Sulfur Plant Configurations for Weird Acid Gases

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1. ABSTRACT

The rise in unconventional natural gas production, along with the growing interest in “clean coal” technologies and other alternative energy sources, has created a number of interesting challenges for sulfur plant designers. More and more, sulfur plants must be designed to recover sulfur from very lean acid gases or acid gases that contain contaminants such as methanol, heavy hydrocarbons, BTEX (benzene, toluene, ethyl-benzene, and xylene), ammonia, and/or cyanide. In addition, national and international emissions standards continue to become more stringent, requiring facilities to achieve increasingly higher recovery levels.

A number of new projects have required non-standard sulfur plant configurations to address the dual challenges of low-quality acid gas and strict emissions requirements, while still preserving the high reliability and ease of operation that sulfur plant operators desire. This paper reviews the capabilities of various sulfur recovery technologies and the ranges of applicability for each, and discusses the impact of various acid gas contaminants on the design of a sulfur recovery facility. In addition, this paper presents information that a sulfur plant designer can use to arrive at an optimum facility configuration for a variety of acid gas compositions and sulfur recovery levels.

2. INTRODUCTION

The global energy portfolio has changed considerably in the last decade. Advances in technology have led to an increase in unconventional natural gas production, as well as an increase in the number of proposed and operating coal gasification facilities world-wide. At the same time, environmental regulations, particularly maximum allowable SO₂ emissions, have become more stringent around the world. The following are the SO₂ emissions standards required by the World Bank, which provides the financing for many new processing facilities:

- Natural Gas Processing: \( 75 \text{ mg/Nm}^3 \) (\( \sim 25 \text{ ppmv} \)) dry, 15% \( \text{ O}_2 \)
- Petroleum Refining: \( 150 \text{ mg/Nm}^3 \) (\( \sim 50 \text{ ppmv} \)) dry, 3% \( \text{ O}_2 \)
- Coal Processing (Gasification): \( 150 \text{ mg/Nm}^3 \) (\( \sim 50 \text{ ppmv} \)) dry, 15% \( \text{ O}_2 \)

For comparison, the United States typically requires less than 250 ppmv of SO₂ on a dry, no excess oxygen basis for refinery sulfur recovery plants.

These changes in both feed streams and emissions limits have created a number of challenges for sulfur plant designers. Sour unconventional natural gas often has a higher CO₂:H₂S ratio than conventional gas sources, which results in leaner (lower H₂S concentration) acid gas feed streams. Likewise, the acid gases produced from treating syngas from coal gasifiers are often much leaner than traditional refinery or gas plant acid gases. In addition, acid gases from both of these sources frequently contain contaminants such as methanol, heavy hydrocarbons, BTEX, ammonia, and/or cyanide, all of which can cause operating problems in sulfur recovery units (SRUs).

The purpose of this paper is to (1) review the various technologies available for recovering sulfur from lean acid gas streams, (2) examine the effects that different contaminants have on these processes and propose strategies to mitigate these effects, (3) attempt to quantify the recovery efficiencies and corresponding SO₂ emissions that can be achieved with various technologies when processing lean or contaminated acid gases, and (4) provide guidance for selecting the optimum facility configuration for various applications.
3. RECOVERY VS. SO₂ EMISSIONS

The single most important piece of information any sulfur plant designer needs to know to begin designing a sulfur recovery facility is the required sulfur recovery efficiency. This requirement will often dictate the process configuration or technology selection because not all of the well-established sulfur recovery processes are capable of achieving the same recovery efficiency. Unfortunately, sulfur plant designers are often given inconsistent or even contradictory recovery specifications. Since the cost of a facility almost always increases with increasing recovery efficiency, this can lead a designer to propose a process design that may be more costly to build than what is really required, or that may not meet all of the specifications for the project.

In very simple terms, the sulfur recovery efficiency is the percentage of the total sulfur (H₂S and other sulfur-containing compounds) in the acid gas feed stream(s) that is recovered as elemental sulfur in a sulfur plant. However, while technically true, that definition is often not very useful. In practice, the sulfur recovery efficiency required for a given facility is almost always dictated by environmental regulations, which vary from state to state, from province to province, and from country to country. In many cases, a more accurate statement is that the required sulfur recovery efficiency is a function of the maximum allowable SO₂ emissions for a given location. Since any sulfur that is not recovered in the sulfur plant is incinerated in the tailgas thermal oxidizer (TTO) to SO₂, the maximum allowable SO₂ emissions in the TTO vent gas effectively dictates the quantity of sulfur that must be recovered in the sulfur plant.

It is worth noting that while sulfur recovery efficiency and SO₂ emissions are directly related, recovery efficiency is typically specified as a percentage, whereas allowable SO₂ emissions are almost always specified as a concentration. In other words, SO₂ emissions (as they are commonly reported) are a function of both the sulfur recovery efficiency and the quantity of other diluents (nitrogen, carbon dioxide, etc.) in the vent gas. This is an important distinction because, while it may seem counter-intuitive, in some cases the technology or plant configuration that achieves the highest sulfur recovery efficiency may not be the technology or configuration that achieves the lowest SO₂ emissions. This is especially true for leaner acid gas streams.

4. SULFUR RECOVERY TECHNOLOGIES

When designing a new sulfur recovery facility, there are a number of well-established technologies to choose from. So, the first step is to understand the ranges of applicability for each type of process, and the sulfur recovery efficiency each type of process can achieve. The following is a list of the sulfur recovery technologies that were considered as part of this study:

<table>
<thead>
<tr>
<th>Primary Sulfur Removal</th>
<th>Tailgas Cleanup</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S Scavengers</td>
<td>Sub-Dewpoint Claus (CBA, MCRTC™, Sulfreen™)</td>
</tr>
<tr>
<td>Liquid Redox (LO-CAT®, SulFerox®, CrystaSulf®)</td>
<td>Direct-Oxidation Claus (SUPERCLAUS®, EUROCLAUS®)</td>
</tr>
<tr>
<td>Biological Processes (THIOPAQ O&amp;G)</td>
<td>Reduction/Absorption/Recycle Tailgas Cleanup (SCOT® and SCOT®-Type)</td>
</tr>
<tr>
<td>Selectox™ &amp; Recycle Selectox™</td>
<td>SO₂ Recycle (CANSOLV® TGT+, ClausMaster™)</td>
</tr>
<tr>
<td>Modified Claus</td>
<td>SO₂ Scrubbing (DynaWave®)</td>
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</tbody>
</table>
Descriptions of each of these technologies are provided in Appendix A. In general, each of these processes or technologies falls into one of two categories: those used for primary (or bulk) sulfur removal from either sour gas or acid gas streams, and those used in addition to a primary sulfur removal process to increase the overall sulfur recovery to 98%-99.9%+. This second type of process is generally referred to as a “Tailgas Cleanup” (TGCU) process.

