8.13 Sulfur Recovery

8.13.1 General

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. Claus sulfur recovery plants typically recover 95 to 99.9 percent of the hydrogen sulfide feedstream depending on the level of control employed.

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 Description

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 gaseous hydrogen sulfide (H₂S) according to the following overall reaction:

\[
2H_2S + O_2 \rightarrow 2S + 2H_2O + \text{heat} \tag{1}
\]

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:

\[
2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O + \text{heat} \tag{2}
\]

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 from the reactor furnace condenser. The cooled gases exiting the condenser are reheated 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:

\[
2H_2S + SO_2 \leftrightarrow 3S + 2H_2O + \text{heat} \tag{3}
\]

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, however, with the condensation and removal of sulfur after each reactor.
high sulfur removal efficiencies can be achieved using 2 or more reactors (or stages are used) in series to recover the with sulfur condensed and recovered after each stage. Each catalytic stage can recover half about 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 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 reheating employed is typically either auxiliary burners or heat exchangers, with steam reheating being used occasionally. If the sulfur recovery unit is located in a crude oil refinery, the typical reheating scheme uses 3536 to 4223 kPa (500 to 600 pounds per square inch guage [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 H₂S, SO₂, 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 used and the reactor temperatures used. Higher recoveries are achieved at lower temperatures, but the traditional Claus reactors must be operated above the dew point of sulfur to prevent sulfur from condensing within the reactor and deactivating the catalyst.

In addition to the oxidation of H₂S to SO₂ and the reaction of SO₂ with H₂S in the reaction furnace, many other side reactions can and do occur in the furnace. Several of these possible side reactions are:

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{S} & \rightarrow \text{COS} + \text{H}_2\text{O} \\
\text{COS} + \text{H}_2\text{S} & \rightarrow \text{CS}_2 + \text{H}_2\text{O} \\
2\text{COS} & \rightarrow \text{CO}_2 + \text{CS}_2 
\end{align*}
\]

The uncondensed vapor leaving the condenser of the final catalytic stage is commonly referred to as “tailgas.” The tailgas contains nitrogen, H₂S, SO₂, sulfur vapor, and traces of other sulfur compounds.
formed as a result of these side reactions. It is frequently necessary to follow the Claus unit with a tailgas treatment unit to achieve higher sulfur recovery efficiencies and/or a thermal incinerator to convert remaining hydrogen sulfide and other sulfur compounds in the tailgas to sulfur dioxide.

8.13.3 Emissions And Controls for SO$_2$\textsuperscript{1-4}

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 of sulfur compounds from the Claus process are directly related to the recovery efficiency. Higher 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 Claus plants without tailgas cleanup, have varying sulfur recovery efficiencies ranging from 92 to 97 percent; Claus plants with tailgas cleanup, have sulfur recovery efficiencies ranging from 99 to 99.9 percent. The efficiency depends upon several factors, including the number of catalytic stages, the concentrations of H$_2$S and contaminants in the feedstream, stoichiometric balance of gaseous components of the inlet, operating temperature, catalyst maintenance, and the type of tailgas cleanup process used. Regardless of whether or not a tailgas cleanup process is used to increase recovery efficiency, most sulfur recovery plants use a thermal oxidizer or incinerator to convert H$_2$S and other sulfur compounds SO$_2$ prior to atmospheric release. Table 8.13-1 shows SO$_2$ emission factors and recovery efficiencies for Claus sulfur recovery plants followed by a thermal oxidizer, incinerator or other oxidative control system. The SO$_2$ emissions factors are expressed in units of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton) of sulfur produced.

Table 8.13-1 (Metric And English Units). SO$_2$ EMISSION FACTORS FOR MODIFIED CLAUS SULFUR RECOVERY PLANTS WITH THERMAL OXIDATIVE CONTROL SYSTEMS*

<table>
<thead>
<tr>
<th>Number of Catalytic Stages</th>
<th>SCC Description</th>
<th>Average % Sulfur Recovery\textsuperscript{c}</th>
<th>SO$_2$ Emissions\textsuperscript{a,d}</th>
<th>EMISSION FACTOR RATING: E</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>kg/Mg Of Sulfur Produced</td>
<td>lb/ton Of Sulfur Produced</td>
</tr>
</tbody>
</table>

\textsuperscript{*}SO$_2$ emission factors are expressed in units of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton) of sulfur produced.

\textsuperscript{a}SO$_2$ emission factors are expressed in units of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton) of sulfur produced.

\textsuperscript{b}Average % Sulfur Recovery is the percentage of sulfur removed from the feedstream.

\textsuperscript{c}Emissions of sulfur compounds from the Claus process are directly related to the recovery efficiency. Higher recovery efficiencies mean less sulfur emitted in the tailgas.

