# SO$_2$ Breakthrough under a Microscope[1]

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## Abstract

The effects of an SO$_2$ breakthrough can be outright devastating to a tail gas treating unit (TGU), and can include dissolved quench column piping, column internals failure, elemental sulfur plugging in the quench water loop, amine system corrosion, loss of selective treating performance, high emissions, and increased solvent makeup/reclaiming needs. These aspects are examined in the context of their chemistry along with techniques for prevention and mitigation. This paper studies how the interaction of NH$_3$ slipped from the SRU Reaction Furnace with varying levels of SO$_2$ ingress impacts the Quench Column pH and amine system performance. A surprising finding from this study is that a major SO$_2$ breakthrough can result from relatively minor (<15%) swings in Claus combustion air if poor analyzer maintenance and reliability practices exist. This work demonstrates how the first SO$_2$ breakthrough can be a self-fulfilling prophesy, review guidelines on setting quench water pH neutralization intervention targets, and investigate the survival of SO$_2$ beyond the quench system.

## Background

Without question, SO$_2$ breakthroughs can be one of the most devastating events for sulfur plant tail gas treating units. Consider some of the damage that can result:

**Quench water loop:**

- corrosion up to and including dissolved quench water piping and column internals,
- internals failure,
- elemental sulfur plugging,
- corrosion product plugging,
- loss of heat transfer leading to unit hydraulic capacity loss,
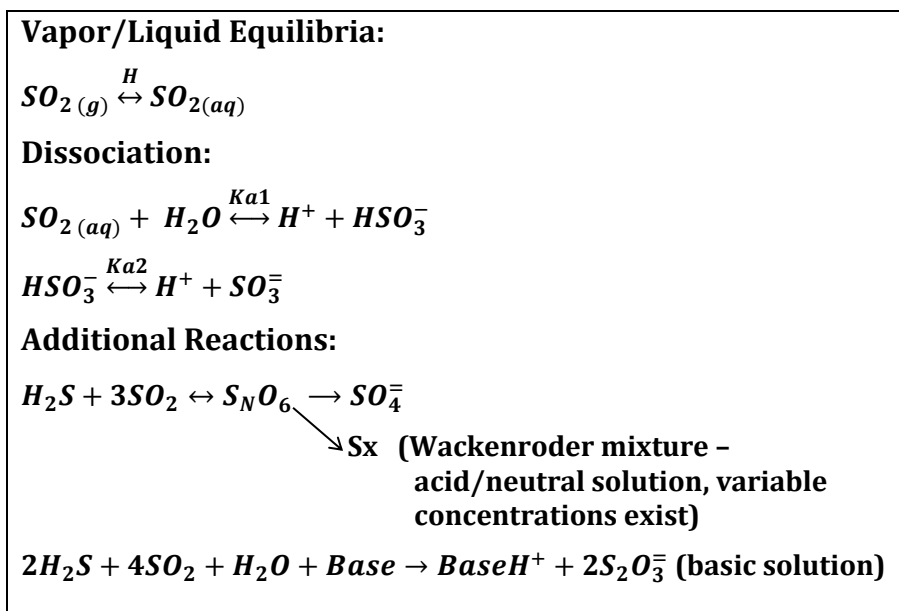- effect on waste water treating;

**TGU amine section:**

- sulfite, sulfate, thiosulfate heat stable salt build-up leading to accelerated corrosion through iron chelation,
- particulates load increase,
- loss of solvent treating capacity,
- plugged internals, loss of containment,
- amine degradation to DEA and MMEA,
- loss of selectivity leading to higher CO$_2$ recycle rates, increased hydraulic load throughout SRU/TGU train, higher COS and stack emissions.

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[1] Sulphur Middle East, 2017

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Table 1 shows the pathway and relevant chemical reactions that occur when $SO_2$ enters an aqueous solution. It is this chemistry that is responsible for the damage mechanisms described above.

