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Mr. David Hendricks
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Dear Mr. Hendricks:

Mr. John Hamilton asked me to send to you a copy of the Sulfur Recovery chapter I wrote for the current revision effort on AP 40. This is enclosed. He suggested you may wish to use excerpts from this chapter in your revision of AP 42; I have no objections.

If you have space, you may wish to consider breaking the sulfur recovery section into three sub-sections: Amine treating, Sulfur Recovery, and Tail Gas Treating. Each of the three is a stand-alone subject, with its own pollution factors and process concerns. A given processing facility may have only one, two, or all three elements depending on the size, feedstocks and processing complexity of the facility.

Regards.

Bruce Scott

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Chemical Process Industry

Sulfur

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INTRODUCTION

Elemental sulfur is recovered as a byproduct of the processing of crude oil and natural gas. This source of recovered sulfur, over 6.5 million tonnes in 1989, represents about 63% of the total elemental sulfur market in the United States, the remainder being derived from Frasch mining or imports[1]. The Frasch mining process has little direct impact on air emissions and will not be discussed in this chapter. Elemental sulfur has a wide variety of industrial uses, the chief being the manufacture of sulfuric acid. From the standpoint of air pollution the sulfur recovery plants operated by petroleum refineries and natural gas plants dramatically reduce the emissions of sulfur compounds into the atmosphere from those facilities.

All crude oils and most natural gases contain sulfur compounds in widely varying amounts. Crude oils may contain from as little as 0.1% sulfur to as much as 5.0%. Natural gas is sometimes sulfur free, or may contain 15 to 20% or more, of hydrogen sulfide (H_2S) or other sulfur compounds. These sulfur compounds are not tolerable in most finished petroleum products, and can prove to be corrosive in refinery processes used to make salable products.

While the sulfur in natural gas is usually H_2S, which can be directly removed by the sulfur recovery plants described in this chapter, the removal of sulfur from raw crude oil is much more complex. In most modern refineries this is usually accomplished by treating distillate cuts from crude oil with hydrogen in the presence of a catalyst at elevated temperature and pressure. This treatment converts the various sulfur compounds into H_2S. Some residual cuts are also desulfurized by this same means to produce low sulfur fuel oil, or to provide feedstocks for further processing. Heavy, nonsalable, cuts are usually cracked into lighter, saleable,fractions. The process of cracking normally converts organic sulfur compounds into H_2S. Being a gas at normal refinery conditions, H_2S tends to concentrate in the off-gas streams used for plant fuel. If this gas were to be burned as is it would frequently result in unacceptable levels of atmospheric sulfur dioxide

(SO_2) pollution.

PROCESS DESCRIPTION

The sulfur recovery facilities used in most refineries and gas plants to prevent this pollution consist of three distinct steps: gas scrubbing to remove the H_2S, sulfur recovery to convert H_2S to elemental sulfur, and tail gas treating to clean the effluent from the sulfur recovery plant to levels appropriate for release to the atmosphere. The refinery or gas plant operator has considerable flexibility in the choice of specific processes he may use to accomplish each of the three steps. This will be discussed in more detail below.

GAS SCRUBBING

The processes described here are used primarily for removing H_2S from gas streams, but are also used to scrub H_2S from liquid streams such as propane and butane. Application to liquids differs from gas scrubbing only in the engineering details and will not be described further here.

Removal of H_2S from gas streams is accomplished by scrubbing with a water solution of an organic amine in a packed or trayed tower(scrubber or absorber). The amine solution is alkaline and the weakly acidic H_2S in the gas stream readily dissolves in it. The acid and base react to form a salt, as illustrated in the following reaction:

$$R_2NH + H_2S \longleftrightarrow R_2NH_2HS + \text{heat} \qquad (1)$$

It should be noted that carbon dioxide (CO_2), is also a weak acid and will react by the same mechanism as reaction (1). Hydrocarbon gases, being insoluble in water and neutral rather than acidic, are not affected by the amine solution and so pass out of the scrubbing tower. As indicated by reaction (1) above, the reaction of H_2S or CO_2 with an amine is exothermic. Reaction (1) is shifted to the right by low temperatures and to the left by high temperatures.

In commercial plants the rich amine solution, loaded with H_2S and CO_2 (acid gases), is sent to a stripping tower (regenerator) where it is boiled and the acid gases stripped out. The amine solution, now containing very little acid gas, is cooled and returned to the scrubbing tower for reuse. Heat exchangers, pumps, filters, and a flash drum complete the equipment list for a typical plant. Frequently, one regenerator serves several absorbers. The acid gases from the stripping tower are cooled and sent to the sulfur recovery plant for conversion to elemental sulfur.

