

1. INTRODUCTION

Catalytic methanation is a key process which is becoming increasingly important to our energy plans in the future. In view of the current and projected natural gas requirements, the development of viable large scale methanation systems is of the utmost importance for our future energy plans. However, before catalytic methanation can be used for the commercial production of synthetic natural gas from synthesis gas, the problem of catalyst deactivation must be solved.

Nickel is a superior methanation catalyst. The metal is relatively cheap; it is very active when present in a form having high surface area, and it is the most selective to methane of all materials. Its main drawback is that it is easily poisoned by sulfur compounds, a fault common to all of the more active methanation catalysts (11,12,16).

This deactivation could result in prohibitive operating costs for catalyst replacement (or regeneration) and could make the process economically impractical (20). One approach to this problem is to develop a methanation pre-treatment process which would effectively remove those trace sulfur impurities responsible for the loss in methanation catalytic activity, to very low levels, e.g., less than 0.1 parts per million (PPM) by volume of total sulfur.

In the 72TPD SYNTHANE coal gasification pilot plant located at Bruceton, Pa., two methanation schemes, Hot Gas Recycle (HGR) and Tube Wall Reactor (TWR) are included (10,13). Since most of the experimental process development unit runs with the HGR and TWR reactors produced an effluent gas with a carbon monoxide content above 0.1%, it was recommended that a final "cleanup" methanation reactor be added. The final cleanup methanator for the SYNTHANE plant consists of a small bed of conventional methanation catalyst. It is general practice for bulk H_2S removal from synthesis gas to use a regenerative liquid absorption process. The purification system chosen for bulk removal of the acid gases (CO_2 and H_2S) in the SYNTHANE plant is the Benfield Hot Potassium Carbonate Process. Sulfur compounds expected in the effluent from a Benfield Hot Potassium Carbonate Process employed to test a coal gasification gas stream include H_2S , COS , CS_2 , mercaptans and thiophenes. The final sulfur removal scheme for the 72TPD SYNTHANE plant was designed to be two fixed beds of activated carbon that can be regenerated. The fixed bed activated carbon system was designed to operate at 95°F and 1000 psig for the adsorption step.

Exxon Research and Engineering Company, under Contract No. E(36-2)-0059 from the United States Department of Energy (previously Energy Research and Development Administration), has carried out a program to investigate trace sulfur compound removal from synthesis gas prior to methanation. The study was aimed at obtaining experimental data that applies to the SYNTHANE gasification process being developed by the Department of Energy. The program included a literature survey, testing unit construction and operation, data and feasibility analysis, and an engineering and economic analysis of the system chosen. In addition, a theoretical analysis was made of the adsorption of sulfur compounds from synthesis gas under an NSF Faculty Research Participation Project.

The program began as a broad paper study to evaluate candidate trace sulfur removal systems and evolved to a detailed experimental evaluation of a metal impregnated carbon using single and multicomponent blends of the trace sulfur compounds of interest. Several candidate systems were systematically reviewed and eliminated from consideration.

This final report summarizes the work conducted on this contract. The remainder of the report is structured as follows -

Section 2 presents a state-of-the-art review of candidate sulfur guard systems.

Section 3 describes the experimental equipment used in the study.

Section 4 presents the experimental results achieved with the selected sulfur guard system and a discussion of these results.

Section 5 presents a summary of the economic and environmental aspects of the evaluated sulfur guard system.

Section 6 gives the major conclusions of the study.

2. STATE-OF-THE-ART ASSESSMENT

A review of the sulfur removal processes was made with respect to their potential as sulfur guard (trace sulfur removal) systems following a Benfield unit.

Several of these have been classified as unlikely candidates for various reasons. Included in these are dimethyl ether of polyethylene glycol (Selexol), amine solutions, and Stretford type solutions, which all represent alternatives or adjuncts to a Benfield hot carbonate acid-gas removal system. Their applicability is best suited to "bulk" sulfur (plus CO₂) removal with typical product sulfur levels at least one or two orders of magnitude higher than the stringent 0.1 ppm total sulfur required of sulfur guard. Cold methanol (Rectisol) is also an unlikely candidate for a sulfur guard system, per se, since it probably represents a viable solution to the total sulfur removal (acid-gas plus sulfur guard) problem if economics can be justified. Other approaches classified as unlikely are caustic (NaOH) solutions and dolomite or limestone because of the huge loss in capacity for sulfur due to the presence of large quantities of CO₂ relative to sulfur compounds (>100/1) in the entering feed. In addition, thiophene probably would not be removed.

As a result of these considerations, all types of sulfur compound removal processes were reviewed with concentration on the more promising solid adsorbents, with some attention being paid to catalytic conversion systems utilizing the hydrogen in the synthesis gas. The potential of absorption processes, solid adsorbents and catalytic conversion for providing the desired characteristics for the sulfur guard system including discussions held with material suppliers is described in the following paragraphs.

2.1 Absorption Processes

Several absorption processes for removing sulfur compound impurities were reviewed and evaluated for their potential for application in the SYNTHANE coal gasification process. These include -

- Amine Scrubbing
- Benfield Hot Potassium Carbonate Process
- The Linde-Lurgi Rectisol Process
- The IFP Sulfur Removal Process
- Holmes-Stretford Process
- Claus Process
- Selexol Process

As indicated above, with the exception of the Rectisol Process, these processes require an additional trace sulfur compound removal system to reduce the sulfur compound concentration to the levels required in the present application, i.e. 0.1 parts per million (ppm) by volume of total sulfur.

2.1.1 Amine Scrubbing

A number of processes are available for licensing that use amine scrubbing to sweeten sour gas (5, 18). Basically, acid gases are absorbed in a basic amine solution and the solution is then regenerated to give a gas rich in H_2S and CO_2 .

Figure 2.1 is a schematic flow diagram of an amine scrubbing process. Sour gas feed with the composition indicated on the figure, is contacted in a scrubber tower with lean monoethanolamine (MEA) solution. The hydrogen sulfide and carbon dioxide are reduced to 20-200 ppm.

The MEA solution containing the acid gas passes to a hydrocarbon disengaging drum where traces of heavier hydrocarbons are removed to be flared. (These traces of hydrocarbons contain negligible amounts of sulfur.) Lighter hydrocarbons, disengaged from the drum, are sent to a low pressure scrubbing system to remove any traces of sulfur compounds and are then used as fuel.

The H_2S laden MEA solution then passes to a regenerator tower where the acid gases are removed and passed to sulfur recovery. The lean MEA solution may contain sludge which is removed in the amine reclaimer. This sludge contains polluting materials and must be further treated.

2.1.2 Benfield Hot Potassium Carbonate Process

The Benfield Promoted Hot Carbonate absorption process uses two independent but compatible circulating solutions in series to achieve a high purity gaseous effluent combined with high efficiency. As a result of the Benfield Process simplicity and low energy requirements, it received special consideration while evaluating the different processes for pre-methanation purification systems.

This process for acid gas removal involves the contacting of a sour gas stream with a solution K_2CO_3 . In addition to H_2S and CO_2 , the product of most coal gasification processes will also contain organic sulfur compounds.

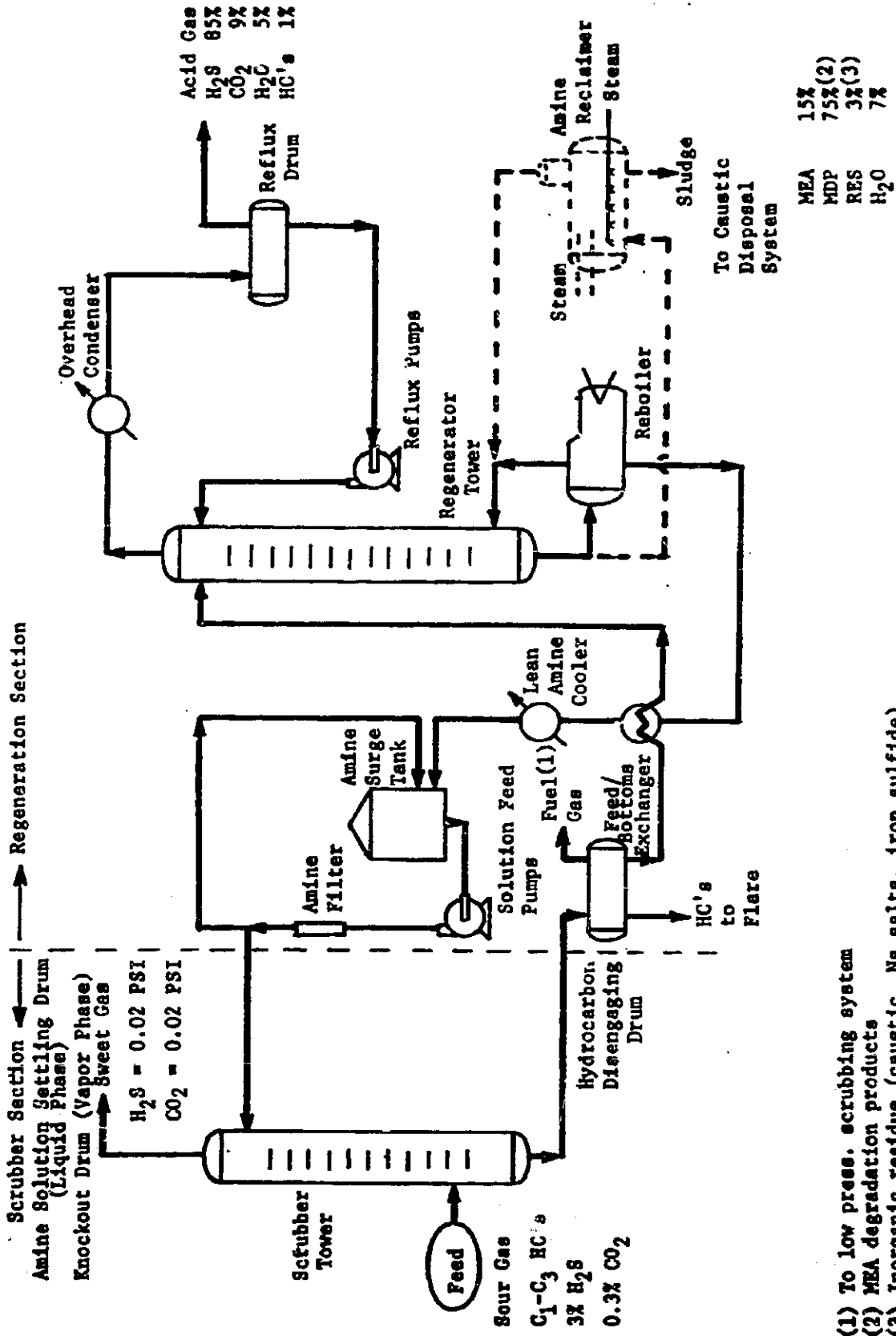
Typical trace sulfur components in coal derived gas are as follows (8):

