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SULFUR RECOVERY FROM ACID GAS BY THE CLAUS PROCCES USING ASPEN HYSYS

This thesis is submitted in partial fulfillment of the requirements for the degree of Bachelor in Degree in Transportation and Refining Engineering

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الآية

قال تعالى:

{ يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ وَاللَّهُ
بِمَا تَعْمَلُونَ خَبِيرٌ }

[المجادلة: 11]

DEDICATION

Most importantly we want to thank Allah for blessing us with graces, health and determination. We dedicate this project to our mothers and fathers for giving us love, patience, support and being the backbone to our achievements. Also, our siblings, we show our sincere appreciation and love. May Allah shower them with life full of blessings and happiness.

Contents

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENT

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ABSTRACT

Due to the many environmental impacts caused by oil refineries worldwide, and the severity of it mainly due to gas flaring of harmful gases such as acid gas, A Sulphur recovery unit consisting of a burner and then a number of reactors to increase the efficiency was used. The study is carried out following standard scientific approach of theoretical study; a simulation was done using Aspen HYSYS which yielded material and energy balance for the process, and optimum oxygen needed as well as overall efficiency which was 97.5%

المستخلص

بسبب المضرات الطبيعة التي تسبب بها مصافي النفط في جميع أرجاء العالم من الكميات الكبيرة التي يتم حرقها من الغازات المضرة ومن أهمهم هو الغاز الحمضي، تم استخدام وحدة استخلاص الكبريت لمعالجته، وتم محاكاة العملية باستخدام برنامج المحاكاة Aspen HYSYS باستخدامه تم الحصول على نتائج موازنة الطاقة والكتلة و أيجاد الكفاءة للعملية التي وصلت الا 97.5% وكمية الاكسوجين المثالية لاستخدام العملية.

CHAPTER 1

INTRODUCTION

1.1 Background

Sulfur removing has become a serious issue in the chemical processing industry because of the lower limits of sulfur content in gasoline, diesel and jet fuels that is being regulated by governments. It is known that H2S in the environment causes health threats, such as, irritation in the breathing system, skin and eyes.H2S is the source of generating a numerous hazardous chemical compounds such as SO2, H2SO3 and H2SO4, therefore, H2S removal is environmentally beneficial and plays an important role in the air pollution.

Raw natural gas is one of the main sources of H2S. Furthermore, of the main impurities that lead to acid rain is SO2.Most of the refineries are using Claus unit for sulfur recovery, particularly for refineries which have a high sulfur content in their crude. In refineries, the element of sulfur converts to H2S in hydrogenation process. After that, H2S goes to sulfur recovery unit and in this step commercial sulfur will produce. Claus process Isa widely used technology for recovering sulfur and energy from acid gases. It is conventionally divided into thermal and catalytic stages in order to achieve very high conversion of acid gas.

The total annual world production of sulfur, as of 2015, was 70 million metric tons. The principal use of sulfur is in the production of sulfuric acid, and is used in a number of specialty applications, although the major end product is for use in fertilizer.

Energy conservation has always been important to the oil and gas industry, but is becoming increasingly critical in the current low oil prices climate. Sulphur recovery facilities are necessary to meet emissions regulations and are therefore often viewed as a cost of production.

However, the Sulphur plant is normally a net energy exporter providing a frequently overlooked benefit to the energy balance of the processing complex. This is because the Claus reaction, which is employed to convert H2S to elemental Sulphur is exothermic, and the waste heat generated from the process can be recovery as steam.

1.2 Statement of the problem

The high emission rates of SO2 and H2S has been an increasing concern for many nations, due to its many adverse health effect and environmental damage it causes.

So instead of just burning up anything that is of no use it can e converted instead into something more useful.

1.3 Research objectives

1.3.1General objectives

The main objective of this thesis is to perform a simulation of sulfur recovery by the Claus process using Aspen HYSYS.

1.3.2 Specific objectives

- To determine the percentage of sulfur recovered from the initial feed.
- To estimate the optimum oxygen needed required to run the process.
- To determine the composition of the remaining feed stream
- To determine the steam generated from the heat exchanger.

1.4 Thesis outline

From the introduction given in this chapter, this thesis has four additional chapters. Chapter 2, which presents a review of related literature of previous studies on this topic. Chapter 3 presents the empirical findings while chapter 4 presents a discussion of the empirical findings in relation to the theoretical framework. The last chapter of the thesis gives the conclusions drawn from the discussion of the findings and also outlines some recommendations.