**Table 1    SO₂ Breakthrough Simplified Chemistry**

> **Vapor/Liquid Equilibria:**
>
> $$SO_{2\,(g)} \overset{H}{\leftrightarrow} SO_{2(aq)}$$
>
> **Dissociation:**
>
> $$SO_{2\,(aq)} + H_2O \overset{Ka1}{\longleftrightarrow} H^+ + HSO_3^-$$
>
> $$HSO_3^- \overset{Ka2}{\longleftrightarrow} H^+ + SO_3^=$$
>
> **Additional Reactions:**
>
> $$H_2S + 3SO_2 \leftrightarrow S_NO_6 \longrightarrow SO_4^=$$
>
> $\searrow$ Sx  **(Wackenroder mixture –**
> **acid/neutral solution, variable**
> **concentrations exist)**
>
> $$2H_2S + 4SO_2 + H_2O + Base \rightarrow BaseH^+ + 2S_2O_3^= \text{ (basic solution)}$$

Keller[1] provides a thorough summary of causes and characteristics of SO₂ breakthroughs that happen in operation. In general, the types of SO₂ breakthroughs can be loosely categorized into:

- Mild SO₂ breakthrough with low or high H₂S
- High SO₂ with low H₂S breakthrough, and
- SO₂ only breakthrough – low and high levels without H₂S.

In this work, we use a "virtual" microscope in the form of the ProTreat® mass transfer rate-based process simulator, to examine what happens at the molecular and ionic chemistry level to accompany the macro-observations that are more familiar to those who have had the misfortune of needing to deal with an SO₂ breakthrough.


**Base Case – Normal Operations**

The sample is prepared for the Microscope by setting some basic assumptions regarding the plant operation prior to the SO₂ breakthrough, i.e. when everything is "normal". Figure 1 shows the overall flowsheet for the SRU/TGU train that was modeled, together with a few key plant details for the base case. The operating data and column details associated with this simulation are from a real operating plant. At the time of data collection, the Claus unit was operating towards the upper end of low-level oxygen enrichment. Consequently, there was plenty of excess hydrogen generated within the Claus unit itself from hydrogen cracking in the thermal section. The first column in Table 2 summarizes the critical key unit operating metrics for this operation and the more important parameters that were studied for the virtual SO₂ breakthrough.