COS	2 to 300 ppm (v/v)
CS_2	0 to 10 ppm (v/v)
Thiophenes	0 to 60 ppm (v/v)
Mercaptans	0 to 60 ppm (v/v)

Analysis of sulfur trace compounds after contacting a bulk removal Hot Potassium carbonate system gave the following approximate removal (2):

<u>Component</u>	<u>Percent Removal</u>
Mercaptans	Over 90%
Carbon Disulfide	75%
Carbonyl Sulfide	75%

FIGURE 2.1
AMINE SCRUBBING



- (1) To low press. scrubbing system
- (2) MEA degradation products
- (3) Inorganic residue (caustic, Na salts, iron sulfide)

Thiophene (C_4H_4S) would not be expected to react chemically with alkaline activated potassium carbonate solution. This expectation has been confirmed in the Benfield Laboratory. However, thiophene removal of about 85% has been reported in a commercial Benfield unit (2,17).

A simplified flow diagram in Figure 2.2 illustrates the carbonate process. The sour gas at elevated pressure (1000-2000 psi) is contacted with recycle, lean K_2CO_3 solution where sulfur compounds are removed to as low as 20 ppm. The pressure on the rich solution is reduced and the acid gases are removed in a regenerator column. The lean K_2CO_3 solution is recycled to the absorber.

The sweet gas (20-100 ppm of sulfur compounds) may be further purified by reaction with Fe_2O_3 or ZnO or by adsorption on activated charcoal or molecular sieves. These trace sulfur compound removal processes are discussed in Section 2.2.

No significant effluent of liquid is purged. Except for small amounts of additives, the solutes are only K_2CO_3 and $KHCO_3$. Heat in the feed gas can be used to supply all or part of the unit's low heat requirements. Unless the CO_2 content is low, it is necessary to treat the acid gas product by means other than a Claus plant.

2.1.3 The Linde-Lurgi Rectisol Process

The Rectisol process, patented and commercialized jointly by Linde and Lurgi, is a technique for removing H_2S , COS and CO_2 from sour gas in such a way that the sulfur containing gases are concentrated sufficiently that they may be processed in a conventional Claus plant. Basically, the Rectisol process involves physical absorption of the acid gases in low temperature methanol and subsequent regeneration of the methanol (24).

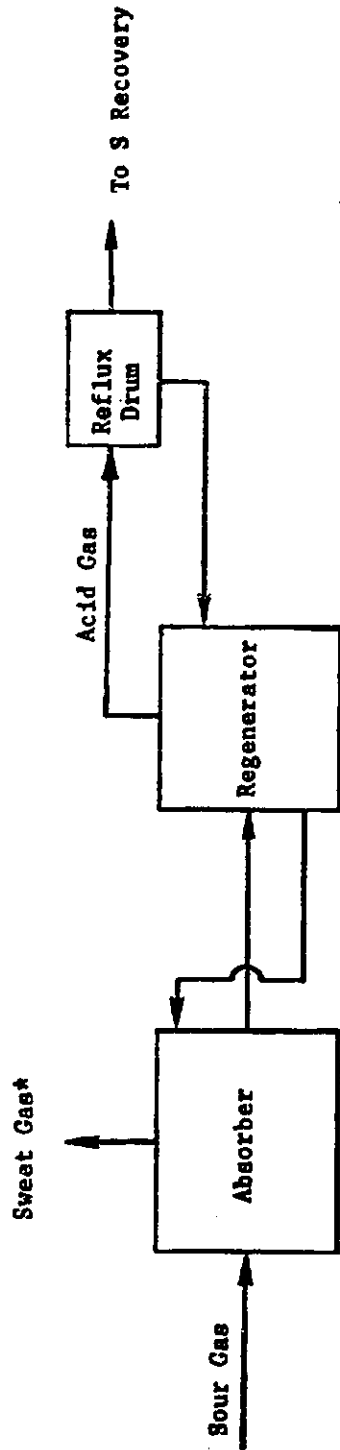
Figure 2.3 shows a two stage Rectisol purification process that produces a high purity synthetic gas and a by-product stream rich in H_2S . The important streams are identified in Table 2.1.

The sour gas enters the first absorber at 441 psia and contacts a stream of low-temperature methanol that has absorbed the equilibrium concentration of carbon dioxide. No CO_2 is removed in this tower and no heat load is imposed. The H_2S in the sweet gas is so low that the gas may be passed to a CO shift converter that utilizes a sulfur-sensitive, low-temperature shift catalyst. After further compression to 725 psia and heat exchange, the gas passes to a second tower where most of the carbon dioxide is removed. The final traces of methanol and CO_2 are removed in an absorber before passing to the nitrogen wash. The carbon dioxide in the methanol from the CO_2 absorber is removed by nitrogen stripping to the point where the methanol- CO_2 solution is in equilibrium with CO_2 in the feed gas. The CO_2 and tail gas contain less than 5 ppm of H_2S .

The methanol from the H_2S absorber still contains too much CO_2 to allow direct use of the gas in a Claus plant. The solution is enriched in H_2S by nitrogen stripping of part of the CO_2 . The H_2S plus some of

FIGURE 2.2

BENFIELD HOT K_2CO_3 PROCESS



*The last traces of acid gases may be removed by passing the gas through Fe_2O_3 , activated charcoal, molecular sieve or ZnO.

