The Aftermath of SO_2 Breakthrough and Ways to Prevent and Mitigate It

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Requirement for Tail Gas Units

Claus sulfur recovery units are not capable of meeting the H_2S or SO_2 emissions guidelines set by most emissions regulating agencies world-wide. Thermodynamic restrictions on the Claus reaction make operating more than 3 catalytic stages uneconomical and impractical. Several recovery booster schemes have been used as "tail gas units" to provide the needed cleanup of the gases from a Claus sulfur recovery unit to meet required emissions regulations.

Classification of Tail Gas Processes

Tail gas units mainly fall into a two categories. One category, once-through processes, typically has one or more conversion steps with the goal of producing a final by-product. Chief among these are sulfur producing technologies such as SuperClaus, Stretford, or CBA, or chemical producing technologies such as sulfuric acid or ammonium thiosulfate (ATS). The other category involves processes generating a recycle stream to the Claus unit containing only one sulfur compound. Cansolv and Wellman-Lord are examples of processes that generate a recycle SO_2 stream, whereas BSR/MDEA, SCOT, Resulf, and other competing processes utilize hydrogenation over a supported Co-Mo sulfide catalyst followed by amine treating to generate a recycle stream containing H_2S.

Elemental Sulfur: The Biggest Challenge Facing Tail Gas Units

No matter the process, one observes that the most challenging part of any of these processes is the presence of the product that was intended to be made by the Claus plant to begin with, elemental sulfur. If it weren't for the presence of elemental sulfur in the TGU feed or as a product of the TGU process, the TGU would be much less complicated and much less expensive. Sulfur's relatively high freezing temperature, insolubility in water, and vapor pressure over liquid makes it a nuisance to have or handle in many different ways.

Liquid water provides a very favorable environment to perform the Claus reaction as the insolubility of the product completely eliminates the Claus chemical equilibrium constraints. However, forming elemental sulfur in water under acidic conditions can lead to severe metal corrosion, production of undesired sulfates or polythionates, and severe plugging problems. Under basic conditions, sulfur is difficult to form from H_2S because oxidation of H_2S by either O_2 or SO_2 tends to make oxy-sulfur anions, mainly thiosulfate ($S_2O_3^{-2}$), instead of elemental sulfur. Catalyst metals such as chelated iron or soluble vanadium salts are needed to convert H_2S to sulfur under basic conditions. An improper

balance of chemical additives or contaminants can lead to difficulties in retrieving the solid sulfur from solution causing plugging somewhere in the unit.

Different solvent based processes such as ClausPol and CrystaSulf have been employed to take advantage of low temperature in producing a favorable Claus equilibrium, but have not gained traction in the industry, likely due to the solids handling portion of the process needed to separate the sulfur.

Elemental sulfur can stop the progress of a catalytic reaction simply by saturating the surface of the catalyst preventing the flow of reactants to and products from the surface. Surfaces below the freezing point of sulfur can allow large deposits of elemental sulfur to accumulate, causing unwanted pressure drop and under-deposit corrosion.

Factors in Choosing a Tail Gas Unit Technology

Choosing a tail gas unit is both a technical and economic decision. Technical considerations start with the regulator‘s requirements for emissions followed by the practical considerations of the technology (plot space, operating complexity, equipment life, safety, etc.). The main economic consideration outside capital cost is what to do with the tail gas products once elemental sulfur is dealt with.

If the tail gas unit produces liquid elemental sulfur by a Claus chemistry variant, the decision is easy; the operator simply incorporates the product into the liquid sulfur that is shipped or formed and shipped. If the tail gas unit produces sulfur in solvent, complications are introduced as the solvent may not be compatible with the liquid sulfur production due to metal or solvent contamination. If the byproduct is not elemental sulfur, the form of the byproduct, the market for the byproduct, and the storage and handling of the byproduct become important considerations.

There are two major routes to non-elemental sulfur byproducts, oxidation to convert all non-SO_2 sulfur to SO_2, and reduction/hydrolysis to convert all non-H_2S sulfur to H_2S. In each of these routes, elemental sulfur handling problems are addressed in a single conversion step. It is important to note that if the conversion to all of one species is not complete, elemental sulfur deposition will foul and eventually cripple the tail gas process because both the oxidation and reduction technologies “go to the water” to complete the process.

When generating SO_2 by oxidation in an incinerator, incomplete conversion of H_2S or elemental sulfur result in the deposition of elemental sulfur once both species enter liquid water as it becomes acidic from dissolving SO_2. This has been observed in ATS and SBS plants where the incinerator operated with no excess oxygen during Claus unit upsets.

As for reduction/hydrolysis, the final stage of this part of the TGU process is a gas drying step, usually in a “quench tower”, where nearly all the water contained in the feeds to the Claus plant along with water generated from all the sulfur recovery reactions is condensed and removed from the process. The drying step allows the tail gas to enter

treatment (usually amine) at low temperature ~100 F (38C) which aids the performance of the amine system. It would appear that quench towers came into use as it is likely that a simple heat exchanger to perform the condensation quickly plugged due to having both Claus ingredients hit the condenser tubes simultaneously during an upset event. It appears the quench tower arrangement is a bit more forgiving, or is it?