5. TECHNOLOGY SELECTION FOR LEAN ACID GASES

One of the primary goals of this paper is to aid sulfur plant designers in selecting the one or two optimum SRU configurations for a given application from the many, many choices available today. Accordingly, a variety of sulfur plant processes and configurations were modeled using Ortloff’s Sulfur Recovery Systems Simulator program, SULFUR. SULFUR can model completely integrated Claus, CBA, Selectox, and oxygen-enriched sulfur plants combined with SCOT®-type tailgas cleanup units and/or incineration systems. The accuracy of the program has been verified in many actual sulfur recovery plants.

The following SRU configurations were modeled:

a. 3-Stage Claus + TTO
b. 2+2-Stage Claus/CBA (2-Stage Claus + 2-bed CBA Sub-Dewpoint) + TTO
c. Recycle Selectox + 2-Stage Claus + TTO
d. Recycle Selectox + 1+2 Claus/CBA (1-Stage Claus + 2-bed CBA Sub-Dewpoint) + TTO
e. 3-Stage Claus + SCOT®-type TGCU + TTO

The compositions of the acid gas feed streams, as well as all other assumptions, utility conditions, etc., are documented in Appendix B.

H₂S scavengers were excluded from this analysis because they are generally recommended for gas streams containing less than 200-400 lb/day (90-180 kg/day) of sulfur. Likewise, liquid redox processes and biological processes were excluded from this analysis because they are generally recommended for gas streams containing less than 20-40 tons/day of sulfur, and both produce a low-quality sulfur product.

Direct-oxidation tailgas cleanup processes were not modeled. However, the literature confirms that the recovery levels achieved with these processes are very similar to those achieved with sub-dewpoint processes. Therefore, where information or generalizations are provided for sub-dewpoint processes, the same conclusions are assumed to apply to direct-oxidation tailgas processes. The SO₂ recycle processes and the SO₂ scrubbing processes were also not modeled. For these processes, the recovery efficiencies, and SO₂ emissions reported are based on results obtained from designs proposed for recent projects.

Table 1 summarizes the ranges of applicability, both in terms of inlet H₂S concentration and achievable recovery efficiency, for all of the technologies listed above. When two technologies, or technology combinations, are considered equally capable of achieving a given recovery efficiency range, both are listed in Table 1. The results presented in Table 1 also assume that there are no problematic contaminants in the acid gas.
The Selectox or Recycle Selectox process, rather than the modified Claus process, is recommended for recovering high-purity sulfur from acid gas feed streams containing less than about 20% H₂S. At less than about 20% H₂S, a stable flame cannot be maintained in a Claus furnace even with a split-flow furnace design so other means, such as firing supplemental fuel gas, or enriching the combustion air with oxygen, are required to maintain a stable flame. However, a stable flame can be maintained at concentrations above 20%, with a split flow furnace and high temperature (>400°F [200°C]) acid gas preheat, without the need for supplemental fuel gas firing or oxygen enrichment. Likewise, a stable flame can be maintained at concentrations above 50% with a straight-through furnace design and either high temperature or low temperature (>200°F [90°C]) acid gas preheat.

If a sulfur recovery efficiency of 92-97% is sufficient to comply with all local environmental regulations, then three Claus catalytic stages following a furnace, or two Claus catalytic stages following a Selectox stage, are generally sufficient. However, if higher recovery efficiencies are required, then some type of tailgas cleanup process must be used in addition to the upstream Claus or Selectox SRU.

A two-bed sub-dewpoint process, like Amoco’s Cold Bed Adsorption (CBA) process, will achieve 97-99% recovery efficiency when installed downstream of a 2-stage Claus or Selectox SRU. Likewise, direct-oxidation Claus processes, such as the SUPERCLAUS® process, can achieve 97-99.4% recovery efficiency when installed downstream of a 2-stage Claus SRU.¹

If even higher recovery levels are required (99.0-99.9%), as is the case for most refineries in the United States, then a reduction/absorption/recycle tailgas cleanup process, such as the SCOT® process licensed by Shell Global Solutions, is typically required. In general, these types of processes can reduce the SO₂ emissions from a sulfur recovery facility to approximately 100-250 ppmv on a dry, no excess air basis. However, provisions such as formulated solvents or acid-aided regeneration may be used to extend the capabilities of these processes.

When ultra-low SO₂ emissions are required (<50 ppmv) or when SO₂ emissions must remain low under all circumstances (startup, shutdown, upset, etc.), then an SO₂ Scrubbing process such as MECS’ DynaWave® SO₂ Scrubbing System, or an SO₂ Recycle process, such as the CANSOLV® TGT+ process, are often the only viable alternatives, especially for lean acid gas streams. Although these types of processes may be installed downstream of a 3-stage Claus or Selectox SRU, the operating costs of the units can be quite high. In order to minimize the consumption of either caustic or solvent and the associated operating costs, it is often better to install these facilities downstream of either a sub-dewpoint Claus process or a direct-oxidation Claus process.
### Table 1 – Sulfur Recovery Technologies for Various H$_2$S Concentrations (No Contaminants)

<table>
<thead>
<tr>
<th>H$_2$S in Acid Gas (%)</th>
<th>SRU</th>
<th>Conversion Stages</th>
<th>TGCU / TGTU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Front-End</td>
<td>Conversion Stages</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Approximate SO$_2$ Emissions (Dry, 0% O$_2$)</td>
<td>&gt;10,000 - 4,000</td>
</tr>
<tr>
<td></td>
<td>Recovery Level</td>
<td>%</td>
<td>92-95%</td>
</tr>
<tr>
<td>0%-100%</td>
<td>H$_2$S Scavengers - Less than 200-400 lb/day - No produced sulfur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%-100%</td>
<td>Liquid Redox - Less than 10-20 T/D - Low Quality Sulfur</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;1%</td>
<td>Biological Processes - Less than 40 T/D - Low Quality Sulfur</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acid Gas Enrichment</td>
<td>2-Stage Claus</td>
<td></td>
</tr>
<tr>
<td>1%-5%</td>
<td>Selectox</td>
<td>1-Stage Claus</td>
<td>Sub-Dewpoint / D.O.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Scrubbing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Recycling</td>
</tr>
<tr>
<td>5%-20%</td>
<td>Recycle Selectox</td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Scrubbing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Recycling</td>
</tr>
<tr>
<td>20%-40%</td>
<td>Hi Temp A.G. Preheat + Split Flow + Air or Hi Temp. A.G. Preheat + Split Flow + 100% O$_2$</td>
<td>3-Stage Claus</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + TGCU</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Recycling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Scrubbing</td>
</tr>
<tr>
<td>40%-50%</td>
<td>Hi Temp A.G. Preheat + Split Flow + Air or Low Temp. A.G. Preheat + Straight Through + O$_2$ Enrichment</td>
<td>3-Stage Claus</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + TGCU</td>
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<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Recycling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Scrubbing</td>
</tr>
<tr>
<td>&gt; 50%</td>
<td>Low Temp. A.G. Preheat (Optional) + Straight Through + Air</td>
<td>3-Stage Claus</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-Stage Claus</td>
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<tr>
<td></td>
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<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Recycling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Stage Claus</td>
<td>Sub-Dewpoint / D.O. + SO$_2$ Scrubbing</td>
</tr>
</tbody>
</table>
6. CONTAMINATES

The concentration of H$_2$S in the inlet acid gas is not the only factor that sulfur plant designers must consider when deciding on the right technology or configuration for a sulfur recovery facility. With a table like the one on the previous page, selecting the best technology or combination of technologies for a given H$_2$S concentration and recovery/emissions specification may seem pretty straightforward. However, contaminants in the acid gas add an additional layer of complexity to determining the best technology for a given application. Contaminants in the acid gas stream can seriously impact the operability and reliability of a sulfur plant. Therefore, designers must determine the most economical means of removing or destroying these contaminants so that they do not negatively affect the performance of the facility.

