

Quench Water pH and NH₃ Destruction “Un-Vailed”¹

Nathan A Hatcher¹, G. Simon A. Weiland¹, Clayton E. Jones¹, Steven M. Fulk¹ & Matthew D. Bailey²

¹Optimized Gas Treating, Inc., 119 Cimarron Park Loop, Suite A, Buda, TX 78610, +1 512-312-9424

²Optimized Gas Treating, Inc., 12337 Jones Rd. Suite 432, Houston, TX 77070, +1 281-970-2700

nate.hatcher@ogtrt.com, clay.jones@ogtrt.com, simon.weiland@ogtrt.com,
steven.fulk@ogtrt.com, matt.bailey@ogtrt.com

ABSTRACT

Recent Brimstone Sulphur Symposia have featured several landmark papers providing insights into Claus unit ammonia destruction, SO₂ breakthroughs into TGU's, and chemistry in the TGU Quench column. Much of this work has been conducted or at least influenced by data collected at Alberta Sulphur Research, Ltd. (ASRL).

In this paper, we present a correlational tool we have developed that can be used to predict Claus unit ammonia destruction from downstream Quench water pH measurements. The tool can be used to infer ammonia slip from operating units so that online adjustments to the Claus furnace operations can be made. In developing the tool, several observations were made between quench water pH, the levels of ammonia destruction, the potential for SO₂ being present in the quench water, and quench water solution corrosion potential. These observations are noted in the paper, and will be presented in an interactive manner to solicit audience feedback about whether perhaps industry best practices should be considered in this area.

The effort to develop this tool ultimately required (1) correlating certain ASRL and other laboratory furnace ammonia destruction data, (2) implementing ammonia as a mass transfer and kinetically controlled rate component in the SulphurPro™ process simulator, (3) correlating simulated ammonia destruction data with simulated quench water pH, and (4) adapting the model to account for real world factors in both the Claus furnace and TGU quench column operations. In the end, the tool represents a successful adaptation of research data to commercial plant performance predictions using a solid, theoretical basis with practical utility for the real world.

¹ Brimstone Sulfur Symposium, Vail, CO, September, 2018

BACKGROUND

Recent Brimstone Sulphur Symposia have featured several landmark papers (Keller, 2012; Hatcher et al., 2016) providing insights into Claus unit ammonia destruction, SO₂ breakthroughs in TGU's, and chemistry in the TGU Quench column. Much of this work has been influenced by data collected at Alberta Sulphur Research, Ltd. (ASRL) and elsewhere. Experimental findings on conditions for predicting SO₂ breakthrough (Prinsloo et al., 2018) support the conclusions presented in the two papers first cited above.

The work reported here began many years ago with observations that were made of an operating SRU/TGU. This particular plant usually processed a moderate H₂S-content amine acid gas from an NGL facility. The pH of the TGU Quench Column circulating water was normally acidic (pH < 7.0) when processing this acid gas. Whenever the adjacent refinery diverted amine acid gas into the NGL acid gas header, the pH of the quench water became alkaline (pH ~ 8.5). The refinery acid gas contained low ammonia levels—the gas-plant acid gas was ammonia free.

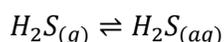
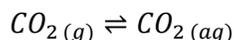
As at many plants, the operators of this unit were under the impression that keeping the quench water pH alkaline would prevent corrosion by eliminating the potential for SO₂ breakthrough corrosion. Over time, the plant began the practice of injecting caustic to hold the pH of the quench water at about 8.5 when the unit was not processing refinery gas. Shortly after this practice began, however, in-line installed corrosion probes began showing an *increase* in corrosion in the quench water loop. A subsequent investigation indicated that the increased corrosion was caused by injected-caustic trapping higher levels of H₂S in the quench water.

Since the time of these plant findings, calculations have become available for reliably predicting the fate of NH₃ in refinery amine systems (Hatcher and Weiland, 2011), ammonia destruction in the Claus furnace (Weiland et al.), ammonia's behavior in TGU Quench and Amine Systems (Hatcher and Weiland, 2012), H₂S corrosion in amine and sour water systems (Hatcher et al., 2014), and modeling SO₂ pickup in TGU Quench Water systems (Hatcher et al., 2016). These calculations are available in the ProTreat® and SulphurPro™ mass transfer and kinetics rate-based simulators.

