Characteristics of Sour Flare Gas Streams that Impact H₂S Treatment Technologies

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Topics

• Introduction
• Design Basis Selection
• Amine Treating of Refinery Flare Gas
• Caustic Scrubbing of Flare Gas
• Solid H$_2$S Scavengers for Flare Gas
• Liquid H$_2$S Scavengers for Flare Gas (In summary only)
• Conclusions
Introduction

• Based on paper with same title. See Trimeric website (www.trimeric.com/publications).
• \( \text{H}_2\text{S} \) removal technology selection based on:
  – Sulfur load (lb/day of S, or LTPD of S)
  – Gas impurities (\( \text{CO}_2 \), \( \text{O}_2 \), \( \text{H}_2 \), etc.)
  – Water content
  – Operating temperature, pressure, and flow rate
• Critical to develop sound design basis
• Covers characteristics that impact: amine, caustic, solid scavengers, and liquid scavengers
Design Basis Selection

• Understand important regulatory drivers:
  – NSPS Ja limit of ~160 ppmv H$_2$S
  – Develop design limit (e.g., 100 ppmv H$_2$S)
  – Eliminate excursions, if permit allows

• Review historical flare gas data due to varying conditions over time

• Average data gives typical operating expenses

• Maximum rates used to size and cost equipment
Example Flow and H₂S Variability (flare gas before treatment)

- Entire range of gas flow used since high H₂S at high flows (limiting design)
- Gas treated even if < 100 ppmv H₂S
- Some high H₂S points allowed by permit
Other Key Characteristics for Design Basis

- Sulfur load: impacts operating costs
- Operating temperature and pressure:
  - Temperatures track ambient (long pipe w/o heat trace or insulation)
  - Pressures generally low (inches WC to a few psig)
- Composition/variability of other gas components
Amine Treating of Flare Gas

- Amine treating common for H₂S removal in refineries
- Dedicated amine unit not economic for flare gas w/ low sulfur load
- Consider new standalone, low dP, amine contactor tied to existing amine circuit
- Determine load capacity of existing amine unit
Example New Amine Contactor

- Simple process
- No chemicals to purchase or dispose of
- Familiar process to operators
- Consider contaminants, VLE for treat ability

Note 1: Either a device to impart flow (Venturi) or a liquid seal pot would be needed to force normal flow through the new amine contactor.
Example VLE for H$_2$S Treat
Caustic Scrubbing of Flare Gas

- NaOH scrubs H$_2$S and CO$_2$ from gas:
  \[ \text{NaOH} + \text{H}_2\text{S} \rightarrow \text{NaHS} + \text{H}_2\text{O} \]  
  \[ \text{NaHS} + \text{NaOH} \rightarrow \text{Na}_2\text{S} + \text{H}_2\text{O} \]  
  \[ \text{NaOH} + \text{CO}_2 \rightarrow \text{NaHCO}_3 \]  
  \[ \text{NaHCO}_3 + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]

- Packed/trayed towers used

- Concerns with caustic scrubbing:
  - Waste of caustic (due to CO$_2$ or high pH)
  - Salts precipitation
  - Blowdown volume and characteristics
Example Caustic Scrubber

- Inexpensive chemical
- Caustic often already present at refinery
- Simple process
- Automated chemical addition
- Many equipment variations

Note 1: Either a device to impart flow (Venturi) or a liquid seal pot would be needed for force normal flow through the caustic scrubber.
Important Gas Characteristics for Caustic Scrubbing

• Operating temperature and pressure:
  – High temperatures limit H₂S removal and result in special materials of construction
  – Low temperatures can result in salt precipitation
  – High pH used to achieve treat at low operating pressures of flare gas
Important Gas Characteristics for Caustic Scrubbing

• Other gas constituents:
  – CO₂ removal not needed and wastes caustic
  – Some organic sulfur, NH₃, and aromatics absorbed

• Refinery factors:
  – Consider pipe lengths between scrubber and existing tankage
  – Available dP dictates type of equipment used
Solid Scavenging of Flare Gas

- Non-regenerable solids react with $H_2S$
- Iron oxide is a common scavenger material
- Desired reaction:
  \[ 3H_2S + H_2O + Fe_2O_3 \rightarrow Fe_2S_3 + 4H_2O \]  
  (5)
- Iron oxide is granular solid or supported on inert, non-flammable substrate
- Two vessels commonly used (one operating, one spare)
Example Solid Scavenger System