CHAPTER 2

LITERATURE REVIEW& THEORETICAL FRAMEWORK

2.1 Claus process

This is an integral unit in most modern refineries, which must adhere to the strict laws and regulations of their government of the maximum allowed emission of SO2 in the atmosphere to prevent present and future environmental damage, thus affecting the wild life and humans alike. In some cases, it seen as an unnecessarily cost which just discourage the investors and hinder the viability of going through the project, so they just opt against constructing the SRU such is the case in Sudan.

This an issue caused by either insufficient study on its feasibility, due to lack of awareness of the process itself or the disregard of the investors of the environmental impacts due to more lenient laws which allow gas flaring without any serious monitoring. The composition of the crude itself doesn't warrant the use of this technology which is more understandable, although this can be argued as an excellent reason, the ability to protect our future no matter how small our affect is, shouldn't we as humans utilize it even at our financial cost.

The Claus process is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. First patented in 1883 by the chemist Carl Friedrich Claus, the Claus process has become the industry standard. C. F. Claus was born in Kassel in the German State of Hessen in 1827, and studied chemistry in Marburg before he immigrated to England in 1852. Claus died in London in the year 1900. [1]

The multi-step Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the by-product gases containing hydrogen sulfide derived from refining crude oil and other industrial processes. The by-product gases mainly originate from physical and chemical gas treatment units (Selexol, Rectisol, Purisol and amine scrubbers) in refineries, natural gas processing plants and gasification or synthesis gas plants.

These by-product gases may also contain hydrogen cyanide, hydrocarbons, sulfur dioxide or ammonia.

Gases with an H2S content of over 25% are suitable for the recovery of sulfur in straight-through Claus plants while alternate configurations such as a split-flow set up or feed and air preheating can be used to process leaner feeds. [2]

Hydrogen sulfide produced, for example, in the hydro-desulfurization of refinery naphtha and other petroleum oils, is converted to sulfur in Claus plants. [3] The reaction proceeds in two steps:

$2\ H_2S + 3\ O_2 \rightarrow 2\ SO_2 + 2\ H_2O$

$4\ H_2S + 2\ SO_2 \rightarrow 3\ S_2 + 4\ H_2O$

The vast majority of the 64,000,000 tons of sulfur produced worldwide in 2005 was byproduct sulfur from refineries and other hydrocarbon processing plants.[4] Sulfur is used for manufacturing sulfuric acid, medicine, cosmetics, fertilizers and rubber products. Elemental sulfur is used as fertilizer and pesticide.

The Claus process is involved in two basic steps in which the hydrogen sulphide is changed to sulphur the first step is the thermal one, while the second one is the chemical one.

The thermal step starts with hydrogen sulfide-laden gas reacts in a sub stoichiometric combustion at temperatures above 850°C Or between 950°C and 1200 °C and even hotter near the flame, [5] such that elemental sulfur precipitates in the downstream process gas cooler.

$2\ H_2S + 3\ O_2 \rightarrow 2\ SO_2 + 2\ H_2O$

This is a strongly exothermic free-flame total oxidation of hydrogen sulfide generating sulfur dioxide that reacts away in subsequent reactions.

The temperature inside Claus furnace is often maintained above 1050°C [6]. This ensures BTEX (Benzene, Toluene, Ethyl benzene and Xylene) destruction which otherwise would clog downstream Claus catalyst [7].

The second part of the process is the catalytic stage, which involves the remaining H_2S, from the Claus furnace, is reacted with the SO_2 at lower temperatures (about 470-620 K) over an alumina- or titanium dioxide-based catalyst to make more sulfur.

