

- **Man-Made Sources of Sulfur**

Although the quantity of sulfur emitted into atmosphere and sulfur cycle due to human activities is very easy to quantify as compared to natural sources, the majority of man-made sulfur resources are due to fossil fuel (like coal, natural gas and petroleum) burning, smelting of ores (nonferrous metals) and various industrial/burning processes. Man-made sulfur emissions into atmosphere began to increase extensively during the 20th century. The increasing trend continued until the 1970s, after which environmental regulations on sulfur emissions were imposed in America and Europe.

Although environmental regulations decreased sulfur emissions; however, it did not eliminate the problems completely.

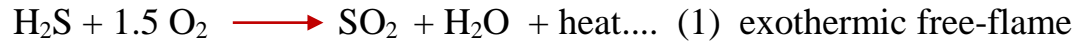
1- Natural Gas

The recovery of sulfur from natural gas starts with H_2S separation. The separation of H_2S is necessary due to its toxicity and corrosive nature. The natural gas constituting H_2S is called sour gas which is made to pass from a solvent (like amines) in which H_2S dissolves and the required percentage of natural gas remains insoluble. Then, the solvent is heated causing H_2S to be removed from the solution. After the separation of several component of natural gas, H_2S is then converted into sulfur by processes like **Claus**. This method produces elemental sulfur as a by-product material.

The Claus process consist of two principal stages:

A- The first stage:

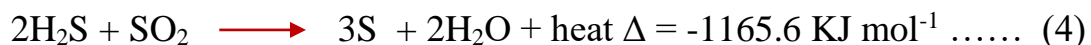
- 1-** A non-catalytic combustion reaction in which one-third of the H_2S in the feed gas is burned in air at a reactor furnace to form sulfur dioxide (SO_2) and water, according to the following reaction:



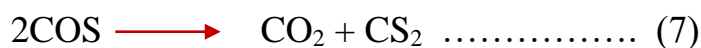
- 2- The furnace normally operates at combustion chamber with temperatures ranging from 980-1540°C and pressures rarely higher than 70 kilopascals (KPa).
- 3- The hot gas from the combustion chamber, cooled by producing high to medium pressure steam in a waste heat boiler, through entering hot gas to condenser.
- 4- The hot gases cool to approximately 325°F, condensing most of the sulfur as liquid Sulfur.
- 5- About 80 percent of the heat released could be recovered as useful energy.
- 6- The resultant Liquid sulfur is removed from the condenser and flows by gravity to a sulfur storage tank. Here it is kept molten, at approximately 280°F, by steam coils.
- 7- Liquid sulfur pumped to trucks or railcars for shipment to end users.
- 8- The remaining cooled gases exiting the condenser are then sent to the catalyst beds at the second stage.

B- The Second stage:

- 1- The remaining uncombusted two-thirds of the hydrogen sulfide undergoes to Claus reaction (remaining gas H_2S reacts with SO_2 generated from the first stage reactions are reheated and enters the first catalytic reactor) to form elemental sulfur as follows:

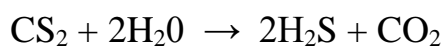
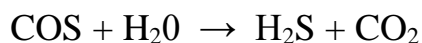


- 2- The catalytic reactors operate done at lower temperatures, ranging from 200 to 315°C. {catalysts are used like: Alumina oxide Al_2O_3 (III) or titanium dioxide (IV) TiO_2 , called **titania catalysts**}.
- 3- At second stage: it is not possible for a Claus plant to convert all sulfur compounds to elemental sulfur.
- 4- Therefore, two or more stages are used in series to recover the sulfur.
- 5- Each catalytic stage can recover half or two-thirds of the incoming sulfur.
- 6- 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 like:



Note:

- 1- Gases with an H_2S content of over 25% are suitable for the recovery of sulfur in straight-through Claus process units.
- 2- The alumina catalyst owes its activity to a very high surface area of 300 m^2/g or higher. About 95 % of that surface area is provided by pores having diameters of less than 8 nm (80 angstroms).
- 3- The catalyst will act to hydrolyzes the carbonyl sulfide (COS) and carbon disulfide (CS_2) that is formed in the reaction furnace:



- 4- Most of the hydrolysis occurs in the first Claus reactor.
- 5- **titania catalysts** and are said to be:

- a- more resistant to thermal aging than the alumina catalysts.
- b- They are also said to have a higher activity for the hydrolysis of COS and CS₂.
- c- higher activity allows the first Claus reactor to operate at lower temperatures compared to alumina catalysts.
- d- However, they are significantly more expensive than the alumina catalysts.

