H₂S PANEL DISCUSSION 2.0: SPECIFICATIONS, REACTION VARIABLES, AND DOWNSTREAM PERSPECTIVES

Umberto Cabarrocas, ASI KECO
Nara Tong, Nalco Champion
Curtis Behr, Valero
QUESTION 1: LEGISLATION, REQUIREMENTS, SPECIFICATIONS FOR H2S LEVELS

• What are the values important at various supply chain points? Is there universality in H2S specs?
H2S in Crude Specifications on Upstream, Midstream and Downstream Sectors

By: Umberto Cabarrockas
Properties of Hydrogen Sulfide (H2S)

1. Toxicity.
2. Flammability and Explosiveness.
5. Marketability of Crude.
1. Toxicity

1.1 Emission Regulations

1.2 Health and Safety Regulations

Severe Impact on:

- Upstream
- Midstream
- Downstream
1.1 Emission Regulations

- **Environmental Regulations by EPA**
  - Only regulated with regards to accidental release (facilities holding 10 Tons or more)

- **Federal Emissions Regulations**
  - Pollutant and Restricted.
  - 10 Tons/ year (Due to SO2)

- **State Emissions and Ambient Air Regulations**
  - Ability to be stricter than Federal
1.1 H2S Emission Regulations

Example of Stricter Regulation on Emissions

- Colorado
  - Fees over 2 Tons/ year

Example of Stricter Regulation on Ambient Air Quality

- Texas (Downwind of O&G Ops.)
  - .03 ppm 30-min TWA (people present)
  - .12 ppm 30-min TWA (people not present)
1.2 Health and Safety Regulations

• Rule 36
  Compliance Requirement
  • Exploration
  • Production
  • Transportation

Subject to: Hydrocarbon fluids that contain H2S of 100 ppm/v or more.
1.2 Health and Safety Regulations

Example of Dispersion Problems

- Case 1
- Case 2
- Case 3

Based on:

100 ppm/v

R.O.E: 50’ and 3,000’

Public Areas and Public Roads
### 1.2 Health and Safety Regulations

<table>
<thead>
<tr>
<th>Country</th>
<th>Institution</th>
<th>Time-Weighted Average (8-hr TWA)</th>
<th>Short-Term Exposure Limit (15-min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>OSH</td>
<td>10 ppm</td>
<td>15 ppm</td>
</tr>
<tr>
<td>Canada</td>
<td>ACGIH</td>
<td>1 ppm</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Germany</td>
<td>EU-OSHA</td>
<td>5 ppm</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Great Britain</td>
<td>NHS</td>
<td>5 ppm</td>
<td>10 ppm</td>
</tr>
<tr>
<td>United States</td>
<td>OSHA</td>
<td>20 ppm</td>
<td>50 ppm</td>
</tr>
</tbody>
</table>
Properties of Hydrogen Sulfide (H2S)

1. Toxicity.
2. Flammability and Explosiveness.
5. Marketability of Crude.
2. Flammability and Explosiveness

2.1 High Auto-ignition

2.2 Explosiveness by concentration

2.3 Creation of Iron-sulfide Scale

Severe Impact on:
- Upstream

Moderate Impact on:
- Midstream
- Downstream
Properties of Hydrogen Sulfide (H2S)

1. Toxicity.
2. Flammability and Explosiveness.
5. Marketability of Crude.
3. Solubility

3.1 Temperature Impacts Solubility

3.2 Weak Sulfuric Acid

Moderate Impact on:
- Upstream

Severe Impact on:
- Midstream
- Downstream
Properties of Hydrogen Sulfide (H2S)

1. Toxicity.
2. Flammability and Explosiveness.
5. Marketability of Crude.
4. Corrosiveness

4.1 Sulfide Stress Cracking
- 4 ppm/w or less
- ISO 15156/ NACE MR-0175

4.2 Pressure Effects
- Severe Impact on:
  - Upstream
  - Midstream
- Moderate Impact on:
  - Downstream
Properties of Hydrogen Sulfide (H2S)

1. Toxicity.
2. Flammability and Explosiveness.
5. Marketability of Crude.
5. Marketability of Crude

( Based on Projects )

- **10 ppm/w Specification**
  - Canada
  - Egypt
  - Indonesia
  - Iraq
  - Kuwait
  - Netherlands
  - Nigeria
  - Qatar
  - Saudi Arabia
  - Turkey
  - Venezuela

- **United States**
  - 10 ppm/w
  - 100 ppm/v
  - 5 ppm/v
  - 10 ppm/v
  - 5 ppm/ w Rail Car
  - 1 ppm/w Truck
Conclusion

• WHY SHOULD H2S BE SPECIFIED?
  • Environmental Impact.
  • Occupational Health and Safety.
  • Infrastructure Integrity.
  • Marketability of USA Crude on International Markets.
Thank You