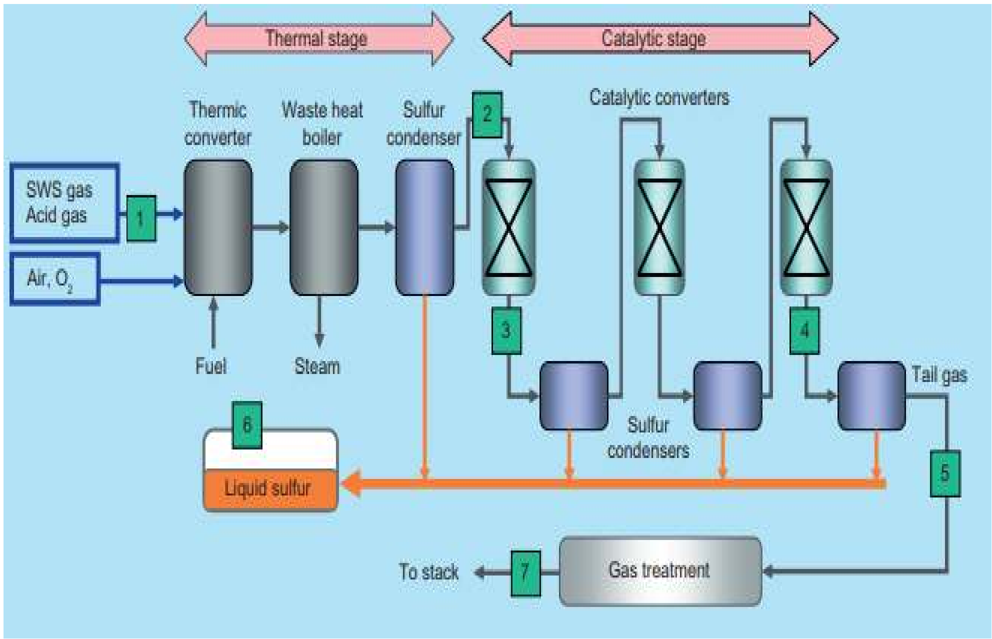

Figure2.1: simplified flow sheet of the Claus process

2.2 Acid gas

Acid gas is a particular typology of natural gas or any other gas mixture containing significant quantities of hydrogen sulfide (H2S), carbon dioxide (CO2), or similar acidic gases.

The terms acid gas and sour gas are often incorrectly treated as synonyms. Strictly speaking, a sour gas is any gas that specifically contains hydrogen sulfide in significant amounts; an acid gas is any gas that contains significant amounts of acidic gases such as carbon dioxide (CO2) or hydrogen sulfide. Thus, carbon dioxide by itself is an acid gas but not a sour gas.

Before a raw natural gas containing hydrogen sulfide and/or carbon dioxide can be used, the raw gas must be treated to reduce impurities to acceptable levels and this is commonly done with an amine gas treating process. [8]

Processes within oil refineries or natural-gas processing plants that remove mercaptans and/or hydrogen sulfide are commonly referred to as 'sweetening' processes because they result in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide.

2.2.1 Amine gas treating

Amine gas treating, also known as amine scrubbing, gas sweetening and acid gas removal, refers to a group of processes that use aqueous solutions of various alkyl amines (commonly referred to simply as amines) to remove hydrogen sulfide (H2S) and carbon dioxide (CO2) from gases. [9] It is a common unit process used in refineries, and is also used in petrochemical plants, natural gas processing plants and other industries.

Processes within oil refineries or chemical processing plants that remove hydrogen sulfide are referred to as "sweetening" processes because the odor of the processed products is improved by the absence of hydrogen sulfide. An alternative to the use of amines involves membrane technology. However, membrane separation is less attractive due to the relatively high capital and operating costs as well as other technical factors. [10]

Gases containing H2S or both H2S and CO2 are commonly referred to as sour gases or acid gases in the hydrocarbon processing industries.

The chemistry involved in the amine treating of such gases varies somewhat with the particular amine being used. For one of the more common amines, monoethanolamine (MEA) denoted as RNH2, the chemistry may be expressed as:

RNH2 + H2S ⇌ RNH3 + SH−

A typical amine gas treating process (the Girbotol process, as shown in the flow diagram below) includes an absorber unit and a regenerator unit as well as accessory equipment. In the absorber, the down flowing amine solution absorbs H2S and CO2 from the up flowing sour gas to produce a sweetened gas stream (i.e., a gas free of hydrogen sulfide and carbon dioxide) as a product and an amine solution rich in the absorbed acid gases. The resultant "rich" amine is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H2S and CO2.

