Ammonia in TGU Quench and Amine Systems

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ABSTRACT

The effects of ammonia ingress and contamination in the acid gas feeds to Claus plants have been well studied and are commonly understood within the context of the Claus unit. This is much less true for the downstream tail gas unit. Most process models presently either ignore the effect of ammonia on the tail gas unit (TGU), or do not account for the resistance to mass transfer that inherently distinguishes real plant operations from hypothetical ideal stages.

In the present work, a mass transfer rate-based model is used to determine the effects of ammonia slip from the Claus unit on TGU Quench water H_2S and CO_2 emissions. Additionally, the accumulation and impact of ammonia on TGU amine system performance is assessed together with material balance estimates of ammonia recontamination of the Claus unit amine acid gas feed. Comparisons to real plant operating data are furnished where available.

1. INTRODUCTION

The tail gas unit immediately downstream from a sulfur plant is arguably one of the most visible units involved in the sulphur processing chain in a refinery or in a gas plant processing sour gas. As a potentially major point of waste excretion from the plant, the TGU is the last line of defense preventing sulfur compounds from entering the environment. And with ever increasing environmental concerns, a poorly performing unit is highly visible, making reliability paramount and demanding close attention be paid to the TGU.

The effects of ammonia ingress and contamination of the acid gas feeds to Claus units are well documented and understood within the context of the sulfur plant. This is much less the case for the downstream tail gas unit. Here, most process models at present either ignore the effect of ammonia on the TGU, or they do not account for the resistance to the mass transfer processes that distinguish real plant operations from such hypotheticals as ideal or equilibrium stages.

Tail gas from a Claus-type sulfur plant contains unreacted H_2S together with SO_2, COS, CS_2, sulfur vapor as well as CO_2 and various inert components such as nitrogen from combustion

air. It can also contain significant amounts of ammonia. Before entering the TGU amine unit for H_2S recovery, the gas is hydrogenated, then cooled by generating LP steam in a heat exchanger, followed by direct contact with water in a Quench Column. The focus of this paper is the TGU Quench and Amine systems, and on using mass transfer rate-based simulation to create a virtual plant in an attempt to answer several questions:

- How effective is the TGU Quench unit at removing ammonia from the hydrogenated tail gas?
- How much H_2S and CO_2 does the absorbed ammonia take with it into the SWS system?
- Is there a relationship between quench water pH and the ammonia content of the gas feed to the Quench Column?
- If nearly all ammonia is picked up in the quench water, can quench water pH be used in to infer upstream reaction furnace ammonia destruction performance?
- How much ammonia enters the TGU Amine unit, where does it end up, and at what concentrations?
- Is there sufficient accumulation of ammonia anywhere in the TGU Amine unit to require purging and how much can purging help reduce ammonia in the acid gas?
- How much contamination of the Claus unit acid gas feed results?

The Quench Column itself is a challenging example of cooling via transpiration of water (humidification) combined with direct-contact, sensible heat transfer, somewhat along the lines of the cooling towers common in power generating stations. Humidification with direct contact heat transfer is already a complex process. However, in a TGU Quench Column there are the added complications of ammonia and acid gas absorption and the accompanying chemical reactions. In particular, the fate of ammonia entering a Quench Tower has potentially important implications for the load placed on the sour water stripper (SWS), for the performance of the TGU Amine unit, and for the extent of recontamination of the acid gas feed to a Claus plant.

This study is limited to reductive-type TGU Quench and Amine systems (e.g., SCOT®). For simplicity, Quench Columns are restricted to single-stage direct-contact type having a quench water pump-around loop—most plants use this approach.
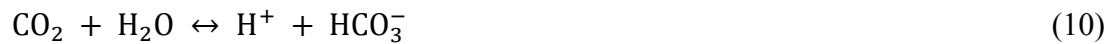
2. PROCESS OVERVIEW AND CHEMISTRY

2.1. Chemistry

Besides nitrogen and argon from combustion air, the gas from a Claus unit contains SO_2, S_x, H_2, CO, COS, CS_2, CO_2 and H_2O. The gas is hydrogenated according to the reactions

$$SO_2 + 3H_2 \leftrightarrow H_2S + 2H_2O \tag{1}$$
$$S_x + xH_2 \leftrightarrow xH_2S \tag{2}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$
$$COS + H_2O \leftrightarrow H_2S \ CO_2 \tag{4}$$
$$CS_2 + 2H_2O \leftrightarrow 2H_2S + CO_2 \tag{5}$$

Thus, a typical feed to a Quench Column consists mostly of nitrogen, water and the acid gases with very small residual amounts of the original reactants in these equations. However, any ammonia in the Claus plant effluent will skate through the hydrogenation reactor and present intact to the quench unit. In the Quench Column the ammonia, being very soluble in water, will tend to absorb. But being alkaline (just like an amine) it will co-absorb and react with CO_2 and its alkalinity will provide a sink for the hydrogen ions liberated when H_2S dissolves.

