The role of tail gas treating unit quench towers

A quench tower cools gas entering a tail gas amine unit but also protects the amine against SO_2 breakthrough

Ralph Weiland, Clayton Jones and Nathan Hatcher *Optimized Gas Treating, Inc*

Tail gas from most sulphur recovery units (SRU) is routed to a reduction quench amine tail gas treating unit (TGTU). A hydrogenation reactor first converts (reduces) residual sulphur species such as SO_2, COS, CS_2, and elemental sulphur into H_2S for eventual recycling back to the SRU. Before its sulphur content is recovered, however, the hot gas from the hydrogenation reactor is quenched to make it cool enough for feeding to the TGTU amine system. Here, the hydrogen sulphide content is captured by a H_2S selective solvent, usually N-methyldiethanolamine (MDEA). This article focuses on the quench tower, which tends to receive little or no engineering attention, despite its very important role in the overall sulphur recovery process.

The primary purpose of the quench tower is to cool the hot gas (500–600°F, 260-315°C) from the hydrogenation reactor to around 100°F (38°C) by direct contact with cooling water. In addition to lowering the temperature, generally about 85% of the water content is removed as well. This water would otherwise need to be purged from the amine system downstream to maintain amine strength. A sometimes poorly appreciated secondary role of the quench tower is to afford some measure of protection of the TGTU from harmful contaminants that would otherwise enter with the quenched tail gas. In particular, any small amounts of ammonia and SO_2 in the gas can be removed in the quench tower. Unless the amine is protected, over a period of time, even small levels of SO_2 contamination can generate heat stable salts and other more reactive amine degradation products of the MDEA solvent, harming the selectivity for hydrogen sulphide.

Trays are rarely used any more in quench towers because of the fast volume decrease that accompanies the rapid drop in temperature, which has a tendency to buckle trays. Today, quench towers are almost always packed, and since high efficiency is not needed to achieve adequate cooling, large diameter random packings are quite suitable. As will be seen later, although cooling itself occurs very rapidly, water removal requires a little more extended contact, and the removal of any ammonia or sulphur dioxide requires even more contact with the cooling water. In other words, very little packed height is needed to achieve cooling, but quite a bit more is needed to remove contaminants. Thus, accurate simulation of the quench tower can benefit operations by predicting how much sulphur dioxide from an SO_2 breakthrough will actually reach the TGTU amine section, how much will be removed in the quench water, and how much ammonia will be captured as well.

How a quench tower performs in terms of heat transfer and protection of the TGTU is discussed in the context of a case study using conditions from an operating refinery unit. In particular, SO_2 breakthroughs and controlling these events using ammonia or caustic injection are addressed.

Case study

For this study, the TGTU quench column and quench water circuit shown in **Figure 1** have been isolated from the overall SRU-TGTU flowsheet The column contains 20 ft (6.1 m) of IMTP 50 random packing. The gas enters at 15 psia (1.03 bara) and 555°F (290°C)[1] with the compo-
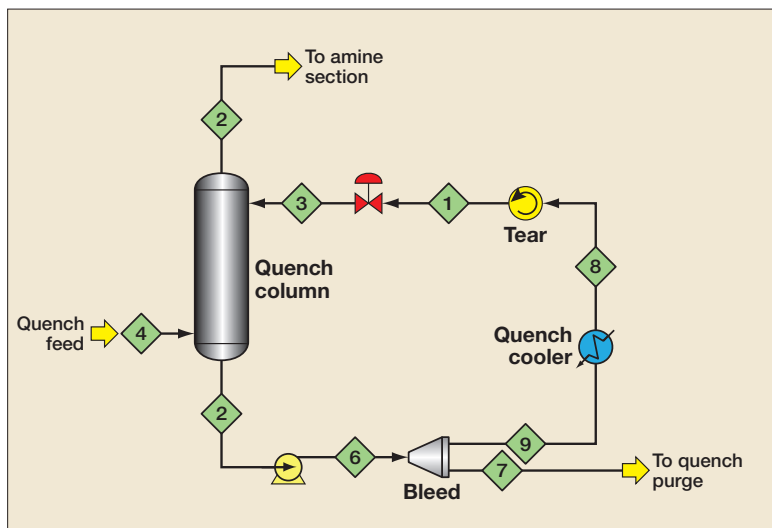
Figure 1 TGTU quench simulation flow sheet

Component flows in quench feed		
	Flow, lbmol/h	Flow, kmol/h
Water	307.1	139.3
Carbon dioxide	82.6	37.5
Hydrogen sulphide	8.3	3.76
Sulphur dioxide	Trace	Trace
Ammonia	0.051	0.023
Hydrogen	41.3	18.7
Carbon monoxide	0.3	0.136
Nitrogen	583.3	264.6
Total	1023	464

Table 1

Figure 2 Gas temperature and water flow profiles

molar ratio was varied from 0.1 to 3.0. Quench water was maintained at 93°F (33.9°C). Condensed water was drawn from the circuit via Stream 7 at whatever rate was necessary to keep the circulating water flow to the quench column constant at 300, 450 or 683 bbl/h (209, 314, 476 std. USgpm or 47.5, 71.2, 108.1 std. m³/h).