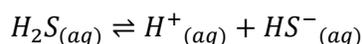
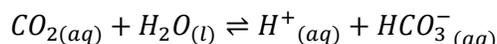
For this work, we studied the relationships between pH of the circulating quench water, ammonia content of the quench water, and ammonia slipped from the Reaction Furnace upstream. A correlation was found that lends itself to online unit monitoring of systems to infer ammonia destruction and slip in the SRU just by knowing the pH of the circulating quench water. The correlation is applicable to any directly coupled SRU/TGU plant that is not actively injecting caustic or ammonia for quench-water pH control.

CHEMISTRY AND RELEVANT VLE

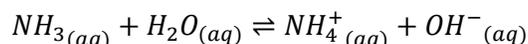
Both H₂S and CO₂ are very sparingly soluble in water, making water alone a profoundly unsuitable solvent for removing them from a gas stream.



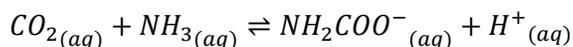
They are very weak acids:



On the other hand, ammonia is quite soluble in water:



It is only weakly alkaline, however, because its solubility is limited by a substantial vapor pressure over aqueous solution. Nonetheless, in a TGU Quench Column it almost entirely dissolves into the quench water. Ammonia binds H₂S and CO₂ by providing alkalinity; however, it also binds CO₂ by forming ammonium carbamate:



As shown by Hatcher and Weiland (2012), ammonia removal in quench water is a simple consequence of the acid-base neutralization reaction between ammonia, and both hydrogen sulfide and carbon dioxide. Ammonia provides a sink for H⁺ ions generated by acid gas dissociation and *vice-versa*. Ammonia, being fairly soluble, encourages the solubilization of the acid gases. Figure 1 shows the percentage of the ammonia in the feed gas to the Quench Tower that is absorbed in the quench water. Figure 2 shows the quench water pH and the corresponding concentrations of NH₃, H₂S and CO₂ as a function of the ammonia concentration in the feed gas to the Quench Tower. The feed gas is 2% H₂S and 12% CO₂ (dry basis) with ammonia levels of 0, 20, 50, 100, 500 ppmv. Figure 1 shows that by far the vast majority of the ammonia that reaches the Quench Column gets removed there and, as expected, the lower the quench temperature the more ammonia is removed. Figure 2 provides some idea of the relative solubility of CO₂, H₂S and ammonia from the case where the gas contains 500 ppmv NH₃. The dissolved NH₃ concentration is about one-half of the CO₂ concentration. In relative terms, ammonia is about 100 times more physically soluble than the acid gases, but the presence of ammonia greatly increases the acid gases' solubility simply because it gives the acid gases something to titrate against as they dissolve. The natural pH of the quench water without ammonia is around 4.6 but with 500 ppmv ammonia in the inlet gas it is slightly above neutral (pH = 7.9–8.0). What this means is that if the pH falls below about 4.0 there is every reason to believe SO₂ has turned up in the feed gas and may be about to cause (or is already causing) problems in the TGU. But the pH does not have to fall below 4.0 for there to be copious SO₂. In other words, low pH is sufficient but not necessary for there to be high SO₂ levels.