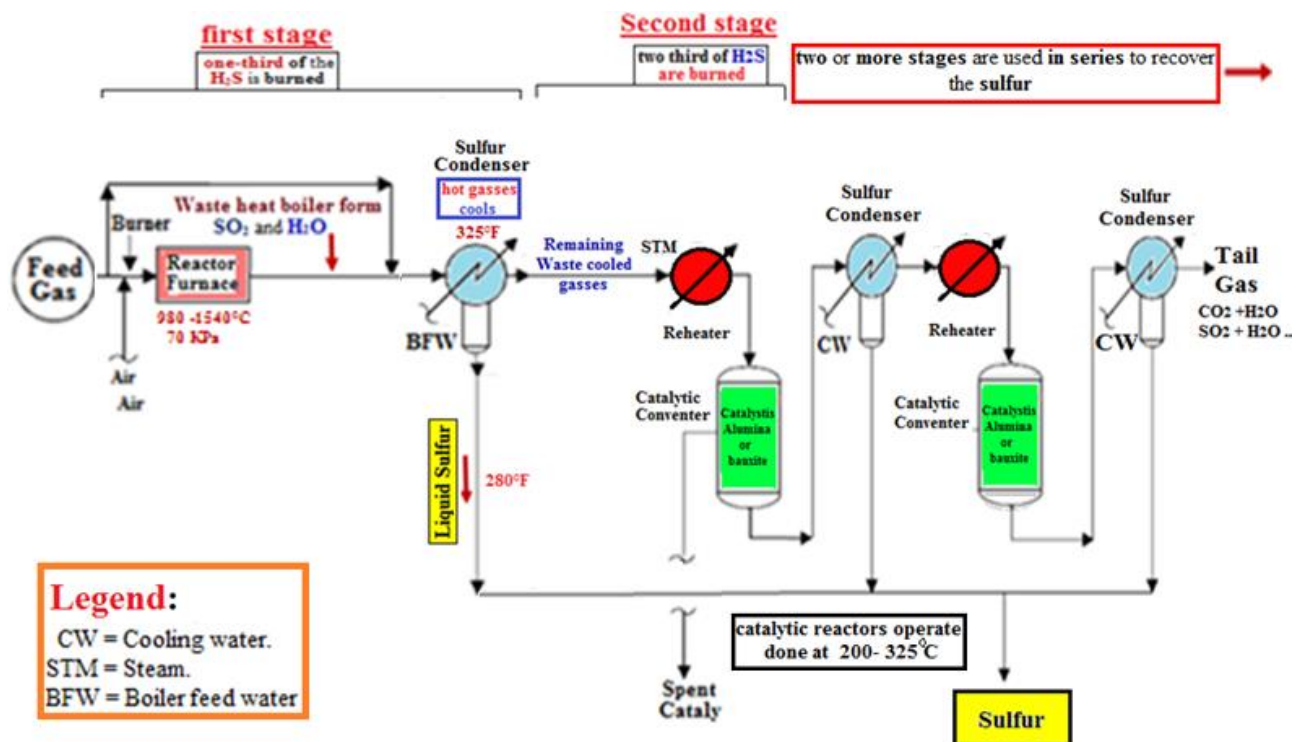


Figure2. Typical Claus sulfur recovery unit.

2- Petroleum

Crude oil generally constitutes carbon (84%), hydrogen (14%), sulfur (1–3%) and nitrogen/oxygen/metals/salt (<1%). The petroleum refining process causes sulfur to separate from the various organic compounds in the form of H₂S. Until the

environmental regulations of the 1970s, H₂S was used as refining fuel which was obtained during the refining process. This process was limited as burned H₂S releases sulfur dioxide into atmosphere. In general, The H₂S produced in oil/petroleum refinery can be further processed to produce elemental sulfur.

