

**SHARING BEST PRACTICES FOR OPTIMIZATION OF
BEAVON STRETFORD TGU's**

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ABSTRACT

This paper shares best practices for optimizing the environmental performance, reliability, and operating run length of reduction-quench type tail gas units (TGUs). While the primary emphasis is on best practices for optimizing TGUs that use the Beavon Stretford process, many of the best practices apply regardless of the TGU's configuration.

This paper begins by exploring operating problems that have historically limited the performance, run length, and reliability of Beavon Stretford TGUs (e.g. plugging tendencies, byproduct salt formation, solution foaming, etc.). Many of the underlying root causes for these operating problems manifest themselves in different forms and to different degrees with other TGU back end configurations. These are compared and contrasted from a high level.

Benchmarked operating performance data from four ConocoPhillips' Beavon Stretford TGU installations will then be shared to demonstrate that many of the issues are interrelated and can be tied to key performance indicators both within the TGU (solution chemistry and hygiene) and also for upstream units (TGU front-end, Claus unit, amine and sour water systems). Under this common understanding, a framework for TGU best practices addressing these root cause issues is laid forth.

Disclaimer

This report is a review of the general findings from detailed studies of actual unit operations at several Beavon Stretford tail gas treating units within the ConocoPhillips Refinery System. Although these recommendations are considered practical and applicable for many unit designs and operating scenarios, the suggested practices are generalizations and should not take the place of detailed site-specific studies and site-specific implementation of good air pollution control practices. Additionally, these technical and regulatory discussions are not intended to be, nor should they be, used as legal advice. To determine the applicability and effect of this information to a particular tail gas treating unit, advice from a competent legal services provider should be sought.

TABLE OF CONTENTS

- 1.0 Introduction
- 2.0 Beavon Stretford Process Background
 - 2.1 Stretford Process Chemistry
 - 2.2 Beavon Stretford TGU Process Flow
 - 2.3 Process Variations
- 3.0 Common Operating Issues with Stretford
 - 3.1 Absorber plugging
 - 3.1.1 Insufficient Stretford solution circulation rate
 - 3.1.2 Excessive amounts of elemental sulfur carried into absorber with lean solution
 - 3.1.3 Foaming/frothing in the bottom of the Stretford absorber
 - 3.1.4 Excessive soluble sulfur salt levels / precipitation of solution components
 - 3.1.5 Very high bisulfide loading in the bottom of the absorber
 - 3.1.6 Packing design issues
 - 3.2 Maintaining proper sulfur froth
 - 3.2.1 Maintaining proper air bubble size
 - 3.2.2 Excessive turbulence in the oxidizer
 - 3.2.3 Maintaining proper optimized operation of the oxidizer weir
 - 3.2.4 Using diesel as a frothing aid
 - 3.3 Foaming
 - 3.3.1 Bacterial contamination
 - 3.3.2 Contamination with hydrocarbon or other surface active compounds
 - 3.3.3 Salts precipitation
 - 3.4 Sulfate and thiosulfate salt buildup
 - 3.4.1 SO₂ breakthrough
 - 3.4.2 Incompletely reacted sulfur species entering oxidizer
 - 3.5 Disposal or on-line regeneration of the Stretford catalyst
 - 3.6 Production & filtration of the sulfur filter cake
 - 3.7 Minimizing emissions of carbonyl sulfide
 - 3.8 Addressing temporary overload of the Stretford solution with H₂S
 - 3.9 Maintaining the optimum alkalinity levels in Stretford solution
- 4.0 Benchmarked Performance of Operating Units
- 5.0 Conclusions
- 6.0 Acknowledgements
- 7.0 References

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1.0 Introduction

The Stretford process is an aqueous sulfur recovery process that removes H₂S from gas streams and catalytically oxidizes the captured H₂S to elemental sulfur. Stretford is sometimes called a ‘liquid redox’ process, in that it relies on an aqueous catalyst solution that is reduced by H₂S and is then re-oxidized by air in a later step. The process was developed in the 1950s, and by the 1980s, approximately 170 units had been constructed (Trofe et. al., 1987). The units were used for treating a wide variety of gas streams, but the three largest use categories in 1986 were Claus tail gas (37 units), coke oven gases (23 units), and geothermal vent gases (15 units). Although it exhibited unique operational issues, the process still achieved widespread use because of its ability to successfully handle wide swings in feed gas composition and flow rate while maintaining low H₂S concentrations in the treated gas. The Stretford process was especially desirable for treating low pressure streams and streams that were then to be vented to atmosphere. In Claus tail gas service, the process was also capable of absorbing significant SO₂ excursions, although not without consequences. Further, the process was also capable of selective H₂S removal in the presence of CO₂.

The Stretford process fell from favor in the 1980s primarily because other processes emerged that were not as prone to plugging and/or waste disposal issues. Process licensors lost interest in actively marketing the Stretford process in North America. In contrast, the alternatives to Stretford were heavily marketed. The “vanadium disposal problem” was a key part of the promotion used. For example, in large-scale sulfur recovery applications using the Claus process with tail gas treating, tertiary amine-based tail gas units (e.g., the SCOT process) that scrubbed H₂S and recycled it to the Claus unit gained favor because, among other things, doing so avoided both the plugging problems and the production of vanadium-contaminated elemental sulfur cake. In other, non-TGU, small-scale sulfur recovery applications, redox processes that used iron instead of vanadium (e.g., LO-CAT, SulFerox) came into favor. Although these other redox processes had many of the same well-known faults (e.g., plugging) as Stretford, the iron-based processes were just as good at removing H₂S and had waste streams without vanadium. The fact that these iron-based processes generally have the same types of operating issues as Stretford and yet have been sold and continue to be sold in preference to Stretford argues that it may have been Stretford’s reliance on vanadium that caused its fall from favor.

Even though it may have been 20 years or more since most Stretford units were built, there are many still in operation.

Best Practices Investigation

ConocoPhillips, the sponsor of this paper, operates Stretford units as TGUs at four US refineries. As part of a recent consent decree between ConocoPhillips, the United States and several states, ConocoPhillips agreed to investigate and share best practices for optimizing the operation of Beavon Stretford TGUs (United States, 2005). This paper is the culmination of the best practices investigation work conducted. Included in this discussion are findings from previous optimization studies undertaken for two of ConocoPhillips' Beavon Stretford TGUs. In addition to considering and including the information from those previous studies, this best practices effort also involved the following:

- A Beavon Stretford best practices round table attended by staff associated with ConocoPhillips' Beavon Stretford units and outside Stretford experts.
- Discussions with owners/operators of 15 other facilities with Stretford units in service on Claus tail gas, geothermal vent gas, and amine acid gas.
- A review of an internal written Stretford troubleshooting guide provided by another Stretford unit operator.
- A review of literature on Stretford systems and Beavon Stretford TGUs.
- A review of procedures at the four ConocoPhillips refineries with Beavon Stretford TGUs.
- Implicit consideration of the regulations having to do with Beavon Stretford TGUs as they apply to the development of these best practices.

The best practices discussed in this paper are meant primarily for the purpose of minimizing emissions and maximizing run times for Beavon Stretford TGUs. Although targeted specifically to Beavon Stretford units, portions of this information may also be useful to:

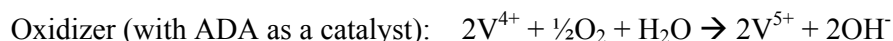
- Other types of TGUs that use reduction/quench type processes on Claus Tail gas.
- Other Stretford units in operation on low-pressure gas streams such as geothermal vent streams and amine acid gas streams.
- Other liquid redox type processes treating a wide variety of feeds.

The remainder of this paper first gives some background on Stretford process chemistry and process flow. Then, the text reviews common operating issues with Beavon Stretford units, including an example 'Why Tree' for one of the most prevalent operating issues, plugging of equipment with elemental sulfur. A subsequent section tabulates operating information from ConocoPhillips' four Beavon Stretford TGUs. Finally, best practices to maximize run length and enhance environmental performance of Beavon Stretford TGUs are provided.

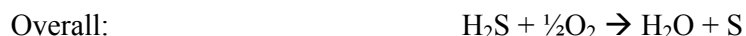
2.0 Beavon Stretford Process Background

2.1 Stretford Process Chemistry

The Stretford process uses an alkaline aqueous solution to absorb H_2S from the gas stream being treated. The primary ingredients of the Stretford solution include a base, vanadium (V), and anthraquinone disulfonic acid (ADA). Once the H_2S has been absorbed into the liquid, the reactions that occur can be generally summarized by the following:



Since both the base (OH^-) and the oxidized vanadium (V^{5+}) reappear in the final line, the Stretford solution containing these species meets the general definition of a catalyst. ADA is another catalyst that promotes the reoxidation of the vanadium in the oxidizer. Overall, the reaction catalyzed by the Stretford solution can be summarized as:



This is the same overall reaction that occurs in other sulfur removal processes such as the modified Claus process and iron-based liquid redox processes. In the case of the Claus process, sulfur is produced in the gas phase and condensed as a liquid product, whereas solid sulfur is produced by the Stretford process and other liquid redox processes.

Although the desired product is elemental sulfur, 1-5% of the inlet H_2S is converted to sulfur byproduct salts in the Stretford system. The byproduct salts formed are thiosulfate ($\text{S}_2\text{O}_3^{2-}$) and sulfate (SO_4^{2-}). If there isn't a continuous purge stream large enough to provide an outlet for all byproduct salts, then the byproduct salts accumulate in the Stretford solution until removed by processing of the solution or until the solution is disposed of and replaced with fresh solution.