6.1 Methanol

Sources

Methanol in acid gas streams is most commonly a result of injecting methanol upstream of the processing facilities at the wellhead or in flow lines for hydrate prevention. Methanol enters the processing facility with the sour gas, is absorbed by the amine, and will often concentrate in the amine stripper reflux stream. Methanol is also the primary component of a commonly used physical solvent and may be found in the associated acid gas stream as a result of carry-over from the solvent system.

Consequences

Although the chemistry of methanol in a Claus sulfur plant is not well documented, it has been reported that methanol reacts with elemental sulfur to form COS and CS$_2$, and that methanol reacts with H$_2$S to form methyl mercaptan. The methyl mercaptan then likely reacts further with sulfur to form a variety of products including CS$_2$, dimethyl disulfide and sulfur-containing polymers. If not converted in the downstream catalyst beds, these reaction products may decrease the overall recovery efficiency of the plant, foul or partially block catalysts beds, or react further with other species to produce H$_2$S, which can disturb the H$_2$S:SO$_2$ ratio in the sulfur plant.$^5$

In addition, methanol, like any other hydrocarbon, may crack and form coke on the catalyst in the sulfur plant reactors. This not only deactivates the catalyst, but can also result in high pressure drop across the catalyst bed and cause dark or discolored sulfur.

Mitigation

High concentrations of methanol in a sour gas or acid gas stream are often removed by contacting the contaminated stream with methanol-free water in a water wash system. Since methanol is highly soluble in water, these systems can significantly decrease the concentration of methanol in a sour gas or acid gas stream. When installed upstream of the amine absorber, these systems will also improve the operability of the amine system by removing particulates and other impurities like ammonia or HCN which can contaminate the amine solvent and cause problems like foaming, poor treating, corrosion, etc.

If water washing is not feasible, or is not sufficient to remove the methanol in an acid gas stream, then methanol can be destroyed in the SRU furnace. This requires routing the entire acid gas stream to the acid gas burner to ensure that any methanol is fully combusted. (In many SRUs, a portion of the amine acid gas is bypassed around the burner and injected into the second zone of
the furnace. Since only one-third of the H2S in the acid gas feed is combusted in the furnace, bypassing a portion of the acid gas around the burner increases the temperature in the front zone of the furnace. However, if the feed stream contains methanol, bypassing a portion of this stream around the burner may allow un-combusted methanol to enter the catalyst beds. If methanol is present in the acid gas feed, routing the entire acid gas stream to the burner should be considered and other means of maintaining a stable flame or a specific furnace temperature, such as burning supplemental fuel gas in the burner or enriching the combustion air with oxygen, may be necessary.

6.2 Ammonia/HCN

Sources

Ammonia is a common contaminant in acid gas feed streams. In petroleum refineries, ammonia is often formed as a byproduct in hydrotreaters and hydrocrackers. It is also commonly used to neutralize strong acids in the overheads of various distillation units. In coal gasification facilities, ammonia and hydrogen cyanide are typically formed during the gasification process.

In both types of facilities, the ammonia (along with H2S) often concentrates in various sour water streams (condensed water, wash water, etc.) and is then stripped from this sour water in a sour water stripper (SWS). The overhead from the SWS is typically routed to one or more SRUs while the stripped water is discharged, or routed back to other processing units for reuse.

Consequences

Ammonia can cause several problems in a sulfur recovery plant. The most troublesome is the formation of ammonia salts in the low-temperature sections of the Claus plant which can lead to plugging and high pressure drop in the unit. Ammonia in the acid gas also impacts recovery. The products of ammonia destruction are nitrogen and water, and water is a product of the Claus reaction. So, the equilibrium conversion to sulfur is limited by both dilution of the H2S and SO2, and the higher water concentration. Finally, ammonia can impact the size of the facility since the combustion products are essentially inert and take up additional space in the piping and equipment.

Hydrogen cyanide in the acid gas can be considered the same as ammonia because in the high temperature atmosphere of the SRU furnace, cyanide will react with other species to form ammonia.

Mitigation

Like methanol, ammonia is highly soluble in water, so contacting the contaminated sour gas, acid gas, or syngas stream with ammonia-free water in a water wash system can significantly decrease the concentration of ammonia in the gas. Obviously, if the source of the ammonia-rich gas stream is a SWS, then this is not a viable option because the contaminated water from the water wash system would typically be routed back to the SWS. However, if the amine acid gas is contaminated with ammonia, a water wash system can be used to remove this ammonia and concentrate it in the SWS gas.

It is generally accepted within the industry that sulfur plants processing ammonia-bearing streams must be designed to destroy essentially all of the ammonia (down to ppm levels) to avoid plugging with ammonia salts in the downstream equipment. Hence, if ammonia is present in an acid gas feed stream, the entire stream must be routed to the acid gas burner to ensure the
maximum amount of ammonia destruction. Amoco and others discovered and demonstrated that ammonia could be successfully destroyed in a Claus sulfur recovery system by thermal decomposition in a reducing atmosphere at temperatures above 2500°F [1370°C] (although recent research suggests a different mechanism for ammonia destruction in an SRU furnace and other designers believe a lower furnace temperature is sufficient).

6.3 BTEX

Sources

Aromatic hydrocarbons such as benzene, toluene, ethyl-benzene, and xylene (BTEX) are often present in produced sour gas streams. When these streams are treated in an amine system, a portion of the BTEX is absorbed in the amine. When the amine is regenerated, this BTEX is stripped from the solvent along with the H₂S and CO₂ and routed to the SRU.

Consequences

There are two significant problems that occur when high concentrations of BTEX are allowed to enter any catalytic conversion stage in an SRU. The first is general deactivation of the catalyst due to accumulation of carbon and/or car sul (a variety of heavy carbon-sulfur compounds) in the pores of the catalyst due to coking of the hydrocarbons. This problem affects all Claus catalysts, both alumina and titania, as well as Selectox catalyst. The second problem with BTEX is rapid deterioration of hydrolysis catalysis in titania catalysts. Titania catalysts have been found to significantly improve the degree of COS and CS₂ hydrolysis over that of alumina catalysts, especially at lower temperatures, and are now used in many plants that require high sulfur recovery efficiency. Unfortunately, field experience and recent laboratory testing have shown that titania catalysts are especially prone to rapid decline in the amount of hydrolysis they catalyze when exposed to BTEX.

