REVIEW OF SELECTED SULFUR RECOVERY PROCESSES FOR SNG PRODUCTION

FINAL REPORT

Prepared by
A.E. COVER, D.A. HUBBARD, S.K. JAIN,
K.V. SHAH, P.B. KONERU AND E.W. WONG

KELLOGG RUST SYNFUELS, INC.
Three Greenway Plaza East
Houston, Texas 77046

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GRI Project Manager
HOWARD S. MEYER
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REVIEW OF SELECTED SULFUR RECOVERY PROCESSES
FOR
SNG PRODUCTION

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1.0 INTRODUCTION AND SUMMARY

Kellogg Rust Synfuels, Inc.(KRSI) has assembled background information for use in evaluating technologies for downstream gas processing, specifically sulfur recovery, as part of work with the GRI/Advisors Planning and Strategy (GAPS) Committee under GRI Contract No. 5082-222-0754. A sulfur recovery process, in the context of coal-to-SNG plant design, is a technology devised to accept the sulfur-bearing gas stream from an acid gas removal unit, to convert the sulfur contained in that stream to its elemental form, and to recover that sulfur for sale as a by-product of SNG manufacture. The sulfur recovery process may or may not operate in tandem with a tail gas or flue gas treatment process for final removal of sulfur from gases to be vented or sold as byproducts.

Using pertinent references and in-house information, KRSI developed a list of 14 technologies for sulfur recovery. The listing has been tabulated in Section 2.0. For each process, the name and location of the developer, a capsule description of the process, typical operating conditions, number of units built or in operation and other comments are included. The listing has also identified the type of reaction, reaction phase (liquid or gas), acceptable H_2S concentration level in the feed gas and gases removed.

The GAPS Committee chose six representative technologies for further evaluation. These were:

- Claus	High H_2S concentration, gas phase Claus reaction. H_2S, COS, SO_2 and CS_2.
- Amoco Direct Oxidation	Medium H_2S concentration, gas phase oxidation and Claus reactions, H_2S and SO_2.
- LO-CAT	Low to medium H_2S concentrations, liquid phase oxidation reaction, H_2S.
- Selectox	Low to medium H_2S concentrations, gas phase oxidation and Claus reactions, H_2S and SO_2.
- Stretford	Low to medium H_2S concentrations, liquid phase oxidation reaction, H_2S.
- Unisulf	Low to medium H_2S concentrations, liquid phase oxidation reaction, H_2S.

A "Status Summary" report has been prepared for each of the six technologies mentioned above. Their directions were to summarize pertinent, recent information within a concise report for each process. Each of the Status Summary reports is divided into the following sections, as applicable:

- General Information
- Historical Background
- Process Chemistry
- Process Description
- Commercial Design Data
- Advantages and Disadvantages
- Commercial Installations
- References

The Status Summary reports appear in Sections 3.0 through 8.0 for the Claus, Amoco Direct Oxidation, LO-CAT, Selectox, Stretford and Unisulf processes, respectively. With the list of processes, these documents comprised the background information needed in further evaluation.

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LIST OF SULFUR RECOVERY PROCESSES

H2S CONCENTRATION	PHASE	REACTION
HIGH (H) : > 25 % H2S	G : GAS	C : CLAUS
MEDIUM (M) : 5-25 % H2S	L : LIQUID	O : OXIDATION
LOW (L) :0.5-5 % H2S		LC: LOW TEMP CLAUS

	NAME OF PROCESS	H2S CONC	PHASE	REACTION	GASES REMOVED
1	AquaClaus(Phosphate)	H,M	L	LC	H2S,SO2
2	CLAUS	H	G	C	H2S,COS,SO2,CS2
3	Citrate	H,M	L	LC	H2S,SO2
4	Cold Bed Adsorption	L	G	LC	H2S,SO2
5	Direct Oxidation-Amoco	M	G	O & C	H2S,SO2
6	IFP-Clauspol 1500	L,M	L	LC	H2S,SO2
7	LO-CAT	M,L	L	O	H2S
8	MCRC	L	G	LC	H2S,SO2
9	Selectox	M,L	G	O & C	H2S,SO2
10	Stretford	M,L	L	O	H2S
11	Sulfint	L	L	O	H2S
12	Sulfreen	L	G	LC	H2S,SO2
13	Takahax	L,M	L	O	H2S
14	Unisulf	M,L	L	O	H2S

LIST OF SULFUR RECOVERY PROCESSES

AQUACLAUS (PHOSPHATE)

Stauffer Chemical Co., Westport, Connecticut

- A Claus reaction process taking place in a buffer solution. The buffer action is produced by phosphate acid and sodium phosphate.
- The process can serve both as a Claus plant tail gas treating unit and a flue gas desulfurization system simultaneously. The process can be applied to coal gasification plants, refineries, and petrochemical plants.
- SO_2 in Claus plant tail gas or boiler flue gas is absorbed into the phosphate solution to form bisulfate ions. An H_2S stream bypassing the Claus plant is used to react with the bisulfate ions to produce elemental sulfur. The sulfur-phosphate slurry is concentrated and molten sulfur is recovered.
- The process can remove essentially all the H_2S and reduce the SO_2 in the treated gas down to less than 200 ppm.
- A 4 MM SCFD unit was started up in 1984 for Helfin Oil Company's Queens City, Texas facility, producing 35 TPD of elemental sulfur.

CITRATE (As designed by M. W. Kellogg)

U.S. Bureau of Mines

- A Claus reaction process taking place in a buffer solution. The buffer action is produced by citric acid and sodium citrate.
- The Citrate process can serve both as a Claus plant tail gas treating unit and a flue gas desulfurization system simultaneously. The process can be applied to coal gasification plants, refineries, petrochemical plants and coke-oven gas plants.

- SO_2 in Claus plant tail gas or boiler flue gas is absorbed into the citrate solution which is subsequently regenerated using H_2S to produce elemental sulfur. The sulfur-citrate slurry is sent to an air flotation tank for sulfur concentration. The sulfur slurry is heated and sulfur is received in a molten form.

- The process can remove essentially all the H_2S and reduce the SO_2 in the treated gas down to less than 200 ppm.

- A commercial size citrate plant was started up in 1983 for treating Claus plant tail gas at the Saber Energy Inc. refinery in Corpus Christi, Texas. Up to 100 TPD of sulfur is being recovered in the citrate unit.

CLAUS

All Engineering Companies in the Sulfur Recovery Field

- The process has been used for many years to recover sulfur from acid gas streams.

- Acid gas and a controlled stoichiometric quantity of air are fed into a reaction furnace, where one-third of the H_2S is burned to SO_2. The H_2S and SO_2 react to form elemental sulfur thermally in the furnace and catalytically in the reactors according to the following Claus reaction:

$$2\ H_2S + SO_2 \text{ ----- } 3S + H_2O + \text{Heat}$$

The catalytic reactions take place at about $650^{\circ}F$. The sulfur formed is then condensed and removed. Successive stages of catalyst beds are used to increase sulfur recovery.

- The process has many variations due to the feed gas conditions and compositions.

  H_2S concentration > 50% - straight through Claus

  H_2S concentration < 50% - feed gas bypass/preheat and air preheat.

- The process can achieve up to 97% sulfur recovery. Therefore, a tail gas treating process is required if higher sulfur recovery is desired or if environmental regulations have not been met.

- The process has been applied to recover sulfur from acid gas streams with H_2S concentration as low as 20 vol%.

COLD BED ADSORPTION

Amoco Production Co., Tulsa, Okla.

- A gas phase catalytic low temperature Claus reaction process taking place over Claus catalyst.
- Claus plant tail gas at about 260°F is passed over a bed of Claus catalyst. Sulfur is formed and adsorbed on the catalyst when loaded with sulfur, the catalyst bed is regenerated by bypassing a slip-stream of the feed to the first Claus reactor. Adsorbed sulfur is vaporized and condensed. One reactor is always in regeneration and one on-stream.
- The process can improve the overall sulfur recovery of a Claus plant to 99+%. The new ULTRA (Ultra Low Temperature Reaction Adsorption) Process - an extension of the CBA Process, increase the overall sulfur recovery to 99.7%.
- Thirteen CBA units are in design or operation with capacities (Claus + CBA) ranging from 2 to 1200 LTPD of sulfur.

DIRECT OXIDATION (AMOCO)

Amoco Production Co., Tulsa, Okla.

- A gas phase reaction where H_2S is oxidized with air over an alumina catalyst to form sulfur.

- The process can be used to recover sulfur from acid gas streams containing less than 15% H_2S.

- The acid gas stream is mixed with air and passed over an alumina catalyst bed. H_2S is directly oxidized to sulfur at about 950°F. The Claus reaction also occurs as a side reaction and the sulfur product is condensed. Depending on the feed gas composition and sulfur recovery desired, a second direct oxidation reactor followed by a coventional Claus reactor might be required.

- Nine commercial units have been constructed since 1959.

IFP CLAUSPOL 1500

Institut Francais du Petrole

- A liquid phase Claus reaction process, with polyethylene glycol as a liquid carrier for the catalyst.

- Acid gas containing H_2S and SO_2 in ratio of 2:1 is countercurrently contacted in a packed tower with a recirculating stream of the liquid carrier. Elemental sulfur formed by the low-temperature (260°F) extension of the Claus reaction sinks to the bottom of the reactor/tower and removed through a seal leg.

- The process can remove H_2S and SO_2 from Claus unit tail gas to 1000 ppm level of SO_2 after incineration. The feed gas can contain up to 20% H_2S.

- Over 30 units in operation with capacities ranging from 30 TPD to 800 TPD.

LO-CAT

ARI Technologies, Inc.

- A liquid phase oxidation process which uses a non-toxic, slightly alkaline solution containing an iron chelate complex as a redox catalyst.

- Gas stream containing H_2S is contacted with aqueous LOCAT solution in a venturi scrubber. The H_2S absorbed in solution is immediately oxidized to elemental sulfur. The reduced catalyst solution is regenerated by air in an oxidizer vessel. Sulfur is removed from the circulating solution by settling in the bottom of the oxidizer or in a separate non-aerated vessel. Sulfur can be recovered from the sulfur slurry by melting or viacentrifuge.

- The process can remove up to 99.9% of H_2S from gas stream with any H_2S concentration.

- To date, 20 units have been operated, mainly in the natural gas processing industry.

MCRC

Enstar Engineering Co. & Mineral & Chemical Resource Co.

- A gas phase low-temperature Claus reaction process taking place over activated alumina catalyst beds.

- The process can handle acid gas streams normally suitable for a Claus plant. A three-converter MCRC process achieves 98.5% sulfur recovery while a four-converter process can achieve 99.2% sulfur recovery.

- The front end of the process is identical to a typical Claus plant with reaction furnace, vapor phase Claus reaction and sulfur condensers. Depending on the recovery desired, one or two conventional Claus reactor beds are used. The last two reactors operate in a adsorption - regeneration mode. A converter in the adsorption mode operates at a temperature below the sulfur dewpoint. The sulfur condenses on the catalyst as it is produced. At the end of a time cycle, the converter is switched to the regeneration mode. Hot gas from the sulfur condensers following the conventional Claus reactors is used to regenerate the catalyst.

- Since 1979, four plants have been constructed and operated. Their production capacities are: 28, 50, 120, and 1100 LTPD of sulfur, respectively.

SELECTOX

R. M. Parsons Co., Pasadena, California and Union Oil of California

- A gas phase catalytic selective H_2S oxidation process taking place over proprietary catalysts.

- The process can be used to recover sulfur from gas streams containing 1 to 40% H_2S. The process has been applied to processing Claus plant tail gas, sour natural gas and geothermal off gas.

- The acid gas stream is mixed with stoichiometric amount of air to oxidize exactly one-third of the H_2S present to SO_2. The classic Claus reaction then occurs between the remaining H_2S and the SO_2 generated. The selective oxidation reaction occurs in the upper few inches of the catalysts bed whereas the Claus reaction occurs in the remainder of the bed. Several stages of catalyst beds can be used following the 1st bed to improve sulfur recovery.

- There are several variations on this process depending on the feed gas compositions and desired sulfur recovery level: Beavon Sulfur Recovery - Selectox: A Beavon reactor (BSR catalyst) is used to hydrogenate all the COS and CS_2 to H_2S before the acid gas is passed over the Selectox catalysts.

  Recycle Selectox Process: When the concentration of the H_2S in the feed is higher than 5%, part of the Selectox reactor effluent is recycled to limit the temperature rise in the reactor.

- A Beavon Sulfur Recovery-Selectox unit went on-stream in 1978 in West Germany for the treating Claus Plant tail gas. A 20 LTPD Recycle Selectox unit went on-stream in 1981 at Carbon & Gasoline Co's Keystone plant in Texas to recover sulfur from an amine unit off gas.

STRETFORD

British Gas Corporation

- A liquid phase oxidation process which uses an aqueous solution containing sodium carbonate, sodium vandate, and anthraquinone disulfonic acid (ADA) as a redox catalyst.

- H_2S is absorbed in the alkaline solution and forms bisulfide. The bisulfide is oxidized by the vanadium to elemental sulfur. The liquor is regenerated by air blowing. The sulfur is removed by froth flotation. Sulfur is recovered either by centrifuging followed by heating or filtration.

- The process can be operated between atmospheric pressure and 1000 psig. Operating temperatures throughout the unit are in the range of ambient to 120°F. The process can remove up to 99.9% of H_2S from gas streams with low H_2S concentrations. Treated gas contains 10 ppm or less of H_2S.

- Over 110 Stretford units were operated or in construction with capacities ranging from 0.1 to 200 MM SCFD.[1] The process has been applied to treat cokeoven gas, Claus plant tail gas, refinery off gas, natural gas and acid gas removal systems regenerator off gas.

- Over the years, substantial improvements were made by various process licensors to improve and extend the application range of the Stretford process. Most notable ones are:

    - Beavon Sulfur Removal Process offered by R. M. Parsons Co., Pasadena, California.

    - Clean Air-Stretford Process offered by J. F. Pritchard Corp., Kansas City, Missouri.

    - Holmes-Stretford Process offered by Peabody Process Systems, Stamford, Connecticut.

SULFINT

Integral Engineering, Vienna, Austria

- A liquid phase oxidation process which uses a non-toxic, alkaline solution containing an iron chelate complex as a redox catalyst.

- H_2S is absorbed in a venturi scrubber and reacted to bisulfide. The bisulfide is oxidized to elemental S (0.1 - 2 mm) and the reduced iron complex is regenerated by air. Sulfur sludge from the oxidizer/settling tank is recovered in a centrifuge decanter.

- The process can remove 99.9% of H_2S from gas streams with low H_2S concentrations (1.3%). Treated gas contains 13 ppm or less of H_2S.

- A small plant for H_2S removal from waste air has been in operation since 1974 while a 18 TPD of sulfur plant was to go onstream in 1984 for cleaning Rectisol off-gases at the coal gasification plant in Usti, CSSR.

SULFREEN

Lurgi Gesellschaft fuer Waerme und Chemotechnik, and Societe Nationale des Petrole D'Aquitaine

- A gas phase low-temperature Claus reaction process taking place over activated alumina catalyst beds.
- Claus tail gas containing H_2S and SO_2 are converted to sulfur at 260 to 300°F. The sulfur produced remains adsorbed on the catalyst bed. Several reactors are operated in a cyclic mode. The regeneration gas is a 570°F slip-stream of the treated tail gas. Sulfur is condensed and removed from the regeneration gas in a standard sulfur condenser.
- The process can treat Claus tail gas containing sulfur compound from 1 to 3%. The Claus reaction conversion efficiency of 84% can be achieved.
- Over 16 units are in operation treating tail gas from Claus plants producing up to 2100 LT/D of sulfur.

TAKAHAX

Tokyo Gas Co. LTD., Japan

- A liquid phase oxidation process which utilizes an alkaline non-toxic solution containing 1,4 - naphthoquinone, 2-sulfonate as a redox catalyst.
- H_2S is absorbed and reacted to bisulfide in an absorber. The bisulfide is oxidized by the catalyst to precipitate sulfur (approx. 2 microns). Reduced catalyst solution is regenerated by air. Sulfur is recovered by filtration of a slipstream.
- The process can remove up to 99.9% of H_2S from gas streams with low H_2S concentrations. Treated gas contains 10 ppm or less of H_2S.
- Over 100 plants have been built and operated in Japan since 1962 for treating coke oven gas, sewage fermentation gas, and chemical and pharmaceutical plants' waste gases.

UNISULF

Union Oil of California, Los Angeles, Cal.