More than the overall performance of the quench system, the study (using the ProTreat mass and heat transfer rate based simulator) was done to expose the inner workings of the column itself, and how it might handle various levels of SO_2 breakthrough from the SRU. In other words, when can the quench column be expected to protect the downstream amine system from an SO_2 breakthrough, what level of protection can be provided, and what can be done operationally to mitigate a higher level breakthrough? First, however, how does the quench fulfill its primary function of cooling the gas?
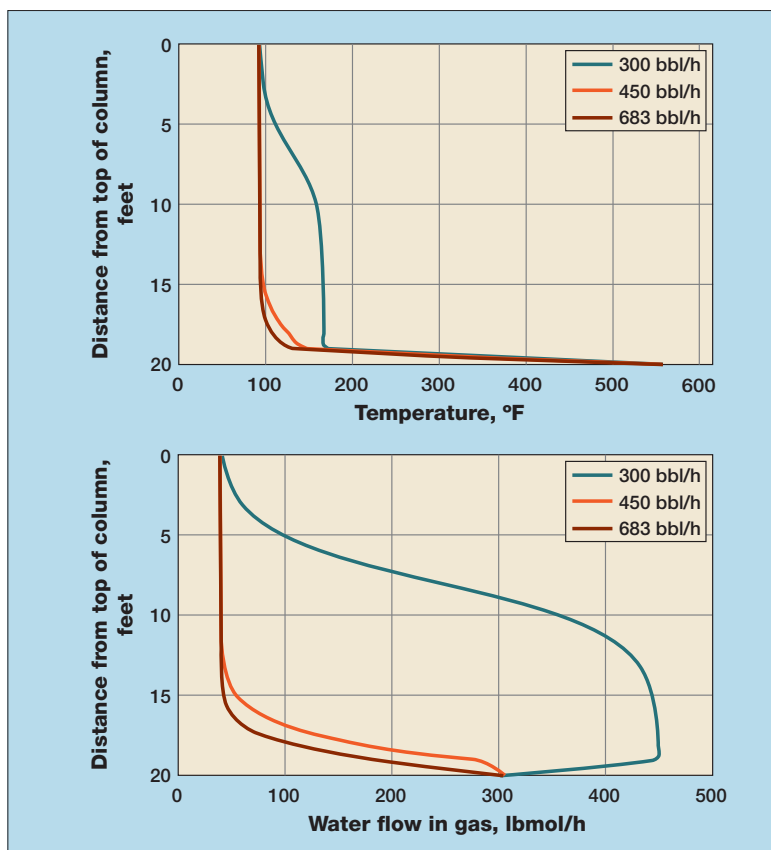
Gas cooling

Figure 2a shows temperature profiles across the column while **Figure 2b** shows the changing flow rate of water in the gas. The parameter in these plots is the circulation rate of the quench water.
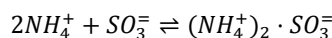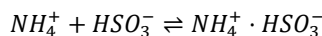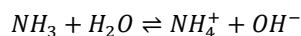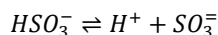
nent molar flows shown in **Table 1**. The ammonia concentration of 50 ppmv is not atypical for the gas going to a quench column in a tail gas treating unit. For the case study the SO_2 to NH_3
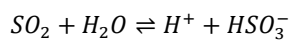
As soon as the gas enters the column, it is immediately quenched by about 400°F. However, at the lowest quench water rate, much of the initial cooling at the bottom of the packing is by evaporation of water (that is, transpiration, or swamp cooling), and the gas remains very high in water until it approaches the upper half of the bed where it meets cooler

| Inlet gas | | Outlet gas | | | | | |
| | | Quench water, 300 bbl/h | | | Quench water, 683 bbl/h | | |
SO_2, ppmv	NH_3, ppmv	Temp, °F	SO_2, ppmv	NH_3, ppmv	Temp, °F	SO_2, ppmv	NH_3, ppmv
25	50	93.0	0.179	0.69	93.6	0.173	1.05
50	50	93.0	3.83	0.070	93.6	3.96	0.10
75	50	93.0	33.3	0.0086	93.6	35.1	0.023
100	50	93.0	66.0	0.0045	93.6	67.0	0.011