SO_2 Breakthrough in a Reduction/Hydrolysis-Amine TGU

Figure 1: Generic Flow Sheet of a Reduction/Hydrolysis TGU

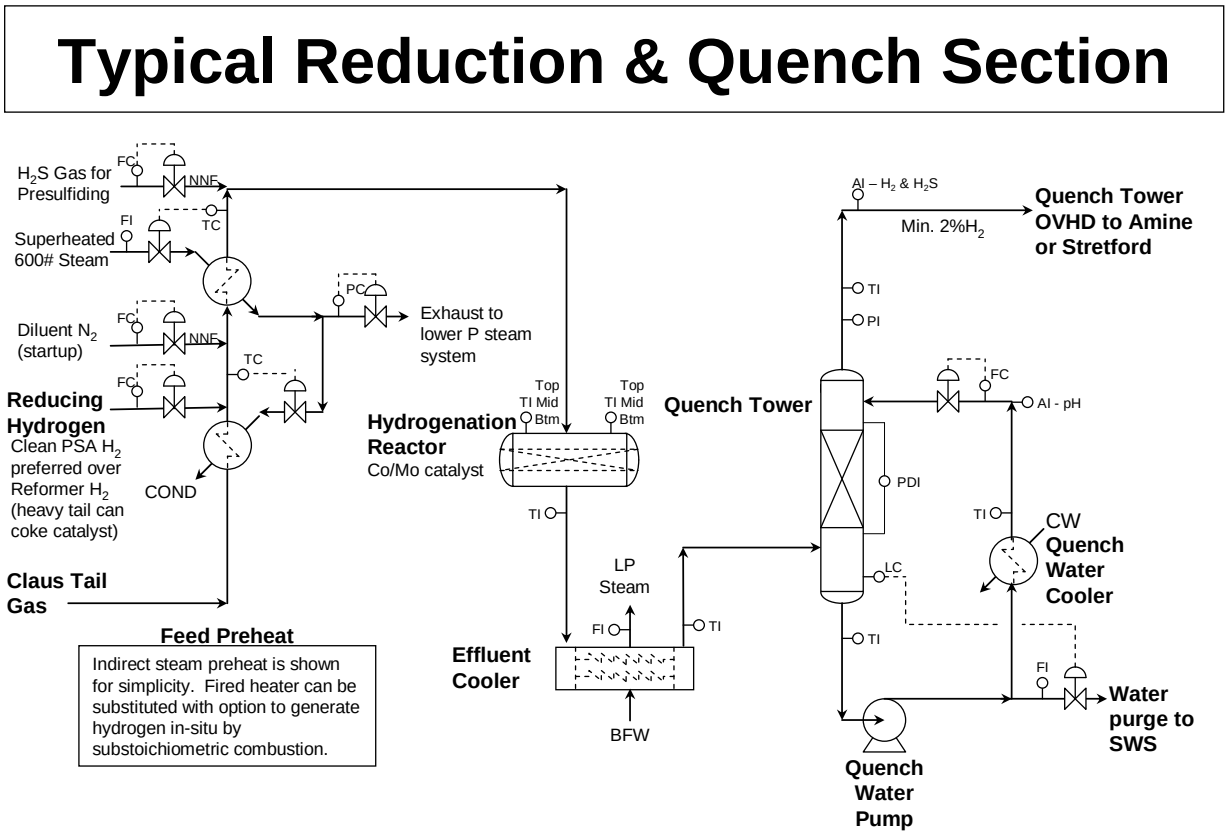


Figure 1 depicts a typical reduction/quench section of a reduction/amine TGU. The main variations in the scheme involve preheat options, how to supplement the amount of hydrogen available from the Claus furnace/WHB, managing heat removal, equipment for startup and catalyst activation, and quench tower layout. In all variations, the chemistry on the catalyst is the same and is usually depicted as follows:

SO_2 conversion:

$$SO_2 + 3\ H_2 \Rightarrow H_2S + 2\ H_2O$$

Elemental sulfur conversion:

$$S_x + x\ H_2 \Rightarrow x\ H_2S \quad (2<x<10)$$

COS/CS_2 hydrolysis:

$$COS + H_2O \Leftrightarrow CO_2 + H_2S$$

$$CS_2 + 2\ H_2O \Leftrightarrow CO_2 + 2\ H_2S$$

Side reactions both beneficial and detrimental occur. The most important side reaction is CO hydrolysis or the water gas shift (WGS) reaction:

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

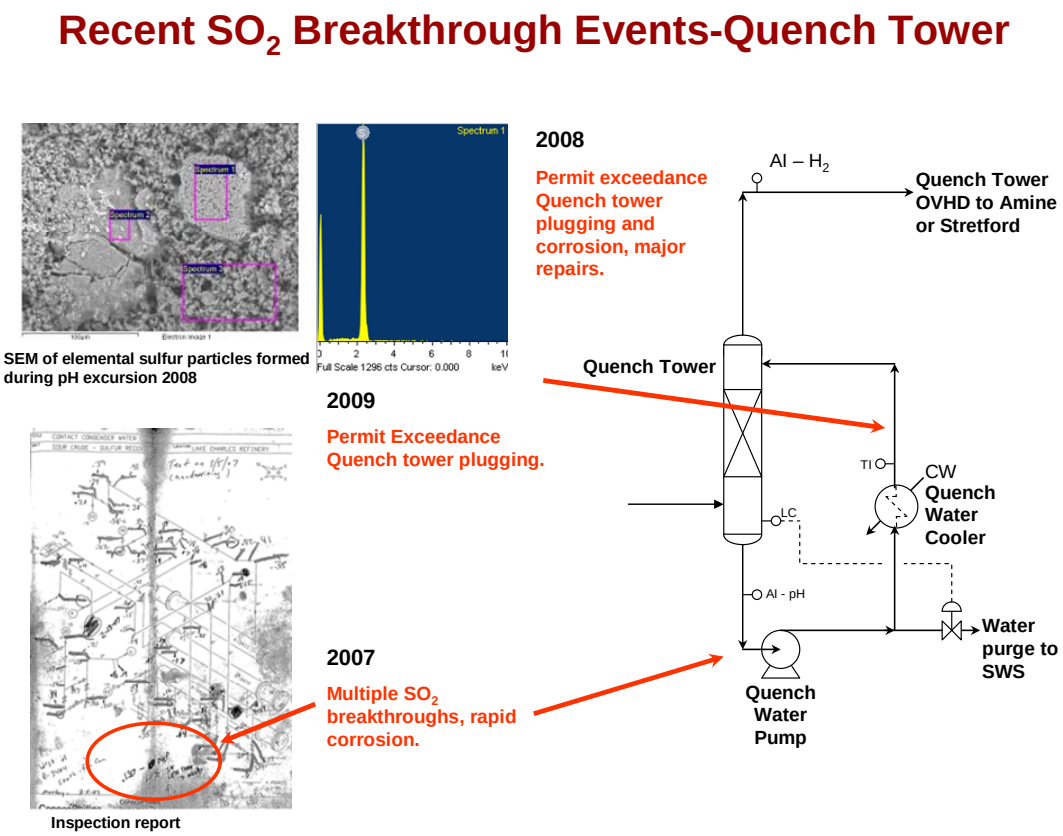
WGS reaction is desirable for three reasons, 1) Hydrogen is generated assisting in maintaining an excess hydrogen environment on the TGU catalyst 2) CO, also a regulated pollutant, is converted under mild conditions and this could reduce the temperature of tail gas incineration needed to destroy any remaining CO, and 3) excess CO is prevented from participating in the sour gas shift (SGS) reaction where H_2S is substituted for H_2O in the WGS reaction:

$$CO + H_2S \Leftrightarrow COS + H_2$$

In WGS, CO_2 is formed; in the analogous SGS reaction COS is formed. In terms of meeting emissions requirements, the lack of CO conversion by WGS and subsequent increase in CO conversion by SGS is likely to be more important on a day to day basis as the catalyst ages and the ability to increase the temperature of the feed to the catalyst bed decreases. In terms of keeping the tail gas unit, and subsequently the sulfur plant(s) they are tied to on line however, the hydrogenation reactions are far more important. If elemental sulfur or a combination of H_2S and SO_2 leave the catalyst bed and reach the quench tower, the unit will plug, corrode, and eventually require drastic measures to clean up the mess usually costing reduced sulfur plant rates and thus reduced hydrocarbon processing rates.

Figures 2 and 3 are representative of the effects of large SO_2 breakthrough events. Such recent events have resulted in significant lost profit opportunity (LPO) or potential LPO as affected units pushed the tolerance of the regulatory agencies for operating in a crippled condition. In **Figure 2**, the quench tower section, the solids in the picture, elemental sulfur, formed a milky white liquid with grayish white to black solids suspended throughout. Although the amine solution that the particles in **Figure 3** were taken from looked almost identical to the quench water that the particles in **Figure 2** came from**,** the nature of the particles (FeS) as demonstrated by the accompanying X-ray data was totally different.

