Managing ROB for Marine and Rail Transport

Presented at Crude Oil Quality Conference, March 7, 2013

Presented by: Waynn Morgan
Written by: Paul Biggerstaff and Waynn Morgan, Baker Hughes
Agenda

- Definition of ROB
- Problems with ROB
- Root causes of ROB
- ROB Management
- Case History
- Conclusion
Definition of ROB

• ROB is the acronym for “Remains on Board” and is the material that remains onboard the marine vessel or rail car following the delivery of cargo
Problems with ROB

• Reduces oil recovery which can result in economic loss

• Increases the Total Cost of Operation by increasing barge or railcar cleaning cycles, longer cleanup times, and a corresponding increase in hazardous waste generation and disposal

• Can create corrosive conditions with either under deposit corrosion or through the generation of H2S by sulfate reducing bacteria

• Others
Root Causes of ROB and Best Practice Actions to reduce frequency of occurrence

- ROB can be composed of:
  - Inorganic solids (i.e. sand, metal oxides)
  - Water/oil emulsions that have fallen out of the crude during transit
  - Asphaltenes
  - Paraffins (predominantly high molecular weight)
  - Basically any material that is not pumped off at disport
Solids Deposition and Oil/Water Emulsions

• Root Causes of Problem: Load port BS&W not correct or specifications waived.

• Pathways to solve problem:
  – Insure that a spec is set prior to loading on the barge;
  – Insure that the sampling protocol is correct;
  – Insure that the analytical techniques are correct;
  – Determine efficiency of the current emulsion breaker
Asphaltene Flocculation

• Root Cause: The asphaltenes become unstable in the crude oil stream and precipitate out of solution. This can be a result of blending incompatibilities or temperature changes resulting in destabilization, precipitation and flocculation of the asphaltenes.
Asphaltene Flocculation (cont.)

• Pathways to solve problem:
  – Establish a compatibility monitoring program that accurately measures the potential for precipitation or flocculation
  – Implement an asphaltene stability treatment program that will aide in the dispersion of the incompatible asphaltenes
  – Install a mixing or agitation system in the vessel that will keep the asphaltenes in suspension
  – Understand the temperature impact and address as needed
Heptane Dispersant Test

HFO BLEND - 380 cSt
Asphaltene Stability Index Test

- ASIT™ Test measures the onset of the flocculation of the asphaltenes with high accuracy by inducing the asphaltene precipitation via titration with a paraffinic solvent.

**Products A & B Best Stabilizers Fuel 1**

**Product A Increases Stability Products B & C Decreases Stability Fuel 3**

ASIT is a trademark of Baker Hughes Incorporated.
Paraffin Precipitation

• Root Causes:
  – Temperature of operation is below the Wax Appearance Temperature (WAT) or onset of wax crystallization which can occur at temperatures >90F in shale oil
  – High melting points due to high molecular weight waxes
• Pathways to solve problem:
  – Insure that the operation remains above the WAT of the oil
  – Implement a paraffin treatment program to:
    • disperse the wax
    • reduce agglomeration and settling
    • reduce potential for wax deposition
  – Implement a pour point depressant (PPD) program to modify the shape of the wax crystals, inhibit growth and improve handling
  – Insure compatibility issues with the crude blend are addressed
The advent and increase in production of shale (particularly Eagle Ford and Utica) has created a greater sense or urgency to better manage the ROB.
Once the ROB becomes excessive, decisions must be made in terms of how to manage the problem. The choices for management are:

- Vessel cleaning and the corresponding downgrade of ROB to waste
- Recovery of the ROB into the hydrocarbons being transported
- Establishment of a preventative action program for future shipments
Vessel Cleaning Option for ROB Management

• Advantages
  – Renders a clean vessel in a short period of time

• Disadvantages
  – Generates hazardous waste
  – Vessel out of service during cleaning time
  – Expensive
  – Is a corrective action instead of a proactive approach
Recovery of the ROB into Hydrocarbon Phase

