

Improve Your Gas Plant's Performance in the Middle East: Part II – The Sulfur Recovery Unit

Abstract

Part one of this series of papers (presented at GPA GCC 21st Annual Technical Conference in 2013) detailed various ways to optimize an amine sweetening unit, particularly sweetening units located in the Middle East (Slagle, 2013). Conditions in the Middle East are often more sour and warmer than other locations in the world. Part two expands on the work completed in part one, focusing on the impact of choices made for the sweetening section on the sulfur recovery unit, while detailing ways to optimize the entire process. Various aspects of the sulfur recovery unit design are impacted by the amine sweetening unit design. The influence amine sweetening technologies have on sulfur recovery units is explored, along with competing sulfur recovery options. The study details choices engineers must make when deciding the number of Claus beds, adding a tail gas treatment unit, using a selective versus non-selective amine and other essential variables.

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Justin C. Slagle

Consulting Engineer

Bryan Research & Engineering, Inc.

3131 Briarcrest Dr. Suite 200

Bryan, TX 77802

USA

J.Slagle@bre.com

+1-979-776-5220

Introduction

Most refineries and gas plants in the Middle East require nearly all the sulfur to be removed from oil and gas. In order to do so, it is common to contact sulfur rich hydrocarbon streams with an amine solution in a regenerative process known as an acid gas removal unit (AGRU) or amine sweetening unit, as shown in **Figure 1**. The acid gas will ideally be rich in H_2S and contain few hydrocarbons. This acid gas is then fed to a sulfur recovery unit (SRU), as shown in **Figure 2**.