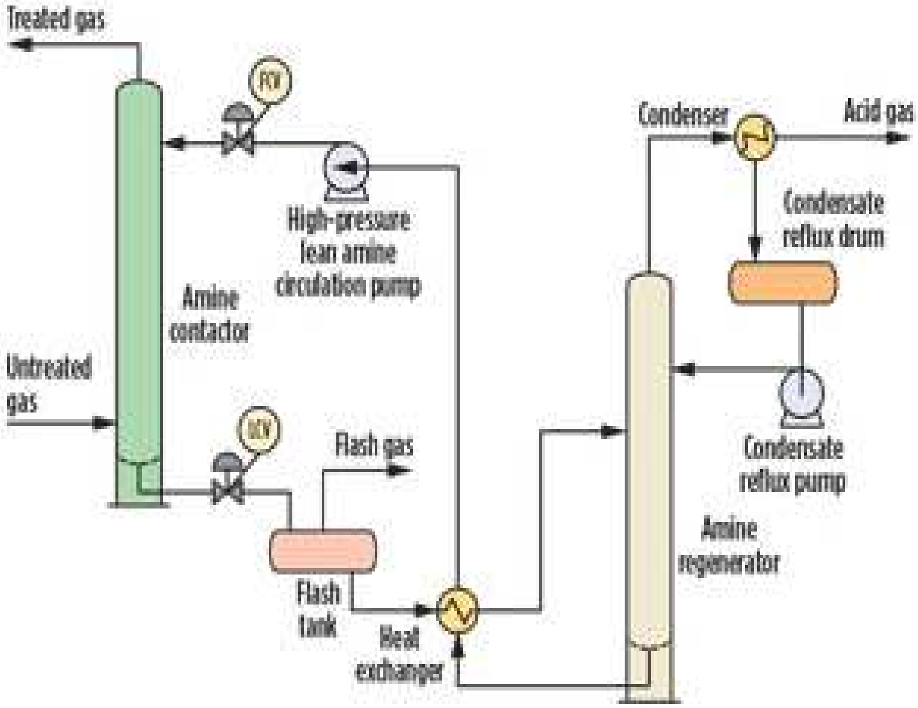

Figure2.2: flowsheet of amine gas treating.

2.2.2Rectisol

Developed by Linde and Lurgi, is a physical acid gas removal process using an organic solvent (typically methanol) at subzero temperatures, and characteristic of physical acid gas removal (AGR) processes, it can purify synthesis gas down to 0.1 ppm total sulfur, including hydrogen sulfide (H2S) and carbonyl sulfide (COS), and carbon dioxide (CO2) in the ppm range. It is also able to remove impurities such as hydrocarbons, ammonia, and hydrogen cyanide, consistent with its origin as a treatment for syngas from the Lurgigasifier which contains these kinds of impurities.

The Rectisol process uses a cheap and easily available, non-proprietary solvent, and is flexible in process configuration. On the other hand, refrigeration is required, associated with significant capital and operating costs, and high vapor pressure of methanol causes solvent losses.

The difference between the rectisol and the amine gas treating is that the first one is purely physical while the other depends on chemical reactions.

