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Designing a Seawater Packed Bed Scrubber for Reducing SO_2 Emissions in Claus Plants

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Abstract — This paper deals with an appropriate and cost effective method for Claus tail gas treating. The most common approach to that treatment is amine based tail gas treatment methods; however a lower installation cost and higher reliability can be achieved by integration of the Superclaus process and a wet gas scrubber. The amount of the daily SO_2 emissions of the understudied plant, due to treatment of 1,160 tons of the acid gas and production of 220-260 ton/day of sulfur, was about 17-18 tons. Due to high pH value of the saline water, using seawater as a solvent for the packed bed scrubber was recommended. The design of the scrubber was done based on the assumption of a 90% efficiency in reduction of H_2S in the Superclaus process. For treating 2,495.40 kmol/h acid gas, the minimum and maximum seawater flow rate were about 5,925 kg/min and 8,887 kg/min, respectively. The scrubber bed height and diameter were estimated 12 and 2.7 m, respectively.

Keyword — Claus, Desulphurization, Scrubber, Sulphur dioxide, Seawater, Tail gas.

Introduction

Because of harmful effects of sulfur related emissions, the control of sulfur dioxide emitted in to the atmosphere is very important in refineries and power plants [1].

In most Natural Gas (NG) refineries, the Claus process is used to produce sulphur from the acid gas. The tail gas of the Claus plant should be treated to prevent releasing SO_2 in to the atmosphere.

The H_2S concentration of the NG in the sample field is about 5,000 ppm. That sour NG is sent to a sweetening unit to remove the H_2S by Methyl Diethanolamine (MDEA). The gas contains a high concentration of H_2S enters the Claus unit. Nominal efficiency of the sulphur recovery unit is 97%. However, due to some complexities in the process, such as an excessive CO_2 in the acid gases, lack of appropriate catalyzers, fluctuations in composition of the Claus units' feed, especially changing in H_2S, CS_2, COS, the actual efficiency in most NG refineries is less than 85 % [2] which can lead to more SO_2 released into the atmosphere. Therefore, the necessity of new technologies to purify the exhaust gases of Claus units which is called Tail Gas Clean Up in Claus unit (TGCUC) becomes more obvious.

Although the most common method for the tail gas treatment in Claus units is amine-based methods, an integration of the superclaus process and wet gas scrubber may reach to a cost effective and reliable treatment method. To achieve that aim, we considered a real Claus plant which produces 220-260 ton/day of sulfur and designed a seawater packed bed scrubber for reducing SO_2 emissions in that plant.

Materials and Methods

Sulphur recovery refers to conversion of hydrogen sulfide (H_2S) to elemental sulfur. Hydrogen sulfide is a by-product of refining of sour natural gas and crude oils. The process consists of a multistage catalytic oxidation of H_2S, as eq.1:

$$2H_2S+SO_2 \leftrightarrow 3S+2H_2O \quad (1)$$

Each catalytic stage consists of a gas reheater, a catalyst chamber and a condenser. Because this reaction occurs in an equilibrium state, it may not be possible for a Claus plant to convert all the incoming sulphur compounds to elemental sulphur. Therefore, there are two or more stages in a Claus unit depending on the desired conversion level. Accordingly, the tail gas, which contains H_2S, SO_2, sulphur vapor and traces of other sulphur compounds, is formed in the combustion section. In the understudied plant, four sulphur recovery trains are fed from a common acid gas header receiving the acid gas from the four gas treating trains. The tail gas, leaving the Claus reactors is routed with the sweeping gas from the degassing unit to the incinerator, where all remained sulphur compounds are converted to SO_2 at the temperature of 800˚C before releasing into atmosphere through the stack. The amount of the daily SO_2 emissions of the understudied plant, due to treatment of 1,160 tons of the acid gas and production of 220-260 ton/day of sulfur, is about 17-18 tons (Fig.1).