A number of amines are in commercial use in gas scrubbing plants. The most common is diethanolamine (DEA), a secondary amine as illustrated in reaction (1). Monoethanolamine (MEA), a primary amine, has been used extensively and is still widely used where its higher reactivity is needed, particularly for CO_2 removal. Methyldiethanolamine (MDEA), a tertiary amine, is coming into greater favor with refiners because of its ability to selectively absorb H_2S and reject most of the CO_2 in the gas stream. There are other amines in use, and the above amines can be blended or otherwise promoted to enhance their performance in specialized applications.

Typical operating conditions in an amine plant are about as follows, although individual plants may vary greatly. Absorbers in refineries are operated at about 90-120^{o}F and at pressures ranging from 80-150 psig in most towers to over 2000 psig in certain applications. Natural gas plant absorbers are operated at the same temperatures but normally at higher pressures, typically 400-1000 psig. Regenerators operate at low pressure, usually 5-25 psig, and at temperatures in the range of 245-265^{o}F.

In some cases, usually very low H_2S in the sour gas, other treatment processes may be used in lieu of amine treatment. These generally use a solid or liquid scrubbing agent that reacts chemically with H_2S, removing it from the gas stream. The spent scrubbing agent is frequently sent directly to disposal, although some can be regenerated and reused. There are a number of these scrubbing agents on the market, and a detailed discussion will not be attempted here.

Sour gases are also sometimes scrubbed directly with liquid Redox solutions. The H_2S is removed and converted directly to elemental sulfur which can be recovered, and the scrubbing solution regenerated for further use. These processes are more often used as tail gas cleanup processes and will be discussed in more detail in that section of this chapter.

SULFUR RECOVERY

Acid gases from the amine plant are processed in a sulfur recovery plant utilizing the CLAUS process in the vast majority of cases. In the Claus process one-third of the H_2S in the acid gas stream is burned with air to form sulfur dioxide (SO_2):

$$H_2S \quad + \quad 3/2\ O_2 \quad \text{--->} \quad SO_2 \quad + \quad H_2O \quad + \quad \text{heat} \qquad (2)$$

The SO_2 reacts with the remaining H_2S to form sulfur, as follows:

$$2\ H_2S\ +\ SO_2\ \longleftrightarrow\ 3\ S\ +\ 2\ H_2O\ +\ \text{heat} \qquad (3)$$

Reaction (3) takes place in the high temperature combustion part of the plant,and accounts for about half of the total conversion. The remaining sulfur is formed in lower temperature catalytic parts of the plant. Because equation (3) represents an equilibrium chemical reaction it is not possible for a Claus plant to convert all the incoming sulfur compounds to elemental sulfur.Each catalytic stage can recover half to two-thirds of the sulfur entering it. Some H_2S, SO_2, sulfur vapor and traces of other sulfur compounds formed in the combustion section escape with the inert gases from the tail end of the plant (tail gas). Thus it is frequently necessary to follow the Claus plant with a tail gas cleanup plant, which will be discussed in the next section of this chapter.

Since the 2:1 ratio of $H_2S:SO_2$ indicated by equation (3) is essential to efficient operation of the plant an extensive control system is usually provided to insure the correct injection of air into the combustion chamber[2].

Many of the engineering differences between Claus plants are centered on the combustion chamber and the need for proper combustion conditions for a wide range of composition and flammability of the acid gas[3]. Hot gas from the combustion chamber is quenched by passing through a waste heat boiler, in which high or medium pressure steam is generated, before entering a sulfur condenser. Since reaction (3) is an equilibrium reaction conversion to sulfur is improved by removing that product.

This is followed by a catalytic stage, consisting of a gas reheater, a catalyst chamber, and a condenser to remove the product sulfur as a liquid. This catalytic stage can be repeated from one to four times depending on the level of conversion desired. Most plants are now built with two stages (some jurisdictions require three), since the need for a tail gas cleanup plant makes the third and fourth stages uneconomic. From the condenser of the final catalytic stage the process stream passes to some form of tail gas treatment process, as described in the next section of this chapter.

The liquid sulfur from the condensers runs through a seal leg into a covered pit from which it is pumped to trucks or rail cars for shipment to end users. Some plants, remote from end users, form molten sulfur into solid pellets or other shapes for shipment.

Claus plants operate at low pressures, rarely higher than 10 psig. Temperatures range from 1800-2800°F in the combustion chamber to 400 -

600°F in the catalytic reactors. Tail gas from the last condenser is at about 270°F. The catalyst used is alumina, sometimes promoted, and sometimes in the form of bauxite.

Claus plants in refineries are frequently used to process gas from the treatment of refinery sour waters. This gas may contain significant quantities of ammonia as well as H_2S. The ammonia can efficiently be converted to nitrogen and water in the Claus plant if proper attention is given to maintaining operating conditions in the right range.

