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Startup Foaming Issues on a New MDEA Tail Gas Unit

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Problem Statement

The Phillips 66 Alliance Refinery started up a brand new MDEA based tail gas unit (TGT) in May 2021. MDEA solution was circulated for five days without incident before Claus tail gas containing H_2S was introduced into TGT. Within hours of introducing H_2S , the amine solution turned black and pressure excursions were reported in the TGT amine regenerator. The pressure excursions were of such a magnitude that the TGT unit was inoperable. A second older TGT unit that operated in parallel did not report any pressure excursions at the same time.

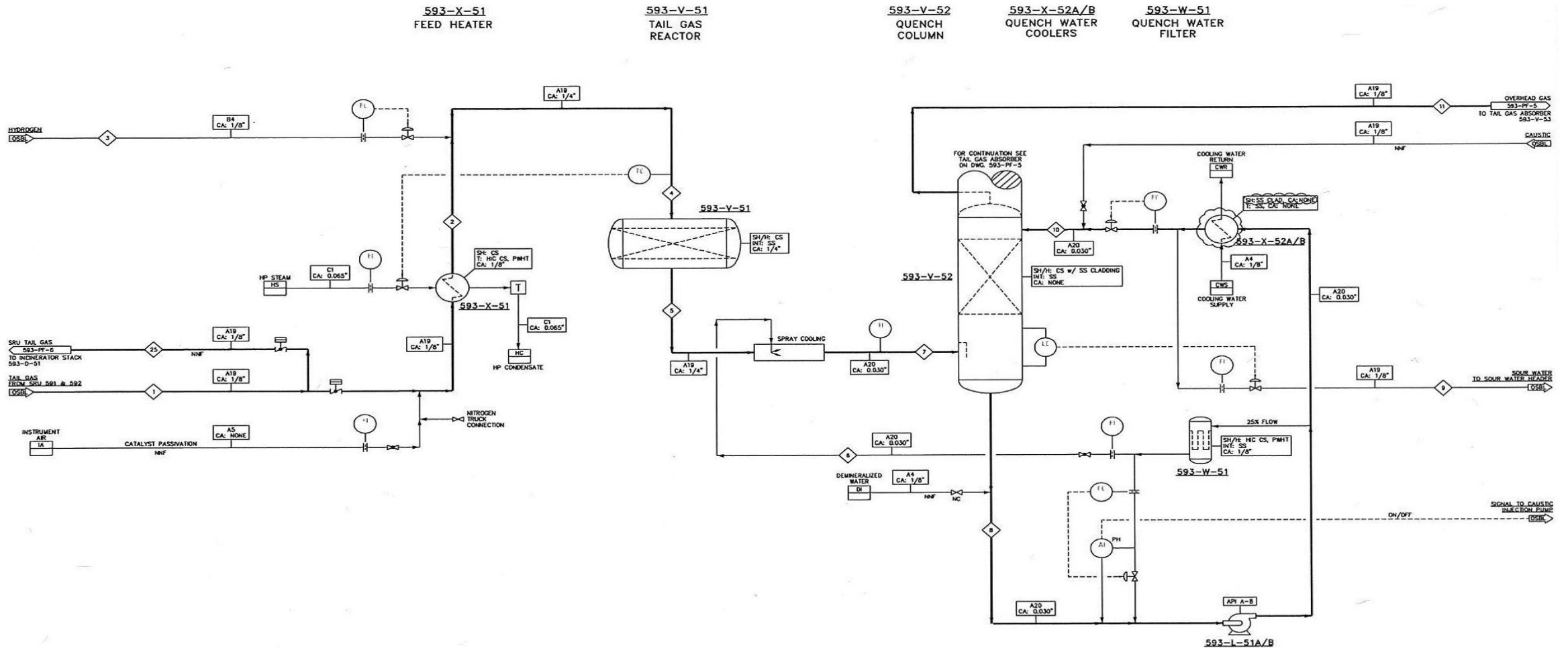
The Alliance team consulted the Phillips 66 Bartlesville lab to identify a contaminant that could cause the pressure excursions.