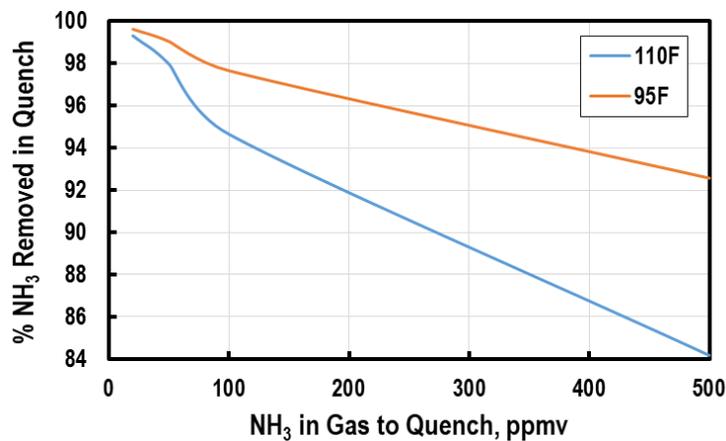


Figure 1 Percentage of Ammonia in Feed Removed in Quench Water

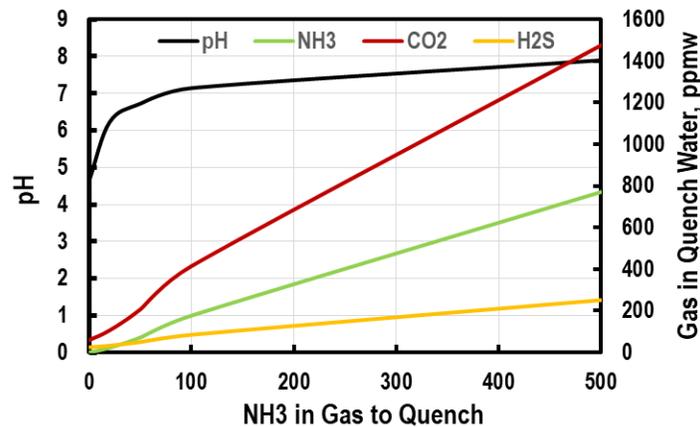


Figure 2 pH and Dissolved Gas Concentrations in Quench Water

As only a single parameter, pH simply cannot be made to stand in for the quench water composition. Rather than signaling a properly and safely operating unit, a neutral pH can hide a multitude of species, any one of which can cause rapid corrosion. In other words, neutral pH does not indicate the quench water is benign. At 25°C the pH of pure water is precisely 7.0 and at 40°C it is 6.77 — both are *neutral* pH values. At 25°C water containing 0.001 mole% H₂S and 0.001 mole% ammonia has a pH of 7.81; for a pH of 7.0 the solution would have to contain 0.00165 mole%

H₂S at this level of ammonia, i.e., the H₂S loading would have to be 1.65 moles H₂S per mole NH₃. However, the same 0.001 mole% NH₃ quench water could contain 0.0005 mole% each of H₂S and SO₂. Indeed, any of the compositions shown in Figure 3 result in neutral pH, demonstrating unequivocally that quench water pH is *not* a measure of corrosivity. For pH to have significance, the system must be understood and the solution speciated as an electrolyte.

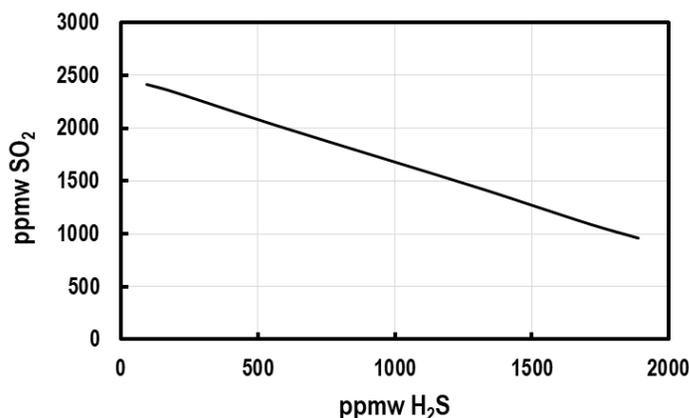


Figure 3 Various Combinations of H₂S and SO₂ that Produce pH = 7 Quench Water with 0.001 mole% (944 ppmw) Ammonia at 25°C

In this case, it was known from previous studies (Hatcher and Weiland, 2012) that NH₃ is picked up almost in its entirety from the process gas stream, so by material balance ammonia in the quench water must represent virtually all the ammonia that slipped from the Reaction Furnace upstream². It is also known that the amount of NH₃ entering the Quench Column is small in proportion to the H₂S and CO₂ in the process gas. The amount of H₂S and CO₂ picked up and the corresponding pH will depend upon a number of factors:

- Operating temperature and pressure in the Quench Column,
- The installed mass transfer internals in the Quench Column,
- The cooled quench water temperature and its circulation rate.

The ProTreat® mass and heat transfer rate-based simulator treats Quench Columns on a strict rate basis and so goes well beyond only analysing the humidification and dehumidification process that take place at various depths within the column's packed bed. It also accurately assess the absorption rates of ammonia and the acid gases and in so doing it achieves a very accurate picture of the composition of the quench water, the process gas, and the gas and water temperature profiles across the column.