• Advantages:
  – Recovery of hydrocarbon component of ROB into oil phase reduces the hazardous waste disposal and recovers usable hydrocarbon
  – Existing successful case history

• Disadvantages:
  – Effectiveness of application can be a challenge
  – May require more than one application as the layers of existing ROB are removed
  – Is a reaction to the problem and not the proactive approach
Establishment of a preventative action plan

• Advantages:
  – Maintains a consistent crude quality from load port to disport
  – Will typically be the least expensive choice
  – Includes monitoring programs, blending protocols, and perhaps chemical treatment
  – Is the proactive approach to prevent or minimize ROB

• Disadvantages
  • More service intensive

© 2013 Baker Hughes Incorporated. All Rights Reserved.
Case History for ROB Recovery

• Recognizing the issues customers are experiencing with the movement of shale oil via barge, rail and transport lines, Baker Hughes has initiated a research project to help manage ROB

• Focus of research has been on the development of technologies that would be effective in
  – minimizing sludge
  – reducing wax deposition
  – improving the handling of shale oil and shale oil blends
  – increasing the amount of oil recovery
Paraffin Dispersion Testing (Utica)

- Product ‘A’ effectively dispersed the paraffin wax in a Utica shale oil sample at ambient temperature over a 72-hr period.

- Treatment was also effective in dropping out water.

Untreated Shale Oil
Product ‘A’ Effect on Shale Oil Viscosity

Significantly improved viscosity down to -10°C
Effect of Product ‘A’ on Wax Deposition (Utica)

- Product ‘A’ was effective in reducing wax deposition by up to 95% at 70°F after 24 hours

<table>
<thead>
<tr>
<th>Condition Temp (°F)</th>
<th>Treatment Temp (°F)</th>
<th>Bulk Oil Temp (°F)</th>
<th>Probe Temp (°F)</th>
<th>Stir Speed (rpm)</th>
<th>Duration (hr:min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>150</td>
<td>95</td>
<td>70</td>
<td>450</td>
<td>24:00:00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Dosage (ppm)</th>
<th>Deposit Wt. (gm)</th>
<th>Deposit Density (gm/m^2)</th>
<th>Wt. % Inhibition (%)</th>
<th>Bare Probe (~%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLANK</td>
<td>N/A</td>
<td>0.5166</td>
<td>90.07</td>
<td>N/A</td>
<td>0%</td>
</tr>
<tr>
<td>Product A</td>
<td>200</td>
<td>0.0782</td>
<td>13.19</td>
<td>85.36%</td>
<td>90%</td>
</tr>
<tr>
<td>Product A</td>
<td>400</td>
<td>0.0485</td>
<td>8.52</td>
<td>90.54%</td>
<td>95%</td>
</tr>
<tr>
<td>Additive #1</td>
<td>200</td>
<td>0.1330</td>
<td>22.84</td>
<td>74.65%</td>
<td>20%</td>
</tr>
<tr>
<td>Additive #2</td>
<td>200</td>
<td>0.2417</td>
<td>40.50</td>
<td>55.04%</td>
<td>10%</td>
</tr>
<tr>
<td>Additive #3</td>
<td>200</td>
<td>0.4297</td>
<td>78.64</td>
<td>12.69%</td>
<td>5%</td>
</tr>
<tr>
<td>Additive #4</td>
<td>200</td>
<td>0.2296</td>
<td>40.64</td>
<td>54.88%</td>
<td>50%</td>
</tr>
</tbody>
</table>
Product ‘A’ Effect on Wax Deposition (Utica)
Several products were effective in dispersing the paraffin wax in an Eagle Ford shale oil sample at ambient temperature for over a month.
## Eagle Ford Shale Oil Cold Finger Test Results

