2.0 UNIT 18 - SULFUR RECOVERY

2.1 PROCESS DESCRIPTION

The Sulfur Recovery Unit will process the combined acid gas streams from the Rectisol Unit, the Gas Liquor Separation Unit, the Phenosolvan Unit and the Ammonia Recovery Unit to produce high quality sulfur.

The process to be used for this unit has not been finalized. The two processes which are being considered for the final design are given below. In both these processes H_2S present in the gas stream is converted to elemental sulfur.

1. Stretford process to be licensed by Peabody-Holmes.
2. Unisulf process to be licensed by Union Oil. (It is expected that this process will be offered to licensee in the near future).

The current process design is based on the Stretford process. Since no licensing agreement has been made with the licensor, the details of design for this unit are not available. The unit has been designed from Fluor in-house data available from other projects.

The reaction mechanism for conversion of H_2S to elemental sulfur is as follows.

The H_2S in the gas stream dissolves in an alkaline solution and ionizes $H_2S \rightleftharpoons H^+ + HS^-$

The disassociation of H_2S is favored under alkaline conditions and is also favored by the oxidation of hydrosulfide ions. In the Stretford process, pentavalent vanadium is used as an oxidizing agent, which is reduced to a tetravalent form and hydrosulfide ions are oxidized to sulfur.

$$HS^- + 2V^{5+} \rightleftharpoons S + H^+ + 2V^{4+}$$

The acid gases from the various process units, -Rectisol (Unit 12), Gas Liquor Separation (Unit 13), Phenosolvan Unit (Unit 16), and Ammonia Recovery (Unit 17) are sent through a contactor where the gas is brought into intimate contact with an aqueous solution containing mainly sodium carbonate, sodium vanadate and anthraquinone disulfonic acid (ADA). Conventional packed tower have been used in the past as contactors. Venturi absorbers have now replaced packed towers in many installations. In this contactor, the

2.1 Unit 18 - Sulfur Recovery (Continued)

hydrogen sulfide present in the gas dissolves in the alkaline solution forming hydrosulfide. The hydrosulfide then reacts with the pentavalent state vanadium present in the solution and is oxidized to elemental sulfur.

The liquor from the contactor flows by gravity to an Oxidizer tank where air supplied from an air blower is blown through the liquid. The air oxidizes the reduced vanadium (V^{4+}) in the solution to the pentavalent state (V^{5+}) through a mechanism involving oxygen transfer via the ADA. Also, air bubbles attach to sulfur particles suspended in the liquid and raise the sulfur to the surface of the oxidizer tank. The sulfur froth is skimmed from the top of the oxidizer into a tank. The tank is equipped with slow speed agitators to prevent settling.

The sulfur froth (5 to 10% by wt. of sulfur) from the tank is then treated for sulfur separation and melting. The sulfur froth is pumped into centrifugal decanters to produce a sulfur cake of about 50 percent sulfur. The sulfur cake is reslurried with water in a tank and the slurry is pumped through a heater where its temperature is increased to 284°F to melt the sulfur. The mixture must be kept under pressure to prevent the water from boiling. The molten sulfur and water pass into a pressure vessel where the sulfur settles out and flows to a molten sulfur storage tank. The water leaves from the top of the vessel through a pressure controlling valve.

2.2 FLOW SHEETS

Flow Sheets for the Sulfur Recovery area are proprietary with the licensors involved. Details of the processes cannot be revealed until a licensing agreement is signed.

2.3 UNIT MATERIAL BALANCE

Stream compositions for the Sulfur Recovery area are proprietary with the licensors involved. Details of the processes cannot be revealed until a licensing agreement is signed.

2.4 ACCOMPLISHMENTS AND DECISIONS

2.4.1 Introduction

The Lurgi portion of the Tri-State project produced a waste gaseous stream (originating primarily in the Rectisol Unit with the following approximate composition

Gas	Percent
H_2S	4.3
CO_2	94.0
Light Hydrocarbon Vapors	1.7
COS	Trace

At Sasol I a similar gas stream was vented to the atmosphere for approximately 20 years. Environmental Regulations enacted in the early 1970's required Sasol to decrease the quantity of sulfur vented.

After careful screening of sulfur recovery technologies, Sasol selected the Stretford process for Sasol I. A contract was awarded to Bischoff of West Germany to design and construct their Stretford plant. Bischoff is a sub-licensor of BGC who is the owner of the process. The design incorporated a tall (approximately 200 feet) wood packed absorber typical of BGC designs.

The startup of the Bischoff Unit was unsuccessful. The absorber failed to function properly. Sulfur deposited on the wood packing and succeeded in plugging the column. The cause for the plugging was attributed to the high CO_2 in the feed gas.

About the time the startup at Sasol I was begun, Sasol II awarded the engineering of their Stretford Unit to Bischoff. When the startup problems at Sasol I surfaced, the design for the absorption section of the plant was awarded to Peabody-Holmes. Peabody-Holmes uses venturi contactors rather than tall wood packed absorbers. They have a unit operating successfully for about 10 years with a feed gas very high in carbon dioxide.

