, 17, 19, 30–35]. The dispersed-phase droplet diameter decreases both with increasing solids concentration and with decreasing particle size [15, 21, 32]. A decrease in the average drop size tends to result in more stable emulsions. Free energy considerations support these observations [36].

Although less well studied, particle density and shape can also be important in emulsion stability. Emulsions created

Demonstrated in -

SEM Images
(Inorganic Solids)

Eastern Montana

Alberta SAGD

BEI 1,500x

BEI 400x
SEM Images (Organic Solids)

LLK 0.45 μm filter [salt & clay]

LLK 0.22 μm filtration of 0.45 μm filtrate [“organic sediment”]
# Table of Solids Testing

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>WCS Sample 1</th>
<th>WCS Sample 2</th>
<th>Oilsands Bitumen 1</th>
<th>US Refiner Desalter interface 1</th>
<th>US Refiner Desalter interface 2</th>
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<tbody>
<tr>
<td>Salt</td>
<td>Halite</td>
<td>58%</td>
<td>61%</td>
<td></td>
<td>9%</td>
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<td></td>
<td>Kaolinite</td>
<td>19%</td>
<td>18%</td>
<td>32%</td>
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<td></td>
<td>Illite</td>
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<td>8%</td>
<td>14%</td>
<td>11%</td>
<td>14%</td>
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<tr>
<td></td>
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<td>13%</td>
<td>7%</td>
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<tr>
<td></td>
<td>Quartz</td>
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<td>10%</td>
<td>21%</td>
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<td>Albite</td>
<td>9%</td>
<td></td>
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<tr>
<td>Clays</td>
<td>Clinohlore</td>
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<td>Iron containing</td>
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<td>MgFeAlSiO(OH),H2O</td>
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<td>5%</td>
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<tr>
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<td>Pyrite</td>
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<tr>
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<td>Ankerite</td>
<td>Ca[Fe,Mg][CO3]2</td>
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<td>12%</td>
<td>4%</td>
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<tr>
<td></td>
<td>Siderite</td>
<td>FeCO3</td>
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<tr>
<td></td>
<td>Dolomite</td>
<td>CaMg[CO3]2</td>
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<tr>
<td></td>
<td>Calcite</td>
<td>CaCO3</td>
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<tr>
<td></td>
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<td>TiO2</td>
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<td></td>
<td>Rutile</td>
<td>TiO2</td>
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<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Interface Sample #1

40% of the solids are <0.45 µ
Interface Sample #2
Emulsion Stabilization by Asphaltene “Aggregates”
Production Problems Associated with Asphaltene Aggregation and Interfacial Adsorption

Emulsion Formation

Pipeline Deposition

Viscosity Issues

Associated issues:
- equipment plugging
- poisoning of refinery catalysts
- altering of desalter efficiency
- equipment cleaning
- addition of chemical dispersants
X-Ray Diffraction of Venezuelan Interface Solids

Other detected elements:
4% sulfur, 960 ppm vanadium
Aggregation States of Asphaltenes

Contributing factors:
- Solvency
- Temperature
- Pressure
- Resins: Asphaltenes
- Chemical Composition
Influence of R/A on Emulsion Stability

Increasing resins improve emulsion resolution

Solid Composition

Organic Coating on Solids

BEI, 100x

EDS

Element

C

O

Na

Mg

Al

Si

S

Cl

Ca

Fe

Intensity

0.000

1.000

2.000

3.000

4.000

5.000

6.000

keV

250 um

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In general, it is easier to obtain solids that are asphaltene-free than asphaltenes that are solids-free.
Phase II
Chemical Behavior

- Incorporated a second approach with the objective: “Reduce Rag with a Better EB”
  - Allow solids to traverse mesophase into aqueous phase
  - Minimize number of interfacial plateau borders available for solids residence
Research Summary

• Testing shows that there maybe an additive to enhance solids removal in desalter

• Lab tests have been completed; the real test is the field
Field Demonstrations

- Low (20-40%) Canadian Crudes...
- High (70-75%) Canadian Crude...
- Heavy and High Viscosity...
- Ultra High Solids Crude (>1100 ppm)...
- High Oil Undercarry
Canadian Crudes - Desalting Improvement

- Cold Lake
- Objective was to increase the amount of Cold Lake processed (230,000bpd crude unit) from 20% to 40%.
- Past problems:
  - Oil undercarry and large volume of oil coated solids.
  - Wide rag approx. 36-48”.
  - Under-sized WWTP.
  - Preheat fouling on the rise.
- Results:
  - Clean effluent and collapse of rag to 6” of emulsion.
  - Reverse emulsion breaker removed.
Trial Results

Before

New EB & Enhanced Solids Removal Add.

W/O Interface

6” 12” 24” 36” 48” 60”
Canadian Crudes - Desalting Improvement++

- WCS (and others) @75%
- Undersized 2-stage desalting; 110,000 bpd crude unit.
- Never designed for high rates of Canadian crudes.
- Past problems:
  - *Wide emulsion layer and 2-5% oil in the effluent.*
  - *Cuff draw on 2nd stage helped, but remained dirty.*
- Results:
  - *Clean effluent and 2nd stage cuff draw (plan to shut off).*
  - *Collapse of rag (increased amount of oil across swingarm).*
  - *Oil and solids free water in bottom of desalter.*
  - *Wetting agent removed.*
  - *Reduced chemical dosage compared to old program*
Pre-trial Performance
2nd Stage Rag Clean Up

Before 1 hour with New EB 4 hours 20 hours 48 hours +
1st Stage Effluent Clean Up

Before New EB  →  4 hours  →  Day 2  →  Day 3  →  Day 4
Trial Results

New EB

New EB & Enhanced Solids Removal Add.
Closing...

- Solids have an impact on refinery economics
- Removing solids as early as possible is the best solution
- Understanding what solids are, how they can behave are the keys to mitigating their impact
- Deciding where to pull the solids out of the system is one of more difficult decisions
- New EB development resolves desalter impacts

“Solids never die ---- they just move around”