TAIL GAS TREATMENT

Gas from the Claus plant still contains 0.8-1.5% of sulfur compounds which must be removed before the gases can be safely vented to the atmosphere. This is done in a tail gas treatment, or cleanup plant. The number and variety of tail gas cleanup options is beyond the scope of this chapter, and only the two most effective types will be described here. These are the amine scrubbing and the liquid redox scrubbing processes.

The Amine Scrubbing process

Tail gas from the Claus plant is heated to about 550°F, hydrogen is added (or generated in the heater, if necessary) and the gas is passed through a catalyst bed where virtually all the sulfur compounds are converted to H_2S; for example:

$$SO_2 \quad + \quad 3\ H_2 \quad \text{--->} \quad H_2S \quad + \quad 2\ H_2O \quad + \quad \text{heat} \qquad (4)$$

Other sulfur compounds are similarly hydrogenated. The hot gas is cooled in a waste heat boiler and passes to a quench column to remove excess water. The cool dry gas stream flows to the bottom of an amine absorber where the H_2S is removed in the same manner as indicated above in the amine section. Acid gas is stripped from the amine, cooled and recycled to the front of the Claus plant to be converted to sulfur. In its general layout this amine plane is quite similar to that described above, although many engineering details are different. Gas from the amine absorber is routed to an incinerator (see below) before being vented to the atmosphere. Newer plants, where proper amines are selected and details engineered, may have low enough sulfur contents to be vented directly.

Liquid Redox Scrubbing process

Tail gas from the Claus plant is treated essentially as indicated above to convert all sulfur compounds to H_2S, cool and dry the gas stream and make it ready for final scrubbing. The gas is contacted in a packed tower with a highly alkaline water solution containing an oxidized Redox catalyst. H_2S is readily absorbed into the alkaline solution and the cleaned tail gas passes from the absorber directly to the atmosphere.

In the scrubbing solution the H_2S is oxidized directly to elemental sulfur by the Redox catalyst, which is reduced. The sulfur is in the form of tiny particles which must be removed from the solution by settling, centrifuging or filtering. The Redox catalyst is reoxidized by sparging air into the scrubbing solution in an oxidation vessel. The regenerated solution is then recirculated to the absorber for further reaction with H_2S. The chemistry of this process can be summarized as follows:

Absorption: $H_2S \text{ (gas)} \longrightarrow 2\ H^+ + S^=$ (5)

Oxidation: $S^= + 2\ V^{+5} \longrightarrow S^o + 2\ V^{+4}$ (6)

Regeneration: $2\ V^{+4} + 2\ H^+ + 1/2\ O_2 \longrightarrow 2\ V^{+5} + H_2O$ (7)

The Redox catalyst is shown as Vanadium in equations (6) and (7) above, but iron is gaining considerable acceptance because of lower toxicity and lower cost.

Other processes

A number of other processes are commercially practiced which are not discussed here because they would not normally meet the criterion of best available control technology. These include processes that continue equation (3) at temperatures below the sulfur dew point to achieve better equilibrium, and oxidation processes, in which sulfur compounds are oxidized to SO_2, and recycled to the claus plant.

While not strictly speaking pollution control devices, most sulfur recovery facilities end by routing the tail gas through a thermal or catalytic incinerator. These convert the small amount of H_2S remaining in the cleaned tail gas to SO_2.

AIR EMISSIONS CHARACTERIZATION

Air emissions are impacted on both ends of the sulfur recovery train. The Amine plant sets the sulfur level in the refinery fuel gas system, which controls stack emissions from furnaces. The tail gas treatment plant controls sulfur emissions from the sulfur recovery complex itself.

Typical refinery amine plants are designed to limit the H_2S content of fuel gases to below 160 ppm, the current EPA limit, and generally are able to clean to well below that level. Uncontrolled emissions from refineries and gas plants could be as high as several thousands of ppms depending on the raw materials and processing equipment used.

Natural gas plants are able to treat gas to below 4 ppm H_2S, the normal pipeline specification. This is better than refineries because of the higher treating pressure, which favors the scrubbing reaction, and the normally lower content of other trace sulfur compounds.

The other pollution issue in amine treating plants involves occasional losses of amines into the plant effluent water system.

Older, or very small (less than 20 LTPD sulfur), Claus plants without tail gas cleanup plants influence air pollution directly by their sulfur recovery efficiency. This is a function of the number of catalytic stages in the plant and the concentration of H_2S in the acid gas fed to the plant. The higher the acid gas concentration and the more stages, the higher the recovery of elemental sulfur. Contaminants (COS, hydrocarbons, water, e.g.) in the acid gas stream also reduce the expected recovery efficiency. While it is difficult to generalize, one would expect a two catalytic bed Claus plant to recover 94-96% of the inlet sulfur as liquid. The range covers acid gas H_2S concentrations from 35 to 90%. The equivalent recoveries from a three bed plant are 96-97.5%, and from a four bed plant 97-98.5%.[4]

The liquid sulfur produced from a Claus plant is saturated with H_2S and, unless degassed, some low ppm levels of H_2S and elemental sulfur will be released from pit and storage tank vents.