2.2 Beavon Stretford TGU Process Flow

Figure 1 shows a schematic of a generic Beavon Stretford TGU. Tail gas from the Claus unit(s) enters a reducing gas generator (RGG). The RGG is a burner that operates with a substoichiometric amount of air. The purpose of the RGG is to heat the tail gas and to provide reducing gas (CO and H_2) for use downstream. The RGG is controlled to maintain the proper inlet temperature to the hydrogenation reactor (typically ~ 520 F minimum) and to maintain the proper excess H_2 concentration in the reactor effluent ($\sim 1.5\%$ to 2% H_2 minimum).

Gas from the RGG enters the hydrogenation reactor (also called the Beavon reactor), where reducing gases react with oxidized sulfur species (e.g., SO_2 , S, COS, & CS_2) to form H_2S . The reactions typically occur over a cobalt-molybdenum catalyst, and all sulfur species are converted into additional H_2S . The hydrogenation reactor operates at a minimum of about 520F.

Temperatures may be raised as the catalyst ages in order to promote the desired reactions and to minimize, if not avoid, SO₂ breakthrough.

Gas exiting the hydrogenation reactor is cooled in a waste heat boiler to generate steam. The gas is then cooled further in a desuperheater / contact condenser (quench tower). The desuperheater section is used to reduce the gas temperature to the adiabatic saturation point by evaporating water.

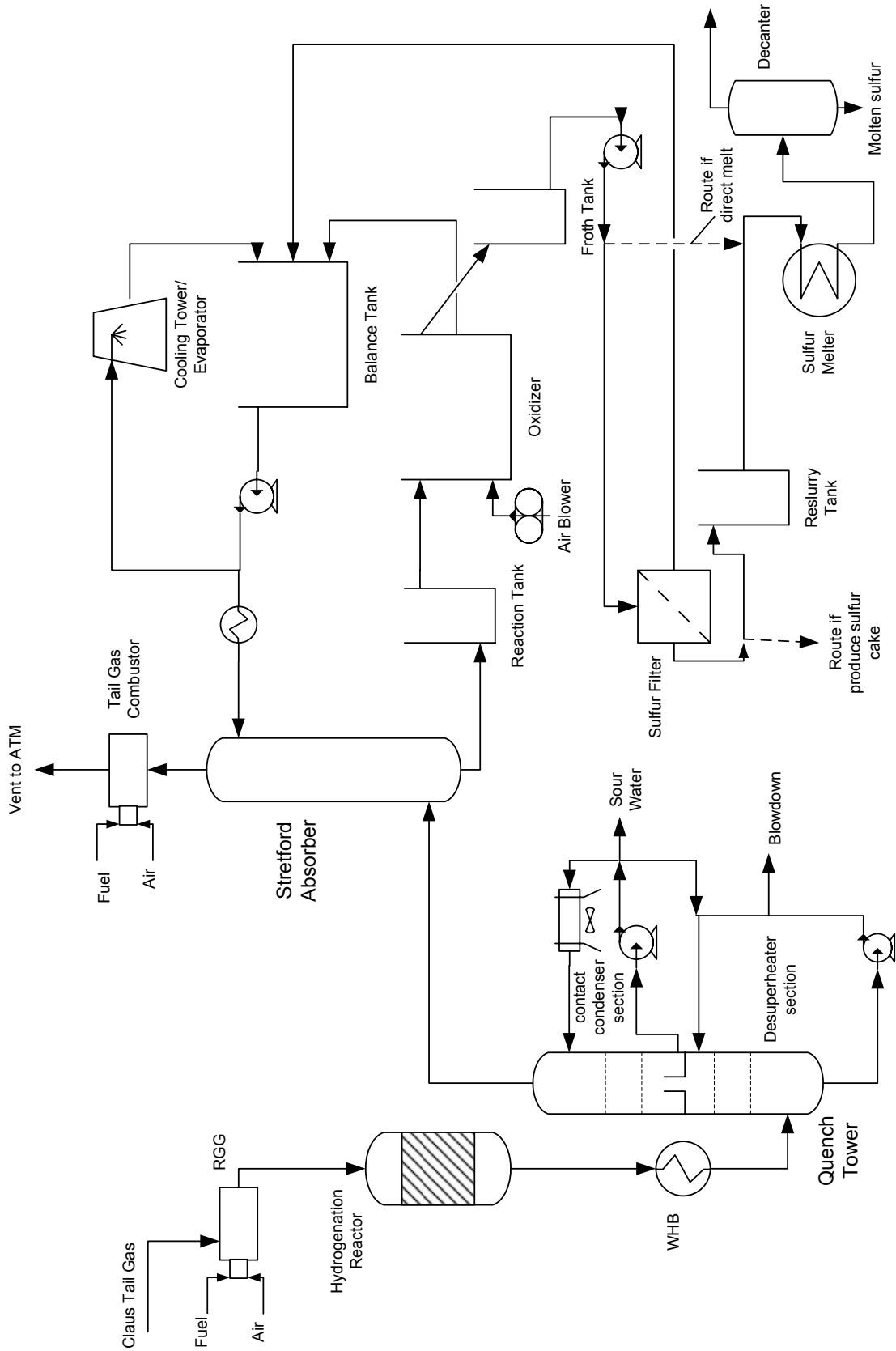


Figure 1. Beavon Stretford TGU Schematic

As water is evaporated into the tail gas, additional water is added to the desuperheater flow loop. A source of alkalinity may also be added to the desuperheater water. One important function of the alkalinity in the desuperheater section is to absorb any SO₂ that happens to break through the hydrogenation reactor during upsets, and to indicate, via measurement of alkalinity and/or pH, whether or not there has been significant SO₂ breakthrough over time.

Gas exiting the desuperheater section passes into a contact condenser section where a cooled recirculating water stream is used to cool and condense water out of the tail gas. Condensed water is bled off to the sour water system.

The cool tail gas then enters the Stretford absorber where it flows upward, countercurrent to the Stretford solution. The absorber is typically filled with an open style, plugging resistant packing (e.g., redwood slats, stainless steel shed decks, or large open random packing). H₂S from the cool tail gas is absorbed into the alkaline Stretford solution. The cleaned tail gas, typically with H₂S at or below 10 ppmv, is then vented to atmosphere or combusted prior to venting to atmosphere.

The rich Stretford solution from the bottom of the absorber flows to a reaction tank. The reaction tank is simply a wide spot in the line that allows enough time for Stretford solution to complete the reaction with dissolved sulfide species to produce elemental sulfur and reduced vanadium. Sometimes the reaction tank is built into the bottom of the Stretford absorber.

Rich Stretford solution from the reaction tank flows to the oxidizers. Frequently, three oxidizers are used in series or one tank with three separate sections in series. Air is sparged into the oxidizers to allow oxygen to be absorbed into the Stretford solution. In the presence of ADA, the reduced vanadium reacts with the dissolved oxygen to produce oxidized vanadium. The lean (re-oxidized) Stretford solution flows by gravity to a balance (or surge) tank. Spent air is vented to atmosphere.

In addition to reoxidizing the vanadium, the air added to the oxidizers also has the purpose of causing the hydrophobic elemental sulfur particles to form a froth that floats on top of the oxidizers. The froth overflows a weir into a mixed froth tank. A slurry pump transfers the elemental sulfur and Stretford solution slurry to a filter to separate sulfur from Stretford solution. The Stretford solution filtrate is returned to the balance tank. The sulfur filter cake may be washed with water and sold or sent to disposal. Alternately, it may be re-slurried with more water and melted to produce higher quality molten sulfur.

A slipstream of the lean Stretford solution passes through a cooling tower. The purpose of the cooling tower is to evaporate excess water out of the Stretford solution.

Lean Stretford solution from the balance tank is pumped back to the top of the Stretford absorber. A heat exchanger may be used to heat or cool the lean Stretford solution as needed to maintain the desired process temperatures inside the absorber.

2.3 *Process Variations*

Some Beavon Stretford TGUs contain only the de-superheater portion of the quench tower. For these units, the Stretford absorber itself acts as the contact condenser. Water that condenses from the tail gas is removed in the cooling tower / evaporator. Given that the Stretford absorber

functions as a contact condenser, it is important to keep careful track of the system temperatures and volumes.

A few other Beavon Stretford TGUs were built without any quench tower. In these units, the Stretford absorber performs the added functions of desuperheating the feed gas and condensing water. In this type of unit, there is no chance for SO₂ excursions to be mitigated by absorption in the quench tower. Units built with this configuration can thus be expected to have a higher rate of byproduct sulfur salt formation than units with a quench tower, and an even larger need to control solution temperatures and water contents.

3.0 Common Operating Issues With Beavon Stretford TGUs

This portion of the paper reviews a number of the common Beavon Stretford TGU operating issues and the controls or best practices for those issues. The focus is on the issues that are most important to maintaining low emissions and longer run times. The issues covered include:

- 3.1 Absorber plugging
- 3.2 Maintaining proper sulfur froth
- 3.3 Foaming
- 3.4 Sulfate and thiosulfate salt buildup
- 3.5 Disposal or on-line regeneration of the Stretford catalyst
- 3.6 Production and filtration of the sulfur filter cake
- 3.7 Minimizing emissions of carbonyl sulfide
- 3.8 Temporary overload of the Stretford solution with H₂S
- 3.9 Maintaining the optimum alkalinity levels in Stretford solution

Where possible, the text lists the primary factors associated with each operating issue, attempts to describe why these factors occur, and then describes best practices that may help alleviate or avoid these problems. An example ‘Why Tree’ is presented for one key issue, elemental sulfur plugging of the absorber. The purpose of the Why Tree is to demonstrate the interrelations between many of the above issues. Many of the causes of problems included in the Why Tree are also common to other tail gas treating technologies, although the problems caused may be significantly different in some cases for those other technologies.