Table 2

water. Cooling is by sensible heat transfer as well as by transpiration cooling. At low circulation rates, much of the 20ft packed bed is necessary to cool the gas — the heat transfer process is not fast. None of this is obvious from inlet and outlet stream measurements, because the outlet gas temperatures in these extreme cases differ by only a fraction of a degree. Furthermore, as will become apparent, the outlet SO_2 concentrations differ by at most 2 ppmv in a total value of 65 ppmv. ProTreat simulation shows that virtually all ammonia is removed, but the fraction of SO_2 removed depends strongly on the SO_2 to NH_3 ratio in the inlet gas.

NH_3 and SO_2 removal in the quench column

Ammonia and sulphur dioxide, being alkaline and acidic respectively, react not just with water, but strongly associate with each other in the water phase:

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$$
$$HSO_3^- \rightleftharpoons H^+ + SO_3^=$$
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$NH_4^+ + HSO_3^- \rightleftharpoons NH_4^+ \cdot HSO_3^-$$
$$2NH_4^+ + SO_3^= \rightleftharpoons (NH_4^+)_2 \cdot SO_3^=$$

Ammonia is highly soluble in water, whereas sulphur dioxide is only sparingly soluble. Any dissolved ammonia will tend to drag an equal amount of SO_2 into the water phase with it through the aqueous acid base

reactions above. Thus, if the SO_2 to NH_3 ratio in the gas is less than one, the cooled gas can be expected to be virtually SO_2 free. Conversely, if this ratio is greater than about one, the gas phase should be ammonia free but will contain whatever SO_2 cannot dissolve physically in the quench water. If the gas has more SO_2 than ammonia, the water will be acidic but if there is more ammonia than SO_2 it will be alkaline. This expected behaviour is why monitoring the pH of
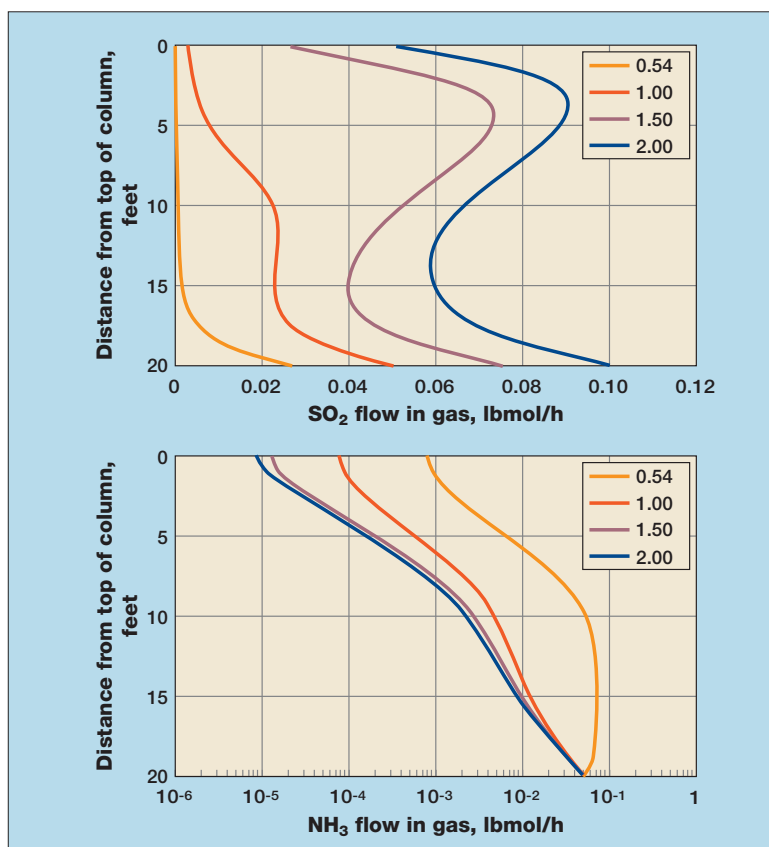