- A liquid phase oxidation process which uses an aqueous solution containing sodium carbonate, bicarbonate, and a vanadium complex as a redox catalyst.
- H_2S is absorbed in the solution and oxidized to elemental sulfur. The solution is regenerated by air oxidation that floats the sulfur off as a slurry. Sulfur is then recovered by filtration or by centrifuges.
- The process is operated at atmospheric pressure with solution temperatures between 90 and 120°F. H_2S containing gas streams with up to 99% CO_2 can be treated. Treated gas normally contains less than 10 ppm H_2S.
- Unisulf solution has been used to successfully treat Rectisol off-gas to recover 26 TPD sulfur at SASOL I in South Africa. Another unit has been constructed in Colorado to treat oil shale retort off-gas.

STATUS SUMMARY

CLAUS SULFUR RECOVERY

1.0 GENERAL INFORMATION

Developer:	Amoco Production Company, Tulsa, Okla.
Licensor:	All engineering companies in the sulfur recovery field.
Type:	A gas phase process where H_2S is partially combusted to form SO_2 and then the remaining H_2S reacts with SO_2 over alumina catalyst to form sulfur.
Conditions:	The feed gas pressure is normally 15 to 20 psig. The adiabatic flame temperature inside the reaction furnace is about 1500 to 3000°F. The catalytic converters operate between 400 to 600°F. The process has many variations depending on the H_2S concentration. For H_2S conc. >50% : Straight thru Claus For H_2S conc. 20-50% : Split flow process with feed gas preheat and/or air preheat. The process can achieve up to 97% sulfur recovery.
Applications:	The process has been applied to recovering sulfur from all kinds of acid gas streams with H_2S concentrations higher than 20% (v).
Status:	Since 1953, 300 plants have been constructed and operated all over the world with capacities ranging from 1 to 3000 TPD.

2.0 HISTORICAL BACKGROUND

The process was first disclosed by C. F. Claus under a British patent in 1883. It involved vapor phase oxidation of hydrogen sulfide with air over bauxite or iron ore catalyst in a simple reactor.

The first commercial application of the art was made about 1937 by I. G. Farbenindustrie. Instead of burning H_2S directly over the catalyst, one-third by volume was burned completely to sulfur dioxide under a waste heat boiler. SO_2 was then reacted with the remaining two-thirds of the hydrogen sulfide gas over bauxite.

Since then, numerous improvements were made to improve the process efficiency and it has become the most widely used process for recovering elemental sulfur from an acid gas stream containing H_2S.

3.0 PROCESS CHEMISTRY

- The reactions taking place in the thermal stage of the reaction furnace are very complicated. However, the overall reactions are quite simple:

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

- If the feed gas contains large amounts of CO_2, small quantities of COS and CS_2 would be formed in the reaction furnace.

$$CO_2 + H_2S \longrightarrow COS + 2H_2O$$

$$CO_2 + 2H_2S \longrightarrow CS_2 + 2H_2O$$

The main reaction taking place in the catalytic converters is:

- As the product effluent cools in the sulfur condensers, sulfur species condense according to:

$$3\ S_2 \longrightarrow S_6\ (v)$$

$$4\ S_2 \longrightarrow S_8\ (v)$$

$$S_6(v) \longrightarrow 6S\ (l)$$

$$S_8 \longrightarrow 8S\ (l)$$

- The maximum conversion of H_2S to elemental sulfur is limited by the thermodynamic equilibrium conversion as shown in Figure 3-1.

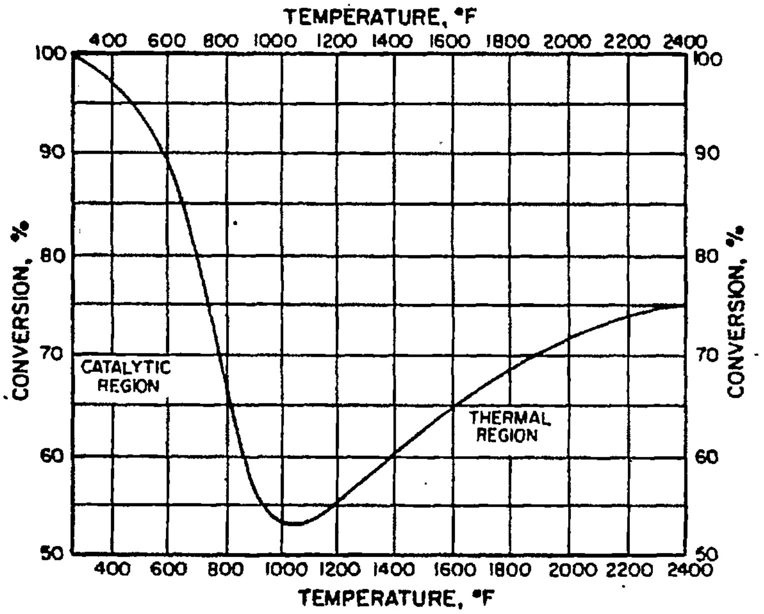

FIG. 3-1 THEORETICAL CONVERSION OF H_2S TO SULFUR VAPOR

Source: Ref. 2

4.0 PROCESS DESCRIPTION

Ouere are two basic forms of the process: the Straight-through process andthe Split-Flow (Bypass) Process. Typical Claus plants have four stages, consisting of a thermal stage followed by three catalytic stages.

Acid gases with H_2S concentration higher than 50% can be processed in the straight-through process. A typical three-stage straight through Claus flowsheet is shown in Figure 4-1. The entire acid-gas stream and the stoichiometric amount of air to burn one-third of the H_2S to SO_2 is fed through a burner to the reaction furnace. At normal furnace temperatures of 1900 to $3000^{\circ}F$, sulfur vapors are also formed. After the thermal stage, the furnace effluent is cooled first in a waste heat boiler and subsequently in a sulfur condenser where the sulfur vapor is condensed.

The reaction gases leaving the sulfur condenser are reheated and flow through the first catalytic converter where additional sulfur is produced by the reaction of H_2S and SO_2. Reheating the gas is necessary to maintain the temperature of the reaction gas above the sulfur dew point as it passes through the catalytic converter because condensation of sulfur leads to rapid catalyst deactivation. The gases leaving the first catalytic converter are again cooled, and sulfur is condensed. The process of reheating, catalytically reacting, and sulfur condensing are repeated in two additional stages.

After leaving the last sulfur condenser, the tail gas, which still contains appreciable amounts of sulfur compounds and a small amount of sulfur vapor,has to be treated in a tail gas treating unit before it can be incinerated and vented to the atmosphere. Depending on the H_2S concentration in the acid gas, conversion efficiencies of 96 to 97% can be achieved with three catalytic stages.

When the H_2S concentration is between 50% and 20% in the acid gas feed, a stable combustion cannot be sustained if the entire gas stream is fed to the reaction furnace. The split-flow (or bypass) process is used. A typical three-stage bypass flowsheet is shown in Figure 4-2. One third of the acid gas is fed to the reaction furnace, and all the H_2S is burned to SO_2 with the stoichiometric amount of air. The hot gases are cooled in a waste heat boiler and then combined with the remaining two thirds of the acid gas before entering the first catalytic conversion stage. The rest of this process is identical to the straight-through process. In this version, most of the reactions to produce sulfur occur in the converters.

As the concentration of H_2S becomes lower than 20%, a point is reached at which a flame cannot be sustained in the reaction furnace. This problem is normally solved in several ways: Preheat acid gas and/or air, or burnsulfur to provide the SO_2 for reaction with H_2S. A typical sulfur-burning process is shown in Figure 4-3. Sulfur from the first converter is pumped to the reaction furnace where it is oxidized to SO_2.
When the H_2S concentration in the feed gas falls below 10%, direct removal and conversion of H_2S is often a more economical route to sulfur removal and recovery.

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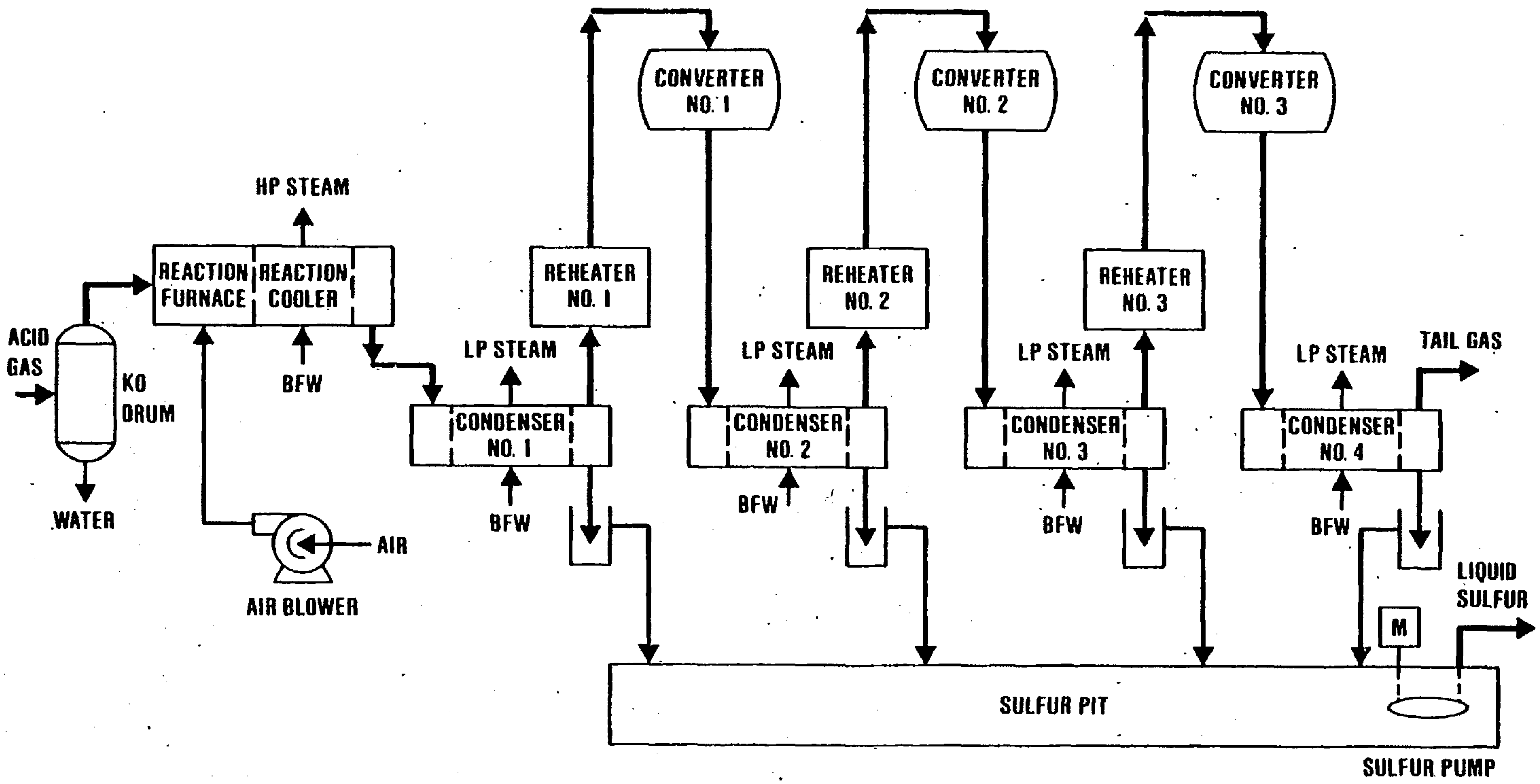
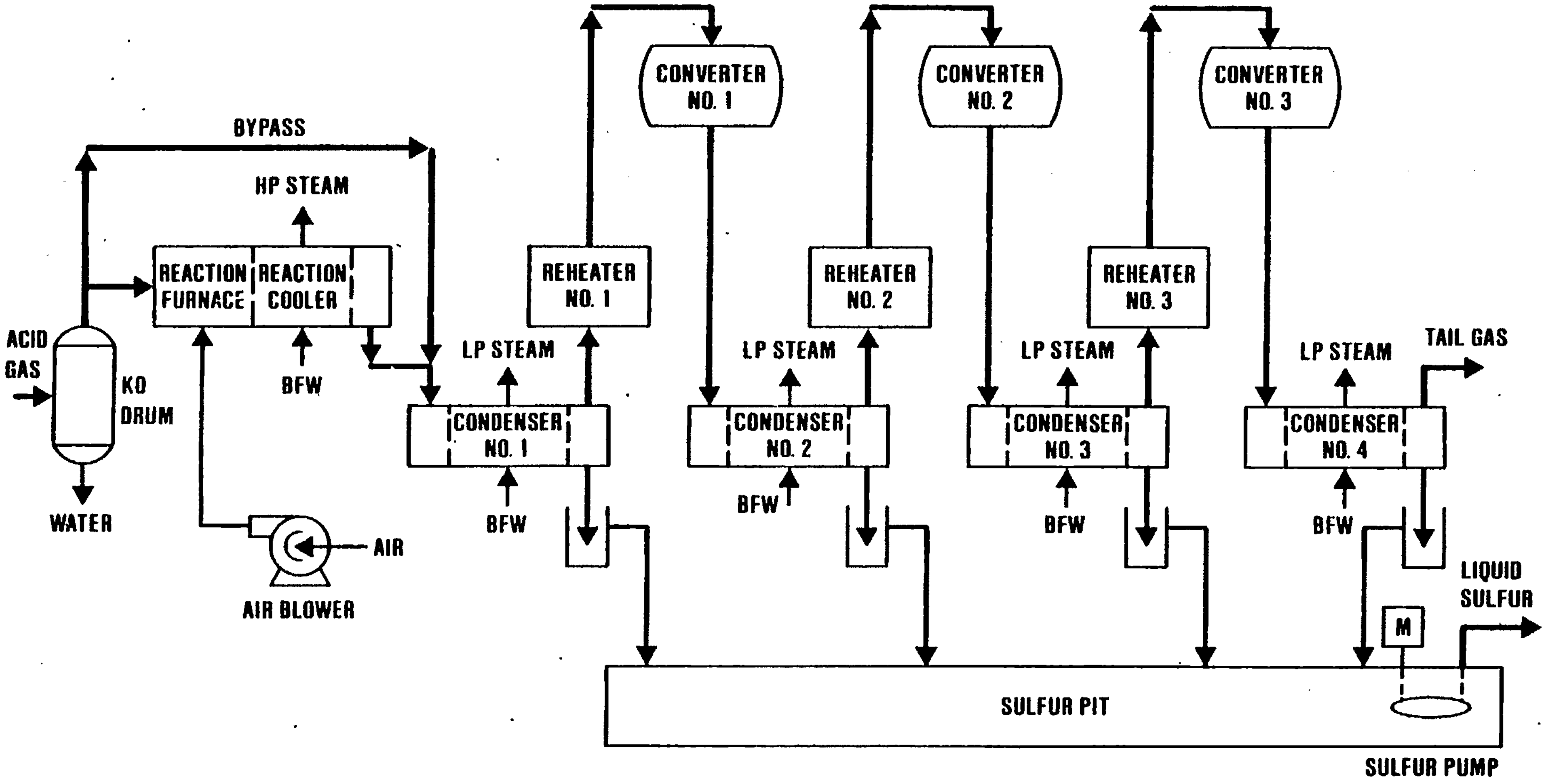