FIGURE 2.3
2 STAGE RECTISOL WASH FOR H₂S AND CO₂-REMOVAL

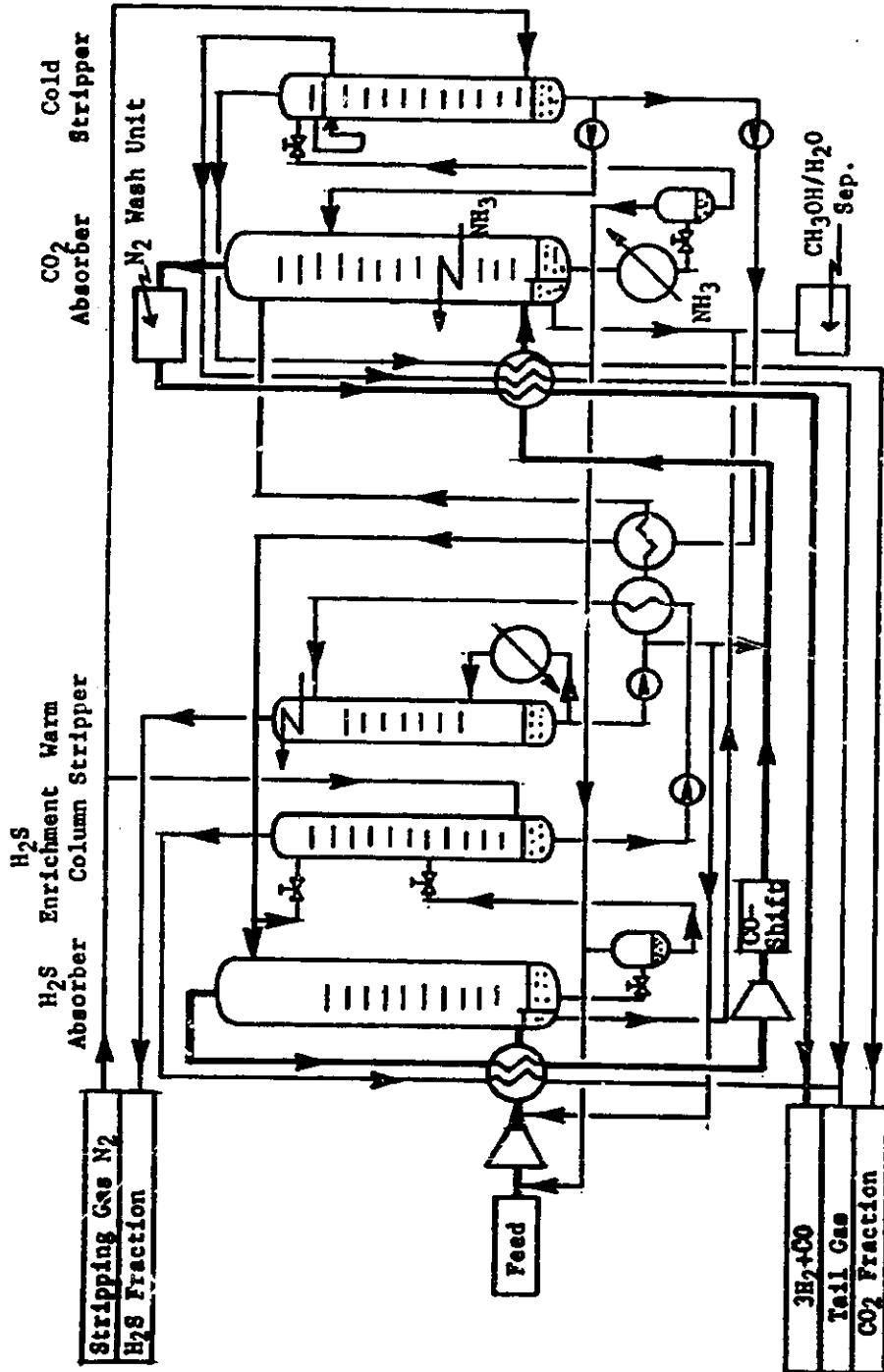


TABLE 2.1

STREAM IDENTIFICATION IN RECTISOL PROCESS (24)

Gas Constituent	Feed Gas to Rectisol I mol %	Feed Gas To Shift mol %	Feed Gas to Rectisol II mol %	Feed Gas to N ₂ Wash mol %	CO ₂ Fraction mol %	Tail Gas mol %	H ₂ S Fraction mol %	Stripping Gas
H ₂	29.32	30.34	54.21	93.15	0.20	0.44	--	100
N ₂ +A	1.52	1.57	1.03	1.78	--	12.10	2.55	
CO	56.62	56.61	2.95	4.97	0.12	0.43	--	
CH ₄	0.10	0.10	0.07	0.10	--	0.01	--	
CO ₂	11.85	11.38	41.74	max. 50 ppm	99.68	87.02	71.95	
H ₂ S	0.59	--	--	--	max 5 ppm	max 5 ppm	25.50	
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total flow	105,000	104,818	159,457	91,423	12,060	61,224	2,632	7,500
	10,324	10,307	15,679	89,895	1,186	6,020	239	737.5
Pressure	31 atm	30 atm	51 atm	49 atm	1.1 atm	1.0 atm	1.5 atm	2.7 atm
	441 psia	427 psia	725 psia	697 psia	15.6 psia	14.2 psia	21.3 psia	38.5 psia

the CO_2 is removed by methanol vapor in a warm stripper. The concentration of H_2S (ca. 25%) is sufficient for sulfur recovery by conventional means.

2.1.4 IFP's Sulfur Removal Process

Gases exiting from a Claus plant still contain considerable sulfur as H_2S , SO_2 , COS , CS_2 . To meet environmental standards this gas may have to be treated further to lower the sulfur content. A process developed by the Institut Francais du Pecrole (IFP) is designed to accomplish this. Basically, the IFP process continues the reaction of H_2S and SO_2 in the liquid phase with a proprietary catalyst in a proprietary solvent.

As indicated in Figure 2.4, the IFP process is very simple and involves only a few pieces of equipment. Claus unit effluent gas at approximately 260°F is injected into the lower part of the packed column. The tower is designed for low pressure drop. Pressure drop across the system is less than 1 psi. Depending on capacity, one or more packed beds with redistribution are used. Sulfur accumulates in a sump at the bottom of the tower and is continuously drawn off under interface control.

The catalyst solvent is continuously circulated from bottom to top of the tower to maximize gas/liquid contact by counter-current flow. Liquid temperature is maintained at $260\text{--}280^\circ\text{F}$, the heat of reaction being removed by vaporization of condensate injected into the solvent pump-around loop just before entering the top of the column. Circulation is governed by level of the solvent/gas interface at the lower bottom.

No solvent degradation has been found to occur. Although vapor pressure is low at reactor temperatures, some solvent is lost in the overhead and is made up through replacement from a storage tank heated with a steam coil.

Conversions ($\text{H}_2\text{S} + \text{SO}_2$ to S) to be expected in the IFP process will depend on the total $\text{H}_2\text{S} + \text{SO}_2$ concentration in the Claus tail gas as shown (26):

<u>Volume % of $\text{H}_2\text{S} + \text{SO}_2$</u>	<u>% Conversion</u>
0.4 - 0.8	80
0.8 - 1.5	90
1.5	95

Typical operating parameters are shown in Table 2.2.

From an operating point of view, only the ratio of H_2S to SO_2 affects conversion rates. The ratio should be held between 1.9 and 2.1 if conversion is to be maximum. In modern refinery practice, this should present no difficulties, for while feeds to the Claus unit will be subject to wide variations in flow and composition, the use of in-line gas chromatographic and UV spectrophotometric monitors permits automatic regulation of the $\text{H}_2\text{S}/\text{SO}_2$ ratio in the Claus effluent to $\pm 5\%$.

Controlling the ratio in this way not only provides conditions for maximum sulfur recovery in the IFP unit, but maintains recovery in the Claus unit at the highest level also.

FIGURE 2.4
CLAUS UNIT TAIL GAS CLEANING
WITH THE IFP PROCESS

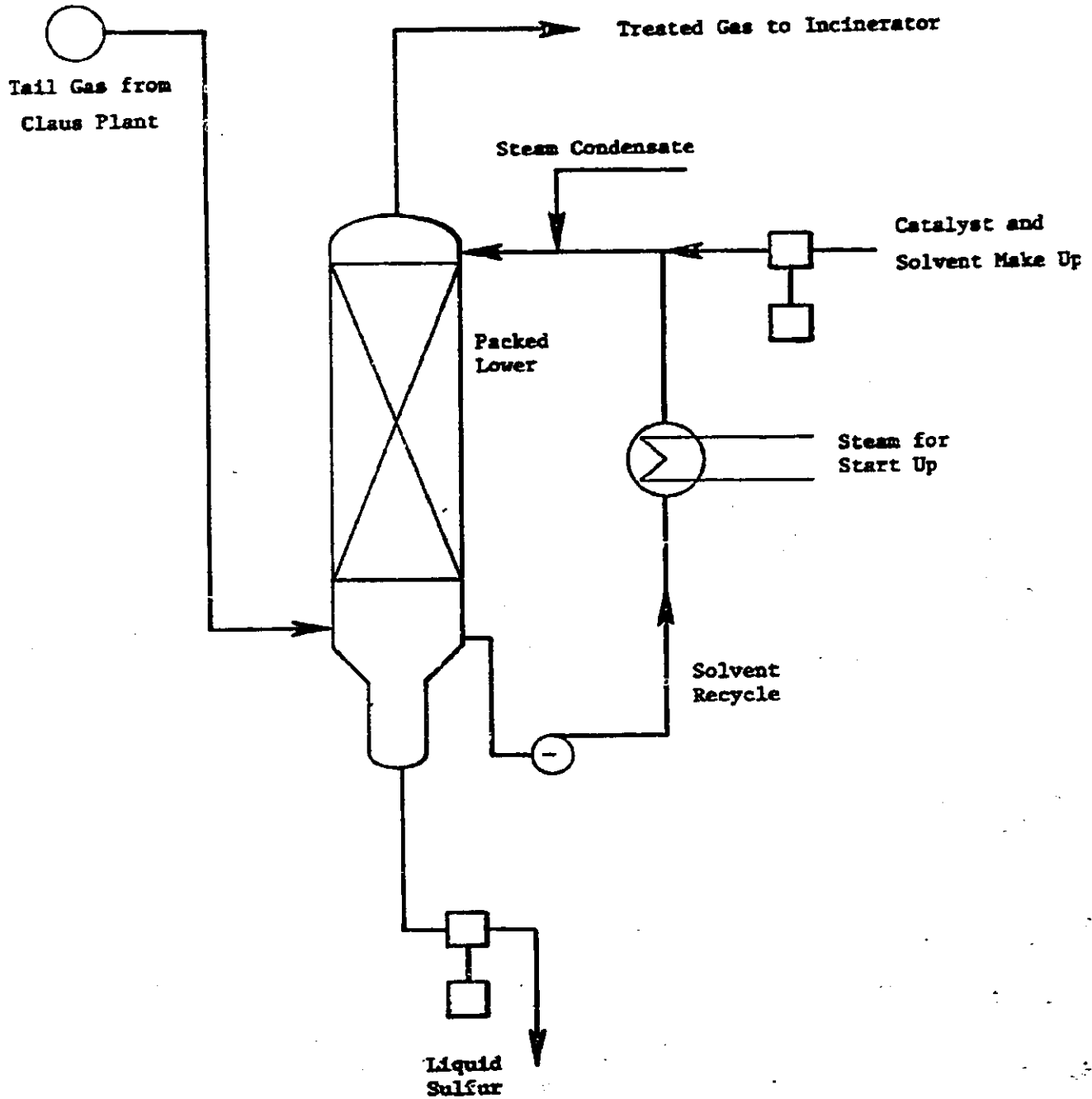


TABLE 2.2
OPERATING PARAMETERS OF IFP PROCESS (26)

		Treating the Tail Gas from a 3 Stage Claus Plant
<u>Tail Gas</u>	Composition Mol.% H ₂ S	0.44
	SO ₂	0.22
	S	0.37
	H ₂ O	37.67
	N ₂ , CO ₂ , Misc.	61.30
Conditions - Temperature °F		260
- Pressure psig		0.5
Flow Rate	lb/mol/hr	2367.06
<u>Sulfur Recovery</u> (on H ₂ S + SO ₂ reaction) %		82
Production lb/hr		420
<u>Treated Gas</u> to incinerator ppm of H ₂ S + SO ₂		1200

The only other variable which can adversely affect sulfur recovery is the concentration of COS and CS₂ in the feed to the IFP unit. While appreciable amounts of these substances are formed in the Claus burner, the first Claus catalytic reactor can reduce the levels well below the 1000-1500 ppm normally encountered in refinery streams. The level will remain essentially constant through the second and third stages, and is unchanged in the IFP unit since the IFP process does not touch COS and CS₂.