Figure 3 Molar flow rate profiles in the gas with quench water flow at 300 bbl/h with varying SO_2 to NH_3 ratio in feed gas
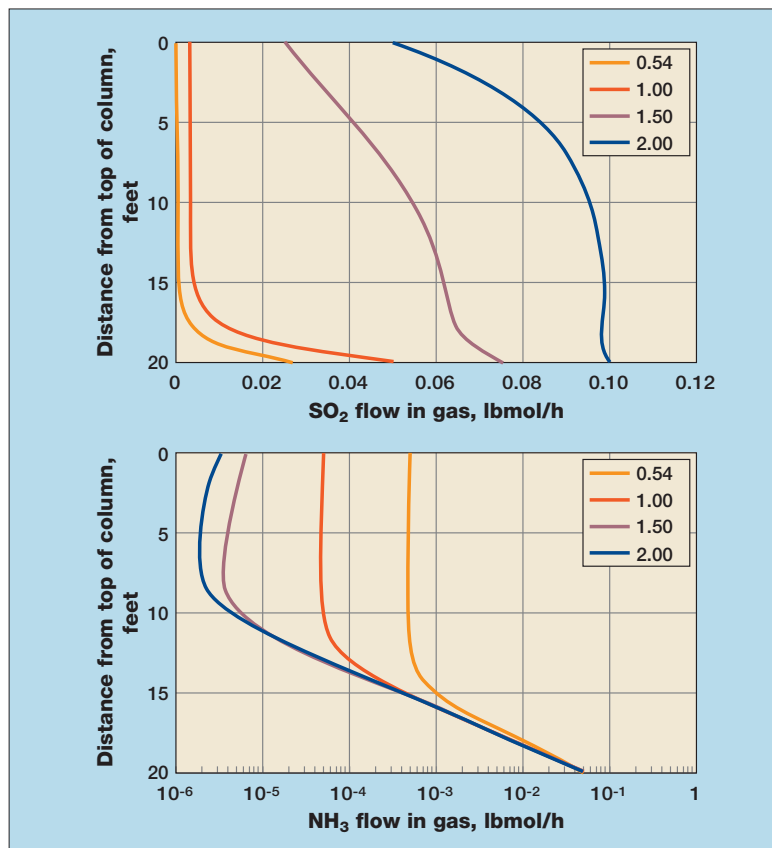
Figure 4 Molar flow rate profiles in the gas with quench water flow at 683 bbl/h with varying SO_2 to NH_3 ratio in feed gas

quench tower pumparound water is a good practice.

First, it is worth noting that the SO_2 and to a lesser extent the NH_3 concentrations predicted to remain in the quenched gas are relatively insensitive to the quench water flow rate (as long as this is high enough to leave the quenched gas temperature relatively unaffected). Therefore, there are almost no external observations that would give any indication of behaviour inside the quench tower. **Table 2** shows these predictions.

The most striking predictions of molar flow rate[2] profiles of SO_2 and ammonia are at the 300 bbl/h quench water rate shown in **Figure 3**. Profiles at the highest quench water flow (683 bbl/h) are shown in **Figure 4** for comparison. When the SO_2 and ammonia levels are equal in the inlet gas (at 300 bbl/h), th SO_2 flow profile through the quench column (blue line in **Figure 3a**) follows the temperature profile (blue line) in **Figure 2a.** The ammonia profile in the lower half

of the column remains fairly steady until it falls through two orders of magnitude in the top half.

At high SO_2 to NH_3 ratios and the lowest quench water rate, SO_2 first absorbs across the lower end of the column, and then strips across the middle section, before absorbing again in the top end. Ammonia absorbs throughout the column because of its high solubility. This has corrosion implications because corrosion is exacerbated by high temperatures and high levels of SO_2 in the water. The S-shaped SO_2 profile is again related to the complex interaction between the temperature profile, the chemical reactivity between the absorbing species, and the high gas phase water content, which begins to fall off only in the upper part of the quench tower. The decreasing water content results in higher SO_2 levels in the gas, driving more SO_2 into the quench water.

A level of 150 ppmv SO_2 in the gas going to the quench column is a fairly high value for an SO_2 breakthrough event. The pH profiles in the tower are revealing (see **Figure 5**). During a significant SO_2 breakthrough, the quench water can become highly acidic with a pH well below four, but if the quench water rate is low pH is lowest in the upper part of the column. This is caused by a high sulphurous acid level in the water there. If the quench water rate is high, the pH will be uniformly low throughout the column once steady state is achieved. Measuring pH in the quench water circuit, either just before entry or after exiting from the quench tower, can be used to indicate when an SO_2 breakthrough is occurring. However, a measurement in this location may not reveal the true extent of the possible corrosion damage being done to the column shell and the packing because the actual pH inside the column may be fully 1 to 1.25 units more acidic than indicated. SO_2 breakthrough results in highly acidic quench water fully capa-

ble of dissolving mild steel and even lower grades of stainless steel such as Type 304. Type 316 will be more resistant although probably not immune from acid attack. The place in the quench tower to look for corrosion damage appears to vary with the quench water flow rate, but the upper half of the quench tower seems to be most susceptible to corrosion damage.