3.1 Absorber Plugging

With all liquid redox systems (e.g., vanadium-based Stretford, iron-based SulFerox and LO-CAT), some amount of elemental sulfur is produced as solid particles in the absorber. Further, due to imperfect separation of the sulfur from the regenerated solution, some amount of elemental sulfur particles are always suspended in the lean solution and pumped back to the absorber. Generally speaking, a gas/liquid absorber operates best if there are only two phases present, the gas and a single liquid-only phase. The presence of elemental sulfur particles in the absorber and throughout the system and the plugging and foaming that occurs as a result can be considered the primary operating concern of all liquid redox processes.

The material that plugs Stretford absorbers is typically elemental sulfur and in some cases vanadium. Plugging is usually traced to one of the following factors:

- Insufficient Stretford circulation rate
- Excessive amounts of elemental sulfur carried into the absorber with lean Stretford solution;
- Foaming/frothing in the bottom of the Stretford absorber;
- Excessive soluble sulfur salt levels (>300 g/L) which:
 - lowers the solubility of vanadium and ADA (an oxidizing agent used in the Stretford process to regenerate the circulating Stretford solution), and
 - may hinder oxidizer performance in oxidizing V^{4+} to V^{5+} because of reduced O_2 solubility in the salt laden solution. The lower V^{5+} concentration could reduce the effectiveness of converting bisulfide to sulfur in the reaction tank, increased bisulfide slip to the Oxidizer, and further sulfur salt formation.
- Very high bisulfide (HS^-) loadings in the bottom of the absorber
- Packing design issues

Figure 2 is a ‘Why Tree’ that includes many of the above items and attempts to illustrate root causes of absorber plugging and how many of the root causes may be inter-related. The items in the list above and some of the items from Figure 2 are further reviewed in the paragraphs that follow.

3.1.1 Insufficient Stretford solution circulation rate

Plugging of the absorber may be caused by insufficient Stretford solution circulation rates. At a typical design solution loading of approximately 500 mg HS^-/L , Stretford units have a circulation rate around 385 gpm for every 1 LTPD of design sulfur capacity. In addition to providing a buffering effect in the event of upstream Claus SRU upsets, solution circulation also provides a means to physically sweep elemental sulfur particles from the absorber thus mitigating some of the plugging concerns.

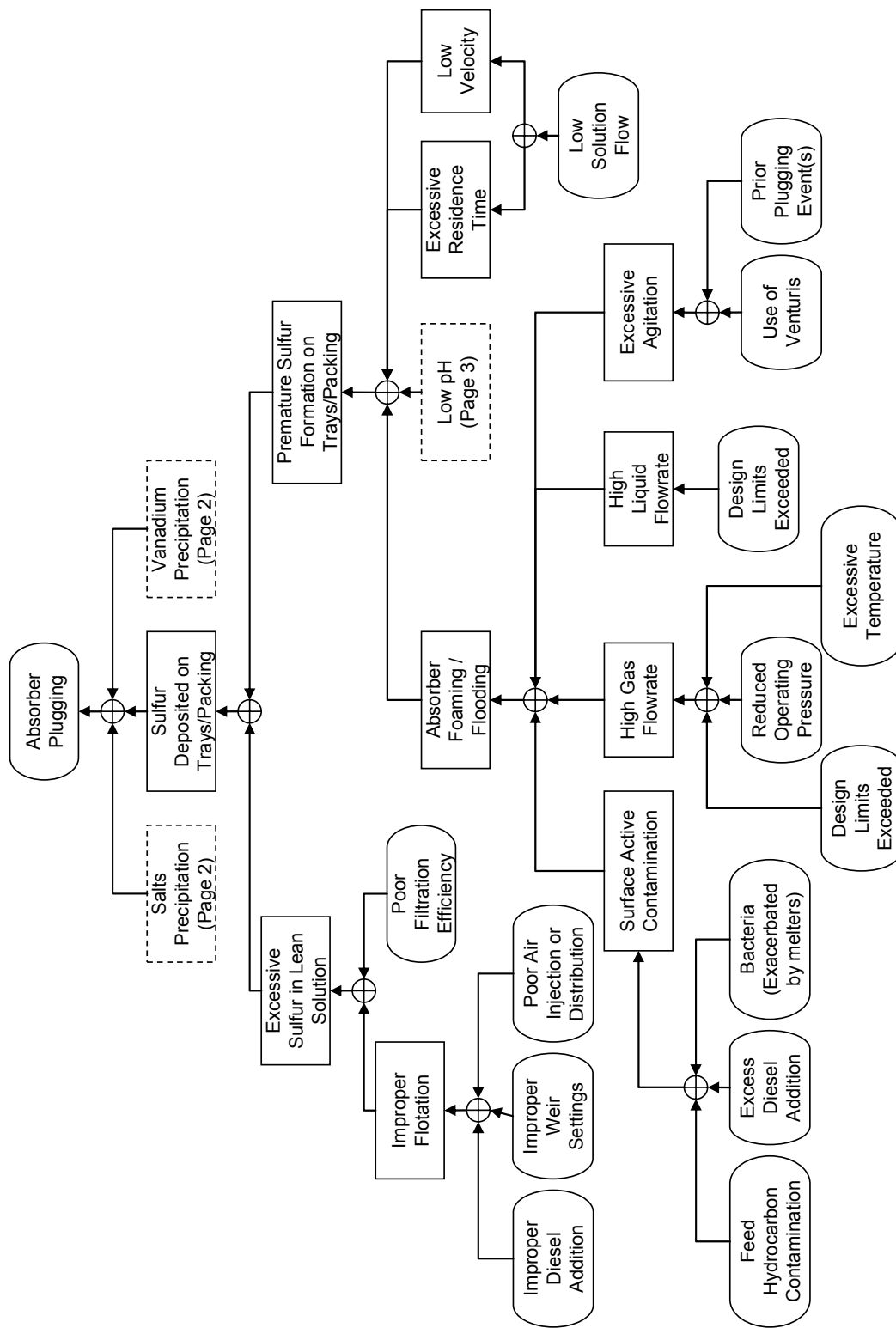
Best Practice: *Maintain full, design solution flow no matter what the actual sulfur loading to the unit. In fact, to the extent that system equipment allows, circulation even higher than design will help to keep sulfur from settling in the absorber.*

3.1.2 Excessive amounts of elemental sulfur carried into the absorber with lean Stretford solution

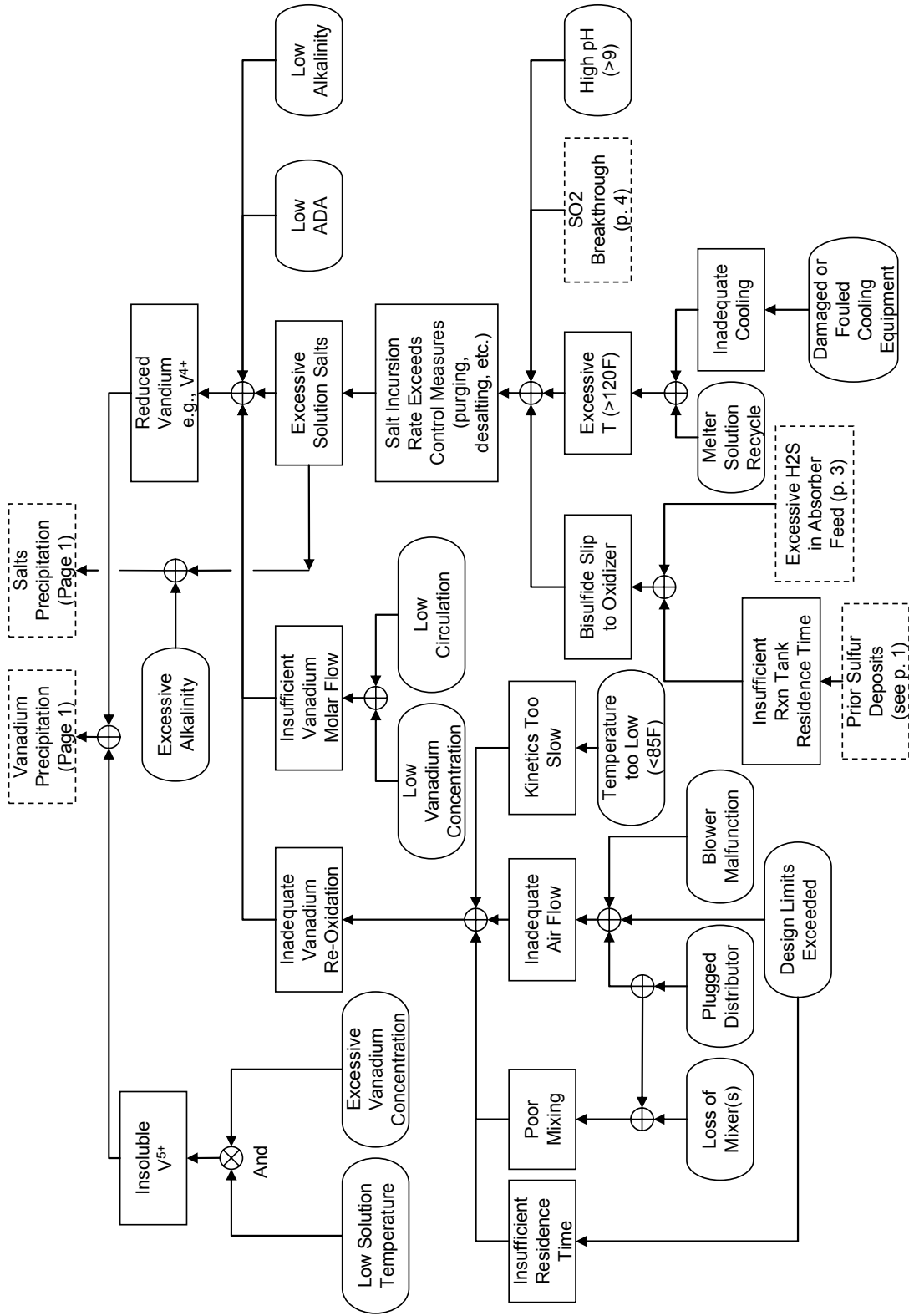
Any elemental sulfur that circulates back to the Stretford absorber in the lean Stretford solution may deposit on the packing in the absorber. The cause of elemental sulfur in the lean Stretford solution is imperfect separation of the elemental sulfur particles from the Stretford solution in the oxidizers via frothing. The most common causes of imperfect separation in the oxidizer can be traced back to improper air addition or distribution, improper froth overflow weir operation, and lack of or improper use of frothing aids. Although it is not possible to get perfect separation, it is generally possible to maintain the lean solution sulfur content at 1 vol% or less.