MODEL VALIDATION

Confidently developing a relationship between quench water pH and Reaction Furnace ammonia slip requires some degree of surety that the following elements can be modeled accurately and consistently:

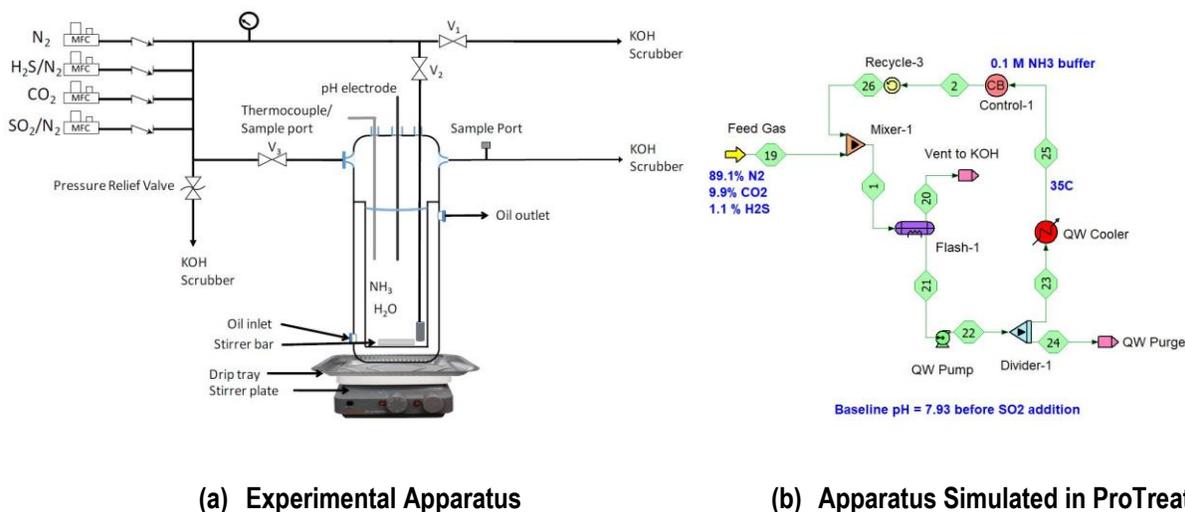
1. Accurate simulation of the upstream Claus SRU,
2. Accurate data and thermodynamic phase-equilibrium model the system NH₃-H₂S-CO₂-H₂O
3. Mass transfer rate-based model of the Quench system that accurately accounts for the transfer of the gases, water, and heat between the process gas and the quench water.

For the Quench Water system, ProTreat uses the same Deshmukh-Mather activity coefficient model for vapor-liquid equilibrium (VLE) model as it has used for 20 years for amine systems. The model accounts for all ionic species and produces a "real" pH. Other software uses "shortcut" methods such as Kent-Eisenberg and API-Sour models and assumes all activity coefficients are exactly unity, i.e., the solutions are essentially ideal and the equilibria amongst components ignore the interacting ionic nature of the solutions. These are gross approximations, and not very good ones.

² Herein lies an assumption and the main limitation of the approach — only a directly-coupled, single SRU/TGU can be modeled with accuracy using this approach.

Veracity of pH Predictions

ProTreat's quench water pH predictions have been validated against the SO_2 -free data reported by Prinsloo et al. (2018, Figure 8). These authors measured pH of quench water using the equipment shown in Figure 4a to simulate a quench vessel. Figure 4b shows the flowsheet used to simulate the laboratory equipment in ProTreat. The quench water contained H_2S and CO_2 in 0.1M ammonia. The measured pH was 7.93 versus ProTreat's prediction of 7.95, well within the uncertainty expectations for a pH meter.



(a) Experimental Apparatus

(b) Apparatus Simulated in ProTreat

Figure 4 Experimental Setup and ProTreat Simulation

Ammonia Destruction in the Reaction Furnace

Alberta Sulphur Research Limited (ASRL) has carried out several valuable experimental studies to establish ammonia destruction kinetics in the Reaction Furnace. Ammonia destruction can occur via several reaction pathways which together form an involved “web” of mutual dependencies. Some reactions are in series, others are in parallel.

The experiments were carried out methodically and carefully. The first round used gases comprised of single sets of reactants so that the kinetics of each individual reaction could be measured. This work proved that the very fast reaction $H_2S + O_2 \rightarrow SO_2$ normally occurs first, followed by the oxidation reaction of SO_2 with NH_3 . There are a number of other pathways, e.g., the thermal decomposition of NH_3 into N_2 and H_2 , direct oxidation of NH_3 by O_2 , and so on, but kinetic measurements demonstrated that these other pathways are slower in typical SRU reaction furnaces. These data set the workings of our model: First, H_2S is allowed to completely oxidize to SO_2 until the limiting reagent (H_2S or O_2 ... typically O_2 unless the plant is in trouble!) is consumed. Next the resulting mixture of NH_3 and SO_2 enters a reactor which calculates the total extent of NH_3 destruction. Thus the model is based on reaction kinetics and is built on the assumption of typical SRU Reaction Furnace chemistry and is accurate for applications within this intended scope, e.g. it does not model kinetically limited combustion of NH_3 when there is no H_2S present.

