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# Sulfur Recovery Technology

An overview of sulfur recovery by the Claus Process with information on flow scheme options, factors affecting sulfur recovery, operating parameters and typical plant deficiencies.

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## INTRODUCTION AND BACKGROUND

The production of sour natural gas and the refining of high sulfur content crude oils is increasing in the world today. The need to recover sulfur from hydrogen sulfide produced from such sources is also on the rise. In today's society there is an increased concern about the potential for air pollution to the well-being of mankind. Therefore various technologies for removing and converting hydrogen sulfide to elemental sulfur are gaining increasing importance in industry. The Claus process was invented by an English scientist named Carl Friedrich Claus and a patent was issued to him in late 1883. In 1938, a German company, I.G. Fabenindustrie A.G., made a significant modification to the original Claus process; and thus, the modified Claus Process was born. Today the majority of the gas that is processed in the United States and throughout the world, and the majority of sour crude oil refined in the world produces hydrogen sulfide which is eventually converted to elemental sulfur by the Claus process. Other technologies have emerged down through the years, but, none have ever come close to making the impact on industry that the Claus process has achieved. It is estimated that some 90 to 95% of recovered sulfur in the world today is produced by the Claus process. There are over 380 Claus plants (specific locations) in operation throughout the world. It is estimated that when these plants are in full production, something like 60,000 long tons per day (LTPD) of sulfur can be produced from these plants.

The Claus process was originally invented for the purpose of recovering sulfur values from a process for the production of soda by the Leblanc method. As years went by, the Claus process was applied to conversion of hydrogen sulfide to elemental sulfur for air pollution abatement purposes. In the late 1930's the Germans saw an opportunity to increase the efficiency of the process dramatically; and, the Claus process took on new meaning for air pollution abatement. In modern times the Claus process is considered to be a potential major air pollutant, since the process typically recovers only 95-97% of the hydrogen sulfide fed to it. New processes, called Tail Gas Clean up Processes, have come into being to increase the overall recovery of a Claus Unit plus a Tail Gas Cleanup Unit to values of 99% or greater.

## GENERAL PROCESS DESCRIPTIONS

### The Claus Process

The original Claus process involved preheating a catalyst bed and introducing a mixture of H<sub>2</sub>S and air (O<sub>2</sub>) over the bed at a somewhat constant temperature. The bed effluent gas was cooled and liquid sulfur was produced.

The overall sulfur recovery was very poor, and the heat of reaction was essentially dissipated to the atmosphere. With the advent of the modified Claus process, the efficiency was improved dramatically. The modification involved burning one third of the H<sub>2</sub>S to SO<sub>2</sub> in a furnace, and removing heat from the effluent gases in a Waste Heat Boiler. About 80% of the heat released could be recovered as useful energy. The cooled gases were then sent to the catalyst beds. The Claus process or modified Claus process is based on some fairly simple chemical reactions that occur both in a free flame (thermal) zone and a catalytic zone (Figure 1). In the burner of the Reaction Furnace, one third of the hydrogen sulfide is burned to sulfur dioxide and the remaining two thirds of the hydrogen sulfide, which was not combusted, undergoes the Claus reaction (in the thermal zone) to yield approximately 70% conversion of the H<sub>2</sub>S to diatomic sulfur vapor (S<sub>2</sub>). The theoretical conversion of hydrogen sulfide to elemental sulfur by the Claus process is depicted in Figure 2. Please notice that there is a thermal region and a catalytic region. In the thermal region, the % conversion is enhanced by higher temperatures, whereas in the catalytic region the inverse is true. Once the Claus reaction occurs in the thermal region, approximately 65-70% of the sulfur that entered in the process in the form of hydrogen sulfide is removed in the first sulfur condenser in the form of liquid elemental sulfur. The remaining gases then go through a series of reheating, conversion and cooling/condensing steps to yield an overall recovery of approximately 95-97%, depending upon the number of catalytic reaction stages and the type of reheat methods used. Figure 3 is an overall flow diagram showing a typical modern day Claus Sulfur Recovery Unit (SRU). In the catalytic converters, H<sub>2</sub>S and SO<sub>2</sub> react to yield further conversion of H<sub>2</sub>S to elemental sulfur. Different sulfur vapor species are formed in the cooler temperatures of the catalytic reactors than in the thermal reactor. Figure 4 demonstrates the relationships between the various major vapor species of sulfur at various temperatures. In addition to the oxidation of H<sub>2</sub>S to SO<sub>2</sub> and the reaction of that SO<sub>2</sub> with H<sub>2</sub>S in the Reaction Furnace, many other side reactions can and do occur in this furnace. Several of these possible side reactions are shown in Figure 5.

