Crude Oil Storage in Salt Domes: Long-term quality considerations

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Harry N. Giles
PetroStorTech LLC
Arlington, VA
COQA

Crude Oil Quality Association

Presented to

Harry N. Giles

In recognition of your outstanding leadership as Executive Director of the COQA 2006-2013, the COQA expresses its deep appreciation and gratitude for your efforts and many accomplishments.

November 2014

Harry N. Giles

Thank you for your many years of dedication to the Crude Oil Quality Association

The Board
Disclaimer

The views and opinions expressed in this presentation are those of the author and do not necessarily state or reflect those of the United States Government or any agency thereof.
Acknowledgement

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Outline

- Can crude oil be stored for a long-term in salt caverns?
- What are the major quality considerations associated with long-term storage?
- Are there other quality issues?
- Concluding comments
Fundamental question

“Can crude oil be stored for 10-20+ years without undergoing deleterious changes in quality?”

- View 1: “Crude oil has been in the ground for millions of years, so why worry?”
- View 2: “Yes, but, once produced, it is exposed to air, injected with chemicals and otherwise treated, so it is susceptible to change.”
Long-term Storage Concerns

- Does stratification or differentiation occur?
- Do microbes degrade stored oil?
- Will oil drawn down from caverns contain excessive water and salt?
- Is sludge formation inevitable?
- How much oil will be irretrievably lost?
- Do other changes in quality occur that may affect drawdown, transportation, and refining?
Experience

- Detailed studies show no adverse effects on physical or chemical properties
  - Geothermally-driven convective mixing mostly prevents differentiation and minimizes stratification
    - Minor differentiation has been observed
    - After 18 – 24 months stratification virtually undetectable
  - Biodegradation does not occur, despite presence of viable bacteria
  - Water, sediment, & salt < pre-storage levels
  - Sludge may form, but only in limited amounts (<0.5%)
  - > 99% of oil recoverable

- No changes found affecting drawdown, transportation, or refining
General Quality Issues

- Ageing
- Biodegradation
- Compatibility
- Sludge
- Vapor Pressure
- Wax
Ageing

- Ageing defined as crude oil becoming more refractory or difficult to refine
  - In general, an increase in asphaltic components

- Crude oil would need to be subjected to conditions not present in caverns
  - Systematic laboratory experiments failed to measurably produce increase in asphaltenes under even extreme conditions
Biodegradation

- Viable anaerobic and aerobic bacteria and fungi found in sludge in many salt caverns
- Lab cultures on crude oil substrate found that all activity ceases when brine concentration exceeds ~20%
- Detailed analyses of sludge and crude oil showed no evidence of biodegradation – aerobic or anaerobic
  - SIRA of CH₄ clearly proved it to be thermogenic and not biogenic in origin
Compatibility

- Different crude oils may or may not be capable of being mixed without adverse reactions
- Accurate predictions elusive
  - Upstream chemicals can promote reactions
  - Incompatibility can take days to be manifest
- Waxes and asphaltenes difficult to redissolve or redisperse once precipitated
- In general, close attention to chemical nature of different crude oils adequate for assessing compatibility
Sludge

- Present in some but not all caverns (Fig. 1)
- Natural phenomenon
  - Waxes, sediment, and water settle in micelle-like structure
  - Asphaltene content somewhat greater than in parent crude oil mixture
  - Oilfield chemicals can stabilize emulsions
- Sludge in caverns differs from that in AG tanks (Tables I & II)
Fig. 1. Cavern Sludge
# Table I. Cavern Sludge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, wt%</td>
<td>1.0 – 52.9</td>
</tr>
<tr>
<td>Gravity, °API</td>
<td>13.0 – 29.5</td>
</tr>
<tr>
<td>Pour Pt, °F</td>
<td>100 – 170</td>
</tr>
<tr>
<td>Salt, lbs/M bbls</td>
<td>750 – 16000</td>
</tr>
<tr>
<td>Wax, wt%</td>
<td>5 – 44.4</td>
</tr>
<tr>
<td>Acid No.</td>
<td>0.15 – 2.8</td>
</tr>
<tr>
<td>Sediment, wt%</td>
<td>0.05 – 6.5</td>
</tr>
<tr>
<td>Ash, wt%</td>
<td>0.02 – 5.0</td>
</tr>
</tbody>
</table>
## Table II. Some Comparative Sludge Characteristics: Caverns vs. Tanks