A second round of experiments used typical SRU feed gases to measure NH_3 destruction rates in the laboratory. This second set of experimental data was used to extract the 2nd-order reaction kinetics; it included “add-on” effects that are present in a real SRU, e.g., including substantial water in the feed gas (just as exists in a real Reaction Furnace), which is known to inhibit some of the NH_3 destruction reactions. Figure 5 shows the efficacy of the final fit contained in the SulphurPro model within ProTreat® v6.0 in April 2016.

The SulphurPro™ model within the ProTreat® simulator accurately predicts NH_3 destruction, NH_3 pickup in the Quench Tower, and quench water pH. The basis for the simulation is electrolyte chemistry, reaction kinetics, and purely rate-based simulation of both the Reaction Furnace and the Quench Column. Fundamental reaction kinetics rather than regressions to error-prone plant performance measurements forms a solid foundation for SulphurPro's truly predictive ability. This level of reliability, based on good science, can only be had from SulphurPro.

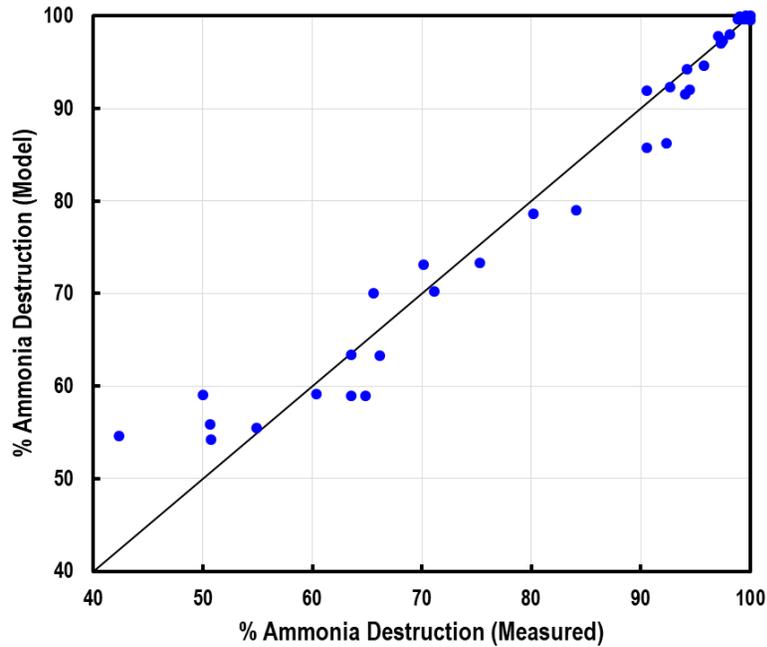


Figure 5 Comparison between Model and Laboratory-Measured Ammonia Destruction under Reaction Furnace Conditions

DATA GENERATION FOR CORRELATION

To generate the data to correlate, the ProTreat and SulphurPro simulation tools were utilized. A three bed Claus unit with an amine based tail gas unit was chosen and fed with typical refinery type Amine Acid Gas (AAG) and Sour Water Acid Gas (SWAG) as shown in Figure 6. The AAG feed contained H_2S , CO_2 , H_2O , CH_4 , and N_2 . The SWAG feed contained equimolar H_2O , H_2S , and NH_3 concentrations. In order to understand the impacts of variant feed quality on ammonia destruction, three concentrations of H_2S and CO_2 in the Amine Acid Gas were evaluated to give a range from lean to rich feed quality at which the ammonia destruction could then be assessed. For each acid gas feed variation, a range of ammonia destruction was obtained by utilizing the SulphurPro kinetic model to better understand the impacts of ammonia slip on the Quench water pH. This gave a data matrix of ammonia destruction versus Claus feed quality. Using a simulator to generate this data is much less risky than making moves on an operating plant, provided that the model is representative of the process. In order to obtain the natural pH of the Quench water circuit, it was assumed that the Hydrogenation Reactor was functioning properly and no SO_2 was slipping to the Quench system. It was also assumed that the plant was not injecting caustic or makeup NH_3 in order to artificially control the Quench system pH.