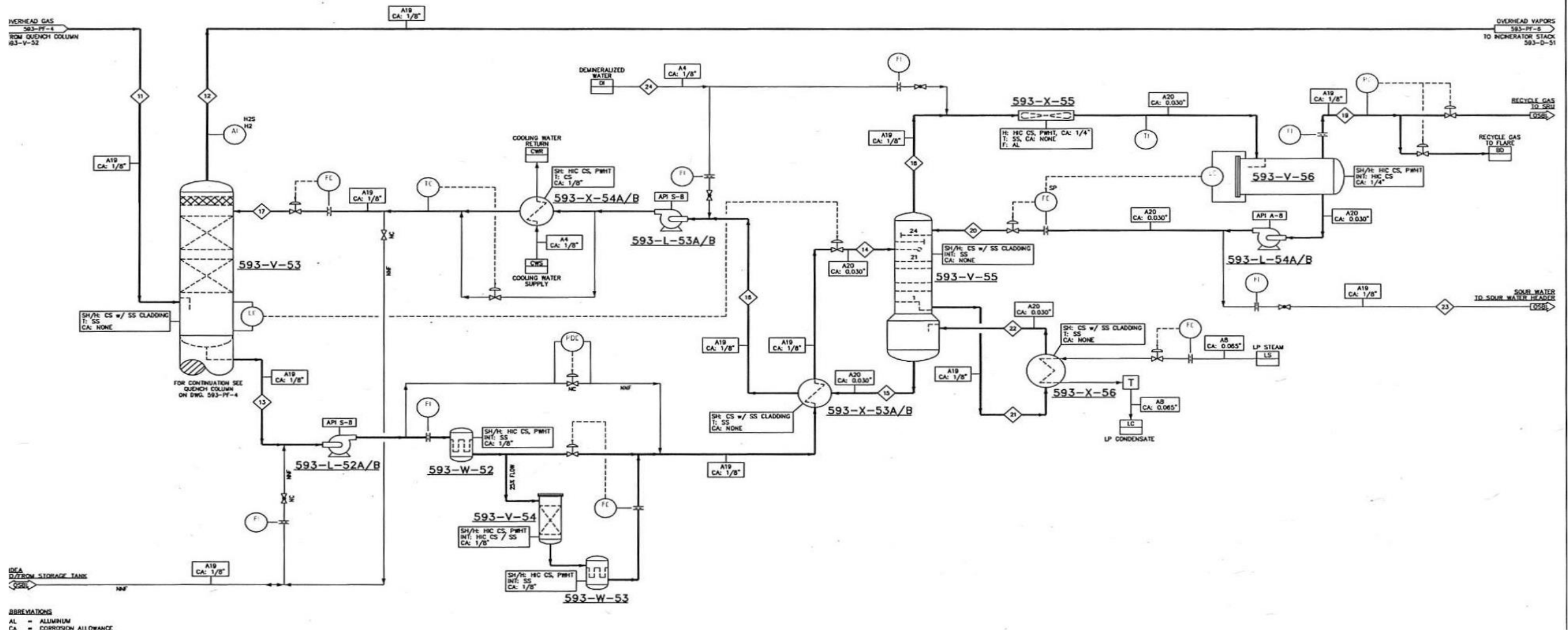
BACKGROUND – NEED FOR A NEW TAIL GAS UNIT

- Alliance refinery has two SRU units that operate in parallel. Capacity < 300 LT/D
- Single TGT unit handled all Claus tail gas. Existing forced draft incinerator for startup and shutdown
- A new TGT was needed to comply with NSPS-J requirements when the existing TGT was undergoing turnaround maintenance and was consequently out of service
- New TGT would allow incremental sulfur processing capacity increase by removing hydraulic constraints in Claus tail gas piping