<table>
<thead>
<tr>
<th>Property</th>
<th>Cavern 1</th>
<th>Cavern 2</th>
<th>Tank 1</th>
<th>Tank 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>API gravity (°)</td>
<td>19.2</td>
<td>21.1</td>
<td>26.9</td>
<td>26.4</td>
</tr>
<tr>
<td>Pour point, °C</td>
<td>78</td>
<td>75</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>Water (KF), mass %</td>
<td>9.3</td>
<td>16.0</td>
<td>18.4</td>
<td>15.9</td>
</tr>
<tr>
<td>Sediment, mass %</td>
<td>1.82</td>
<td>1.24</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Ash, mass %</td>
<td>1.48</td>
<td>0.86</td>
<td>0.017</td>
<td>0.017</td>
</tr>
<tr>
<td>Salt, ppm (mass)</td>
<td>&gt;3000</td>
<td>2050</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>Sulfur, mass %</td>
<td>2.11</td>
<td>2.03</td>
<td>2.84</td>
<td>2.86</td>
</tr>
<tr>
<td>Nitrogen, mass %</td>
<td>0.119</td>
<td>0.127</td>
<td>0.159</td>
<td>0.166</td>
</tr>
<tr>
<td>Acid No., mg KOH/g</td>
<td>0.60</td>
<td>0.51</td>
<td>0.30</td>
<td>0.31</td>
</tr>
<tr>
<td>Wax, mass %</td>
<td>38.0</td>
<td>29.6</td>
<td>0.42</td>
<td>0.79</td>
</tr>
<tr>
<td>Asphaltenes, mass %</td>
<td>4.2</td>
<td>3.1</td>
<td>3.59</td>
<td>3.57</td>
</tr>
</tbody>
</table>
Sludge Consequences

- Loss of valuable commodity
- Loss of crude oil storage capacity
- Can result in dramatically reduced pumping rates and severe clogging of tubulars
- Difficult and expensive to dispose of
Gamma-ray density logs accurately define depth and thickness of layer.
Sludge Prevention

- Avoid commingling dissimilar crude oils
- Natural convective mixing in caverns helpful
- Allow crude oil to settle before storage
  - S & W appear to be necessary for micelle formation
Vapor Pressure

- During prolonged storage, vapor pressure of crude oil increases due, in part, to geothermal heating
  - Gradient 2 - 4°C/100 m
  - Temperature of oil may reach 55°C
- And, to an increase of light HC and other gases
  - CH₄, CO₂, and N₂ occur naturally in Gulf Coast domal salt
  - N₂ “salts out” from leach water
- Stocks can exceed atmospheric pressure when drawn down
Wax

- Many streams have high wax appearance temperature ("cloud point")

- Wax precipitation can contribute to
  - Excessive remain-on-board losses
  - Clogged pipelines (Fig. 2)
  - Fouling and metering errors
  - Sludge accumulation

- Wax dispersants not recommended for crude oils to be stored, especially if commingled
Fig. 2. Wax
Other Quality Issues

- Hydrogen sulfide
- Mercury
Hydrogen Sulfide

- Naturally present in many crude oils
- During drawdown, emissions may exceed permissible levels
  - Potential health hazard and public nuisance
- Use of sequestering or passivating agent may be necessary on delivered crude oil or at drawdown
  - Presence of amines becoming of increasing concern
Hg: Why the Concern?

- Contributes to increased corrosion rates
- Accumulates in cooler zones of towers, posing health hazard during maintenance
- Poisons catalysts
- Emissions pose severe health hazard
- Subject of API/EPA/AFPM (NPRA) project to “determine the Hg content of crude oil processed in the U.S.”
Hg Research Study

- ~110 samples analyzed
  - Numerous domestic & other foreign streams, stockpiled crude oils, and cavern sludge
- Concentration ranged from 0.03 – 10.5 ng/g
  - Well below EPA default value of 1.5 μg/g
- Settling occurs during storage with 2–3+ orders of magnitude increase near interface (Fig. 3) and in sludge (Fig. 4)
- Not known if Hg accumulates in cavern brine or sediment
Figure 3. Cavern without sludge
Figure 4. Cavern with sludge
Conclusions

- Crude oil can be safely and effectively stored in salt caverns for many years.
- Crude oil can be stored in aboveground tanks for a number of years, but with precautions.
- Of primary concern:
  - Compatibility of commingled crude oils
  - Potential sludge formation and its disposal
  - Vapor pressure of stocks when drawn down
Thank you.
Questions?