Tail gas treatment plants are rated by the concentration of sulfur compounds in the treated vent gas, corrected for moisture and air dilution. Amine scrubbing plants normally release 50-250 ppm of sulfur compounds, but new, specifically designed plants may be expected to release no more that 20-25 ppm, and of this less than 15 ppm H_2S. Liquid Redox type plants should release below 40 ppm, although older plants may be designed for less efficient cleanup. Current EPA limits are 250 ppmv.

Both amine and liquid Redox processes are subject to leakage of scrubbing solution into effluent water systems.

AIR POLLUTION CONTROL MEASURES

Measures taken by plant operators to maintain the pollution control efficiency of their sulfur recovery facilities include the following:

GAS SCRUBBING

The principle cause of excess emissions from an amine plant is foaming of the amine solution in the absorber. Foaming can be caused be excessive particulate contamination, presence of liquid hydrocarbons in a gas scrubber, and contamination by surface active chemicals. Thus, the operator's first concern must be for the cleanliness of the amine solution. Strongly acidic compounds in the gas stream, or oxygen which will form acidic compounds, react with the amine to form salts that will not decompose in the stripper. These are called heat stable salts (HSS) and will gradually cause the performance of the amine to deteriorate. At levels above 4-5% in the amine solution HSS promote corrosion, which can lead to foaming and equipment failure. Amines (and H_2S) are known to cause cracking in the welds of carbon steel vessels. Care must be exercised in the fabrication and repair of steel equipment for this service, and stress relief of vessel welds is required.

SULFUR RECOVERY

Careful control of the air injection rate in to the Claus plant is the chief factor affecting the recovery efficiency. In addition to the front end control system, most plants have a "tail gas ratio" analyzer to measure the concentrations of H_2S and SO_2 in the gas leaving the last condenser. Poor combustion control can cause the catalyst to "sulfate" and lose activity. Periodic rejuvenations can temporarily control this phenomenon. Because of the toxic nature of H_2S Claus plants must be equipped with an interlock system to automatically put the plant into a safe condition in case of a critical failure. Some plants remove (degas) the H_2S dissolved in the liquid sulfur produced. This may reduce the emissions from the complex slightly, but its main value is in transportation safety. It is possible to reach explosive levels of H_2S in the vapor space of rail cars with undegassed sulfur.

TAIL GAS TREATMENT

The pollution control concerns in the two principle processes discussed include maintaining proper air:fuel ratios in the heater, adequate hydrogen to accomplish the necessary hydrogenation, and control of the pH of the quench tower water. Concerns in the amine process parallel those of the amine gas scrubbing process, with the extra need to insure adequate stripping of the amine. Amine stripping sets the H_2S leak rate through the absorber.

Emissions from the liquid Redox plants are controlled primarily by maintaining the proper alkalinity and flow rate of the scrubbing solution. Attention must be paid to the cleanliness of the solution as well. Build up of sulfur particles, catalyst degradation products and salts can cause mechanical problems which can interfere with efficient scrubbing. Biological infestations can also cause foaming problems. Most plants purge a small stream of scrubbing solution from the plant to keep the salts levels under control.

Incinerators must operate at a temperature of 1200^{o}F or higher if all the H_2S is to be combusted. Proper air:fuel ratios are needed to eliminate pluming from the incinerator stack. Stacks should be equipped with analyzers to monitor the SO_2 level.

REFERENCES

1. "The United States sulphur industry", Sulphur 209, 17, 1990
2. "Control: the key to successful claus sulphur recovery", Sulphur 202, 24, 1989.
3. J. B. Hyne, "Optimum furnace configuration for sulphur recovery units", Sulphur 198, 24, 1988.
4. H. G. Paskall, Capability of the modified claus process, Western Research, Calgary, 1979, p 172.

BIBLIOGRAPHY

A. L. Kohl and F. C. Riesenfeld, Gas Purification, 4th ed.,Gulf Publishing Co. Houston, 1988.
U. H. F. Sander, H. Fischer et al., Sulphur, Sulphur Dioxide and Sulphuric Acid, The British Sulphur Corp. Ltd., London, 1984
"Sweetening of natural gas: I", Sulphur 192, 30, 1987.
"Sweetening of natural gas: II", Sulphur 193, 30, 1987.

KEYWORDS

AMINE TREATING
    DEA
    MEA
    MDEA
GAS SCRUBBING
CLAUS
SULFUR RECOVERY
HYDROGEN SULFIDE
TAIL GAS CLEANUP (TREATMENT)
INCINERATOR
TREATING