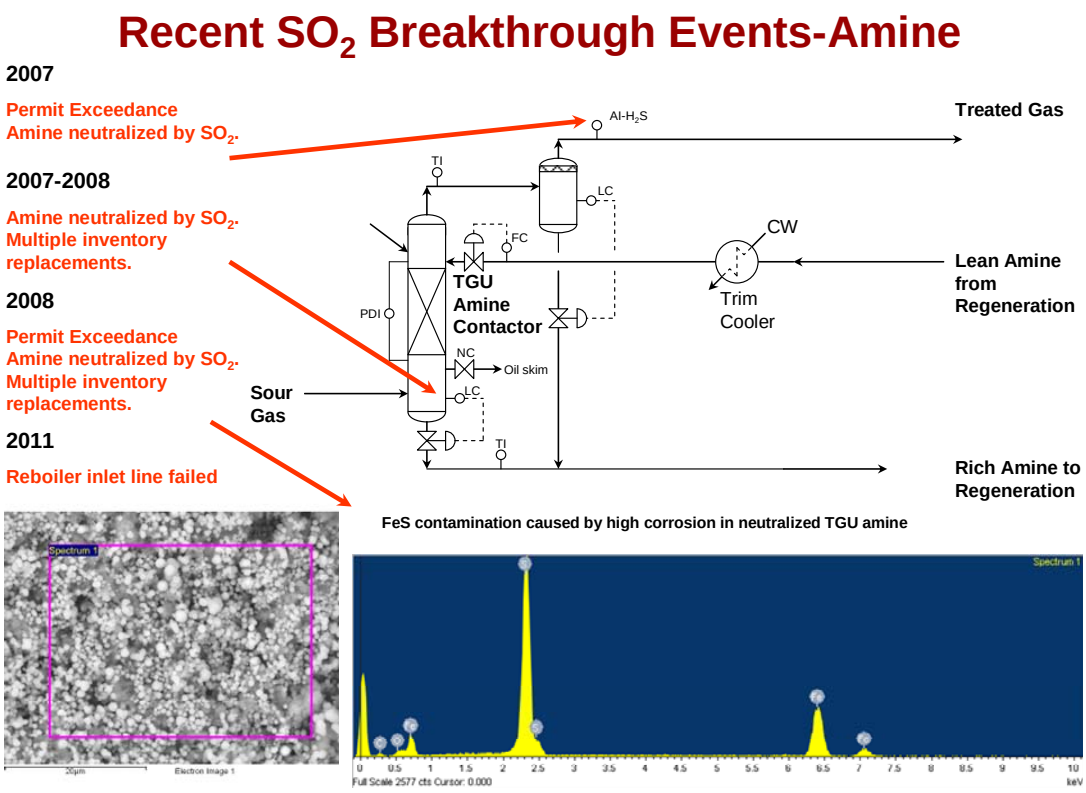
Figure 2: Results from Massive SO_2 Breakthrough in Quench Section of TGU



The lessons learned from the incidents summarized in these figures serve as axioms for understanding the nature of SO_2 breakthrough in reduction-amine style TGU's. First and plain to see, these events can have devastating effects on the operation and mechanical integrity of the TGU. Second, not plain to see, but felt deep down inside, these incidents are preventable under almost all circumstances. Even though these incidents are preventable in most normal operations, power failures or mechanical failures do happen, so operations must be ready.

Although these ideas are axiomatic, the approaches to dealing with SO_2 breakthrough are not. As with geometry, where we are asked to start with a few axioms and develop proof of geometric relationships; with SO_2 breakthrough we have to start with some basic chemistry, operations knowledge, and apply some additional skills to understand the more complex nature of SO_2 breakthrough consequences and develop effective strategies to deal with them.

Figure 3: Results from Massive SO_2 Breakthrough in Amine Section of TGU



Types of SO_2 Breakthrough

Different types of SO_2 breakthrough occur with different causes. While the effects differ, only bad effects accompany unmitigated SO_2 breakthrough. SO_2 breakthrough comes in two types. The first type, SO_2 only breakthrough, results mainly from non-standard operations such as startup, presulfiding, and hot standby. SO_2 breakthrough accompanied by H_2S is the second type nominally occurring during normal acid gas operations. Both high SO_2/low H_2S and low SO_2/high H_2S breakthrough can take place, the former causing much more severe problems due to the shortage of H_2S in the quench water at low pH.

Tables 1-3 summarize the conditions of each of these SO_2 breakthrough scenarios, roughly in order of the speed at which catastrophic failure or plugging takes place. The italicized items have been noticed in recent events because some of the usual events surrounding SO_2 breakthrough, namely sulfur plugging, did not occur.

Table 1: Causes and Characteristics of SO_2 only Breakthrough

SO_2 Only Breakthrough	
Causes	**Characteristics**
Complete H_2S consumption in Claus and complete H_2 consumption in hydrogenation (Air Demand Analyzer, ADA, or air control failure)	**Rapid pH plunge to <3 without solid sulfur formation**
Conversion of TGU catalyst from metal sulfide to oxide	**High corrosion rates even to SS**
Direct oxidation of H_2S to SO_2 over TGU metal oxide catalyst	**Rapid TGU amine neutralization,** ***MDEA degradation***
	Amine bisulfite corrosion

Table 2: Causes and Characteristics of High SO_2/low H_2S Breakthrough

High SO_2 with Low H_2S Breakthrough	
Causes	**Characteristics**
Disabled ADA or TGU hydrogen analyzer	**Plunge to low pH (<3) with solid sulfur formation-rapid plugging**
Manual air control	**Higher corrosion rates due to sulfurous acid attack**
Shortage or loss of hydrogen	**Neutralization of TGU amine**
	Increased corrosivity of TGU amine

Table 3: Causes and Characteristics of Low SO_2/High H_2S Breakthrough

Low SO_2 with High H_2S Breakthrough	
Causes	**Characteristics**
Disabled ADA or TGU hydrogen analyzer	**Lowered or drifting pH**
Manual air control	**Accelerated, but not catastrophic corrosion rates**
Shortage or loss of hydrogen	**Steady neutralization of TGU amine**
	Erratic stack emission performance

A recent major finding is aggressive corrosion of carbon steel in hot lean amine sections of the TGU. Recent failures in this section of the TGU include reboiler inlet lines, regenerator wall thinning, lean amine pumps, valves, and the lean side of the lean/rich exchanger. This damage does not appear to be the result of either the presence or absence of lean loading (over or under stripping), and only seems to be aggravated after a massive SO_2 breakthrough. **Figure 4** shows some of this aggressive corrosion in a carbon steel TGU reboiler inlet line.

Figure 4: Aggressive Corrosion in Hot Lean Amine Following SO_2 Breakthrough

Severe TGU reboiler inlet line corrosion likely caused by $MDEAH^+HSO_3^-$ accumulation after SO_2 breakthrough.

Caught off-guard: The problem with pH

One might ask, "How is it that a thriving operation can be sent into such a tailspin so rapidly?" One reason may be the absolute reliance that many operators and their supporting engineers have on the pH meter sitting in the quench tower circulation. The pH meter seems to be all-knowing, bestowing a wealth of information on the health of the TGU when in fact it is nothing more than a "low-low" alarm, if working properly. In its appropriate role as low-low alarm, the pH meter warns of immediate danger that can cause loss of containment, something the industry labels as a safe operating limit or SOL. This means that when the alarm goes off, operations must immediately respond to return the unit to a safe operating envelope. A big problem is that the pH meter is good for telling us when the unit is in trouble, but not very good at telling us that the unit is getting into trouble or has gotten out of trouble.

Confusion surrounding the mystery of pH leads to what one would colloquially refer to as "Old Wives' Tales" about the quench tower and SO_2 breakthrough. Some come to believe that they can take their time getting to the neutralizer injection without any

urgency. Others might have heard the pH 7 means neutral, so that must be ok. Still others may think that one quick blast from the neutralizer clears everything up and will prevent the kinds of problems shown in **Figure 4**. Some quench towers are equipped with a section containing a batch of "caustic" that should neutralize any SO_2 breakthrough. In all these cases, the same assumption about the quality of information from the pH appears to be made, that it tells us everything we need to know about the solution it is measuring.

What does pH tells operators?

There are many things that we would like the pH meter to be telling operations. We would want pH to tell them which species of dissolved SO_2 are present. Some are aggressively corrosive, some aren't. If pH could tell us the concentration of dissolved SO_2 species, it would give us useful information about how corrosive the solution is. We would also like pH to tell us the composition of the quench water, the potential to form solid sulfur in the quench tower, and the potential to neutralize the TGU amine.