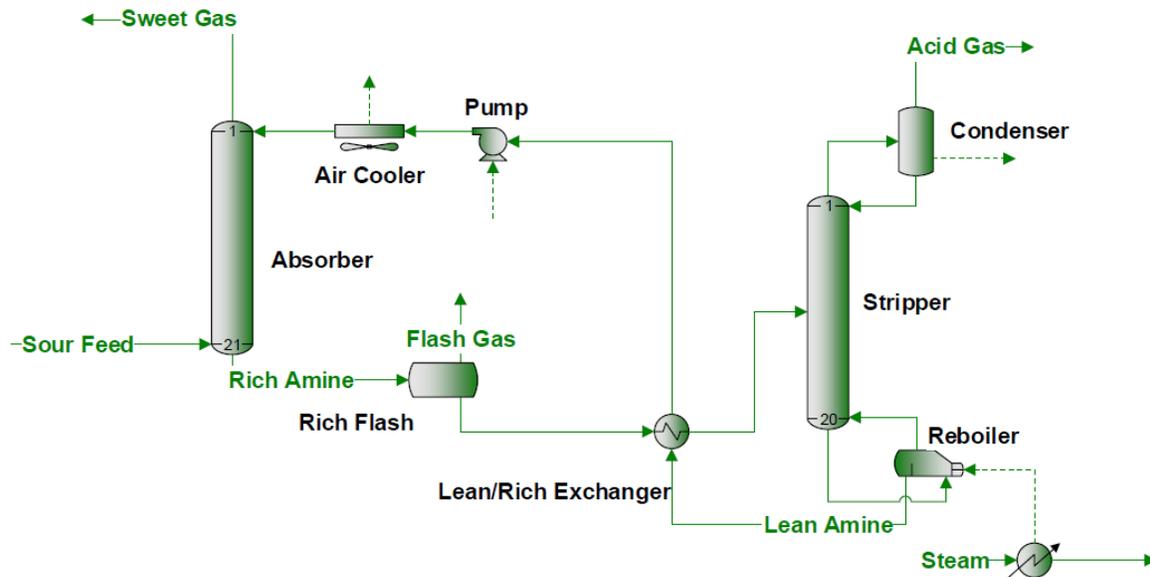


Figure 1: Typical Amine Sweetening Unit

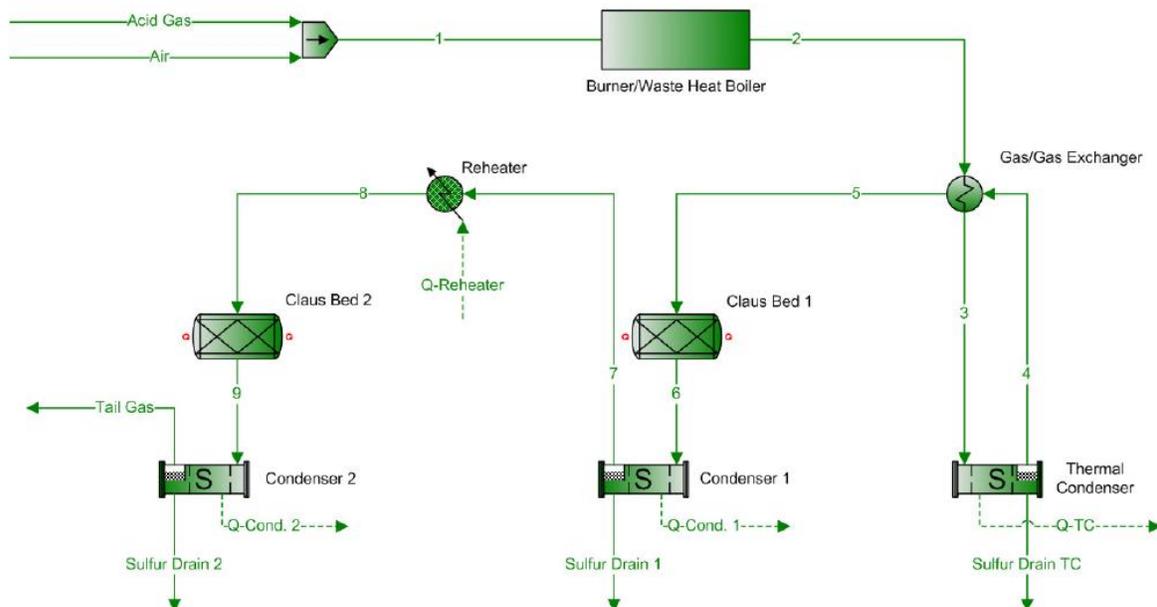


Figure 2: Basic Sulfur Recovery Unit

Naturally, the AGRU should effect the SRU process, as it controls the feed composition and flow rate to the SRU. Optimization of the AGRU is essential in any gas plant or refinery. Part I of this study studied ways to optimize the AGRU independently of the SRU.

The best way to study the impact the AGRU has on the SRU is to use a process simulator. This study models both the AGRU and SRU using ProMax 4.0 (Bryan Research & Engineering, Inc., 2014). This simulator offers a number of advantages including the benefit of connecting the AGRU to the SRU when performing any case studies. ProMax 4.0 is based on data from hundreds of operating plants. It has been proven to predictively match operating data (Ochieng, et al., 2012) (Skowlund, Hlavinka, Lopez, & Fitz, 2012) (Spears, Hagan, Bullin, & Michalik, 1996).

First, the study compares different AGRU process variables' impact on the acid gas composition and flow rate. Then, the study compares different configurations of the SRU, including straight through Claus beds, low temperature Claus beds, partial oxidation and amine based tail gas treatment. Finally, rules of thumb for sulfur recovery are compiled.

Background

Acid Gas Removal

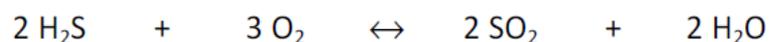
The acid gas is the starting point for any study concerning the sulfur recovery unit. A sour gas contains H₂S and CO₂ among other less concentrated sulfur containing compounds. Generally, H₂S and any other sulfur components are desired to enter the SRU. However, in most cases it is unavoidable to send at least some CO₂ to the SRU (Kohl & Nielsen, 1997).

Due to different sweet gas specifications and operating conditions, different processes and solvents are used (Polasek & Bullin, 1994). As far as the SRU is concerned, the main components to enter the main burner from the acid gas are H₂S, CO₂, other sulfur containing compounds like mercaptans, and hydrocarbons. With adequate air flow rate the mercaptans and hydrocarbons should completely combust. Therefore, H₂S and CO₂ are the primary concerns. Selective acid gas removal processes, such as amine sweetening with MDEA, are used to limit the concentration of CO₂ entering the main burner of the SRU.