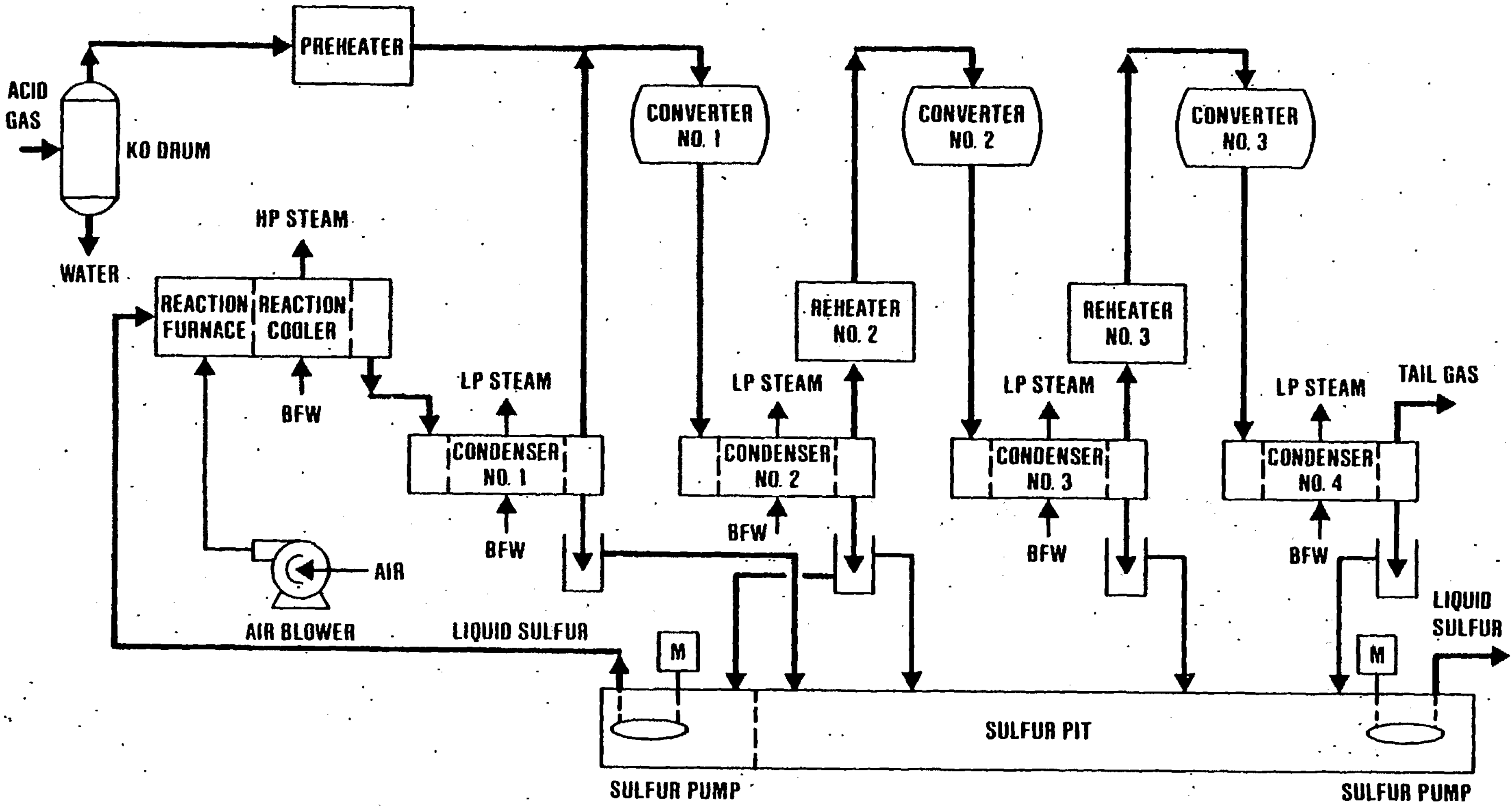
FIG. 4-1 Claus Three-Stage Sulfur Recovery Process

Source: Ref. 1



Source: Ref. 1

FIG. 4-2 Bypass Claus Three-Stage Sulfur Recovery Process



Source: Ref. 1

FIG. 4-3 Claus Sulfur-Burning Three-Stage Sulfur Recovery Process

5.0 COMMERCIAL DESIGN DATA

Table 5-1 provides design data for a Claus sulfur recovery unit in a 250 billion Btu/day coal-to-SNG plant and the contribution to gas cost in a coal-to-SNG plant is presented in table 5-2.

TABLE 5-1

DESIGN DATA FOR A THREE-STAGE CLAUS SULFUR RECOVERY SYSTEM IN A 250 BILLION BTU/DAY COAL-TO-SNG PLANT

	ACID GAS Mol %	AIR Mol %	FUEL GAS Mol %	SULFUR Mol %	TAIL GAS Mol %
H_2S	37.04				0.48
COS	0.01				
CO_2	44.16		2.66		23.05
CO	8.63				
H_2	2.04		0.76		
CH_4	4.13		95.01		
N_2 & Ar	0.05	78.20	1.56		54.19
O_2		20.80			
SO_2					0.24
S_2					0.01
H_2O	3.94	1.00	0.01	100.00	22.03
	100.00	100.00	100.00	100.00	100.00
TOTAL #/HR	169,428	242,390	2,108	53,224	360,702

HP STEAM GENERATION	110.6 MM BTU/HR
LP STEAM GENERATION	35.5 MM BTU/HR
BFW HEATING	7.4 MM BTU/HR

Source: Ref. 3

TABLE 5-2

CALCULATION OF CONTRIBUTION TO GAS COST
CLAUS SULFUR RECOVERY

Coal Type	N.Dakota lignite
Evaluator	Kellogg Rust Synfuels, Inc. (5)
Project Report No.	None
Date Published	1985
Plant Capacity	250 Billion Btu/day SNG

CAPITAL COSTS :	$ MM (Mid-1982)
Installed Equipment	11.0
Contingency @ 15%	1.7
DFCI	12.7
Home-Office costs @ 12%	1.5
TFCI	14.2
Royalties	0.2
Initial Catalyst Charge	0.02
Total Plant Investment	14.42

OPERATING COSTS :			$/hr
Consumed			
Steam(600 psig)	686 #/hr	@ $ 5.50/ 1000 lb.	3.8
Electricity	638 Kw	@ $ 0.05/ Kwh	31.9
Catalyst Make-up	0.0902 cu ft.	@ $ 0.384/ lb.	1.5
Produced			
Steam Credit(600 psig)	25,229 #/hr	@ $ 5.50/ 1000 lb.	-138.8
Steam Credit(60 psig)	39,152 #/hr	@ $ 3.85/ 1000 lb.	-150.7
Sulfur Credit	3,990 #/hr	@ $ 120/ LT	-213.8
TOTAL			-466.1

Total Operating Cost, $ MM/yr at 100 % Stream factor =-4.08 MM $/Yr

CONTRIBUTION TO GAS COSTS :	Specific Cost, $/MM Btu-Yr	Charge Rate, Year	Contribution, $/MM Btu
Capital Related	0.18	0.089 (*)	0.02
Operating	-0.05	1.000	-0.05
Total			-0.03

(*) Capital charge rate calculated based on GRI Gas Cost Guidelines.

6.0 ADVANTAGES & DISADVANTAGES

- **Advantages**

  --Well proven process technology for recovering sulfur from acid gas streams.

- **Disadvantages**

  --The process is not economical and/or might not be operable when the concentration of H_2S is below 20%.

  --The process can only achieve a sulfur recovery of 96%, hence, a tail gas treatment unit is required if complete removal of sulfur is necessary.

  --Presence of hydrocarbons heavier than C_3^+ will lead to catalyst fouling and deactivation and a lower quality sulfur product.

7.0 COMMERCIAL INSTALLATIONS

Since 1953, a total of 300 plants have been designed and constructed by AMOCO's licensed technology around the world with capacities between 1 and 3000 tpd. A list of Claus plants owned and operated by Amoco is shown in Table 7-1.

TABLE 7-1

SULFUR RECOVERY PLANTS OPERATED BY AMOCO

AT NATURAL GAS PLANTS	DATE OF CONSTRUCTION	PRESENT CAPACITY (TPD SULFUR)
Elk Basin, WY	1949	110
North Cowden, TX	1952	16
Slaughter, TX	1952	48
Midland Farms, TX	1956	12
Empire Abo, NM	1960	67
West Yantis, TX	1963	80
Edgewood, TX	1964	350
Beaver Creek, WY	1965	70
South Fullerton, TX	1967	5
West Whitecourt, ALT, CANADA	1964	1200
Bigstone, ALT, CANADA	1968	320
East Crossfield, ALT, CANADA	1968	1767
Kharg Island, PERSIAN GULF	1969	570
AT REFINERIES		
Yorktown, VA	1957	50
Sugar Creek, MS	1970	86
Whiting, IN	1971,1972	260
Texas City, TX	1975	400
Cremona, ITALY	1965	11
Brisbane, AUSTRALIA	1967	13
Milford Haven, WALES, UK	1973	35

Source: Ref. 4

8.0 REFERENCES

1. **Clute, A. E., "Sulfur Recovery from Low Hydrogen Sulfide Gases"**, Chemical Engineering Progress, 78 (10), October 1982, pp 61.

2. **"Coal Conversion Systems Techical Data Book"**, by Institute of Gas Technology, March 1984, DOE/FE/05157-5, Section VF.30.2, pp3.

3. **Kellogg In-House Data**

4. **Palm, J. W.,"Sulfur Recovery Plant Operation"**, Sulfur, No. 143; July 1979.

5. **Kellogg Rust Synfuels, Inc., "Design and Economics of Lignite to SNG facility using Lurgi Gasifiers"**, for Gas Research Institute, to be published, 1985, GRI Contract 5082-222-0754.

STATUS SUMMARY

AMOCO - DIRECT OXIDATION & SULFUR RECOVERY

- 1.0 GENERAL INFORMATION
- 2.0 PROCESS DEVELOPMENT
- 3.0 PROCESS CHEMISTRY
- 4.0 PROCESS DESCRIPTION
- 5.0 ADVANTAGES & DISADVANTAGES
- 6.0 COMMERCIAL INSTALLATIONS
- 7.0 REFERENCES

1.0 GENERAL INFORMATION

Developer: Amoco Production Company,
Tulsa, Okla.

Licensor: Same as Above

Type: A gas phase catalytic process where H_2S is oxidized by air over alumina catalyst to form sulfur.

Conditions: Operating pressures are near atmospneric. The maximum exit temperature from the direct oxidation reactors are between 800 to 1000°F. Gas streams containing less than 15% H_2S can be processed.

Applications: The process has been applied to recover sulfur from an amine unit off-gas.

Status: Nine commercial units have been constructed since 1959.

2.0 PROCESS DEVELOPMENT

- Pan American Petroleum Corp. (Now Amoco Production Co.) first published research and development information on the direct oxidation of hydrogen sulfide to sulfur in 1959.

- The first direct oxidation plant was owned and operated by Sinclair Oil & Gas Co. with a recovery capacity of 4 LTPD near Tatum, New Mexico. The plant was designed and built by Austin Rankin Corporation under license from Pan American Petroleum Corportion and was started up in 1961.

- To date, nine commercial units have been constructed.

3.0 PROCESS CHEMISTRY

- The chemistry of this heterogenous catalytic process is very similar to the Claus process. In the first reactor, H_2S is oxidized to S and SO_2 by O_2 in the stoichiometric injected air according to:

$$H_2S + 1/2\ O_2 \longrightarrow S + H_2O$$

$$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O$$

- The partial oxidation of H_2S to sulfur and water predominates over the complete oxidation to sulfur dioxide and water.

- The products of the above reactions react with unconverted H_2S and reach equilibrium according to the Claus reaction

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

- Side reactions that normally take place in a Claus reactor are also present.

$$S + O_2 \longrightarrow SO_2$$

$$3S_2 \longrightarrow S_6$$

$$4S_2 \longrightarrow S_8$$

4.0 PROCESS DESCRIPTION

In this process, a lean H_2S gas stream is preheated to a suitable temperature before it is fed to the direct oxidation reactor. Oxygen in the air reacts with H_2S over an alumina catalyst to produce sulfur. The products of the reaction are cooled to remove sulfur and the remaining gases are preheated with bypass gas from the first reactor, mixed with additional air and passed to a second reactor. The gases from the second reactor are cooled to remove the sulfur and then vented. A simplified process flow diagram is shown in Figure 4-1. Sometimes, when treating a clean acid gas stream (i.e., without any hydrocarbons), a Claus cleanup reactor is used to improve the sulfur removal. This process is shown in Figure 4-2.

The direct oxidation process can recover up to $90^+\%$ of the sulfur. However, it is important that the acid gas feed contain minimum hydrocarbons, especially C_3^+, since they can cause rapid catalyst deactivation and also produce off-color sulfur product.

FIG. 4-1 **DIRECT OXIDATION PROCESS**

Source: Ref. 1

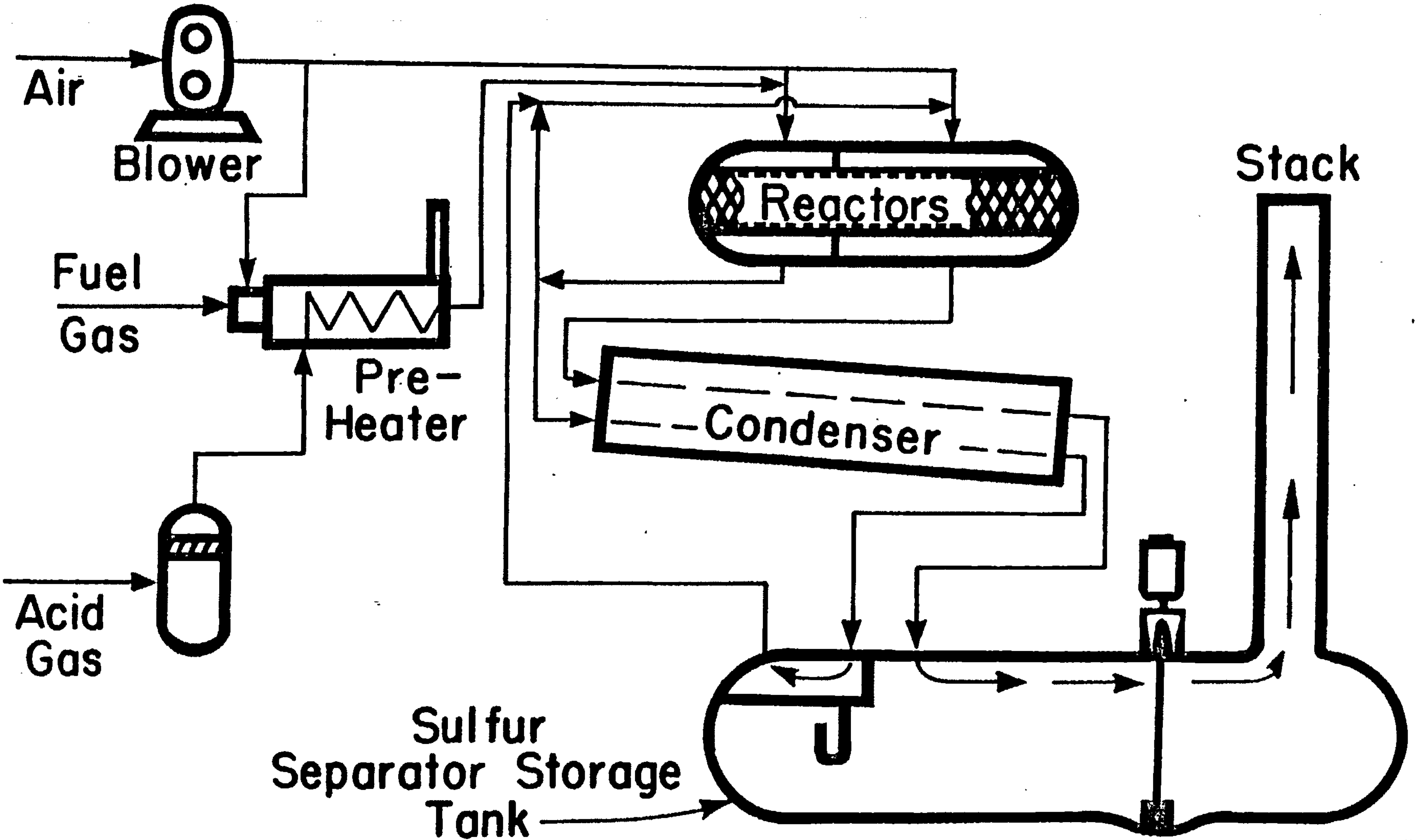
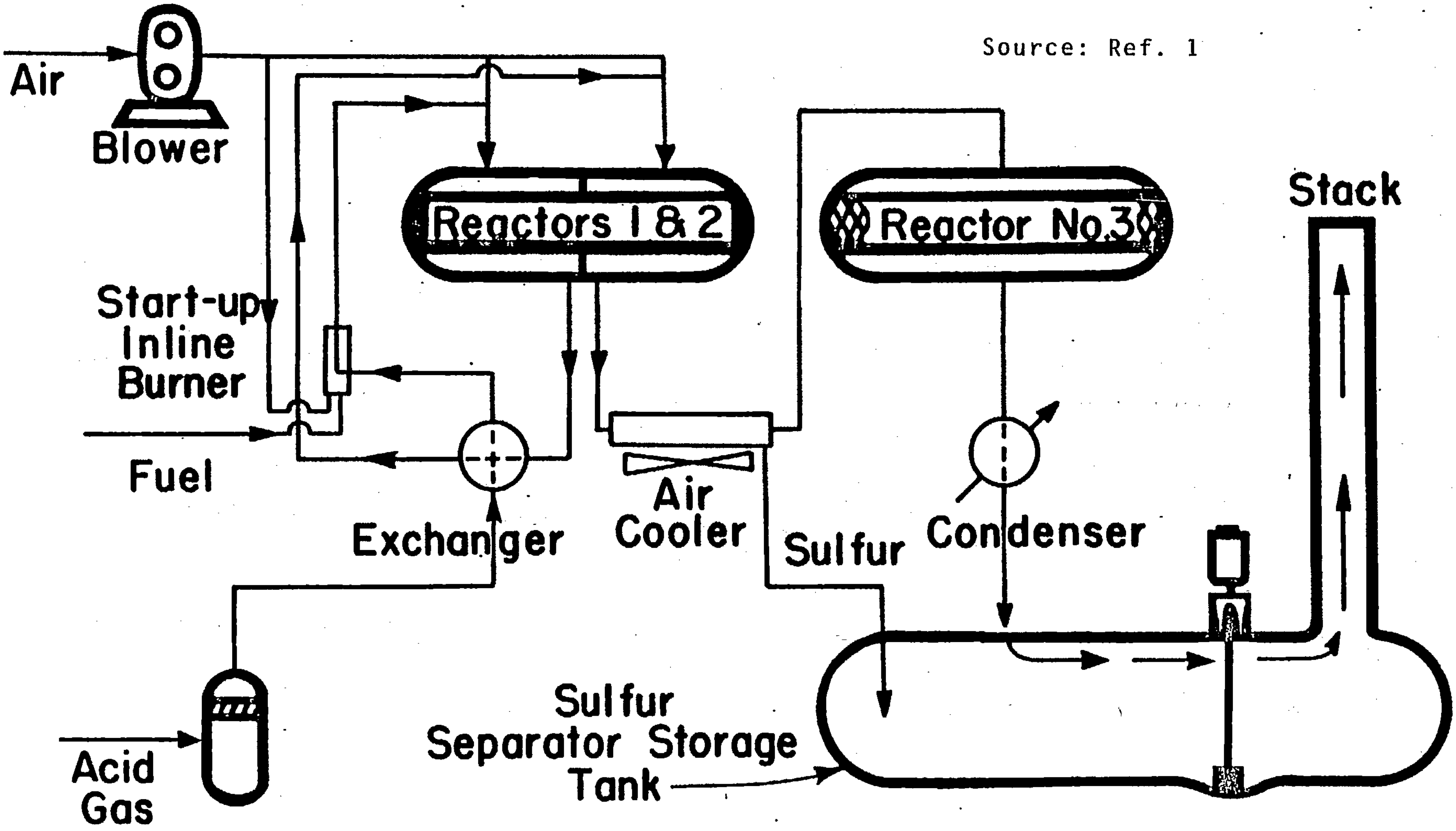