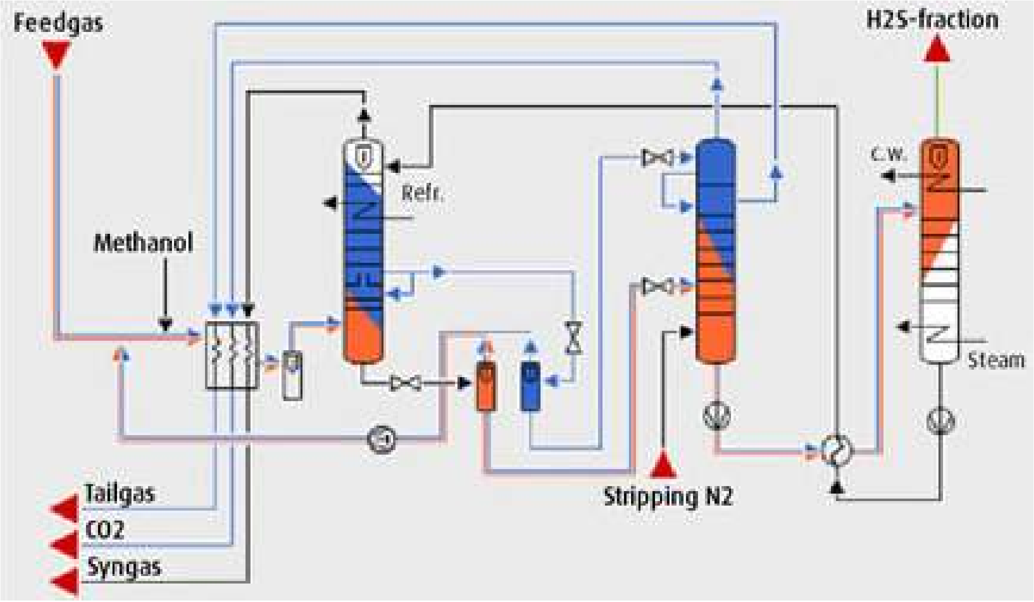

Figure2.3: Flowsheet of rectisol process

2.2.3 Sour water stripping

Sour water stripping is a fairly simple process in which either external steam, steam generated by a reboiler, or even a hot hydrocarbon stripping vapor is used to shift chemical reaction equilibria by heating the sour water.

The steam is the “gaseous solvent” used to remove and carry the ammonia and H2S out of the system. In other words, the application of heat generates internal stripping steam (equivalently, live steam injection can be used) and carries ammonia, H2S, and CO2 out of the water by, heating the sour water feed to boiling point, reversing chemical reactions, and diluting the partial pressure of the gases stripped by furnishing excess steam.

This sounds a lot like an amine regenerator, and it is. Figure2.4 shows a typical SWS column with heating by the injection of live steam. Because a sour water stripper does not form a fully closed loop like an amine regenerator does, maintaining a water balance is unnecessary. This means that live steam can be used as a stripping agent either alone or in conjunction with a conventional reboiler and the additional water added by the condensate simply added to the refinery’s water inventory. Typical energy usage in the stripping process is in the range 1.0– 1.5 lb of 50 psig equivalent saturated steam per gallon of sour water.

When an external reboiler is used, steam pressure is often higher than in an amine regenerator to minimize heat exchange surface. In an amine regenerator, amine degradation limits temperatures. In a sour water stripper, ammonia recycle in the stripped sour water is undesirable to begin with, so these concerns do not exist. However, there is a practical limit of 400-450°F where coking heavy hydrocarbons can lead to fouling and solids deposition in the reboiler, and corrosion is always a concern.

Higher NH3 and H2S concentrations require more stripping energy, but a higher concentration is also a more efficient way to store and transport the NH3 and H2S removed from upstream units. Because high H2S solubility relies on the presence of ammonia, the molar concentration of H2S very rarely exceeds that of ammonia, and then usually only in dilute systems. A typical molar ratio of H2S to ammonia is 0.5-0.8 in the combined SWS feed water of a typical refinery. Ammonia levels in the water are often determined by upstream process conditions, and they can be highly specific to the process licensor and crude slate in operation. Obviously, higher concentrations of NH3 and H2S are preferred from a water consumption perspective. However, there is a practical limit of between one and several weight percent ammonium disulfide equivalent in the sour water feed before metallurgy must be significantly upgraded.

Trays have historically been used in SWSs, but random packing is beginning to see use in units processing relatively clean water. Trays with directional, fixed valves have been reported to be more resistant to fouling because the horizontal velocity imparted as the gas leaves each valve tends to sweep clean the area near the valves. Stripped sour water specifications for NH3 and H2S can be highly dependent upon the locale where the unit is installed and the final discharge requirements. NH3 is harder to strip than H2S and typical targets for NH3 are 30-80 ppmw in the stripped water versus undetectable to less than 0.1 ppmw for H2S. Typical recent installations involve 35-45 actual trays with tray efficiencies quoted anywhere from 25 to 45%.

In some cases, other alkaline contaminants besides ammonia may be present in sour water. Amine can carry over into the regenerator purge or it can be present from injection into the crude unit overhead for corrosion control. Sodium, potassium, and magnesium may also be present from impurities in the makeup water (hardness) or by water-contacting various products containing these compounds within the upstream units. These species can chemically trap additional H2S and prevent the H2S from being stripped. In order to spring the H2S, acid then must be added to the water. Other contaminants and their effect will be deferred to the next section on the chemistry of ammonia-acid gas systems.

