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# Investigation and diagnosis of startup foaming issues at a new tail gas treater

In May 2021, Phillips 66 started up a new methyl diethanolamine (MDEA)-based tail gas unit at its Belle Chasse, Louisiana, refinery. Shortly after startup, foaming in the amine regenerator forced the unit to shut down. Amine manufacturers had declared *force majeure* after the February 2021 cold snap in Texas, so the refinery was forced to find alternative solutions to changing out the amine. This article will discuss interpretations of ion chromatography (IC), along with comprehensive two-dimensional gas chromatography-mass spectrometry results that pertain to the root cause of foaming. Also discussed will be acceptable regenerator steam and reflux accumulator purge rates, the appropriate antifoam injection locations, the use of carbon beds for contaminant removal, and the utilization of carbon beds to remove submicron iron sulfide particles, as well as tray ratings, equipment design details and sulfur recovery unit (SRU) operation.

**Background.** Prior to 2021, the Belle Chasse refinery operated with two parallel Claus SRUs that sent tail gas to a single MDEA-based tail gas unit. The refinery could divert SRU tail gas from either SRU to a single forced draft incinerator during startups, shutdowns and emergencies. The refinery needed a new tail gas treating unit (TGTU) to provide redundant TGT capacity for the refinery, thus allowing the refinery to continue to operate and comply with New Source Performance Standards (NSPS) Subpart J requirements while the existing TGTU was undergoing turnaround maintenance and was consequently out of service.

**New TGTU design—Process flow diagram.** The new TGTU was designed to handle Claus tail gas from two SRUs that have an operating capacity of roughly 50-long-tpd and 75-long-tpd sulfur, respectively. A new natural draft incinerator was provided to complement the existing incinerator.

Claus plant tail gas from either SRU can be sent to the new TGTU. The Claus plant tail gas is first heated by a 600-psig steam heater to attain adequate reaction temperatures for the cobalt molybdenum (CoMo) catalyst to convert sulfur species to hydrogen sulfide (H<sub>2</sub>S) (FIG. 1). The hydrogen necessary for the reactions in the CoMo catalyst bed to proceed is supplied by reformer hydrogen. There is no waste heat boiler downstream of the CoMo catalyst bed. The new TGTU was originally designed with a spray cooler on the quench column inlet piping, but the spray cooler was never installed. The

quench water heat exchangers, which use cooling water, provide all the cooling for the quench column. The quench column has a single bed of random packing. The circulating quench water has a filter designed for 25% of the normal quench water flow. Quench water pH is continuously monitored online upstream of the quench water coolers. If the quench water pH drops, caustic [sodium hydroxide (NaOH)] is added automatically to increase the pH of the quench water.

The MDEA section of the TGTU uses generic MDEA. Designed MDEA circulation is 130 gpm of 30 wt% MDEA solution. The 4 ft-diameter MDEA absorber is a column with two 12 ft-deep beds of random packing and an overhead demister (FIG. 2). Absorber overhead is sent directly to the incinerator. A carbon bed is provided on the rich amine leaving the absorber. Particulate filters are provided upstream of the carbon bed to prevent

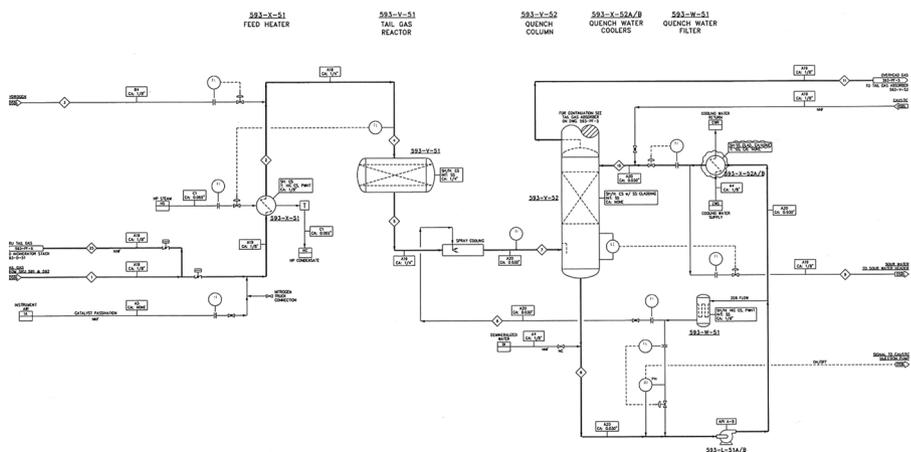


FIG. 1. CoMo reactor and quench column.