FIG. 4-2 **DIRECT OXIDATION PROCESS**



Source: Ref. 1

5.0 ADVANTAGES & DISADVANTAGES

- Advantages

  --Can process feed gas containing less than 15% H_2S.

- Disadvantages

  --Can only process acid gas containing little hydrocarbons and no heavy (C_3+) hydrocarbons.

  --Only 90+% of the sulfur can be recovered, so an additional tailgas treatment unit would usually be required.

6.0 COMMERCIAL INSTALLATIONS

Nine commercial units have been started up. A listing of these units is given with their location, name plate capacity and the year of startup.

i National Sulfur Company, Midland, Texas, 12 LTPD, 1965.
ii Sinclair Oil & Gas Co., Tatum, New Mexico, 4 LTPD, 1961.
iii Climax Chemical Co., Monument, New Mexico, 17 LTPD, 1962.
iv National Sulfur Company, 1 LTPD, 1958.
v W. R. Grace & Co., 2 LTPD, 1966.
vi Home Oil & Carstairs, Alberta, Canada, 50 LTPD, 1967.
vii Pioneer National Gas Co., Waha, Texas, 2 LTPD, 1968.
viii Intertex Gas Co., Texas, 23 LTPD, 1970.
ix Linestar Gas Co., Warwick Field, Texas, 35 LTPD, 1973.

7.0 REFERENCES

1. **Mungen, R. and H. Grekel, "Pan American's Direct Oxidation Sulfur Recovery Process"**, paper presented at the Natural Gas Processing Symposium of the Chemical Institute of Canada, June 6-8, 1966, Saskatoon, Saskatchewan, Canada.

STATUS SUMMARY

LO-CAT SULFUR RECOVERY

1.0 GENERAL INFORMATION

Developer: ARI Technologies Inc.
Palatine, IL 60067

Licensors: ARI Technologies, Inc.(in USA)
Palatine, IL 60067

Type: A liquid phase oxidation process which uses a non-toxic, iron chelate complex as the catalyst reagent.

Conditions: The absorption and regeneration takes place at ambient temperatures. Feed gas pressures can range from atmospheric to 1300 psig. H_2S content in feed gas can range from 100 grains/100 SCF to 30%. Both aerobic and anaerobic gas streams can be processed. Treated gas contains less than 5 ppm H_2S.

Applications: The process has been applied to treating gas streams from: Several manufacturing processes, sewage plants lift stations, waste water treatment plants, amine regenerator offgas, natural gas and oil shale pilot plant.

Process Schemes: Several variations of the process are possible depending on the application. For a typical coal-to-SNG plant, schemes can be applied to treat the off-gas from a removal system.

Status: Over twenty units are in operation or under construction.

2.0 PROCESS DEVELOPMENT

- The process was first developed by Humphreys and Glasgow in 1965 as the chelated iron process. Ethylene Diamine Tetra Acetic Acid (EDTA) was used to hold the iron in solution.
- In 1972, ARI Technologies Inc. began work on the development of a process for the removal of H_2S from ventilating air.
- ARI overcame the principal stability problem of the chelated iron compound by addition of a polyhydroxylated sugar (Type B chelating agent) to the EDTA (Type A chelate). A patent was issued to Thompson in 1980. The result of this development was called the LO-CAT (Liquid Oxidation-Catalytic) Process. The catalytic reagent utilized was designated ARI-300.
- An installation was made at the Plateau Refining Co. in Bloomfield, NM in 1977.
- In 1982, a more stable catalytic reagent, ARI-310 was introduced.

3.0 PROCESS CHEMISTRY

The LO-CAT process uses chelated iron as a catalyst reagent to promote the overall reaction

$$H_2S + 1/2\ O_2 \longrightarrow H_2O + S$$

In the absorber, the sulfide ions are oxidized by the iron ions:

$$H_2S \longrightarrow 2H^+ + S^{-2}$$

$$Fe^{-3} + S^{-2} \longrightarrow 2\ Fe^{+2} + S$$

In the oxidizer, the reduced iron ions are regenerated (oxidized) by dissolved oxygen for reuse:

$$2\ Fe^{+2} + 1/2O_2 + H_2O \longrightarrow 2\ Fe^{+3} + 2OH^-$$

The organic chelating agents are present to prevent the precipitation of ferric hydroxide or ferrous sulfide.

The F^{+2}/Fe^{+3} reaction is very fast so minimum excess S^{2-} ions are carried over into the oxidizer. Hence, the unwanted byproduct, thiosulfate salts, are not formed by the side reaction:

$$2S^{-2} + 3/2\ O_2 \longrightarrow S_2O_3^{-2}$$

Also, excess dissolved O_2 is limited by the presence of Fe^{+2} ions in the regenerated solution.

The presence of high partial pressures of CO_2 in the process gas stream leads to a reduction in pH of the LO-CAT solution and therefore a buffer solution such as ammonium, sodium or potassium carbonate is added. However, the H_2S absorption reaction is very fast as compared with CO_2 absorption, so high selectivity of H_2S removal can be achieved.

4.0 PROCESS DESCRIPTION

The LO-CAT process has essentially two basic systems. One is an aerobic system where oxygen is present together with H2S in the gas stream to be processed. The other is an anaerobic system where the processed gas stream does not contain 02 and a separate air stream is used for solution regeneration.

Aerobic System:

The flow scheme for this type of system is shown in Figure 4-1..1. Gas to be purified is contacted with the catalyst reagent in an absorber tailored to the type of gas being treated and the maximum H_2S concentration in the feed. The H_2S is absorbed and ionized in the solution. The S^{2-} and HS^{2-} ions react almost instantaneously to form elemental sulfur. The sulfur leaves the absorber with the catalyst solution. The oxygen in the aerobic gas stream is absorbed in the solution and the solution is reoxidized while it is passing through the absorber.

Anaerobic System:

In an anaerobic unit, the H2S removal and conversion to sulfur takes place in an absorber. The spent solution is circulated to an oxidizer where it is regenerated by contact with air.

Sulfur which forms in the absorber is carried into the oxidizer, where it settles and is removed as a slurry. In small units, the slurry is discarded as a non-hazardous waste without further treatment. In larger units, sulfur is recovered by centrifuges or continuous melters. The catalyst solution can be recycled.

Depending on the application, different types of absorbers and flow schemes are used, as discussed below:

Conventional Scheme (Figure 4-2).

- This system is used for low pressure (150 psig) operations. A venturi-absorber and atmospheric pressure oxidizer are used.

High Pressure Autocirculation Scheme (Figure 4-3)

- A liquid filled column is used as both the oxidizer and absorber.

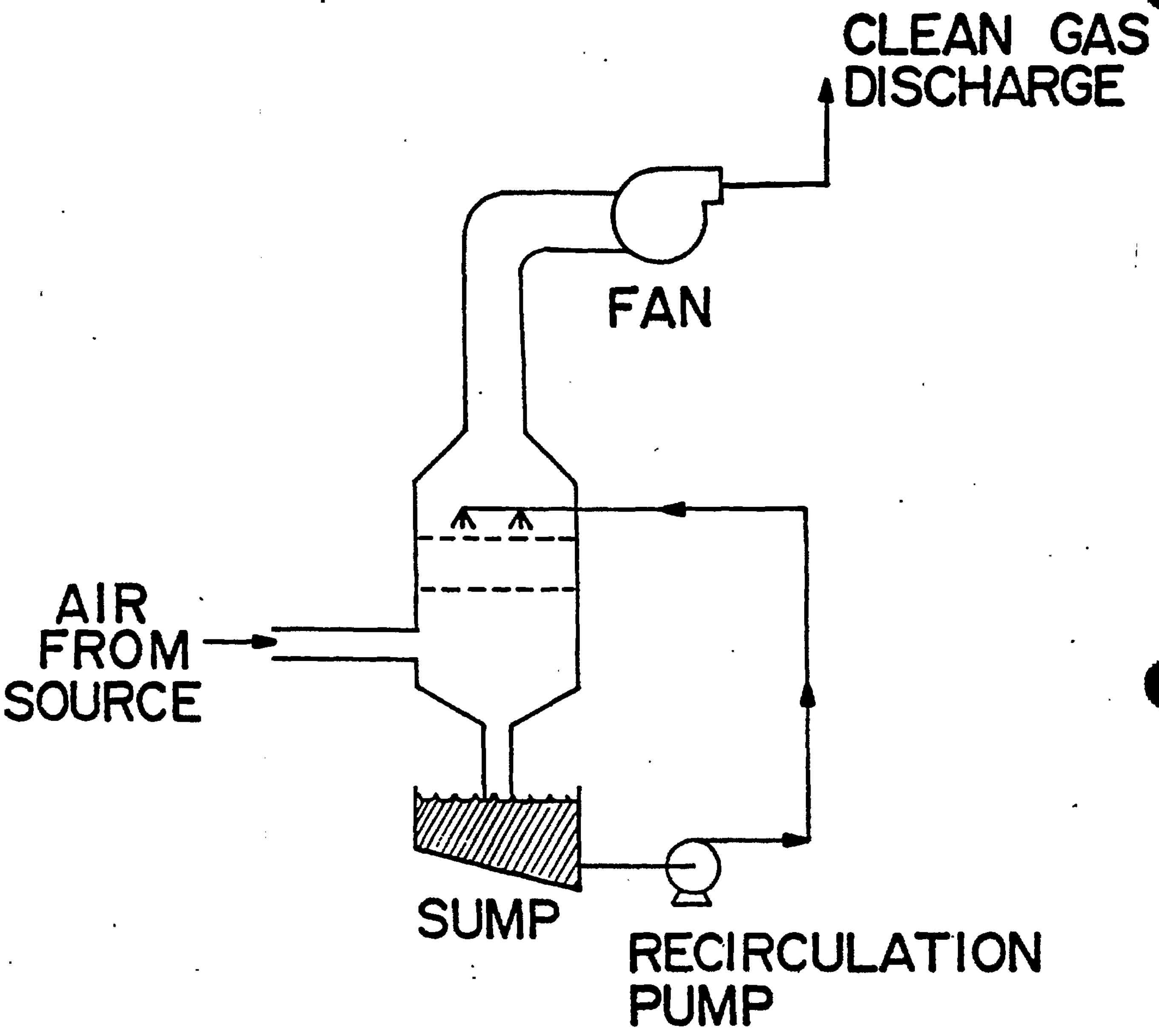
CO2 Treating Scheme (Figure 4-4)

- This system uses a packed tower absorber and a separate oxidizer. This system is suitable when a CO2 product stream is required, e.g., for EOR or for food and beverage applications.

Atmospheric Autocirculation scheme (Figure 4-5)

- This system is best suited for low CO2, high H2S applications for treating amine regenerator off-gas. It has no circulation pumps, temperature controls or complicated machinery.

The type of absorber chosen for a particular application depends on the gas volume processed, the H2S content of the gas and the allowable pressure drop. Figure 4-6 can be used to make a preliminary selection of the absorber type best suited for a specific application.