REACTION	TYPE REACTION
$H_2S + 3/2 O_2 \rightarrow SO_2 + H_2O$	BURN
$2H_2S + SO_2 \rightarrow 3/2 S_2 + 2H_2O$	CLAUS
$H_2S + 1/2 O_2 \rightarrow 1/2 S_2 + H_2O$	OVERALL
$2NH_3 + 3/2 O_2 \rightarrow N_2 + 3 H_2O$	AMMONIA
$CH_4 + 2 O_2 \rightarrow CO_2 + 2H_2O$	HYDROCARBON

Figure 1. Claus Plant reactions.

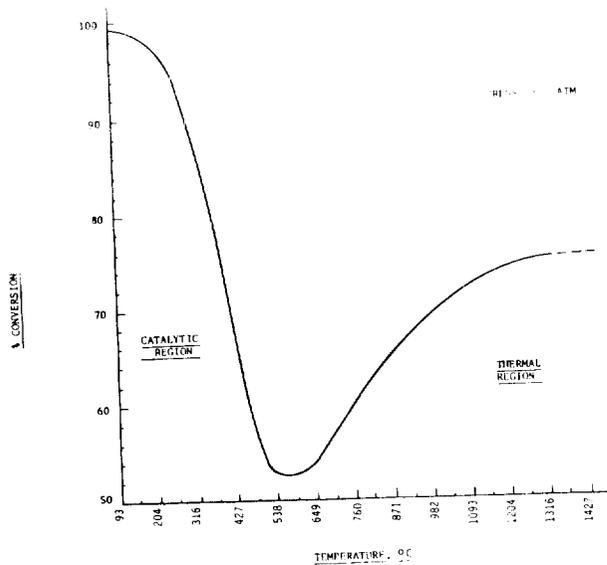


Figure 2. Theoretical conversion of  $H_2S$  to elemental sulfur by Claus Reaction<sup>1</sup> overall reaction:  $H_2S + 1/2 O_2 \rightarrow S + H_2O$ .

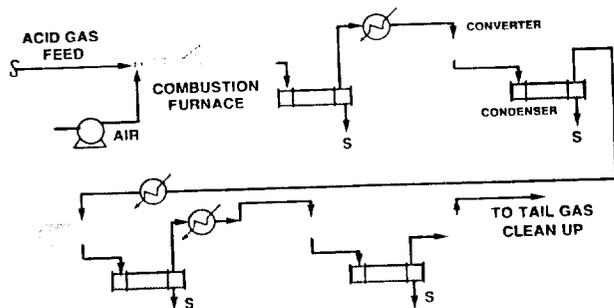


Figure 3. Conventional Claus sulfur recovery unit.