it from plugging, and provided downstream of the carbon bed to catch carbon particles. Rich amine passes through two lean/rich shell-and-tube heat exchangers before entering the trayed amine regen-

erator. The 3-ft-diameter amine regenerator has an overhead air-cooled heat exchanger designed to cool the overhead gases to 120°F (48.89°C). Reflux is sent back to the three-tray reflux section in the

amine regenerator. Facilities are provided to purge a small portion of the reflux. A cooling-water heat exchanger cools the lean amine to a 100°F (37.78°C) design temperature before entering the absorber. The quench column, amine absorber and amine regenerator are stainless-steel clad.

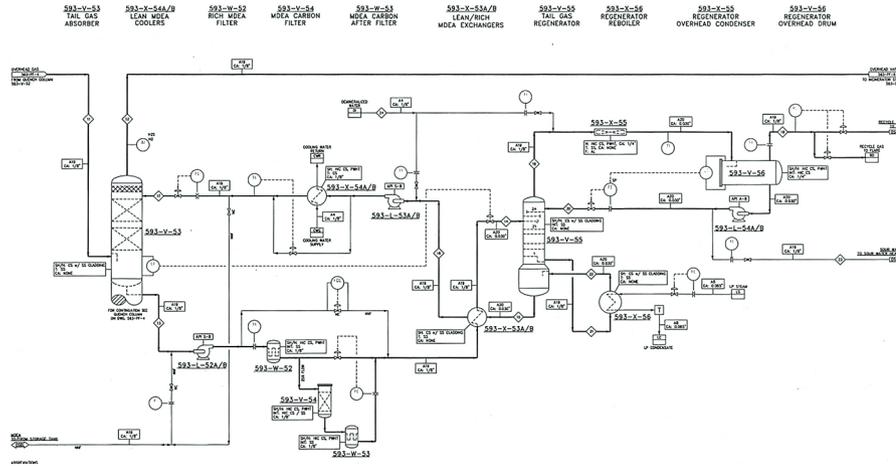


FIG. 2. MDEA section of the new TGTU.

**Equipment preparation highlights.**

New towers and piping were washed with hot condensate to remove debris and chemical contaminants from the new equipment. The tail gas catalyst was pre-activated offsite with a vendor's proprietary process to avoid the use of acid gas for presulfiding, and so that the catalyst could be stored in situ without a nitrogen blanket.

**Initial startup.** The tail gas catalyst bed temperature was raised to a minimum of 420°F (215.56°C) before adding H<sub>2</sub>S-containing gas to the TGTU. Plant nitrogen was used as the process gas to heat the catalyst. MDEA solution was circulated for 5 d before any H<sub>2</sub>S-containing gases were routed to the new TGTU. Quench column circulation was also established before adding feed. The unit started up in the second week of May 2021.

Claus tail gas from the smaller Claus unit was initially added to the new TGTU. This Claus unit does not process ammonia acid gas from a sour water stripper and would be a stable source of Claus tail gas for the startup. The MDEA solution was water-white before Claus tail gas was added. Within hours of introducing Claus tail gas, however, the amine solution turned black. Engineering staff interpreted the source of the black color to be iron sulfide particles generated as the H<sub>2</sub>S-containing amine began establishing a protective iron sulfide on carbon-steel piping and equipment. Engineering's initial course of action was to let the new 10-micron particulate filters remove particles in the amine. At this time, some differential pressure excursions were reported in the amine regenerator. The operations team maintained staffing at high levels to accommodate the frequent filter changes. Within 72 hr, the amine was water-white again, although frequent filter changes were required. Unfortunately, even though the amine solution color was good, foaming issues on the amine regenerator were frequent and severe enough that stack emissions were rising.