Unfortunately this is not the case. pH has a specific definition. For dilute solutions of reasonable ionic strength, the pH meter tells us the molar (gram moles/liter designated by ***M***) concentration of hydrogen ion $[H^+]$ over a wide range of concentrations from 10^{-14} to 1 ***M***. A log scale from the definition of pH = –log $[H^+]$ makes it convenient to work with changes in $[H^+]$ over several orders of magnitude, especially when doing analytical work. Unlike the computations used to put together some of the graphs later on, the accuracy of a typical pH meter is only about +/- 0.03 to 0.05 pH units. Outside of H^+ concentration, the pH meter tells us NOTHING else about the remainder of the solution.

Things about the solution can be inferred from the number only if the chemistry is completely defined, and the changes to the solution are only associated with the defined chemistry. The art of pH titration and the development of certain titration related analytical methods use the assumption of defined chemistry to determine the concentrations of acids or bases, as with amine strength. It can also be used to predict the behavior of acid/base systems once we know all the original constituents of a solution and their corresponding equilibrium characteristics. Once we step outside the defined chemistry however, we can no longer trust pH to tell us what is in the solution at what concentration outside of the one thing it is designed to measure, $[H^+]$.

pH tends to tell operations what normal looks like. Unfortunately, what normal looks like may be completely different for plants operating with completely different feeds and Claus unit configurations. An example of the variety of conditions and the resultant normal operating pH for several refinery units are given in **Table 4** below.

Table 4: Quench Water pH Readings for Varying SRU Configurations

Unit	64	65	64	64	A Train	592	U43 A&B Claus	#2 SRU
Sampling date	6/19/06	6/19/06	12/11/06	12/12/06	6/8/06	7/14/06	8/7/06	8/9/06
Reaction Furnace Type	Straight through	Straight through	Straight through	Straight through	Split Flow	Split Flow	Split Flow	Straight through
NH3 in quench water, ppm	69	228	227	76	112	1185	98	55
Quench water pH	8.3	7.8	8.1	7.4	6.9	8.8	7.9	8.1
%NH3 in feed destroyed	99.87	99.63	99.59	99.88	99.74	99.14	99.93 (avg)	99.94

There appears to be little correlation between overall computed ammonia destruction and quench water pH, and little correlation between SRU furnace types and quench water pH. One would expect that less ammonia destruction and higher ammonia in the quench water would produce a higher pH as "592" shows, but that correlation is shattered looking at identical parallel units "64" and "65". There is no indication of what drives the pH to this number other than knowing the ammonia content of the water. With no information provided on acid gas composition, temperature, and pressure, we can only be left to guess what else is there. This same problem gets even more complicated to decipher or compute for quench towers employing a "desuperheater" where caustic solution is added to the circulating water stream to "neutralize" incoming SO_2. The pH of this solution may start out >14, but will drop steadily to a lower number as the caustic reacts with acid gases (H_2S and CO_2) in the TGU reactor effluent.

pH Discloses Dissolved Species Distribution and Not Concentration

Using the techniques outlined in **Fundamentals of Analytical Chemistry 3rd. ed**., D. A. Skoog and D. M. West, 1976, pp 233-235 as shown in **Figure 5**, we can readily see that the relative fractions of the total dissolved species can be computed as a function of pH. What this means in the case of any di-basic acid such as dissolved H_2S, CO_2 or SO_2 is that at a certain measured pH, whatever total concentration of the dissolved species, the fractions of each species will be the same. Because the equations can be manipulated to eliminate absolute concentrations, this essentially eliminates knowledge of the total concentration of the dissolved material as a function of pH. This becomes apparent in **Figure 6**.

Figure 6 shows the results of computing the distribution of dissolved SO_2 as a function of pH for two different situations, a 0.1 molal (g moles/kg of water) SO_2 with varying levels of sodium ion, Na^+, added to the mix to adjust pH, and 1.0 molal SO_2 with varying levels of ammonium ion, NH_4^+. Both equilibrium relationships for all species and charge balance requirements had to be satisfied to determine the distribution of species in solution. This is relatively easy for a spreadsheet with a solver as pH can be varied to solve an objective function which is merely satisfying the charge balance (sum of cation charge + sum of anion charge = 0). Additional accuracy is provided by computing activity coefficients of the various species which causes some, but not very much distortion of the species distribution over the range of pH values.

Figure 5: Computing Distribution of Dissolved SO_2 as a function of pH

Equilibrium Relationships:

$$SO_2(g) \Leftrightarrow SO_2(aq)$$

$$SO_2(aq) + H_2O \Leftrightarrow H_2SO_3$$

$$H_2SO_3 \Leftrightarrow H^+ + HSO_3^- \quad (K_1=1.72 \times 10^{-2})$$

$$HSO_3^- \Leftrightarrow H^+ + SO_3^{-2} \quad (K_2=6.43 \times 10^{-8})$$

Computing Distribution

$$C_T = [H_2SO_3] + [HSO_3^-] + [SO_3^{-2}]$$

$$A_0 = [H_2SO_3]/C_T \longrightarrow A_0 = [H^+]/([H^+]^2 + K_1[H^+] + K_1K_2)$$

$$A_1 = [HSO_3^-]/C_T \longrightarrow A_1 = K_1[H^+]/([H^+]^2 + K_1[H^+] + K_1K_2)$$

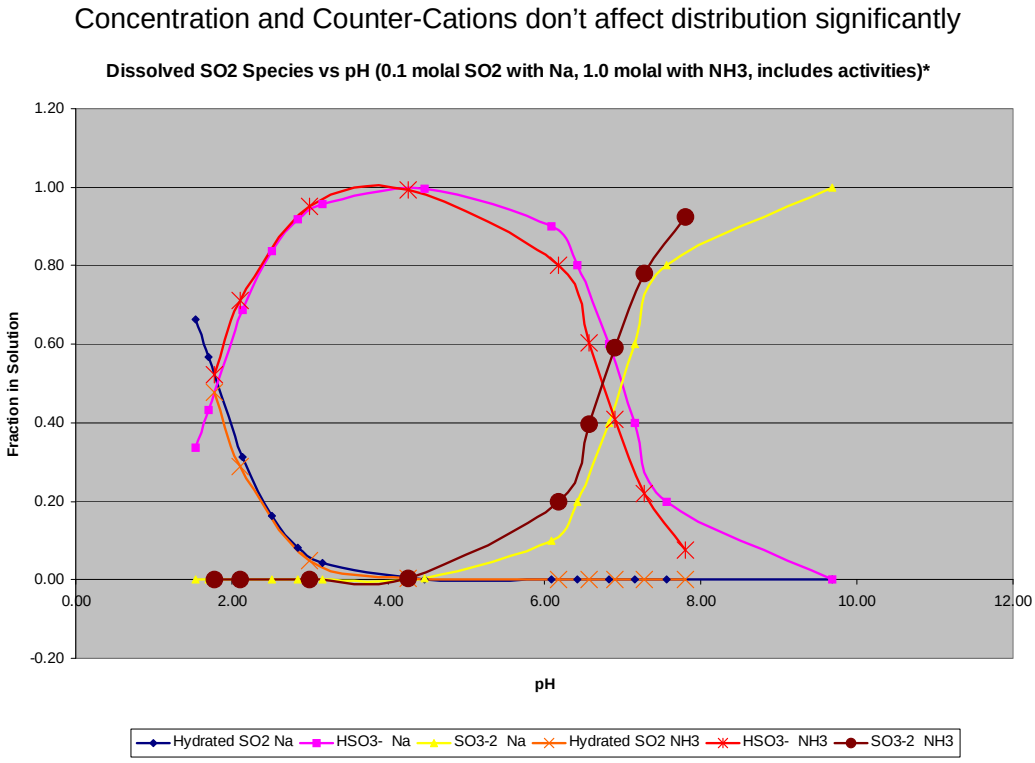
$$A_2 = [SO_3^{-2}]/C_T \longrightarrow A_2 = K_1K_2/([H^+]^2 + K_1[H^+] + K_1K_2)$$

As depicted above, the dissolved SO_2 makes sulfurous acid, H_2SO_3, the bisulfite ion, HSO_3^-, then sulfite ion, SO_3^{-2}, as the pH increases. Carbon steel (Fe) corrosion takes place when H^+ reacts with iron to form iron (II) ion, Fe^{+2}, and hydrogen gas via the equation:

$$Fe^0 + 2\ H^+ \Rightarrow Fe^{+2} + H_2(g)$$

Thus any species providing the solution H^+ will support corrosion. What **Figure 6** shows is the corrosivity of a solution with dissolved SO_2 species extends into what we might consider a safe operating pH range of 6-8 as bisulfite ion, which can supply H^+, is still present as an ample fraction of the total dissolved SO_2 in solution. Because the distribution is known, pH can tell us that corrosive materials *may* be present, but won't tell us how corrosive the solution is because pH does not reveal absolute concentrations.