The reactions involving ammonia and the acid gases are:

$$NH_3 + H^+ \leftrightarrow NH_4^+ \tag{6}$$
$$H_2O \leftrightarrow H^+ + OH^- \tag{7}$$
$$H_2S \leftrightarrow H^+ + HS^- \tag{8}$$
$$HS^- \leftrightarrow H^+ + S^= \tag{9}$$
$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{10}$$
$$HCO_3^- \leftrightarrow H^+ + CO_3^= \tag{11}$$
$$NH_3 + CO_2 \leftrightarrow NH_2COO^- + H^+ \tag{12}$$

and these are the same reactions that occur when CO_2 and H_2S dissolve in and primary or secondary alkanolamine system. In that sense, ammonia is just another amine—it is the simplest amine, containing no carbon. However, it has high volatility. Ammonia influences all these reactions by virtue of Equation (6) where it acts as a sink for hydrogen ions by forming ammonium ions. As written (for an absorber or Quench Column), all the other reactions form hydrogen ion and by virtue of ammonia's alkalinity, Equation (7) acts as the sink for the hydrogen ions so formed.

Understanding Quench Columns, SWSs, and amine units processing ammonia-contaminated gas depends on knowledge of

- Vapor-liquid equilibria,
- Kinetics of the carbamate forming reaction, Equation (7), and
- Appreciation of absorption and stripping as mass transfer rate processes where Henry's law applies.

The ProTreat® process modeling and simulation tool that will be used is genuinely mass and heat transfer rate-based. Nevertheless, it uses vapor liquid equilibrium (VLE) as one of its building blocks[1] and its VLE relies on the thermodynamic framework of Deshmukh and Mather (1982).

2.2. Process Overview

Typically, gas from the hydrogenation unit first is cooled to 320–350°F by raising low pressure (LP) steam at 40–50 psig (2.75–3.5 barg) in a waste-heat exchanger. The Quench Column itself takes this gas and reduces its temperature by counter-current, direct-contact heat transfer against cool circulating water in a packed or trayed column. When the gas first enters the Quench Column, it is superheated at the entering temperature so initially it causes water to evaporate which

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[1] Unlike ideal-stage models, VLE is not the only building block in a real mass transfer rate-based model.

actually cools the quench water. Within a few inches of the bottom of the bed or above the first tray the gas starts to cool and water then condenses. Most of the initial water content ultimately condenses (30–35% water is reduced to a few percent). In most plants, the quench water is pumped in a loop through a conventional fin-fan cooler or cooling water exchanger and passed back to the top of the quench tower. A portion of the quench water (equivalent to the water condensed from the hot gas) is bled from the system on a bottoms level control and into the sour water stripper (SWS) system. Depending on the components in the gas, the quench water and purge may contain CO_2, H_2S and ammonia and their concentrations may be fairly high because reactions between ammonia and the acid gases remove the Henry's Law solubility limitation. These components must be removed in the SWS before the condensed water can be sent to the bug pond (waste water treatment plant).

A secondary purpose of the Quench Column is to guard the TGU Amine system from SO_2 breakthrough from the TGU Reaction section (hydrogenation). Ammonia may be present in the quench water, either by slip from the SRU, or by intentional, direct addition to buffer the quench water by controlling pH. Some plants use caustic injection for the same purpose. The overhead gas from the Quench Column is then fed to a selective amine system to scrub H_2S to less than a few 100 ppmv (or even to as low as 10ppmv) and slip as much CO_2 as possible out of the system. The resulting acid gas is then recycled back to the Claus unit. The most common solvent is generic MDEA, but FLEXSORB®-SE and FLEXSORB®-SE Plus are gaining ever more recognition as providing better CO_2 slip; hence lower solvent rates and reduced energy usage.

3. MASS AND HEAT TRANSFER RATE-BASED SIMULATION MODEL

ProTreat® simulation is the tool used in this study. ProTreat's column model is a genuinely mass (and heat) transfer rate-based rendition of all the processes happening within a column containing any of a variety of trays, random packing, and structured packing in any combination of internals type, variety, size, tray geometry, and materials. This approach has been used for complex distillation processes (extractive, azeotropic, reactive, three-phase) since the mid 1980s with outstanding success and has been offered to the gas industry via the ProTreat simulator since 1998. As originally released, ProTreat was limited to the generic amines and their blends, but it has since been expanded to include glycol dehydration, the physical solvent DMPEG[2], numerous additional reactive solvent components, promoted HotPot, and heat stable salts. One of the latest additions is sour water stripping and applications involving ammonia. All models are genuinely mass transfer rate-based meaning that the separations are calculated on the basis of individual (vapour and liquid) phase mass transfer coefficients, interfacial areas, and concentration difference driving forces.