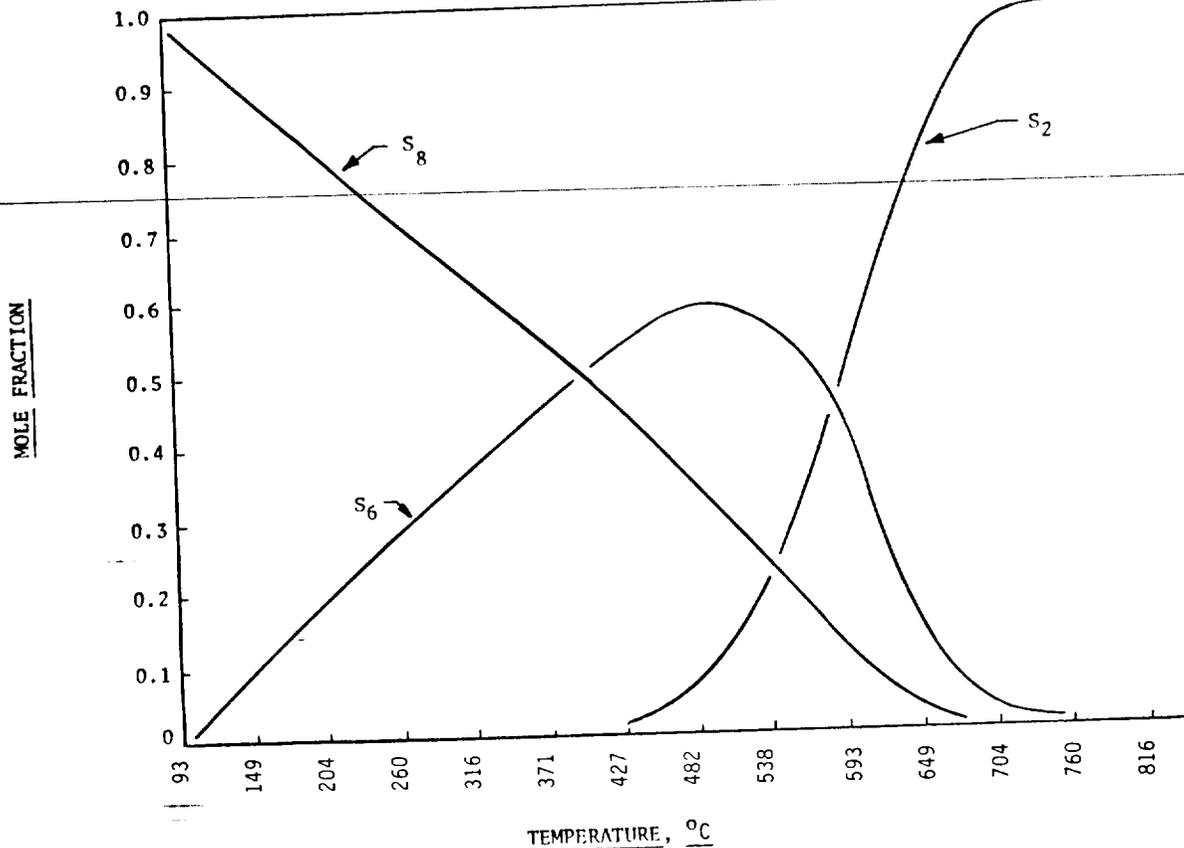


Figure 4. Equilibrium between the major molecular species of sulfur in vapor phase.<sup>1</sup>

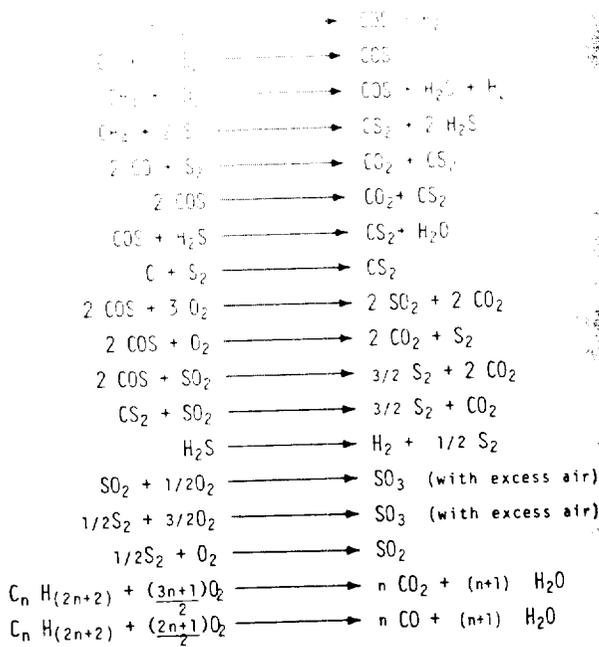


Figure 5. Claus process: typical possible side reactions.

If the acid gas feed to the Claus Sulfur Recovery Unit contains approximately 45 mol % or more hydrogen sulfide (on a wet basis), then a straight-through type configuration is typically used. At  $H_2S$  concentrations below 40 mol %, a split-stream type Claus process configuration is typically used. Modern day Claus units typically employ one thermal reactor stage and three catalytic conversion stages. If the Sulfur Recovery Unit is located in a gas processing plant, the type of reheat employed is typi-

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ally either auxiliary burners or reheat exchangers, with steam reheat being used occasionally. If the Sulfur Recovery Unit is located in a refinery, the typical reheat scheme uses 400-600 psig steam for reheating purposes. The type of reheat used has a significant impact on the amount of overall sulfur recovery achieved.