Two theory behind origin of Sulfur and Sulfur compounds in crude oil:

1- Sulfur creates generally from the decomposition of organic matter, and with the passage of time and of gradual settling into strata, the sulfur segregates from crude oil in the form of hydrogen sulfide that appears in the associated gas, and some portion of sulfur stays with the liquid.

2- Sulfur creates from the reduction of sulfates as:

First: reduction of sulfates (SO₄) by hydrogen (H) and by bacterial action of the type (desulforibrio desulfuricans):



(H): comes from the reservoir fluid.

(SO₄): are kept in the reservoir rock.

As a result, hydrogen sulfide (H₂S) is generated.

Second: H₂S formed can react with the sulfates or rock to form sulfur:



Third: The remains of H₂S in composition of crude, under the conditions of pressure, temperature and period of formation of the reservoir H₂S:

(H₂S) also can react with the hydrocarbons to give sulfur compounds.

Sulfur compounds are the most important non-hydrocarbon heteroatom.

There is a relationship between sulfur content and density of crude oil as below:

a- the higher the density of the crude oil, well be the higher the sulfur content.

- b-** The total sulfur in crude oil can vary from: 0.04% w/w for light crude oil to about 5% w/w for heavy crude oil and tar sand bitumen.

The sulfur compounds determined in crude oil are classified into chemical groups like:

a. Free elemental sulfur (S):

Free elemental sulfur is rarely found in crude oil; however, it can be present in a suspension or dissolved in the liquid. While crude oil is heated, partially reacts with hydrocarbons and the result will be separating of Sulfur:



b. Hydrogen sulfide (H₂S):

H₂S is found in reservoir gas and dissolved in the reservoir liquid (<50 ppm By weight). Often the appearance of H₂S in petroleum fractions is a consequence of thermal decomposition of organosulfur compounds.

c. Thiols

Thiols or mercaptans: are organosulfur compounds that contain a sulfhydryl group (SH), that is composed of a sulfur atom and a hydrogen atom attached to a carbon atom. It should be noted that the content of mercaptans in crude varies from 0.1 -15 % mass from total content of sulfur compounds.

d. Sulfides:

The sulfides: are organosulfur compounds which can have a linear or ring structure. The boiling points of sulfides are higher than of mercaptans (for molecules of equal carbon number). The bulk of sulfur containing in the kerosene and gas oil is equal to 50-80% of total sulfur compounds.

e. Disulfides:

The disulfides (general formula: $R - S - S - R$) are found in small quantities in petroleum fractions with a boiling point up to 300°C . They account for 7-15% of the total sulfur.

3- Oil Sands

One of the problems of oil sand reserves development is a rise of sulfur and nitrogen deposition in that region. Mainly this oil is intensely buried and steam injection is needed which causes a variety of emissions including H_2S , CO_2 and H_2 . Sands contribute to a significant source of sulfur, which are predominantly found in Canada where approximately 300 billion barrels of extractable oil having 3.5–5% sulfur. Generally, oil sands are a combined form of bitumen, clay, water and sand. Oil sands having 10% and 7% bitumen are considered to be rich and not cost effective. The improvement of oil sand refinery must be done to obtain a significant amount of sulfur. In particular, it could be said that the production of H_2S is under special attention as on the one hand, it plays a role in oil partial desulphurization and on the other hand, due to its toxicity, there is some difficulty to handle and transport it.

4- Sulfide Smelting

Combined sulfur can be obtained through nonferrous metal smelting. Smelter gases having SO_2 is transformed into H_2SO_4 and liquid sulfur. In the US (1990), approximately 11% of sulfur was produced through H_2SO_4 obtained from smelting nonferrous metals. Sulfur can also be obtained from SO_2 emissions. In order to obtain useful sulfur or to dispose it, the desulfurization process can be applied which uses compounds like CaO , NaCO_3 , MgO to get SO_2 while it produces elemental sulfur, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, liquid sulfur and H_2SO_4 . Figure 3 shows a schematic shape of flash smelting furnace where the slag component is mixed with sulfate mineral

concentrate which will be injected into the furnace with enriched oxygen until oxidation reaction shapes. Thereafter, the molten matte and slag which are heavier will be separated and fall down to the bottom of the furnace.

