

8.13 Sulfur Recovery

8.13.1 General¹⁻²

Sulfur recovery refers to the conversion of hydrogen sulfide (H₂S) to elemental sulfur. Hydrogen sulfide is a byproduct of processing natural gas and refining high-sulfur crude oils. The most common conversion method used is the Claus process. Approximately 90 to 95 percent of recovered sulfur is produced by the Claus process. The Claus process typically recovers 95 to 97 percent of the hydrogen sulfide feedstream.

Over 5.9 million megagrams (Mg) (6.5 million tons) of sulfur were recovered in 1989, representing about 63 percent of the total elemental sulfur market in the U. S. The remainder was mined or imported. The average production rate of a sulfur recovery plant in the U. S. varies from 51 to 203 Mg (56 to 224 tons) per day.

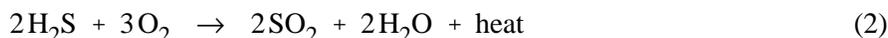
8.13.2 Process Description¹⁻²

Hydrogen sulfide, a byproduct of crude oil and natural gas processing, is recovered and converted to elemental sulfur by the Claus process. Figure 8.13-1 shows a typical Claus sulfur recovery unit. The process consists of multistage catalytic oxidation of hydrogen sulfide according to the following overall reaction:



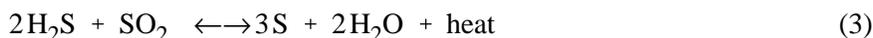
Each catalytic stage consists of a gas reheater, a catalyst chamber, and a condenser.

The Claus process involves burning one-third of the H₂S with air in a reactor furnace to form sulfur dioxide (SO₂) according to the following reaction:



The furnace normally operates at combustion chamber temperatures ranging from 980 to 1540°C (1800 to 2800°F) with pressures rarely higher than 70 kilopascals (kPa) (10 pounds per square inch absolute). Before entering a sulfur condenser, hot gas from the combustion chamber is quenched in a waste heat boiler that generates high to medium pressure steam. About 80 percent of the heat released could be recovered as useful energy. Liquid sulfur from the condenser runs through a seal leg into a covered pit from which it is pumped to trucks or railcars for shipment to end users. Approximately 65 to 70 percent of the sulfur is recovered. The cooled gases exiting the condenser are then sent to the catalyst beds.

The remaining uncombusted two-thirds of the hydrogen sulfide undergoes Claus reaction (reacts with SO₂) to form elemental sulfur as follows:



The catalytic reactors operate at lower temperatures, ranging from 200 to 315°C (400 to 600°F). Alumina or bauxite is sometimes used as a catalyst. Because this reaction represents an equilibrium chemical reaction, it is not possible for a Claus plant to convert all the incoming sulfur compounds to elemental sulfur. Therefore, 2 or more stages are used in series to recover the sulfur. Each catalytic stage can recover half to two-thirds of the incoming sulfur. The number of catalytic stages depends upon the level of conversion desired. It is estimated that 95 to 97 percent overall recovery can be