Best Practice: *The best practices for this issue (excessive amounts of elemental sulfur in lean solution) are the same best practices that are followed to maintain proper sulfur froth – refer to section 3.2.*

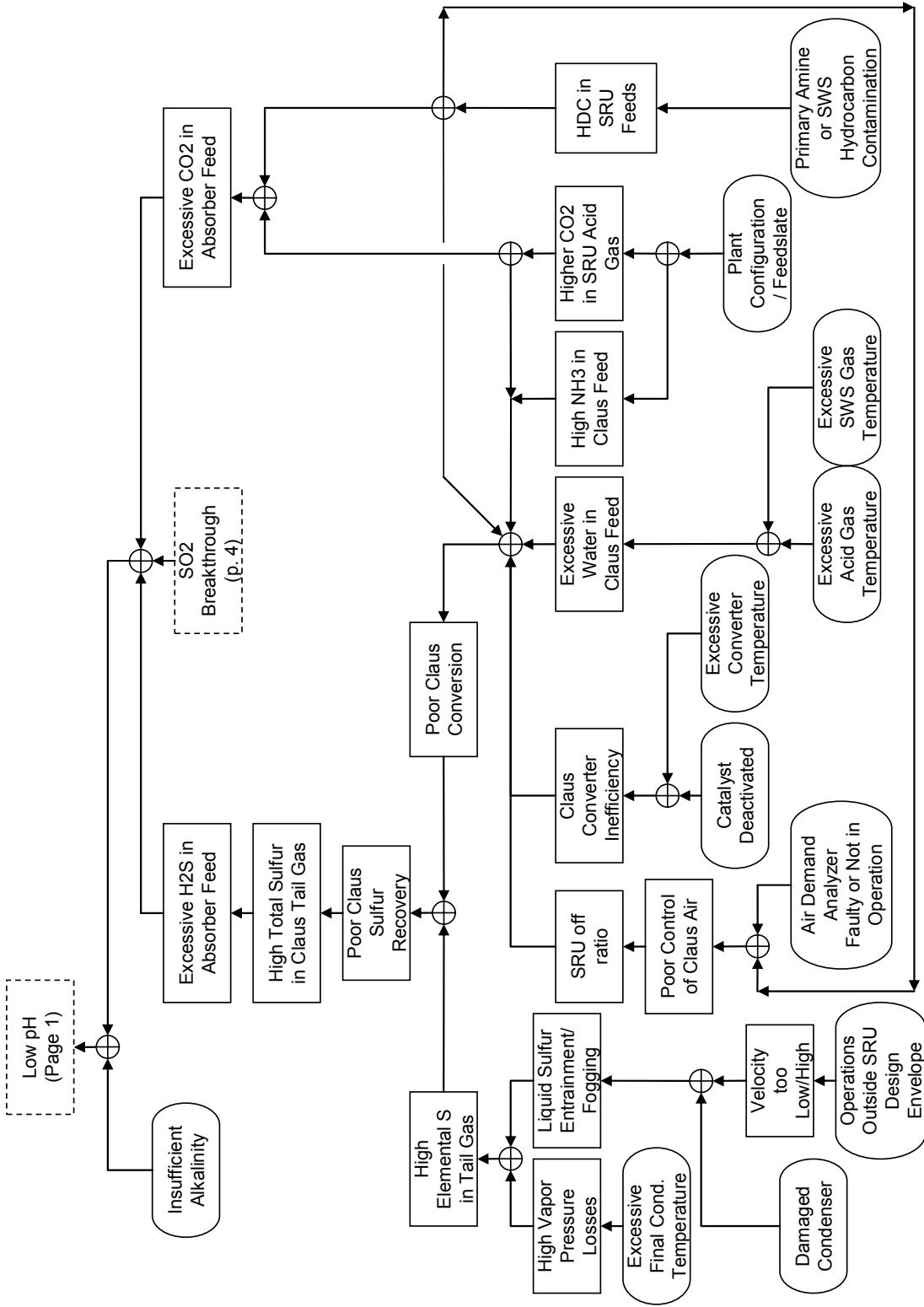
Why Tree - Preventing Beavon Stretford Absorber Plugging (1)



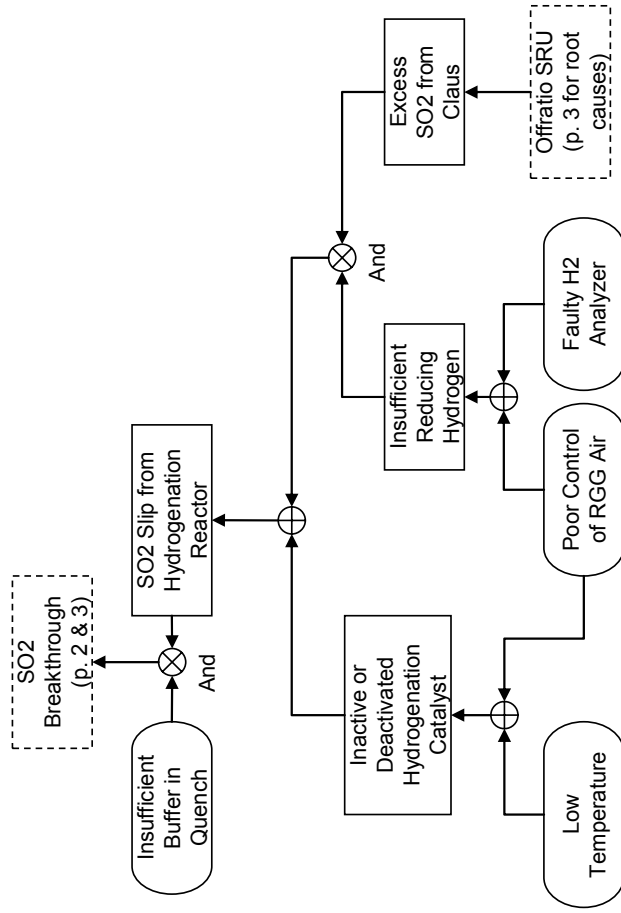
Why Tree - Preventing Beavon Stretford Absorber Plugging (2)



Why Tree - Preventing Beavon Stretford Absorber Plugging (3)



Why Tree - Preventing Beavon Stretford Absorber Plugging (4)



3.1.3 Foaming / frothing in the bottom of the Stretford absorber

The presence of elemental sulfur particles in the Stretford absorber can also promote foaming and frothing in the bottom of the absorber. Foam is stabilized by small particles, such as elemental sulfur. As a result, uncontrolled foam that grows up into the packing will transport elemental sulfur into the packing or keep elemental sulfur from flowing downward. If foam is present in the packing, elemental sulfur particles can settle, harden, and eventually plug the packing. Thus, foam control is important to limit absorber plugging. For Beavon Stretford units, one method that has proven effective at controlling foam is to spray a slipstream of the lean solution upward onto the lower levels of packing and/or downward into the rising gas.

Best Practice: *Continuously irrigate the bottom section of the absorber with relatively coarse spray to control foam. For Stretford absorbers with redwood slat splash packing, it is also common to remove every other board from the bottom section of the packing, further improving the ability of the sprays to wash solids away from the lower section of packing. Instrumentation to detect absorber pressure drop is another good practice, and can be used to provide earlier warning of absorber plugging, if it were to occur.*

3.1.4 Excessive soluble sulfur salt levels / precipitation of solution components

V^{4+} is less soluble than V^{5+} . Further, both vanadium compounds are less soluble in Stretford solution with high salts contents. Thus, if the concentration of sulfur byproduct salts (e.g., thiosulfate) is allowed to get too high, it can cause precipitation of vanadium compounds in the bottom of the Stretford absorber and/or in the reaction tank, because these are the places where the concentration of the V^{4+} is highest. The industry guideline is to maintain less than 300 g/L total soluble sulfur salts. Salt removal methods include removal of salts via crystallization (e.g., British Gas Desalting process) or by purging a portion of the solution and replacing it with fresh solution. The causes of high salts concentrations are several and are covered further in Figure 2 and in section 3.4 of this report.

Best Practice: *Control the formation and buildup of byproduct sulfate and thiosulfate salts concentrations through the best practices discussed in sections 3.4 and 3.5.*

3.1.5 Very high bisulfide loading in bottom of absorber

Plugging in the Stretford absorber is usually monitored using the pressure drop across the absorber. ConocoPhillips has observed that the pressure drop across the absorber does not increase uniformly over a plant's run length. Notable step increases in pressure drop often occur after a plant upset. One hypothesis is that sulfur accumulates in the absorber packing due to rapid sulfur formation when bisulfide loading is temporarily very high due to poor sulfur conversion in the Claus plant during an upset. The presence of excess reactant (HS^-) could tend to force the reactions toward the formation of elemental sulfur before the solution can get into the reaction tank. Elemental sulfur formed while the solution is still flowing over the packing could then lead to laydown of sulfur on the packing. In other cases, the excess bisulfide concentration could overwhelm the concentration of vanadium catalyst in solution as discussed later in this paper. Unreacted bisulfide that enters the

oxidizer carries the potential to: 1) rob oxygen required to regenerate vanadium, and 2) increase byproduct salt formation rates.