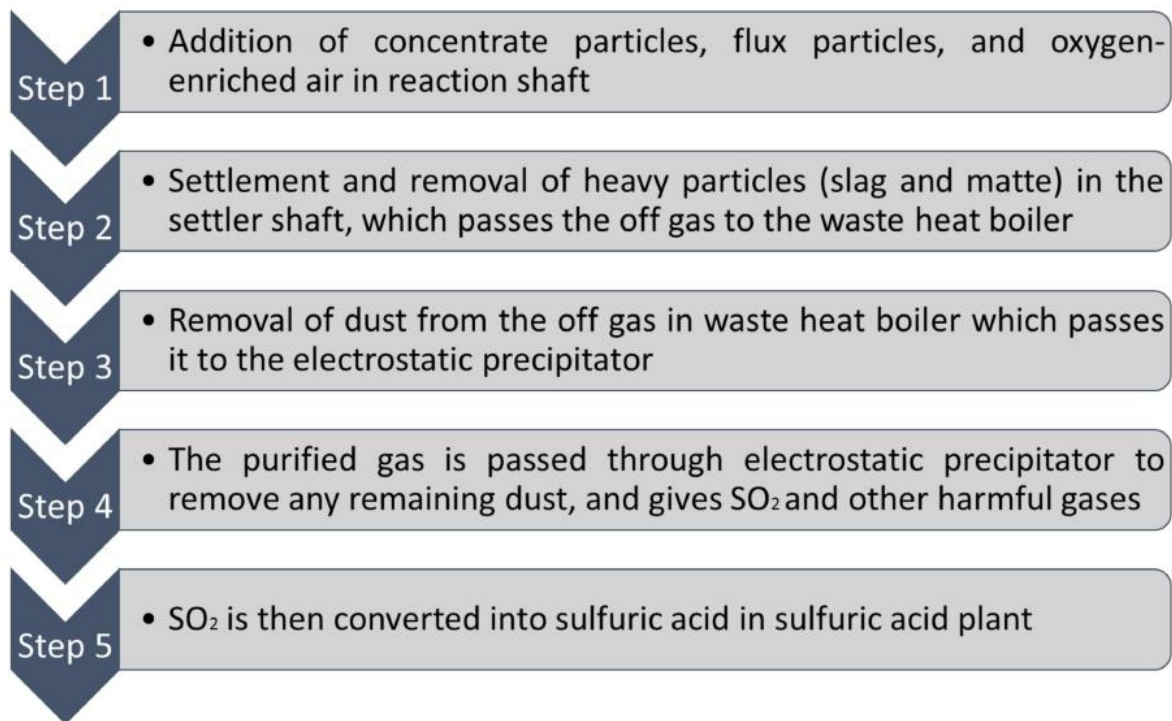


Figure 3. Schematic of Flash Smelting Furnace

This process makes SO₂ and other harmful emissions. Throughout the process, the gas given off is converted to sulfuric acid, which can be used as a by-product.

5- Coal:

Coal known as solid fossil fuel, much of the sulfur in low sulfur coal derives from the sulfur content of the plant material making up the original peat. Sulfur contents in coal greater than the sulfur derive from the depositional environment. Sea water or brackish water in the coal beds also contain sulfur as sulfates.

The sulfates undergo bacterial reduction changed to H_2S which reacts:

- (1) React with iron in the water to form pyrite.
- (2) React with the organic material or the sulfate reducing bacteria to form the organic sulfur structures.