To keep COS and CS₂ concentrations at a minimum, it is advisable to run the first Claus converter hotter than usual, and to replace the bauxite with a more sophisticated catalyst. The slightly lower conversion due to running this stage hotter will be compensated for by the higher overall sulfur recovery in the IFP unit.

The sulfur level in the tail gas can be reduced to 200 ppm at considerably greater expense. The more elaborate schemes involve incinerating the Claus tail gas, scrubbing with an ammonia solution and reduction of sulfate ion to SO₂. The SO₂ is mixed with a gas containing H₂S and reacted in the IFP process as described above. Ammonia is recycled. The final gas to the incinerator then contains a maximum of 200 ppm of sulfur and 50 ppm of NH₃.

If the H₂S/SO₂ ratio is held within the range 1.0-2.1, and if the first Claus reactor is run to keep down COS and CS₂, the overall sulfur recovery for the combined Claus/IFP system can be in excess of 99.2%, equivalent to stack SO₂ emissions of about 1500 ppm. The only source of pollution is the stack gas.

2.1.5 Holmes-Stretford Process

The Holmes-Stretford Process is a method of removing hydrogen sulfide from gases and converting them directly to elemental sulfur. This highly developed chemical process is a key to economical desulfurization of gas streams from coke ovens, SNG plants, refineries and new coal gasification processes. Figure 2.5 gives a flow diagram for this process.

The gas to be purified is countercurrently scrubbed in a scrubber with an alkaline solution containing a vanadium salt along with anthraquinone disulfonic acid (ADA). The hydrogen sulfide is just dissolved in the circulating liquor and then oxidized to free sulfur by reducing the vanadium from its pentavalent form to its quadrivalent state.



The H₂S is converted to elemental sulfur by the vanadic salt which itself is reduced to the vanadium form, from pentavalent to quadrivalent. To make the cycle reversible, anthraquinonic disulfonic acid is employed as an oxidant to restore the quadrivalent vanadium back to the pentavalent state. During this reaction, the ADA is reduced to semiquinone.

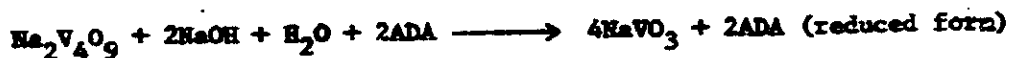
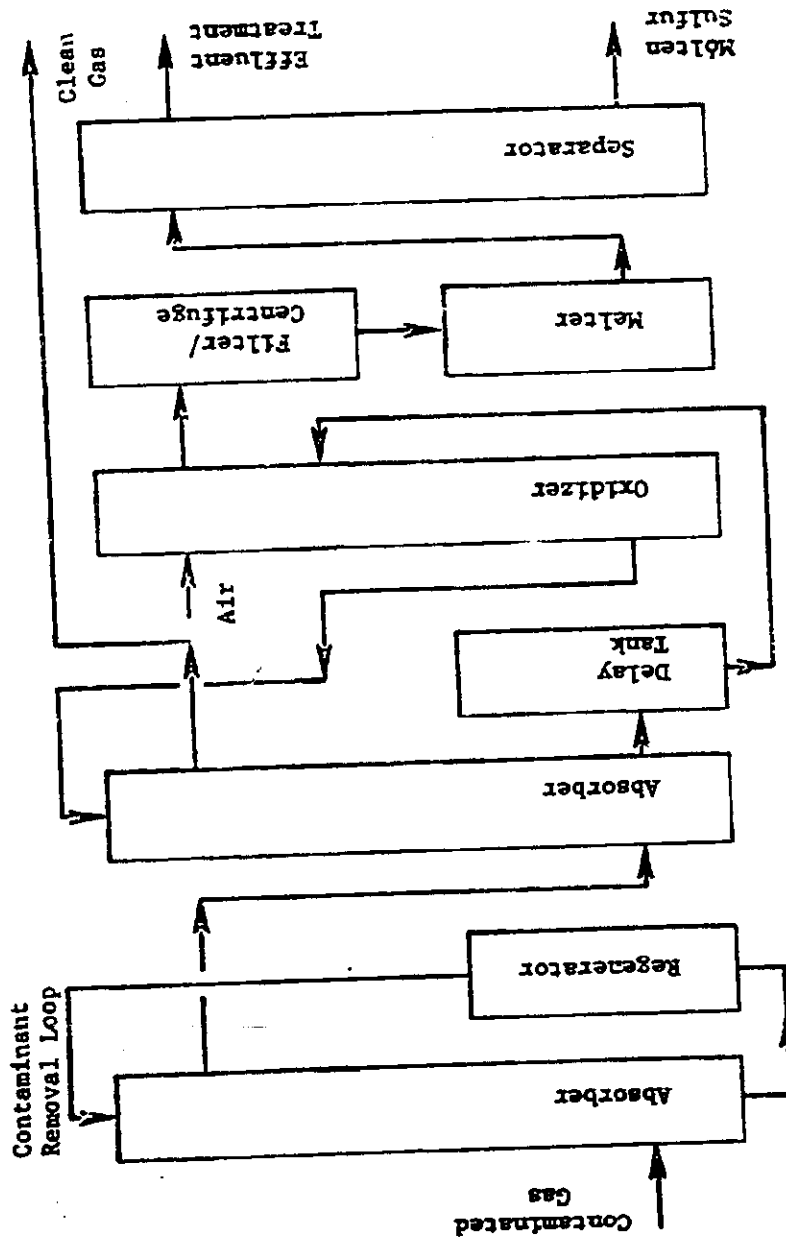
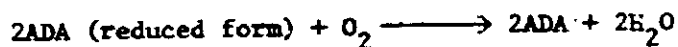


FIGURE 2.5
HOLMES-STRETTFORD PROCESS



The ADA is subsequently reoxidized with air in separate oxidizer vessels back to the original ADA configuration.



Due to the formation of by-product salts such as sodium sulfate and sodium thiocyanate, it is necessary to purge liquor from the process system. The Holmes Stretford Process includes a new technique for the treatment of this liquor resulting in zero effluent discharge. Purity of the sulfur will be of the order of 99.5% depending on the contaminants of the feed gas. Potential contaminants include unsaturated hydrocarbons, tar fog, free carbon and oil mist.

The effluent stream from the Stretford process containing sodium thiosulfate and sodium thiocyanate (in some cases) must be treated prior to discharge. Holmes has developed and piloted four alternate methods to handle effluents from this process:

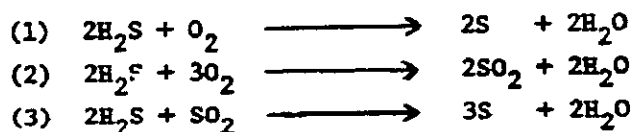
- Evaporation or spray drying
- Biological degradation
- Oxidative combustion
- Reductive incineration

The reductive incineration process results in a zero effluent discharge because all the products from this step are recycled.

The Holmes-Stretford Process is capable of handling gas flow rates of 0.1 to 190 million SCFD, the inlet concentrations of H_2S in the coal gas is reduced from 0.03 to 95% V/V in the inlet gas stream to 1.0 to 500 ppm V/V in the outlet gas stream.