NEW TGT – Hydrogenation Reactor and Quench Column



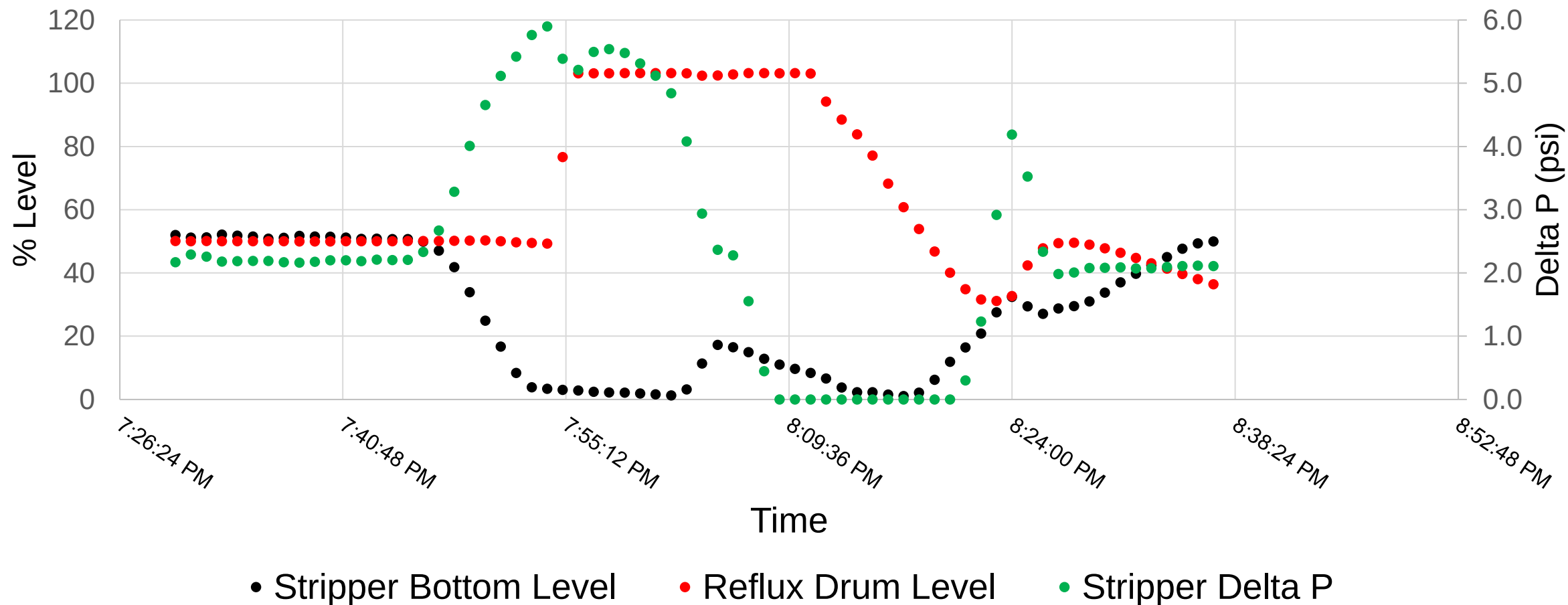
NEW TGT – MDEA Absorber and Regenerator



Mention packed vs. trayed columns, antifoam injection facilities, no hydrocarbon skim on reflux accumulator, purge, particulate and hydrocarbon filters on rich amine, demister pad on absorber, position of condensate injection