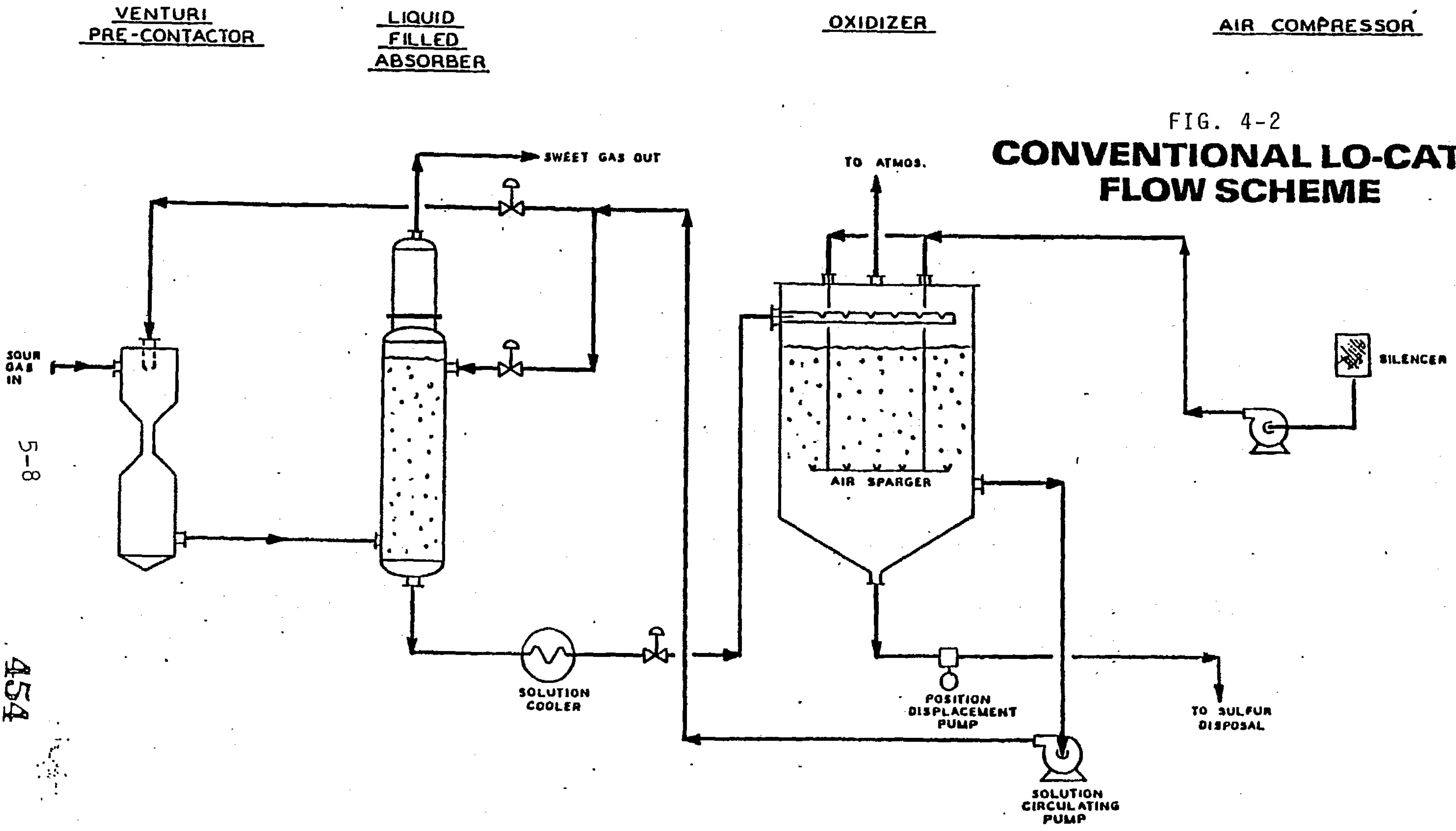


Source: Ref. 1

FIG. 4-1 LO-CAT AEROBIC SYSTEM

FIG. 4-2

CONVENTIONAL LO-CAT™
FLOW SCHEME

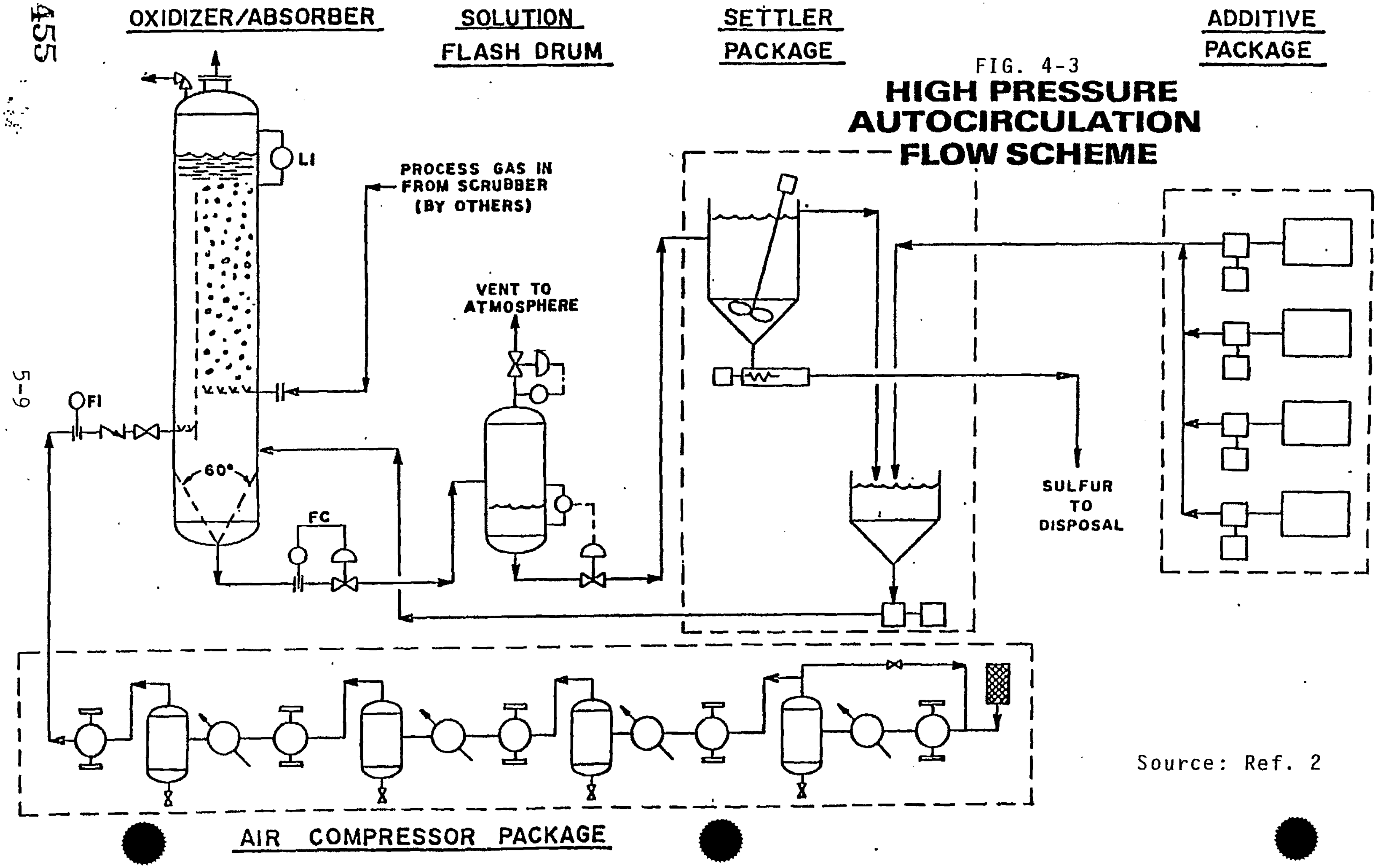


NOTE:
CHEMICAL ADDITION EQUIPMENT NOT SHOWN.

Source: Ref. 2

FIG. 4-3

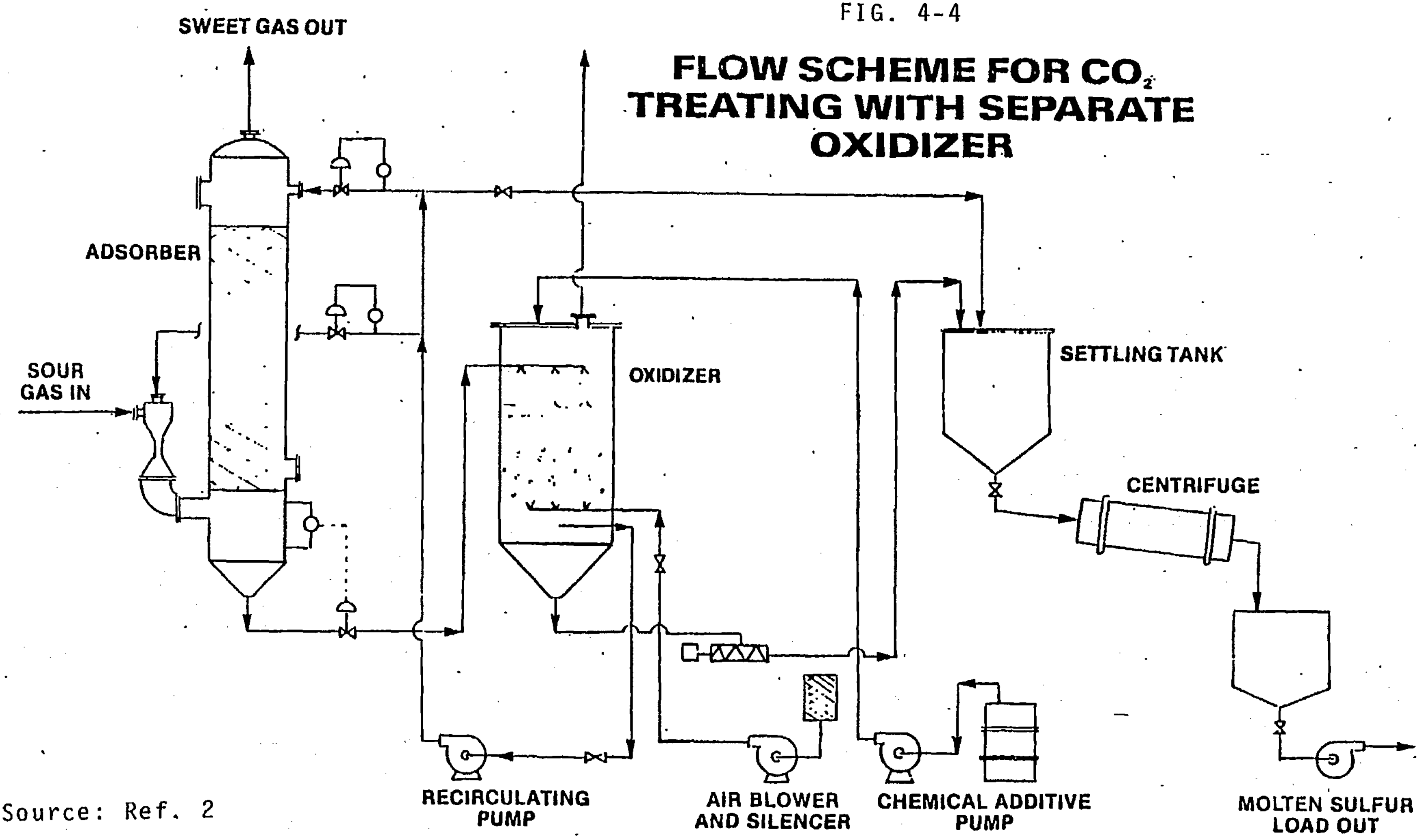
HIGH PRESSURE AUTOCIRCULATION FLOW SCHEME



Source: Ref. 2

FIG. 4-4

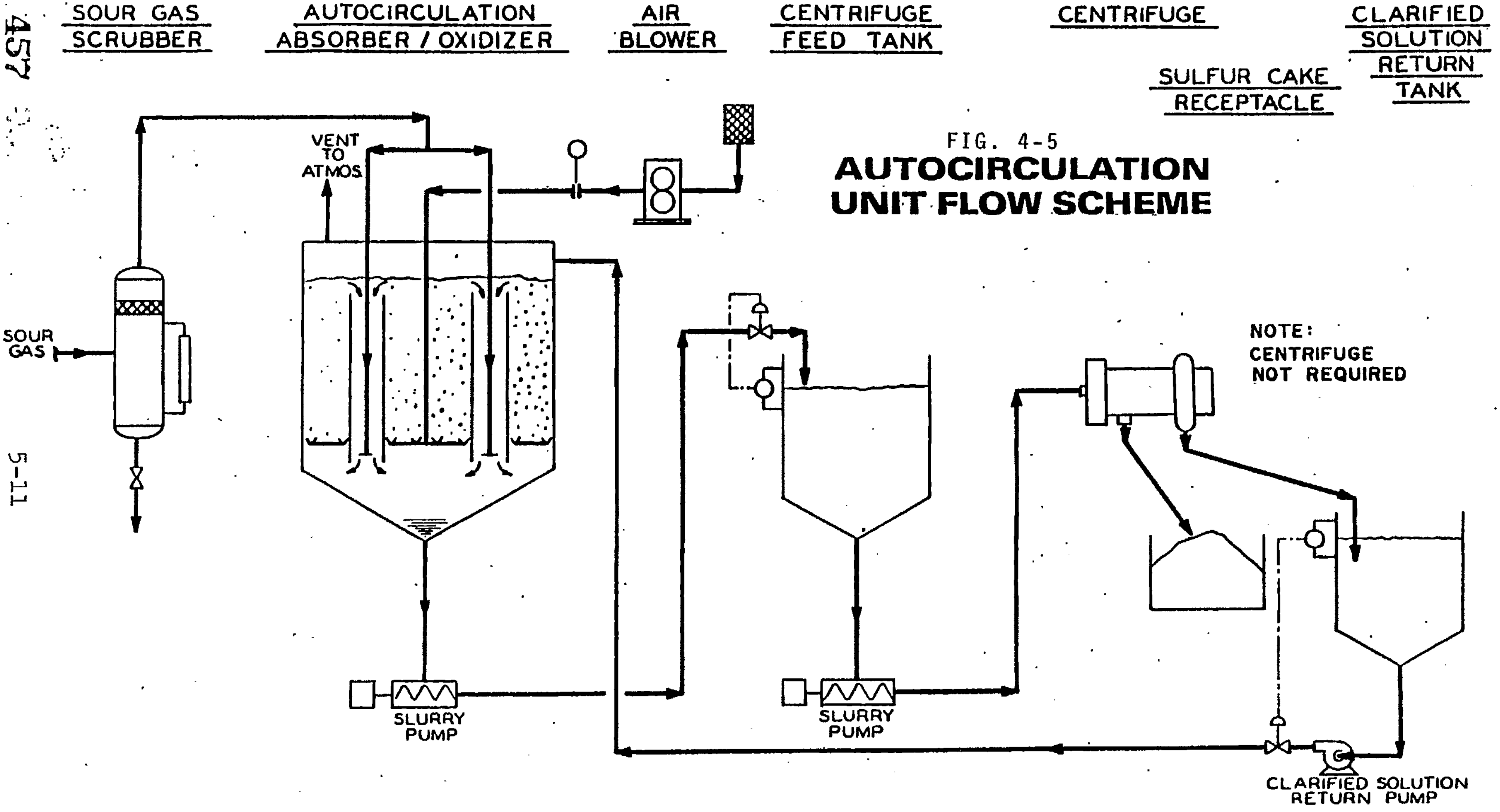
FLOW SCHEME FOR CO_2 TREATING WITH SEPARATE OXIDIZER



Source: Ref. 2

FIG. 4-5

AUTOCIRCULATION UNIT FLOW SCHEME



NOTE: CHEMICAL ADDITION EQUIPMENT NOT SHOWN.

Source: Ref. 2

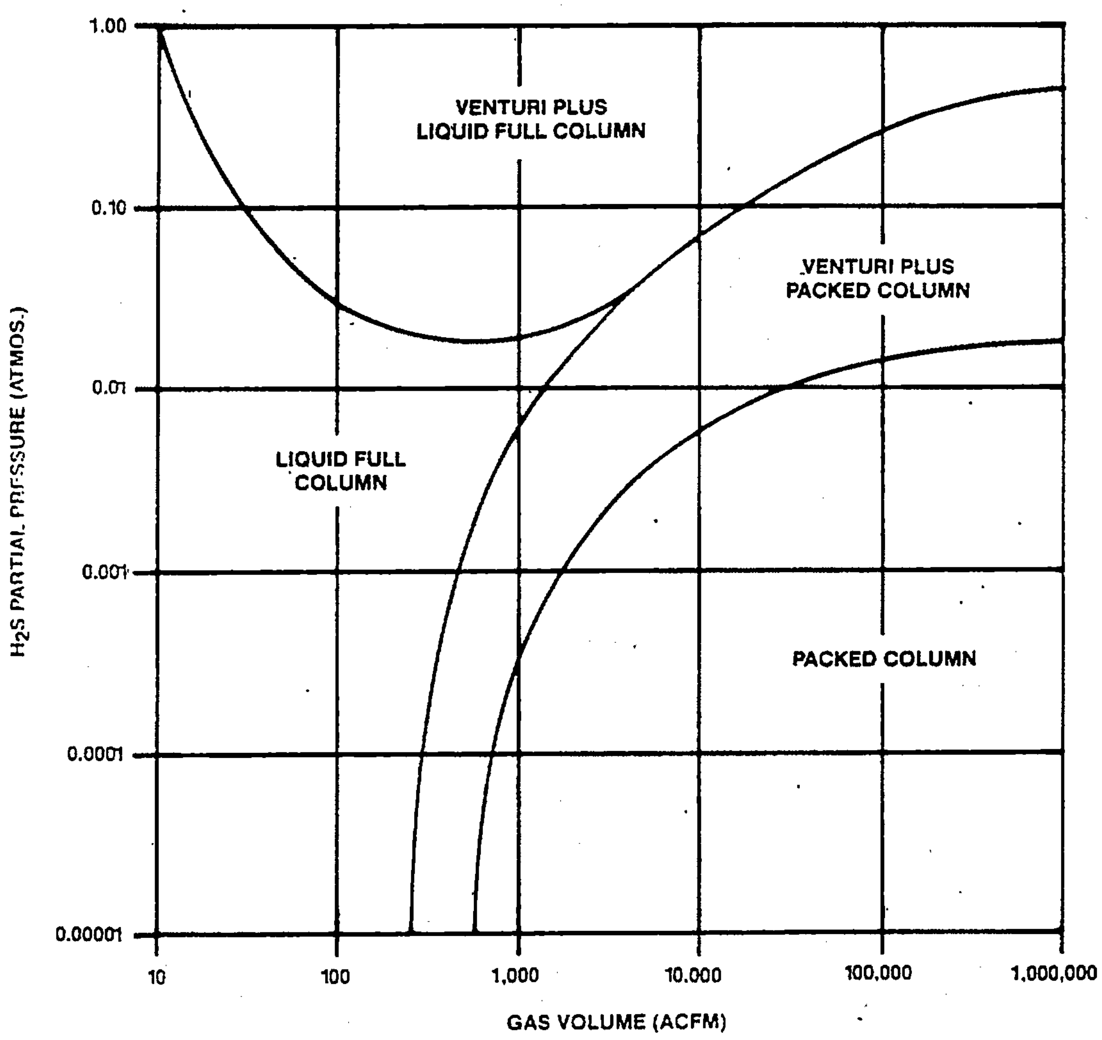


FIG. 4-6 DIFFERENT TYPES OF ABSORBER DESIGNS FOR LO-CAT SULFUR RECOVERY PROCESS

Source: Ref. 3

5.0 COMMERCIAL ECONOMICS DATA

Table 5-1 shows the costs for the equipment and operation of atmospheric autorecirculation units. Table 5-2 gives the operating costs for a LO-CAT unit which processes 10 MMSCFD of amine system off-gas containing over 99.6% CO2 and water.