Figure 6: SO_2 Species Distribution with Varying SO_2 Concentration and Different Counter Cations



*Computations from sour VLE spreadsheet developed by Phillips 66

Although we say that pH 7 is neutral, this does not mean non-corrosive. Neutral only means $[H^+] = [OH^-] = 10^{-7}$ ***M***. It does not mean that HSO_3^- is incapable of donating its proton to the corrosion mechanism.

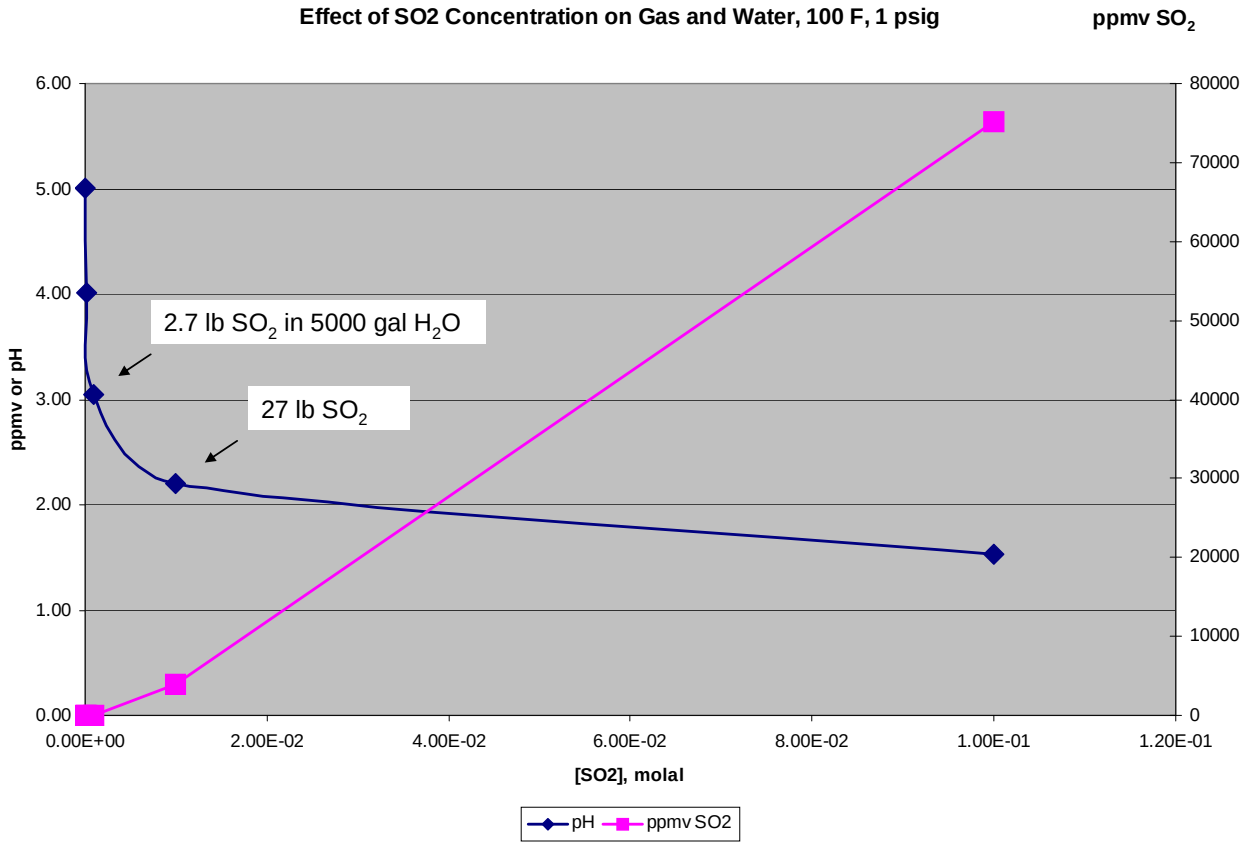
This can be further illustrated by considering the manufacture of sodium bisulfite and ammonium bisulfite from absorbing SO_2 in a flue gas (such as a Claus tail gas incinerator effluent) using solutions of sodium carbonate or aqueous ammonia. These products are produced at concentrations of about 38 wt% and 67 wt% respectively. The product part of a typical two-stage absorption process usually operates in the pH 5-5.5 range, and the emissions control stage runs in the 6.5-7.5 range. Generally these vessels are built using FRP (Fiberglass Reinforced Plastic) as they are extremely corrosive to almost all plain metals and alloys.

pH Measurements and SO_2 only Breakthrough

It would be ideal to sequester SO_2 from the hydrogenation reactor in the quench tower and not allow it to reach the amine solution to neutralize the amine making it useless for acid gas pickup and making it corrosive as was shown in **Figure 4**. Plain water will dissolve considerably more SO_2 than either H_2S or CO_2 as it is a much stronger acid

when dissolved allowing the solution equilibrium to shift toward the formation of bisulfite and eventually sulfite ion. However, it shares the same properties as H_2S and CO_2 in that its solubility is limited and saturated solutions may have a considerable vapor pressure of SO_2 above them. As with the other acid gases, a small amount of SO_2 will quickly acidify the water in a quench column (assuming no neutralizer section) as demonstrated in **Figure 7** and as the solution gets saturated send gas containing potentially high concentrations of SO_2 on to the amine which has plenty of buffering capability to absorb the remainder of the SO_2.

Figure 7: Effect of SO_2-Only Breakthrough on Typical 100 LTPD Quench Water Inventory



Amine bisulfite aggressive corrosion is not the only consequence of failing to capture SO_2 in the quench tower. As shown in **Figure 8**, there is a considerable effect on the quality of the MDEA normally used in TGU amine systems. Note the sharp increase in DEA and Methyl Mono Ethanol Amine, MMEA or $CH_3NH(CH_2CH2OH)$ after an SO_2-only breakthrough event at another refinery that experienced the same failure as the unit in **Figure 4**. Degradation of the MDEA to these secondary amines is always observed in Phillips 66 refinery monthly system samples from TGU amine that shows a rapid thiosulfate ion increase, a sign of SO_2 breakthrough.

Figure 8: MDEA Analysis by Ion Chromatography Before and After SO_2-Only Breakthrough Event

Recent Case: Before and After SO_2-Only Breakthrough

Unit run in hot standby mode at end of June 2011. Oxygen bleed from main burner generated SO_2 (no H_2S or H_2 available) for 3 days.

ions in ug/ml		
NAME	U39.1 MDEA	U39.1 MDEA
Date	8-Jun	21-Jul
Sodium	207	187
Formate	1,443	2,372
Acetate	724	1,014
Chloride	171	150
Sulfate	111	276
Sulfite	0	0
Thiosulfate	4,137	24,638
Thiocyanate	2	20
Sulfide	0	0
Oxalate	184	381
Phosphate	17	29
MMEA	2,844	8,826
Ammonium	0	0
MEA	503	278
DEA	12,744	15,427
MDEA	399,628	476,394
DIPA	0	0

Sulfites reacted to thiosulfates when exposed to H_2S when unit resumed normal operations.