\textsuperscript{d}The efficiency depends upon several factors, including the number of catalytic stages, the concentrations of H$_2$S and contaminants in the feedstream, stoichiometric balance of gaseous components of the inlet, operating temperature, catalyst maintenance, and the type of tailgas cleanup process used. Regardless of whether or not a tailgas cleanup process is used to increase recovery efficiency, most sulfur recovery plants use a thermal oxidizer or incinerator to convert H$_2$S and other sulfur compounds SO$_2$ prior to atmospheric release.

\textsuperscript{e}Regardless of whether or not a tailgas cleanup process is used to increase recovery efficiency, most sulfur recovery plants use a thermal oxidizer or incinerator to convert H$_2$S and other sulfur compounds SO$_2$ prior to atmospheric release.
The emission factors were determined assuming all sulfur compounds are converted to SO$_2$ prior to atmospheric release. These emission factors are applicable to all Claus sulfur recovery plants whether or not the sulfur recovery plant employs a tailgas cleanup system provided the emissions are controlled using a thermal incinerator or thermal oxidizer. These emissions factors are also applicable for Claus sulfur recovery plants with oxidative tailgas cleanup systems that do not use incineration.

**Controlled Removal**

<table>
<thead>
<tr>
<th>Other Not Classified [99% Removal]</th>
<th>96.8</th>
<th>65–20</th>
<th>429–40</th>
</tr>
</thead>
<tbody>
<tr>
<td>30103299</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**

- The emission factors were determined assuming all sulfur compounds are converted to SO$_2$ prior to atmospheric release. These emission factors are applicable to all Claus sulfur recovery plants whether or not the sulfur recovery plant employs a tailgas cleanup system provided the emissions are controlled using a thermal incinerator or thermal oxidizer. These emissions factors are also applicable for Claus sulfur recovery plants with oxidative tailgas cleanup systems that do not use incineration.

- SCC = Source Classification Code. Emissions may be reported under other general sulfur recovery SCC codes such as 030603301 or 31000208, but the emissions factor should be selected based on the SCC descriptions (control efficiencies) included in the table.

- Efficiencies are for feedgas streams with high H$_2$S concentrations. Gases with lower H$_2$S concentrations would have lower efficiencies. For example, a 2- or 3-stage plant could have a recovery efficiency of 95% for a 90% H$_2$S stream, 93% for 50% H$_2$S, and 90% for 15% H$_2$S.

<table>
<thead>
<tr>
<th>SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
</tr>
</tbody>
</table>

- 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:

  \[
  \text{SO}_2\text{ emissions (kg/Mg)} = \frac{(100\% - \%\text{recovery}) \times \text{MW}_{t\text{SO}_2}}{\text{MW}_t\text{S} \times 1000}
  \]

  \[
  \text{SO}_2\text{ emissions (lb/ton)} = \frac{(100\% - \%\text{recovery}) \times \text{MW}_{t\text{SO}_2}}{\text{MW}_t\text{S} \times 2000}
  \]

  Where the ratio of the molecular weights of SO$_2$ and S, $\frac{\text{MW}_{t\text{SO}_2}}{\text{MW}_t\text{S}}$, is 2.00.

- Use for Claus units with scrubbing type of tail gas treatment units and other systems that achieve 99.9 percent sulfur recovery.

- Use for Claus units with technologies that extend the Claus reaction and other systems that achieve 99 percent sulfur recovery.

A 2-bed catalytic Claus plant typically achieves 92 to 96% percent sulfur recovery efficiency. Recoveries range from 96 to 97.5% percent for a 3-bed catalytic plant and range from 97.5 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. In 2008, the new source performance standards were revised to include requirements for sulfur recovery plants less than 20.32 Mg (22.40 ton) per day capacity to have SO₂ emissions of 0.25 percent by volume or less (2,500 ppmv), dry basis at zero percent oxygen. This is comparable to the 99 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, and thereby increase sulfur recovery efficiencies, (2) adding a scrubbing process to the Claus exhaust stream for the purposes of increasing sulfur recovery efficiencies, or (3) incinerating the sulfur compounds to SO₂ and using conventional flue gas desulfurization (FGD) scrubbing techniques to reduce the SO₂ emissions. Incineration is also commonly used to control the emissions of H₂S and other reduced sulfur compounds in the tailgas, whether or not there are other tailgas cleanup processes employed. Incineration by itself does not reduce the total sulfur emissions from the sulfur recovery unit; it only reduces H₂S and other reduced sulfur compound emissions while increasing the SO₂ emissions.

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, for the purposes of increasing sulfur recovery. 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 Aquaclaus, 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:

\[
\text{SO}_2 + \text{Na}_2 \text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3
\]  (7)

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:

\[
2\text{NaHSO}_3 \rightarrow \text{Na}_2 \text{SO}_3 \downarrow + \text{H}_2\text{O} + \text{SO}_2
\]  (8)
Sulfite crystals are separated and redissolved for reuse as lean solution in the absorber. The wet SO$_2$ gas is directed to a partial condenser where most of the water is condensed and reused to dissolve sulfite crystals. The enriched SO$_2$ 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 H$_2$S 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 H$_2$S 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, H$_2$S is converted to sulfur outside the Claus unit using a lean H$_2$S-to-sulfur process (the Strefford process). The other 3 processes utilize conventional amine scrubbing and regeneration to remove H$_2$S and recycle back as Claus feed. These processes can achieve approximately 99.9 percent sulfur recovery and can be used to meet new source performance limits of 300 ppmv or less reduced sulfur compound emissions or, if the reductive tailgas scrubber is followed by incineration, SO$_2$ emissions of 250 ppmv (dry basis, 0 percent oxygen).