- Simple process
- Low operator attention
- Media change-out
- Nonhazardous media (unless hazardous gas component adsorbed)

Note 1: Either a device to impart flow (Venturi) or a liquid seal pot would be needed to force normal flow through the solid scavenger vessel.
Important Gas Characteristics for Solid Scavenging

• Sulfur load: usually used below ~0.4 LTPD due to high cost of scavenger material

• Operating temperature and pressure:
  – Media performance decreases below 45-50F
  – Temperatures up to 200F extend life of media
  – No significant impact of operating pressure (vessel size changed to give same residence time regardless of pressure)
Important Gas Characteristics for Solid Scavenging

• Other gas constituents:
  – Saturate gas with water to extend iron-oxide life
  – One vendor cannot guarantee removal with >10 % H₂; another claims no effect / has high H₂ refinery application in operation
  – Oxygen speeds up reaction and increases capacity, but may complicate media removal
  – High H₂S & O₂ give high H₂S heat of reaction
• Refinery factors: very low pressure drop can be achieved
Liquid Scavenging of Flare Gas

- Different liquid H₂S scavengers available
- Triazine commonly used
- Triazine makes water-soluble products w/ H₂S, if not over spent
- Spent solution typically 100% liquid (solids form if over spent)
- Loadings range from 0.5 lb/gal to 2-3 lb/gal
- Direct injection is common (batch also possible)
Important Gas Characteristics for Liquid Scavenging

- **Sulfur load**: used < 0.1 LTPD due to high chemical cost

- Operating temperature and pressure:
  - Temperatures of 60-120F typical
  - Low T = slow kinetics
  - High T = decompose
  - H$_2$S removal difficult at low P
Important Gas Characteristics for Liquid Scavenging

• Other gas constituents:
  – Water addition if gas not saturated
  – Triazine reacts selectively with $H_2S$

• Refinery Factors:
  – Flow changes impact removal with direct injection
  – Atomizing agent important
  – Odor and WWTP issues (biocide)
## Summary Tables

<table>
<thead>
<tr>
<th></th>
<th>Typical Sulfur Load</th>
<th>Other Flare Gas Components</th>
<th>Temp. Impacts</th>
<th>Operating Pressure Impact</th>
<th>Other Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amine</strong></td>
<td>All: Economics Favored at High Loads</td>
<td>(O_2): Degrade amine</td>
<td>\textbf{High T}: Limits Treat</td>
<td>\textbf{Low P}: Limits Treat</td>
<td>Piping runs for amine.</td>
</tr>
<tr>
<td><strong>Caustic</strong></td>
<td>All: Economics Favored at Low (0.1 – 1 LTPD)</td>
<td>(CO_2), other S: Consume Caustic (NH_3): Odor</td>
<td>\textbf{High T}: Limits Treat, Materials issues \textbf{Low T}: Salts</td>
<td>Negligible</td>
<td>Piping/tanks for caustic.</td>
</tr>
<tr>
<td><strong>Solid Scavengers</strong></td>
<td>Low: &lt; 0.4 LTPD</td>
<td>(O_2): Heat-up (H_2): Performance (H_2O): Saturated Gas Recommended</td>
<td>\textbf{Typical}: 60 – 120 F \textbf{High T}: Degrade \textbf{Low T}: Slow Kinetics</td>
<td>\textbf{Low P}: Limits Treat</td>
<td>Easy to Implement (Direct Injection).</td>
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Conclusions

- Typical sulfur loads: 0.1 LTPD to much greater
- Impact of operating temperature, pressure, and other gas constituents varies greatly
- Need to establish representative design basis over wide range of conditions
- Factors give refiners better sense of flare gas information needed to select H₂S treating system
Questions

Thank you

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Background on H$_2$S Removal & Sulfur Recovery Niches

• Technology niches for H$_2$S removal
  – Large-scale niche – over ~20 LTPD of sulfur (amine/Claus/TGT process common)
  – Medium-scale niche – ~0.1 to ~20 LTPD sulfur (amine/Claus, liquid redox, other regenerable liquid chemical processes common)
  – Small-scale niche – less than ~0.1 LTPD sulfur (nonregenerable liquid or solid chemicals common)

• Size refers to amount of sulfur, not gas rate

• Niches assume new build and continuous operation (temporary or standby service favors nonregenerables)
Niches are guidelines only; technologies should be evaluated on a case-by-case basis because feed gas conditions, treatment goals, and other parameters can impact technology selection.