Mitigation

One method for reducing the concentration of BTEX in an acid gas stream is to install an acid gas enrichment unit (AGE) upstream of the SRU. Although these systems are very similar to the upstream amine units, they operate at a much lower absorber pressure (generally 10-20 PSIG) so that the partial pressure of BTEX in the inlet acid gas is much lower. Consequently, very little (if any) BTEX is absorbed by the solvent, and it (along with a significant portion of the CO₂ in the acid gas) leaves the absorber and is routed to the TTO while the H₂S is absorbed by the solvent. The solvent is then regenerated and the resulting acid gas, which has both a higher H₂S concentration and less BTEX, is routed to the SRU.

Another method for removing BTEX from acid gas is to install activated carbon beds upstream of the SRU. Two large processing facilities in the Middle East were experiencing chronic Claus catalyst deactivation and low sulfur recovery as a result of BTEX in the feed streams to their SRUs. Regenerable activated carbon beds were installed upstream of the SRUs and the catalyst life improved dramatically.

If reducing the BTEX concentration in the feed gas with either an AGE or an activated carbon system is not feasible, then the BTEX must be fully destroyed in the SRU furnace. There is very little data available regarding BTEX destruction in SRU furnaces, so establishing the furnace design parameters for preventing BTEX from escaping the furnace is currently a matter of engineering judgment. Field testing has indicated that raising the furnace temperature to 2100-2200°F (1150-1200°C) by burning supplemental fuel gas reduces the BTEX content of the
furnace effluent to negligible levels (less than 5-10 ppmv). Like ammonia and methanol, this also requires routing the entire acid gas stream to the burner. Any BTEX that is allowed to bypass the burner, as in a split-flow configuration, will enter the downstream catalyst beds and deactivate them.

6.4 Heavy Hydrocarbons and Mercaptans

Sources
Like aromatic hydrocarbons, heavy hydrocarbons (C₆⁺) and mercaptans are often present in produced sour gas streams and when contacted with amine in an amine absorber, will be partially absorbed by the amine. In some cases, the cool amine solvent will also condense heavy hydrocarbons forming a second liquid phase. Careful attention to the amine system design, including adequate residence time and provisions for skimming hydrocarbons in the amine flash drum, can prevent a significant amount of hydrocarbon from entering the downstream SRU. However, these components are still commonly found in acid gas streams.

Consequences
Many of the consequences of heavy hydrocarbon contamination are the same as the consequences of BTEX and methanol contamination. These include catalyst deactivation from coking, decreased recovery efficiency, increased facility size, and contaminated sulfur. Additional hydrocarbon contamination also increases the formation of COS and CS₂ in the SRU furnace.

In addition to the consequences stated above, mercaptans in the acid gas feed will increase the SO₂ emissions since the sulfur in these compounds is not recovered in the Claus reactors if the mercaptans are not oxidized in the furnace.

Mitigation
Like the other contaminants discussed previously, heavy hydrocarbons (excluding BTEX) must be removed or destroyed upstream of the reactor beds in an SRU to prevent deactivation of the catalyst. Activated carbon systems and AGE systems can both be employed to remove heavy hydrocarbons from acid gas stream. However, since the overhead gas from an AGE is routed to the TTO, this will not solve the emissions issues created by mercaptans in the feed. These components can also be destroyed in the SRU furnace by combustion in the burner. A furnace temperature of about 2000°F (1090°C) has been suggested by some as adequate to destroy any heavy hydrocarbons or mercaptans in an acid gas feed stream.
7. RESULTS/TRENDS

The following charts illustrate some key trends from the simulation results.

Chart 1 shows the calculated recovery efficiency and SO$_2$ emissions (on a dry, 0% oxygen basis) as a function of the inlet H$_2$S concentration for a 3-Stage Claus plant.

Chart 2 shows the calculated recovery efficiency and SO$_2$ emissions (on a dry, 0% oxygen basis) as a function of the inlet H$_2$S concentration for a 2+2-Stage Claus/CBA SRU.

The dashed lines represent the results obtained when oxygen enrichment (100% or lower, as limited by furnace temperature) is used in the SRU, while the solid lines represent the results for a traditional air-blown SRU. In both charts, the acid gas feed streams contain no contaminants.

![Chart 1 – Recovery Efficiency and SO$_2$ Emissions for a 3-Stage Claus SRU](image)
As one would expect, the recovery efficiency decreases with decreasing H₂S concentration in both cases. Likewise, the recovery efficiency is higher in both cases for oxygen-enriched SRUs as a result of the higher partial pressure of H₂S and SO₂ in the furnace and reactors. However, what might be more surprising is that the SO₂ emissions also decrease with decreasing H₂S concentration. In addition, the SO₂ emissions for SRUs without oxygen enrichment are actually less (in some cases significantly less) than the emissions from oxygen-enriched SRUs even though the latter achieve a higher recovery efficiency.

As stated previously, SO₂ emissions (as they are commonly reported) are a function of both the sulfur recovery efficiency and the quantity of other diluents in the vent gas stream. Leaner acid gas streams contain more inert components (usually CO₂) that dilute the vent gas from the TTO and reduce the SO₂ emissions on a concentration basis (but not necessarily on a mass basis). The nitrogen that enters with the SRU combustion air is also an inert that dilutes the vent gas stream and reduces the SO₂ emissions on a concentration basis. When the SRU combustion air is enriched with oxygen, a portion of the nitrogen that acts as diluent is removed, resulting in higher SO₂ emissions on a concentration basis.
Chart 3 shows the recovery efficiency impact of including titania catalyst in the first reactor bed of a 3-Stage Claus SRU and a 2+2 Claus/CBA SRU. As stated previously, titania catalysts have been found to significantly improve the degree of COS and CS$_2$ hydrolysis over that of alumina catalysts, especially at lower temperatures, and are now used in many plants that require high sulfur recovery efficiency.

Chart 3 also show the recovery impact when titania catalyst is used in a 2+2 Claus/CBA SRU that processes a feed stream contaminated with ammonia. When the acid gas feed to a Claus plant is contaminated with ammonia, it is generally accepted that all of the ammonia must be destroyed in the SRU furnace. This requires operating the SRU furnace at a higher temperature and routing the entire feed stream to the acid gas burner. Unfortunately, since a split-flow furnace design cannot be used to maintain the required furnace temperature, supplemental fuel gas firing is typically required, especially with lean acid gas feeds. Since the amount of COS and CS$_2$ that is formed in the furnace increases with increasing supplemental fuel gas firing, the recovery impact of using titania catalyst is even more pronounced for SRUs that require considerable supplemental fuel gas firing in the furnace.