Bisulfide loading is determined by the flow and hydrogen sulfide concentration in the gas entering the Stretford absorber as well as the solution circulation rate. Like many other TGU problems, excess bisulfide loading is often traced to proper control and management of the upstream amine, sour water stripper, and Claus units. For example, the concentration of hydrogen sulfide in the tail gas feeding the Stretford absorber can be minimized by optimizing the performance of the upstream Claus plant. To help promote sulfur recovery in the Claus unit(s), the air-to-acid gas ratio and converter temperatures should be carefully monitored and controlled.

Upsets often result when hydrocarbon is carried into the acid gas feeding the Claus plant. The presence of the flammable hydrocarbon throws off the Claus plant air-to-acid gas ratio, which in turn causes higher levels of sulfur to be fed to the tail gas unit. (The effect of air-to-acid gas ratios is illustrated further in a subsequent section.) The best way to minimize the severity of a hydrocarbon excursion is to have an accurate air demand analyzer with an automated control valve feeding air to the Claus reaction furnace. Compared to a manual control valve arrangement, an automated air control valve can react faster to the air requirements of the Claus process and does a better job of maintaining the 2:1 H₂S to SO₂ ratio. As discussed previously in section 3.2 on maintaining proper sulfur froth, adequate equipment and operating practices to prevent hydrocarbons from entering the acid gas feeds to the Claus plant is necessary.

Best Practice: *The best practices for this issue (very high bisulfide loading) are the same best practices that are followed to mitigate temporary overloading and SO₂ excursions – refer to sections 3.4 and 3.8 for further details.*

3.1.6 Packing design issues

Among other plausible factors for absorber plugging, packing design is one that has been improved at some of the ConocoPhillips Beavon Stretford TGUs. In one case, the 4th (bottom-most) bed of redwood slats was completely removed from the Stretford absorber and replaced with spray headers. Later, portions of the redwood board packing were removed to create a more open gas-liquid contact area in the 3rd bed of packing. Finally, the rectangular board packing was removed completely, and replaced with splash packing that had a pitched or angled slope (also called ‘shed decks’) to eliminate flat surfaces on which sulfur could collect easily. Use of this angled packing has reportedly led to longer periods between absorber plugging in some plants.

Other Beavon Stretford units at other refineries have reportedly attempted to address absorber plugging issues by the installation of random packing designs. ConocoPhillips experience has been that random packing may be more prone to plugging than either redwood slats or pitched slope splash packing. As a result, some of these other units have reportedly had to resort to frequent (e.g., weekly or monthly) caustic washing of the absorber packing to remove sulfur deposits.

Best Practice: *Using coarse sprays in the bottom of the absorber along with plugging resistant packing designs above is best practice in this area. Avoid use of traditional random packing.*

3.2 *Maintaining Proper Sulfur Froth*

The primary means of removing sulfur from the Stretford solution is by causing it to form a froth on top of the oxidizers so that the froth can overflow to the froth tank. Sulfur is hydrophobic. Frothing is aided by appropriately small air bubble sizes, by providing even distribution of these air bubbles and, in some cases, by the addition of frothing agents such as diesel fuel.

The failure to form a good froth can cause high amounts of sulfur in the lean Stretford solution, which is circulated to the absorber. This in turn can lead to plugging of equipment, especially the absorber packing. A poor or unstable froth in the oxidizer may be the result of improper bubble size, poor air distribution, excessive turbulence, improper froth weir setting, or formation of foam instead of a froth in the oxidizers. The causes of poor bubble size may be improper air flow (too low) or poor mixing for oxidizers that use a turbine style mixer to achieve appropriately small bubble.

Once a good stable froth is formed, the froth is removed from the oxidizer by a weir baffle system. Froth that overflows is moved to the froth tank for further processing. Maintaining optimized operation of the weir baffle system is important to minimize sulfur in the lean Stretford solution.

3.2.1 *Maintaining proper air bubble size*

The critical equipment which determines air bubble size is the air sparging system in the oxidizer. Keeping the air flowing to the sparging systems in the oxidizer at design flow rates, under all conditions, even low loads, helps to keep the air spargers free of sulfur deposits, and thus maintains good air bubble size. In addition, maintaining design air flow rates ensures maximum re-oxidation of the vanadium. It is possible that one may run into an argument of reduced electricity costs with reduced air rates or an argument that higher air rates might promote higher salt formation. However, the benefits of maintaining proper sulfur froth (minimizing sulfur circulation and plugging) and re-oxidation generally outweigh any savings in electricity that might be had from turning down air rates. Further, and as explained elsewhere in this report, maintaining the vanadium in an oxidized state tends to reduce sulfur byproducts formation. As far as this investigation could determine, high air flow tends to favor reduced sulfur salts formation rates and has the added benefit of enhancing vanadium oxidation. Inadequate air flow tends to favor high salts formation rates and all the negative consequences thereof.

Best Practice: *Keep the air flowing at design flow rates to all oxidizers under all conditions, even low loads, in order to maintain a good froth.*

3.2.2 *Excessive turbulence in the oxidizer*

Excessive turbulence in the oxidizers can cause collapse of sulfur froth. Excessive turbulence is usually caused by failure of an oxidizer mixer or plugging of an oxidizer air sparger which leads to air maldistribution. Therefore, if an oxidizer mixer fails or if an air sparger becomes plugged, it is important to repair these items and return them to full service as quickly as possible.

Best Practice: *Maintain appropriate spares of mixing and sparging equipment. For example, if the motor or gear box of an oxidizer mixer is a critical item at a particular installation, then suitable spare parts should be considered for on-site storage.*

It is important to note that occasionally, excessive turbulence may lead to the reverse phenomenon of an overly healthy froth or foam that grows out of the oxidizer. However, overflowing froth or foam is usually traced to foam-causing or foam-stabilizing agents. Refer to section 3.3 below for more information.

3.2.3 Maintaining proper optimized operation of the oxidizer weir

If the oxidizer froth weir is set improperly, this could result in excessive froth height. Absorber plugging could result from the high sulfur solids content in the lean solution. Alternatively, if the weir setting allows inadequate froth height, then the amount of elemental sulfur in the lean solution may be lower, but the froth tank and subsequent downstream filtration or melting equipment may be overcome by excessive amounts of Stretford solution. Many operators desire spare froth tank capacity to allow for periodic maintenance outages in product sulfur material handling equipment. Hence, optimum weir operation gives the proper balance between the amount of sulfur circulated to the absorber and the amount of solution entering the froth tank.

Best Practice: *Adjust or experiment with the froth weir settings as recommended by the unit designer until the optimum weir setting is determined; this is a site specific setting.*

3.2.4 Using diesel as a frothing aid

As mentioned earlier, diesel addition is sometimes used as a frothing aid. If used, diesel is added to the liquid flowing from the reaction tank to the first oxidizer. Opinions vary on the value of diesel as a frothing aid. Some experts recommend against adding diesel, as hydrocarbon contamination is known to cause foaming problems in the absorber (see section 3.3). However, direct evidence at one ConocoPhillips Beavon Stretford unit indicates froth failure when diesel addition is halted. When diesel is added, the recommended starting rate based upon our experience is one tenth of a gallon per long ton of sulfur. This starting rate may be equivalent to something in the range of 2-3 drips/min per LTPD of sulfur throughput. However, the starting rate is adjusted as necessary based on the observed effects at each site. Because of the noted differences of opinion with regard to diesel addition, this is not presented as a “best practice” here, but is included for informational purposes.

3.3 Foaming

Foaming is generally an infrequently occurring problem in most Beavon Stretford TGUs. Potential causes of foaming or causes of foam stabilization include bacterial contamination, contamination with hydrocarbon or other foreign surface active compound, or precipitation of salts. In turn, foaming can cause the oxidizers to foam over, which may cause operations to reduce air flow, which can cause insufficient re-oxidation of the Stretford solution and increased salts formation rates.

3.3.1 Bacterial contamination

When foaming is caused by bacteria, it is usually when a sulfur melter is part of the system and when the aqueous liquid from the sulfur melter is returned to the Stretford system. The theory is that the high temperatures of the melter cause the bacteria to die and release their surface active cell contents, which leads to foaming (Trofe, et. al., 1993). ConocoPhillips has one Stretford unit with direct melting where the aqueous liquid from the sulfur melter is returned to the Stretford unit, and this unit has noted foaming when the melter is run for long periods of time.

Best Practice: *Avoid returning the aqueous liquid from the sulfur melter to the Stretford system, if at all possible, in order to control bacterial-induced foaming. If this is not possible, then running the sulfur melter for as short of a period as possible may help alleviate foaming.*

Although bacteria are usually not a problem unless a melter is present in the system, bacteria can also be controlled by using a biocide. Thiocyanate is one such biocide. The presence of a sufficient level of thiocyanate (in addition to causing a shift in the primary sulfur salt byproduct, as discussed later in the paper), tends to effectively control the number of bacteria present.

3.3.2 Contamination with hydrocarbon or other surface active compounds

When foaming is caused by hydrocarbon or other surface active compounds, it can often be traced back to hydrocarbon incursion into the upstream Claus unit(s).

Best Practice: *Prevent and mitigate hydrocarbon ingress into upstream amine units and sour water strippers. This may take the form of proper phase separations upstream of the amine units and sour water strippers, as well as adequate phase separation between the amine units/sour water strippers and the Claus unit.*

Additionally, using clean fuel gas or high purity hydrogen sources in any direct-fired inline burners is important to minimize hydrocarbon incursion. Since these burners require substoichiometric combustion, heavier hydrocarbons may pass through to downstream units. Refinery hydrogen and refinery fuel gas commonly contain significant fractions of gasoline and other heavy vapors, and thus are not good fuel sources.