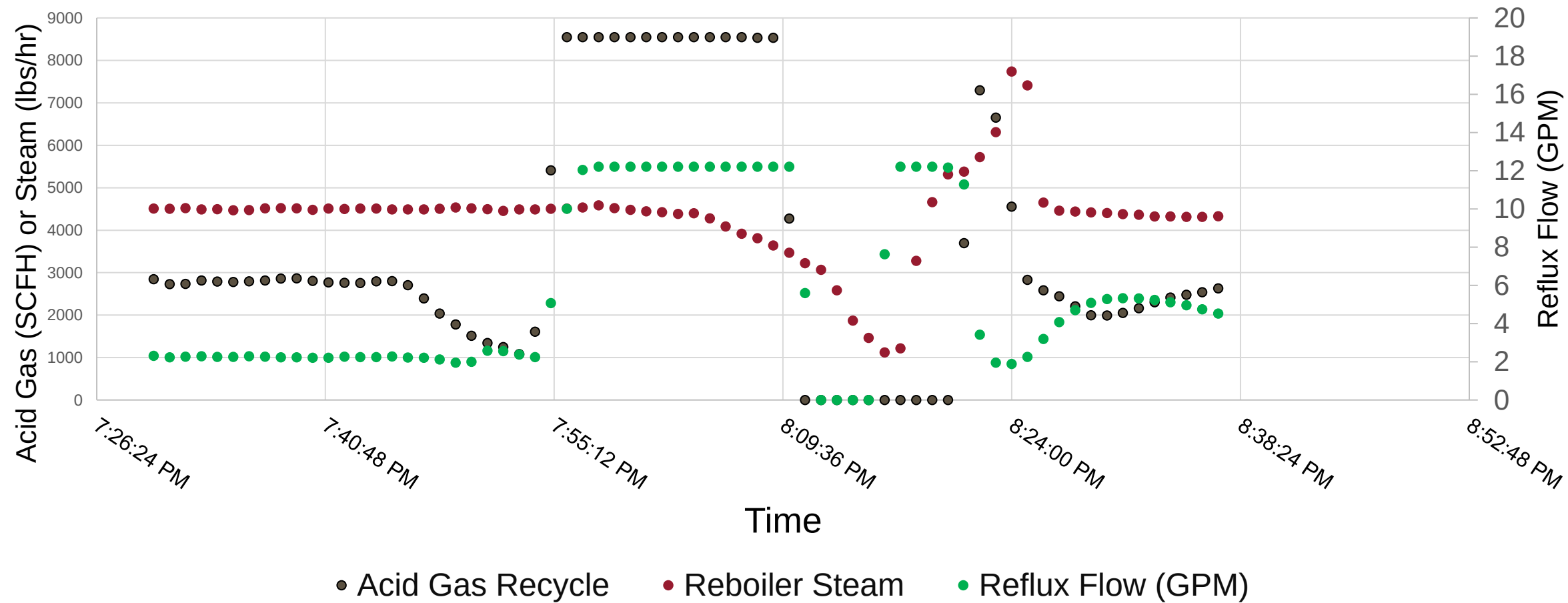
Regenerator Foaming – Part I

Figure 1: TGT Regenerator Performance



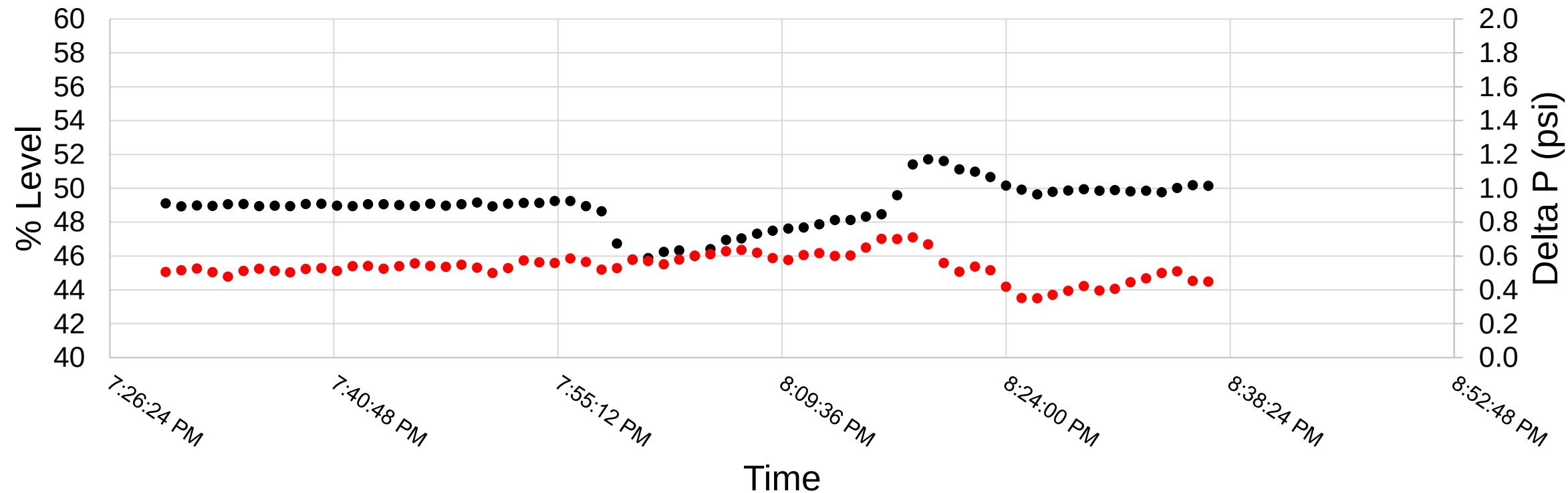
Regenerator Foaming – Part 2

Regenerator Acid Gas Recycle and Reflux Flow



Foaming Analysis – TGT Absorber – Minimal Foaming Behavior

Figure 3: TGT Absorber Performance

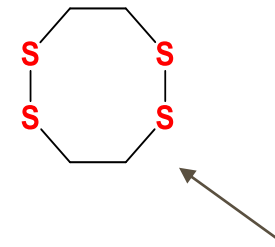


- Absorber Btms Level
- Absorber Delta P

Start Root Cause Analysis

Alliance was experiencing foaming problems on their new tail gas amine unit 593. The team believed that either hydrocarbons from the Reformer hydrogen stream or polysulfides could be contributing with the foaming situation. Amine samples were provided for analysis.

The Alliance team was interested on identifying the presence of polysulfides that might be formed from the reaction of SO_2 with amines. Polysulfides include both organic polysulfides (RS_nR) and inorganic polysulfides (H_2S_n).