6.0 ADVANTAGES & DISADVANTAGES

- **Advantages**
  - Non-toxic chemicals are used in the catalyst reagent ARI-310.
  - The catalyst is readily available and at low cost.
  - The catalyst is stable at any pH, hence low catalyst consumption.
  - High turndown (nearly 100%) capacity.
  - Produces elemental sulfur without flotation.
  - The catalyst reagent tolerates CO2, NH3 and other gas contaminants.
  - The process is adaptable to aerobic or anaerobic gas streams.
  - Essentially complete removal of H2S from acid gas streams with low H2S content.
- **Disadvantages**
  - The catalyst reagent is mildly corrosive, so equipment cannot be fabricated from carbon steel.
  - The process can only remove H2S, so a hydrogenation reactor is required to convert all other sulfur compounds to H2S

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TABLE 5-1

LO-CAT SULFUR RECOVERY PROCESS
CAPITAL COST FOR LOW-PRESSURE AUTOCIRCULATION UNIT

CAPACITY TONS/DAY	PROCESS DESIGN	BASIC EQUIPMENT PACKAGE	CENTRIFUGE PACKAGE	TOTAL
0.1	$ 10,000	$ 110,000	Not Applicable	$ 120,000
0.5	10,000	160,000	Not Applicable	170,000
1.0	10,000	230,000	$ 120,000	360,000
3.0	10,000	350,000	120,000	480,000

Feed gas contains 30% H_2S
All costs in 1983 Dollars

Source: Ref. 4

TABLE 5-2

LO-CAT SULFUR RECOVERY PROCESS
OPERATING COST FOR LOW-PRESSURE AUTOCIRCULATION UNIT

	$/Year
CHEMICALS:	
Catalyst Concentrate	9,960
Catalyst Makeup	7,680
Buffer (KOH)	9,110
ELECTRICITY	13,700
TOTAL	40,450

Feed gas contains 30% H_2S
All costs in 1983 Dollars

Source: Ref. 4

7.0 COMMERCIAL INSTALLATIONS

More than twenty units have been installed for various applications as follows:

- Manufacturing process ventilation air,
- sewage plant lift stations,
- waste water treatment plants
- amine regenerator off-gas treatment
- natural gas sweetening,
- oil shale pilot plant off-gas.

Size of units installed range from 0.1 to 17 LTPD of sulfur.

8.0 REFERENCES

1. **Hardison, L. C., "Application of the LO-CAT H_2S Oxidation Process to Natural Gas Treating"**, paper presented at the 14th Annual Spring Meeting, Marietta College Student Chapter of the Society of Petroleum Engineers of AIME, Marietta, OH, April 27, 1979.

2. **Hardison, L. C. "Applications of the LO-CAT Process to Sweetening Natural Gas"**, paper presented at the 34th Annual Gas Conditioing Conference, University of Oklahoma, Newman, OK, March 5-7, 1984.

3. **ARI Technologies Inc., "ARI presents the new LO-CAT hydrogen sulfide oxidation process".**

4. **Hardison, L. C., "Catalytic Gas-Sweetening process selectively converts H_2S to sulfur, treats acid gas"**, Oil & Gas Journal, 82 (23), June 4 1984, pp 60.

STATUS SUMMARY

SELECTOX SULFUR RECOVERY

1.0 GENERAL INFORMATION

Developers:	Union Oil Co. of California Union Science & Technology Division Brea, CA 92621 and The Ralph M. Parsons Co. Pasadena, CA 91124 (Recycle Selectox and BSR/Selectox)
Licensor(s):	Same as Above
Type:	A gas phase catalytic selective H_2S oxydation process taking place over a proprietary catalyst.
Conditions:	Operating pressures are near atmospheric. Operating temperatures are 350 - 700°F for the Selectox reactor. Gas streams from 1 to 40% H_2S can be treated.
Applications:	The process has been applied to treating a Claus plant tailgas and amine unit off-gas. Non-condensible gases from geothermal operations can also be treated.
Status:	A BSR/Selectox unit went on stream in 1978 for treating Claus plant tailgas. A 20 TPD Recycle Selectox unit went on stream in 1981 to recover sulfur from an amine unit off-gas.

2.0 PROCESS DEVELOPMENT

The Selectox catalyst was developed in the early 70's by Union Oil Company of California's Union Science and Technology Division.

Ralph M. Parsons Company adapted the process together with its Beavon catalyst and introduced an early version of the BSR/Selectox process under the name Beavon Mark II.

In the late 70's, improved versions of the Beavon catalysts and Selectox catalysts were developed and the processes were marketed under BSR/Selectox, once-through Selectox and Recycle Selectox processes.

3.0 PROCESS CHEMISTRY

The chemistry of this heterogenous catalytic process is very similar to the Claus process. The process employs an active catalyst that selectively oxidizes H_2S to S using air at low temperatures. One third of the H_2S entering the reactor reacts with oxygen at the injected air on the surface of the Selectox catalyst to SO_2:

$$H_2S + 3/2\ O_2 \longrightarrow SO_2 + H_2O$$

Almost simultaneously, a substantial portion of the SO_2 is reduced to elemental sulfur by reacting with H_2S according to the Claus reaction:

$$2H_2S + SO_2 \longrightarrow 3S + 2\ H_2O$$

The overall reaction occurring over the Selectox Cobalt Molybdate catalyst is:

$$H_2S + 1/2\ O_2 \longrightarrow S + H_2O$$

Thus the gaseous products leaving the Selectox reactor are sulfur vapor and unconverted H_2S and SO_2 in 2:1 mole ratio.

The Selectox catalyst oxidizes H_2S to S and SO_2 selectively, without forming SO_3 and without oxidizing either H_2 or saturated hydrocarbons.[3] COS and NH_3 are inerts although some trace mercaptans might be oxidized. Olefins and aromatics present in the feed will poison the catalyst.

A BSR (Beavon) reactor is sometimes installed upstream of the Selectox reactor to convert sulfur compounds other than H_2S to H_2S via the following reactions:

$$SO_2 + 3H_2 \longrightarrow H_2S + H_2O$$

$$S_x + xH_2 \longrightarrow xH_2S$$

$$COS + H_2O \longrightarrow CO_2 + H_2S$$

$$CS_2 + 2H_2O \longrightarrow 2H_2S + CO_2$$

4.0 PROCESS DESCRIPTION

There are three operating modes of the Selectox process depending on the H_2S content of the feed gas stream.

The first is the Once-through Selectox process illustrated in Figure 4-1. It is useful for recovering sulfur from gas streams containing about 5% H_2S or less. Lean acid gas mixed with stoichiometric air is fed directly to the first stage. About 82% of the H_2S is converted to elemental sulfur over the Selectox catalyst. H_2S and SO_2, leaving the first stage in a 2:1 mole ratio, react to form an additional 14% sulfur over Claus catalyst present in the second and third stages. The overall sulfur recovery is about 96%. The tail gas leaving the third stage can be catalytically incinerated over a bed of Selectox catalyst using air. The Once-through Selectox process has been studied at Union Oil's pilot plant where sulfur is recovered from the H_2S present in non-condensible gas streams, present ingeothermal operations.

For acid gases containing 5-40 mole % of H_2S, the Recycle Selectox process (Figure 4-2) is used. Since the selective oxidation of H_2S to S reaction is highly exothermic, the H_2S concentration in the acid gas feed is reduced to about 5 mole % by mixing with the spent gas from the first-stage condenser. Hence the reactor temperature rise is controlled by use of recycle gas. The balance of the spent gas containing unconverted H_2S and SO_2 in a 2:1 mole ratio is sent to one or two stages of Claus catalyst for conversion to sulfur. About 82% of the product sulfur is recovered from gases leaving the first stage, 12% in the second stage, and an additional 2% in the third stage. The overall sulfur recovery is about 96%.

The BSR/Selectox Process, shown in Figure 4-3, is a special application of the Once-through Selectox process to recover sulfur from Claus tail gas. Claus tail gas is heated to reaction temperature by mixing with the hot combustion products generated in a patented reducing gas generator using fuel gas and air. The resulting gas contains hydrogen and carbon monoxide as reagents for hydrogenation.The hot gas mixture next passes through a bed of BSR cobalt molybdate catalyst where all non-H_2S compounds are converted to H_2S. The hydrogenated gas stream is first cooled in a steam generator and then by direct contact condenser to near ambient temperature to condense and separate water. The cooled gas is now heated up and mixed with stoichiometric air before being fed to a Selectox catalyst reactor. About 80% of the H_2S reaching the Selectox catalyst is converted and recovered as elemental sulfur. The overall sulfur recovery (including Claus) is therefore above 99%.

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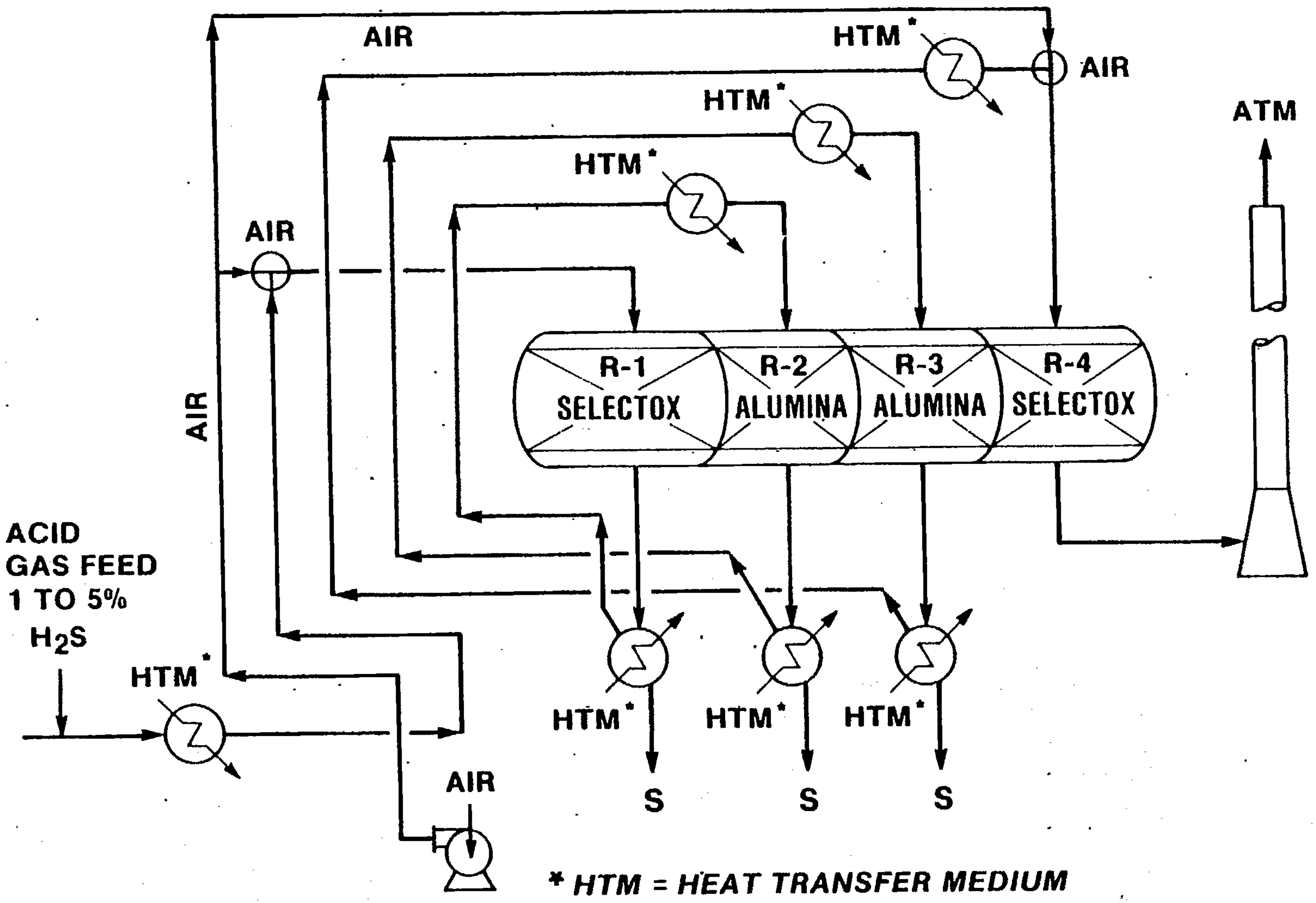