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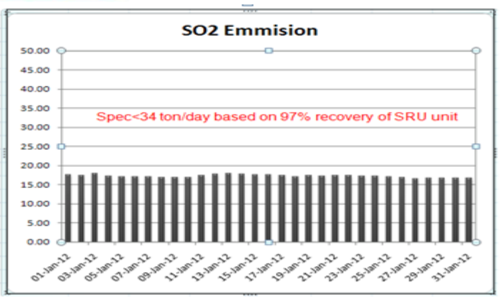

Fig.1. The SO_2 emissions in the flue gas of the plant

Selecting an appropriate and cost effective tail gas treatment method for Claus plants is challenging. Generally, the tail gas treatment methods can be divided into two categories [3]:

1) Dry bed processes that consist of two following main processes;
1-1) Oxidization of SO_2 and then absorption or reaction which consists of SFGD, WESTVACO and SNPA/TOPSOE methods.
1-2) Extension of Claus reactions on a solid bed which contains SULFREEN, AMOCO-CBA, MCRC, and MAXISULF (DMI) methods.
2) Wet scrubber processes that consist of three following processes;
2-1) Extending Claus reaction in liquid phase with a catalyst that consists of IFP-1, TOWNSEND and ASR SULFOXID methods.
2-2) Oxidizing SO_2 and then absorb or react, that contains the WELLMAN-LORD, CHIYODA101-VSB MCITRATE, ATS, UCAP, AQVACLAUS, SAABERG-HOTEI methods.
2-3) Reducing the H_2S and then absorb or react which includes SCOT, BSRP (Beovon / stretfod), CLEAN AIR, TRENCOR-M, BSR/MDEA, BSR/SELECTOX methods.

The Claus tail gas treatment process proposed in this paper is an integration of a superclaus process and a wet gas scrubber as a cost effective alternative to amine-based methods. By using this treatment method, sulphur recovery and sulphur dioxide emission reduction requirements can be met at a lower operating and capital costs and higher reliability.

Superclaus process

Application of the Superclaus process leads to a higher sulphur recovery thanks to a retarded SO_2 formation in the Claus stages, and selectively oxidising of H_2S in the presence of oxygen and a catalyst. This method contains a combustion stage followed by at least three catalytic reaction stages, with sulphur removed between stages by condensers. The first reactors are packed with a standard Claus catalyst, while the final reactor is packed with selective oxidation catalyst. In the combustion stage, the acid gas is burned with a low amount of air, such that the tail gas leaving the last Claus reactor contains typically 0.8-1.0 volumetric percent of H_2S. The selective oxidation catalyst in the final reactor oxidizes the H_2S to sulphur. The efficiency of such method is about 90%.

Superclaus process controls the H_2S concentration entering the Superclaus stage while the conventional Claus processes do not. The Superclaus catalyst is sensitive neither to excess oxygen, nor to the presence of water or sulphur dioxide. That is because the selective oxidation reaction is not based on a equilibrium state unlike the Claus reaction.

Claus reaction: $2H_2S+SO_2 \leftrightarrow 3S+2H_2O$ (2)

Superclaus reaction: $H_2S+½O_2 \rightarrow S+H_2O$ (3)

For a three-bed Claus system, the Superclaus process makes the following modifications and additions [4]:

- The catalyst in the third bed is replaced with the Superclaus catalyst.
- A slipstream of air is taken from the inlet burner and added to the gas entering the Superclaus reactors. The excess air must be maintained to prevent sulphating the catalyst.
- The Superclaus reactor inlet temperature is kept at around 220˚C (430˚F) and the reheater must be modified if it cannot heat the gas to this temperature to achieve this temperature. The company of Jacobs introduced a system for that purpose which called the Advanced Burner Control, ABC system [4].

Seawater scrubber

A Seawater scrubber is designed to remove the SO_2 emission. In this process a small amount of the NO_x, CO_2 and H_2S are also removed but that isn't the primary purpose of the system [5].The process is applicable mainly to oil and coal fired boilers as well as the process gas in refineries where seawater is available. Although the most important parameter in term of SO_2 absorption in seawater seems to be the alkalinity [6], other factors may play a vital role. The Flakt-Hydro Process utilizes seawater's inherent properties to absorb and neutralize sulfur dioxide. In the understudied plant, seawater is available in a large amount at the power station as a coolant of the condensers. Therefore, the seawater can be reused at the downstream of condensers for the treatment purpose. The absorption of SO_2 takes place in an absorber, where the seawater and flue gas are brought into a close contact in a counter-current flow.

