Corrosivity of High Acid Crudes

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Crude purchase is the main expense of a refinery. Thus, processing discounted HAC have a positive financial impact.

World production of high Acid Crudes (HAC) is expected to increase to 10-15% by 2010 and processing HAC will soon be a necessity rather than a choice.

HAC may accelerate corrosion, fouling, furnace coking, desalting problems and need to be understood before processing them.

Focus of presentation is about available tools for predicting corrosion impact of HAC in the distillation unit.
Corrosion in Distillation Unit (1)

Area 1 – High velocity naphthenic acid corrosion
Area 2 – Dew point corrosion
Area 3 – Condensing Naphthenic acid corrosion
Area 1 - Furnace, transfer lines and side cuts

- Classical naphthenic acid corrosion affected by:
  - Temperature
  - Material of construction
  - Acid content
  - H₂S content
  - Shear stress (velocity)

- At high shear stress, a small amount of acid can increase rapidly H₂S corrosion (e.g. high corrosion even at TAN lower than 0.5)

- At low shear stress, H₂S may inhibit acid corrosion.
Area 2 – Overhead or Dew Point Corrosion

- Hydrochloric acid, formed from the hydrolysis of calcium and magnesium chlorides in the crude, is the principal strong acid responsible for corrosion in crude unit overhead. Software is available to calculate water dew point at several levels of HCl. Neutralizer and corrosion inhibitors are injected.

- Carbon dioxide and low molecular weight acids are released from HAC. They buffer the acid solution formed and require more neutralizer inducing fouling.

- Released hydrogen sulfide, increase significantly dew point requiring a change in injection point.
Area 2 – Vacuum Unit Corrosion

- Condensing naphthenic acid corrosion affected by:
  - Temperature
  - Material of construction
  - Acid content
  - H₂S content

- A high H₂S content is needed to inhibit naphthenic acid corrosion. Thus, need to blend HAC with crude having high H₂S release at 700+.

- No or little effect of shear stress.
Acids Analysis

- **Total acid number per ASTM D664**
  Current method using potentiometric titration of a small amount of oil with alcoholic KOH.

- **Mobil Method # 1463-89** - Extraction of the acids by chromatography then analysis by FT-IR.

- **Electrospray Ionization-Mass Spectrometry** - Extraction of the acids by chromatography then analysis by EI-MS.
Total Acid Number

<table>
<thead>
<tr>
<th>Location</th>
<th>Sulfur %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brent</td>
<td>0.74</td>
</tr>
<tr>
<td>Kansas</td>
<td>0.58</td>
</tr>
<tr>
<td>Ratawi</td>
<td>4.45</td>
</tr>
<tr>
<td>WTS</td>
<td>2.55</td>
</tr>
<tr>
<td>Captain</td>
<td>0.74</td>
</tr>
<tr>
<td>Mariner</td>
<td>1.17</td>
</tr>
<tr>
<td>Midway</td>
<td>2.08</td>
</tr>
<tr>
<td>Heimdal</td>
<td>1.44</td>
</tr>
</tbody>
</table>
Sulfur Content vs. \( \text{H}_2\text{S} \) Evolution

Graph showing the relationship between sulfur content (Wt%) and total \( \text{H}_2\text{S} \) evolved for different locations: Kansas, Brent, Captain, Mariner, Hemdall, MS, WTS, and Ratawi.
H₂S Evolution Analysis

- **Captain (1213 ppm - 0.74% S)**
- **Heimdall (1264 ppm - 1.44% S)**
- **Ratawi (352 ppm - 4.45% S)**
- **WTS (949 ppm - 2.55% S)**

Temperature vs. H₂S Evolved (ppm)
Corrosion Test Results (1)

Graph showing total corrosion rate (mpy) and TAN x H2S evolved for different locations.
EI-MS of Captain Crude
## Captain Crude