The details of mass transfer rate modeling have been described at length elsewhere (Weiland et al., 2003; Weiland and Dingman, 2001). Suffice it to say that the kinetics of the NH_3-CO_2 reaction (Equation 12) have been properly accounted for using known kinetic parameters and the usual enhancement factor approach. The beauty of the *mass transfer* rate approach is that the resulting process model is a virtual plant on a computer, in which all the fundamental physical and chemical processes occurring are properly accounted for and mimicked. The computer simulation is a direct one-for-one prediction of both column and process performance completely without recourse to user estimates of any parameters whatsoever. All that is required is the actual process

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[2] Dimethylether of polyethyleneglycol, marketed commercially under the names SELEXOL™ and Genosorb®

flow sheet configuration, tower internals details, and values for process parameters such as gas or water flow and composition, tower pressures and imposed heat loads.

The SWS model itself has been validated against more than a half-dozen sets of stripper performance data by two refining companies and an engineering firm, with what were reported by them as excellent results. It will be validated further in this paper by comparison with additional plant performance data, this time from a Quench Column. Using a virtual plant in the form of a precise computer model, the remainder of this paper tries to provide answers to the questions raised in the Introduction.

4. TGU QUENCH AND AMINE SYSTEM

Figure 1 shows an overall process flow diagram with all the features needed to analyse and discuss the processes and the effect of process parameters intelligently. For example, there is the possibility of blowing down part of the regenerator condenser water via a purge. There is also the ability to inject caustic soda or even ammonia into the quench water circuit to control the effect of contaminants such as heat stable salts and to control quench water pH. We are not particularly interested in the effect of such conventionally-controlled process parameters as circulation rates and amine strength. Instead the focus is on how performance is impacted by small amounts of ammonia in the quench gas, quench water temperature, and whether caustic is intentionally injected or not, i.e., the effect of pH control on how much ammonia and H_2S are picked up in the quench water.
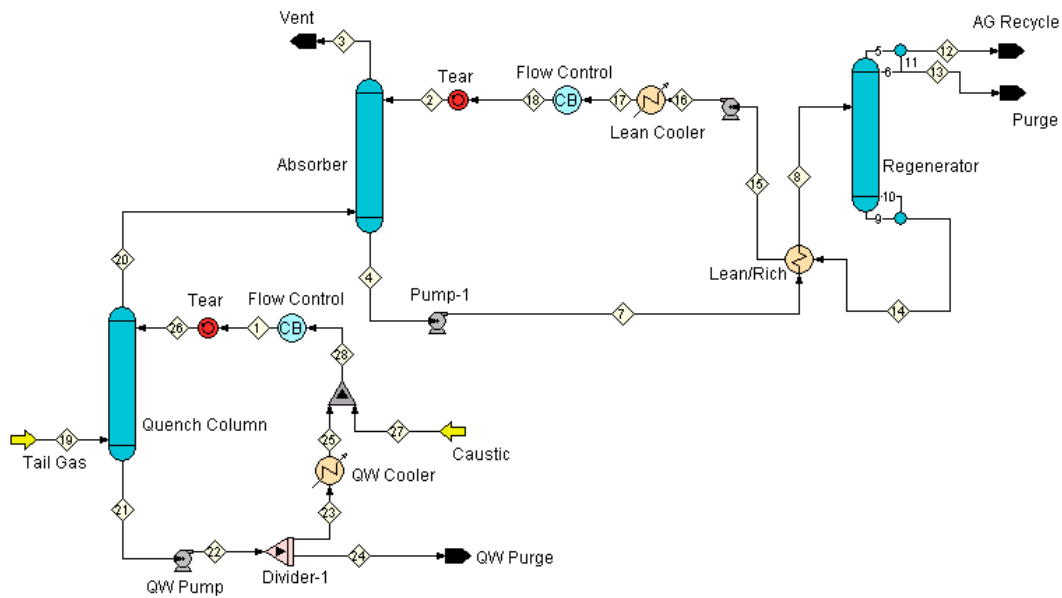

Figure 1   PFD of Quench & Amine System

The composition and condition of the entering tail gas are shown in Table 1, together with the quench water flow rate and its temperature from the quench water cooler. The Quench Column contained 10-ft of 2-in Nutter Rings and was 7.5-ft diameter at 60% flood. Table 2 shows relevant parameters for the TGU Amine circuit. As far as hardware is concerned, the absorber contained 12 valve trays with 12.5% downcomers in a 7-ft shell and operated at just below 75% jet flood and 30% downcomer choke flood. The regenerator was trayed also, but with 32 valve trays, again with

12.5% downcomers, but in a 5-ft shell. The regenerator operated at 78% jet flood and 70% downcomer choke flood.

