Silicon in Crude Oil

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Baker Petrolite
Agenda

• Not discussion of problems and applications in refineries
• Define terms
• Discuss various test methods
• Outline test protocol
Terms for Silicon

- Silicon the element -Si
- Silica- SiO₂ –
- Silicate – (Na₂O)ₓ(SiO₂)ᵧ(H₂O)z
- Silicone – Polymeric material based on repeating units of (SiOR₂)
- PDMS – Poly Di Methyl Siloxane is most common silicone
- Si containing surfactants and emulsion breakers
Poly dimethylsiloxane
Sample: SN 31592
Size: 21.3392 mg
Method: ORGANIC - SLOW RATE
Comment: 20 DEGREES PER MINUTE TO 850 DEGREES CENTIGRADE - NITROGEN

97.11% TOTAL LOSS
(20.72 mg)
Sample: SN 31591
Size: 6.3456 mg
Method: ORGANIC - SLOW RATE
Comment: 20 DEGREES PER MINUTE TO 850 DEGREES CENTIGRADE - ZERO AIR

94.62 % TOTAL LOSS
(6.004 mg)
Conclusion

• Obtain different products in reducing and oxidizing environments
• Method of ashing sample will affect recovery of silicon
Cyclic Trimer Breakdown Products
## Boiling Point of PDMS

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>Cyclic D3</td>
<td>134</td>
<td>273</td>
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<tr>
<td>Cyclic D4</td>
<td>175.8</td>
<td>348</td>
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<tr>
<td>Cyclic D5</td>
<td>210</td>
<td>410</td>
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<tr>
<td>Cyclic D6</td>
<td>245</td>
<td>473</td>
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</table>
Measurement of Silicon

• Preparation (All use dilution)
  – Direct injection ***
  – Ashing
  – Bomb digestion ***

• Determination
  – ICP ***
  – AA
## Silicon in Products

<table>
<thead>
<tr>
<th></th>
<th>New Defoamer</th>
<th>Digestion</th>
<th>Direct Inject</th>
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<tr>
<td>Naphthha</td>
<td></td>
<td>8.6ppm</td>
<td>8.2ppm</td>
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<tr>
<td>LCGO</td>
<td></td>
<td>3.5</td>
<td>3.2</td>
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<tr>
<td>HCGO</td>
<td></td>
<td>1.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Old Defoamer</td>
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<tr>
<td>Naphthha</td>
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<td>33.8</td>
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<tr>
<td>LCGO</td>
<td></td>
<td>23.6</td>
<td>28.7</td>
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<tr>
<td>HCGO</td>
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<td>4.3</td>
<td>1.8</td>
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</table>
Complicating Factors

- Coker products relatively pure
- Crude oil contains Filterable solids
  - Sand – silica
  - Clay – Aluminum silicates
- Could contain water soluble silicates
- Could contain oragano-silicon compounds
  - Silicone
  - Surfactants
  - Emulsion breakers
  - ???
Silicate
SLOP TREATMENT EXAMPLE

• CPI skimmings 50% oil, 40% H2O, 10% solids
• Treat with 5,000 to 10,000 ppm BPR 23595
• 0.1% solids, 0.1% H2O, <50 ppm Na in recovered oil
• Solids and silicate in water
• After 3+ years treatment, no sign of Si deposits
### Table 8

**Analysis of Ash from Oil-Soluble Constituents of Crude Oils**

(On Water-Free and Sediment-Free Oils)

<table>
<thead>
<tr>
<th>Region</th>
<th>NiO (ppm)</th>
<th>Na$_2$O</th>
<th>SiO$_2$</th>
<th>V$_2$O$_5$</th>
<th>Fe$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>SO$_3$</th>
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<tr>
<td>North Louisiana</td>
<td>44</td>
<td>1.7</td>
<td>46.5</td>
<td>4.3</td>
<td>3.3</td>
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<td>2.8</td>
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<td>Louisiana-Miss.</td>
<td>11</td>
<td>0.1</td>
<td>61.7</td>
<td>3.2</td>
<td>0.1</td>
<td>2.7</td>
<td>1.1</td>
<td>6.1</td>
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<tr>
<td>Mississippi (Eucutta)</td>
<td>319</td>
<td>2.4</td>
<td>16.3</td>
<td>8.6</td>
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<td>...</td>
<td>50.7</td>
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<tr>
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<td>4.1</td>
<td>11.7</td>
<td>63.3</td>
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<td>2.4</td>
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<td>46.1</td>
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<td>...</td>
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<td>...</td>
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<td>9.1</td>
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<td>...</td>
<td>47.7</td>
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<tr>
<td>Oklahoma-Kansas</td>
<td>49</td>
<td>2.0</td>
<td>33.3</td>
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<td>10.9</td>
<td>1.0</td>
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<td>2.8</td>
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<tr>
<td>Wyoming (Big Horn)</td>
<td>44</td>
<td>10.4</td>
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<tr>
<td>&quot; (San Joaquin)</td>
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<td>29.5</td>
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<td>12.8</td>
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<tr>
<td>California (Sta. Maria)</td>
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<td>...</td>
<td>20.0</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
Desalter Emulsion Band SEM Analysis

- **Inorganic**
  - Silicon 38.6%
  - Iron 24.2%
  - Sulfur 21.8%
  - Zinc 15.3%

480X
Desalter Emulsion Band
SEM Analysis

- Silicon 32.3%
- Iron 22.0%
- Sulfur 18.2%
- Aluminum 13.4%
- Calcium 11.6%
- Potassium 2.5%

50X
Conclusions

- Speciation not practical in most cases
- Problem is complex
- Silicon can be measured down to ppm level relatively accurately
Baker Petrolite Test Protocol

- Define Si species by solubility class
- Water wash to remove water soluble Si
- Filter to remove particulate Si
- Prepare sample (dilution with both)
  - Direct injection
  - Bomb digestion ***
- Detect
  - ICP
  - XRF (for solids)
Acknowledgements

- Tom Falkler
- Chuck Harper
- Larry Lutes
- Bill Matlach