Best Practice: *The best fuels for the RGG and other in-line burners are methane (natural gas) or clean, high-purity (PSA-quality) hydrogen.*

3.3.3 Salts precipitation

When foaming is caused by precipitation of salts, this may be due to overly large batch chemical addition. In this context, chemical addition includes caustic (or other source of base), vanadium, and ADA. If chemicals are added in large doses, localized high concentrations may result, which can cause precipitation and particle stabilized foaming.

Best Practice: *Add caustic continuously with adjustment based on analytical results to avoid high localized caustic concentrations and salts precipitation. Similarly, it is best to add vanadium and ADA in smaller more frequent batches based on analytical results.*

3.4 Sulfate and Thiosulfate Salt Buildup

The primary causes for the formation of sulfate and thiosulfate in a Beavon Stretford TGU system are 1) SO₂ breakthrough to the Stretford absorber, and 2) the presence of unreacted or partially reacted sulfur species (bisulfide and polysulfide) in the rich solvent feed to the Stretford oxidizers, and 3) operation at temperatures above 120 F. Other secondary causes exist such as oxidation of elemental sulfur in the oxidizers, but these causes are largely a characteristic of the Stretford process overall and generally of lower importance.

3.4.1 SO₂ breakthrough

SO₂ breakthrough from the hydrogenation and quench section can lead to rapid accumulation of sulfate and thiosulfate salts. It follows then that preventing and mitigating SO₂ breakthrough is paramount in managing levels of sulfur salts in the Stretford solution. One advantage of Stretford over amine based TGU configurations is that Stretford has the ability to absorb comparatively massive SO₂ upsets without immediate deterioration in treating performance. The only immediate symptoms may be black Stretford solution, increased chemicals make-up requirements, or increased salts concentrations from analysis of the solution. However, the damage being done to the Stretford system during such an SO₂ upset may not be noticed until the enough vanadium salts precipitate out of solution in the absorber and cause premature pressure drop rise, effectively limiting capacity and the run length.

To prevent SO₂ breakthrough to the Stretford solution, it is important to properly control, operate and maintain the reducing gas generator (RGG), hydrogenation reactor, and quench tower. These items become difficult to properly control when the Claus air control is not tight. Hydrocarbon ingress into the Claus unit is one of the primary causes of severe upsets in Claus unit air demand.

Best Practice: *Just as it was important for foam control, managing and preventing hydrocarbon contamination in the treating operations upstream of the Claus unit is also critical for Stretford salts control*

The RGG must heat the tail gas up to at least 520 F and be operated so that the hydrogenation reactor effluent contains a minimum of 1.5-2% H₂. The most common causes of RGG malfunction include poor heater air:fuel ratio control to the RGG and poor feed quality. Refinery hydrogen and refinery fuel gas feeds commonly contain significant fractions of gasoline and other heavy vapors. Furthermore, the composition of these streams may swing significantly over time making the stoichiometric air:fuel ratio a moving target.

Best Practice: *The best fuels for the RGG and other upstream direct fired heaters are methane (natural gas) or clean, high-purity (PSA-quality) hydrogen. Where a optimal choice of fuel can not be made, the composition needs to be known*

through online gas chromatographic analysis to permit the stoichiometric air:fuel ratio to be computed.

The hydrogenation reactor catalyst activity will decline over time as the catalyst is degraded. If SO₂ begins to be detected downstream, the temperature of the feed to the hydrogenation reactor can be raised (up to a point) in order to improve the kinetics of sulfur species conversion to H₂S. The hydrolysis reactions of COS and CO tend to fall off well before hydrogenation reactions of SO₂ and elemental sulfur. Tracking the conversion of these species over time can provide earlier warning of when to ramp up reactor feed temperature. Ramping up the reactor feed temperature based on COS and CO concentrations will also minimize the back end emissions due to COS, which is not absorbed into the Stretford solution to the same extent as H₂S. This observation also applies to amine based TGUs. Just as importantly, operating with excess hydrogen concentration can also partially overcome some of these kinetic limitations.

Best Practice: *Operate the RGG and external make-up H₂ (if available by the design) so that a minimum H₂ concentration in the hydrogenation reactor effluent of 1.5-2.0% is maintained. Section 3.8 discusses further details on ramping up hydrogenation reactor temperature to minimize the emissions of COS. This technique can also be used in more severe catalyst deactivation scenarios to compensate for SO₂ and elemental sulfur hydrogenation activity loss.*

The desuperheater section of the quench tower represents another chance to mitigate SO₂ breakthrough. In the desuperheater section, water is evaporated into the tail gas until it reaches adiabatic saturation. Additional water is added to the desuperheater as needed to make up for the evaporated water. If a contact condenser section is present above the desuperheater section, then the water feed to the desuperheater may come from the contact condenser loop. In any case, since the desuperheater does not routinely discharge water, it is possible to maintain it at a high alkalinity / high pH. The high alkalinity water can absorb SO₂ if it breaks through, preventing the SO₂ from reaching the Stretford solution. The basic environment also prevents the formation of elemental sulfur deposits and plugging within the contact condenser which is important in maintaining long term cooling and hydraulic capacity in the circuit.

The pH of the desuperheater water may not always be a good indicator of a high alkalinity. Trace levels of NH₃ in the tail gas may cause a relatively high pH (e.g., pH 7.5 - 9) even though alkalinity levels are very low. Thus, if pH is used as a process indicator, it may be necessary to maintain it at a level above that which would naturally be present due to NH₃. For example, if the tail gas normally contained 100 ppmv of NH₃, then it might cause a pH of ~7.5 in the quench water even without any appreciable alkalinity. Thus, the quench water might need to be maintained at a high enough alkalinity to give a normal pH of 8.5 or 9. Any alarms based on pH would also need to be set somewhat above the pH that the system would equilibrate to without alkalinity. Alternatively, operators can rely on routine analytical measurements.

Best Practice: *Take routine alkalinity measurements and adjust caustic addition to the desuperheater section accordingly, or make sure that operating pH set points and alarms are well above the level that would occur naturally due to any trace NH₃ that may be left in the Claus tail gas.*

3.4.2 Incompletely reacted sulfur species entering oxidizer:

The presence of unreacted or partially reacted sulfur species (bisulfide and polysulfide) in the rich solution fed to the Stretford oxidizers can lead to thiosulfate salt formation in the oxidizer. Within the Stretford unit, the primary causes of bisulfide and polysulfide being fed to the oxidizers may be attributed to insufficient Stretford chemical concentrations, inadequate reoxidation of Stretford solution, excessive sulfur salt byproduct concentrations, or sulfur deposition in the reaction tank causing reduced reaction time. A discussion on each of these factors follows. An additional factor, temporary overloading due to very high bisulfide loadings, is discussed in section 3.8.

Insufficient Stretford chemical concentrations

In order to avoid unreacted sulfur species entering the oxidizer, there must be enough vanadium present to convert the sulfide species to elemental sulfur. Generally speaking, 50% to 100% excess of vanadium is recommended (Trofe et. al, 1993). To be conservative, one should figure the 50%-100% based on the design sulfur loading rather than the actual sulfur loading. For example, a concentration of 2.3 g/L is sufficient to provide 50% excess vanadium (based on a 2:1 ratio of vanadium to bisulfide) for a unit designed for 500 mg/L bisulfide loading. Maintaining 3.1 g/L of vanadium would give 100% excess at the same 500 mg/L design loading. Keeping a healthy excess of vanadium also helps to prevent temporary overloading. For example, a unit that typically sees 250 mg HS⁻/L under normal operations will be much more forgiving of temporary overloading of up to 1000 mg HS⁻/L (4x increase in H₂S loading) for a short period if they have been maintaining 3.1 g/L of vanadium in the solution.

ADA aids in the reoxidation of the vanadium and also has been shown to suppress the formation of thiosulfate in the oxidizer. The optimum ADA concentration range is generally accepted to be 1.5 to 3 g/L (Trofe, et. al., 1993), again for units designed for a maximum of 500 mg/L bisulfide loading.

Best Practice: *Perform routine analytical testing, and add chemical accordingly to maintain vanadium and ADA concentrations.*

Inadequate reoxidation of Stretford solution

Hand in hand with the proper concentrations of Stretford chemicals is proper reoxidation of those Stretford chemicals. Air rates should be maintained at design levels at all times. Maintaining adequate alkalinity has also been shown to aid in reoxidation of vanadium as discussed further in section 3.9.

Best Practice: *Alkalinity levels should be maintained in the 20 g/L and higher range. Maintain oxidizer air rates at design levels at all times.*

Excessive sulfur salt byproduct concentrations

High salt concentrations may reduce the rate of re-oxidation of vanadium. One potential mechanism is simply due to the reduced solubility of O₂ in salt laden solutions. Section 3.5 discusses methods to control sulfur salts in further detail.

Sulfur deposition / reduced residence time in reaction tank

Plugging of the reaction tank with elemental sulfur may reduce residence time and allow unreacted sulfide species into the oxidizer. Some plugging is inevitable. As mentioned previously, maintaining adequate circulation rates can help sweep particles through the system and prevent plugging of the reaction tank. ConocoPhillips has some Stretford TGUs where the reaction tank is built into the bottom of the absorber. These reaction tank designs are more prone to plugging with significant volumes of elemental sulfur. In these units, skim pumps are present to remove sulfur on the top and bottom of the reaction tank.

Best Practice: *Operate skim pumps on the reaction tank intermittently to remove accumulated sulfur particles before residence time is compromised.*

Operation at high temperature:

Operation at temperatures above about 120 F causes higher byproduct formation rates.