Table 1   Tail Gas and Quench Water Data

Tail Gas	
Temperature (°F)	350
Pressure (psig)	4
Component Flows (lbmol/hr)	
Water	600
Carbon Dioxide	195
Hydrogen Sulphide	32
Carbonyl Sulfide	0.1
Hydrogen	63
Carbon Monoxide	0.6
Nitrogen	1326
Ammonia (ppmv, Variable)	0, 20, 50, 100, 500
Quench Water	
Flow (lb/h)	375 000
Temperature (°F, Variable)	95, 110

Table 2   Process Parameters for TGU Amine Circuit

MDEA Strength (wt%)	34
Phosphoric Acid Additive (ppmw)	3 400
Circulation Rate (USgpm)	343
Temperature (°F)	100
Rich Amine to Regenerator (°F)	235
Reboiler Steam Flow (klb/h at 50 psig)	22.6

Simulations were performed to determine the sensitivity of a number of process parameters to quench water temperature and caustic injection. Tables 3 and 4 summarise the results without pH control, and with pH controlled to 8.0, respectively. Turning first to the results absent pH control, it appears that the quench water pH tracks the ammonia in the raw gas (i.e., the ammonia escaping from the Claus plant) quite nicely even when substantial amounts of H_2S and CO_2 are co-absorbed. Perhaps this is because most of the ammonia is picked up in the Quench Column leaving very little to carry over into the amine unit, except at the highest inlet ammonia level of 500 ppmv. These findings are even slightly more emphatic when the quench water is colder.

The quench water CO_2 content appears strikingly high. Because ammonia reacts with CO_2 and is a good sink for the hydrogen ions that accompany H_2S absorption, it is more revealing to compare quench water ammonia, CO_2 and H_2S levels on a molar loading basis. With 500 ppmv NH_3 in the gas, the ammonia in the quench water is loaded to roughly 0.17 mol H_2S/mol NH_3 and 0.75 mol CO_2/mol NH_3. When there is 50 ppmv NH_3 in the gas the corresponding loadings are 0.34

Table 3   Effect of Ammonia in Feed Gas at Two Quench Water Temperatures on Performance Measures

	a 110F Quench						b 95F Quench				
	No Na+ added for pH adjustment						No Na+ added for pH adjustment				
NH3 ppmv	0	20	50	100	500		0	20	50	100	500
pH	4.64	6.22	6.72	7.14	7.90		4.63	6.20	6.74	7.15	7.96
Quench Water NH3 (ppmw)	0.0	22.83	71.91	177.1	771.1		0.0	23.29	78.93	195.6	898.8
Quench Water H2S (ppmw)	25.264	33.036	50.115	85.168	251.662		28.545	35.653	53.462	89.648	275
Quench Water CO2 (ppmw)	59.416	106.051	206.836	414.916	1475.993		67.404	115.918	233.489	473.730	1817
NH3 Pickup in Quench Column	0.0	99.3	98.0	94.7	84.166		0.0	99.63	99.05	97.66	92.57
% NH3 pickup in Absorber	0.0	90.2	98.2	99.2	99.5		0.0	97.90	99.4	99.7	99.8
ppmw NH3 in reflux water	0.0	7.068	22.330	104.400	1520.0		0.0	4.250	12.270	47.500	762.1
Lean H2S loadings	0.000094	0.000094	0.000095	0.000095	0.000095		0.000098	0.000098	0.000098	0.000098	0.000095
Lean CO2 loadings	0.000186	0.000186	0.000186	0.000186	0.000186		0.000192	0.000192	0.000192	0.000192	0.000186
Quenched Gas ppmv NH3	0.00000	0.12420	0.92430	4.90800	72.430		0.0	0.00707	0.449	2.215	35.160
Quenched Gas mol% H2S	1.81000	1.81000	1.81000	1.80900	1.8050		1.873	1.873	1.872	1.872	1.868
Treated Gas ppmv NH3	0.00000	0.01243	0.01711	0.03987	0.3599		0.00000	0.00015	0.00259	0.00741	0.0725
Treated Gas ppmv H2S	40.0	39.9	39.8	39.7	39.37		7.29	7.29	7.28	7.28	7.25
ppmw NH3 in lean amine	0.0	0.0006	0.0015	0.0058	0.0520		0.0	0.0004	0.0009	0.0032	0.03057
% CO2 pickup in Absorber	5.32	5.32	5.32	5.32	5.30		6.01	6.01	6.01	6.01	6.01
Quench Gas Temp (oF)	111.79	111.78	111.78	111.79	111.81		96.12	96.12	96.12	96.12	96.14