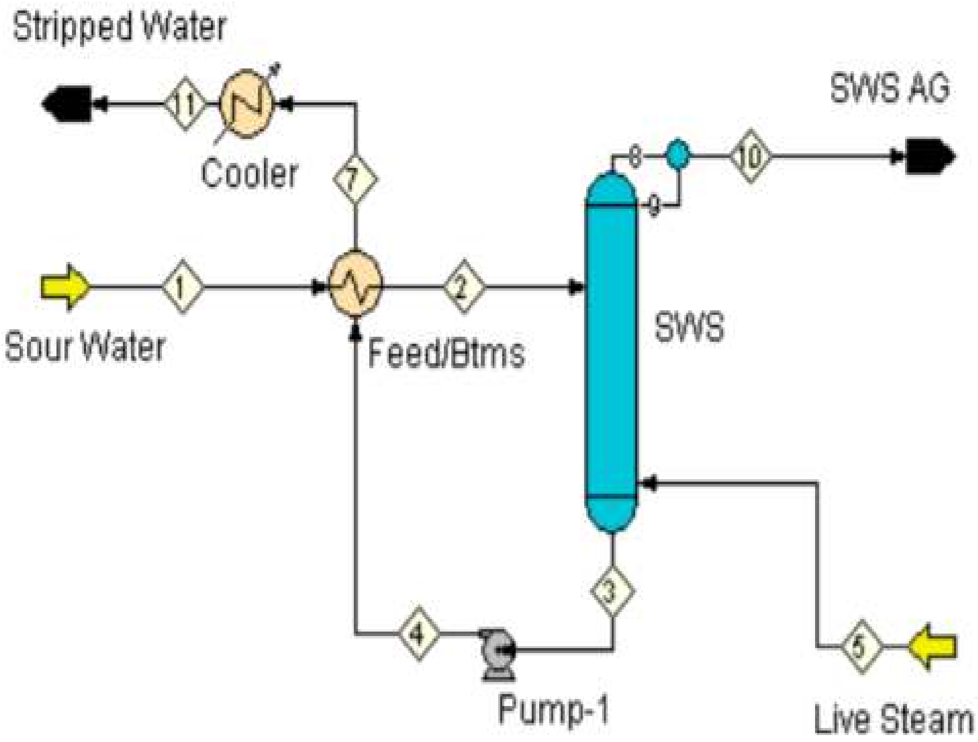

Figure2.4 Flowsheet of SWS unit

2.3 Sulphur

Sulphur belongs to group 16 of the periodic table, along with O, Se and Te. The element has an atomic number of 16, an atomic mass of 32, four oxidation states (-2, +2, +4 and +6) and four naturally occurring isotopes (32S, 33S, 34S and 36S), of which 32S is most abundant at 95% of the mass.

Figure2.5 Produced Sulphur

Sulphur primarily occurs in four oxidation states in geological environments: S2- (sulphides and sulphosalts), S0 (elemental sulphur), S4+ (SO2 in volcanic gas) and S6+ (SO3 in volcanic gas). Its oxidation state determines how S is incorporated into mineral phases. The most important occurrence of S associated with igneous rocks is in metal sulphide mineralization. Many metals exhibit chalcophilic tendencies, leading to the formation of many sulphide and sulphosalt ore minerals, such as chalcosite Cu2S, pyrite FeS2, sphaleriteZnS, galena PbS, cinnabar HgS, stibnite Sb2S3 and oldhamiteCaS. Evaporate minerals generally take the form of anhydrous or hydrated sulphates, e.g., barite BaSO4, gypsum CaSO4.2H2O, anhydrite CaSO4 and epsomite MgSO4.7H2O.

Pyrite present in sediments is another source of sulphate. Common rock-forming silicate minerals, including feldspar, mica and pyroxene, also contain significant amounts of sulphur, typically in the range 20 to 500 mg kg-1. Sodalite commonly contains S up to percentage levels, and non-silicates, such as apatite, can contain up to 1100 mg kg-1 S. Ultramafic and mafic rock types contain the highest concentrations of sulphur, typically between 300 and 23,000 mg kg-1.

Intermediate and felsic rock types contain proportionally much less sulphur, with ranges of 60–3600 mg kg-1 and 45-3900 mg kg-1 respectively. Carbonate sediments generally contain more SO4 2- (4550 mg kg-1) than shale (1850 mg kg-1) and sandstone (945 mg kg-1) . Organic-rich sedimentary rock types, such as black shale (ca. 7%) and coal (up to 3%) tend to have the highest sulphur concentrations, although evaporate deposits, including gypsum and anhydrite, generally contain ca. 20% sulphur. Carbonate rocks and sandstone commonly contain less than 1% S. The mobility of SO4 2- in soil is constrained by processes of adsorption and reduction.