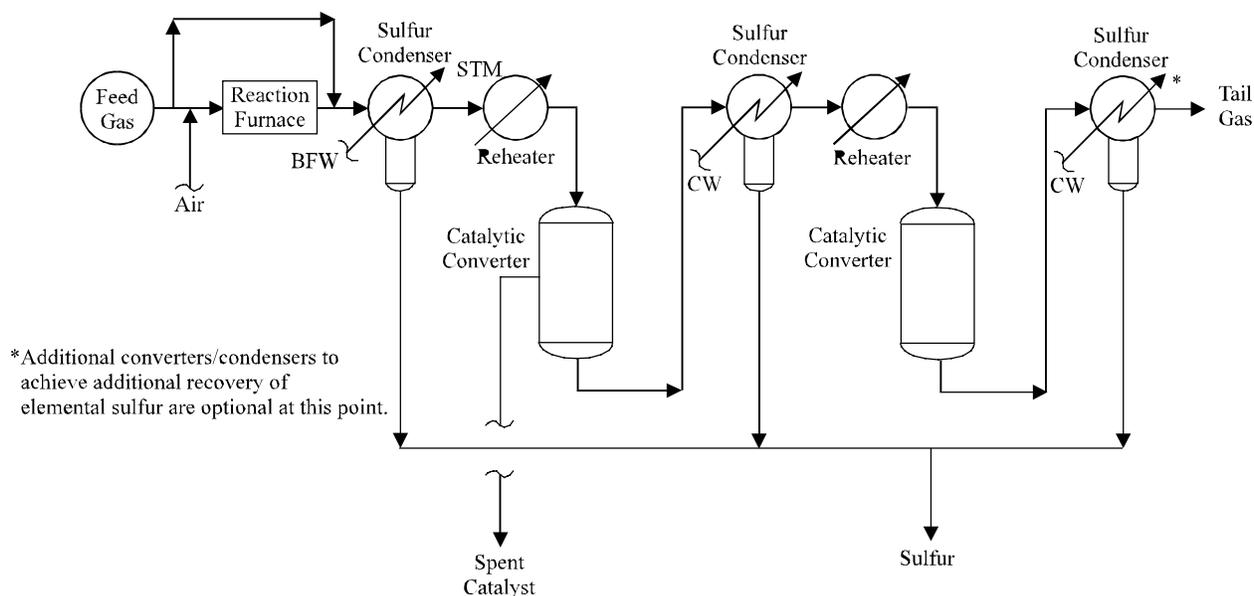


Figure 8.13-1. Typical Claus sulfur recovery unit. CW = Cooling water. STM = Steam. BFW = Boiler feed water.

achieved depending on the number of catalytic reaction stages and the type of reheating method used. If the sulfur recovery unit is located in a natural gas processing plant, the type of reheat employed is typically either auxiliary burners or heat exchangers, with steam reheat being used occasionally. If the sulfur recovery unit is located in a crude oil refinery, the typical reheat scheme uses 3536 to 4223 kPa (500 to 600 pounds per square inch gauge [psig]) steam for reheating purposes. Most plants are now built with 2 catalytic stages, although some air quality jurisdictions require 3. From the condenser of the final catalytic stage, the process stream passes to some form of tailgas treatment process. The tailgas, containing H_2S , SO_2 , sulfur vapor, and traces of other sulfur compounds formed in the combustion section, escapes with the inert gases from the tail end of the plant. Thus, it is frequently necessary to follow the Claus unit with a tailgas cleanup unit to achieve higher recovery.

In addition to the oxidation of H_2S to SO_2 and the reaction of SO_2 with H_2S in the reaction furnace, many other side reactions can and do occur in the furnace. Several of these possible side reactions are:



8.13.3 Emissions And Controls¹⁻⁴

Table 8.13-1 shows emission factors and recovery efficiencies for modified Claus sulfur recovery plants. Factors are expressed in units of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton). Emissions from the Claus process are directly related to the recovery efficiency. Higher

Table 8.13-1 (Metric And English Units). EMISSION FACTORS FOR MODIFIED CLAUS SULFUR RECOVERY PLANTS

EMISSION FACTOR RATING: E

Number of Catalytic Stages	Average % Sulfur Recovery ^a	SO ₂ Emissions	
		kg/Mg Of Sulfur Produced	lb/ton Of Sulfur Produced
1, Uncontrolled	93.5 ^b	139 ^{b,c}	278 ^{b,c}
3, Uncontrolled	95.5 ^d	94 ^{c,d}	188 ^{c,d}
4, Uncontrolled	96.5 ^e	73 ^{c,e}	145 ^{c,e}
2, Controlled ^f	98.6	29	57
3, Controlled ^g	96.8	65	129

^a Efficiencies are for feedgas streams with high H₂S concentrations. Gases with lower H₂S concentrations would have lower efficiencies. For example, a 2- or 3-stage plant could have a recovery efficiency of 95% for a 90% H₂S stream, 93% for 50% H₂S, and 90% for 15% H₂S.

^b Reference 5. Based on net weight of pure sulfur produced. The emission factors were determined using the average of the percentage recovery of sulfur. Sulfur dioxide emissions are calculated from percentage sulfur recovery by one of the following equations:

$$\text{SO}_2 \text{ emissions (kg/Mg)} = \frac{(100\% \text{ recovery})}{\% \text{ recovery}} 2000$$

$$\text{SO}_2 \text{ emissions (lb/ton)} = \frac{(100\% \text{ recovery})}{\% \text{ recovery}} 4000$$

^c Typical sulfur recovery ranges from 92 to 95%.

^d Typical sulfur recovery ranges from 95 to 96%.

^e Typical sulfur recovery ranges from 96 to 97%.

^f Reference 6. EMISSION FACTOR RATING: B. Test data indicated sulfur recovery ranges from 98.3 to 98.8%.

^g References 7-9. EMISSION FACTOR RATING: B. Test data indicated sulfur recovery ranges from 95 to 99.8%. recovery efficiencies. The efficiency depends upon several factors, including the number of catalytic stages, the concentrations of H₂S and contaminants in the feedstream, stoichiometric balance of gaseous components of the inlet, operating temperature, and catalyst maintenance.

recovery efficiencies mean less sulfur emitted in the tailgas. Older plants, or very small Claus plants producing less than 20 Mg (22 tons) per day of sulfur without tailgas cleanup, have varying sulfur recovery efficiencies. The efficiency depends upon several factors, including the number of catalytic stages, the concentrations of H₂S and contaminants in the feedstream, stoichiometric balance of gaseous components of the inlet, operating temperature, and catalyst maintenance.