2.1.6 Claus Process

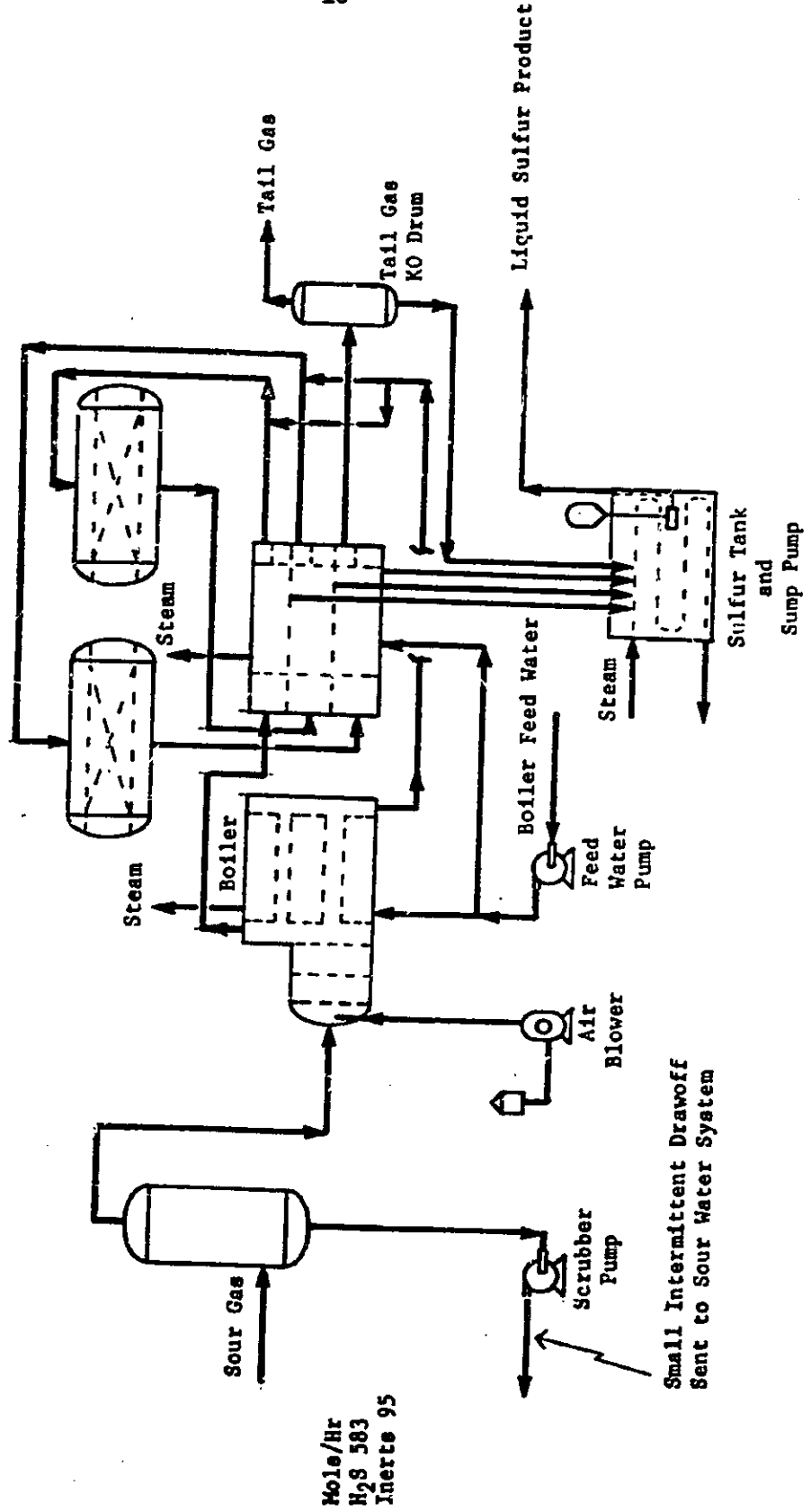
Recovery of sulfur from hydrogen sulfide streams is usually effected by the Claus process. The process involves burning a portion of the hydrogen sulfide to produce a gas stream with an $\text{H}_2\text{S}/\text{SO}_2$ ratio of 2. The hydrogen sulfide and sulfur dioxide are then converted to elemental sulfur in one or more reactors containing activated alumina or bauxite as catalyst. The reactions involved are:



Claus plants can be operated in a number of configurations. A typical configuration is presented in Figure 2.6.

Figure 2.6 is an example of a Claus plant with two converters. Often three converters are used and, if the concentration of H_2S is 15-25 mole percent, only one-third of the acid gas passes through the burner in

FIGURE 2.6
TYPICAL CLAUS PLANT



order to maintain a flame. The H₂S rich gas is usually the product of an absorption process used to clean up a gas stream.

The feed gas passes through a knockout drum to remove sour water and then enters a furnace where it is mixed with sufficient air to burn any hydrocarbons plus one-third of the H₂S. The oxidation takes place at temperatures greater than 1800°F. Heat is recovered from the hot gas stream in a waste heat boiler. Part of the stream passes through a condenser where it is cooled to about 400°F by producing steam. Sulfur is thereby condensed and passed to a heated sulfur tank in the liquid state.

After the first condenser, the cooled gas is mixed with sufficient hot gas from the waste heat boiler to raise the temperature to that required for conversion (greater than 450°F). The gas then enters the primary converter where sulfur is produced by reaction 3. The sulfur produced in the first converter is condensed in a second condenser and the gas from this condenser is again re-heated by mixing with hot gas from the waste heat boiler. The heated gas passes through a second catalyst bed, a third condenser and to a knock-out drum where the last sulfur is removed.

The tail gas still contains appreciable quantities of sulfur (0.5% or more). A third converter will reduce the sulfur content but the effluent will still be too high in sulfur content to allow direct venting. In the past, the tail gas has been incinerated and vented through a stack.

2.1.7 Selexol Process

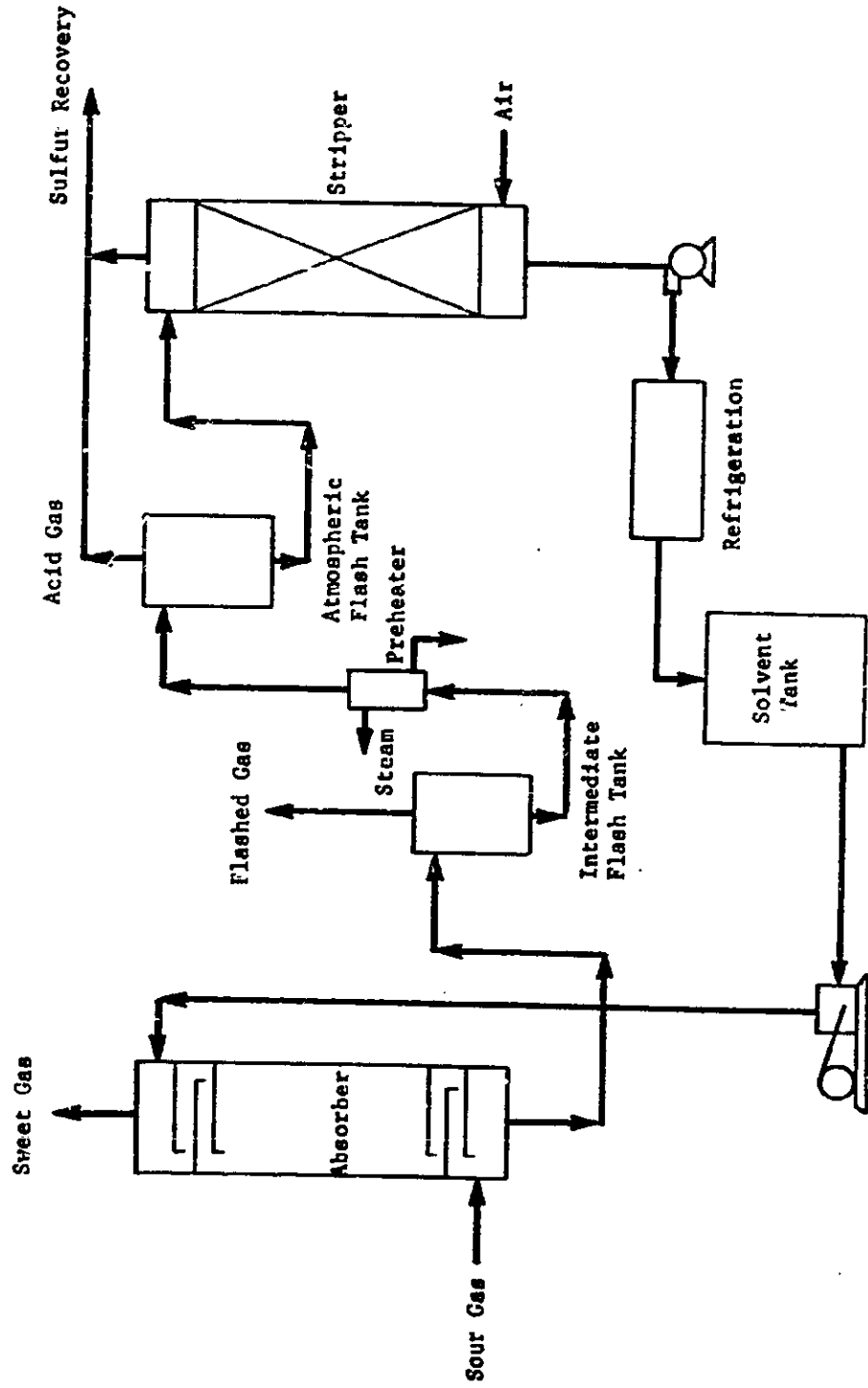
The Selexol Process, at first used to extract CO₂ from synthesis gas, has now been adapted to the treatment of natural gas. It offers a direct economical means for removal of acid gases to produce sweet dry gas. Process solvent consists of the dimethyl ether of polyethylene glycol (DMPEG). It displays high physical absorption capacity for the acid gases, including hydrogen sulfide, carbon dioxide, carbonyl sulfide and mercaptans (25).

"Sour" gas is admitted at the bottom of the absorber, Selexol's solvent is sprayed from the top of the absorber. The sour gas contacts the Selexol solvent countercurrently in the absorber. The Selexol's solvent absorbs the acid gases out of the sour gas. The sweet gases thus obtained exit from the top of the absorber. The acid gas rich solvent, at first, is flashed in an intermediate flash tank where some of the acid gases are flashed off. The intermediate Selexol solvent is preheated and then sent to an atmosphere flash tank where acid gases are further flashed. The hot solvent is sprayed from the top of a stripper. Air is blown in from the bottom of this stripper. This air strips all the sulfur constituents from the Selexol's solvent. The sulfur compounds along with acid gases are treated in a sulfur recovery unit. The lean Selexol's solvent is pumped out from the bottom of the stripper and cooled in a refrigeration unit and stored in the solvent storage tank for recirculation to the absorber.