<table>
<thead>
<tr>
<th>Cond. Temp (°F)</th>
<th>Treat Temp (°F)</th>
<th>Bulk Oil Temp (°F)</th>
<th>Probe Temp (°F)</th>
<th>Stir Speed (rpm)</th>
<th>Duration (hr:min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>150</td>
<td>103</td>
<td>73</td>
<td>750</td>
<td>18:00:00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Dosage (ppm)</th>
<th>Deposit Wt. (gm)</th>
<th>Deposit Density (gm/m²)</th>
<th>Wt. % Inhibition (%)</th>
<th>Bare Probe (~%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLANK</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.0%</td>
<td>0%</td>
</tr>
<tr>
<td>Product 'B'</td>
<td>300</td>
<td>0.0784</td>
<td>13.92</td>
<td>84.1%</td>
<td>75%</td>
</tr>
<tr>
<td>Product 'B'</td>
<td>600</td>
<td>0.0562</td>
<td>9.47</td>
<td>89.2%</td>
<td>90%</td>
</tr>
<tr>
<td>Candidate 2</td>
<td>300</td>
<td>0.2759</td>
<td>49.13</td>
<td>44.0%</td>
<td>40%</td>
</tr>
<tr>
<td>Candidate 2</td>
<td>600</td>
<td>0.0893</td>
<td>15.80</td>
<td>82.0%</td>
<td>60%</td>
</tr>
<tr>
<td>Candidate 3</td>
<td>300</td>
<td>0.3746</td>
<td>61.66</td>
<td>29.7%</td>
<td>25%</td>
</tr>
<tr>
<td>Candidate 3</td>
<td>600</td>
<td>0.1748</td>
<td>28.91</td>
<td>67.1%</td>
<td>60%</td>
</tr>
<tr>
<td>Candidate 4</td>
<td>300</td>
<td>0.4055</td>
<td>66.74</td>
<td>23.9%</td>
<td>10%</td>
</tr>
</tbody>
</table>

- Product ‘B’ was effective in reducing wax deposition by up to 90% at 73°F after 18 hours.
Product ‘B’ Effect on Wax Deposition (Eagle Ford)

Blank  
300 ppm  
Product ‘B’  
300 ppm  
Candidate 3  
300 ppm  
Candidate 5
Case History for ROB Recovery

- Vessel had a significant amount of paraffin sludge that required cleaning prior to transferring vessel lease to another company

- Patent pending chemistry was applied to ROB layer and allowed to soak

- Another load of hydrocarbon was loaded onto vessel

- ROB was checked after this load and a significant amount of material had been removed. The remaining material was much lower in viscosity as well
Viscosity of ROB Before Treatment

ROB from untreated compartment
Viscosity of ROB after treatment

ROB from treated compartment
• After treatment with Product ‘A’, the ROB in that compartment had significantly lower pour point and viscosity

### Eagle Ford Sludge Handling Properties (Field Trial Results)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pour Point, °F</th>
<th>KV @ 60°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge Untreated</td>
<td>+25</td>
<td>---*</td>
</tr>
<tr>
<td>Sludge 2S (Candidate 5)</td>
<td>+5</td>
<td>6160</td>
</tr>
<tr>
<td>Sludge 2P (Product ‘A’)</td>
<td>-40</td>
<td>372</td>
</tr>
</tbody>
</table>

*Viscosity could not be measured at 60°F*
After treatment with Product ‘A’, the ROB on the vessel exhibited
– 75% reduction in inorganic material
– Virtually no filterable solids
– ~50% reduction in high MW (C20+) paraffin content

<table>
<thead>
<tr>
<th>Sample</th>
<th>Organics, Wt%</th>
<th>Inorganics, Wt%</th>
<th>Filterable Solids (ppm)</th>
<th>Paraffin Wax, C20+ Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge Untreated</td>
<td>83</td>
<td>17</td>
<td>5170</td>
<td>10.23</td>
</tr>
<tr>
<td>Sludge 2P (Product 'A')</td>
<td>96</td>
<td>4</td>
<td>&lt;10*</td>
<td>4.91</td>
</tr>
</tbody>
</table>
Conclusion

• ROB is an ongoing concern for Crude Oil Transportation

• The characteristics of the ROB must be understood in order to develop a proper management program

• The advent of shale into the marketplace has increased the interest level in ROB and ROB Management

• Technologies exist to aide in addressing ROB Management programs