Assessing How to Effectively Deliver Scavenger Chemical and Reduce H₂S Concentrations

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Key Terminology Used

- **Efficiency** - Chemical Required / Chemical Injected
- **Over Treating** - Using Excessive Amounts of Chemical
- **Over Spending** - Using Insufficient Amounts of Chemical (Fouling)
- **Triazine** – Active Component. Molecule is a 6-sided ring structure with alternating C and N atoms. N can be any primary amine (MEA)
- **Dithiazine** - Desired *Liquid* Reaction Byproduct
- **Trithiane** - Undesired *Solid* Reaction Byproduct
Triazine’s Chemical Structure
H$_2$S Scavenger Reactions

- **1$^{st}$ & 2$^{nd}$ Reactions Combined**
  - 1 mole of Triazine reacts with 2 mole H$_2$S

\[
\text{Triazine} + 2 \text{H}_2\text{S} \rightarrow \text{Dithiazine} + 2 \text{NH}_2\text{R}
\]

- Desired byproduct is dithiazine (liquid)

- **3$^{rd}$ Reaction**
  - Byproduct is trithiane (solid) & occurs when Efficiency $\geq$ 100%

\[
\text{Trithiane}
\]
Trithiane Foulant

Eagle Ford Asset – Gonzales, Texas
Reaction Chart

Low Fluctuation H2S/Gas

High Efficiency

Solid Formation

High Fluctuation H2S/Gas

Liquid Dithiazine

Over Spending (Not Enough Chemical)
100% Target

Ultrafab HSS
80% Target

Over Treating (Too Much Chemical)
Chemical Waste
Marathon’s Choice for a Sulfide Scavenger

- Water-Based Chemical with Triazine as the Active Component

- Gas Treatment Chemical A:
  - Triazine
  - Methanol

- Gas Treatment Chemical B:
  - Triazine
  - Methanol
  - 2-Butoxyethanol
Review of In-Line Chemical Injection

- Injection of Chemical into a Flowing Pipeline
- The Chemical and H$_2$S Come in Contact Resulting in a Reaction
- H$_2$S is Removed from the Production Gas
Reaction Mechanics of Direct Injection

- Direct injection relies on contact occurring on bottom of the pipe
- Reaction is instantaneous
- Process is dependent on physical contact in pipe
- Other liquids in the pipeline will affect the contact surface
Contact is Increased by using an Atomizer

- Increases surface area of chemical contacting gas

- Chemical flows in the same direction as gas, thereby remaining in contact with the same gas

- As H₂S is reduced downstream of injection point, the reactions near completion leave fewer reaction sites on the chemical

\[ \text{Chemical} + 2 \text{H}_2\text{S} \rightarrow \text{Product} + 2 \text{NH}_2\text{R} \]

- Fewer reaction sites on the chemical results in a lower capability for chemical to react with H₂S
Why MRO Uses Ultrafab Modular Systems

- Original Ultrafab (UF) Industries Units installed by Hilcorp for gas H$_2$S removal pre-MRO acquisition

- In 2013, MRO’s Central Engineering Gas Study Team recommended continuing with distributed UF strategy vs. centralized Amine treating

- Ultrafab Criticality Team formed 2nd Qtr of 2014 to focus on efficiency & reliability of UF Modular Units
Ultrafab Unit’s Skid Mounted Equipment

1. Contactor
2. Separator
3. $\text{H}_2\text{S}$ Analyzer
4. Chemical Injection Pumps (Primary and Secondary)
5. Fuel Gas Conditioning System
6. $\text{H}_2\text{S}$ Sample Stream
Ultrafab Contactor Tower

- Largest Vessel on the Skid
- Responsible for 100% of the H₂S removal
- Liquid Filled with Packing
- Designed to Lift Spent Scavenger (Heavier) to Top
- Displaces Spent Scavenger by Injecting Fresh Scavenger at Base
1. Ensure Gas Measurement Exists at Central Facility

2. Install Chemical Injection Meters
   - Turbine Meters ✗
   - Pulsation Dampeners ✗
   - Calibrated Gear Meters ✓
Ultrafab Pre-Test Modifications

3. Bring Ultrafab Unit Data into SCADA

4. Use Lead-Acetate Analyzers
Ultrafab Efficiency – Performance Testing

- Tests Performed at Eagle Ford’s 3 Largest Chemical Consumers
- Defining Ideal Operating Parameters – Inlet Conditions

**Target operations (idealized)**

- **Inlet H2S ppm**
- **Chemical rate**
- **Time**

- **Pumps 1&2**
- **Pump 1**
Defining Ideal Set Points – Outlet Conditions

**UF outlet H2S (idealized)**

![Graph showing UF outlet H2S (idealized)]

- **Pump #1 Over Injection**
- **Optimum**
- **1.5ppm H2S**
Performance Test Conditions

- During the beginning of the Test, construction was being performed at the CF resulting in gas “swings” between two independent “process trains”

- After the construction was completed and conditions stabilized, a higher efficiency was obtained
Variables that Affected Chemical Efficiency

- Decreasing pump injection rates (GPD)
- Increasing pump start H₂S concentrations (ppm)
- Gas production stabilizing by processing 50% of total CF gas per train
- 65% of total CF gas processed through Train 1 resulted in 77% efficiency (15% increase)
Train 1 Performance Test Results

Ultrafab Efficiency
12/24/14 - 5/12/15
Hydrolysis of Triazine

Triazine $\xrightarrow{k_1} \text{Hydrolysed triazine (Formaldehyde)} \xrightarrow{H_2S} \text{Thioformaldehyde} \xrightarrow{} \text{Polymer Goo}$

$\text{Thiadiazine} \xrightarrow{k_3} \text{Dithiazine} \xrightarrow{k_4} \text{Trithiane}$
Hydrolysis of Triazine

1. Triazine + H₂O → Formaldehyde + Ethanolamine

2. Formaldehyde + H₂S → Thioformaldehyde + H₂O

Eagle Ford Asset – Gonzales, Texas
Hydrolysis of Triazine – further reactions

3. thioformaldehyde + dithiazine

4. dithiazine + polymer
Polymer