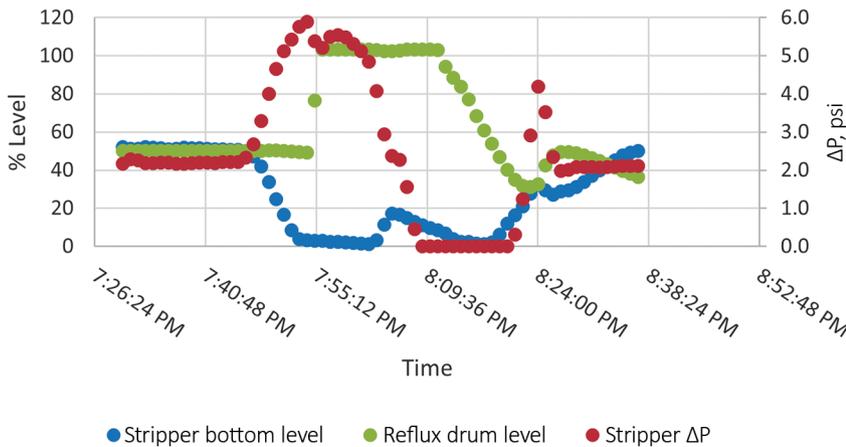


FIG. 3. TGTU regenerator performance.

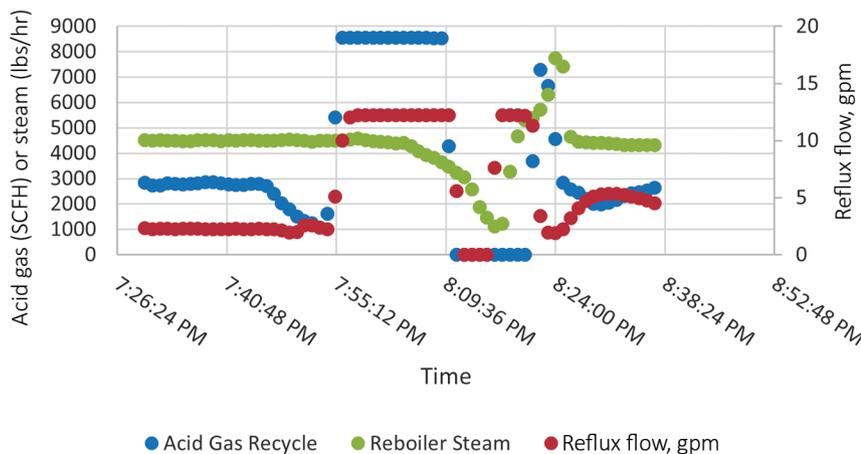


FIG. 4. TGTU regenerator performance.

**Foaming diagnosis.** The TGTU amine regenerator performance during 1 hr in June 2021 is illustrated in FIGS. 3 and 4. The stripper bottom level and reflux drum level shown in FIG. 3 are stable until the stripper tray pressure drop starts rising quickly at approximately 7:45 p.m. Minutes later, the stripper bottom level drops quickly, followed by the reflux drum level quickly rising to 100%. FIG. 4 shows that acid gas recycle initially drops when the stripper pressure drop starts rising, and then goes off scale high when all the liquid holdup in the column is pushed overhead into the reflux accumulator. The behavior shown in FIGS. 3 and 4 is consistent with foam starting first in the stripping section of the regenerator, with amine unable to reach the bottom of the regenerator and then “burping” into the reflux accumulator. FIG. 4 also indicates reflux flowback to the stripper going off scale high as the operations team attempted to reduce the reflux accumulator level. FIG. 4 shows that steam had to be cut to lower the stripper pressure drop and to avoid a reflux accumulator overflow. FIGS. 3 and 4 indicate classic foaming behavior, with foaming far worse in the trayed amine regenerator than in the packed amine absorber. The TGTU MDEA absorber’s  $\Delta P$  and level control were not affected as significantly during the same time interval. The TGTU absorber bottoms level was maintained in the 45%–52% range, and the TGTU absorber  $\Delta P$  stayed within a tight range of 0.35 psi–0.71 psi. Similar behavior repeated itself during similar time periods for the next few weeks.