A 2-bed catalytic Claus plant can achieve 94 to 96 percent efficiency. Recoveries range from 96 to 97.5 percent for a 3-bed catalytic plant and range from 97 to 98.5 percent for a 4-bed catalytic

plant. At normal operating temperatures and pressures, the Claus reaction is thermodynamically limited to 97 to 98 percent recovery. Tailgas from the Claus plant still contains 0.8 to 1.5 percent sulfur compounds.

Existing new source performance standards limit sulfur emissions from Claus sulfur recovery plants of greater than 20.32 Mg (22.40 ton) per day capacity to 0.025 percent by volume (250 parts per million volume [ppmv]). This limitation is effective at 0 percent oxygen on a dry basis if emissions are controlled by an oxidation control system or a reduction control system followed by incineration. This is comparable to the 99.8 to 99.9 percent control level for reduced sulfur.

Emissions from the Claus process may be reduced by: (1) extending the Claus reaction into a lower temperature liquid phase, (2) adding a scrubbing process to the Claus exhaust stream, or (3) incinerating the hydrogen sulfide gases to form sulfur dioxide.

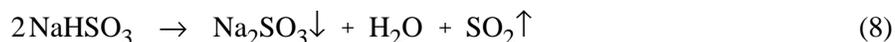
Currently, there are 5 processes available that extend the Claus reaction into a lower temperature liquid phase including the BSR/selectox, Sulfreen, Cold Bed Absorption, Maxisulf, and IFP-1 processes. These processes take advantage of the enhanced Claus conversion at cooler temperatures in the catalytic stages. All of these processes give higher overall sulfur recoveries of 98 to 99 percent when following downstream of a typical 2- or 3-stage Claus sulfur recovery unit, and therefore reduce sulfur emissions.

Sulfur emissions can also be reduced by adding a scrubber at the tail end of the plant. There are essentially 2 generic types of tailgas scrubbing processes: oxidation tailgas scrubbers and reduction tailgas scrubbers. The first scrubbing process is used to scrub SO₂ from incinerated tailgas and recycle the concentrated SO₂ stream back to the Claus process for conversion to elemental sulfur. There are at least 3 oxidation scrubbing processes: the Wellman-Lord, Stauffer Aquaclus, and IFP-2. Only the Wellman-Lord process has been applied successfully to U. S. refineries.

The Wellman-Lord process uses a wet generative process to reduce stack gas sulfur dioxide concentration to less than 250 ppmv and can achieve approximately 99.9 percent sulfur recovery. Claus plant tailgas is incinerated and all sulfur species are oxidized to form SO₂ in the Wellman-Lord process. Gases are then cooled and quenched to remove excess water and to reduce gas temperature to absorber conditions. The rich SO₂ gas is then reacted with a solution of sodium sulfite (Na₂SO₃) and sodium bisulfite (NaHSO₃) to form the bisulfite:



The offgas is reheated and vented to the atmosphere. The resulting bisulfite solution is boiled in an evaporator-crystallizer, where it decomposes to SO₂ and water (H₂O) vapor and sodium sulfite is precipitated:



Sulfite crystals are separated and redissolved for reuse as lean solution in the absorber. The wet SO₂ gas is directed to a partial condenser where most of the water is condensed and reused to dissolve sulfite crystals. The enriched SO₂ stream is then recycled back to the Claus plant for conversion to elemental sulfur.

In the second type of scrubbing process, sulfur in the tailgas is converted to H₂S by hydrogenation in a reduction step. After hydrogenation, the tailgas is cooled and water is removed. The cooled tailgas is then sent to the scrubber for H₂S removal prior to venting. There are at least 4 reduction scrubbing processes developed for tailgas sulfur removal: Beavon, Beavon MDEA, SCOT, and ARCO. In the Beavon process, H₂S is converted to sulfur outside the Claus unit using a lean H₂S-to-sulfur process (the Strefford process). The other 3 processes utilize conventional amine scrubbing and regeneration to remove H₂S and recycle back as Claus feed.

Emissions from the Claus process may also be reduced by incinerating sulfur-containing tailgases to form sulfur dioxide. In order to properly remove the sulfur, incinerators must operate at a temperature of 650°C (1,200°F) or higher if all the H₂S is to be combusted. Proper air-to-fuel ratios are needed to eliminate pluming from the incinerator stack. The stack should be equipped with analyzers to monitor the SO₂ level.

References For Section 8.13

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