Time for Questions
QUESTION 2: REACTION VARIABLES

• What are the effects of temp, viscosity, time, and interferences on H2S scavenging? Is reversion possible? What are the ultimate fates of additive technologies?
GLOBAL H₂S SCAVENGERS MARKET

- **REGENERATIVE H₂S SCAVENGERS**
  - Monoethanolamine (MEA)
  - Diethanolamine (DEA)
  - N-methyldiethanolamine (MDEA)
  
  **53%**

- **TRIAZINE-BASED H₂S SCAVENGERS**
  - Monoethanolamine triazone
  - Methylamine triazone
  
  **16%**

- **ALDEHYDE-BASED H₂S SCAVENGERS**
  - Formaldehyde
  - Acrolein
  - Glyoxal
  
  **5%**

- **MATEL-BASED H₂S SCAVENGERS**
  - Metal oxides
  - Metal carboxylates and chelates
  
  **4%**

- **OTHER H₂S SCAVENGERS**
  - Oxidizing chemicals
  - Solid scavengers
  
  **22%**

*Source: Research N Reports Analysis, 2015*
COMMODITY AMINE H₂S SCAVENGERS

CONDITIONS THAT AFFECT REACTION EFFICIENCY
- Composition of hydrocarbon streams – CO₂, COS, and other competing reactions
- Residence time – reaction kinetics varies depending on the type of amine
- Temperature
- Mixing

REVERSIBLE REACTION
- Reaction products are usually heated to regenerate amine and H₂S for further processing

POSSIBLE FATE OF THE SCAVENGER AND REACTION PRODUCT
- Regeneration unit
- Claus process to form elemental sulfur
TRIAZINE-BASED H$_2$S SCAVENGERS

CONDITIONS THAT AFFECT REACTION EFFICIENCY

- Crude oil composition – organic acids, mercaptans
- Residence time – reaction is fast
- Temperature – higher temperature facilitates reaction; product may decompose at 120 °C - 150 °C
- Viscosity and mixing

IRREVERSIBLE REACTION

- Some reaction products will decompose when exposed to the crude unit temperature
- Decompose compounds: oxazolidine and minor components

POSSIBLE FATE OF THE SCAVENGER AND REACTION PRODUCT

- Desalter effluent brine – depending on the partition coefficient of the chemical
- Crude unit
- Distillates
ALDEHYDE-BASED H₂S SCAVENGERS

CONDITIONS THAT AFFECT REACTION EFFICIENCY

› Crude oil composition – base, oxidizing agent, and other competing reactions
› Residence time – reaction is slower than triazine’s
› Temperature – higher temperature helps to reach activation energy
› Viscosity and mixing

IRREVERSIBLE REACTION

› Some reaction products will decompose when exposed to the crude unit temperature

POSSIBLE FATE OF THE SCAVENGER AND REACTION PRODUCT

› Desalter effluent brine – may cause low pH in wash water
› Crude unit
› Distillates
METAL-BASED H₂S SCAVENGERS

CONDITIONS THAT AFFECT REACTION EFFICIENCY
- Hydrocarbon stream composition – reducing agents, organic acids, and other competing reactions
- Residence time – reaction is rapid
- Temperature – higher temperature helps to reach activation energy
- Viscosity and mixing

REACTION MAY REVERSE UNDER HARSH CONDITIONS
- Metallic sulfides react with strong acids to re-liberate H₂S

POSSIBLE FATE OF THE SCAVENGER AND REACTION PRODUCT
- Treated hydrocarbon streams
- Desalter effluent brine – may lead to stabilized emulsions
QUESTION 3: DOWNSTREAM PERSPECTIVE

• WHAT DO END USERS CONSIDER TO BE BENEFITS/RISKS OF H2S SCAVENGING? PLEASE PROVIDE BACKGROUNDS/SOLUTIONS TO CHALLENGES SEEN BY INDUSTRY IN GENERAL
Benefits/Risks of \( \text{H}_2\text{S} \) Scavengers to End Users

Curtis Behr
Benefits of H2S Scavengers

- Allows some refiners to be able to comply with environmental permits.
- Safety / convenience benefits on vessels to allow inspectors to sample without need for fresh air equipment.
- Has the potential to mitigate corrosion of pipelines, tanks, and vessels.
- In general, low H₂S concentrations are more often required for intermediates and finished products than crude.
- Many streams within a refinery may be treated with H₂S scavengers for compliance with specifications and environmental regulations.
Risks of H2S Scavengers

• Amine based scavengers, such as triazine, are problematic for refinery equipment
  – Corrosion and fouling on Atmospheric tower upper trays, overhead lines, exchangers, and coolers
  – Fouling of Vacuum Tower overhead circuit
  – Can create more stable emulsions in desalter
  – Amines in desalter effluent impact waste water treatment plants (high COD load)

• For other refinery feedstocks, H$_2$S scavengers of any type are less likely to cause issues as hydrotreating destroys the problematic compounds
  – Metals in some scavengers, however, can poison catalyst
Examples of Equipment Fouling