Mitigating an SO_2 breakthrough

When an SO_2 breakthrough from the SRU occurs, it is important to:

• Detect the breakthrough,

• Protect the quench tower and its internals from rapid acidic corrosion

• Prevent or minimise SO_2 ingress into the downstream amine system.

If SO_2 does get into the amine system, it will act as a heat stable salt and increasingly deactivate the amine and increase solution corrosivity at higher concentrations. Over time, degradation of the MDEA into secondary fragments such as DEA and MMEA will occur causing increased reactivity with CO_2 and lowering the selectivity achievable in the TGTU. Reduced selectivity means more CO_2 gets recycled back to the front of the SRU, both reducing the quality of the feed gas and possibly overloading the TGTU with additional inert gas (CO_2).

SO_2 can essentially be totally removed from the quench water by maintaining it pH-neutral or slightly alkaline. Adding caustic soda to the quench water is a common way to do this. But it should be recognised that any excess caustic will serve to remove H_2S and CO_2 with the quench purge. Keeping the pH alkaline also ensures that SO_2 is converted by H_2S to thiosulphate rather than elemental sulphur. Rather than adding yet another species (sodium) to the system, it might be better just to add enough ammonia to keep the quench water neutral.

Conclusion

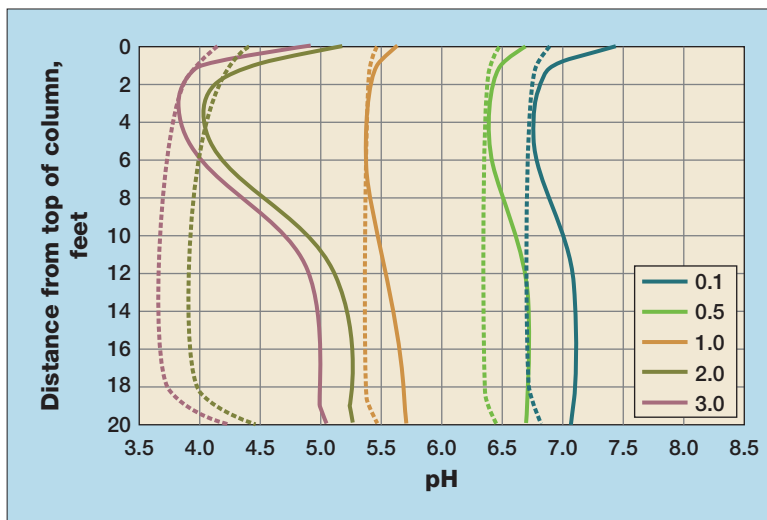The quench tower in an SRU-TGTU system does more than cool the gas before it enters the TGTU amine system. When operated properly, the quench tower can also protect the amine from SO_2 breakthroughs. However, when an SO_2 breakthrough occurs, if action is not taken promptly to control the quench water pH, serious corrosion in the upper reaches of the quench tower and its internals can result because of the highly acidic environment. As shown by ProTreat simulation, the level of acidity inside the column is not truly indicated by measuring the pH of the entering or leaving quench water stream. Elemental sulphur will also form when H_2S hits SO_2 laden quench water, plugging the internals. All of this can happen without any indication from outlet pH measurements. In the end, the capacity reductions and corrosion implications mandate close attention to this important piece of equipment.

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Figure 5 pH Profile in the quench column at 300 bbl/h (solid lines) and 683 bbl/d (dashed lines) quench water rate, SO_2 to NH_3 ratio as parameter, and 100 ppmv SO_2 in the gas. Parameter is SO_2 to NH_3 ratio in feed gas to quench tower

Notes

1 This is not a typical feed gas temperature. Many plants have a waste heat recovery exchanger upstream of the quench tower generating LP steam (3 to 4 barg).

2 The discussion is in terms of molar flow rates rather than molar concentrations because the large changes in water concentration significantly affect the concentrations of other species and can mask important variations.

Ralph H Weiland is President of Optimized Gas Treating, Inc (OGT). He holds BASc, MASc and PhD degrees in chemical engineering from the University of Toronto.
Email: Ralph.Weiland@ogtrt.com

Nathan (Nate) A Hatcher is Vice President, technology development for OGT. He holds a BS in chemical engineering from the University of Kansas.
Email: Nathan.Hatcher@ogtrt.com

Clayton Jones joined Optimized Gas Treating, Inc as a Software Development Engineer in 2012. He holds a BS in chemical engineering from McNeese State University and a MS in chemical engineering from the University of New Mexico.