#### Other Types of Sulfur Recovery Processes

Due to the occurrence of very dilute hydrogen sulfide streams in certain industrial applications, a group of processes has emerged which basically employ the Claus process chemistry, but are conducted in a manner somewhat different than the process configuration described above. In the late 1950's, AMOCO introduced a process called the Direct Oxidation Process. This process did not use a thermal reactor, but only catalytic stages. Due to the extreme sensitivity of the process to the highly exothermic reactions across the first catalyst bed and the usual occurrence of hydrocarbons in such feed gas streams, the process set with much difficulty in the few commercial applications built. In 1959 a process was introduced in England called the Stretford process. It was primarily designed for the removal of hydrogen sulfide from brewery sewage gases and manufactured gases in England. This process uses a wet chemistry (red/ox) technique for reacting hydrogen sulfide with oxygen in the presence of vanadium and other reaction promoters. The Stretford process was brought to the United States in the mid to late 1960's and was applied to several applications which were different from those originally encountered in England. The few Stretford plants that were built for direct treatment of sour natural gas and resultant production of elemental sulfur have met with much difficulty and usually have not been successful. The Stretford process has been applied to Tail Gas Cleanup Processes, which will be talked about in a later paper, and has found general success in that application. In modern day times, another version of the Claus process has emerged which is called the Cold Bed Sub-dewpoint type processes. This technique takes advantage of the enhanced Claus conversion at cooler temperatures in the catalytic stages, and allows the catalyst to operate actually below the sulfur dewpoint, with a resultant deposition of liquid sulfur on the catalyst. Eventually the liquid sulfur poisons the activity of the catalyst, and the beds must be switched and regenerated with a cyclic type of flow configuration. Troublesome switching valves have been employed to accomplish bed cycling.

#### MODERN DAY INNOVATIONS

##### Cold Bed Sub-dewpoint Processes

The Cold Bed Sub-dewpoint type Claus processes have come into favor, especially for large Sulfur Recovery Units in Canada, France and Germany. The first such process to be introduced was called Sulfreen. It was introduced and developed by SNEA(P) and Lurgi of Europe in the late 1960's. Several large Sulfreen units were built in Canada, and have been extremely successful in their operation for achieving something like 98-99% overall recovery when following a 2-stage or 3-stage Claus Sulfur Recovery Unit. In the early 1970's, AMOCO introduced their CBA (Cold Bed Adsorption) process which is quite similar to the Sulfreen process, but uses a regeneration stream which is indigenous to the process rather than an external recirculation loop as used in the Sulfreen scheme. A further improvement on the CBA technique was introduced by MCRC or Delta Projects Ltd. in the early 1980's and was named the MCRC Process. In this scheme, there is no regeneration gas as such; but, there is a sequence of switching beds so that the hot portion of the process gas first comes in contact with the bed to be regenerated and then flows through the subsequent beds (on adsorption)

in series. All of these Cold Bed Sub-dewpoint processes give typical overall sulfur recoveries of 98-99%, when following downstream of a typical 2-bed or 3-bed Claus Sulfur Recovery Unit. It is our understanding that Davy McKee International has introduced a similar process a few years ago in Europe called the Maxisulf Process (one plant), which uses the Cold Bed Sub-dewpoint type of concept. These processes will be described in more detail in a later paper.

##### Selectox Process

In early 1978, The Ralph M. Parsons Company built the world's first BSR/Selectox Tail Gas Cleanup Process Unit for a company called Wintershall A.G. at a refinery at Lingen, W. Germany. The demonstration of the Selectox catalyst in such an application was highly successful and led to further development of the Recycle Selectox process. In late 1981, the world's first Recycle Selectox Plant was placed on stream for the Sid Richardson Carbon and Gasoline Company in Kermit, Texas. Selectox is a process which is all catalytic in nature and does not employ the burning (combustion) of a portion of the hydrogen sulfide to SO<sub>2</sub> in a thermal reactor. Instead the acid gas feed, which typically contains less than 20-40 Mol % hydrogen sulfide, is preheated and mixed with a stoichiometric amount of air (oxygen) and fed to a Selectox catalyst bed. Highly exothermic reactions occur across the Selectox bed. A severe temperature rise would occur, except for the use of a Recycle Blower, which takes a portion of the first condenser gas effluent, and recycles it back to the inlet of the Selectox bed. Selectox was developed primarily for utilization on lean acid gas streams which typically will not support combustion of one third of the hydrogen sulfide to SO<sub>2</sub>. However, it can be applied to much richer streams (40-70 Mol % H<sub>2</sub>S) in small applications. The Sid Richardson Selectox plant (13 mol % H<sub>2</sub>S and 20 LTPD) has been in operation for over four years, and has had an extremely high on-stream factor and a very successful operation. Figure 6 is a simplified flow diagram of a Recycle Selectox SRU.