An organic sulfide or thiane

Regenerator Tray Rating

- 24 Trays total – 3 reflux trays and 21 stripping trays
- Phillips 66 Fractionation Experts used commercial tray rating programs:
 - Jet flood ranged from 41-63% as the system factor varied from 1 to 0.65
 - Downcomer flood ranged from 42-64% as system factor varied from 1 to 0.65
 - Stripping trays not flooding
 - Stripping trays not believed to be operating in the spray regime

Reflux Accumulator Sizing

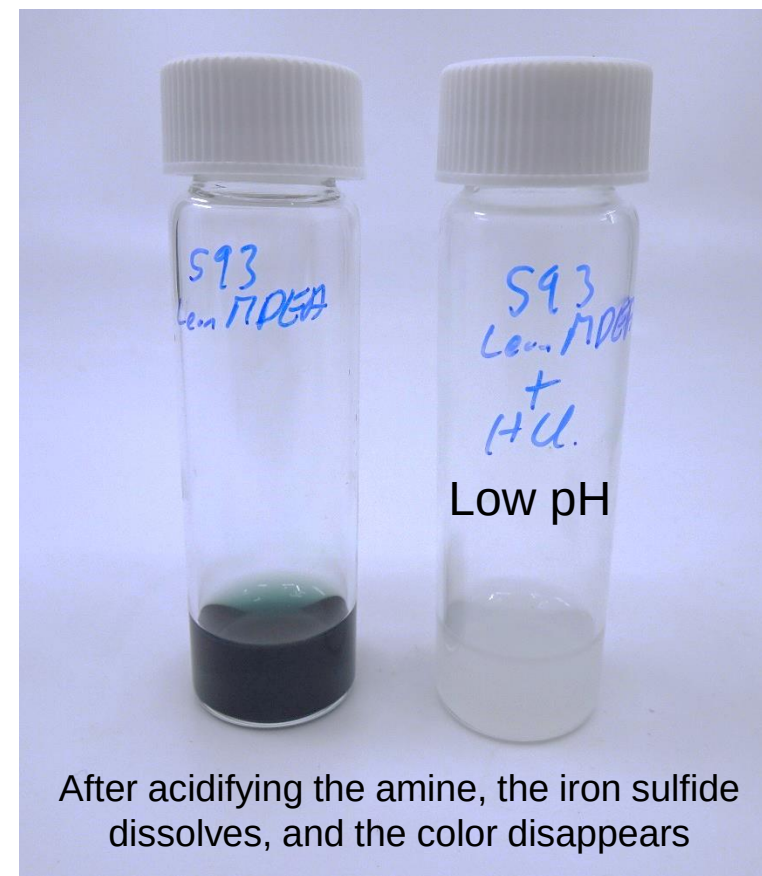
- Two Foot Diameter Horizontal Drum
- No hydrocarbon skim piping or instrumentation
- About 9 ft² area for gravity assisted separation in regenerator. Only about 1.5 ft² of gas flow area in the reflux drum at 50% full with gravity working perpendicular to the flow direction
- Foaming Mitigation was not considered in the design of this drum!