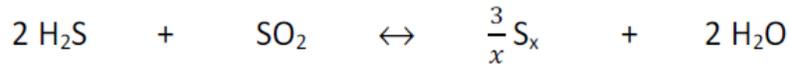
Sulfur Recovery Unit

The SRU exists to properly dispose of acid gas removed from a number of upstream processes. While refineries may have multiple sources of acid gas, gas plants will normally have two sources AGRUs and Sour Water Strippers (SWS). The purpose of the unit is to convert environmentally hazardous gaseous H₂S (and other sulfur compounds) to stable solid elemental sulfur.

There are two primary reactions (or rather summations of numerous intermediate reactions) necessary for the conversion to elemental sulfur, as shown in **Equations 1 and 2**.



Equation 1: SO₂ Formation



Equation 2: S_x Formation

As shown, it is important to observe that H₂S is a necessary reactant for both reactions. That means complete destruction of H₂S is to be avoided in the first reaction. While S₁-S₈ sulfur allotropes are rigorously modeled, all allotropes are combined and called elemental sulfur, or S_x, for this discussion.

The most basic configuration of a Claus bed SRU is called the straight-through process, as shown in **Figure 2**.

The straight-through process was originally developed to remove about 95% of atomic sulfur from the acid gas. It has since lost favor to more complex processes, which all still have the straight-through Claus bed process at the center. The H₂S content of the acid gas needs to be roughly 50% for straight-through configurations without additional clean-up units.

The burner, shown in **Figure 3**, has many parts to it.

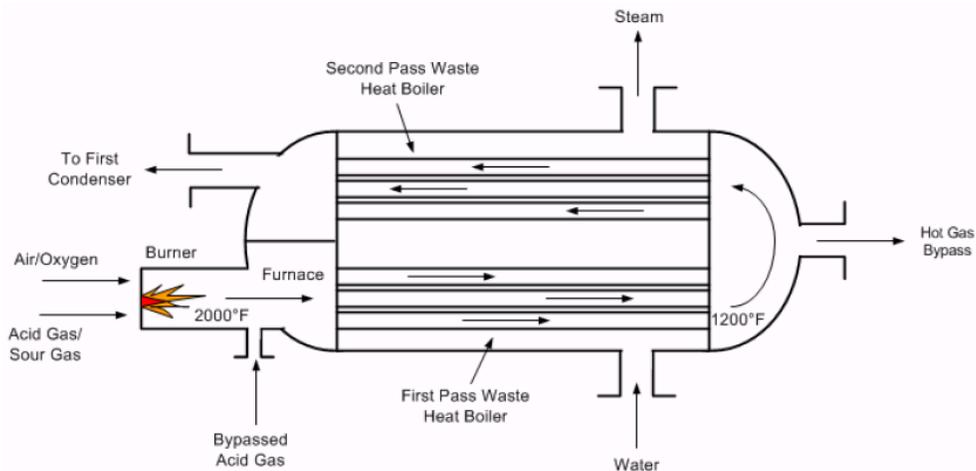


Figure 3: Acid Gas Burner with Waste Heat Boiler

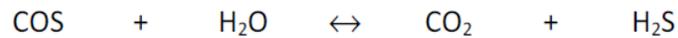
First, the gas encounters the flame, the first of three reaction zones. The reaction detailed in **Equation 2** shows that 2 moles of H₂S are required for each mole of SO₂, which is controlled by the O₂ in **Equation 1**. Therefore, in order to control the 2:1 H₂S to SO₂ ratio, the air flow rate must be controlled. The air flow rate should maintain a H₂S:SO₂ ratio of equal to or greater than two in the tail gas in order to ensure the reaction beds always have the necessary reactants. The temperature should be in excess of 980°C. The presence of CO₂ and hydrocarbons in the acid gas also allows side reactions to occur, forming COS, CS₂ and CO, which reduce sulfur recovery. In most cases, this cannot be avoided, although may be properly handled in the first Claus bed with a high temperature hydrolyzing catalyst. If NH₃ is present in the acid gas, it must be fully destroyed before entering the burner, which requires temperatures in excess of 1370°C (Gas Processors Suppliers Association, 1998).

