H₂S AND CRUDE QUALITY

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QUESTION 1

• H2S IS PREDOMINANTLY ASSOCIATED WITH HEALTH, SAFETY, ENVIRONMENTAL CONCERNS, THOUGH IT ALSO IMPACTS SULFIDE STRESS CRACKING (SSC) CORROSION IN SOUR SERVICE CARRIER SYSTEMS. DESCRIBE THE RELATIVE RISK AND MITIGATION PRIORITIES IN PRODUCTION, GATHERING, PIPELINING, REFINERY OPERATIONS.
QUESTION 2

• **H2S** can be measured directly in liquid crude oil streams and/or in the vapor space above the liquid crude. *Which test method is most appropriate where, and for what purpose?*

• **How should the values derived by testing be interpreted?**

• **Is it critical to include test method used in the reporting and interpretation of results?**
H2S Test Methods

Although H2S is a single molecule, it is hard to determine exact levels in crude and many methods are available.

Sample integrity is a key factor:
- Storage temperature
- Container
- Age of sample

Garbage in = Garbage out

There is no standardized test method specific to crude oil. Test methods were designed for light petroleum liquids and fuel oils.

Critical to state what method was used and units in those results along with any modifications that were made by the inspection lab.

Results are critical for H2S scavenging, safety and contract specs. with traders.

Liquid Phase Test Methods


UOP 163: Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration.

Vapor Phase Test Methods

ASTM 5705: Measurement of Hydrogen Sulfide in the Vapor Phase Above Residual Fuel Oils (Results in ppmv mole % in vapor)

ASTM D7621: Standard Test Method for Determination of Hydrogen Sulfide in Fuel Oils by Rapid Liquid Phase Extraction (Results in ppmw mg/kg)
Relation between different test methods:
Should not assume there is correlation between methods.

<table>
<thead>
<tr>
<th></th>
<th>UOP-163</th>
<th>ASTM D5705</th>
<th>ASTM D5623</th>
<th>IP570 for crude</th>
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<tr>
<td></td>
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</table>

Testing done by CCQTA confirmed a lack of correlation between test methods.

Recommend on using one test method and sticking to it throughout the process.

In the US we mostly see UOP 163 and ASTM 5705 being used (either or both). ASTM 5705 variations are fit for field use, minimal equipment required.

ASTM 5705 pitfalls:
- Modifications implemented by inspection labs to fit test for crude. No standardized temperature for testing crude in practice.
- Difficult to read stain tubes.

UOP 163 pitfalls:
- Interference of chemical contaminants including scavengers with titration.
- Technicians may interpret curves in different ways.

QUESTION 3

• What H2S specific language is typically included in transport or custody transfer contract language?

• Are there, or could there be, documentation methods that track treatment for H2S?
QUESTION 4

• PROVIDE A HIGH LEVEL, NON-PROPRIETARY DESCRIPTION OF H2S MITIGATION TECHNIQUES (BOTH PHYSICAL METHODS SUCH AS WELLHEAD STRIPPING/BURNING AND CHEMICAL METHODS SUCH AS REACTION AND SUPPRESSION ADDITIVES COULD BE HELPFUL).
H2S Mitigation Technologies

- Mechanical/Operational
- Chemical
Mechanical/Operational

Crude Oil/Condensate Stripping
- Pressure letdown Separator
- Gas induced stripping not routinely done in crude production
  - Some patented processes are available
  - 10%+ losses
  - Recycle and compress minimize losses
  - Small streams 6-9 kbpd
- Steam stripping done as part of SAGD production

Drilling muds may include triazine or other H2S scavengers
**Gas Production**

- **Contact towers**
  - Glycols, triazine
  - Losses of 10%+
- **Solid bed H2S absorbent beds**
  - Zn, Fe, Mixed metals
  - Sludge generation
- **Direct inject (triazine & other additives)**

Drilling muds may include triazine or other H2S scavengers.
## Additives

<table>
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<tr>
<th>H2S Scavenger Additive Type</th>
<th>Description</th>
<th>Advantages/Disadvantages</th>
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</table>
| Alkaline Hydroxides         | - Sodium hydroxide (caustic) is readily available to refineries and is by far the cheapest option.  
                            - Potassium hydroxide is also used although more costly | - The major problem with caustic injection however is the addition of sodium, which not only increases the sodium level in the fuel oil, but also gives rise to fouling, catalyst poisoning, and corrosion problems in furnaces and downstream units. e.g. Crude Unit, FCCU, Visbreakers and Cokers.  
                            - Sludge generation  
                            - The neutralization process is reversible if the pH is not kept sufficiently high enough (pH > 11) to render the medium alkaline. |
| Formaldehyde                | - Formaldehyde, paraformaldehyde | - These products while effective and inexpensive pose handling issues. For one thing, formaldehyde is categorized as a Class 3 carcinogen. Not surprisingly, most refiners in are very reluctant to use such a material. Nevertheless, formaldehyde is still used at some facilities. |
| Simple Amines               | - Simple amines such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are typically used in these formulations.  
                            - These organic amines are weak bases, while H2S is a weak acid. | - Low cost  
                            - The amine salts formed easily dissociate when thermally stressed, re-releasing H2S into the vapor space. This problem has been observed in Industry and hence the practice is now rare. |
| Complex Proprietary Amines and Amine Complexes | - Some patented proprietary products react with H2S to form heat stable, oil soluble materials, which do not subsequently breakdown on heating to release H2S | - Fouling due to amine salts |
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| **Triazines** (aldol condensates) | - Triazine based products which on reaction with H2S forms oil soluble alkyl diathiazines and monoalkylamines are the most prevalent compounds in this classification  
- Reaction product of formaldehyde/paraformaldehyde | - Additive costs dropped with the advent of some manufactures utilizing a continuous process and is now considered a commodity  
- Diathazines and monoalkylamine byproducts are recognized as being troublesome in some refinery operations. Fouling and corrosion are the most problematic issues  
- Industry is looking for alternatives to this low cost solution |
| **Metal Based** (inorganic and organic) | - Inorganic metal based compounds oxides, salts, carbonates  
  o FeCl3, Fe2O3, ZnCl2, Zn2O3, ZNCO3, CuCO3  
- Organic Carboxylates  
  o Zn, and Fe carboxylates  
  o Used often in contact tower as well as direct inject | - Inorganic are low cost; organic versions are higher cost  
- Sludge generation, fouling of equipment, emulsion stabilizer  
- Corrosivity from chloride salts |
| **Aldehydes** | - Includes amine aldehydes (condensation products of amines and formaldehyde)  
- Glyoxal | - Used instead of triazines but at higher treat cost  
- Aldehyde reactions are slow compare to triazines  
- Glyoxal has slow reaction time and but is used in triazine sensitive situations; Corrosive to carbon steel |
| **Other Additives** | - Sodium nitrite (contact towers)  
- Glycol–based | - CAPEX for facilities  
- Glycols are slow to react |
QUESTION 5

• **In the application of chemical additives, how is effectiveness tracked?**

• **Is H2S routinely measured before and after treatment? Is it only measured before a stoichiometric additive calculation and addition is done?**

• **What are typical “just in case” overdose levels?**
Application of H$_2$S Scavenger

- Scavenger
  - Process T, P Reynolds No. >2300
  - Scavenger
- Oil Storage Tank
- Secondary Injection
- Loading Dock

Maximize mixing and reaction time to reduce consumption