# Figure 1    Claus/TGU Configuration Studied
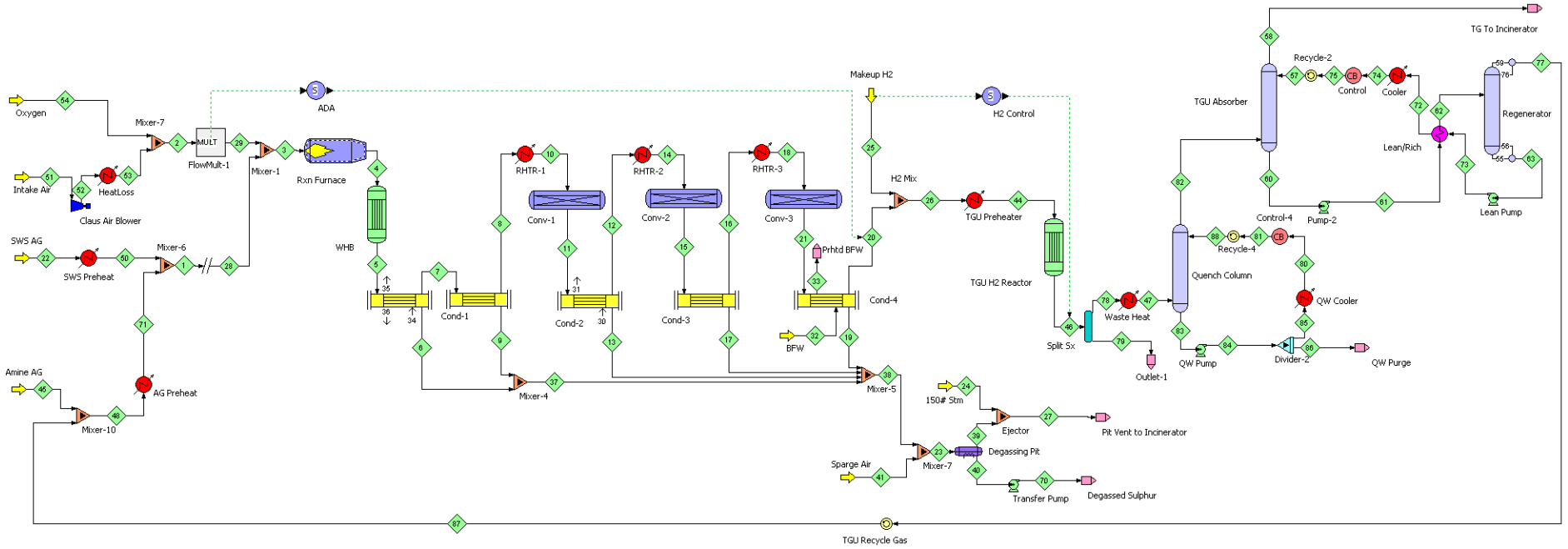
**SO₂ Breakthrough Case Studies**

One of the more common scenarios that can lead to an $SO_2$ breakthrough event results from either faulty or poorly maintained analyzers that are either ignored or placed in manual. The air demand analyzer (ADA in Figure 1) and Claus combustion trim air feedback control are perhaps the most important loops critical to keeping operational and in cascade control. The reasons will become quite evident after examining the case studies in this work. Within the TGU itself, the hydrogen analyzer ($H_2$ Control in Figure 1) is important to watch as excess hydrogen <u>must</u> be present to hydrogenate $SO_2$ and elemental sulfur to $H_2S$. Furthermore, the quench water pH analyzer can indicate when an $SO_2$ breakthrough is in progress so that mitigating actions can be taken.

To simulate the process of an $SO_2$ breakthrough in our virtual microscope, the Claus unit air demand feedback control loop was placed in manual. Hydrogen make-up was assumed to be in manual and held closed while perturbing the Claus combustion air (steam 29) upwards. Table 2 outlines key process parameters that change during this process. Percent excess Claus air refers to the amount of excess air relative to the amount required for a 2:1 ratio of $H_2S$ to $SO_2$ in the Claus tail gas. Cautionary parameters are shown in yellow. Damage can be expected for the parameters that are highlighted in red.

As excess air is increased in the Claus unit, the first sign of impending doom is the dramatic increase in the outlet temperature from the TGU Hydrogenation Reactor. If left going for long enough, most seasoned operators would notice this tattle tale. At roughly 5% excess air, the temperature across the catalyst bed has increased by 90°F, which is one of the reasons why this part of the plant is often refractory lined. At 10% excess air, the bed outlet temperature is a whopping 745°F! However, many of these events can occur quickly over the period of just seconds to minutes and be gone before the thermal mass of catalyst is fully heated up, masking the problem.

As excess air increases, the extra $SO_2$ being fed to the TGU Hydrogenation Reactor consumes more and more of the excess $H_2$. At 10% excess air, the virtual hydrogen analyzer shows 2.1%. Although this is a shade on the low side, most in the industry would consider there still to be plenty of hydrogen to take care of the hydrogenation in the Co/Mo catalyst.

Between 10 and 12% excess air, there is a subtle change that occurs within the TGU front end. Hydrogen is consumed rapidly and $SO_2$ begins to emerge from the Hydrogenation Reactor. At 12% excess air, there is 0.2 ppmv $SO_2$ in the feed to the Quench Tower. The $SO_2$ breakthrough has begun! Nevertheless, there appear to be no further malicious indicators within the Quench Tower or amine system. However, as shown below, the unit is on the precipice of a very serious unit upset.