Reboiler inlet line lost half of wall thickness (CS pipe with 3/16" corrosion allowance). Unit started up in 2009.

MMEA and DEA routinely show up in greater amounts after massive SO_2 breakthrough.

The Role of H_2S in SO_2 Breakthrough

The scenario above assumed that no bases were present nor was H_2S or CO_2 present in the water in the quench tower at the time of the incident. As previously noted, these incidents take place when SO_2 generation takes place in the absence of acid gas combustion as in a startup or shutdown scenario caused by oxidation of sulfur or metal sulfides, or as a recent incident showed, direct SO_2 formation by oxidizing the presulfiding H_2S over the metal oxide form of the TGU catalyst. In these scenarios, no elemental sulfur was formed in the quench tower.

During normal operations with acid gas, there is an expectation, even under upset conditions, that some H_2S will accompany SO_2 breakthrough into the quench tower. H_2S plays a significant role because it is reactive with the SO_2, not only through the Claus reaction, but in a complex set of reactions revolving around a variety of sulfur and oxygen containing anions. Bases in the quench water essentially regulate the H_2S and CO_2 content of the solution in normal operations, so the reserve of H_2S that can react

with incoming SO_2 will be determined by the quantity and nature of the base. As stable sulfur-oxygen anions such as thiosulfate and sulfate form, bases already added or incoming with the tail gas will be paired as salts of these anions making them unavailable to hold H_2S in solution. This is when the quench water will get ugly with elemental sulfur and polythionic acid formation.

A situation to demonstrate the role of H_2S in SO_2 breakthrough is outlined in **Figure 9**.

Figure 9: Flow Sheet for a 2 Stage Quench with Pre-Loaded Neutralizer

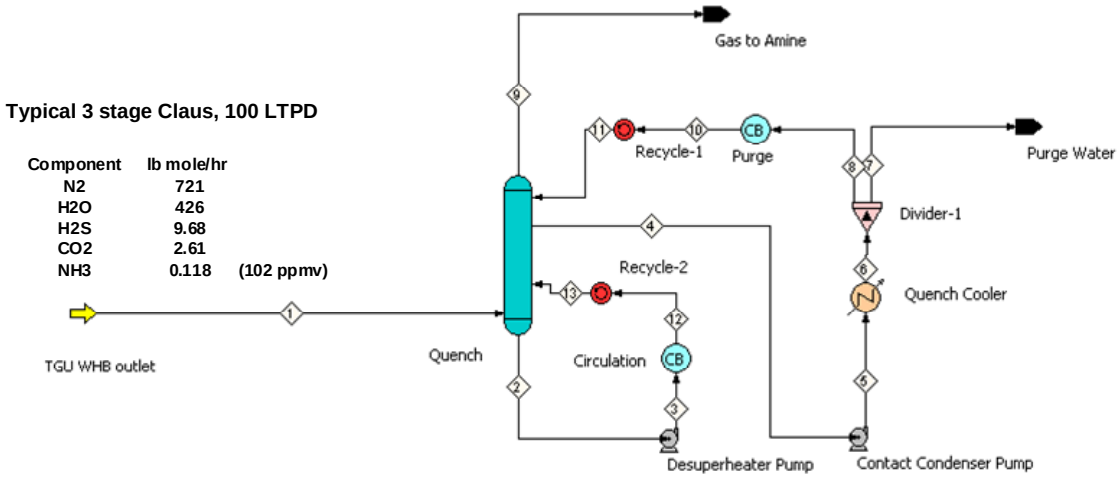
A Case Study of SO_2 Breakthrough with H_2S Present:

Two stage quench tower with caustic added to "desuperheater" section

10 wt% NaOH charge in desuperheater

ProTreat™ simulator using ammonia package to account for undestroyed NH_3

Assumption: Absorbed SO_2 reacts with dissolved H_2S to thiosulfate, simulation computes resultant steady state conditions after each incremental breakthrough



Figures 10 and 11 represent the idealized chemistry of a rather complex system. As the conditions go to very low pH, the complexity is increased to the level where the mixture is just referred to as "Wackenroder Liquid"[1] where many "disproportionation" reactions take place among sulfur species in varying oxidation states. Eventually, the most stable species emerge from this mess, thiosulfate, sulfate, and elemental sulfur.

Figure 10: Pre-loaded Caustic Chemistry under Acid Gas Operations

$$CO_2(g) \Leftrightarrow CO_2(aq)$$
$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3$$
$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow H^+ + CO_3^{-2}$$
$$H_2S(g) \Leftrightarrow H_2S(aq)$$
$$H_2S(aq) \Leftrightarrow H^+ + HS^-$$
$$NaOH + H^+ \Rightarrow Na^+ + H_2O$$

Figure 11: H_2S and SO_2 Interactions at Varying Solution pH

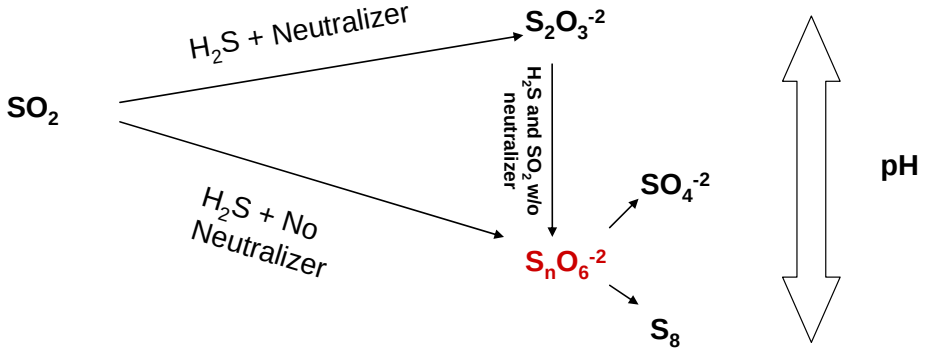
What Happens to H_2S during SO_2 Breakthrough

$$SO_2\,(aq) \Leftrightarrow HSO_3^- \Leftrightarrow SO_3^{-2}$$

$$4\,SO_3^{-2} + 2\,HS^- + H_2O \Rightarrow 3\,S_2O_3^{-2} + 4\,OH^- \quad (pH>9)$$

$$2\,HSO_3^- + 2\,SO_3^{-2} + 2\,HS^- + H_2O \Rightarrow 3\,S_2O_3^{-2} + 2\,OH^- \quad (4<pH<9)$$

$$2H_2S(aq) + SO_2\,(aq) + 2HSO_3^- \Rightarrow 2\,O_3SS_3SO_3^{-2} + 2H^+ + 2\,H_2O \quad (pH<4)$$