Table 4   Effect of pH Control on Performance Measures

NH3 ppmv	0	20	50	100	500		0	20	50	100	500
Quench pH @ T_{Quench}	8.08	8.08	8.05	8.02	7.90		7.99	7.99	7.99	7.99	7.96
Na+ Used for pH = 8 (lb/hr)	360	358	340	300	0		360	358	340	300	0
Quench Water NH3 (ppmw)	0.0	11.3	58.6	155.8	771.1		0.0	14.6	72.0	185.4	898.8
Quench Water H2S (ppmw)	266	268	270	271	252		247	250	255	262	275
Quench Water CO2 (ppmw)	1512	1520	1531	1545	1476		1554	1569	1605	1660	1817
NH3 pickup in Quench Column	0.0	94.15	87.33	82.98	84.158		0.0	97.22	94.40	92.64	92.57
% NH3 pickup in Absorber	0.0	98.37	99.38	99.41	99.5		0.0	99.54	99.68	99.73	99.8
ppmw NH3 in reflux water	0.0	25.3	122.9	329.6	1520.0		0.0	13.1	56.8	143.2	762.1
Lean H2S loadings	0.000094	0.000094	0.000094	0.000094	0.000095		0.000098	0.000098	0.000098	0.000098	0.000095
Lean CO2 loadings	0.000186	0.000186	0.000186	0.000186	0.000186		0.000192	0.000192	0.000192	0.000192	0.000186
Quenched Gas ppmv NH3	0.0	1.070	5.799	15.610	72.430		0.0	0.526	2.652	6.986	35.160
Quenched Gas mol% H2S	1.806	1.805	1.805	1.805	1.805		1.869	1.869	1.868	1.868	1.868
Treated Gas ppmv NH3	0.0	0.01789	0.04477	0.09497	0.3599		0.0	0.00247	0.00869	0.01915	0.0725
Treated Gas ppmv H2S	39.14	39.12	39.12	39.14	39.37		7.25	7.25	7.25	7.25	7.25
ppmw NH3 in lean amine	0.0	0.00164	0.00999	0.01518	0.05201		0.0	0.00098	0.00372	0.00825	0.03057
% CO2 pickup in Absorber	5.32	5.32	5.30	5.30	5.30		6.01	6.01	6.01	6.01	6.01
Quench Gas Temp (oF)	111.784	111.785	111.787	111.790	111.810		96.121	96.121	96.122	96.126	96.14

and 1.1 while at 20 ppmv ammonia in the gas, the H_2S and CO_2 loadings are 0.72 and 1.8. What is instructive about these particular results is that although there is six times more CO_2 in the gas than there is H_2S, the CO_2 is not absorbed six times more strongly. In fact, on a relative basis, H_2S is more strongly absorbed than CO_2 in this instance. On the other hand, when the quench water pH is controlled to 8.0 (Table 4), the *acid gas* levels in the quench water are almost *independent* from the ammonia content of the gas, but the ammonia in the quench water is in direct proportion to the ammonia level in the gas, just as it is without pH control, and independent from quench water temperature. When quench water pH is controlled with caustic, the H_2S and CO_2 levels in the quench water to the SWS can be several times higher than when caustic is not used. This may have implications for sour water handling and reuse.

It is also noteworthy that there can be significant levels of ammonia in the quenched gas going to the amine unit. Although this does not reappear to any great extent in the stripped amine (being always < 0.1 ppmw), this is not to say that ammonia will not accumulate in the regenerator. Before addressing that issue, however, it is worth directly comparing ammonia removal in the Quench Column as a function of quench water temperature and the ammonia level in the incoming gas. This is done in Figure 2. Regardless of quench temperature, controlling pH always results in

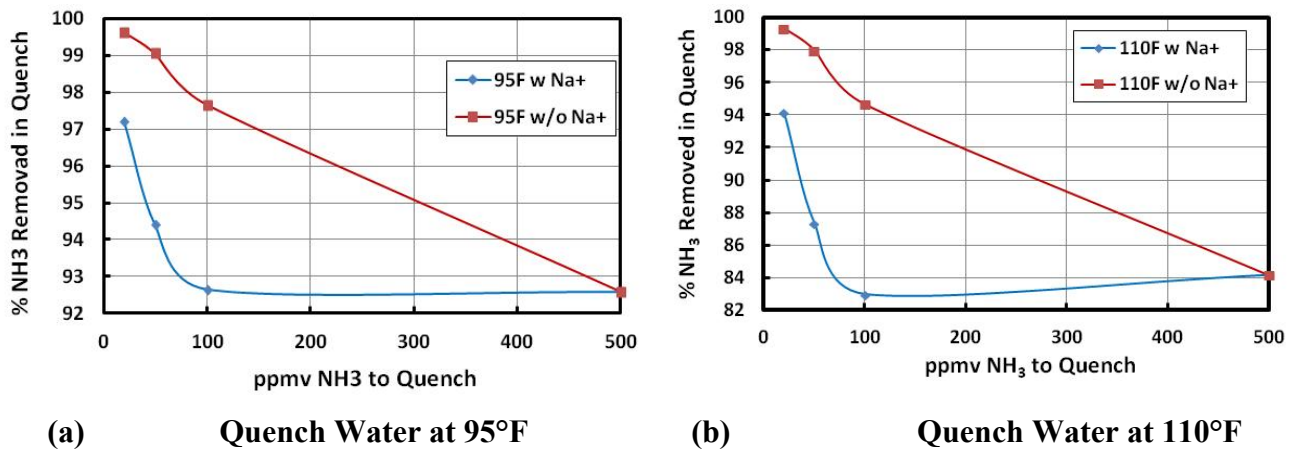| (a) | Quench Water at 95°F | (b) | Quench Water at 110°F |