**SRU troubleshooting.** The larger 75-long-tpd SRU had plugging concerns during the startup of the new TGTU. Sulfur carryover from the final condenser into the TGTU catalyst bed was also hypothesized. It was initially thought that these issues might be related to TGTU foaming, and troubleshooting efforts began to resolve these issues.

The largest pressure drop in the SRU was measured across the first converter catalyst bed. Heat transfer in the first converter bed reheater was also severely limited, resulting in poor SRU conversion during the new TGTU startup. During this time, a low outlet temperature from the first sulfur condenser was evident. The plugging could be temporarily alleviated by unplugging the seal leg, leav-

ing the first condenser. When the first seal leg started flowing liquid sulfur, the performance of the first reheater gradually improved as sulfur melted away from the first reheater. As the reheater performance improved, the temperature of the first catalyst bed started rising, improving overall sulfur plant conversion.

At this time, the refinery hypothesized that there was a water leak in the first condenser that was plugging the sulfur rundown leg and allowing sulfur to accumulate and then get entrained and carried into the first reheater where the sulfur stuck onto cold parts of the reheater. There were also some thoughts that the carryover was due to poor heat transfer from the steam tracing on the aboveground sulfur seal legs. To prove conclusively that there was a water leak from the condenser and not from the upstream waste heat boiler, the refinery decided to conduct radioactive tracer testing on the upstream waste heat boiler and the first condenser.

Radioactive tracer was injected into the boiler feed water that supplied the waste heat boiler and first condenser. Tracer was injected on separate days into the boiler and condenser. Tracer levels were measured in the TGTU’s quench water on each day. Radioactive tracer tests showed conclusively that the first condenser was leaking—and that there was no leak in the waste heat boiler. Maintenance efforts could be concentrated on fixing the first condenser.

### Sulfur carryover from the final condenser and TGTU catalyst activity.

Heat transfer issues around the final seal leg in the larger 75-long-tpd sulfur plant led to a decision to raise the final condenser temperature to 290°F–300°F (143.33°C–148.89°C) in June 2021. Shortly after raising the temperature, refinery personnel noticed that the top of the TGTU hydrogenation catalyst bed activity started dropping, while the middle of the catalyst bed increased (FIG. 5). Total catalyst activity—in terms of  $\Delta T$ —remained the same (FIG. 5).

Phillips 66 interpreted this catalyst behavior as sulfur entrainment affecting catalyst bed performance. Sulfur hydrogenation is a slower reaction vs. other reactions that occur in the tail gas catalyst bed, and, consequently, the bulk of the tail gas reactor exotherm has been shifted lower in the bed. There was no change in emissions associated with the changing  $\Delta T$  in the tail gas catalyst bed.

SRU troubleshooting efforts began before laboratory results of the TGTU amine analysis were obtained. While SRU issues contributed to overall SRU/TGTU performance, SRU issues were not the root cause of the foaming issues.

**Amine regenerator tray rating.** Phillips 66 fractionation experts rated the amine regenerator stripping trays at typical operating rates prior to the foaming events. Jet flood ranged from 41%–63% as the system factor was varied from 1