Process performance is illustrated by data obtained from the (pilot-plant) unit shown in Figure 2.7 with 580 psig feed gas containing 25 vol. % H₂S and 10% CO₂, presented in the table below (25).

FIGURE 2.7

SELEXOL PLANT



Feed Gas (Vol. %)	
H ₂ S	25
CO ₂	10
COS	0.110
CH ₃ SH	0.020
Pressure, psig	500

	<u>Solvent Removal</u>	<u>Complete Removal</u>
Solvent loading (scf acid gas/ gallon solvent)	10.40	4.50
Sweet gas (Vol. %)		
H ₂ S	0.0001	0.0001
COS + CH ₃ SH	0.00015	0.00015
CO ₂	7.5	0.3
Acid gas (Vol. % hydrocarbon)	<2.0	<2.0

2.2 Trace Sulfur Compound Cleanup Processes

With the exception of the Rectisol process, none of the processes described in 2.1 can reduce sulfur compound levels to that required for protection of the methanation nickel catalyst in the SYNTHANE Process. Another (trace sulfur compound) removal system used in series with one of the above processes is required to obtain levels of the order of 0.1 ppmv sulfur impurities. Candidate processes that have the potential to accomplish this include -

- Dry Box Process
- Seaboard Process
- Caustic Soda Scrubbing
- Cyclic Use of Calcined Dolomite
- Molecular Sieves
- Catalytic Conversion
- Zinc Oxide
- Iron Oxide
- Activated Carbon
- Metal Impregnated Activated Carbon

Each of these processes/systems is briefly discussed below.

2.2.1 Dry Box Process

Of perhaps greatest economic importance is the "dry-box" process for removing hydrogen sulfide from coke-oven gases and other industrial gases. In this process, hydrated iron oxide is coated on shavings or other supporting material spread on trays in rectangular boxes. The gas, to which sufficient air has been added to provide an oxygen concentration of 0.6-1.0%, is passed over the iron oxide. The hydrogen sulfide reacts to form ferric sulfide, which, in turn, is reoxidized by the added oxygen to the original iron oxide and sulfur. After some use, it is necessary to remove the iron oxide and allow it to become thoroughly revived in the air before returning it to the boxes for further use. The iron oxide is finally discarded when the total sulfur content reaches 50 to 60%. When used for final cleanup, the oxide may be discarded with a sulfur content as low as 30%. The advantages of the dry-box process are the completeness of removal of hydrogen sulfide and the simplicity of the process. The dry-box process is one of the most selective methods of removing hydrogen sulfide in the presence of carbon dioxide. A process related to the dry-box process has been used in several plants in Germany. In this process, gas to which the stoichiometric amount of oxygen and 330-500 ppm of ammonia have been added, is passed over activated carbon. The hydrogen sulfide is thereby converted into sulfur, which can then be recovered by extraction with ammonium sulfide solution. The hydrogen sulfide content of the treated gas is reduced to about 1 ppm.

2.2.2 The Seaboard Process

This process was developed by Koppers Company in 1920. Large volumes of air are employed to strip the hydrogen sulfide from the absorbent. The hydrogen sulfide is not usually recoverable from this process. The air used in the reactivation operation tends to oxidize some of the hydrogen sulfide to thiosulfate; hence, it is necessary to discard some of the absorbent periodically and add fresh solution to maintain the desired composition (3.0-3.5% Na_2CO_3). Somewhat related to the Seaboard process for recovering hydrogen sulfide as elementary sulfur are the ferrox process and the nickel process. In the ferrox process, a suspension of iron oxide is used as catalyst and in the nickel process, nickel sulfate is generally employed.

2.2.3 Gas Cleaning Using Caustic Soda Solution

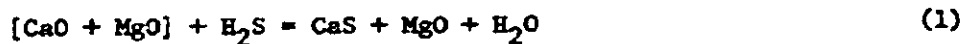
Where complete removal of relatively small quantities of hydrogen sulfide is necessary, it is the practice to use sodium hydroxide solutions. This is normally a batch operation, the solution being replaced when most of the sodium hydroxide has been converted into sodium sulfide. Gas-liquid contacting devices employed to effect this reaction include packed towers, jet scrubbing devices, and simple bubbling of the gas through the solutions. In some cases the removal of hydrogen sulfide is carried out in two stages, the gas being first contacted with a solution of sodium sulfide, which is converted to the hydrosulfide, concentrated, and sold. The gas is then contacted with a solution of sodium hydroxide, which completely removes the remaining traces of hydrogen sulfide from the gas, the solution being converted to sodium sulfide, which is later converted to sodium hydrosulfide.

Calcium hydroxide is a less expensive base, but its insolubility and that of calcium sulfide cause processing difficulties. It is therefore less frequently used than sodium hydroxide.

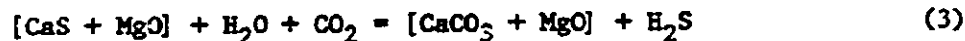
Where hydrogen sulfide must be removed from acid gases such as carbon dioxide, alkaline absorbents cannot be used. In these cases, oxidizing agents such as potassium permanganate solution or a buffered solution of sodium dichromate and zinc sulfate are used.

2.2.4 Cyclic Use of Calcined Dolomite to Desulfurize Fuels Undergoing Gasification

Clean power systems are being developed in which coal or oil would be either gasified or pyrolyzed at high pressure in fuel treating processes. In such processes, sulfur in the fuel would be converted to H₂S, which would be captured by either fully calcined or half-calcined dolomite.



Reaction (2) can be conducted in reverse to regenerate half calcined dolomite and to obtain H₂S at a concentration sufficient for conversion to elemental sulfur in a Claus system:



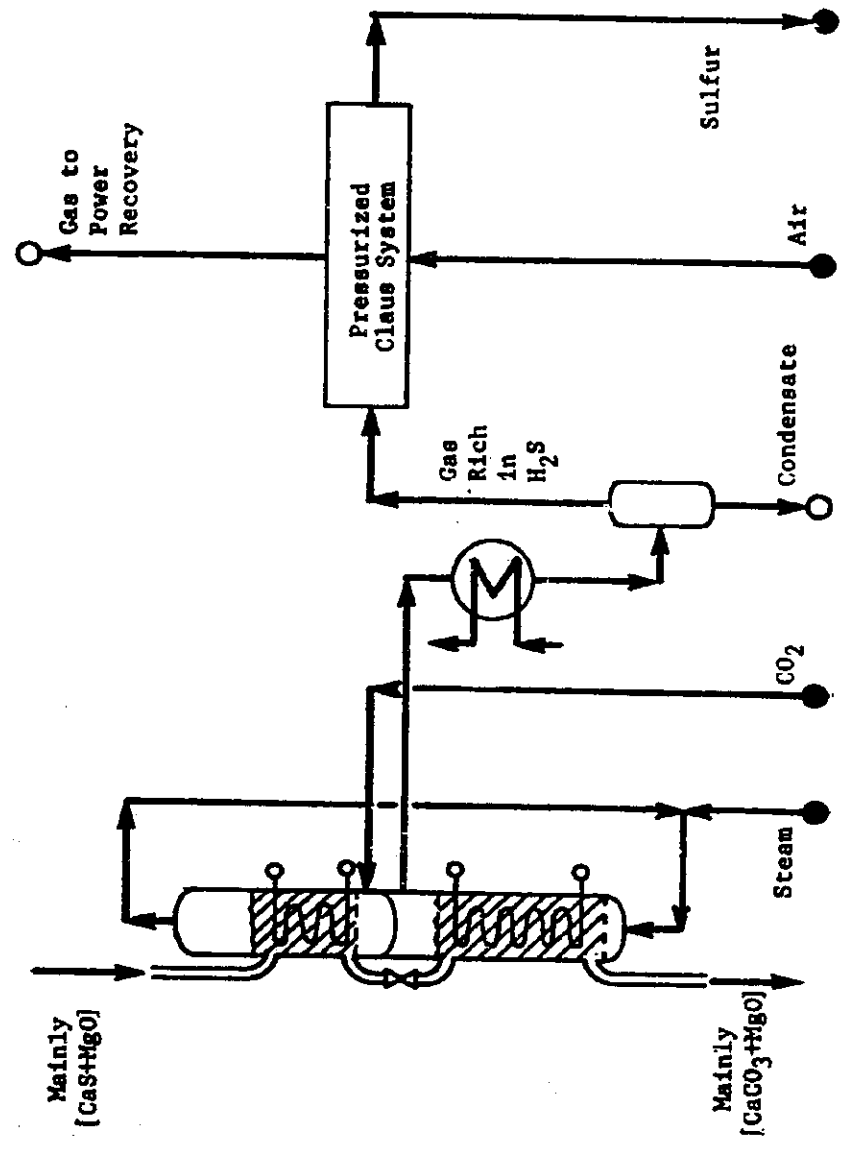
Equilibrium for reaction (2) or (3) is a strong function of temperature, the regeneration being favored at low temperature. The primary interest is in the application of the reactions in systems where the solid is used cyclically.