In solid fossil fuels (such as coals ranking from brown coals and lignite up to anthracite, peat and other forms like oil shale's *etc.*,) sulfur is present as:

a- Two inorganic forms, being as:

- Sulfide like: pyritic sulfur (FeS_2).
- Sulfate like: (Na_2SO_4 , $CaSO_4$, $FeSO_4$).

b- Organic Sulfur is bound in these fuels as:

- Organic compounds like: sulfide, mercaptans, disulfide, thiophenes.
- Present as gases like: hydrogen sulfide (H_2S) and carbonyl sulfide (COS) in petroleum, heavy fuel oils and natural gas generally.

c- Small amounts of elemental sulfur.

d- Sulfur in organic structures of a variety of types.

e- Biomass fuels such as waste wood, bagasse (residual from sugar cane) contain very small amounts of sulfur.

Note: The removal of the organic sulfur from organic sulfur structures in coal is much more difficult than the Pyritic Sulfur, because it is part of the organic coal structure itself.

6- Origin of Sulfur in Sedimentary Environment:

Sulfur occurs most abundantly in Sedimentary environments as:

- 1-** A decomposition product of sulfide components, like Pyrite (iron sulfide) and Galena (lead sulfide).

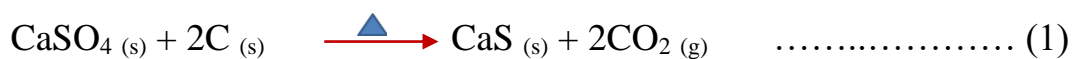
- 2- A bed associated with limestone and gypsum. The Sulfurs deposits in gypsum beds may result from reduction of the gypsum by organic matter and reduction bacteria.

Deposits of gypsum and anhydrite are processed by anaerobic bacteria, especially where hydrocarbons are available as food for the bacteria, which reduce the sulfate to sulfur (SO_4 to S), with the emission of CO_2 and H_2S :

- a- The CO_2 reacts with the calcium present to make the mineral calcite, and limestone. $\text{Ca} + \text{CO}_2 \longrightarrow \text{CaCO}_3$ (Calcite)
- b- The H_2S may escape, or especially if trapped, may be oxidized by oxygen-containing surface waters that have ^(a)percolated into the area to elemental sulfur, ^(b)or by biological action.
- c- In this way, bedded sulfur is created, associated with limestone and gypsum or anhydrite.

The basic steps of the sulfur recovery process from gypsum (at the Lab.) are:

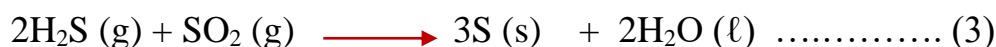
- 1- Reduction of gypsum (CaSO_4) to calcium sulfide using reducing agents, for example, coal (C) or activated carbon (Eq. (1)):

