H2S Abatement and its Impact on Refining

Lawrence Kremer
Baker Petrolite
COQG
H₂S in Hydrocarbons

• Naturally occurring H₂S
  – Crude Oils

• Generated by refinery processes
  – Cracking
  – Stripping
  – Elemental Sulphur
H$_2$S Issues

- **Toxicity**
  - Employee exposure
  - Environmental releases
- **Corrosion**
  - Storage tanks
  - Fuel quality
- **Odor**
  - Tank vents, sewers, sulphur pits
  - Neighborhood complaints
- **Specifications**
  - Fuel quality
  - Environment
## Products Treated with H$_2$S Scavengers

### Intermediates
- Crude oil
- Desalter effluent
- Sewers
- Coker wash water
- Flare gas

### Finished Fuels
- Natural gas, C$_3$s, C$_4$s, LPG
- Naphtha as reformer feed
- Mid-distillates and blend components
- Gasoline and blend components
- Furnace fuel oil
- Residual fuel
- Asphalt

© 2008 Baker Hughes Incorporated. All Rights Reserved.
Crude Oil Quality Group
Crude Oil Supply System
Treatment Locations

• Oilfield
  – Can be treated at Wellheads
    ➢ Treatments carried out by production chemical vendors

• Transshipment
  – Treated at Load port
    ➢ Treatment by P2R services application

• Refinery
  – Treated at Refinery Terminal
    ➢ Treatment during offloading
  – In Refinery treatment
    ➢ Typically products treated as needed

• Downstream
  – Downstream product treatment
    ➢ P2R services treatment at terminal or on board vessel
Oilfield Treatment

- Hydrogen Sulfide Scavengers added into sour crude wells
- Many different type additives used
- Crude field production can have multiple vendors
- Triazines, neutralizers, formaldehyde, acrolein used
- Water Separation in field will carry out some sulfur species
- Some amines can be entrained in crude
Transshipment

- Scavenger added at load port
  - Complex logistics
  - P2R services
- Scavenger added at intermediate terminal
  - Terminal set up for treatment
  - Added cost
  - P2R services
- Scavenger added on vessel
  - Difficult for crude oil
  - Limited mixing
  - Very complex logistics
  - P2R services
Typical Terminal Specifications

• **North America**
  – 10-100 ppm in Vapor
  – 10-50 ppm ASTM D5705
  – Highest Level – 100 ppm in Vapor
  – Lowest Level - <10 ppm in Vapor

• **Europe**
  – <2 ppm in Liquid

• **Far East**
  – < 100 ppm in Vapor
  – < 100 ppm in ASTM D5705
Shipping

• IMO considering H₂S specification
• Personal Monitors set at 10ppm
  – Loading/Offloading operation stopped if the alarm is activated
• Accidents still occur despite precautions
Chemical Removal of H₂S

- Oxidizers
- Neutralizers (organic amines, inorganic bases)
- Metals
- Reactants
  - Organic Bases
  - Triazines
  - Formaldehyde, Acrolein
  - Effective in a wide range of fuels
    - Minimizes number of additives needed
    - Reduces product rejections and shipping delays
    - Reduces additive odor, corrosion and safety problems
Oxidizers

• Peroxides, Permanganates
  – Advantages
    ➢ Very fast
    ➢ Water soluble products, sulfites
  – Disadvantages
    ➢ Dangerous
    ➢ Explosive
  – Not used
Formaldehyde

- **Advantages**
  - Inexpensive
  - Oil soluble product
  - Does not contain nitrogen or metals

- **Disadvantages**
  - Carcinogen
  - Can be slow reaction
Acrolein Reactions

- Reaction with H2S
- Reaction with FeS
- Reaction is irreversible
- Also can be used as biocide
- Hydration (breakdown) in the system
Neutralizers

\[ \text{H}_2\text{S} + \text{Amine Neutralizer} \leftrightarrow \text{Salt} \]

- **Advantages:**
  - Fast reaction
  - No sodium

- **Disadvantages**
  - Reaction is reversible
  - Weak acid/base equilibrium
  - Not specific for H\(_2\)S
  - Amines regenerated
    - Wastewater effects – increased nitrogen
Inorganic Bases

\[ \text{H}_2\text{S} + \text{NaOH} \leftrightarrow \text{Salt} \]

- **Advantages**
  - Fast reaction, cheap
  - Use alone or in combination
  - Thermally stable products
- **Disadvantages**
  - Non-selective for H$_2$S
  - Reaction is reversible
  - Ash forming
  - Increases fuel sodium content
  - Limited safe injection temperature
Reaction/Conversion Additives

$\text{H}_2\text{S} + \text{SULFIX® product} \rightarrow \text{Inert sulphur species}$

- **Advantages:**
  - Non-reversible at typical usage temperatures
  - Rapid reaction depending on mixing and dosage
  - Selective for $\text{H}_2\text{S}$
  - May be used at elevated temperature and with caustic
  - Extensive no-harm testing
  - Successful industry track-record
  - Effective in wide range of fuels
Oil-Soluble H₂S Scavengers

H₂S + SULFIX® product →

R-S-R or R-S-S-R

• Proprietary, patented products
• Ideal for high temperature applications or applications where water is undesirable
• Reduced amine refinery impacts
• More expensive
Refinery Impacts & Mitigation Strategies
Amines

• Sources
  – Hydrogen sulfide treatment
  – Corrosion inhibitors and neutralizers
  – Naturally occurring amines
  – In refinery sources
• Problems
  – Stabilize emulsion in desalter
  – Tower corrosion and fouling
  – Impact WWTP
Potential Amine Salt Fouling and Corrosion
Stainless Steel Distillation Tray Damage from Exposure to Solid Hydrochloride Salts
Overhead Vapor Condensing System Pipe Damaged by Liquid Hydrochloride Salts
Metals

• Na, Fe, etc. are catalyst poisons
• Contribute to ash
• Some metals such as Zn, Cu undesirable in WWTP
Mitigation Strategies

• Discontinue crude oil purchase
• Fix damage
• **Change additive use in field**
• Remove contaminant in refinery
• Monitor and predict problem
H2S Treatment of Crude Oil

- Not easily controlled at well
- Traders can control at load port, transshipment, or off loading
  - Safety main concern
  - Low Cost prime criteria
  - End user not consulted
Treating Partnership

• Cooperation for better results
  – Trader controlling the treat
  – Refiner with concerns on impact
  – Knowledgeable chemical supplier

• Design program based on refinery impact
  – May be more expensive
  – Communicate chemistry to refinery
  – Optimize treatment to reduce over treatment
H₂S and Mercaptan Scavengers

• Baker Petrolite: the Industry Leader in solving H₂S and mercaptan issues
  
  • Long, successful track-record
  • Customized products and programs for different applications
  • Over 16 patents in force
  • Prepared-To-Respond™ services
Prepared To Respond™ Services

A service providing an effective, quick response to help refiners, traders, terminals and pipeline companies manage situations where problems with product quality and contamination of petroleum products occur.