There are many uses that we can gain from the element Sulphur, which give it its industrial and household uses alike, thus giving an economical benefit besides the environmental one for the Sulphur recovery unit. Like for manufacturing of drugs and other pharmaceuticals, in making of pesticides, but the main two applications are for the use for soil fertilizer and most recently in the manufacturing of concrete.

2.3.1 Manufacture of soil fertilizer

Sulphur (S) is an essential plant nutrient required by all crops for optimum production. Plants take up and use S in the sulphate (SO4 -S) form, which like nitrate (NO3 -N), is very mobile in the soil and is prone to leaching in wet soil conditions, particularly in sandy soils. Sulphur deficiencies are becoming increasingly common. Deficiencies can be easily corrected with fertilizers containing sulphate. Generally, S is the third most limiting soil nutrient in cereal, oilseed and forage crop production, it is third only to nitrogen (N) and phosphorus (P) in fertilizers.

Sulphur is essential in the structural and enzymatic components in plants. Sulphur is a key component of some essential amino acids and is needed for protein synthesis. Chlorophyll synthesis also requires S. Sulphur is not readily translocated within plants, so all plants need a continuous supply of sulphur from emergence to crop maturity. Therefore, in S-deficient plants, older leaves may appear healthier, while newer leaves and tissue may have stunted growth and a lighter green or even yellow appearance. A sulphur deficiency at any growth stage can result in reduced crop growth and yield. Adequate S results in rapid crop growth and earlier maturity.

Because ammonium sulphate fertilizers are so rapidly available to crops, they can be applied to crops in various ways. Normally, the uptake efficiency of soluble sulphate fertilizer is better when banded in soil versus broadcast and incorporation. When sulphate-S is sided banded near the seed or seed-placed, uptake efficiency tends to be best. Further, banded S fertilizer may favor crop growth versus weed growth, since this method places the fertilizer close to the crop roots. Normally broadcast application onto snow is not recommended. Some sulphate loss due to redistribution in runoff may occur if ammonium sulphate fertilizers are broadcast on snow deeper than 4 inches (10 cm) covering frozen ground, particularly on slopes greater the 4 per cent. If detected early enough, S deficiency can be corrected in many crops by broadcasting ammonium sulphate. In the case of canola, broadcasting ammonium sulphate until the early flowering stage may help correct an S deficiency provided there is enough rain to dissolve and move the SO4 -S into the root zone (Figure 7). The greatest risk from using soluble sulphate fertilizers occurs on sandy soils subjected to heavy rainfall. Under these conditions, SO4 -S may leach below the rooting zone.

2.3.2 Manufacture of sulphur concrete

Process of the sulphur concrete manufacture is based on the “hot” technology. In which all the mixed components are heated until 140–150o C. The sulphur used in the sulphur concrete production can be mixed with any type of traditional aggregate. Dosage should be optimized according to practical criteria as well as the mechanical properties. Optimal amount for sulphur mortar is about 30% of the bond while for the sulphur concrete is about 15% of the bond. The sulphur matrix with the percentage of mineral extender is 5% for mortar and 10% for concrete (on sulphur mass basis).

Process of sulphur concrete production is based on the Sulphur’s properties of changing its viscosity with the change of the temperature (in 119–122o C sulphur completely turns from the solid into the liquid). The technology of the sulphur concrete is very similar to the technology of the asphalt concrete. The sulphur concrete production process it consists of heating up the mixture until 150o C, melting of modified sulphur and mixing the components, molding samples into metal molds which were initially heated to the same temperature as the mixture, and then cooling the samples to the ambient temperature.

It’s used in building roads, drainage systems, industrial and harbor engineering, and agriculture. Comparison of selected sulphur concrete’s features with the cement concrete’s ones are presented, the sulphur concrete can be used for anti-radiation protective shields. The use of sulphur concrete for manufactures production gives an opportunity to create new, effective material solutions creating new standard in building elements. Among the most popular manufactures are for tanks for various substances, cesspits, drains, sewerage pipes, drainages, sewerage channels, and weights for electric traction lines.

The sulphur concrete are characterized by high resistance to biological and chemical corrosion. In some cases, its mechanical and physical properties can even transcend the properties of traditional concrete so can it can be assumed as a better solution for some building constructions. It should be expected that the interests in the sulphur concrete and its development within next several years should not deteriorate.