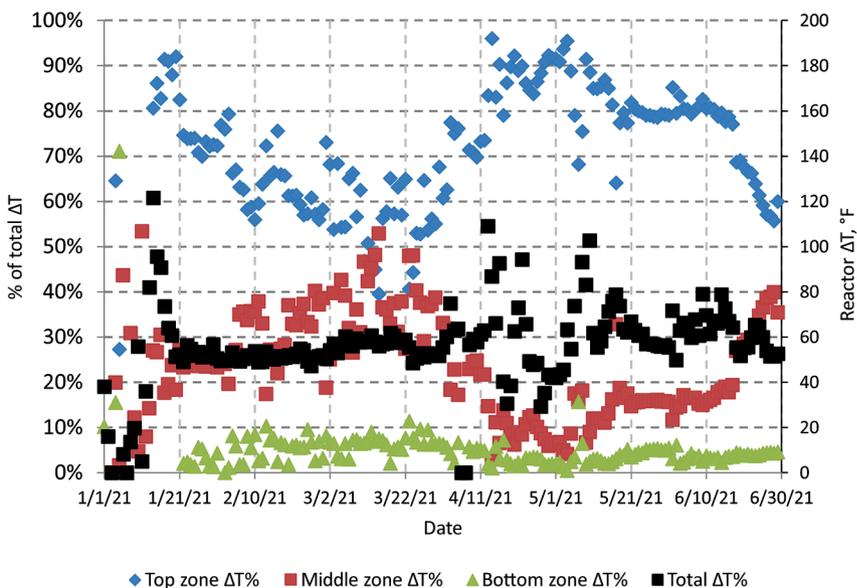


FIG. 5. TGTU reactor zone’s  $\Delta T\%$  and total  $\Delta T$  (°F).

to 0.65. Downcomer flood ranged from 42%–64% for the same range of system factors. The trays were not believed to be flooding. Dry tray pressure drop was greater than 1 in. H<sub>2</sub>O, which is above typical weeping limits.

The stripping trays have positive downcomer clearance and were running slightly above the weir loading where unsealing has been observed. The trays were not believed to be operating in the spray regime.

**Activated carbon beds and iron sulfide removal.** Amine samples taken during a foaming event were sent to the Phillips 66 lab in Bartlesville, Oklahoma. The samples were dark green to blue in color (FIG. 6), and the refinery wanted to determine whether the foaming was related to either: 1) reformer hydrogen used for the tail gas catalyst that could have aromatics in it, or 2) the presence of polysulfides that amine vendors have stated could be formed from the reaction of sulfur dioxide (SO<sub>2</sub>) and tail-gas amine. The amine turned this color again, even though its color had previously been markedly improved by using the unit's rich amine par-

ticulate filters. The Phillips 66 Bartlesville lab showed conclusively that the emerald green color was due to the presence of extremely small colloidal iron sulfide particles. After acidifying the amine, the iron sulfide dissolved, and the color disappeared from the solution (FIG. 6).

The Bartlesville lab passed the amine solution through small 0.45-micron filters, a smaller-than-practical field filter element. The 0.45-micron filters were ineffective at removing the color-producing particles. The lab then tested activated carbon as a filter media, and it was found to be effective (FIG. 7). The lab ran foam tests, using air as the process gas. The refinery amine showed a higher foam column *before* passing through activated carbon, rather than *after* passing through it (FIG. 8). Both color and foaming propensity concerns were mitigated after passing the amine through activated carbon. The authors believe that the foaming propensity was reduced because the activated carbon was removing organic compounds, such as surfactants that contribute to foaming. Further, the authors believe that the activated carbon removed the colloi-

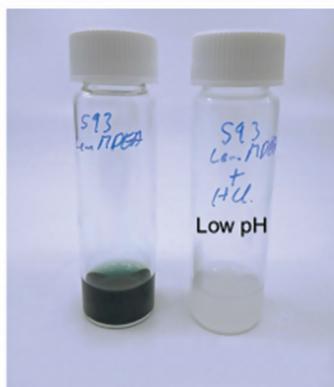
dal iron sulfide particles, thereby reducing the stability of any foam that was formed.

To make optimum use of the carbon bed as an iron sulfide filtration device, the carbon vendor was asked if there were any limits on amine circulation through the carbon bed. The recommended practice per the vendor was 2 gpm/ft<sup>2</sup> to 4 gpm/ft<sup>2</sup> for amine flow through the carbon bed, with a minimum contact time of 15 min. Based on that feedback, amine flow through the carbon bed was limited to about 28 gpm, which corresponded to a contact time of about 24 min. Flow-rates higher than 28 gpm would reduce the efficiency of the carbon bed for iron sulfide removal.