Figure 2.8 shows equipment suitable for sulfur recovery when desulfurization is accomplished by means of reaction (1) so that the solid charged to the sulfur desorber contains CaO. The sulfur desorber in the figure houses two fluidized beds: a lower bed for conducting reaction (3) and an upper bed in which CaO is converted to CaCO₃ in the absence of steam. Provision of the upper bed allows one to use a higher stream partial pressure in reaction (3) than would otherwise be possible, for one does not have to worry about the formation of Ca(OH)₂. Both beds of the figure might operate at 1100°F.

2.2.5 Gas Sweetening Using Molecular Sieve Method

Numerous crystalline aluminosilicates have been synthesized. Their structural properties have been presented as follows (4):

FIGURE 2.8
CYCLIC USE OF CALCINED DOLOMITE
SULFUR DESORBER AND SULFUR RECOVERY



Type	Chemical Formula	Crystalline Structure
4A	$0.96 \pm 0.04 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ $1.92 \pm 0.09 \text{SiO}_2 \cdot n\text{H}_2\text{O}$	cubic $a = 12.3$
5A	Similar to 4A, 75% Na ion replaced by Ca ion	cubic $a = 13$
13X	$0.83 \pm 0.05 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ $2.48 \pm 0.03 \text{SiO}_2 \cdot n\text{H}_2\text{O}$	cubic $a = 24.95 \text{ \AA}$

Trace sulfur cleanup involves the use of the type 13X. These molecular sieves have a pore diameter of 8.9 Å. Hydrogen sulfide and mercaptans have molecular dimensions small enough to enter these pores. This particular application of removing sulfur compounds is an example of selective adsorption. The more polar sulfur compounds are more strongly adsorbed than the hydrocarbons. The CO₂ influences the amount of H₂S adsorbed, reducing it by 5-10 percent at high CO₂ concentrations. In some streams, water is present. The water is removed very quickly at the inlet end of the adsorber. The weight of adsorbent in this water adsorption zone must be added to the bed requirements for the sulfur removal. In the removal of sulfur compounds, it is necessary to stop the adsorption when the sulfur compounds first appear in the effluent. The next step is removal of the entrained liquid in the bed and depressurization to 60-120 psig. The desorption step consists of passing hot purge gas at 60-120 psig in the same direction as the sour gas feed. Regeneration is performed at 400-500°F. The lower temperatures remove the H₂S and the higher temperatures the mercaptans. The gas requirement is 20-25 mol for 100 lb of molecular sieve. It is desirable that the purge gas be dry, sweet and contain no oxygen. The oxygen would react with the H₂S to form sulfur which would be deposited in the absorber and poison the adsorbent. The cooling is accomplished by introducing liquid feed or product at the bed top. This cooling liquid should contain less than 1 grain of sulfur per 100 cu. ft. A cooling flow of 4 gallons per minute per square ft. of bed cross-section has been found adequate.

Among the potentially limiting handicaps associated with molecular sieves mentioned is that dealing with its ability to handle COS. Not only are questions of limited sorption kinetics and capacity involved, but also the fact that sieves have been reported to promote the reaction between CO₂ and H₂S to form COS and H₂O. A quantitative indication of the extent of this problem was recently reported by Cines, et al. (3). These workers used various molecular sieves (manufacturers not specified) to treat natural gas containing only H₂S as sulfur at 33 ppm levels. Approximate operating conditions were 50 atm pressure, ambient temperature, space velocity of 5000 hr⁻¹, and 2.2% CO₂ in feed. With Type 13X sieves (10 Å pore size, Na form), they found that at H₂S breakthrough (1 ppm in effluent), 88% of the H₂S that had apparently been adsorbed by the sieve had actually been eluted by their column as COS. Considerably lower conversions (5-17%, defined as above) were found with Type 5A sieves (5 Å pore size, Ca form) but these are generally considered to offer limited capacity for larger organic sulfur molecules. It is possible that reduced space velocity would

lessen this effect by allowing increased COS sorption. Use of 5A followed by 13X sieves might have potential under some circumstances. In any event, the problem represented a serious limitation with respect to the present application. Sieve manufacturers are apparently working on methods to reduce COS formation tendency (see, e.g., Turnock, et al. (21)).

2.2.6 Catalytic Conversion

Satterfield, et al. (22) have recently published some results on hydrodesulfurization of thiophene over molybdenum-based catalysts. For example, using a Ni/Mo catalyst in a once-thru tubular reactor with 1% thiophene in pure hydrogen at 11 atm total pressure and a space velocity of ca. 7500 hrs⁻¹, essentially complete conversion (>99%) of thiophene was achieved at ca. 300°C. The authors also noted the fractional conversion of thiophene in pure H₂ increased with decrease in thiophene partial pressure and claimed conversion rate was nearly zero order with respect to initial thiophene partial pressure. This latter result was actually based on runs using a Co/Mo catalyst at thiophene partial pressures ranging from ca. 30-150 mm Hg, but the authors implied a similar trend was expected with Ni/Mo. If, indeed, this trend is extrapolative down to lower thiophene partial pressures and total system pressure is not greatly influential (the 45 ppm thiophene level at 70 atm total pressure planned for investigation in our program represents a partial pressure of 2.4 mm Hg), the above results are encouraging. However, the authors indicate that, based on past work, H₂S in feed gas does inhibit the reaction.

A consultation was held with Prof. C. N. Satterfield to discuss catalytic hydrodesulfurization matters specific to our program. As indicated, Satterfield and others have recently published some information on thiophene conversion over molybdenum-based catalysts. Over the range of conditions used in that study, they found conversion rate was nearly zero order with respect to initial thiophene partial pressure (per cent conversion being inversely proportional to concentration). Professor Satterfield did feel, however, that at the very low thiophene partial pressures to be used in our work, the conversion rate would likely be first order in thiophene concentration. He bases this mainly on earlier work published by Satterfield and Roberts (23) where they studied the hydrogenolysis kinetics of thiophene over Co/Mo catalyst in a differential reactor, at 1 atm pressure, and found that rate was correlated by a Langmuir-Hinshelwood type of kinetic expression. If one uses the model and appropriate rate and adsorption constants derived by them, both of the above discussed behavior trends manifest themselves when appropriate values of thiophene partial pressure are used.

It is stressed that their model was based on experimentation per partial pressure, and accordingly, the effects of extrapolation to the low partial pressures planned in our program are not known. With this in mind, the model does predict the magnitude of the inhibition effect due to H₂S. This turns out to be essentially unimportant at low H₂S levels.

With regard to the important question of catalyst poisoning effect due to the high (15%) CO levels in synthesis gas, Professor Satterfield indicated that he did not have any first hand knowledge.

Neither was he aware of information to quantitatively predict the extent of methanation over presulfided Ni/Mo or Co/Mo catalysts in our range of interest.

Regarding other poisons in coal-derived synthesis gas, he did point out that aromatics (especially three ring aromatics), olefins, diolefins, etc., will compete for catalyst sites thereby reducing HDS activity. This should not be much of a problem for an HDS sulfur guard catalyst downstream of a Benfield unit since the feed at that point, in theory, should be essentially free of such materials. A more likely area for concern would be in connection with the upstream Co/Mo catalyst planned for water-gas shifting (one-half the total gas stream) in the SYNTHANE process train. Although specifically designed to carry out the shift reaction, this unit has also been envisioned to effect a large conversion of organic sulfur contained in the feed to H₂S. Thus, system upsets in the oil scrubbing system upstream of the shift reactor could be a problem.

It is possible that catalytic conversion of organic sulfur to H₂S would be required as part of an overall sulfur guard system. The major difficulty here involves selecting a candidate that can achieve relatively high conversion (via hydrogenation or hydrolysis) of the very low level organic sulfur compounds, while allowing little or no methanation or shifting to occur in the bulk gas stream. A major problem with methanation and, to a lesser extent, shifting involves the fact that both are exothermic reactions and more costly processing schemes than simple once-through fixed bed reactors would be required to remove generated heat and avoid runaway reaction.

An important consideration regarding catalytic conversion involves position of the reactor within the overall processing train. For example, placement before the acid-gas removal step would be desirable in order to take advantage of the H₂S removal capacity of that system which would not be affected at all by the incremental increase in loading. Furthermore, the gas is hot and would require no additional heating. However, high concentrations of H₂S and CO₂ would unfavorably influence hydrogenation or hydrolysis equilibrium, and other impurities retained in the gas at this point might affect catalyst performance and life. Placement directly before a ZnO reactor (and possibly downstream of activated carbon) might prove feasible as long as total sulfur loading to the conversion reactor was sufficiently low not to impose an uneconomically high H₂S loading on non-regenerable ZnO.

Another variation might be placement downstream of acid-gas treatment but upstream of activated carbon and zinc oxide. This would require an additional heating and cooling step, however. Finally, placement within the acid-gas treatment step might be possible, for example, with a system such as the Benfield "Hi Pure" system which uses a DEA scrubber for additional gas cleanup to supplement the primary hot-carbonate scrubber. Placement of the conversion step could be between both scrubbers. This would have the advantage of working with a relatively clean gas stream that was low in CO₂ and H₂S, as well as allowing the incremental H₂S to be sent directly to the DEA scrubber without having to overburden downstream sulfur guard units such as activated carbon and/or zinc oxide. At least one disadvantage would, of course, be the incorporation of an additional heating and cooling step. Problems of physical incompatibility with "Hi Pure" might also be restrictive.