Best Practice: *Maintain a temperature below 120 F (preferably below 110F) throughout the Stretford unit.*

3.5 *Disposal or On-line Regeneration of the Stretford Catalyst*

Even if all of the best practices mentioned previously to minimize or prevent the formation of sulfur byproduct salts are followed, 1-5% of the inlet sulfur species will be converted to sulfur byproduct salts in the Stretford system. If the loss of these salts via the product sulfur or solution purge is insufficient, the salts levels will build over time. The salts must be removed before they reach high levels for a variety of reasons, as discussed above and as shown in Figure 2. The methods used to deal with high salt levels in Stretford are no different than with an amine treating unit. These methods include:

- Desalting of the solution.
- Continuous purge of Stretford solution in order to maintain reasonable salt levels.
- Replacement of the Stretford solution with fresh solution.

For the majority of Beavon Stretford systems, thiosulfate is the primary sulfur salt species formed. Thiosulfate may be removed from the system via the British Gas Desalting process. The process involves the conversion of thiosulfate to sulfate and the subsequent crystallization of sulfate as Glaubers Salt. Global Sulfur Systems offers contract desalting services which can be performed on line.

In a few cases, especially when thiocyanate is present in the system, sulfate (versus thiosulfate) is the primary salt formation product. Sulfate may be crystallized directly from the Stretford solution. When sulfate is the primary byproduct, sulfate levels generally must be kept below roughly 100 g/L, depending on the temperature, to prevent precipitation of sulfate salts, which are less soluble than thiosulfate salts. One of ConocoPhillips' Beavon Stretford units utilizes

NaSCN addition to promote sulfate as the primary byproduct. This plant has a permanent desalting system for sulfate removal. Using this system, sulfate levels are kept below 60 g/L. Although only applicable to systems where sulfate is the primary byproduct, use of such a system represents best practice for on-line regeneration. In such systems where an agent such as thiocyanate is used, it is important to keep thiocyanate levels high enough to continue producing sulfate as the primary byproduct.

In cases where it is infeasible to perform on-line desalting, a continuous purge to a suitable and properly permitted waste water treatment system may be used to maintain salts levels. Alternately, the solution may be replaced. A number of potential disposal options may be available (Rueter, 1990).

Best Practice: *Employ desalting or other techniques to maintain salts at acceptable levels. When thiosulfate is the primary salt byproduct, thiosulfate levels should be maintained below 250 g/L (Trofe, et. al, 1993). When sulfate is the primary salt byproduct, sulfate levels should be maintained below 100 g/L.*

3.6 *Production and Filtration of the Sulfur Filter Cake*

The sulfur produced in Beavon Stretford units can be melted and added to Claus sulfur or produced as a filter cake.

If direct melting is used, as it is in one of ConocoPhillips's Beavon Stretford units, it is important to maintain the melter temperature as close to the sulfur melting point as possible, preferably around 260F if acceptable melter operation can be achieved. Lower melter temperatures are preferred because units with direct melting usually return the Stretford solution from the melter back to the Stretford unit to preserve solution inventory. The decanted solution from the melter contains high salts levels because higher temperatures cause higher rates of sulfur salts formation in the melter.

If filtration is used, it is important to wash the sulfur adequately to reduce vanadium losses. In this case, the use of warm wash water is preferred, because vanadium compounds have a higher solubility in warm water, and a cleaner cake can be produced. It is desirable to have a low vanadium content so that the sulfur can be re-used for agricultural purposes and or disposed of as non-hazardous waste.

3.7 *Minimizing Emissions of Carbonyl Sulfide*

COS emissions are primarily a function of the feeds and operation of the upstream Claus SRU, the reducing gas generator, and the hydrogenation reactor. Since Stretford is able to treat down to very low H₂S levels, COS contribution can become a larger percentage of the total sulfur emissions. Stretford has a much more limited capability to remove COS compared to the H₂S removal efficiency.

In the TGU hydrogenation reactor, hydrolysis of COS is a natural occurrence under normal operations. The kinetics of this reaction can be further promoted by operating the hydrogenation reactor at a higher temperature, albeit with a slightly higher equilibrium concentration of COS.

Best Practice: *As the hydrogenation catalyst ages, the hydrogenation reactor temperature can be raised in discrete, small increments as necessary to maintain emissions within required limits. The first Claus Converter operating temperature can also be raised (if the design configuration permits) to offload the TGU hydrogenation reactor COS hydrolysis (GPSA Data Book, Paskall). Finally, maintaining design Stretford circulation will maximize removal in the Stretford system.*

3.8 Addressing Temporary Overload of the Stretford Solution with H₂S

The Stretford system may be in perfect operation and control and still be easily upset with very high bisulfide loading caused by excessive H₂S in the feed, which in turn is due to an upset or problem in the Claus unit(s). Referring to Figure 3 below, a typical 3-bed Claus unit recovering 97.9% of the sulfur present in the feeds would only recover 89.0% of the sulfur for 10% air deficient operations. As a result, the H₂S loading on the Stretford absorber would increase by more than a factor of five, i.e. $(1-89\%/100) / (1-97.9\%/100) = 5.2$.

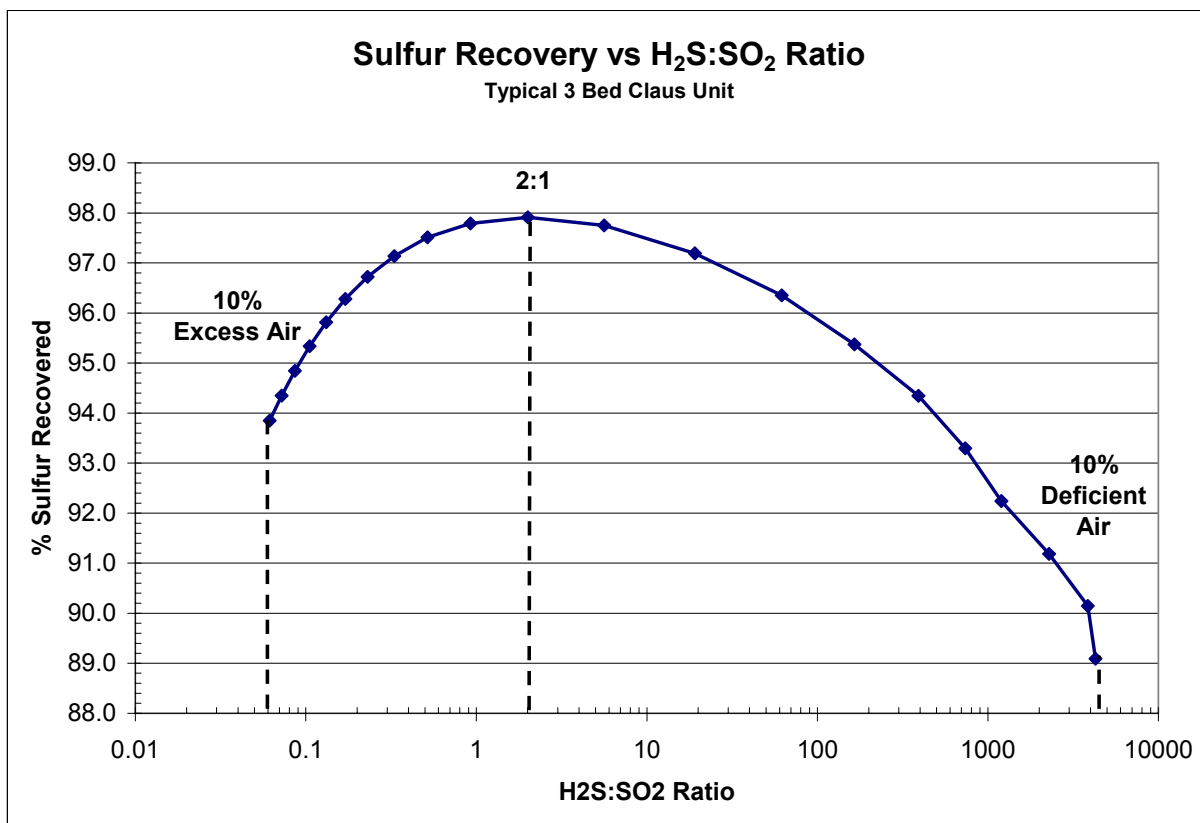
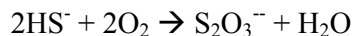


Figure 3. Illustration of Effects of Off-ratio Claus Air Control

The immediate consequence of this sort of upset can be bisulfide slip into the oxidizers and a subsequent increased salt formation rate. Most Stretford operators can attest to the solution turning jet black during this temporary overloading. From a microscopic viewpoint, the reaction below robs oxygen required for vanadium reoxidation (Kohl & Riesenfeld, 1985).



The reduced vanadium species (e.g., V^{4+}) give the solution its black color. Deposits gathered from a number of Stretford absorbers during turnaround maintenance were observed to consist of alternating layers of elemental sulfur and vanadium, much like growth rings in trees. In these cases, the reduced vanadium layers may have resulted from massive vanadium precipitation events spawned from temporary Stretford solution overloading. The presence of elevated salts in solution may have also reduced oxygen solubility in the oxidizer, thus compounding the problem.

Best Practice: *The importance of tight air control in the Claus unit cannot be overstated for the reason that it prevents temporary Stretford solution overloading. This requires a properly operating and calibrated air demand analyzer that “trims” the air fed to the front of the Claus unit by a feedback control system. It is also imperative to minimize hydrocarbon related upsets to avoid overwhelming the Claus air control system. In the event that this prevention measure is lost, overwhelmed or not available, there are other Best Practices to mitigate temporary Stretford solution overloading from upsets. These include operating with higher initial alkalinity in the Stretford solution and rapidly increasing the alkalinity of the desuperheater water and of the Stretford solution in the oxidizers. The tactic of rapidly increasing caustic addition to the Stretford oxidizers is discussed further below.*

Overloading with H_2S can be mitigated by maintaining full design solution circulation under all conditions and by maintaining adequate chemical concentrations as discussed previously. Otherwise, it is important to monitor the color of the Stretford solution several times per operation shift. If the color begins to darken from the usual red / orange to the characteristic overload color of black, immediate steps must be taken to correct the cause of the high loading to the Stretford unit by correcting the problem at the upstream Claus unit (e.g. adjusting air to acid gas ratio).