With only a small additional perturbation from 12 to 12.3% excess air, the train derails. The following sequence of events is observed from Table 2:

- $SO_2$ increases from 0.2 to 74 ppmv in the Quench Column feed.
- Excess hydrogen drops nearly to zero.
- The cold quench water pH plummets from 7.13 to 4.35. On the hot side, the column bottoms pH has dropped from 6.72 to 3.83.
- $SO_2$ has entered the amine system, leading to further complications:
    - A significant portion of the MDEA has been neutralized (0.13 mole/mole loading x 2 moles of MDEA per mole of dissolved $SO_2$ = 0.26 or 26% neutralized), resulting in lost scrubbing capacity for $H_2S$.

- H2S removal is no longer acceptable. The normal overhead concentration of 30-40 ppmv H2S is now over 3500 ppmv!
- With H2S present in the circulating amine, as long as the solution is kept basic, the sulfite can be expected to convert to thiosulfate over time as noted previously in Table 1. However, the kinetics of this conversion are not immediate by any means and are not well understood. In our opinion, it is not inconceivable that sulfite will survive and enter the Regenerator. Under the extreme case of no conversion to thiosulfate or elemental sulfur, ProTreat shows that some SO2 will actually be present in the vapor inside the Regenerator with somewhere between 1-7 ppmv in the Regenerator Reboiler vapor return. Herein lies proof by simulation of a damage mechanism that was correctly postulated by Keller[1]. The Regenerator reflux water could be almost as aggressive as the Quench Tower water if the breakthrough remains unchecked.
- It should be noted that the model does not presently include provision for the aqua-Claus reaction to elemental sulfur, so some of the destructive nature of the SO2 in solution could in reality be transferred to the problems with elemental sulfur formed in the amine system.

So exactly what happened?

At 12% excess air, there was enough residual ammonia present to buffer the quench water. The ratio of SO2 to ammonia in the Quench Tower feed is only 0.0036 per Table 2. At 12.3% excess air, however, there is now 1.3 times as much SO2 as there is ammonia. Ammonia is a weak base and hydrolyzes by the reaction:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
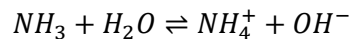
The hydroxyl ion (OH$^-$) is available to react with SO2 providing SO2 the incentive to be scrubbed out of the gas when there is excess ammonia by the simplified overall chemistry below:

$$SO_2 + NH_3 + H_2O \rightleftharpoons NH_4^+ + HSO_3^-$$

$$SO_2 + 2NH_3 + H_2O \rightleftharpoons 2NH_4^+ + SO_3^=$$
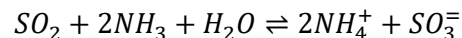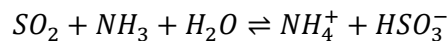
Ammonia serves as the neutralizer for SO2 breakthroughs. Indeed, many plants use ammonia injection to protect the quench tower against SO2 damage. Other plants use caustic (NaOH) injection to neutralize the SO2. Neutralization is an important damage control mitigation measure in designs.

The ammonia itself comes from whatever ammonia slip emerges from the SRU Reaction Furnace. The ProTreat® kinetic ammonia destruction model shows less ammonia slip as a consequence of increasing excess air as noted in Table 2. This qualitative behavior is in agreement with observations and recent data[2] collected by Alberta Sulphur Research Ltd. This represents one (and perhaps the only) bad consequence of better ammonia destruction in the SRU front-end.

Further excess air above 12.3% results in simply more exacerbated conditions as noted in Table 2. In terms of process control thinking, 12.3% is not an extreme excursion. In terms of safety and mechanical integrity, the consequences can be dreadful, so we leave it to the reader to conclude whether operating the Claus/TGU in manual or without adequately maintaining instruments and analyzers is a wise strategy.