Since titania catalyst clearly improves the recovery efficiency in Claus SRUs, all other results are based on including titania catalyst in the first reactor bed (including the results presented in Charts 1 & 2).
Chart 4 shows the recovery efficiency as a function of the inlet H$_2$S concentration for different technologies (3-Stage Claus, 2+2 Claus/CBA, 3-Stage Claus + SCOT$^\text{R}$-type TGCU, and 2+2 Claus/CBA + SO$_2$ scrubbing) assuming there are no contaminants in the acid gas feed. Note that the recovery efficiency for the 2+2 Claus/CBA + SO$_2$ Scrubbing process is defined as the percentage of sulfur in the feed stream recovered as molten sulfur or removed in the scrubbing unit.

Recovery efficiencies are not shown for direct-oxidation processes, but they are assumed to be similar to the results for the 2+2 Claus/CBA SRU. Likewise, results are not shown for a 2+2 Claus/CBA + SO$_2$ Recycle process, but they are assumed to be similar to those shown for the 2+2 Claus/CBA + SO$_2$ Scrubbing process.

*Chart 4 – Recovery Efficiencies for Various Technologies and Technology Combinations.*
Chart 5 shows the SO₂ emissions (dry, 0% oxygen) as a function of the inlet H₂S concentration for different technologies (3-Stage Claus, 2+2 Claus-CBA, 3-Stage Claus + SCOT®-type TGCU, and 2+2 Claus/CBA + SO₂ scrubbing) assuming there are no contaminants in the acid gas feed. Not surprisingly, the higher the recovery efficiency achievable for a given technology, the lower the corresponding SO₂ emissions. However, as discussed previously, oxygen enrichment may increase the SO₂ emissions from a facility because it eliminates a portion of the nitrogen than acts as diluent in the vent gas. Therefore designers and owner/operators must be very careful when modifying a facility to use oxygen enrichment. If a given facility is having trouble meeting their emissions limits, or is operating close to their emissions limit, then adding oxygen enrichment to increase their capacity may cause them to go out of compliance if no other modifications are included.

Chart 5 – SO₂ Emissions for Various Technologies and Technology Combinations.
Chart 6 shows the effect of different contaminants on the recovery efficiency for a 3-Stage Claus SRU and a 2+2 Claus/CBA SRU. The contaminants examined were ammonia, BTEX and heavy hydrocarbons (C₆⁺). However, it should be noted that the effect of HCN in the feed would be very similar to the effect of ammonia and the effect of methanol or mercaptans in the feed would be similar to the effect of C₆⁺ hydrocarbons, because each require a similar furnace temperature for destruction.

As discussed previously, all of these contaminants must be fully destroyed in the SRU furnace so that they do not damage the downstream catalyst beds. Consequently a split-flow furnace design cannot be used to maintain the appropriate furnace temperature when any of these contaminants are present. Instead, other means, such as supplemental fuel gas firing, must be used to maintain the desired furnace temperature. The amount of supplemental fuel gas, and the corresponding recovery impact, depends on the required furnace temperature. Supplemental fuel gas firing impacts the recovery by 1) producing water which is a product of the Claus reaction and 2) by diluting the gas stream and lowering the partial pressure of H₂S and SO₂ in the reactors. Since ammonia destruction requires the highest furnace temperature (~2500°F [1370ºC]), and therefore the greatest amount of supplemental fuel gas, the recovery impact is largest for ammonia-contaminated streams. BTEX requires a lower furnace temperature (2100-2200°F [1150-1200ºC]) and other hydrocarbons require an even lower temperature (1800-2000°F [980-1090ºC]), so the corresponding recoveries are higher.

![Chart 6 – Recovery Efficiencies with Different Contaminants in the Feed Stream.](chart6.png)
Chart 7 shows the effect of different contaminants on the SO₂ emissions (dry, 0% oxygen basis) from a 3-Stage Claus SRU and a 2+2 Claus/CBA SRU. What is particularly interesting about this chart is that in some cases there is clearly a breakpoint in the H₂S concentration where the benefits from dilution begin to outweigh the negative impacts on recovery.

As stated previously, when processing streams with contaminants, supplemental fuel gas firing or oxygen enrichment is often required to maintain the appropriate furnace temperature. Since oxygen enrichment has been shown to increase SO₂ emissions, only supplemental fuel gas firing has been considered for this chart. At H₂S concentrations greater than 30-40%, the SO₂ emissions that result when processing feeds containing contaminants are actually less than those for uncontaminated acid gases. One may conclude that, while the recovery efficiency is less for these streams (as illustrated in Chart 6), the combustion products formed from burning supplemental fuel gas actually dilute the vent stream so that the SO₂ emissions are less than when processing uncontaminated acid gas. One may also conclude that the more fuel gas that is required, the lower the SO₂ emissions because the emissions when processing ammonia-contaminated streams are less than the emissions from processing BTEX or hydrocarbon-contaminated streams.

However, at concentrations less than 30-40%, the SO₂ emissions that result when processing uncontaminated acid gases are significantly lower than those when processing contaminated acid gases. Therefore, one may conclude that at this point the negative impact on recovery from burning supplemental fuel gas begins to outweigh the advantage obtained from SO₂ dilution.

![Chart 7 – SO₂ Emissions with Different Contaminants in the Feed Stream.](image-url)

Although these effects are particularly obvious when looking at the SO₂ emissions from 3-Stage Claus SRUs, the same trends can be seen in the SO₂ emissions from 2+2 Claus/CBA SRUs.
Interestingly, this trend breaks down when examining the SO\textsubscript{2} emissions from a 3-Stage Claus SRU followed by a SCOT\textsuperscript{®}-type TGCU. Although the recovery efficiencies are certainly less for these facilities when processing acid gases containing contaminants, the dilution affect, coupled with the ability of these systems to achieve fairly high H\textsubscript{2}S removal efficiencies even at low H\textsubscript{2}S partial pressures, means that these systems can often achieve the same SO\textsubscript{2} emissions with or without contaminants in the feed. That being said, the solvent circulation rate required and the steam rate required in the stripper reboiler are significantly higher for SRU/TGCUs processing contaminated acid gas streams. This is because the total amount of H\textsubscript{2}S in the absorber inlet is higher (due to lower recovery in the SRU), and the H\textsubscript{2}S:CO\textsubscript{2} ratio is lower.

Although these results may lead a sulfur plant designer to consider destroying any contaminants in the sulfur plant rather than removing them upstream, there are some significant disadvantages with this approach. Chart 8 shows the relative plant size for a facility processing various contaminants.

Obviously, as the amount of supplemental fuel gas firing increases, so does the size of the facility and the capital cost of the facility. This larger capital cost, as well as the OPEX cost associated with continuous fuel gas consumption, must be weighed against the cost of the additional facilities required to remove the contaminant(s) upstream of the sulfur plant.