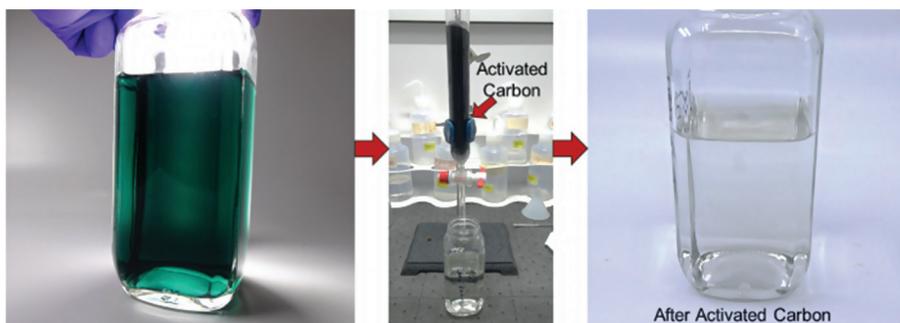
**Root cause of foaming.** A graphical representation of the results of a comprehensive two-dimensional gas chromatography-mass spectrometry analysis of the refinery tail gas amine is shown in FIG. 9. The results indicated the presence of thianes, which are sometimes called “organic polysulfides,” and the presences of fatty acids, including palmitic and stearic acids. The fatty acids are foam-producing agents commonly used in commercial soaps. Fatty acids react with a base, such as caustic or an amine forming a fatty acid salt, which, by definition, is a soap or surfactant. Therefore, the presence of fatty acids in an amine system is expected to cause foaming. Most likely, these fatty acids came from machining or lubricating oils used in metal-fabrication processes. The authors believe that these fatty acids are the root cause of the foaming and that thiane compounds are not surface-active agents and are not responsible for the foaming. No inorganic polysulfides were found.

Phillips 66 checked with the vendor that preactivated the catalyst with a proprietary process<sup>a</sup>. This process uses H<sub>2</sub>S, hydrogen and heat in a vapor phase to sulfide the catalyst. It does not have any polysulfides in the process, per vendor feedback. At this time, the authors do not know where the thianes originated. A hypothesis is that the amine samples were shipped to the Bartlesville lab without a nitrogen blanket. Oxygen in the air mixed with H<sub>2</sub>S in the amine due to high lean loading may have resulted in thiane production; however, this hypothesis has not been verified.

**Antifoam.** Based on laboratory tests, a vendor-supplied polyglycol antifoam



**FIG. 6.** Samples of amine taken during a foaming event. The samples were dark green to blue in color (left). After acidifying the amine, the iron sulfide dissolved, and the color disappeared from the solution (right).



**FIG. 7.** Removal of amine color with activated carbon.

was effective in this case. Unfortunately, the unit was not built with antifoam injection facilities that would allow antifoam injection directly into the amine regenerator where the foaming problems were manifesting. The only as-built antifoam injection point was directed into the amine absorber, a packed column where foam is less likely to occur than in the trayed regenerator. Any antifoam injected into the absorber would have to pass through the activated carbon beds, where it would be adsorbed before getting into the trayed regenerator. Consequently, the refinery had to build a new antifoam injection facility that allowed antifoam injection into the regenerator reflux piping. The antifoam was effective when used at this location.

The unit engineer contacted the carbon vendor and verified that the activated charcoal used in the unit<sup>b</sup> will adsorb polypropylene glycol antifoam. Simple shake tests indicated that the amine was foaming more on the outlet of the activated carbon bed than on the inlet of the carbon bed, which indicated that the carbon bed was completely spent at times and needed to be changed out. It is also possible that the activated carbon was removing the antifoam and preventing its access to the regenerator. The unit engineers changed out the activated carbon to a fresh bed prior to the next startup.

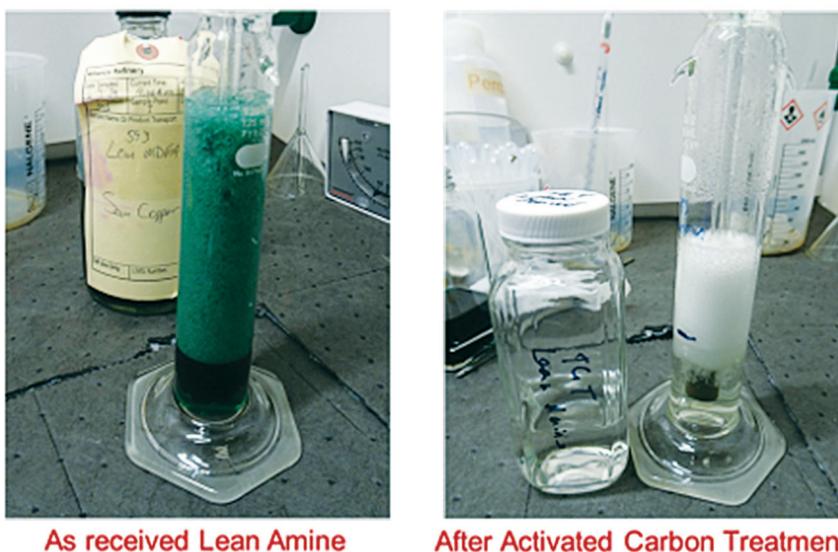
**TABLE 1.** IC analysis of the amine sample