<table>
<thead>
<tr>
<th></th>
<th>Whole Crude</th>
<th>Light Naphta</th>
<th>Medium Naphta</th>
<th>Heavy Naphta</th>
<th>Kero</th>
<th>Atm Gas Oil</th>
<th>Light VGO</th>
<th>Heavy VGO</th>
<th>Vacuum Resid</th>
<th>Atm Resid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp at Start (F)</td>
<td>Start</td>
<td>305</td>
<td>305</td>
<td>305</td>
<td>400</td>
<td>500</td>
<td>650</td>
<td>850</td>
<td>1050</td>
<td>650</td>
</tr>
<tr>
<td>Temp at End (F)</td>
<td>End</td>
<td>305</td>
<td>305</td>
<td>400</td>
<td>500</td>
<td>650</td>
<td>850</td>
<td>1050</td>
<td>End</td>
<td>End</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>0.70</td>
<td>0.04</td>
<td>0.10</td>
<td>0.27</td>
<td>0.56</td>
<td>0.75</td>
<td>1.15</td>
<td>0.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercaptan (ppm)</td>
<td>11</td>
<td>7</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2S (ppm)</td>
<td>834</td>
<td>156</td>
<td>156</td>
<td>101</td>
<td>84</td>
<td>57</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAN</td>
<td>2.4</td>
<td>0.1</td>
<td>0.4</td>
<td>1.3</td>
<td>2.4</td>
<td>2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid (% of total)</td>
<td>0.0</td>
<td>6.0</td>
<td>29.2</td>
<td>44.9</td>
<td>15.8</td>
<td>4.41</td>
<td>65</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Ratawi Crude

<table>
<thead>
<tr>
<th></th>
<th>Whole Crude</th>
<th>Light Naphta</th>
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<th>Heavy Naphta</th>
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<td>305</td>
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<td>305</td>
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<td>850</td>
<td>1050</td>
<td>650</td>
</tr>
<tr>
<td>Temp at End (F)</td>
<td>End</td>
<td>305</td>
<td>305</td>
<td>400</td>
<td>500</td>
<td>650</td>
<td>850</td>
<td>1050</td>
<td>End</td>
<td>End</td>
</tr>
<tr>
<td>Sulfur (%)</td>
<td>3.88</td>
<td>0.01</td>
<td>0.08</td>
<td>0.33</td>
<td>0.98</td>
<td>2.42</td>
<td>3.50</td>
<td>4.20</td>
<td>6.96</td>
<td>5.41</td>
</tr>
<tr>
<td>Mercaptan (ppm)</td>
<td>274</td>
<td>597</td>
<td>258</td>
<td>72</td>
<td>29</td>
<td>8</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2S (ppm)</td>
<td>40</td>
<td>12</td>
<td>12</td>
<td>14</td>
<td>22</td>
<td>62</td>
<td>236</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TAN</td>
<td>0.14</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid (%) of total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.8</td>
<td>48.0</td>
<td>26.7</td>
<td>6.1</td>
<td>3.7</td>
<td>36.4</td>
<td></td>
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</tbody>
</table>
The amount of H$_2$S and acid in each area of unit are additive and can be calculated knowing the proportion of each crude in a basket.

The analysis of the oil or blend can then be used:

- To change proportion of each crude to minimize corrosion in critical areas.
- To add specific crude to basket. E.g. one that releases high H$_2$S amount at 700 +F to inhibit corrosion of vacuum unit.
- To change injection point of neutralizer/inhibitor in overhead to account for higher dew point.
- To evaluate the effect of adding a specific HAC on corrosion of distillation unit.
Conclusions

- There is no correlation between total sulfur content and \( \text{H}_2\text{S} \) evolved.
- \( \text{H}_2\text{S} \) evolution data analysis allows the determination of the specific concentration of \( \text{H}_2\text{S} \) in each area of the distillation unit.
- TAN values are higher than actual acid concentration especially if crude has a high sulfur content.
- Electrospray data analysis allows the determination of where the acids concentrate in the unit.
- \( \text{H}_2\text{S} \) and EI-MS analysis are simple, rapid and cost effective. Only a 100 ml of sample is needed. They yield critical information about corrosivity missing in a typical crude assay.
Thank you for your attention

Any Questions ?