## Table 2    SO₂ Breakthrough Case Study Results

| Parameter | Base Normal Ops | Excess Air Case Study | | | | |
|---|---|---|---|---|---|---|
| Enriched Claus combustion air % stoich | 100.0 | 105.2 | 110.0 | 112.0 | 112.3 | 112.5 |
| H2S:SO2 in claus tail gas | 2.0 | 0.20 | 0.08 | 0.06 | 0.06 | 0.056 |
| % sulfur recovery | 97.99 | 96.62 | 94.68 | 93.84 | 93.71 | 93.61 |
| NH3 slip, ppmv out Claus WHB | 73 | 63 | 55 | 52 | 52 | 51 |
| Hydrogenation Reactor $\Delta$T, deg F | 46.8 | 136 | 225 | 261 | 267 | 264 |
| Hydrogenation Reactor Outlet T, deg F | 567 | 656 | 745 | 781 | 787 | 784 |
| Quench Column | | | | | | |
|   SO2 in feed, ppmv | 0 | 0 | 0 | 0.20 | 74 | 401 |
|   SO2:NH3 ratio in feed | 0 | 0 | 0 | 0.0036 | 1.3 | 7.2 |
|   SO2 in OHD, ppmv | 0 | 0 | 0 | 0 | 31 | 583 |
|   NH3 in OHD, ppmv | 0.7 | 0.4 | 0.3 | 0.3 | 0.0 | 0.0 |
|   %H2 in OHD | 11.0 | 6.6 | 2.1 | 0.288 | 0.043 | 0.024 |
|   Hot btms water pH | 7.05 | 6.92 | 6.78 | 6.72 | 3.83 | 2.78 |
|   Cooled quench water pH | 7.46 | 7.32 | 7.18 | 7.13 | 4.35 | 3.16 |
| Amine System | | | | | | |
|   Lean amine | | | | | | |
|     SO2 loading, mole/mole MDEA | 0 | 0 | 0 | 0 | 0.13 | 0.41 |
|     Cooler outlet pH | 11.00 | 10.99 | 10.98 | 10.98 | 9.28 | 8.05 |
|   Absorber overhead gas | | | | | | |
|     ppmv H2S | 33.2 | 35 | 37 | 38 | 3554 | 32800 |
|     ppmv SO2 | 0 | 0 | 0 | 0 | 1.3E-05 | 9.7E-03 |
|   SO2 in acid gas recycle[2], % | 0 | 0 | 0 | 0 | 0 | 0.42 |
|   Reflux water | | | | | | |
|     SO2, mole% | 0 | 0 | 0 | 0 | 2.39E-04 | 2.47E-02 |
|     NH3, mole% | 0.003 | 0.001 | 0.001 | 0.001 | 0.000 | 0.000 |
|     H2S, mole% | 0.20 | 0.21 | 0.21 | 0.22 | 0.22 | 0.20 |
|     pH | 4.96 | 4.60 | 4.36 | 4.28 | 3.74 | 2.14 |
|   Reboiler inlet pH | 9.24 | 9.23 | 9.22 | 9.21 | 7.77 | 6.99 |
|   SO2 in reboiler vapor out, ppmv | 0 | 0 | 0 | 0 | 1-7[3] | 273 |

**Notes:**

1. ppmv figures are on a wet basis

2. Recycle acid gas loop wasn't closed in simulations so result is illustrative.

3. Range of SO2 where main amine recycle loop would converge within a reasonable tolerance.

### A Better Resolution Microscope

One of the key findings from the case study above was the importance of the ratio of SO₂ to NH₃ in the Quench Column feed. Because the SO₂ slip is so sensitive to excess air in the Claus unit, a second case study was performed to break the flowsheet at the quench column feed to allow the amount of SO₂ in the Quench Column feed to be directly varied. In this second case study, the Quench Column itself was examined under a 1:1 and 2:1 ratio of ammonia to SO₂. Figure 2 shows profiles of temperature, pH and vapor concentration of SO₂ and NH₃ across the Quench Column for a 1:1 ratio of NH₃ to SO₂ (left plots) and with excess ammonia at a 2:1 NH₃ to SO₂ ratio (right plots).