Ions, µg/mL	593-102 TGT lean MDEA
Sodium	1.6
Ammonium	5.6
2-methylaminoethanol	586.9
MDEA	130,539.7
Diethanolamine	1,685.1
Chloride	31.7
Nitrate	< 0.1
Phosphate	< 0.1
<b>Sulfate</b>	<b>894.6</b>
<b>Sulfite</b>	<b>535.6</b>
Thiocyanate	< 0.1
<b>Thiosulfate</b>	<b>1,503.4</b>
Acetate	< 0.1
Formate	76.9
Sulfide	4,107.7
Carbonate	1,715.2

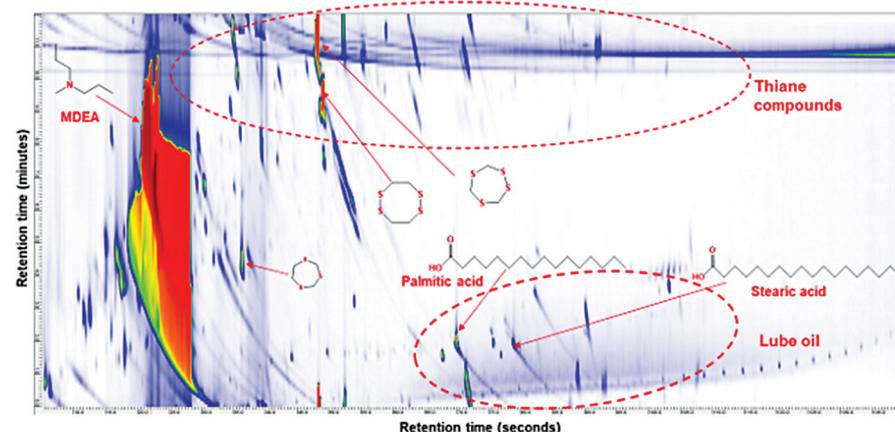
**Ion chromatography.** IC results from a sample of lean TGT amine are shown in **TABLE 1**. Thiosulfate, sulfite and sulfate are present at noticeable levels. These data were initially interpreted as the results of an SO<sub>2</sub> breakthrough, which could explain the green amine, since SO<sub>2</sub> is corrosive in amine. However, the sulfide content was very high for tail gas MDEA (4,107 ppmw). High sulfide content means that the lean H<sub>2</sub>S loading of the sample is high. This sulfide content or lean loading is so high that it would explain any stack emissions issues encountered at this unit. When lean (or rich) amine loading is high, thiosulfates, sulfites and sulfates are very likely to be generated by oxygen in the sample bottles contacting the amine solution and reacting with the sulfides. Based

on this IC result, there was no reason to focus on SO<sub>2</sub> breakthroughs. The focus was put on amine regenerator operation to reduce the lean loading of the amine. It is most plausible that much of the color and iron sulfide in the amine resulted from inadequate regeneration, leading to high HS<sup>-</sup> concentrations in the amine contacting the hot section of the amine plant that has carbon-steel components.

Another reason to strip the amine adequately in the regenerator is to remove heavy hydrocarbons that might accumulate in the tail-gas amine. The source of hydrogen in this refinery is reformer hydrogen that can contain small amounts of aromatic hydrocarbons. Maintaining adequate tail gas regenerator overhead temperatures [ $> 115.56^{\circ}\text{C}$  ( $> 240^{\circ}\text{F}$ )]



**FIG. 8.** Foaming propensity test.



**FIG. 9.** A graphical representation of the results of a comprehensive two-dimensional gas chromatography-mass spectrometry analysis of the refinery tail gas amine.

can only assist in removing hydrocarbons from the amine. Engineering staff also made the decision to continuously purge 2 gpm from the reflux accumulator as a method to continuously remove hydrocarbons and other foaming species from the amine.