If oxygen enrichment is used in addition to, or instead of, supplemental fuel gas firing, then the facility size decreases significantly. However this benefit must be weighed against the increase in SO\textsubscript{2} emissions and the cost associated with continuous oxygen consumption.

![Chart 8 – Relative Facility Size When Processing Feed Streams with Various Contaminants.](image-url)
Finally, for very lean acid gases (<20% H$_2$S) the Selectox and Recycle Selectox processes can often achieve higher recovery efficiencies than the traditional modified Claus process. At H$_2$S concentrations less than about 20%, a stable flame cannot be maintained in a split-flow Claus furnace without oxygen enrichment so firing supplemental fuel gas is required to maintain a stable flame. Likewise, at H$_2$S concentrations less than about 10%, a stable flame cannot be maintained in a split-flow Claus furnace even with oxygen enrichment and supplemental fuel gas firing is required. As stated previously, supplemental fuel gas firing impacts the recovery by 1) producing water which is a product of the Claus reaction and 2) by diluting the gas stream and lowering the partial pressure of H$_2$S and SO$_2$ in the reactors. Chart 9 shows the recovery efficiencies for a Recycle Selectox SRU, a Recycle Selectox-CBA SRU, a 3-Stage Claus SRU, and a 2+2 Claus/CBA SRU when processing an acid gas containing no contaminants.

![Chart 9 – Recovery Efficiency for Selectox vs. Modified Claus Processes](image-url)
8. ECONOMIC CONSIDERATIONS

It would be simple to say that sulfur plant designers should always design a facility that will achieve the highest possible recovery efficiency (or perhaps the lowest possible SO₂ emissions). That would certainly eliminate many of the questions and trade-offs sulfur plant designers face when trying to determine the best technology or plant configuration for a given application. However, sulfur, while a valuable commodity, is hardly a profit center for most facilities and designing for the highest possible recovery efficiency can result in a significantly more costly facility than what is actually required. The following table shows the approximate relative capital cost for different technologies or combinations of technologies.

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<th>Technology</th>
<th>Recovery Efficiency</th>
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<tr>
<td>3-Stage Claus + TTO</td>
<td>92-97%</td>
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<tr>
<td>2+2-Stage Claus/CBA + TTO</td>
<td>98-99%</td>
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<td>98-99%</td>
<td>1.3-1.4</td>
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<td>3-Stage Claus + SCOT®-type TGCU + TTO</td>
<td>99-99.9%</td>
<td>1.8-2.0</td>
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<tr>
<td>2-Stage Claus + CBA + TTO + SO₂ Scrubbing</td>
<td>99-99.9+%</td>
<td>1.4-1.5</td>
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<tr>
<td>2-Stage Claus + D.O. + TTO + SO₂ Scrubbing</td>
<td>99-99.9+%</td>
<td>1.4¹⁰</td>
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<tr>
<td>3-Stage Claus + TTO + SO₂ Recycle</td>
<td>99-99.9+%</td>
<td>1.8-2.0</td>
</tr>
</tbody>
</table>

In general, as the required recovery efficiency increases, so does the cost of the facility. Therefore, a better statement might be that sulfur plant designers should always strive to design the lowest cost facility that will meet the required SO₂ emissions limit (or achieve the required recovery efficiency).

Unfortunately, that is often more difficult because costs are generally harder to quantify and it may be tough for a designer to balance high recovery (or low emissions) with low capital cost and low operating costs. For instance, the charts above illustrate that firing supplemental fuel gas to destroy contaminants can result in lower SO₂ emissions on a concentration basis (although not on a mass basis.) However, fuel gas consumption is a continuous operating cost. Chart 10 shows the cost per ton of sulfur produced when firing supplemental fuel gas. Likewise, the charts above illustrate that oxygen enrichment may be used to reduce the size of a facility or increase the capacity of an existing facility, but oxygen consumption is also a continuous operating cost. Chart 11 shows the cost of oxygen and fuel gas (if required) per ton of sulfur produced for facilities with oxygen enrichment. Finally, the table above indicates that an SO₂ scrubbing system downstream of a sub-dewpoint or direct-oxidation tailgas process can achieve the lowest SO₂ emissions for the lowest capital cost. However, this type of process consumes caustic in order to achieve these low emissions. Chart 12 shows the cost of caustic per ton of sulfur produced when this combination of technologies is used.
Chart 10 – Fuel Gas Costs When Processing Acid Gases Containing Different Contaminants

Chart 11 – Oxygen & Fuel Gas Costs When Processing Acid Gases Containing Different Contaminants
9. OTHER CONSIDERATIONS

A sulfur plant designer must also consider the impacts of other regulations and agreements on a sulfur recovery facility. In many places, but particularly in the United States, the consequences of non-compliance with emissions limits are becoming more severe. Consent decrees, which are binding legal agreements between the federal government, the state government, and the owner/operator of a facility, often force operators to pay penalties for each day they are out of compliance, or for each non-compliance event. This can cost owner/operators thousands of dollars a day for facilities that experience frequent exceedances. The United States has also recently adopted 40 C.F.R. Part 60, Subpart OOOO which eliminates the startup, shutdown, and malfunction exemption from emissions standards found in the NSPS general provisions in 40 C.F.R. Part 60, Subpart A.11

While these agreements and new regulations may not actually change the SO₂ emissions limits for the facilities they apply to, they place additional burdens on the owner/operator to meet those limits at all times and under all circumstances. Consequently, these requirements may drive sulfur plant designers to consider alternative technologies that will both meet the required emissions limits and meet them under all circumstances including startup, shutdown and malfunction.
10. CONCLUSIONS

A sulfur plant designer must consider a variety of factors when preparing a design for a new facility. These include:

- The required sulfur recovery efficiency
- The maximum allowable SO₂ emissions
- The presence of contaminants
- The capital cost of the facility
- The operating costs of a facility
- Any other regulatory restrictions or requirements

As we have demonstrated, the required sulfur recovery efficiency is not an independent specification. Instead, it is almost always driven by the maximum allowable SO₂ emissions and those vary from state to state, province to province, and country to country. In addition, because SO₂ emissions are almost always specified as a concentration, high recovery efficiency does not necessarily mean low SO₂ emissions. Lower emissions can often be achieved at lower recovery efficiencies because of dilution. This is especially true for lean acid gas streams. Therefore, it is imperative that a sulfur plant designer know both the required recovery efficiency and the maximum allowable SO₂ emissions so that they can design for the most stringent requirement. It is also imperative that an owner, client, or client’s representative not specify a lower emissions limit (or higher recovery efficiency) than what is required by regulators or financers because the cost and complexity of a facility increase significantly with increasing recovery efficiency.