Figure 2   Ammonia Removed in Quench Column vs. Ammonia in Gas

less ammonia removal into the quench water, i.e., higher ammonia levels in the quench gas to the amine unit, and the hotter the quench water the more ammonia is pushed into the amine system. Interestingly, beyond about 100 ppmv ammonia in the gas, the fractional removal becomes independent of how much ammonia there is in the gas; whereas, without pH control, fractional removal falls with increasing amounts of ammonia in the incoming gas.

The TGU Amine unit is a real concentrator of ammonia. In this case there were four wash trays and 28 stripping trays in the regenerator. Without a purge on the reflux from the condenser, a 500 ppmv ammonia gas to the Quench Column translated into only 35 ppmv in the TGU Amine feed gas (no pH control used) but the regenerator accumulated enough ammonia to produce an acid gas to the Claus plant containing *0.12 mol% ammonia*! With a 10% purge of the regenerator reflux water this falls to 700 ppmv. Thus, when even a few ppmv of ammonia are present, it might be worthwhile to take a small purge from the reflux as it will reduce ammonia to the sulfur plant enormously. If a two-zone Reaction Furnace is being employed for ammonia destruction in the

Claus unit, the design may be relying upon a clean (low NH_3 content) acid gas source to bypass to the colder back chamber.

5. COMPARISON WITH PERFORMANCE DATA FROM A TGU QUENCH COLUMN

To this point, one might view the foregoing as being "only" simulation, with no indication of just how good or bad the simulator itself might be. The proof of any simulator is comparison against solid plant data (*not against another simulator*). Figure 3 shows the flowsheet and measured process conditions for a Quench Column operating in a refinery. Table 5 lists the conditions of the
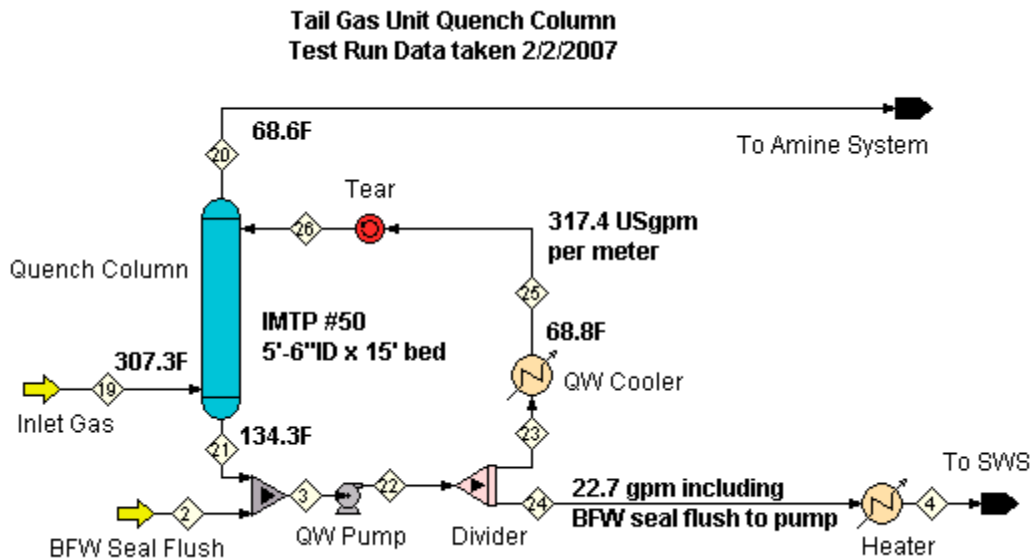
Figure 3   Process Conditions of Refinery Quench Unit

inlet gas. Before test data were collected, meters were zeroed and spanned so measured flows were felt to be reliable and accurate to within normal meter calibration standards. The unmeasured quantity was the Inlet Gas flow rate; this was by material balance calculated around the hydrogenation unit and the ammonia concentration of the gas entering that unit was estimated by calculation around the sulphur plant. Thus, although the overall composition data in Table 5 were by analysis, the gas flow rate and the ammonia level are subject to accumulated error.

