SULFA-CHECK™
Hydrogen Sulfide Abatement

John Garcia Energy Services

Crude Oil Quality Group Conference
Marriott Hotel – West Loop, Houston, Texas
September 29, 2005
Sulfa-Check™ H₂S Abatement Programs

Agenda

• Share experience with sour crude oils and crude slates
• Overview of Nalco’s applications
• Sensitization of the Market
• Common questions regarding H₂S abatement
• Review liquid and vapor phase H₂S test methods
• Highlight Energy Services’ crude oil H₂S abatement technology
• Share experience from the South China Sea
• Summary
Nalco’s Worldwide Experience

Sour Crude and Crude Slates

• Extensive field experience
  – Africa (Kuito)
  – Arabia (Qatar Marine)
  – China (Liuhua)
  – Russia (Urals)
  – Latin America (Hamaca)
  – Mexico (Maya)
  – Middle East (Brega)
  – United States (ANS)

• Experience with high H₂S crude oils such as Arab Light/Heavy, Basra, Eocene, Orion and Olmeca used in various crude slates
Nalco’s Worldwide Experience

Applications within the Industry

• Crude oil production
  – Offshore: Floating Production Storage and Off-Loading
  – Oil field: Producing Wells

• Outside the refinery
  – Marine terminals
  – Oil Traders and Brokers
  – Pipeline network leading to refinery

• In the Refinery
  – Tank farms
  – In process

• Non-Traditional
  – Strategic Petroleum Reserves
Sensitization of the Market

Off-Spec Cargos

- Cargos refused – Resulting in traders incurring significant losses due to delays in product acceptance and demurrage costs

- Testing – Requires monitoring and testing to meet target liquid or vapor phase H₂S specifications

- Tanker Treats - Treated during loading or off-loading operations at the wharf or off-shore

- Tank Treats – Chemical injection into rundown line to and from tankage
Sensitization of the Market

Treating with Amine Scavengers

- Typically, amine based scavengers are used to abate H₂S from sour crude oil.

- On the refining side, processing treated crude oils has led to:
  - Observed increases in pH in crude unit overhead water.
  - At one location, reported pressure drop in the overhead pump around system.
  - Separate location, monoethanolamine (MEA) found entrained in top pump around strainer deposit.

- Formation of amine salts
  - Potentially leading to overhead corrosion issues.

- Depending on amine type
  - Amine may carryover to a side cut in the atmospheric tower.
  - Some amount of amine partitions into desalter effluent.
Hydrogen Sulfide Abatement

Common Questions

• Why are crude oils contaminated with H₂S?
• How can I measure the H₂S content?
• What is the best H₂S control program?
• How is an H₂S abatement program applied?
Why are crude oils contaminated with H$_2$S?

Liberation of H$_2$S

Low and high sulfur crude oils can generate excessive quantities of H$_2$S.

- H$_2$S is liberated into vapor space by two processes:
  - Free (dissolved H$_2$S)
  - Thermal degradation of organosulfur compounds (evolved H$_2$S)

- Rate of thermal degradation dependent on:
  - Sulfur compound type
  - Temperature
  - Time
Why are crude oils contaminated with $H_2S$?

**Sulfur Distribution in Crude Oil**

- **Mercaptans**
  - Alkyls, Cyclic
  - Aromatic

- **Sulfides**
  - Alkyls, Cyclic

- **Disulfides**
  - Alkyls, Dialkyl
  - Cyclic, Alkylaryl

- **Thiophenes**
  - Alkyls, Benzo
  - Thieno, Dibenzo

- **Bicyclic sulfides**

---

©Copyright 2005 Nalco Company. All rights reserved
Why are crude oils contaminated with H₂S?

H₂S Partitioning into the Vapor Space

• H₂S migrates into the vapor headspace above a confined crude oil through an equilibration process

• Equilibration is dependent on Henry’s Law

• The rate at which equilibrium is reached depends on time, temperature, mixing, and viscosity
How do I measure the H$_2$S content?

Vapor and Liquid Phase Test Methods

- Vapor Space Determinations
  - Can Test Method (ASTM D5705 or In-House variations)
  - Drager or Sensidyne H$_2$S detector tubes

- Liquid Phase Determinations
  - Dilute and Purge Method
  - Strips H$_2$S from sample solution
How do I measure the $H_2S$ content?

**Vapor Phase – Can Test Method**

**Required Equipment**

- Drager Bellows Pump
- Drager Tubes (1 -200 ppm, 100 - 2000 ppm, 0.2 - 7%)
- Quart Metal Cans with caps and 3/4” mouth
- #8 Rubber stopper
- Hot water bath or oven
How do I measure the $H_2S$ content?

Liquid Phase – $N_2$ Purge Test Method

- Nitrogen Source
- Fine Metering Valve
- Pressure Regulator
- Flowmeter
- 50 ML/Min
- Nitrogen Vent Stream
- H2S Collected
What is the best \( H_2S \) control program?