##### Oxygen Enrichment (COPE<sup>SM</sup>) Process

For many years the value of substituting oxygen for air in a Claus type plant has been realized, and papers on this subject have appeared in the literature. In March 1985, Goar, Arrington & Associates, Inc. and Air Products and Chemicals, Inc. introduced the COPE<sup>SM</sup> (Claus Oxygen-based Process Expansion) process to industry. This process permits the utilization of up to 100% oxygen in lieu of the air stream for oxidation of H<sub>2</sub>S to SO<sub>2</sub> in the Reaction Furnace. The use of O<sub>2</sub> gives an increase in H<sub>2</sub>S handling capacity and a significant reduction in the tail gas volume from a Claus unit, due to the elimination of nitrogen present in the air stream. The unique feature of the COPE process is the utilization of a Recycle Blower to take a portion of the No. 1 Condenser effluent and recycle it back to the burner of the Reaction Furnace to act as the flame moderant or coolant to keep the temperature rise in the furnace under control. A U.S. patent on this technique has been issued. Also, a special proprietary burner (to safely handle the O<sub>2</sub>) is used in the process. The COPE process may be used in a typical refinery Sulfur Recovery Unit application (80 ± % H<sub>2</sub>S) to double the capacity of the unit for handling H<sub>2</sub>S, and at the same time to reduce the tail gas volume to approximately 75-80% of what the tail gas flow was when handling the original design basis of acid gas feed and using air. At the same time, there is a dramatic reduction in the utility requirements of the downstream tail gas unit; and, savings in utilities of the TGCU Unit can approach, or possibly even completely offset, the cost of purchased oxygen. It is believed in some applications, that the