* HTM = HEAT TRANSFER MEDIUM

Source: Ref. 1

FIG. 4-1 **Once-Through Selectox Process.**

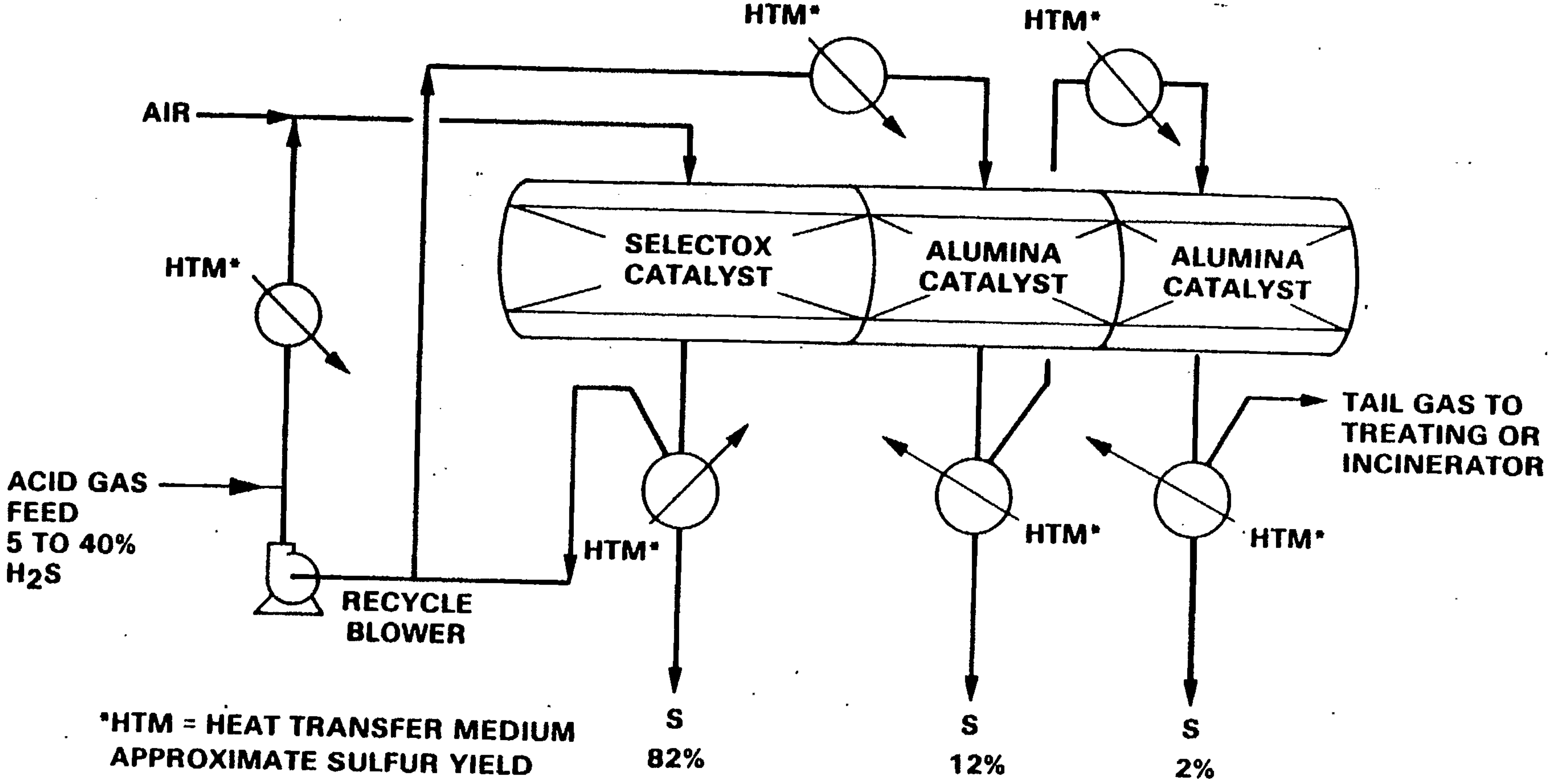

FIG. 4-2. **Three-Stage Selectox Process with Recycle.**

Source: Ref. 1

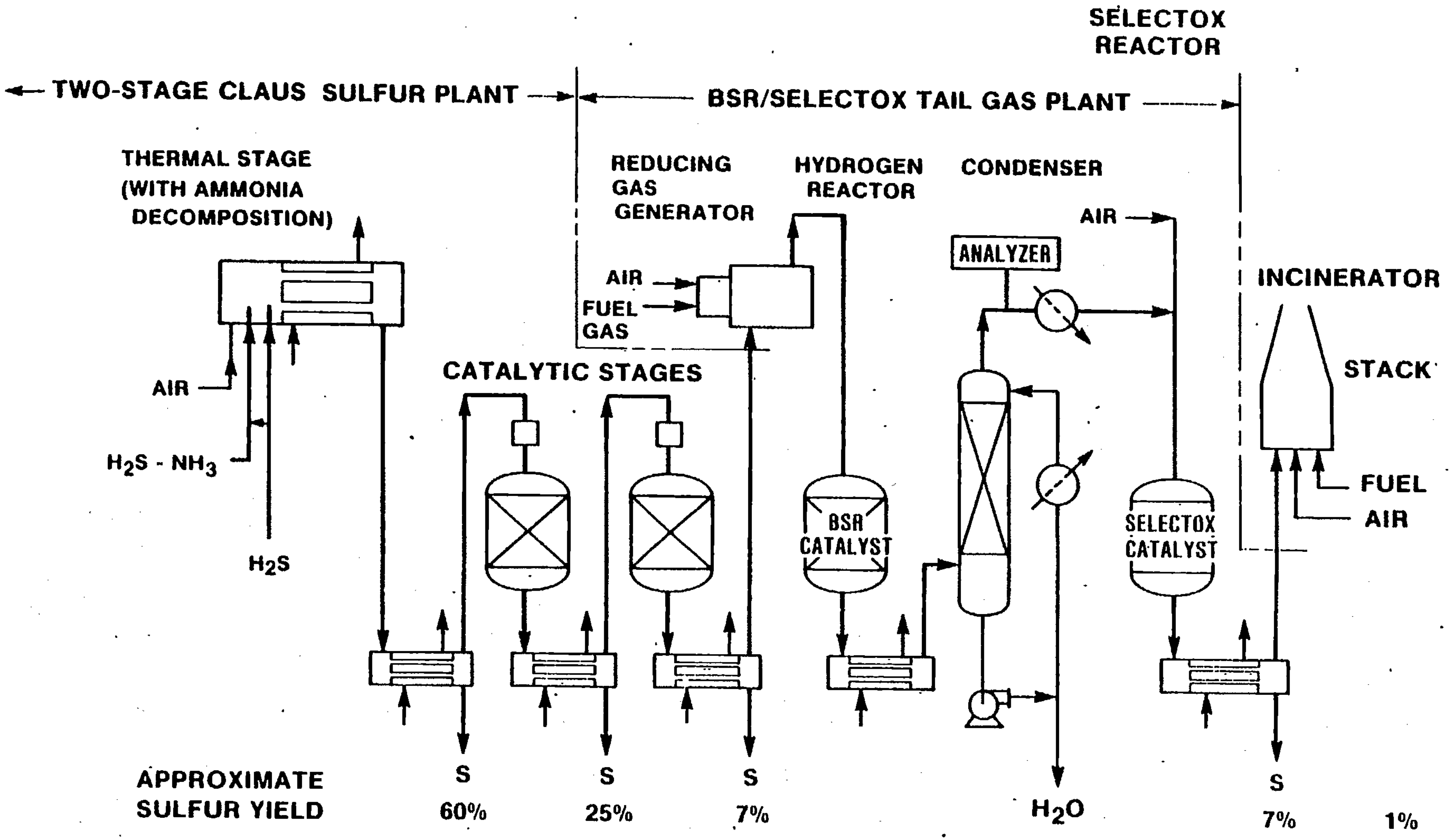

FIG. 4-3 **BSR/Selectox Abating Claus Emissions.**

Source: Ref. 1

5.0 COMMERCIAL ECONOMICS DATA

The economics of sulfur recovery using the Selectox process have been reported by the Ralph Parsons Co. and summarized in Table 5-1.

6.0 ADVANTAGES & DISADVANTAGES

Advantages

- Process can feed gas containing a wide range of H_2S concentrations.
- The Selectox catalyst can also serve as a catalyst for catalytic incineration.

Disadvantages

- Acid gas containing olefins and aromatics cannot be processed due to danger of catalyst fouling.
- Except for BSR/Selectox, only 96% of the total sulfur can be recovered without an additional tailgas treatment unit.

TABLE 5-1

CAPITAL & OPERATING COSTS FOR A 100 TPD SELECTOX SULFUR RECOVERY SYST

	H_2S 20% IN CO_2		H_2S 50% IN CO_2
	3 - STAGE RECYCLE SELECTOX	BSR/SELECTOX	BSR/SELECTOX
INVESTMENT COSTS, $MM			
CLAUS - 2 STAGES		5.07	3.73
BSR UNIT		1.80	1.42
SELECTOX UNIT	5.78	1.33	0.84
ACCESSORIES	2.68	2.25	1.48
TOTAL	8.46	10.45	7.47
UTILITIES, CATALYSTS, & CHEMICALS COST, $/DAY	114.67	195.00	101.00
SULFUR RECOVERY, %	96.00	99.00	99.00

All Costs in Jan. 1981 Prices
Source: Ref. 1

7.0 COMMERCIAL INSTALLATIONS

The first commercial application of the BSR/Selectox process was built for Wintershall AG. at Lingen, West Germany. It was started up in January 1978 and was used to treat Claus plant tail gas. The total capacity of the plant (including Claus unit) is 75 LTPD.

The first Recycle Selectox plant was built for Sid Richardson Carbon & Gasoline Co. at their Keystone plant near Kermit, Texas. The plant was commissioned in late 1981 and was used to treat acid gas feed with 13 mol% H_2S from an amine plant. The capacity of the plant is about 20 LTPD.

An existing Claus plant was retrofitted to a two-stage (one Selectox, one Claus) recycle Selectox plant at the M. Vida plant near Pecos, Texas for the Intratex Gas Company. The overall capacity is 25 LTPD of sulfur. H_2S concentration in the feed gas stream range from 6% to 15% H_2S. Project is underway currently.

Chevron USA will install two 10 LTPD recycle Selectox plants at Gaviota, CA. Start-up is scheduled for 1986.

8.0 REFERENCES

1. **Hass, R. H., D. M. Fenton, H. W. Gowdy and F. E. Bringham, "Selectox and UNISULF: New Technologies for Sulfur Recovery "**, paper presented at International Sulfur 1982 Conference, London, England, November 14-17, 1982.

STATUS SUMMARY

STRETFORD SULFUR RECOVERY

1.0 GENERAL INFORMATION

Developer: North Western Gas Board
Manchester, UK
Clayton Aniline Co. Ltd.,
Manchester, UK

Licensor: British Gas Corporation
London, UK

Improved Processes: Over the years, substantial improvements were were made made by various process licensors to improve and extend the application ranges of the Stretford process. They included:

- Beavon Sulfur Removal Process (BSRP) offered by R. M. Parsons Co., Pasadena, CA and Union Oil Co. of California, Brea., CA.
- Holmes-Stretford Process offered by Peabody Systems, Stamford, CT.
- Cleanair-Stretford Process offered by J. F. Pritchard Corporation, Kansas City, Missouri.

Type: A liquid phase oxidation process which uses an aqueous solution containing sodium carbonate, sodium vanadate, and anthraquinone disulfonic acid (ADA) as a redox catalyst.

Conditions: The process can be operated between atmospheric pressure and 1000 psig. Operating temperatures throughout the unit are in the range of ambient to 120°F. The process can remove up to 99.9% of H_2S concentration. Treated gas contains 10 ppm or less of H_2S.

Applications: The process has been applied to treat coke oven gas, Claus plant tail gas, refinery off-gas, natural gas, and acid gas removal systems regenerator off-gas.

Status: Over 110 Stretford units were operated or in construction with capacities ranging from 0.1 to 200 MMSCFD of acid gas feed.

2.0 PROCESS DEVELOPMENT

The process was developed jointly by the North western Gas Board and the Clayton Aniline Co. Ltd. in 1959. It was intended initially to replace the iron oxide purification system (the Manchester Process) for the removal of H_2S from coal gas.

The process was licensed to various engineering contractors who made improvements and modifications to the original process.

W. C. Holmes Ltd. (now Peabody Engineered Systems) made major improvements to the original process to handle coke-oven gas, producer gas, and town gas and marketed the technology under the Cleanair Process.

R. M. Parsons Co. and Union Oil Co. of California added a catalytic converter upstream of the Stretford process to treat Claus Plant tailgas and marketed the technology under the Beavon Sulfur Removal Process (BSRP).

Recent developments by the British Gas Corporation include operation of a high pressure pilot plant at Pantington; development of the Desalting Process to treat purge effluent, and study of the microbiological growth on the effluent and product streams.

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3.0 PROCESS CHEMISTRY

A typical Stretford solution consists of an aqueous solution of:

Anthraquinone disulfonic acid (ADA),
Vanadium (as sodium meta-vandate), and
Sodium Carbonate.

In the absorber, H_2S is absorbed and ionized to HS^- in the Stretford solution. The HS^- ions are then oxidized to elemental sulfur by the pentavalent vanadium ions in solution:

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

The reduced vanadium ions are then reoxidized by the ADA, which act as an oxygen carrier. The reduced ADA itself is reoxidized by oxygen in the air. These coupled redox reactions are:

$$V^{+4} + \text{ADA} \longrightarrow V^{+5} + \text{ADA (reduced)}$$

$$H^+ + \text{ADA (reduced)} + 1/2O_2 \longrightarrow \text{ADA} + OH^-$$

Hence, the overall reaction is the liquid phase oxidation of H_2S to elemental sulfur:

$$H_2S + 1/2\ O_2 \longrightarrow S + H_2O$$

Excess HS^- ions are oxidized to thiosulfates and sulfates by the oxygen in the air.

$$2HS^- + 2\,O_2 \longrightarrow S_2O_3^{-2} + H_2O$$

$$S_2O_3^{-2} + 5/2\ O_2 \longrightarrow 2\,SO_4^{-2}$$

HCN in the feed gas reacts with free sulfur in solution to form thiocyanates:

$$CN^- + S \longrightarrow CNS$$

Other sulfur compounds are hydrolyzed and converted to a limited extent:

$$COS + H_2O \longrightarrow CO_2 + H_2S$$

$$CS_2 + H_2O \longrightarrow COS + H_2S$$

$$R\text{-}SH + Na_2CO_3 \longrightarrow R\text{-}SNa + NaHCO_3$$

During the reaction process, part of the sodium carbonate becomes bicarbonate. Due to the alkaline nature of the solution, small amounts of CO_2 in the feed gas is also absorbed:

$$CO_3^{-2} + H^+ \longrightarrow HCO_3^-$$

4.0 PROCESS DESCRIPTION

A schematic flow diagram of the Stretford process is shown in Figure 4-1. The raw gas is contacted countercurrently with the Stretford solution in the absorber where essentially all the H_2S is removed. The treated gas contains less than 10 ppm of H_2S. The solution flows from the absorber to a reaction tank where the conversion of HS^- ions to elemental sulfur is completed. The reaction tank could be the bottom section of the absorber or a separate vessel. From the reaction tank, the solution flows by gravity to the oxidizer where it is regenerated by air sparged at the base of the tank. The air also causes froth flotation of the solid sulfur particles which are produced in the reaction. The sulfur slurry froth overflows into the slurry tank. The bulk of the regenerated Stretford solution flows into the balance tank where it is then recirculated to the absorber. The sulfur slurry is further processed in filters or centrifuges to separate the solution remaining in the slurry. The sulfur cake is then washed with water to recover chemicals contained in the solution and to produce relatively pure sulfur. The wash water is then evaporated off and the sulfur is melted in an autoclave.

Over the years, different engineering licensors have improved the original design and they market their new designs. The most notable processes are described below:

Holmes-Stretford Process - Process modifications and improvements made to the original Stretford process are: feed gas pre-treatment, sulfur recovery and effluent treatment. Holmes-Stretford designs can handle acid gas containing hydrogen cyanide (such as coke oven gas). Old versions of the process includes an HCN removalstep where the HCN in the feed gas stream is removed separately in a pre-absorber. This is accomplished by reacting HCN with sodium polysulfide solution and more than 97% of the HCN can be removed in this step. To prevent buildup of thiocyanates, a small effluent slipstream is required. New Holmes-Stretford plants have eliminated the pre-absorber and use a "Fixed Salts Recovery" process to treat the final waste effluent stream, allowing a zero-effluent discharge because all the products from this step are recycled. In this process, the Stretford effluent stream containing sodium thiocyanate, sodium thiosulfate and sodium sulfate are first concentrated in an evaporator. The concentrated stream is then fed to the top of a reactor where a reducing atmosphere is maintained by sub-stoichiometric combustion of fuel and air. This reductive incineration method produces a gas containing CO_2, N_2 and H_2S which is recycled to the Stretford absorber and a liquid stream containing vanadium salts and sodium carbonate is also recycled. Small amounts of ADA are decomposed to H_2O and CO_2. In the sulfur recovery area, the Holmes-Stretford design uses continuously-operating centrifuges and continuous sulfur melters to minimize plant labor requirements. Figure 4-2 shows a simplified Holmes-Stretford process flow diagram. Figure 4-3 shows a simplified process flow diagram for the "Fixed Salts Recovery" section of the plant.

Cleanair Process - This process is designed to provide an overall removal efficiency of 99.9% of the sulfur compounds fed to a Claus plant. The process consists of three major steps. The first step is the reduction of the COS and CS_2 compounds from about 1200 ppmv to 150 ppmv by operating modified-Claus reactors at elevated temperatures. The second step involves aqueous quenching of the Claus tailgas from 130°C to 50°C in a tower. This cooling step is used simultaneously to achieve a further Claus redox reaction between the H_2S and SO_2 content of the tail gas. Essentially all SO_2 is consumed before the excess H_2S is passed to the final step, which is the Stretford unit. A simplified process flow diagram for the quench and Stretford sections of the Cleanair process is shown in Figure 4-4.

Beavon Sulfur Recovery Process (BSRP) - This process consists of two main steps: (1) Catalytic hydrogenation and hydrolysis of all sulfur species to H_2S; and (2) conversion of H_2S to elemental sulfur by the Stretford process. The process is specially designed to treat Claus plant tailgas. A simplified process flow diagram is shown in Figure 4-5. In the first step, Claus plant tailgas is heated to reaction temperature by mixing with the hot combustion products of fuel gas and air from a reducing gas generator. The resulting gas contains hydrogen and carbon monoxide as reagents for hydrogenation. The hot gas mixture next passes through a bed of BSR cobalt molybdenum catalyst where all non-H_2S compounds are converted to H_2S. The hydrogenated gas stream is first cooled in a steam generator and then by direct-contact condenser to near ambient temperature to condense and remove the water. The cooled gas then enters the Stretford unit where H_2S is removed. Several improvements to the Stretford section were made in the BSRP process. These include modifications to the mechanical designs of the absorbers and oxidizers to avoid plugging and the direct autoclaving of the sulfur froth in the sulfur recovery step.