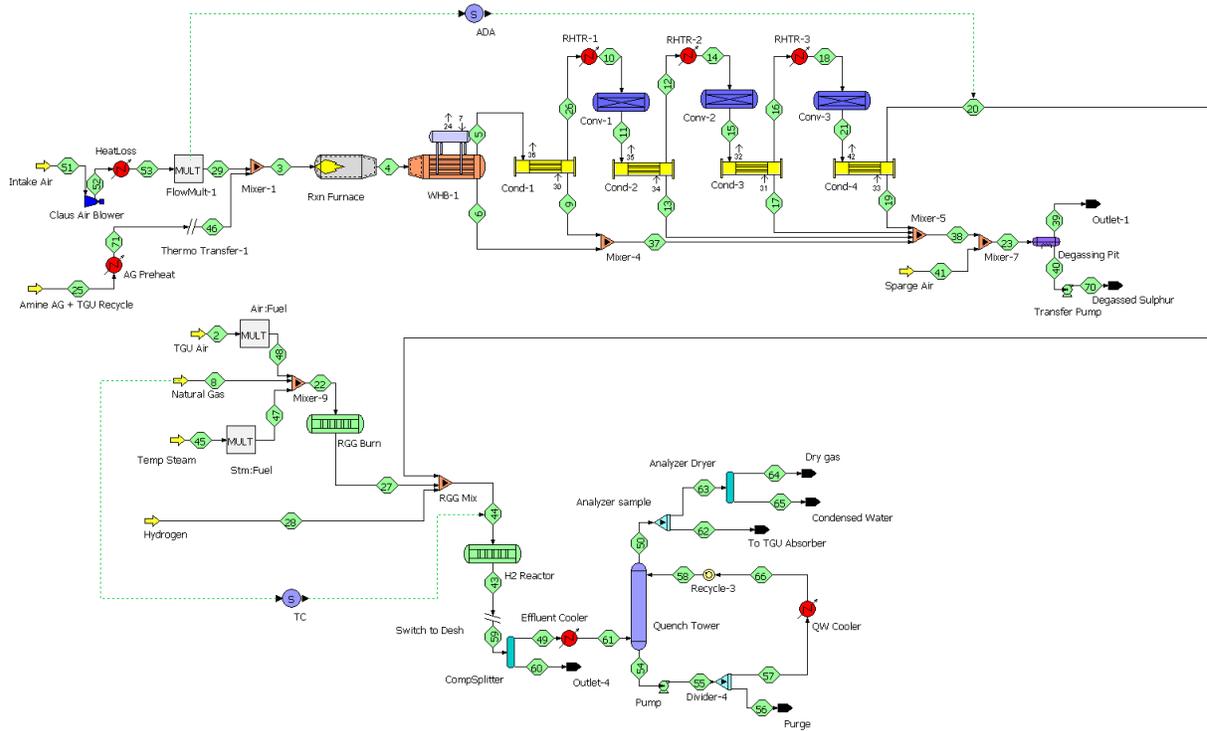


Figure 6 ProTreat® and SulphurPro™ Flowsheet Setup

CORRELATION RESULTS

After generating the data points, a correlation was found to fit the calculated dry outlet NH_3 concentration from the Reaction Furnace as a function of Quench water pH at 77°F. Each curve in Figure 7 represents a different wet Amine Acid Gas H_2S concentration ranging from a lean acid gas to a rich feed. The feed composition is a weak, but significant player in the level of ammonia destruction. The difference in feed quality weakens as the ammonia destruction approaches 100%, or towards the acidic range. Assuming that a given plant configuration runs with a feed composition that is not subject to huge variations, the pH of the Quench Water will naturally equilibrate to a level fixed by the ammonia destruction in the Reaction Furnace. The Reaction Furnace ammonia slip can be inferred by measuring dissolved NH_3 in the Quench Water or having a specialized testing firm, such as Brimstone STS, survey the plant.