Next, the hot gas enters the first pass of the waste heat boiler, which serves as an area to remove heat in the form of steam generation. The S_x conversion is best at low temperature; so it is necessary to

reduce the temperature. As the heat is removed, some S_x , H_2 and H_2O react to form H_2S and SO_2 until temperatures drop below $650^\circ C$.

As the temperature drops below $650^\circ C$, the gas enters the third reaction zone and the second pass of the waste heat boiler. The third reaction zone is also known as the sulfur redistribution zone due to the S_x allotropes shifting from high temperature stable forms to molecular forms stable at low temperatures. Further shifts in allotropes will occur downstream, but to a significantly lesser degree. The bulk of the redistribution has occurred by the time the gas drops to $370^\circ C$.

Subsequent equipment is used to further convert sulfur species to S_x . The Claus Beds operate to maximize conversion by contacting the gas with a catalyst, most often Al_2O_3 (activated alumina) (Gas Processors Suppliers Association, 1998). As mentioned earlier, COS and CS_2 present an additional obstacle. A Claus Bed with TiO_2 is often used to convert those sulfur molecules to H_2S , as shown in **Equations 3 and 4**.



Equation 3: Hydrolyzing COS



Equation 4: Hydrolyzing CS_2

The reactions shown in **Equations 3 and 4** prefer to occur at higher temperatures than standard Claus Beds, normally about $325^\circ C$. Sometimes a mixture of TiO_2 and Al_2O_3 is used to reduce catalyst costs.

While **Equations 3 and 4** prefer high temperatures, **Equations 1 and 2** prefer low temperatures. However, it is important to avoid sulfur condensation on Al_2O_3 catalysts. That is why the reheater upstream of each Claus Bed is used to maintain a temperature such that the stream never reaches the sulfur dew point in the reactor, but also careful not to maintain too high of a temperature. The simulator is able to calculate the dew point and the correct reheater temperature so the operator has a set point to control the reheater.

Cold Claus Bed catalysts are also available on the market

Once the gas exits the Claus Bed, it must enter a sulfur condenser to drop out the S_x formed through the reactor. The condensers usually operate at about $150^\circ C$.

The tail gas is important to maintain a 2:1 $H_2S:SO_2$ mole ratio at a minimum, to insure there is enough H_2S to react through all Claus Beds. At this point, the tail gas may be handled in a few different ways. It may be incinerated or treated before incineration.

SRU Comparisons

The tail gas handling is an important discussion. The SRU with no tail gas handling is the base case, to be compared to Cold Bed Absorption, Partial Oxidation and Tail Gas Treatment using MDEA to recycle H_2S back to the SRU burner.

Two acid gas cases are evaluated – acid gas from an MDEA AGRU and acid gas from an AGRU with a non-selective chemical solvent, such as DGA or MDEA + piperazine. DEA, DGA and MDEA + piperazine are all observed to give roughly the same acid gas concentrations, with some slight variations in hydrocarbon content.

Acid Gas from the two cases are shown in **Table 1**.

	Acid Gas (mol%)						MMSCFD
	C1	C2	C3	H ₂ S	CO ₂	H ₂ O	
MDEA	0.088	0.011	0.005	49.6	39.1	11.1	29.5
Non-selective amine	0.167	0.012	0.020	40.8	47.9	11.1	36.1

Table 1: Inlet Acid Gas Composition to Main Burner

The different acid gases are used to calculate the correct operating conditions and resulting total sulfur recovery for the different sulfur recovery processes.

As mentioned earlier, cold bed absorption is possible when using a different catalyst. This type of catalyst takes advantage of the increased reaction rate at lower temperatures. The temperature may now drop below the sulfur dew point, but not below the dew point of other components. Simulation may help maintain the correct temperature. A cold bed is displayed in **Figure 4**.