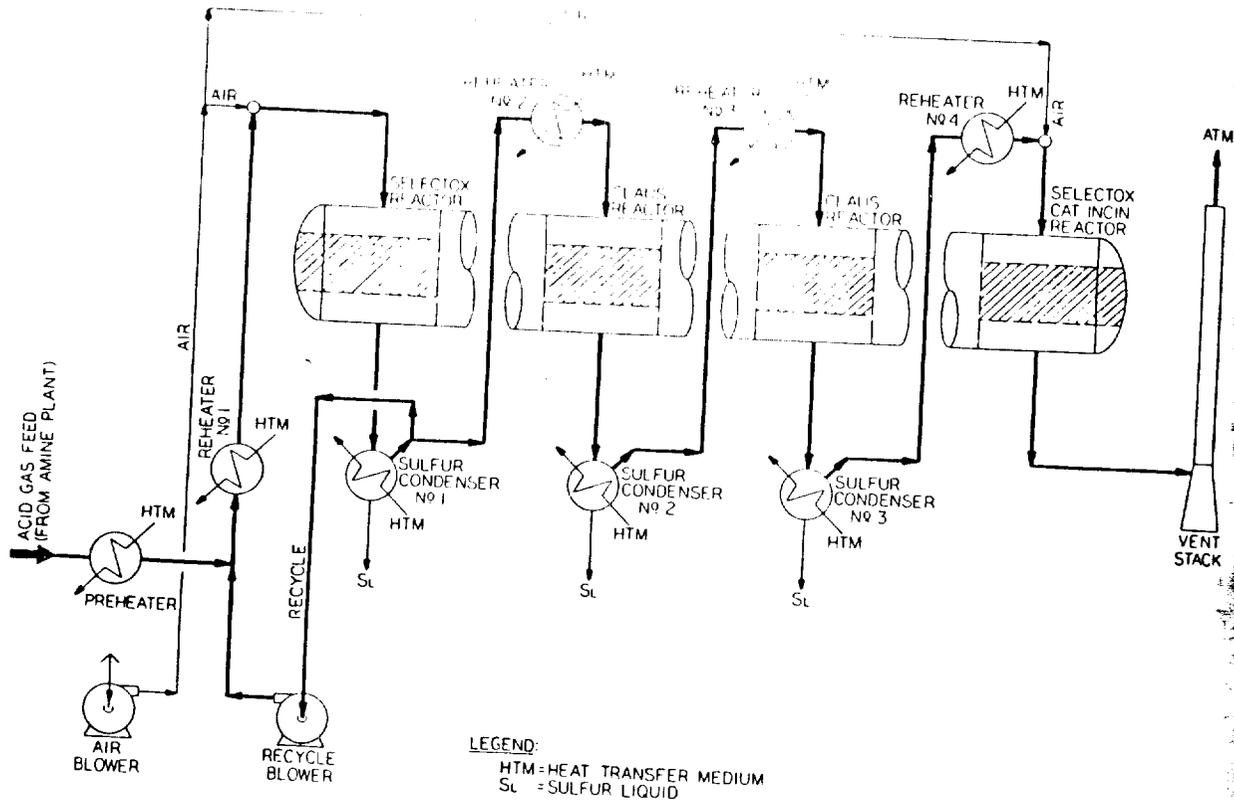


Figure 6. Recycle selectox sulfur recovery process. Simplified process flow diagram.

amount of SO<sub>2</sub> emissions can be reduced (in absolute value) when handling essentially twice the amount of H<sub>2</sub>S in a Claus unit employing the COPE process. Two commercial units have been in operation now for several months in a major oil company's Gulf Coast refinery. The first was commissioned in March 1985. It is felt that the COPE process should be considered for new grass roots plants, as well as retrofits to existing plants that require more capacity. Figure 7 is a simplified flow diagram of the COPE process.

#### LO-CAT Process

The ARI "LO-CAT" process was introduced to industry approximately 10 years ago. This process utilizes an iron chelate system to remove H<sub>2</sub>S directly from a gas stream by an oxidation/reduction reaction where the H<sub>2</sub>S is converted directly to solid sulfur in the aqueous solution. It is believed that the LO-CAT process is most applicable to very lean streams that contain less than 1 to 2 LTPD of sulfur, and which do not require the production of a marketable sulfur product. Most LO-CAT units built to date have met with operational difficulty and relatively high chemical usage costs. Also, the sulfur produced typically must be disposed of in a landfill or by other means.

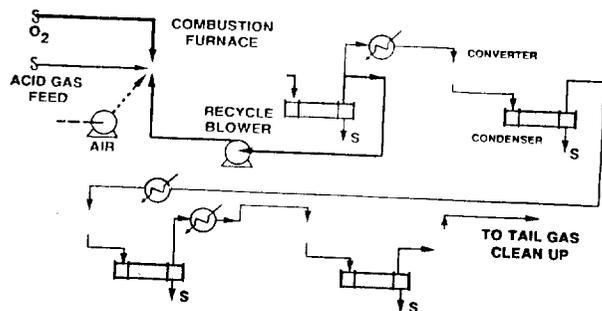


Figure 7. COPE<sup>SM</sup> sulfur recovery unit.

#### Selective Caustic Process

Selective caustic treating has been used in the industry to remove H<sub>2</sub>S from a gas stream. This is typically not a sulfur recovery process, but a sulfur removal technique which is discussed in the literature.

#### SUMMARY AND CONCLUSION

In summary, it may be said that the Claus process has been the true major workhorse in the sulfur recovery industry for over 100 years. It has had many innovations and many changes since its introduction in late 1883. Most of the newer techniques have been aimed at improving the overall recovery of the process and yielding lower emissions at the same time, while producing sulfur for a higher economical return (ROI). The large majority of hydrogen sulfide produced in the world today is converted to elemental sulfur by the Claus process. It is anticipated that the Claus process will continue to be of major importance to the sour gas and sour crude refining industries in the future. The smallest sulfur recovery train built in the world is approximately 2 LTPD; and, the largest sulfur train is approximately 1,750 LTPD. There are over 380 sulfur recovery units located throughout the world. The average size of these will vary from 50 to 200 LTPD in the United States, and from 1000 to 1500 LTPD in Canada. Elemental sulfur is an essential element to mankind. World sulfur demand is predicted to exceed the known supply through the year 2000, unless new sulfur reserves or production are found. It is believed that the Claus process will continue to be a significant process well into the future. Other improvements are sure to be made.

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