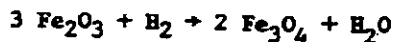
2.2.7 Zinc Oxide

Zinc oxide was another active material considered for this application (1). It is probably unsurpassed in its potential to achieve ultra-low levels of sulfur, in the form of H₂S, in treated gas streams. The reaction between ZnO and H₂S to form ZnS and H₂O is so strongly favored thermodynamically that equilibrium levels of 1 ppb or less H₂S are predicted over the normal operating temperature range (350-400°C) for gas streams containing 0.1% H₂O. Under practical operating conditions, H₂S levels of <0.1 ppm are claimed by suppliers. High temperature operation is required for two reasons. First of all, although low temperatures thermodynamically favor formation of ZnS, the absorption capacity of the material drops rapidly when operation falls below ca 350°C. (Absorption capacity varies greatly according to processing conditions, but capacities of approximately 20 wt % sulfur are typically claimed by suppliers for commercial operation before exiting H₂S levels exceed 0.1 ppm.)

Another reason for high temperature operation of ZnO is that other sulfur compounds must be thermally decomposed to H₂S before any significant removal is noted. Removal of such compounds as methyl mercaptan and carbon disulfide is not generally considered as presenting great difficulty. Carbonyl sulfide removal is more controversial with success apparently dependent on the specifics of the operation. The major limitation of ZnO, as expected, involves thiophene which is thermally quite stable. Thermal decomposition data on thiophene, specific to our needs, have not yet been found, but preliminary indication is that very little decomposition occurs at temperatures approaching 500°C. Because the formation of ZnS is so strongly favored, even at high temperature, regeneration of ZnO is generally considered to be uneconomical and is not practiced. As a result, sulfur loadings to ZnO must be minimized in order to achieve economic operation. Various ZnO absorption catalysts are commercially available (e.g. Girdler's G-72, Katalco's 32-4, Topsoe's BTZ)*.

2.2.8 Iron Oxide

In general, in order to avoid iron carbonyl formation, iron oxide catalyst is usually run at temperatures >200°C. Temperatures in the range of 350-400°C, similar to those often used for zinc oxide, are sometimes used. This is done presumably for the same reasons as for zinc oxide; namely to increase sorbent capacity and help promote decomposition of the so-called "reactive sulfur compounds" (mercaptans, CS₂, COS (?)). Above 175°C, in the presence of H₂, Fe₃O₄ is considered the active sorbent/catalyst because the following reaction is favored



Thus, the H₂S desulfurization reaction is



while for zinc oxide it is



*Specification of tradenames in this report does not constitute endorsement by the U.S. Department of Energy.

Using thermodynamic equilibrium data provided by Imperial Chemical Industries, the following approximate equilibrium H₂S levels are predicted (19):

Temp (°C)	H ₂ O =	Equil. H ₂ S (ppm) Over Metal Oxide*			
		Fe ₃ O ₄		ZnO	
		0.17%	1.7%	0.17%	1.7%
200		0.03	0.5	1 x 10 ⁻⁵	1 x 10 ⁻⁴
250		0.05	1.1	9 x 10 ⁻⁵	9 x 10 ⁻⁴
300		0.07	1.5	3 x 10 ⁻⁴	3 x 10 ⁻³
370		0.13	2.7	2 x 10 ⁻³	2 x 10 ⁻²
400		0.15	3.2	3 x 10 ⁻³	3 x 10 ⁻²

*Gas contains 45% H₂.

As indicated, for streams containing 0.17% H₂O (comparable to the 0.1-0.2% in simulated SYNTHANE syntheses gas feed), even at temperatures of 400°C, equilibrium H₂S levels over zinc oxide are approximately 50x lower than over iron oxide. (Much larger differences are predicted at lower temperatures.) It should be pointed out that under actual commercial run conditions, dynamic equilibrium values would, no doubt, be higher than the above figures. However, <0.1 ppm H₂S levels using zinc oxide are often claimed by suppliers, depending on processing conditions.

2.2.9 Activated Carbon

Fixed beds of activated carbons have historically been used for removing odorous compounds from gaseous streams. Specially treated activated carbons have been formulated by catalyst manufacturers for the removal of sulfur compounds, including hydrogen sulfide, carbonyl sulfide and mercaptans from hydrocarbon streams. A typical activated sorbent is coconut shell char containing 5% (wt) copper made by Girdler (G-32 J). The physical properties of G-32 J are (9):

Surface Area	900 m ² /g
Pore Volume	0.6 cm ³ /g
Bulk Density	0.56 to 0.61 g/cm ³
Particle Size	4 x 8 mesh granules 8 x 30 mesh granules

Activated carbon has a desulfurization capacity of about 2 x 10⁵ ft³ of natural gas per pound of sorbent in reducing sulfur mole fraction from about 30 ppm (v/v) to 0.2 ppm (v/v). High molecular weight hydrocarbons can severely reduce adsorption capacity and must be removed prior to entering the bed. Alternatively, they must be removed during regeneration or the duty cycle may be reduced to 10% that of a fresh bed.

The useful life of activated carbon sorbents has been found to be about 2 years in most applications. The sorbent is generally regenerated with superheated steam at 400 to 500°F near atmospheric pressure. Usually

this requires 12 to 25 pounds of steam per hour per cubic foot of carbon. After steaming, the carbon bed should be purged with inert or process gas prior to putting it back on stream. Carbon beds are generally operated at ambient temperatures. Oxygen or air must be excluded from these beds since activated carbon can act as oxidation catalysts, thus destroying the bed due to excessive temperature rise.

2.2.10 Metal (CuO/Cr₂O₃) Impregnated Activated Carbon

Pittsburgh Carbon 7-2 (Katalco FCA) is the adsorbent that was planned for the SYNTHANE 72 TPD unit. Pittsburgh Carbon is the original supplier of both Katalco 7-1 (unimpregnated) and 7-2 carbons (their designation being BPL and FCA, respectively). Girdler's G-32W grade of metal-impregnated activated carbon is also supplied by Pittsburgh Carbon and is apparently equivalent to FCA. The metallic impregnants are copper and chromium. The copper, apparently present as the oxide, provides for bulk H₂S desulfurization by forming the corresponding metal sulfide. The role of the chromium species is less certain but it may promote conversion of some organic sulfur to H₂S. The precise nature and composition of impregnants is confidential although non-proprietary information published by Girdler describing their G-32W material indicates approximately 6 wt % copper and 3.4 wt % chromium (as metals). Both BPL and FCA (7-1 and 7-2) are produced from identical coal-based carbon sources with the only major difference, besides metal impregnation, being in surface area. According to Pittsburgh Carbon, the impregnation process lowers the original BPL surface area of ca 1050 m²/g to approximately 750 m²/g for FCA. Accordingly, some loss in absolute adsorptive capacity of the carbon portion of the material is likely for FCA relative to BPL.

Regarding the expected performance of activated carbon, Pittsburgh Carbon agreed with other catalyst suppliers consulted (CCI, Katalco, Girdler) that COS represented the most difficult sulfur compound to adsorb. However, in general disagreement with the others, Pittsburgh Carbon was quite optimistic with respect to the ability of activated carbon to handle most of the thiophene. None of the above firms supplied specific information to support their predictions. It is likely that some of this apparent contradiction may be due to the fact that performance is no doubt highly dependent on the numerous specifics of the operation, not the least of which includes the fact that adsorption of specific species is often dependent on the nature and concentration of other adsorbates present in the gas stream.

Allytic and Chemicals, Inc., Louisville, Kentucky, was quite emphatic in their belief that activated carbon (plain or impregnated grades) would not be suitable for the spectrum of sulfur compounds (hydrogen sulfide, methyl mercaptan, carbonyl sulfide, carbon disulfide, and thiophene) at the expected levels (10-80 ppm) requiring removal down to 0.1 ppm sulfur. It was felt that only in the case of methyl mercaptan (maximum levels of ca 20 ppm predicted) would system loading capacity and removal efficiency possibly prove activated carbon to be a viable approach to sulfur guard. They indicated that capacities for H₂S, CS₂, and C₄H₄S were considerably lower (1/2-1/3 or less of that for CH₃SH) so that target removal efficiencies could not be economically achieved. Finally, and perhaps most importantly,

it has been their experience that activated carbon has little or no value as a system for removing carbonyl sulfide (which, at ca 80 ppm maximum predicted levels could represent the most prevalent sulfur compound feed to a premethanator sulfur guard system). This is despite the fact that adsorption isotherm data in the literature for COS on activated carbon indicate very high equilibrium adsorption (8).

Regarding the expected performance of activated carbon, representatives of Katalco offered reservations similar to those advanced in discussions with CCI. The most important of these involves the probability of reduced capacity for thiophene compared to methyl mercaptan, and poor performance with respect to removal of carbonyl sulfide. If the limitation regarding COS proves real, it may not represent a crucial limitation. This is despite the fact that COS may represent the predominant sulfur compound exiting a hot carbonate scrubber if one assumes a minimal COS removal efficiency of 75% as has been reported in some commercial installations (7). This is because special designs of the Benfield system (e.g. their "Hi-Pure" process which employs a dual scrubbing system consisting of hot potassium carbonate followed by diethanolamine) are claimed by the manufacturer to be able to approach 99% removal efficiency and achieve <10 ppm COS levels without great difficulty (7).