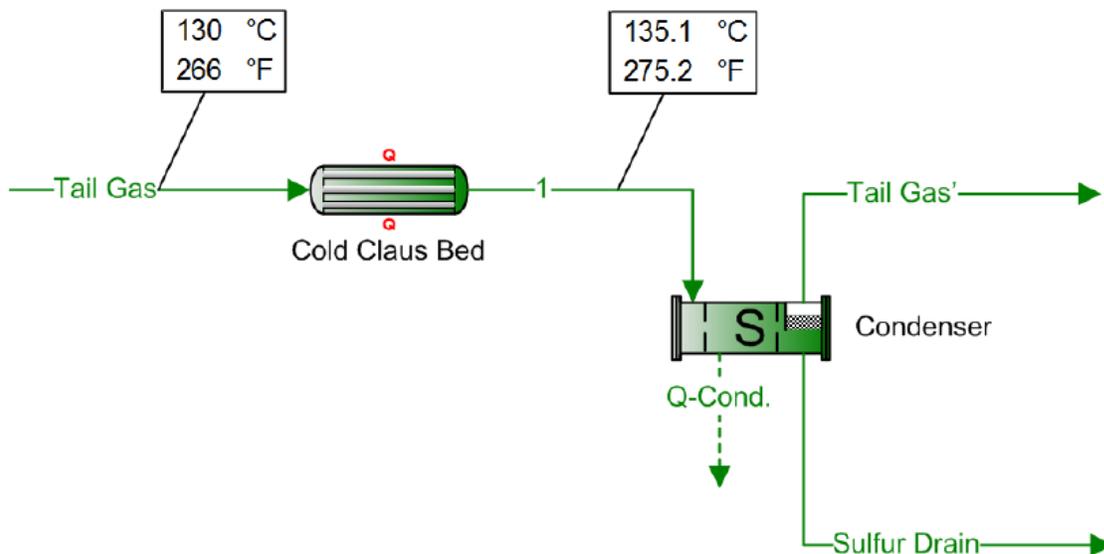


Figure 4: Sub-Sulfur-Dew Point Claus Bed

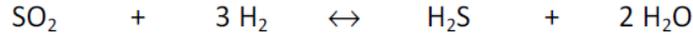
Partial oxidation, also known as SUPERCLAUS, uses a specialty catalyst to partially oxidize H₂S with O₂ provided from air, as shown in **Equation 5**.



Equation 5: Partial Oxidation of H₂S

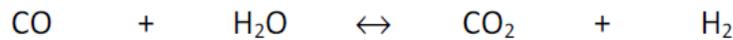
SO₂ is not a reactant in **Equation 5**; therefore, the tail gas ratio of 2:1 H₂S:SO₂ is no longer required. Prior to partial oxidation, it is necessary to hydrolyze any remaining COS and CS₂ back to H₂S and CO₂, as shown in **Equations 3 and 4**.

It is equally important to convert SO₂ to H₂S, as shown in **Equation 6**.



Equation 6: Conversion of H₂S to SO₂

The above reaction also requires hydrogenating CO in order to produce H₂, as shown in **Equation 7**.



Equation 7: Hydrogenation of CO

Depending on conditions of the tail gas, the partial oxidation process should operate between 260 and 370 °C. The partial oxidation process is displayed in **Figure 5**.