IC Analysis of the amine sample

- This lean amine sample result was originally thought to be result of SO₂ breakthrough
- Notice very high sulfide result – which is high lean loading
- The presence of sulfite, sulfate and thiosulfate are likely as a result of oxidation of the lean loading.
- No reaction with SO₂ is detected.
- Very high sulfide result – this is really rich amine based on sulfides – explains green and black amine samples

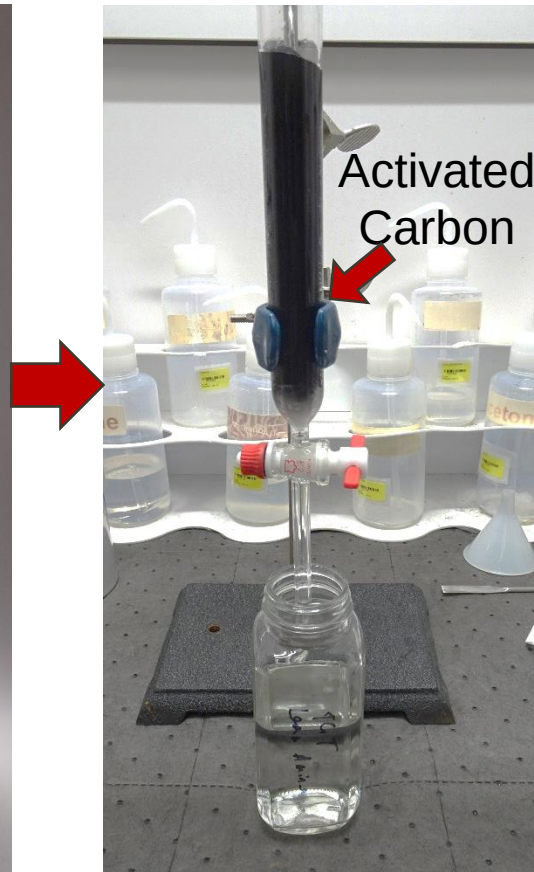
	593-102 TGT Lean MDEA
	09-Jun-21 09:00
Ions (µg/mL)	
Sodium (Na)	1.64
Ammonium	5.56
2-methylaminoethanol	586.87
Methyl diethanolamine	130539.75
Diethanolamine	1685.13
Chloride (Cl-)	31.65
Nitrite	<0.1
Nitrate	<0.1
Phosphate	<0.1
Sulfate	894.61
Sulfite	535.62
Thiocyanate	<0.1
Thiosulfate	1503.38
Acetate	<0.1
Formate	76.96
Sulfide	4107.66
Carbonate	1715.21

Origin of Blue-Green Color in Amine Sample



- The Emerald greenish color is known to be from the presence of extremely small colloidal iron sulfide particles in solution.
- Acidification of the amines with hydrochloric acid dissolves the iron sulfide particles making the color disappear.

Removal of Amine Color with Activated Carbon



- The current iron sulfide particles cannot be removed with filters (0.45 microns) but activated carbon can help remove them (see picture).
- The colloidal iron sulfide particles will eventually agglomerate into filterable particles.