Table 5   Condition of Inlet Gas

Temperature (°F)	307.3
Pressure (psia)	17.1
Total Flow (lbmol/h)	1,192.
Nitrogen (mol%)	59.19
Carbon Dioxide (mol%)	2.305
Hydrogen Sulphide (mol%)	0.655
Water (mol%)	35.01
Carbon Monoxide (mol%)	0.01
Hydrogen (mol%)	2.83
Ammonia (ppmv)	≈127

The quench water cooler duty was accurately calculated to be 11.14 MMBtu/h but the most accurate measurement was felt to be the quench water temperature exiting the bottom of the Quench Column. The temperature measured there was 134.3°F. To achieve a heat balance, and match the Quench Column bottoms temperature, the inlet gas flow had to be increased from 1,192 lbmol/h to 1,325 lbmol/h, an 11% increase and well within the uncertainty in the estimated total flow. This flow allowed both the bottom temperature to be perfectly matched and the cooler duty to be matched to within 7%. This is quite respectable agreement for commercial plant operating data. The measured and calculated purge flow rates agreed perfectly. To match the measured ammonia concentration in the purge stream of 226.6 ppmv, the ammonia in the inlet gas had to be decreased from the estimated 127 ppmv to 115 ppmv. By making small adjustments in quantities that were only estimated in the first place, complete agreement with measured operating data were obtained.

It may be of interest to show how the temperature and water content of the gas varied across the Quench Column. These are shown in Figures 4(a) and (b), respectively. The 15-ft deep packed bed was divided into 45 small (4-in deep) segments to approximate the continuous nature of the contacting. The gas is completely quenched by the first 5–6 feet and the water has been removed to its final value by the first 8 feet of packing. Obviously, in this particular case a 15-ft bed was very conservative. It is also noteworthy that quench water temperature shows a small bulge at about the 4-in mark from the bottom of the bed. As mentioned earlier, the entering gas is under saturated with water (superheated) which causes water first to evaporate (resulting in cooling of the quench water) before it begins to condense as the gas flows up through the packing. Ammonia is removed by the first 12 feet of packing although by the time the gas has passed through the first 8 feet of packing the residual ammonia is already < 1 ppmv (wet basis).
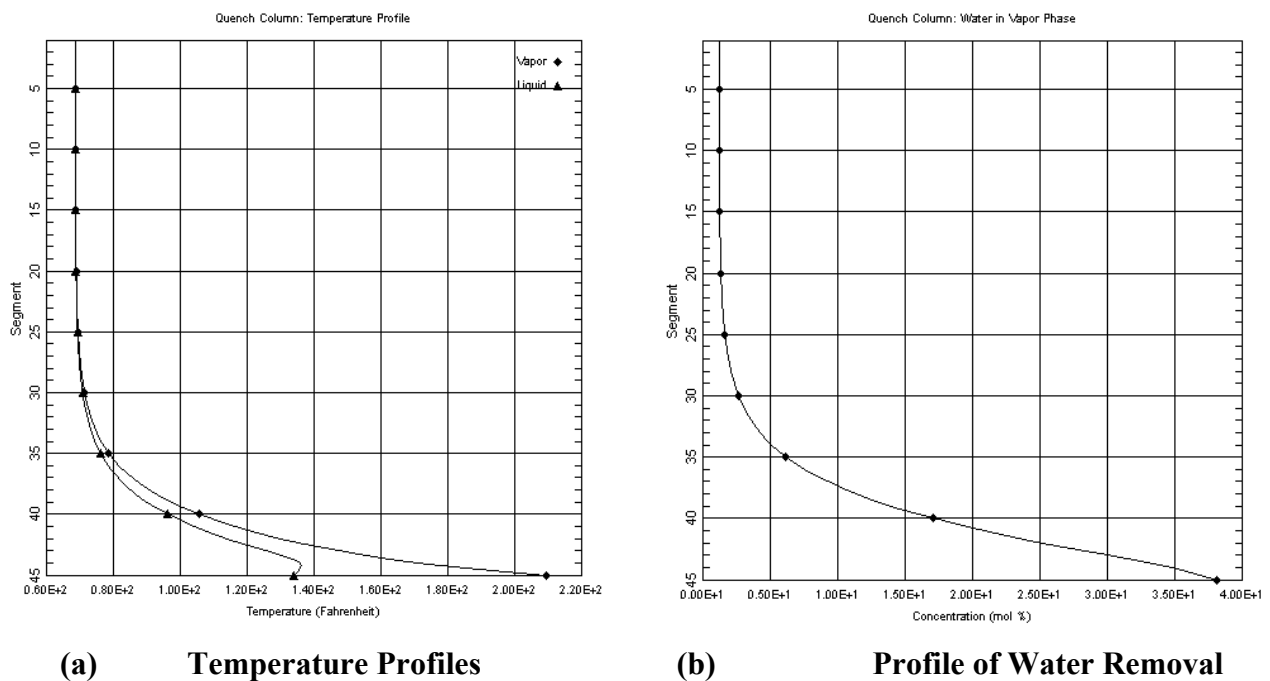

(a)   **Temperature Profiles**   (b)   **Profile of Water Removal**

Figure 4   Temperature and Water Removal Profiles in Quench Column

This level of detail is an added bonus provided by a mass transfer rate-based model. The fact of a small liquid-phase temperature bulge may be somewhat erudite, but it is certainly pertinent to know what packed bed depth (or the numbers of a specific tray) are actually required to perform a given function. At the very least, it gives one design confidence and a known margin of uncertainty.