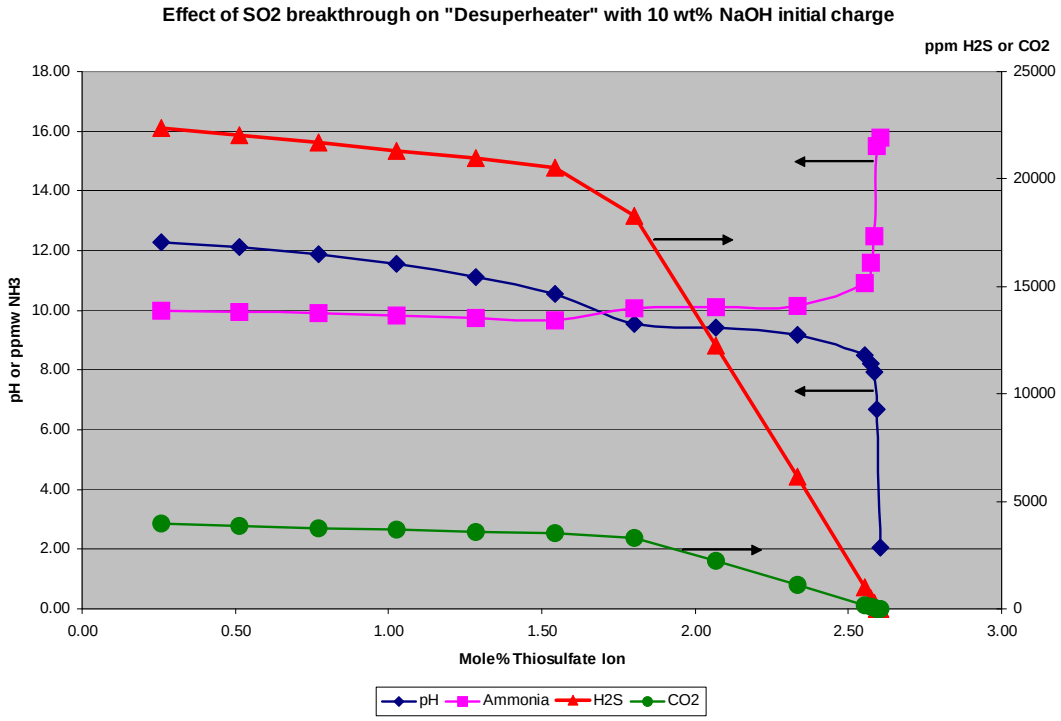


Polythionate formation and
Disproportionation (Wackenroder Liquid)

Using the ProTreat™ simulator with the assumptions shown in **Figure 9**, the graphs in **Figures 12 and 13** were constructed for an incremental amount of SO_2 reacted with the

contents of the quench water to form thiosulfate ion above pH 4 according to the reactions in **Figure 11**.

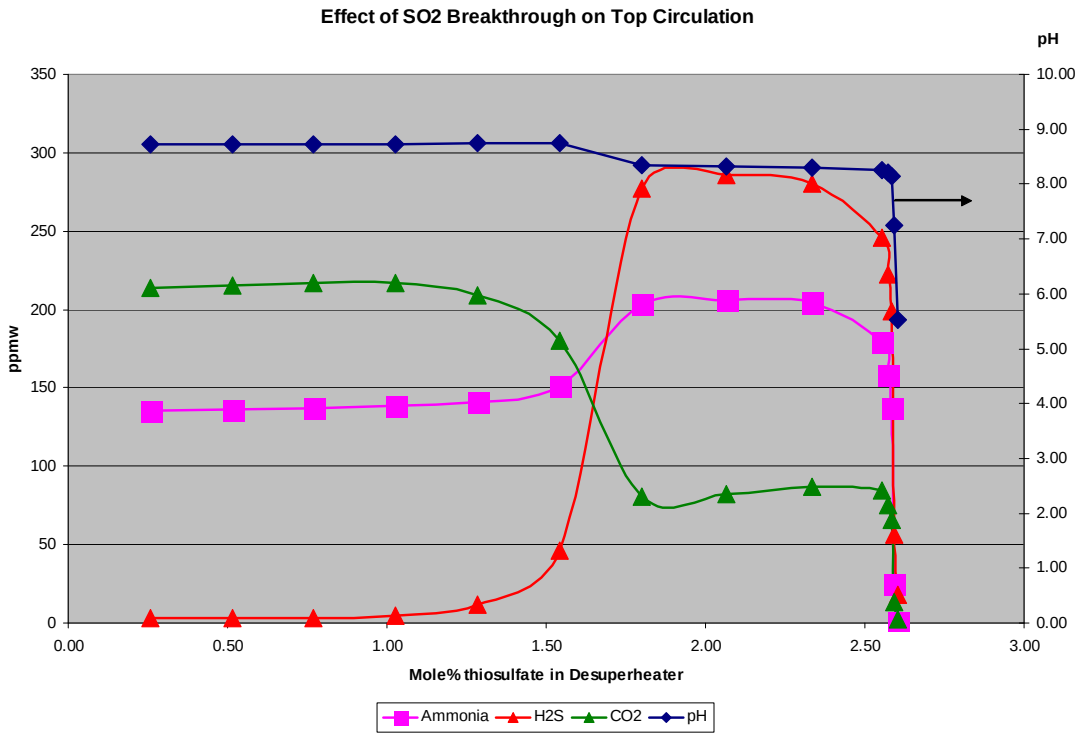
Figure 12: Desuperheater Stage Component Concentration and pH as SO_2 Breakthrough Progresses



The mixture in the desuperheater after acid gas operations commence is primarily sodium bisulfide, carbonate, and bicarbonate with only a tiny fraction of either sulfide ion or free H_2S or CO_2. As thiosulfate forms during an SO_2 breakthrough and the pH slips below 10, there is a dramatic shift downward in both the H_2S and CO_2 content of the solution. Some would consider this pH to be a very safe zone to operate in when actually the quench tower is beginning its approach to the "cliff". At a pH approaching 8, everything may still look "ok" but the reservoir of H_2S needed to react with the SO_2 and turn it into benign, soluble thiosulfate is nearly depleted. Although ammonia does begin to accumulate in the water, it is quickly paired with incoming SO_2 as corrosive ammonium bisulfite which does not help the situation.

After this, it only takes a teeeeeeeny bit of SO_2 to hurl the tower over the "cliff" as the pH line shows. At this point, Wackenroder chemistry becomes the order quickly filling the system with elemental sulfur and corrosive sulfurous acid and bisulfite ion.

Figure 13: Top Section Component and pH Progression during SO_2 Breakthrough



The top section has virtually no protection because the incoming base is constantly purged with the condensed water. While the bottom still has capacity to react SO_2 with H_2S, the gas leaving the top should still be free of SO_2. However, immediately as the bottom reaches the cliff and goes over, the top does the same and SO_2 will begin to go to the amine system in massive quantities causing the plant stack to go out of compliance due to amine neutralization.

In a way, relying on pH to tell us what is going on in the quench tower, either one stage or two stages is akin to putting the stop sign at the edge of the cliff. Some aren't going to be able to stop in time.

Prevention and Mitigation of SO_2 Breakthrough

As with amine hygiene[2], a combination of prevention and mitigation measures is needed to address SO_2 breakthrough without relying on the pH meter for anything but an alarm point/trigger for a neutralizer injection system.

Prevention

The most effective prevention measure is, surprisingly, cooperation. Artificial geographic boundaries are important for states, nations, and property lines, but they

generally erect artificial barriers to cooperation in a plant, especially a refinery setting. Whether normal or unplanned, startup and shutdown are the times where lack of cooperation between amine users, sour water generators, and acid gas handling areas of the plant can cause slugs of hydrocarbons to be sent to the SRU. Cycles of air starving followed by excess air by trying to keep a struggling unit in manual control during a hydrocarbon slug episode is a recipe for SO_2 related disaster.

One of the worst problems noted over the years is the separation of the sour water storage tank from the main processing units. Left out in a tank farm, designed with no real time readings from level instrumentation, sulfur plant operations are often left with one to two tank interface level checks per day. In one instance a broken level instrument in an upstream unit lead to filling the sour water tank with gasoline because the interface detection was not available real time. Amine systems can be as much of a problem for the sulfur plant as they usually represent the bulk of acid gases run in the plant. The methods for prevention and mitigation for amine contamination in reference 2 should be followed to keep amine system performance stable and the acid gas free of hydrocarbons.