The presence of contaminants in the acid gas feed adds an additional layer of complexity when designing a sulfur recovery facility. Many common contaminants can damage the catalyst in the downstream catalyst beds or increase the SO₂ emissions if they cannot be converted in the catalyst beds. Consequently they must be fully destroyed in the SRU furnace which precludes bypassing a portion of the acid gas around the burner. With this common method of temperature control unavailable, other means of maintaining a stable flame or a desired temperature in the SRU furnace must be employed - like firing supplemental fuel gas or enriching the combustion air with oxygen. Unfortunately, both of these options come with advantages and disadvantages that must be weighed against the cost of upstream facilities to remove the contaminants.

Supplemental fuel gas firing in the SRU furnace will result in a larger facility since the combustion products and the nitrogen from the associated combustion air take up additional space in the facility. Fuel gas consumption is also a continuous operating cost for a facility. However, in some cases, this strategy can result in lower SO₂ emissions on a concentration basis because of the additional diluent. For acid gas with more than 30-40% H₂S, burning supplemental fuel gas decreases the SO₂ emissions compared to a facility where fuel gas firing is not required, but for acid gases with H₂S concentrations less than 30-40%, the negative impact on recovery outweighs the positive impact from dilution and the resulting emissions are higher.

On the other hand, oxygen enrichment will decrease the size of a sulfur recovery facility or increase the capacity of an existing facility. However, oxygen enrichment also removes a portion of the nitrogen that acts as diluent in the vent gas and the result can be higher overall SO₂ emissions. So, if a facility is currently operating very close to their SO₂ emissions limit, adding oxygen enrichment capabilities may
cause the facility to go out of compliance. Oxygen is also a continuous operating cost for most facilities.

Unfortunately, there is no simple or systematic answer to the question “What is the best way to recover sulfur from weird acid gas streams?” A sulfur plant designer must be fully informed of all of the parameters that may influence the design, including contaminants, recovery efficiency, regulations, and economic considerations, in order to develop a design that best meets the needs of a given project or facility.

REFERENCES FOR THIS PAPER

6 Palm, J. W., Canadian Patent No. 928,043.
9 Private correspondence.
APPENDIX A

Sulfur Recovery Technologies

**H₂S Scavengers (e.g., Triazines, SULFATREAT™, SULFUR-RITE®)**

Solid or liquid chemicals that react with H₂S; newer technologies are more environmentally-friendly than iron sponge. Often non-regenerable, so use is limited to very low sulfur production rates and low H₂S concentrations where other sulfur recovery technologies are not economical.

**Range of applicability**
- Sulfur production: <200-400 lb/day (<0.1-0.2 T/D)
- H₂S in the feed gas: 0-100%
- Typical feed gas: natural gas
- Economical scavenger options vary by application specifics

**Liquid Redox (e.g., LO-CAT®, LO-CAT® II, SULFEROX®, CRYSTA SULF®)**

These processes absorb H₂S from gas streams into solutions containing oxidizing/reducing agents, which react with the H₂S to form sulfur and water. Solid elemental sulfur is recovered from the circulating solution.

**Range of applicability**
- Sulfur production: 0.1-20 T/D
- H₂S in the feed gas: 0-100%
- Typical feed gas: natural gas or tailgas from TGCU reduction/cooling sections

**Biological Processes (e.g., THIOPAQ O&G)**

A selective gas treating process using naturally-occurring bacteria to oxidize H₂S to elemental sulfur. Solid elemental sulfur is recovered from the circulating solution.

**Range of applicability**
- Sulfur production: 0.1-40 T/D, conservatively
  0.05-150 T/D, potentially economical
- H₂S in the feed gas: 100 ppmv - 100%
- Typical feed gas: natural gas or tailgas from TGCU reduction/cooling sections

**Selectox™ and Recycle Selectox™**

The proprietary Selectox™ catalysts catalyze both the equilibrium conversion of H₂S to sulfur via the two-step Claus reactions and the direct oxidation of H₂S to sulfur. Using a Selectox catalyst bed at the front end of an SRU, instead of an acid gas burner and furnace, allows processing very lean acid gas streams that cannot be processed in a conventional modified Claus SRU.
RANGE OF APPLICABILITY

The Once-Through Selectox™ SRU process is recommended for recovering high-purity sulfur from acid gas feed streams containing 0.5-5% H₂S. The Recycle Selectox™ SRU process is recommended for acid gas feed streams containing 5-20% H₂S. However, for small sulfur recovery units (less than 50 T/D), the Selectox process may be used for acid gas feed streams containing up to 45% H₂S.

The Selectox™ process has been demonstrated in facilities producing as little as 0.5 T/D and as much as 46 T/D of sulfur. However, there is really no upper limit on sulfur production.

- Sulfur production: 0.5-50 T/D
- H₂S in the feed gas: 2-20% optimal; 0.5-45% applicable
- Typical feed gas: acid gas from natural gas, refinery gas, or syngas treating, tailgas from TGCU reduction/cooling sections

MODIFIED CLAUS¹⁵,¹⁶

Most sulfur plants use the modified Claus process, which carries out the Claus reaction in two steps. First, ⅓ of the H₂S is combusted to SO₂, which then reacts with the remaining ⅔ of the H₂S to form elemental sulfur and water:

(1)  \( H_2S + \frac{3}{2} O_2 \rightleftharpoons SO_2 + H_2O \)
(2)  \( 2 H_2S + SO_2 \rightleftharpoons \frac{3}{n} S_n + 2 H_2O \)

The overall reaction for the process is:

(3)  \( 3 H_2S + \frac{3}{2} O_2 \rightleftharpoons \frac{3}{n} S_n + 3 H_2O \) (the 1-step Claus reaction, i.e., direct-oxidation)

Each modified Claus sulfur plant contains one non-catalytic conversion stage (the reactor furnace) and two or three catalytic conversion stages in series. The Claus reaction is highly exothermic, releasing a great deal of heat energy that is recovered as high and low pressure steam in heat exchangers following the conversion stages.

RANGE OF APPLICABILITY

- Sulfur production: >15 T/D optimal; 3-15 T/D applicable
- H₂S in the feed gas: 20-100%
- Typical feed gas: acid gas from natural gas, refinery gas, or syngas treating

SUB-DEWPOINT CLAUS (E.G., CBA, MCRC™, SULFREEN™)¹⁷

The conventional Claus sulfur recovery process is limited by reaction equilibrium considerations to sulfur recoveries in the range of 93-97%. For applications requiring an intermediate level (97.5-99.5%) of sulfur recovery, the so-called “sub-dewpoint” Claus processes can be used. These processes include the Cold Bed Adsorption (CBA) process, the Maximum Claus Recovery Concept (MCRC™) process, and the Sulfreen™ process. All of these processes extend the capability of the Claus process by operating the Claus reaction at a lower temperature, so that the sulfur produced by the reaction condenses. Since the Claus reaction occurs in the gas phase, this liquid sulfur does not inhibit the reaction like sulfur vapor does, resulting in a favorable shift in the reaction equilibrium and higher sulfur conversion. The condensed sulfur is adsorbed in the Claus catalyst, so the process operates in a cyclic fashion to periodically regenerate the catalyst.
SULFUR PLANT CONFIGURATIONS FOR WEIRD ACID GASES
LRGCC - Laurance Reid Gas Conditioning Conference - February 24-27, 2013

- Sulfur production: >15 T/D optimal; 5-15 T/D applicable (nominal sulfur plant capacity)
- H₂S/SO₂ in the feed gas: 1-5% typical
- Typical feed gas: Claus tailgas

**DIRECT OXIDATION CLAUS (E.G., SUPERCLAUS®, EUROCLAUS®)**

These technologies use proprietary catalyst to directly oxidize H₂S to sulfur. This conversion is not defined by Claus equilibrium. The Claus unit operates off-ratio (~10-15 to 1 H₂S:SO₂) to suppress the SO₂ content in the Claus tailgas, which is combined with air and routed to the direct oxidation reactor. EUROCLAUS® is like SUPERCLAUS®, but with hydrogenation step added prior to the direct oxidation step.