The temperature profiles in Figure 2 appear to be nearly identical for the two ratios studied. However, the pH for the 2:1 ratio of $NH_3$:$SO_2$ (right side) is nearly an entire pH unit higher. This allows the $SO_2$ to be removed to less than 0.1 ppmv. The learning here is that danger for an $SO_2$ breakthrough may be increased at pH levels below approximately 6.5 for this particular plant. There is no guarantee, however, that $SO_2$ is present if the pH drops to below this figure. The normal pH equilibration level for this particular system is 7.4-7.5 at the oxygen enrichment level that was in operation when the data was collected. The normal equilibration can be quite different for different operating conditions and for different units, so this is a situation where generalizations cannot be reliably made. Guidelines for caustic or ammonia injection neutralization targets can be constructed by running simulation case studies *for a specific plant's feed conditions and installed hardware* using the ProTreat® simulator.

With the 1:1 $NH_3$:$SO_2$ ratio (left side Figure 2), about 1 ppmv $SO_2$ slips into the amine system. So is 1 ppmv $SO_2$ really bad? Since $SO_2$ tends to stay in the liquid water phase, a little $SO_2$ in the feed vapor can result in surprisingly high levels of $SO_2$ when the circulating amine has come to steady state. Consequently, the recycle convergence tolerance for $SO_2$ breakthrough simulations usually has to be considerably tighter than for other simulations. After allowing 1 ppmv $SO_2$ in the feed vapor to build up in the amine loop in our virtual model, the $SO_2$ had accumulated to about 0.3 mole% or an equivalent loading of 0.041 mole/mole MDEA. The $H_2S$ in the treated gas was still at acceptable levels. We can conclude that the amine system performance would decline somewhere between a 1:1 and 1.3:1 ratio of $SO_2$ to $NH_3$ (note the inverted definition) by considering these results together with the case study in Table 2.

**More Bad News**

The industry is gaining increasing awareness that degradation products such as MMEA and DEA are formed as a result of MDEA degradation with repeated and prolonged bludgeoning of the TGU amine. Originally hypothesized as early as 1999 by Jenkins and Critchfield[3], selectivity reduction and its associated effects on the SRU and ultimate capacity loss are realities that can be expected from $SO_2$ breakthroughs[1,3, 4]. Although the accumulation itself over time cannot be predicted yet, the effects on amine system performance can now be quantified[4].

**Gas Plant SRU/TGU Implications**

Since gas plants typically do not process ammonia, there is no natural pH buffer to work with. Consequently, *any* $SO_2$ slip into the Quench Tower in a gas plant will cause the same problems as discussed in this paper in the context of refining systems with excess $SO_2$. This begs the question as to whether some continual pH buffering should added. We leave this as a question to answer in the future. However, it is fortunate that gas plant SRU's typically operate with less hydrocarbon upsets and fluctuations in the feeds, making $SO_2$ breakthroughs less likely in general.