Ammonia in RF Effluent vs. Quench pH

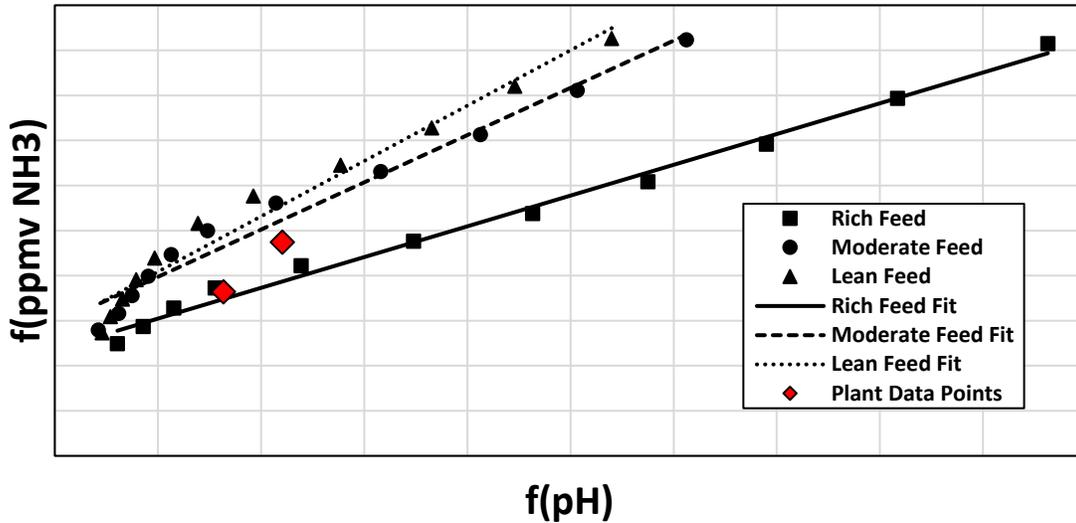


Figure 7 Data Set Generated and Resulting Correlation Results with Measured Plant Data Overlaid

For a given feed composition and plant configuration, the slope of the proprietary relationship can be used to generate predictions for the ammonia concentration slipping from the Reaction Furnace. While the predictions are not pin-point accurate, they do provide the necessary precision to tell when high levels of NH_3 are slipping from the Reaction Furnace. This tool can now assist plant engineers and operators in identifying when the Reaction Furnace ammonia destruction system is not optimally operating and provide a quicker way to infer either potential burner damage or the system becoming overwhelmed with NH_3 . This relationship can aid also in making zone split and preheat decisions leading to quicker optimization moves of the Claus unit. As noted by the actual plant data points that are overlaid on Figure 7, in principle, a minimum of two data points are required to establish an operating slope and performance predictions.

A sensitivity study was conducted looking at variations in the operating conditions and plant configurations to gauge the validity of the correlation for these variations. The original work assumed a three bed Claus unit with no Oxygen enrichment and is represented by the circles in Figure 8. The first variation was to look at a two bed Claus plant, which did not seem to have much, if any, impact on the results as represented by the triangles in Figure 8. We then went back to the three bed Claus unit and added in a low level of oxygen enrichment, 28% oxygen. These results are represented as diamonds also in Figure 8. From this sensitivity study, it can be inferred that Claus plants operating with oxygen enrichment will have an offset to plants that are on air only. As such, a Claus plant running Oxygen enrichment will have a higher concentration of ammonia from the Reaction Furnace than a Claus plant running air only for the same measured pH value, as shown in Figure 8.