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) and using conventional FGD scrubbing techniques to remove SO$_2$. This control method is different from the scrubbing processes described previously in that this control technique does not increase sulfur recovery efficiencies. FGD systems used for sulfur recovery plants employ an alkaline reagent in a wet scrubber to absorb SO$_2$ from the incinerator exhaust. The sulfates formed in the wet scrubber remain in the scrubbing water; spent scrubbing water typically requires treatment to remove dissolved solids or special disposal techniques, such as deep well injection. FGD wet scrubber control efficiencies typically range from 90 to 98 percent depending on the scrubber design and alkaline reagent used. The use of FGD systems for sulfur recovery plants is typically limited to smaller sulfur recovery plants (plants with capacities of less than 20.32 Mg (22.40 ton) per day). Disadvantages of an FGD system for sulfur plant control include no increase in sulfur recovery efficiency and creation of a wastewater stream; advantages of an FGD system for sulfur plant control is that the system can be used to reduce SO$_2$ emissions even when there are operational issues with the upstream Claus process. Scrubbing processes that recycle H$_2$S or SO$_2$ ton the Claus feed become ineffective when there are operational issues with the upstream Claus process.

**Emissions from the Claus process may also be controlled by incinerating sulfur-containing tailgases to form SO$_2$.** Incineration on its own does not reduce the sulfur compound emissions from the sulfur recovery plant; it merely converts all sulfur emissions to SO$_2$. In order to properly control reduced sulfur compound emissions, incinerators must operate at a temperature of 650°C (1,200°F) or higher if all the H$_2$S 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 SO$_2$ level.

### 8.13.4 Emissions And Controls for Other Pollutants 10-33

Other pollutants emitted from sulfur recovery units include oxides of nitrogen (NOx), carbon monoxide (CO), and total hydrocarbon (THC). NOx and CO emissions are typically generated when the sulfur-containing tailgases are sent to an incinerator or thermal oxidizer. Trace amounts of hydrocarbons can be carried over in the sour gas feed to the sulfur recovery unit when hydrocarbon gases, such as natural gas and refinery fuel gas, are treated to remove H$_2$S. Table 8.13-2 shows emission factors for these other pollutants from sulfur recovery plants. These factors are expressed in units of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton) of sulfur produced. Test data are available for NOx, CO, and THC emissions for sulfur recovery plants with combustion-type control devices such as thermal incinerators or thermal oxidizers. All of the data available for NOx, CO, and THC are for units with tailgas clean-up units designed to increase the sulfur recovery efficiencies to 99.9 percent; however, the
emissions of these pollutants is not expected to be as closely tied to sulfur recovery efficiencies as emissions of SO\textsubscript{2}. Therefore, the emission factors in Table 8.13-2 are expected to be applicable to Claus sulfur recovery plants regardless of the number of stages.

Table 8.13-2 (Metric And English Units). EMISSION FACTORS FOR OTHER POLLUTANTS FOR CLAUS SULFUR RECOVERY PLANTS

<table>
<thead>
<tr>
<th>SCC(^{c})</th>
<th>Description</th>
<th>NO\textsubscript{x} Emissions(^{a})</th>
<th>CO Emissions(^{b})</th>
<th>THC Emissions(^{c,d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>301032</td>
<td>Controlled (e.g., incinerator)(^{f})</td>
<td>0.093</td>
<td>0.72</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.19</td>
<td>1.4</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Representativeness: Moderately, Moderately, Poorly

\(^{a}\) References 10, 11, and 13-31.
\(^{b}\) References 10-16, 18-22, and 24-32.
\(^{c}\) References 12, 14, 21, 22, 25, and 33.
\(^{d}\) THC emissions measured as propane by EPA Method 25A.
\(^{e}\) SCC = Source Classification Code. Emission factors were developed specifically for units with tail gas treatment units (e.g., SCC 30103204). The 6-digit SCC code is listed here as these data are expected to apply to all types of sulfur recovery units (30103201; 30103202; 30103203; 30103204; 30103299). The emissions factors are also expected to apply to other general sulfur recovery SCC codes such as 030603301 or 31000208.
\(^{f}\) The emission factors apply only to sulfur recovery units that are controlled with combustion-type control devices, e.g., thermal incinerators or thermal oxidizers.

References For Section 8.13

2. Written communication from Bruce Scott, Bruce Scott, Inc., San Rafael, CA, to David Hendricks, Pacific Environmental Services, Inc., Research Triangle Park, NC, February 28, 1992.