**Figure 2       Quench Column Temperature, pH and Concentration Profiles**

**1:1 NH₃:SO₂ Ratio**                                    **2:1 NH₃:SO₂ Ratio**
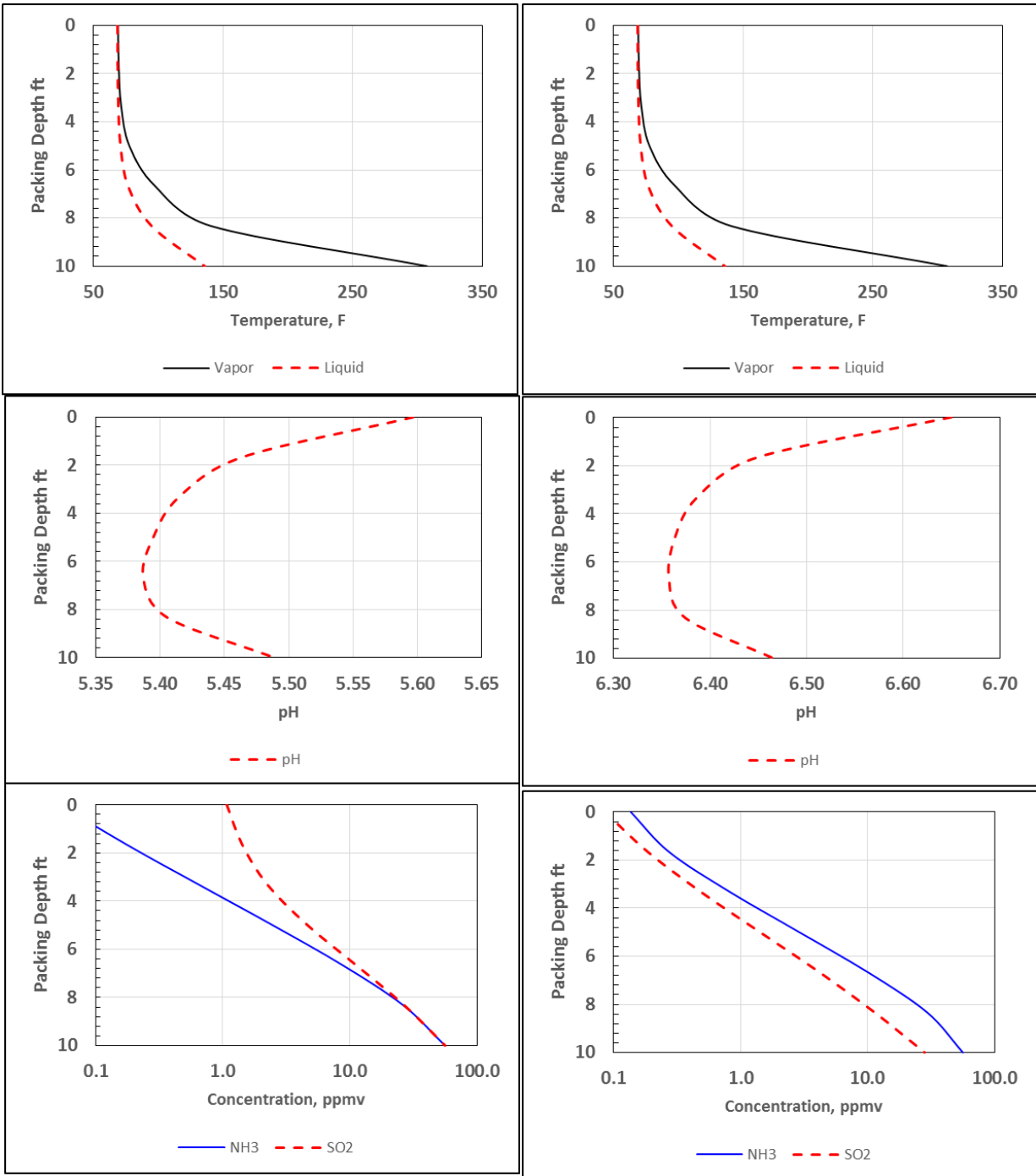
## Summary & Conclusions

This paper has revealed the sensitivity of TGU's to $SO_2$ breakthroughs. Through the use of a virtual microscope in the form of ProTreat® mass transfer rate-based simulation, the impacts have been quantified.

Perhaps the most significant finding from this work is that **any non-zero** $SO_2$ concentration leaving the quench tower will wreck the TGU amine ***over time*** as the $SO_2$ accumulates in the circulating amine loop. This can happen even with the $SO_2$ concentration in the quench tower overhead vapor stream is so low that it is difficult or impossible to measure (<1 ppmv) in practice.

The findings of this paper are in complete alignment with why the industry has adopted best practices to: (1) keep controls in good condition, (2) perform diligent analyzer maintenance, (3) and install rapid pH buffering injection systems in the Quench Column.

## References

1. "The Aftermath of $SO_2$ Breakthrough and Ways to Prevent and Mitigate It", Keller, A., Proceedings of the 2012 Brimstone Sulfur Symposium, Vail, CO.
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3. "Evidence of MDEA Degradation in Tail Gas Treating Plants", Critchfield, J. E., Jenkins, J. L., PTQ, Spring, 1999.
4. "Effect of MMEA on the Performance of Tail Gas and AGE Units", Weiland, R.H., Hatcher, N.A., Weiland, G.S.A., Proceedings of the 2015 Sour Oil Gas and Technology Conference, Abu Dhabi, U.A.E.