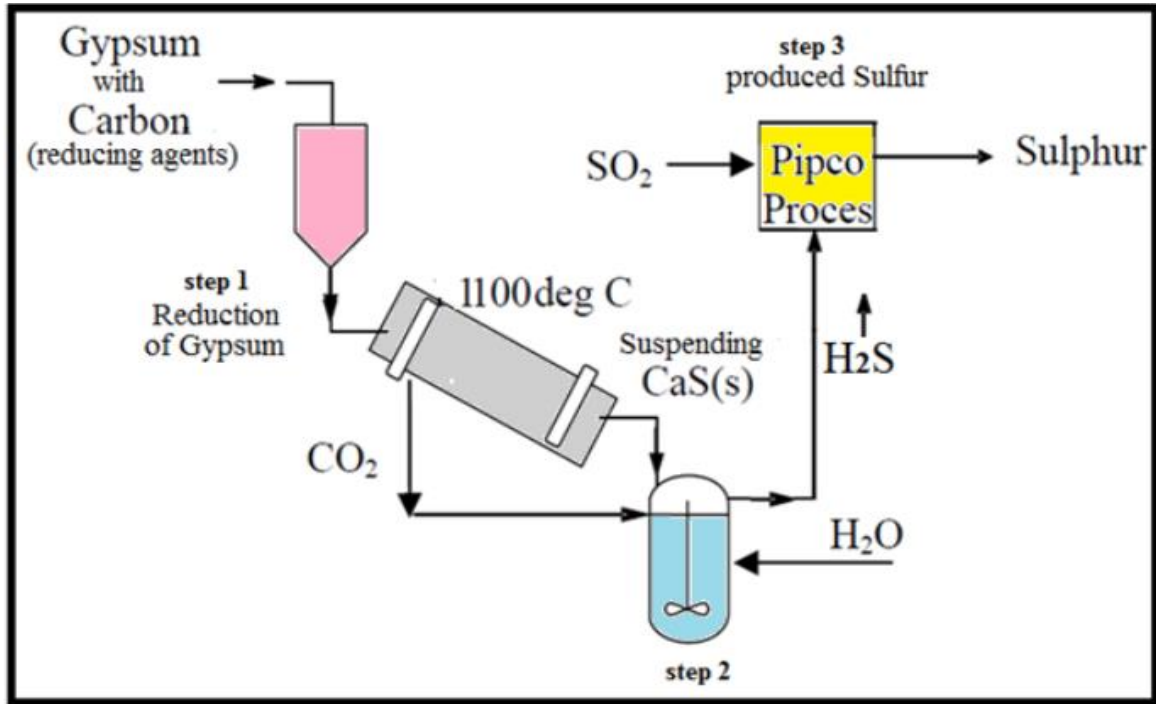


- 2- Suspending the calcium sulfide obtained (CaS) from Eq. (1), reacted with water (H_2O) to form H_2S , which is stripped off with CO_2 (Eq. (2))



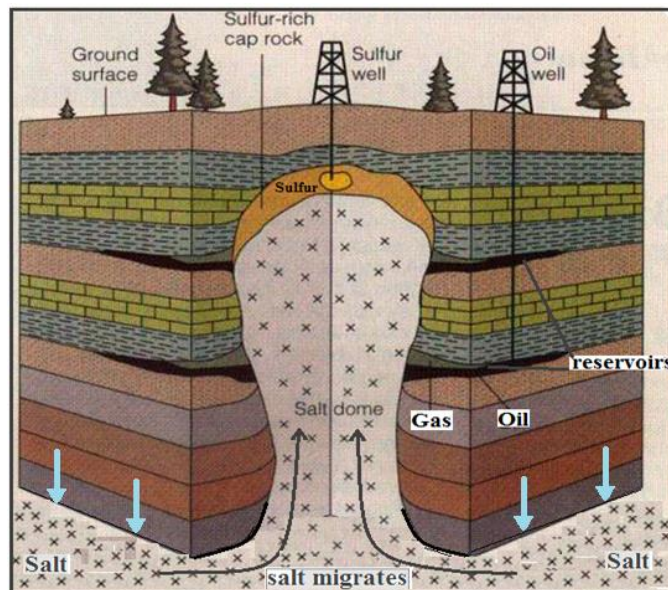
- 3- H_2S gas reacted with SO_2 gas and produced Sulfur (Eq. (3)):





Create of Sulfur:

- 1- Salt domes are made of marine evaporate deposits.
- 2- These domes are mostly composed of salts and other evaporate minerals, including halite, calcite, gypsum, and anhydrite.



- 3- When the salt rises up it will be in contact with meteoric ground water which will preferentially dissolve and carry away Salt Halite (NaCl) as the most soluble mineral there.
- 4- Hence, the concentration of less soluble evaporates rises in the upper part of the salt dome (as cap rock).
- 5- The Salt Domes from the upper part to the lower part of the cap are usually composed of:
 - a- Salt-Halite (NaCl), which is the most soluble evaporate.
 - b- Calcite (CaCO₃).
 - c- Gypsum (CaSO₄.2H₂O).
 - d- Anhydrite (CaSO₄).
- 6- Crude oil is often associated with salt domes.
- 7- Oil and other hydrocarbons are lightweight and tend to migrate upward.
- 8- Oil reservoirs form when there is a trap.
- 9- The common structural traps for oil are salt domes.
- 10- Seepage hydrocarbons help as energy source for certain bacteria as food and undertake certain chemical reactions (which in simplified form look like):



- 11- Waste product of the bacterial metabolism, like hydrogen sulfide (H₂S) will react with oxygen (O₂) to form elemental sulfur (S):