2.4.1 Accomplishments and Decisions (Continued)

The startup of the sulfur plant at Sasol II was put on "hold" pending completion of research on the Unisulf process by Union Oil Company. This process utilizes a proprietary solvent to replace the Stretford solution in a Stretford plant. Bench scale tests in the U.S. and full scale tests in South Africa have been successful. The full scale tests ran for several months producing a marketable sulfur product. Union Oil Company is prepared to licenses this process to others.

2.4.2 Sulfur Recovery Technologies

Several sulfur recovery technologies were considered for the Tri-State project. They include the following:

a. Stretford

b. Unisulf

c. Selectox

d. ADIP-Claus

e. Incineration/FGD

2.4.2.1 Stretford - The Sulfur Recovery Unit for the Tri-State feasibility study was the Peabody-Holmes version of the Stretford Process. Peabody-Holmes is a sub-licensor of BGC. They have a long history of process designs for the Stretford process. The design of the Sulfur Recovery Unit included Venturi contactors to replace the wood packed absorbers. Centrifuges and continuous melters were used to purify the sulfur. The Tri-State design is similar to the design of the Stretford Unit installed at Sasol II and Sasol III. Peabody-Holmes is confident that the Sasol units will operate successfully.

The high concentration of CO_2 in the feed gas changes the normal rate of circulation for the Stretford solution. The chemistry of the Stretford process is very complex, and the absorption of CO_2 into the solution changes the characteristics of the process. The success of the operating plant with high CO_2 demonstrates that Peabody-Holmes has learned to compensate for the CO_2.

The Stretford process was rejected by TSSC after problems at SASOL developed with their Stretford process.

2.4.2.2 Unisulf - Union Oil has several Stretford units installed in their refineries. As a part of their normal work on these units, they developed a proprietary solvent they felt was an improvement over the Stretford solution.

The composition of the Unisulf solution is proprietary. It can replace the Stretford solution in a Stretford plant. This process has been tested over several months on a commercial scale and proven itself. Union Oil Company is now offering this process for licensing.

2.4.2.2 Unisulf (Continued)

The economics for the process are unknown. Union Oil Company has declined to divulge the composition of their solution. Statements have been made indicating that the solution is stable, losses are negligible and the solution does not degrade over long usage.

2.4.2.3 Selectox - This is a new process developed by Union Oil Company that converts H_2S to elemental sulfur. The process was developed specifically to treat H_2S in the presence of saturated paraffinic hydrocarbons. With olefinic material, Union Oil says their process will produce brown sulfur. The feed gas for the Tri-State project contains olefinic material. Before committing to produce brown sulfur, saleability of the brown sulfur should be discussed with potential buyers of the material.

This process was not evaluated economically. This evaluation was scheduled to begin after more consultation with Union Oil. The technical feasibility has not been determined.

2.4.2.4 ADIP/Claus - The concentration of H_2S in the feed gas to a Claus Unit should be as high as possible. Concentrations in the range of 15-20 percent are at the absolute minimum. The Tri-State gas is only 4.3 percent. One way to increase this concentration is the use of the Shell ADIP process. This process produced a Claus feed for Tri-State at 35 percent H_2S and 65 percent CO_2.

A selective Rectisol will produce a feed stream to Claus that is high enough in H_2S but it will contain C_2+ hydrocarbon vapors. A process such as ADIP is needed to separate the hydrocarbons from the H_2S.

Claus is the conventional process for converting H_2S to elemental sulfur. A partial oxidation of the H_2S produces a reaction gas containing H_2S and SO_2. These two compounds reacts to form elemental sulfur and water.

Tail gas from a Claus Unit is too high in sulfur to be vented to the atmosphere. Several processes are available to treat this gas. Union Oil/Parsons offers the Beavon process to recycle the sulfur in the tail gas. In the Beavon process, the SO_2 in the tail gas is converted to H_2S and the tail gas is fed to a Stretford Unit. The Shell SCOT Unit also converts the SO_2 to H_2S and then the H_2S is recycled back to the Claus Unit. The Shell SCOT process was selected for the Tri-State project.

2.4.2.4 ADIP/Claus (Continued)

The ADIP/Claus process combination was found to have a high capital cost, increased operating complexity plus increased catalyst and chemical costs. It was rejected for the Tri-State project.

2.4.2.5 Incineration/FGD - For this option the gas previously fed to a Sulfur Recovery Unit is incinerated and the combustion products are combined with boiler plant stack gas and fed to Flue Gas Desulfurization (FGD) Units. The FGD units are an integral part of the steam generating plant. Addition of the incinerated gas to the FGD feed adds only a slight incremental cost to the FGD unit capital cost.

This option was rejected for the Tri-State project. The loss of sulfur revenue, increased chemical costs and the huge increase in sludge disposal volume made this choice uneconomic.

2.5 CURRENT STATUS

The Stretford process is the current design basis for this unit. When the project is reactivated, a decision has to be made between the above processes depending mainly on the licensing status of the Unisulf process and experience gathered by other processes.

2.6 LICENSORS AND EVALUATIONS

Peabody-Holmes is the potential licensor for the Stretford process. The Unisulf process is licensed by the Union Oil Company.

When the project is reactivated, a secrecy agreement will have to be made with either Peabody-Holmes for the Stretford process, or with Union Oil for the Unisulf process.