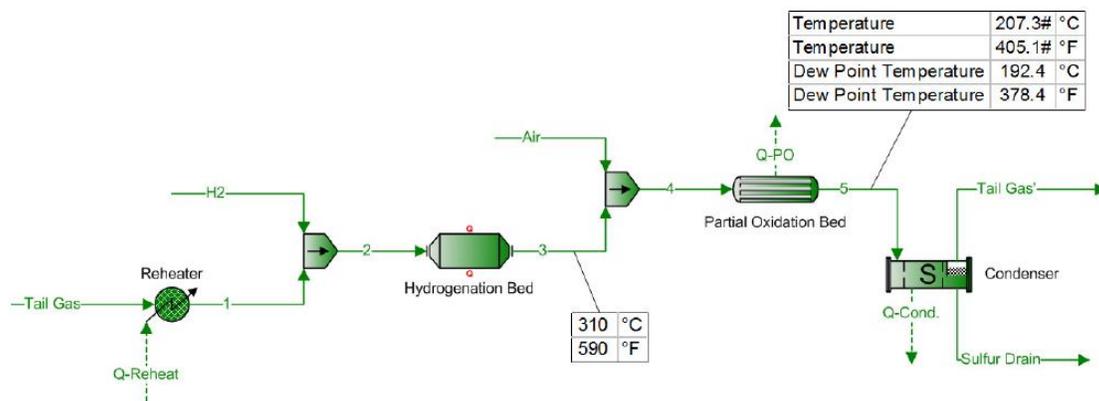


Figure 5: Partial Oxidation Process

The last tail gas treatment option studied is tail gas treatment using MDEA and recycling the H₂S back to the SRU main burner. This method utilizes a hydrogenation reactor to convert sulfur species in the tail gas back to H₂S before sending it to a MDEA unit. The MDEA will produce off gas (sent to the incinerator) and acid gas (recycled to burner). MDEA or another H₂S selective amine is used, to avoid absorbing CO₂, letting it enter the incinerator instead. The hydrogenation reaction usually occurs at an elevated temperature of 300 °C.

The three cases based on acid gas from Part I are shown in **Table 2**.

No TG Cleanup	Sulfur Recovery (%)		
	Cold Bed	Partial Oxidation	MDEA TGTU
97.935	98.989	99.570	99.995

Table 2: Optimized Total Sulfur Recovery Process Comparison

The above table shows the MDEA TGTU has the deepest sulfur recovery of the four options. Of course, no tail gas treatment has the lowest total sulfur recovery. Even when the model takes the increased CO₂ into account, the processes are still able to achieve these recovery rates. The main drawback to CO₂ in the acid gas is the size of equipment and increased air flow rate.

Conclusions

It is best to evaluate all options when optimizing a SRU. Some common rules of thumb are outlined in **Table 3** as a starting point for engineers undergoing SRU optimization and design projects.

SRU Rules of Thumb*	
<i>Straight Through Process</i>	
Tail Gas Ratio (H ₂ S:SO ₂)	2 mole/mole
Burner Temperature without NH ₃	Above 980 °C
Burner Temperature with NH ₃	Above 1370 °C
WHB 1st Pass Temperature	650 °C
WHB 2nd Pass Temperature	370 °C
1st Claus Bed Catalyst	TiO ₃ or mixed with Al ₂ O ₃
1st Claus Bed Temperature	315 °C
2nd and 3rd Claus Bed Catalysts	Al ₂ O ₃
2nd and 3rd Claus Bed Temperature	10-15 °C above Sulfur dew point
Sulfur Condenser Temperatures	150 °C
<i>Cold Bed Process for Tail Gas Treatment</i>	
Cold Bed Temperature	Below Sulfur dew point and above other species' dew points
<i>Partial Oxidation of Tail Gas</i>	
Reactor Temperature	260-370 °C
Tail Gas Ratio (H ₂ S:SO ₂)	Minimize SO ₂ entering reactor
Catalyst	Contact vendor for proprietary catalysts
<i>Tail Gas Treatment with MDEA</i>	
Hydrogenation Temperature	300 °C
Water wash Temperature	50 °C
<p>*The above rules of thumb are just starting points. Rigorous ProMax simulation is required to optimize individual units. (Gas Processors Suppliers Association, 1998) (Kohl & Nielsen, 1997) (Bryan Research & Engineering, Inc., 2014)</p>	

Table 3: General Rules of Thumb for Sulfur Recovery

MDEA TGTUs provide the deepest removal of sulfur, as shown in this study.

While there is no impact on the total sulfur recovery, the choice of amine upstream of the SRU will impact the size of the plant and the resulting operating costs. The OPEX and CAPEX of a SRU will increase as the concentration of CO₂ in the acid gas increases. **Table 1** shows the increase in flow rate of the acid gas due to the additional absorption of the CO₂ by the non-selective amine.

Part III Preview

The third part of this series will show the impact of optimizing a NGL recovery plant. The study will show how upstream amine and glycol units effect ethane recovery and rejection. Part III will also show optimization steps for cryogenic NGL recovery plants.

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