- Sulfur production: >15 T/D optimal; 5-15 T/D applicable (nominal sulfur plant capacity)
- H₂S in the feed gas: 0.8-3%
- Typical feed gas: Claus tailgas with minimal SO₂

**REDUCTION/ABSORPTION/RECYCLE (E.G., SCOT® AND SCOT®-TYPE)**

In applications where a high level (more than 99.5%) of overall sulfur recovery is required, an amine-based tailgas cleanup process can be used to achieve high overall sulfur recovery performance. This type of tailgas cleanup process reduces all of the sulfur compounds in the tailgas leaving the front-end Claus sulfur plant back to hydrogen sulfide (H₂S), then uses selective amine absorption to remove the H₂S while allowing most of the carbon dioxide (CO₂) to “slip” by. The H₂S and CO₂ removed by the amine are stripped from the amine and recycled back to the Claus plant, allowing an overall sulfur recovery in excess of 99.5%.

- Sulfur production: >15 T/D optimal; 5-15 T/D applicable (nominal sulfur plant capacity)
- H₂S/SO₂ in the feed gas: 1-5% typical
- Typical feed gas: Claus tailgas

**SO₂ RECYCLE (E.G., CANSOLV® TGT+, CLAUSMASTER™)**

CANSOLV® TGT+ uses a regenerable proprietary amine to absorb SO₂. ClausMaster™ uses a proprietary SO₂ physical absorbent solution. These are emerging technologies for Claus plant applications with the potential to make it easier to achieve very low SO₂ emissions, especially when processing “weird” acid gases.

- Sulfur production: >15 T/D optimal; 5-15 T/D applicable (nominal sulfur plant capacity)
- SO₂ in the feed gas: 0.08-1.2% typical
- Typical feed gas: partially cooled tailgas from the sulfur plant TTO

**Claus Tail Gas Treating**: Both CANSOLV® TGT+ and ClausMaster™ processes are oxidation/absorption/recycle alternatives to a conventional reduction/absorption/recycle SCOT® or SCOT®-type TGCU. First, essentially all the sulfur compounds in the Claus tailgas are oxidized to SO₂ by incineration. After cooling, the solution selectively absorbs SO₂ from the oxidizer tailgas. This treated gas can meet
emissions specifications in the range of 10-250 ppmv total SO₂. The SO₂ from solution regeneration is recycled to the Claus SRU.

**Problematic Acid Gas Processing:** Since CANSOLV® TGT+ can capture and recycle SO₂, the process is well-suited for scrubbing the combustion products of any streams (containing sulfur-bearing compounds) that cannot easily be processed in a conventional Claus plant, e.g., high hydrocarbon content acid gas, ammonia-bearing SWS gas, spent degassing air, sulfur pit sweep air, disulfide oils, etc. In these cases, the problematic stream can be combusted in the sulfur plant TTO, scrubbed with CANSOLV® TGT+, and the SO₂ stripped from the solvent can be recycled back to the sulfur plant.

**SOₓ Scrubbing (e.g., DynaWave®)²³,²⁴**

SOₓ scrubbing systems are often used when environmental regulations require very low SOₓ emissions (less than 25-100 ppmv) from a sulfur recovery facility. These systems remove essentially all of the SOₓ contained in the feed gases by contacting the feed with a circulating solution of sodium hydroxide (NaOH) or another alkaline reagent. The scrubbing system is located downstream of the TTO, which means emissions are low during startup, shutdown, and upset conditions.

- Sulfur production: >15 T/D optimal; 5-15 T/D applicable (nominal sulfur plant capacity)
- SOₓ in the feed gas: 0.08-1.2% typical
- Typical feed gas: partially cooled tailgas from the sulfur plant TTO

**REFERENCES FOR APPENDIX A**


### APPENDIX B

#### ACID GAS COMPOSITIONS:

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SULFUR PLANT CONFIGURATIONS FOR WEIRD ACID GASES
LRGCC - Laurance Reid Gas Conditioning Conference - February 24-27, 2013

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FUEL GAS COMPOSITION:

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HYDROGEN COMPOSITION:

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Temperature | 60 ºF (15.6 ºC)
LHV | 1000.5 BTU/SCF (9412 kcal/Nm³)

MISCELLANEOUS ASSUMPTIONS:

- Ambient Conditions: 100ºF (38ºC) Maximum, 14.7 PSIA (1.013 bar(a))
- Steam Pressure Levels:
  - High Pressure (HP) – 650 PSIG (44.8 bar(g))
  - Low Pressure (LP) – 50 PSIG (3.4 bar(g))
  - Low-Low Pressure (LLP) – 15 PSIG (1.03 bar(g))
- Boiler Feed Water Temperature: 230ºF (110ºC), 2% blow-down assumed
- 3-Stage Claus SRU
  - Waste Heat Boiler generates HP Steam
  - Sulfur Condensers 1-4 generate LP Steam
  - Reactor beds contain new alumina and titania catalysts
    - 100% approach to equilibrium
- 2+2-Stage Claus/CBA SRU
  - Waste Heat Boiler generates HP Steam
  - Sulfur Condensers 1-2 generate LP Steam
  - Sulfur Condensers 3-4 generate LLP Steam
  - Reactor beds contain new alumina and titania catalysts
    - 100% approach to equilibrium

- Tailgas Thermal Oxidizer:
  - Furnace Temperature - 1500°F (815°C)
  - TTO operates with a minimum of 25% excess air
  - Spent degassing air is routed to the TTO
  - Sulfur pit sweep air is routed to the TTO

- SCOT® and SCOT®-type Tailgas Cleanup Unit:
  - Steam-heated
  - Low-temperature hydrogenation catalyst
  - Cooling water available for quench water and lean solvent trim cooling

- Cost Data
  - Fuel Gas – US $3.00 per MMBTU (US $11.90 per 10⁶ kcal)
  - Oxygen – US $50.00 per ton
  - Caustic – US $450.00 per ton