**Reflux accumulator sizing.** The reflux drum is a horizontal 2-ft-diameter drum, which was not overly effective at stopping foam once it rolled out of the column. There is a roughly 9-ft<sup>2</sup> area for gravity-assisted vertical separation in the regenerator upstream flowing into a horizontal 2-ft piece of pipe for the reflux drum. With the reflux drum operated half full, there is roughly 1.5 ft<sup>2</sup> of flow area, and gravity is working at a 90° angle to the gas flow. Foaming event mitigation was not considered in the design of the tail gas unit, but this should be considered for future Phillips 66 designs. The tail gas reflux drum does not include a hydrocarbon skim.

**Summary of operating improvements.** After these collective learnings, several improvements were implemented at the refinery, including:

- Increasing steam to the reboiler to target 120°C (248°F) on regenerator overhead. This move was made to decrease lean loading in amine, reduce iron-sulfide particle generation, and decrease H<sub>2</sub>S vapor pressure over the lean amine to reduce stack SO<sub>2</sub> emissions.
- Adding antifoam injection points, so that antifoam does not have to pass through carbon beds and extra piping and equipment in the rich amine before entering the regenerator.
- Reducing amine circulation through carbon filters, so that amine flow was within design rates. Carbon filters for the new TGTU were installed on the rich amine piping. Carbon can be used to remove contaminants that cause foaming (e.g., fatty acids), and it can also remove submicron iron-sulfide particles, per Phillips 66 lab measurements.
- Establishing a constant purge rate of 2 gpm from the amine regenerator overhead accumulator to remove contaminants from the system. The purge rate helps to remove heavy hydrocarbons that might accumulate

otherwise, due to their influx from the reformer hydrogen.

**Takeaways.** The following are the primary takeaway points from the investigation of foaming in the TGTU:

- The root cause of the foaming was identified from the lab measurements as fatty acids from rust inhibitors or metalworking additives. The authors believe that iron sulfide particles were acting to stabilize foam in the regenerator. Removal of the iron sulfide particles, along with fatty acids, has mitigated foaming considerably. The removal of only iron sulfide may reduce foam stability, but it is not the root cause of foaming itself. The MDEA still needs a foaming agent—in this case, fatty acids—to exhibit the foaming shown.
- New equipment in amine service should be rinsed with alkaline material to remove lubricants from the new equipment. Operating companies have recommended low-strength caustic (< 10 wt% NaOH) for years. The amine columns were only rinsed with hot condensate before this startup.
- Reducing steam to the amine regenerator reboiler to mitigate foamovers or “burping” liquid overhead can be worse than the foaming itself. Improperly regenerated amine can lead to emissions excursions, just as foaming does. Phillips 66 has found that operating tail gas amine regenerators with a target overhead temperature of 118.33°C–121.11°C (245°F–250°F) is a reliable way to control contaminants that lead to foaming in tail gas amine regenerators.
- Antifoam injection facilities must be provided to both absorbers and regenerators, as antifoam should not have to travel through an activated carbon bed to reach a column.
- 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 3 ft. Phillips 66’s operational experience has been that a trayed regenerator is more likely to foam than the packed regenerator.

Industry experts suggest that packed towers can reduce the likelihood of foaming in the tail gas regenerator, provided there is proper liquid distribution. One further consideration is that, with large amounts of colloidal iron sulfide particles present, it is possible that packing would foul quickly, resulting in reduced separation efficiency in a packed amine regenerator.

- Activated carbon beds can be used to remove submicron colloidal iron sulfide particles. Although this is not desirable to the hydrocarbon removal capacity of the carbon beds, it is an effective stop-gap measure that can be considered to help preserve amine inventory. **HP**

#### NOTES

<sup>a</sup> Eurecat’s TOTSUCAT process

<sup>b</sup> Calgon Carbon Corp.’s Sorbamine, AT 4x10

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