Sensitivity Study for Configuration and O₂ Enrichment

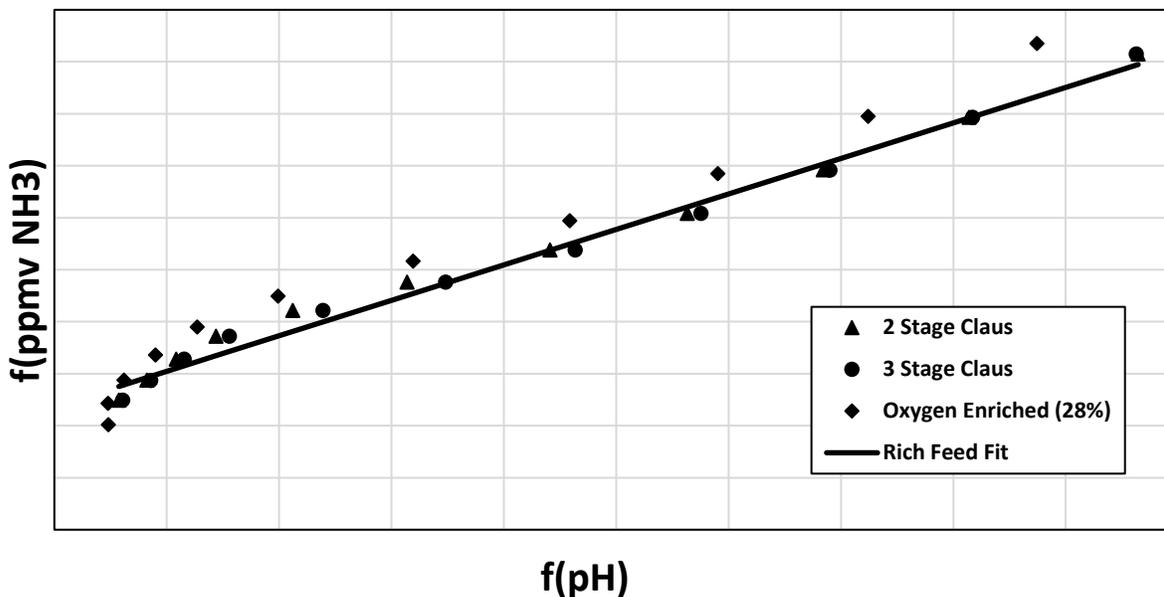


Figure 8 Sensitivity Study for Configuration and Oxygen Enrichment

A number high level rules-of-thumb can be procured from this work. Plants processing a rich acid gas feed and Sour Water Acid Gas with a natural Quench Water pH of approximately 8 or higher can be assumed to have higher levels of ammonia slip from the furnace and, as such, have an enhanced risk of ammonia plugging problems. Likewise, plants processing moderate to low quality acid gas and Sour Water Acid Gas with a natural Quench Water pH of around 7.25 or higher are also at a higher risk of ammonia plugging due to the higher ammonia slip from the furnace. On the other hand, any plant with a quench water pH less than 4 is most likely experiencing an SO₂ breakthrough from the TGTU Reactor to the Quench system, and may be experiencing SO₂ breakthrough to the amine system. This could potentially have disastrous consequences such as highly corrosive conditions, irreversible amine degradation, off-specification treating all of which could either render the plant inoperable or cause an unplanned shutdown to occur.

CONCLUSIONS

A correlation was successfully developed to infer Reaction Furnace ammonia slip from Quench Tower pH measurements. With the development of this correlation, quicker decisions can be made by plant operations personnel to optimize and troubleshoot ammonia destruction systems. We are looking for a pilot facility to set up a monitoring and prediction program on line. Although the correlation was initially developed for ProTreat/SulphurPro generated data, the form of this correlation lends itself to use on *any* plant configuration, as long as the feed concentration is relatively consistent from day to day and two or more plant measurements are made to calibrate the model. The two actual plant measurements to date are in the range of expectations from the SulphurPro/ProTreat predictions. Given the complex nature of the factors that play into Claus unit ammonia destruction and TGU plant performance, only a model based upon truly first principles science can represent this system well.

REFERENCES

Nathan A Hatcher, P.E., Clayton E. Jones, MS, P.E., G. Simon A. Weiland, *SO₂ Breakthrough under a Microscope*, Brimstone-STS Sulfur Recovery Symposium, Vail, CO, 2016.

R. Prinsloo, Robert A. Marriott, Norman I. Dowling, *Investigating Quench Tower Conditions for Predicting SO₂ Breakthrough*, Laurence Reid Gas Conditioning Conference, Norman, OK, 2018.

Keller, A., *The Aftermath of SO₂ Breakthrough and Ways to Prevent and Mitigate It*, Brimstone-STS Sulfur Recovery Symposium, Vail, CO, 2012.

Nathan A. Hatcher, Ralph H. Weiland, *The Fate of Ammonia in Refinery Amine Systems*, Brimstone-STS Sulfur Recovery Symposium, Vail, CO, 2011.

G. Simon A. Weiland, Nathan A. Hatcher, Clayton E. Jones, Ralph H. Weiland, *Ammonia Destruction in the Reaction Furnace*, Petroleum Technology Quarterly, Q4, 2016.

Nathan A. Hatcher, Ralph H. Weiland, *Ammonia in TGU Quench and Amine Systems*, SOGAT 2012, Abu Dhabi, UAE, March, 2012.

Nathan A. Hatcher, Clayton E. Jones, G. Simon Weiland, Ralph H. Weiland, *Predicting Corrosion Rates in Amine and Sour Water Systems*, Petroleum Technology Quarterly, Gas, 2014.