Having a fast air control system on the front of the SRU is also critical to making the adjustments necessary to handle reasonable sized upsets or feed changes such as happen in startups or coker switching operations. Manual air control is not fast enough.

While the previous information appears to have "picked on" the poor old pH meter, this is not a reason to neglect it or any of the other key analyzers needed to run this plant. In fact this is a wake-up call to protect the integrity of each of these analyzers. Observations point to the sampling systems of these analyzers as the main contributor to analyzer mal-operation.

Air Demand Analyzers require sampling systems that are steam jacketed, and preferably have a way to free drain condensed or entrained/coalesced elemental sulfur back to the process. Hydrogen analyzers should be placed on the drier gas streams in the TGU (quench or absorber overhead) to prevent the condensation of acidic, corrosive water that can lead to plugging of the sample system or damage to the analyzer. The pH meter station should have a way to verify that water from the process is flowing past the pH probe at all times. After a plugging episode, the pH meter, usually on a slipstream to the main line will become plugged and prevent the meter from "seeing" a problem.

A hydrogen analyzer is useless without any excess hydrogen to measure. Having an outside source of hydrogen, while a practical "must have" in the refinery setting is more difficult in a gas plant setting. Isolated locations are forced into using "reducing gas generators" (RGG) to generate hydrogen and CO for WGS. Fired RGG's require good mixing burners that are capable of incorporating steam injection to control soot deposition when firing in sub-stoichiometric conditions. Claus unit conditions can also be used to help generate and keep more of the hydrogen byproduct from H_2S combustion in the main reaction furnace. Steps to increase flame temperature and speed heat transfer at the front end of the WHB can be used to maximize hydrogen production.

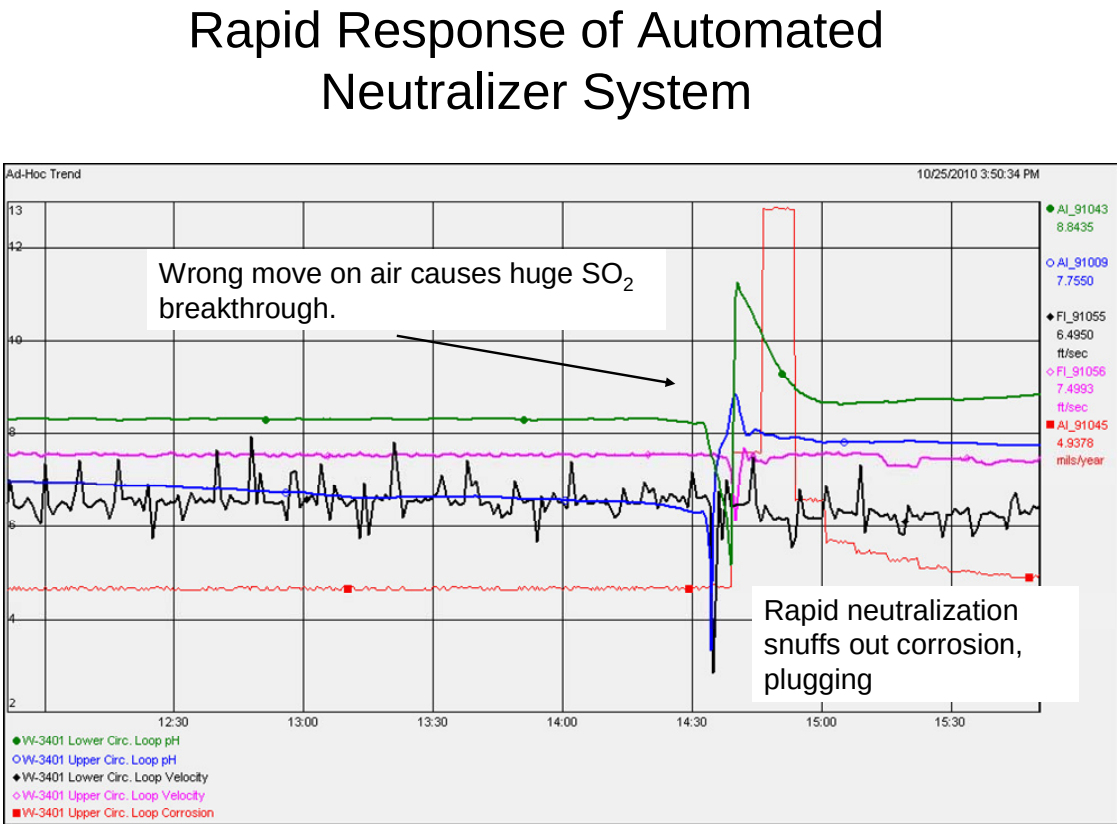
No matter how the hydrogen gets supplied, if there is not enough to stay in excess at the outlet of the hydrogenation reactor, SO_2 breakthrough is guaranteed.

Mitigation

From the graph in **Figure 6**, we can see that in order to eliminate any corrosive dissolved SO_2 species in the quench tower water, the pH of the solution must be raised above 9 in order to convert all SO_2 species to the sulfite ion. As soon as the pH "drops off the cliff" and plunges down to about 2, neutralizer must *immediately* be injected. Not only does this stop the corrosion, but it also minimizes the migration of SO_2 in the gas going to the amine system.

Figure 14 depicts the response of an automated 20% NaOH injection in a two stage quench tower system (no pre-loaded caustic in the bottom section after implementation of the rapid injection system).

Figure 14: Rapid Neutralization Response



The blue and green lines represent pH readings in the upper and lower circulating systems, the red line is depicts readings from a corrosion probe in one of the loops. The pH rapidly drops in both loops due to switching the unit to manual air control during an upset putting far too much air in the unit. The automated neutralizer system is triggered

on the rapidly dropping pH getting the pH of both loops over 9. The red corrosion meter output line temporarily jumps to very high levels but after the injection rapidly returns to normal.

Recommendations:

Prevent SO_2 breakthrough with effective contaminant control in the amine and SWS systems providing feed to the SUR/TGU. Work on inter-plant cooperation skills to prevent contaminant slug events during startups, shutdowns, and unplanned emergencies.

Avoid manual air control operations. Air controllers should have fast acting valves.

Insure the sampling systems for the Air Demand, Hydrogen, and pH analyzers are kept verifiably clear of obstructions from solids or corrosive liquids. Calibrate these instruments using a routine maintenance schedule

Install a pH meter on all quench tower circulation loops. Don't rely on a quench tower pH meter to infer anything about the concentrations of solution components or corrosivity of the quench solution. Use ion chromatography (anion and cation) to understand what drives the normal value of quench water pH. Don't use neutralizer to "control" pH.

Make neutralizer injection an automated system triggered by a reliable pH meter for most rapid response to SO_2 breakthrough to prevent excessive corrosion, sulfur formation, amine neutralization and degradation, and aggressive amine bisulfite corrosion. Have a plentiful supply of neutralizer. Inject neutralizer to keep pH of each quench tower circulating loop above 9 until the SRU upset can be straightened out. Inject neutralizer downstream of the pH meter to prevent under dosing.

Install a rapid purge for spent solution in desuperheater sections of two stage quench towers that use pre-loaded caustic, and install a way to rapidly reintroduce fresh caustic solution after purging.

For plants using generic MDEA for primary and TGU amine, consider an amine swapping system between the larger primary and smaller TGU systems. A permanent heat stable salt removal system on the larger primary amine system is required.

References

1. **Advanced Inorganic Chemistry, 4th ed.** F. A. Cotton and G. Wilkinson, J. Wiley & Sons, New York, 1980 pg. 537
2. *Grime Doesn't Pay*, A. Cummings and A. Keller, Brimstone Sulfur Symposium, September 2004