If the Claus unit problem can't be corrected rapidly enough, then additional caustic can be added to the desuperheater water to buy some time to remedy the upstream problem. Further, one ConocoPhillips' site adds caustic soda to the solution in the oxidizers at higher than normal flow rates until the solution turns reddish orange again indicating adequate reoxidation of the Stretford solution. Note: steady, continuous chemical addition is advocated as a best practice in another section of this paper for *normal operations*. Practices such as this should be weighed by the individual site based upon the trade-off between preventing salts formation versus the increased risk of bulk precipitation of chemicals in solution.

3.9 *Maintaining the Optimum Alkalinity Levels in Stretford Solution.*

It is generally not possible to independently adjust the pH and the alkalinity of the solution in a Stretford unit. If the Stretford unit were processing a gas stream without any CO_2 present, then it

might be possible to adjust alkalinity and pH independently. However, since CO₂ is present in Claus tail gas, the two cannot be adjusted independently. Higher alkalinity equates to higher pH and vice versa. The source of the base added to adjust alkalinity is also generally not important. Regardless of whether one uses NaHCO₃, Na₂CO₃, or NaOH, the alkalinity and the pH will change the same way. However, the reaction of NaOH with CO₂ results in the production of some water, so if there is a water balance issue, then it may be preferable to add NaHCO₃ rather than NaOH.

As mentioned previously, maintaining an appropriate level of alkalinity has been proven to aid in the reoxidation of vanadium. Recommended alkalinity levels are generally in the 20 g/L range, and higher in some cases. Most units add caustic to maintain alkalinity.

Best Practice: *Continuously add caustic in a location for good mixing, and adjust the addition rate based on routine analytical testing to maintain the alkalinity at or above 20 g/L.*

If allowed within bicarbonate solubility limits and if allowed by equipment configuration, it may be beneficial to run at elevated alkalinity levels for at least three reasons. First, elevated alkalinity levels have been shown to improve vanadium reoxidation (Trofe-2, et. al., 1993). Second, elevated alkalinity levels can provide some amount of buffer against H₂S emissions during temporary overload events. Third, elevated alkalinity levels have been shown to reduce thiosulfate and overall salt formation rates (Trofe, et. al, 1993).

Regarding this third point, caution is advised. Although the research showed reduced total salt formation rates, very high alkalinity levels can cause the sulfur salt byproducts to be produced as sulfate rather than the usual thiosulfate. Sulfate is less soluble than thiosulfate, and it may be necessary to have a system suited to the production of sulfate before running at very high alkalinities.

4.0 Benchmarked Performance of Operating Units

Table 1 provides some approximate operating data for 4 Beavon Stretford TGUs in ConocoPhillips US refineries. An observation can be made that the units with the lowest H₂S loading (mg HS⁻/L) have the longest run lengths. As a rule, high circulation rates and low sulfur loadings are conducive to both good H₂S removal and high reliability for all types of liquid redox sulfur recovery units (Stretford, SulFerox, LO-CAT, etc.). This observation is not surprising, but it does point out the importance of optimizing the upstream Claus train sulfur recovery in order to minimize load on the TGU.

A second observation is that the units with the lowest salts concentrations have the longest run lengths. As pointed out previously throughout this document, high salts concentrations are detrimental for a variety of reasons including: reduced vanadium reoxidation rates, higher salt production rates, causes precipitation of vanadium and other salts, etc. Salt concentration management is a key issue with Stretford TGUs. The Why Tree in Figure 2 suggests that bisulfide loading and salts formation are inter-related.

Sites C and D have recently switched absorber internals from redwood slats in favor of stainless steel shed decks with hopes of obtaining longer operating runs between absorber cleanings. Neither of these revamps have been in service long enough to assess benefits. However, since switching to the shed decks, site C has observed a slightly higher baseline start of run pressure drop accompanied by a significantly lower H₂S concentration in the treated gas. These observations point to improved mass transfer with the shed decks versus traditional redwood slats.

Finally, net accumulation of sulfur salts at site C dropped to essentially zero after melter operations were discontinued in favor of a filter press operated by a third party. This result is believed to be a cumulative effect of lower thiosulfate generation rate from operations without the high temperature melter coupled with increased Stretford solution losses into the filter cake. The plant is currently experimenting with water washing techniques to optimize the quality of the filter cake.

Table 1 -- Approximate Operating Parameters for 4 ConocoPhillips Beavon Stretford TGUs

Unit	A	B	C ^a	C ^b	D	Typical Industry Guideline ⁹
Typical loading (mg HS ⁻ /L)	220-320	~180	375-500	375-500	200-480	< 500
Avg. TSS (vol%)	0.2	0.6		0.1	0.3	< 1
TSS range (vol%)	0.1-0.7	0.1-3.0	0-0.2	0-0.2 target	0.1-1	< 1
TDS (g/L)	85	140-180	40	40	280-450	< 350
Thiosulfate (g/L)	10-25	130-160	150-450 ⁴	140-170	140-430	< 250
Sulfate (g/L)	45-60	- ³	-	-	38-116	< 100 ⁸
Stretford temperature to absorber (F)	80-105	80-100	95-105	95-105	60-100	< 120
Vanadium (g/L)	1.5-3.0	1.7-2.2	3	1.5-2.5	2.3-4.7	2.3-3.1
ADA (g/L)	1.5-3.0	1.7-2.3	1.9-2.2	1.8-2.5	1.8-2.2	1.5-3.0
Stretford pH	8.7-9.4	8.6-9		8.5-9	8.5-9.2	< 9
Desuperheater pH	9.5-10	7-8		9-9.5	8.5-9.5	-
Stretford total alkalinity (g/L)	16-23	30-50	14-18	20-25	14-24	> 20
SCN ⁻ (g/L)	10-15	-	-	-	-	-
Frequency of 3 rd party desalting (events/yr)	na ¹	na ²	2-3	na ⁵	4	-
Absorber packing type	Redwood slats	Redwood slats	Redwood slats	Redwood slats ⁶	Top 3: Redwood slats Btm: SS shed deck	-
Time between downtime caused by absorber plugging (yrs)	na ⁷	~4	0.9	2	1.1	-
C ^a – Stretford TGU with melter in operation						
C ^b – Stretford TGU with melter out of operation, filtration of sulfur cake						
1 – unit has permanent dedicated salts removal system on site						
2 – unit has continuous small solution purge to prevent salts accumulation						
3 – data lacking/inconsistent (no sulfate data, thiosulfate plus total alkalinity add up to more than TDS)						
4 – during period of cyclic salt buildup followed by 3 rd party desalting						
5 – no desalting necessary after ceasing melter operation						
6 – redwood slats were in use for this data, however, unit has subsequently been converted to SS shed decks (pitched angle)						
7 – absorber plugging does not require downtime between scheduled TGU turnarounds (5 year cycle)						
8 – applicable for units that produce sulfate as the primary byproduct salt based upon authors' experience						
9 – Trofe, et. al, 1993 was used as the primary reference for these guidelines						

5.0 Conclusions

Although it has a number of unique operating issues, the Beavon Stretford TGU process has proven to be a very capable emission control device in Claus tail gas treating service. Compared to other TGU processes, a Beavon Stretford TGU may have the best ability to absorb a large system shock (e.g., an SO₂ or H₂S excursion) while maintaining good emission control and, with proper counter-measures, recover quickly. As is the case with other TGU technologies, good operating practices in the upstream amine, sour water stripper, and Claus units goes a long way toward preventing most of the major operating problems with Beavon Stretford TGUs.

Other than sound control of the units feeding the Beavon Stretford TGU, the next most important set of best practices cover managing sulfur byproduct salts. High levels of salts have many negative consequences, such as reducing the solubility of the Stretford catalyst species, interfering with re-oxidation of the solution and precipitation of salt species themselves. It is very important to maintain good control those factors that lead to excessive salt formation. Even with the best control of temperatures, air rates, and other items, the salts may still build over time. Thus, it is important to remove the salts from the system by on-line regeneration, solution purging or other means before they reach maximum recommended levels.

As with many processes, the outward symptoms of some Stretford operating problems can occur long after the events that initiated the problem. For example, in the case of absorber plugging, the chronic symptom of high absorber pressure drop may occur weeks or months after repeated Claus unit upsets. Because the cause of a problem is sometimes separated by a significant time lapse from the onset of symptoms, problem solving becomes a more difficult exercise. By sharing views of the root causes of these problems and corresponding best practices identified, the authors hope to provide the industry with a better understanding of the important variables to closely monitor and control to consistently maximize the overall performance of Beavon Stretford TGUs.

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- ConocoPhillips staff who participated in the best practices round table
- ConocoPhillips staff who participated in this investigation by providing plant data and review of this report.
- Operating staff representing the ~15 other Stretford units who provided feedback during the conduct of this best practices investigation.
- Dr. O.E. Hileman & T.W. Trofe for discussion of some aspects of the history and decline of the Stretford process.

7.0 References

Note: Many of the original Stretford process licensors published articles on the issues discussed in this paper. While the references given below are primarily from a later period of time, these references did include and consider that previous body of licensors' literature. Even so, it may be useful for the reader to refer to some of the early papers by Parsons, British Gas, Peabody Holmes, and others for certain specific items.

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