*Nalco’s Crude Oil \( H_2S \) Abatement Technology*

- **SULFA-CHECK™ EC9085A**
  - EC9085A, Patent since 1998
  - Extensively used for sour crude oils
  - SULFA-CHECK™ alternatives

- Injection Technology – NALGUARD™ Quill:
  - Patent since 1994
  - Optimizes contact and mixing
  - Maximized absorption capacity improves cost performance - “Economics”

- Developing a Sulfa-Check™ Program requires:
  - Product screening determines scavenging efficiencies
  - Monitoring while administering chemical treatment program
  - Define field treatment effectiveness and optimize feed rates
**Crude Oil – $H_2S$ Control Options**

**SULFA-CHECK™ Product Line**

- SULFA-CHECK™ – Proprietary products providing true reaction chemistry
- Stoichiometric reaction – Two moles $H_2S$ per mole scavenger
- Incorporates $H_2S$ into scavenging compound
- Splits off two moles of amine
- Produces thermally stable, oil soluble sulfide derivative
- Does not form salts (No acid-base reactions)
- No downstream side affects
Crude Oil – \( \text{H}_2\text{S} \) Control Options

\[ \text{SULFA-CHECK}^{\text{TM}} \text{ EC9085A} \]

- Fate of organosulfur derivative
  - Organosulfur derivative is oil soluble
  - Bp of reaction product is 365\(^\circ\)F (185\(^\circ\)C)
  - Will find its way to the heavy end of the gasoline distillation range or light jet fuel fraction
  - Thermal degradation does not re-liberate \( \text{H}_2\text{S} \), but forms simple C-S and C-C fragments

- Fate of amine
  - Partitioning of amine into desalter effluent brine is minimal
  - Majority of amine will go overhead
  - Increases the pH of overhead system, 2 – 3 pH units
  - No overhead corrosion or fouling issues encountered
What is the best $\text{H}_2\text{S}$ Control Program?

Nalco Patented Injection Technology

- NALGUARD™ Quill
  - Stinger across pipe diameter
  - Install suction side of transfer pipe
  - Utilize inline mixers

- Properly sized pump
  - Sufficient capacity
  - Sufficient discharge pressures
  - Pulse inhibitors

NALGUARD™ is a registered trademark of Nalco Company
Case Study – Southern California

NALGUARD™ Quill Optimizes Program Efficiency

NALGUARD™ is a registered trademark of Nalco Company
Vapor phase data at 140°F:

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TREATMENT</th>
<th>DOSAGE</th>
<th>INITIAL H2S CONC.</th>
<th>FINAL H2S CONC.</th>
<th>AMOUNT CONSUMED</th>
<th>PERCENT REDUCED</th>
<th>REACTION RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EC9085A</td>
<td>250 ppm</td>
<td>1200 ppm</td>
<td>40 ppm</td>
<td>1160 ppm</td>
<td>96.7 %</td>
<td>0.22:1</td>
</tr>
<tr>
<td>2</td>
<td>EC9085A</td>
<td>375 ppm</td>
<td>1400 ppm</td>
<td>40 ppm</td>
<td>1360 ppm</td>
<td>97.1 %</td>
<td>0.28:1</td>
</tr>
</tbody>
</table>

Liquid phase data at 140°F:

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TREATMENT</th>
<th>DOSAGE</th>
<th>INITIAL H2S CONC.</th>
<th>FINAL H2S CONC.</th>
<th>AMOUNT CONSUMED</th>
<th>PERCENT REDUCED</th>
<th>REACTION RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EC9085A</td>
<td>250 ppm</td>
<td>39 ppm</td>
<td>16 ppm</td>
<td>23 ppm</td>
<td>59.0 %</td>
<td>11:1</td>
</tr>
<tr>
<td>2</td>
<td>EC9085A</td>
<td>375 ppm</td>
<td>35 ppm</td>
<td>9 ppm</td>
<td>26 ppm</td>
<td>74.0 %</td>
<td>14:1</td>
</tr>
</tbody>
</table>

Note: Reaction ratio refers to the ppm of chemical additive required to react with 1 ppm of H₂S in the either the liquid or vapor phase.
The South China Sea – Liuhua Crude

Floating Production Storage & Off-Loading

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>INITIAL LIQUID H₂S CONCENTRATION</th>
<th>INITIAL VAPOR H₂S CONCENTRATION</th>
<th>VAPOR/LIQUID RATIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39 ppm</td>
<td>1200 ppm</td>
<td>31:1</td>
</tr>
<tr>
<td>2</td>
<td>35 ppm</td>
<td>1400 ppm</td>
<td>40:1</td>
</tr>
</tbody>
</table>
Nalco’s Worldwide Experience

Cost of Treating Sour Crude Oil

• Typical refinery spot treat costs – Mobilization and demobilization included
  - Low range: 100 – 300 ppm H₂S in the vapor headspace
    - US $0.15 – $0.30/bbl
  - High Range: 700 – 1,000 ppm H₂S in the vapor headspace
    - US $0.50 - $0.60/bbl

• Permanent installations for continuous treats are generally lower

• Oil production treating costs (212,000 BPD) – Projecting ppm H₂S in gas phase based on ppm H₂S in the oil phase targeting 0 ppm in the gas phase

<table>
<thead>
<tr>
<th>ppm H₂S in Oil</th>
<th>ppm H₂S in gas</th>
<th>ppm Scavenger</th>
<th>US $/bbl</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>200</td>
<td>1,000</td>
<td>0.24</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>2,000</td>
<td>0.49</td>
</tr>
<tr>
<td>200</td>
<td>800</td>
<td>3,000</td>
<td>0.73</td>
</tr>
</tbody>
</table>
SULFA-CHECK™ H₂S Abatement

Summary

• Nalco Energy Services’ Worldwide experience is extensive

• H₂S concentrations vary widely – crude dependent

• H₂S headspace concentrations are influenced by:
  – Liquid phase concentrations
  – Thermal decomposition of organosulfur compounds
  – Time, temperature, and mixing

• Test methods available, which reliably determine liquid and vapor phase H₂S concentrations

• Proper product selection, application, monitoring leads to successful chemical treatment programs at economically attractive costs