Foaming Propensity Test



As received Lean Amine



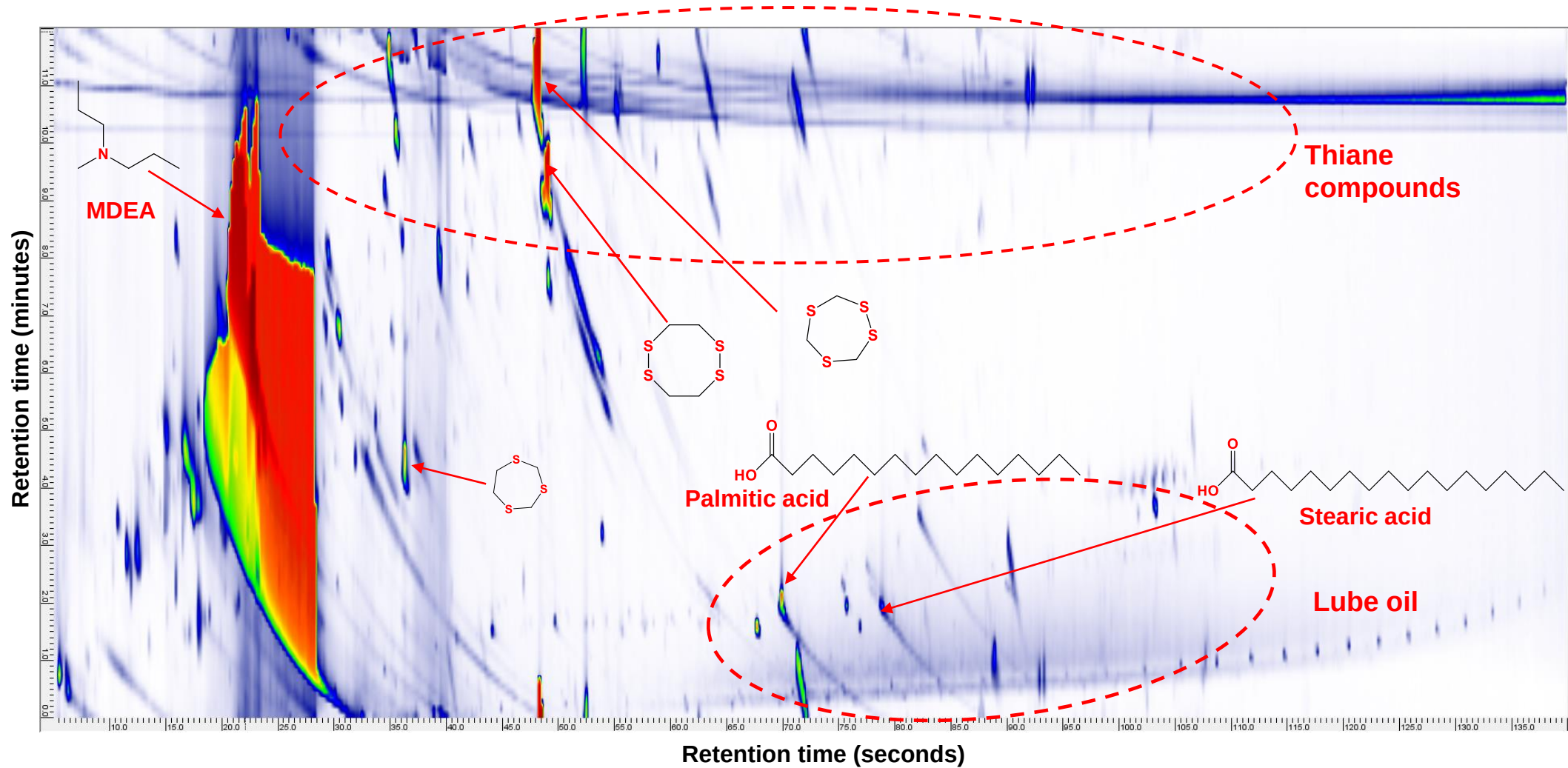
After Activated Carbon Treatment

- The as received lean amine shows a higher foam column compared with the amine after activated carbon treatment.
- Passing the lean amine through activated carbon helps remove organic compounds that contributes with foaming.