6. CONCLUSIONS

Using a genuine mass and heat transfer rate-based simulation model for amine and quench columns treating streams containing ammonia has revealed several aspects of these processes that have remained hidden, and has provided answers to the questions asked in the introduction. Acid gases react with ammonia which tends to increase greatly ammonia concentrations in water and in aqueous amine systems because the acid components convert dissolved ammonia to ammonium ion and this species has almost unlimited solubility in aqueous solutions.

In answer to the original questions, the TGU Quench unit seems extremely effective at removing most of the ammonia from the incoming gas, leaving perhaps a few tens of parts per million to find its way into the amine system. At the same time, it carries from one to nearly three times its own molar flow of total acid gas into the SWS system. At typical tail gas compositions, CO_2 is at quite a bit higher levels than the more troublesome H_2S and, depending on the original ammonia level in the incoming gas, the accompanying H_2S flow was found to range from 15% of the ammonia flow in the purge at 500 ppmv NH_3 in the feed to 70% when the gas contains 20 ppmv ammonia. But for the relatively higher CO_2 concentration in the case, H_2S carry into the SWS would be much higher. However, just because most of the ammonia is removed in the Quench Column, does not mean ammonia is not a problem in the TGU Amine unit.

The residual ammonia from the Quench Column enters the amine system and concentrates in the product acid gas from that unit. For example, 35 ppmv in the TGU Amine feed gas was found to cause the regenerator to accumulate enough ammonia for the acid gas to the Claus plant to contain *0.12 mol% (1,200 ppmv) ammonia*! A 10% purge of the regenerator reflux water reduced this to 700 ppmv, i.e., by nearly a factor of two. Thus, when even a few tens of ppmv of ammonia are present, it may be worthwhile to take a small purge from the stripper reflux to reduce ammonia to the sulfur plant.

Because nearly all the ammonia is removed in the Quench Column, could monitoring the ammonia level in the purge water provide a good measure of the ammonia destruction in the Claus plant? The simulation results in Table 3 suggest this might be viable. The relationship is more easily
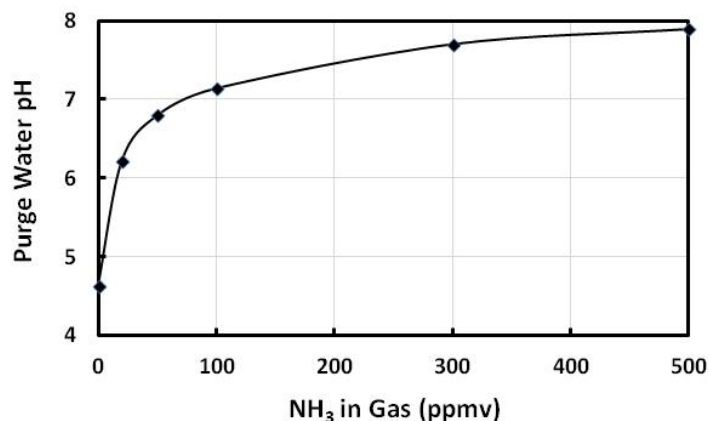

Figure 5   Sensitivity of Purge Water pH (at Purge Temperature) to NH_3 in the Inlet Gas

visualized in Figure 5. At moderate ammonia levels in the gas (<100 ppmv) the purge water pH (as determined at the temperature of the purge stream) responses very nicely to changes in ammonia concentration, and the lower the ammonia is, the more sensitive is the pH. Of course, it hardly needs emphasizing that pH can be used as a tool only if pH control is not being practiced. When the ammonia concentration is high, (>300 ppmv) the purge water needs no pH control as it is already in the vicinity of 8.0.

ProTreat's mass transfer rate-based column model allows an engineer to build a very rational model of their plant to the extent that the model becomes a virtual plant. The unprecedented reliability and accuracy can be leveraged to allow design margins to be drastically reduced, it makes designs more cost effective and competitive, and it makes troubleshooting a more precise art. All of this is a direct consequence of modeling equipment using fundamentally sound and correct engineering science as opposed to the idealizations of equilibrium stages, tray efficiencies and HETPs.

7. ACKNOWLEDGEMENT

8. REFERENCES

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