The advantages of using the seawater scrubber for Claus tail gas treating are as follows:

- High reliability thanks to the simplicity of the process.
- Seawater is naturally alkaline with a typical pH value of 8.0 to 8.3. Therefore, it is suitable for absorption of the acidic gas.
- The absorbed SO_2 is oxidized to harmless sulphate ion which is already a natural constituent of the seawater.

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- The seawater has properties of a suitable solvent such as high solubility of gas, low vapor pressure, low viscosity, low cost, low toxicity [7].
- No need to add chemicals to the scrubber.
- No disposals.
- The scrubbers are not subjected to clogging.
- Low investment costs and low revenue requirements due to the simplicity of design and operation.
- The scrubber efficiency in case of using saline water and brine is more than that of brackish and fresh water but has no linear correlation with salinity [8].
- The acidic absorber effluent flows by gravity to a Seawater Treatment Plant (SWTP), where the absorbed SO_2 is oxidized to SO_4^{2-} before discharge.

The counter current packed bed scrubber was chosen because of the followings;

- This type of scrubber is one of the wet scrubbers with a low power consumption.
- It is the best option for removals of SO_2 emission of the Claus unit due to absence of particulates.
- Fewer problems in the column.
- Flexibility.
- Less corrosion problems.
- Low pressure drop.
- Low investment costs.

The ceramic Inatox Saddle Ring as a tower structure (Fig.2) is selected. That is because of the followings;

- It is more applicable than other forms due to a better efficiency and some other benefits.
- High resistance due to a smooth surface.
- The cost of production is cheaper than other types due to a simple structure [9,10,11].
- It is widely used as regenerative thermal oxidizers, acid gas scrubber, dryer towers, tail gas scrubbers and impasse towers [9,12].

Fig. 2. Ceramic Inatox Saddles Ring structure.

An integration of a selective oxidation process and a wet gas scrubber is proposed for Claus tail gas treating in the understudied plant because of the followings;

- The efficiencies of both selective oxidation process and wet gas scrubber for removing sulfur is about 99.9% [4].
- Compared to amine based Claus tail gas treatment methods, the proposed process has 35% less equipment [4,13,14].
- Approximately, 20% savings can be achieved by the proposed process [4,15,16,17].
- Reduction of operating cost of the Claus unit.
- Seawater is available because the understudied plant is located near a sea.
- The equipment to transfer seawater after a physical treatment is available in the understudied plant.
- The seawater at the understudied plant has 3.9% salinity and the pH value is 8.3[10,14,15].
- The capability to take care of an increased pollutant concentrations during start up, shout down and malfunction.
- There are a waste water treatment plant and an aeration process in the understudied plant. In the aeration basins, the ambient air is blown into the seawater by fans.
- Approximately, 40% less space required for the proposed process[4,16,17].
- The design assumptions are shown in Table 1. The components of the Claus tail gas are given in Table 2 in detail.

Results and Discussion

The results of designing the packed bed scrubber which uses seawater as a solvent, are shown in Table 3. As seen in Table 3, if the refinery owners use the proposed process for Claus tail gas treating, the amount of the exhausted H_2S will be reduced from 5.45 kmol/h to 0.45 kmol/h via the Superclaus process and the amount of SO_2 in the packed bed scrubber is reduced from 2.73 kmol/h to 0.14 kmol/h.

The data of SO_2 solubility in seawater with salinity of 3.9% was used. If the salinity is increased, the solubility of SO_2 will be increased and therefore, the seawater consumption will be decreased.

Another possible improvement could have been adding a small amount of alkalinity such as limestone, quicklime, hydrated lime, sodium carbonate, magnesium carbonate or ammonia for increasing the effect of desulfurization and reducing the amount of seawater required for the process and also the size of the scrubber. The amount of sulfate in the seawater would limit the performance of the scrubber [18]. That amount was 4696 mg/lit in the seawater used in this plant.