Antifoam and Activated Carbon Design

- The existing polypropylene glycol antifoam was effective at reducing foam in the unit. The activated carbon vendor said that its carbon, Sorbamine 4x10, would remove the antifoam from the amine.
- Simple shake tests showed more foam in samples of amine leaving carbon beds vs. those samples taken before the carbon beds. Phillips 66 interpreted this data as indicating carbon bed was spent.
- Amine flowrate limited to 28 GPM based on 15 minutes minimum contact time in carbon bed per vendor
- The unit was designed with single antifoam injection point into lean amine
- Phillips 66 had to add an antifoam injection point so that the antifoam would not have to pass through the carbon bed
- Antifoam added to new injection point on regenerator reflux was effective for controlling pressure excursions due to foaming

GCxGC MS of Amine Extract



- The amine sample shows the presence of thianes, lube oil, palmitic/stearic acid (potentially rust inhibitor or metal working additives).
- The organic acids in the presence of the amine can form a salt that behaves like a surfactant (soap) and contribute to foaming.

Possible Sources of Thianes

- Air safe presulfided catalyst used with Criterion catalyst – TOTSUCAT® process
- This process uses H₂S, hydrogen, and heat in a vapor phase to sulfide the catalyst. It does not have any thianes or polysulfides in the process per vendor feedback.
- Lean loading was very high. Is it possible that air in the sample bottle could have reacted with H₂S in amine solution to make thianes.
- Any data in our industry that indicates thianes would be a foaming agent? None that we know of.
- No traditional inorganic polysulfides found.

Summary of Operating Improvements

- Increased steam to reboiler to target 248°F on regenerator overhead. This move was made to decrease lean loading in amine, reduce iron sulfide particle generation, and reduce H₂S vapor pressure over the lean amine to reduce stack SO₂ emissions.
- Added antifoam injection points so that antifoam doesn't have to pass through carbon beds on rich amine before entering the regenerator
- Reduce amine circulation through carbon filters so that amine flow was within design flow rates. Carbon filters at the new TGT are installed on the rich amine piping. Carbon can be used to remove contaminants that can cause foaming, such as fatty acids, and also to remove submicron iron sulfide particles per Bartlesville experiments
- Established a constant purge rate of 2 GPM from the amine regenerator overhead accumulator to remove contaminants from the system. Helps remove heavy hydrocarbons that might accumulate due to their presence in reformer hydrogen

Conclusions

- The amine sample shows presence of lube oil and palmitic/stearic acid additives. The acids which potentially originate from rust inhibitors or metal working additives, would react with the amines forming a surfactant (soap) causing foaming. Phillips 66 believes these fatty acids are the root cause of the foaming.
- New equipment in amine service should be rinsed with alkaline material to remove lubricants from new equipment. Low strength caustic ($< 10\%$ wt NaOH) has been recommended by operating companies for years.
- Reducing steam to mitigate foamovers can exacerbate foaming by increasing lean loading to such an extent that iron sulfide particulates which stabilize foam are created by the high lean loading.
- Antifoam injection facilities must be provided to both amine regenerators and absorber. Antifoam can't travel through an activated carbon bed.

Conclusions

- The dark green color of the amine is due to the presence of extremely small colloidal iron sulfide particles.
- Thianes were present but no inorganic polysulfides. No reason to believe thianes are a foaming agent at this time.
- The colloidal iron sulfides in the sample could not be removed by normal filtration. Activated carbon was shown to remove the iron sulfide particles. Over time the particles can agglomerate and could be filtered out.
- It is not clear what advantage having a trayed regenerator vs. a packed regenerator provides in a tail gas unit, especially when the column diameter is only three feet. Phillips 66 operational experience has been that trayed regenerators are more likely to foam than packed regenerators.