Conclusion

The most common approach for Claus tail gas treatment was to install an amine-based tail gas treatment unit (TGCU); however it is possible to reduce the installation cost and increase the reliability by integrating the Superclaus process and wet gas scrubber. In this research, an appropriate and cost effective tail gas treatment process in an existing Claus plant was designed. The amount of the daily SO_2 emissions of the understudied plant is about 17-18 tons due to treatment of 1160 tons of acid gas and production of 220 to 260 ton per day of sulphur. Because the understudied plant was located near

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the sea and the pH value of the seawater water is relatively high, the seawater was used as a solvent for the packed bed scrubber. The design of scrubber was based on the assumption of a 90% efficiency in reduction of H_2S in the Superclaus process. For treating 2495.40 kmol/h acid gas, the minimum seawater flowrate is about 5925 kg/min and the maximum flow rate is calculated as 8887 kg/min. The height and diameter of the scrubber bed were calculated as 12 and 2.7 m, respectively. It is concluded that if the refinery owners use the proposed method for Claus tail gas treating, the amount of the exhausted H_2S will be reduced from 5.45 kmol/h to 0.45 kmol/h via the Superclaus process and the amount of SO_2 in a packed bed scrubber will be reduced from 2.73 kmol/h to 0.14 kmol/h.

In this paper, the design was based on the packed bed scrubber with no water recirculation. Therefore, designing the scrubber with water recirculation capability is the subject of the author's next paper.

Table 1. The assumptions for designing the scrubber

Type of scrubber	Countercurrent packed bed no water recirculation
Superclaus efficiency for reducing H_2S	90%
Scrubber efficiency	95%
Tower structure	Ceramic intalox saddle ring
Structure size	2 inch
Tail gas molecular weight (calculated exhausted gas from Claus unit)	35.17
Seawater molecular weight with 39 ppt salinity	18.7
Main purpose of scrubbing	SO_2 removal
Seawater temperature	30°C
Gas profile to scrubbing	Accordingtable2
SO_2 concentration in solvent (seawater)	0 (no water recirculation)
H_2S concentration after Superclaus	0.45Kmol/hr

Table 2. The components and amount of the Claus tail gas in the understudied plant

Component	Design case	
	Design flow	
	kmol/h	mol %
H_2S	5.45	0.22
SO_2	2.73	0.11
H_2O	735.85	29.49
COS	2.44	0.10
CS_2	0.40	0.02
CO	45.54	1.82
CO_2	675.03	27.04
H_2	26.42	1.06
N_2	1001.52	40.13
O_2	0	0
NH_3	0	0
SX	0.14	0.01
Total	2495.49	100%
Temperature (°C)	125	-
Pressure (bar g)	1.06	-

Table 3. The results of designing the packed bed seawater scrubber.

Characteristics	Rate	Unit
Scrubber inlet gas flow	1462.8	kg/min
Minimum liquid flow rate	5924.78	kg/min
Actual liquid flow rate	8887.17	kg/min
Minimum liquid volumetric flow rate	95.4	lit/s
Actual liquid volumetric flow rate	143.11	lit/s
Inlet so_2 concentration	2.73	kmol/hr
Outlet so_2 concentration	0.14	kmol/hr
So_2 in solvent	0	
Bed factor	131	m^2/m^3
Cross section area of scrubber	5.7	m^2
Scrubber diameter	2.7	m
Pressure drop	0.0808 1	m of water/m of packing inch of water/ft of packing
Pressure drop in flooding	1.5	inch of water/ft of packing
Tower height	12	m
Scrubber inlet gas temperature	125	°C
Gas velocity at the bottom of the tower	3.78	m/s
Gas velocity at the top of the tower	3.14	m/s
Average gas velocity	3.45	m/s
Average gas velocity in bed	4.37	m/s
Degree of wetting	1.9176×10^{-4}	$m^3/m.s$
Number of distributors	4	-

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