The Holmes-Stretford process removes HCN from the feed gas prior to the Stretford absorber. An aqueous sodium polysulfide (Na_2Sn+1) solution reacts with the CN$^-$ ions to form CNS$^-$ in a separate absorber. The required polysulfide solution is formed in a separate polysulfide generator:

$$CN^- + Na_2Sn+1 \longrightarrow CNS^- + Na_2S_n$$

$$Na_2S_n + S \longrightarrow Na_2S_{n+1}$$

The reductive incineration reactions in the "fixed salts recovery" step (discussed in Section 4.0) in the Holmes Stretford process involve complex chemistry. The following shows the major reactions taking place:

$$NaCNS + 4H_2O \longrightarrow Na_2CO_3 + CO + N_2 + 2H_2S + 2H_2$$

$$Na_2S_2O_3 + H_2O \longrightarrow Na_2SO_4 + H_2S$$

$$Na_2SO_4 + CO + 3H_2 \longrightarrow Na_2CO_3 + H_2S + H_2O$$

The Cleanair process consists of a quench section upstream of the Stretford absorber. SO_2 is removed in this section by a Claus type redox reaction in a proprietary aqueous solution. The SO_2 ionizes in solution to HSO_3^- which then react with HS$^-$ to form elemental sulfur:

$$2\ H_2S \longrightarrow 2H^+ + 2\ HS^-$$

$$SO_2 + H_2O \longrightarrow H^+ + HSO_3^-$$

$$2HS^- + HSO_3 \longrightarrow 3S + 3OH^-$$

Hence the overall reaction is:

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

The Beavon Sulfur Recovery Process (BSRP) consists of a catalytic reactor upstream of the Stretford absorber to hydrogenate and hydrolyze all sulfur species to H_2S. The catalyst (BSR) is a cobalt-molybdenum catalyst in the sulfided state. The reactions occurring are:

$$COS + H_2O \longrightarrow CO_2 + H_2S$$

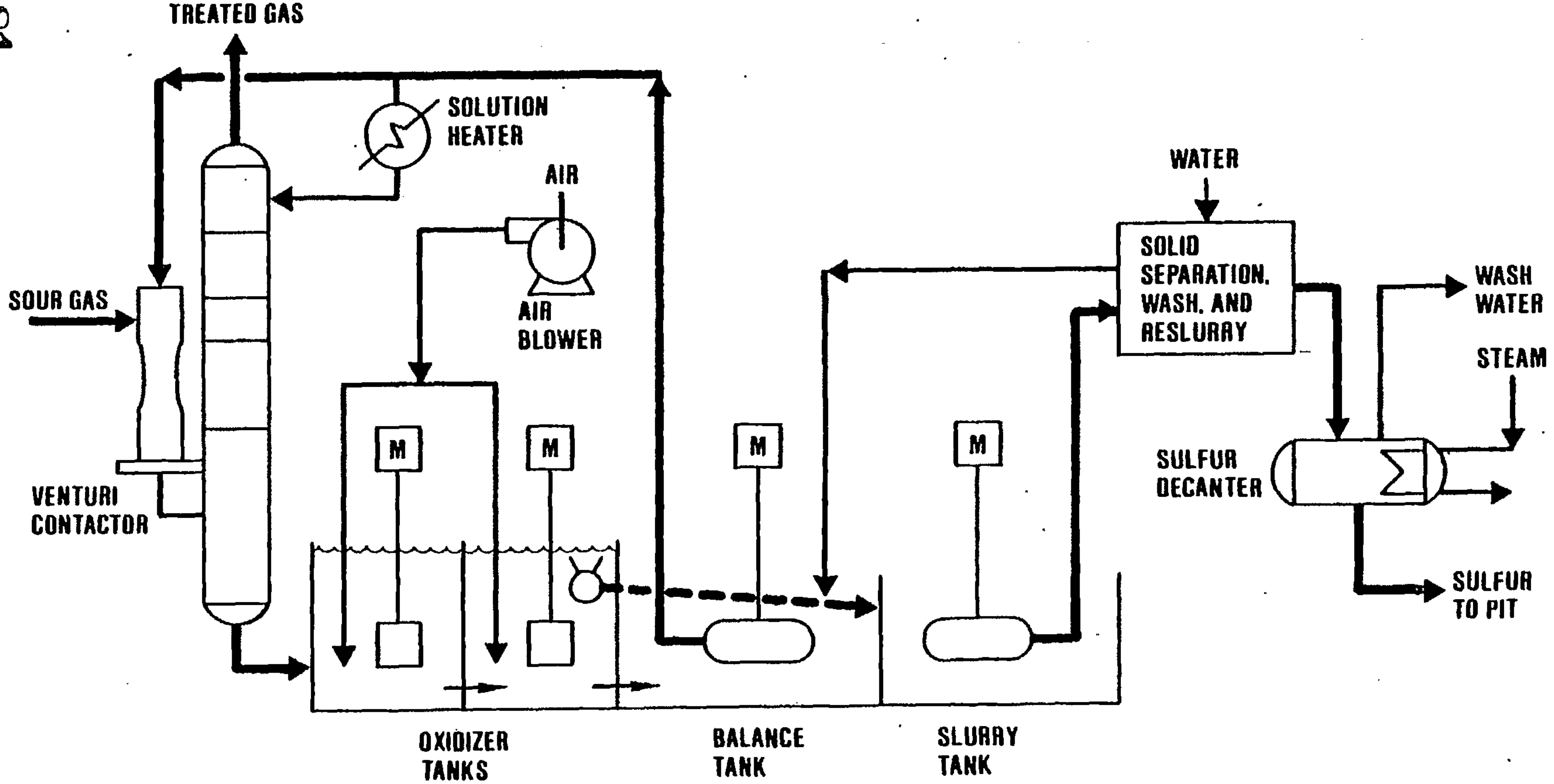
$$CS_2 + 2H_2O \longrightarrow CO_2 + 2H_2S$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$SO_2 + 3H_2 \longrightarrow H_2S + 2H_2O$$

$$CH_3SH + H_2 \longrightarrow H_2S + CH_4$$

$$Sx + xH_2 \longrightarrow xH_2S$$



Source: Ref. 2

FIG. 4-1 Stretford Process

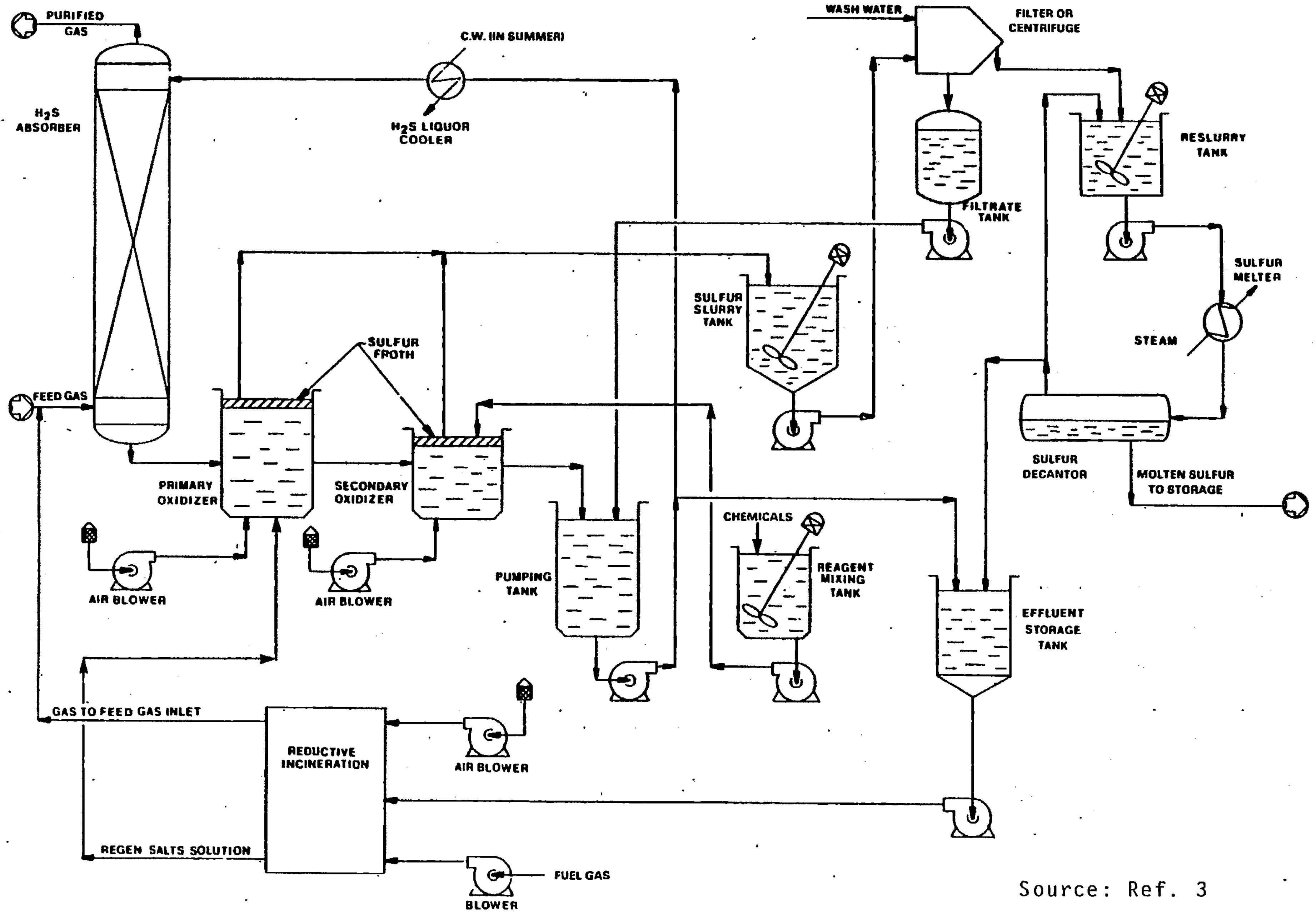


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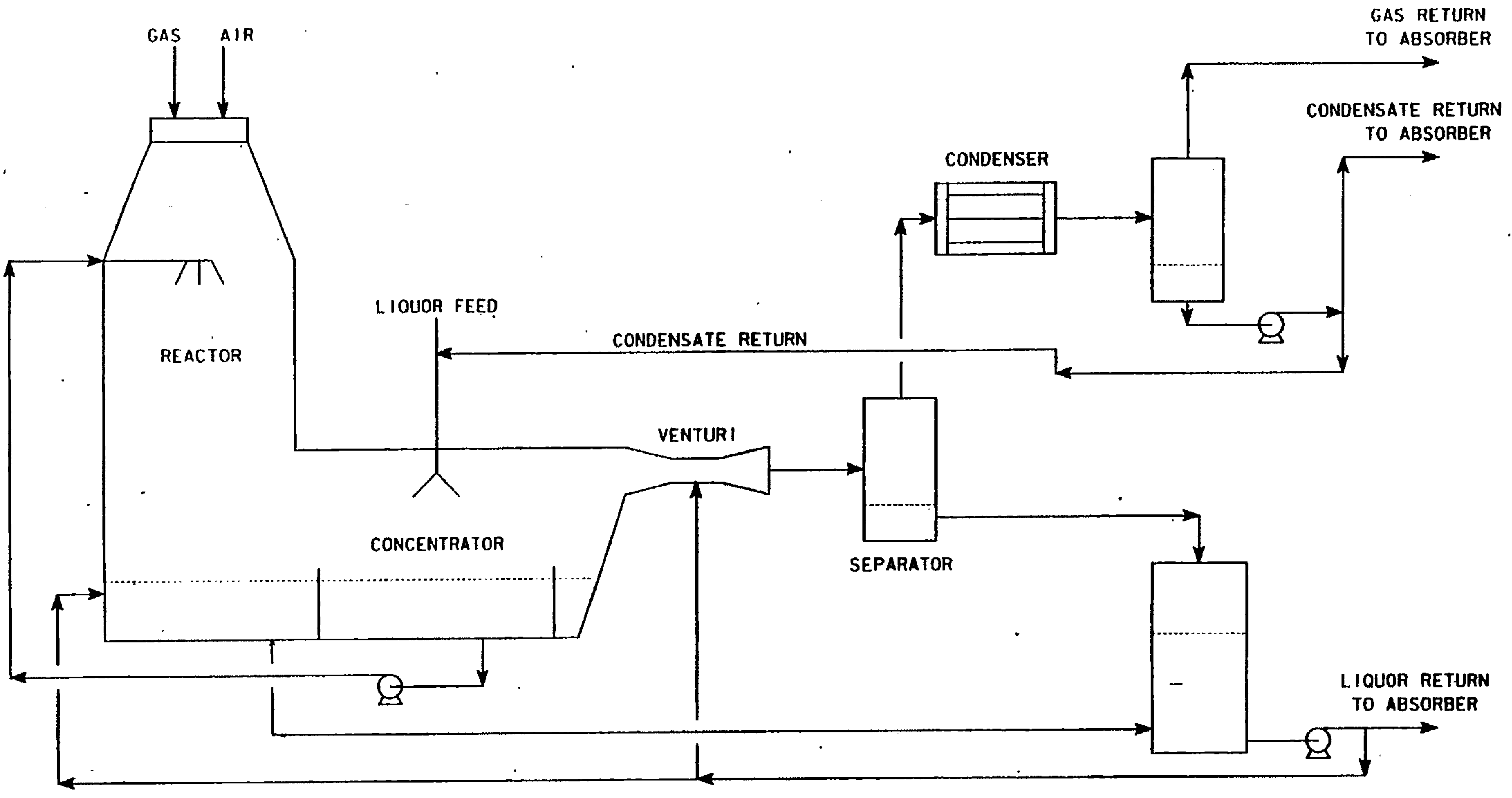
FIG. 4-2 HOLMES-STRETFORD PROCESS



Source: Adapted from Ref. 4

KELLOGG RUST SYNFUELS, INC.

GAS RESEARCH INSTITUTE
HOLMES-STRETFORD
FIXED SALTS RECOVERY PLANT
FIGURE 4.3

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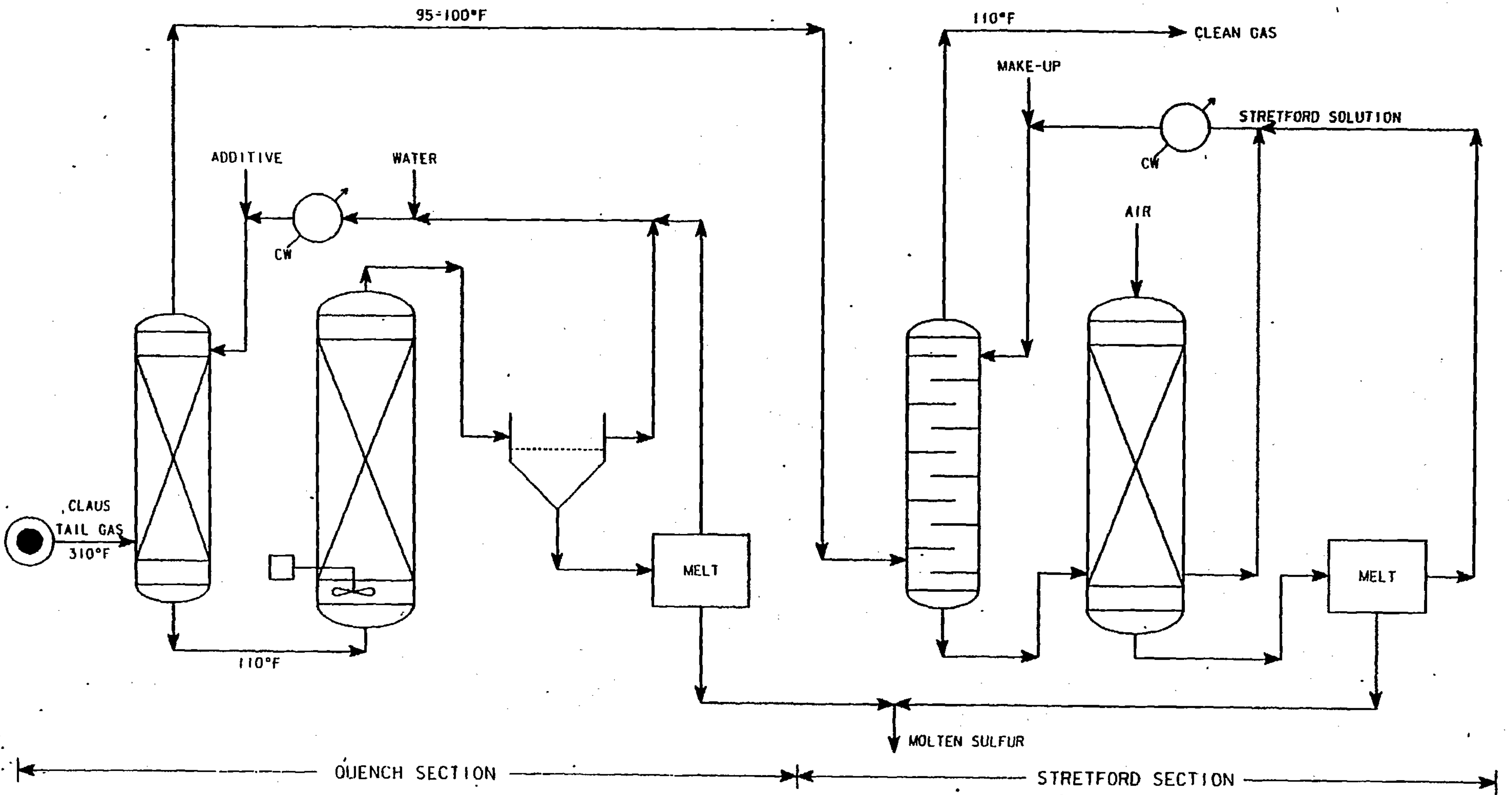

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KELLOGG RUST SYNFUELS, INC.

GAS RESEARCH INSTITUTE
CLEANAIR/STRETFORD
SULFUR RECOVERY PROCESS
FIGURE 4.4

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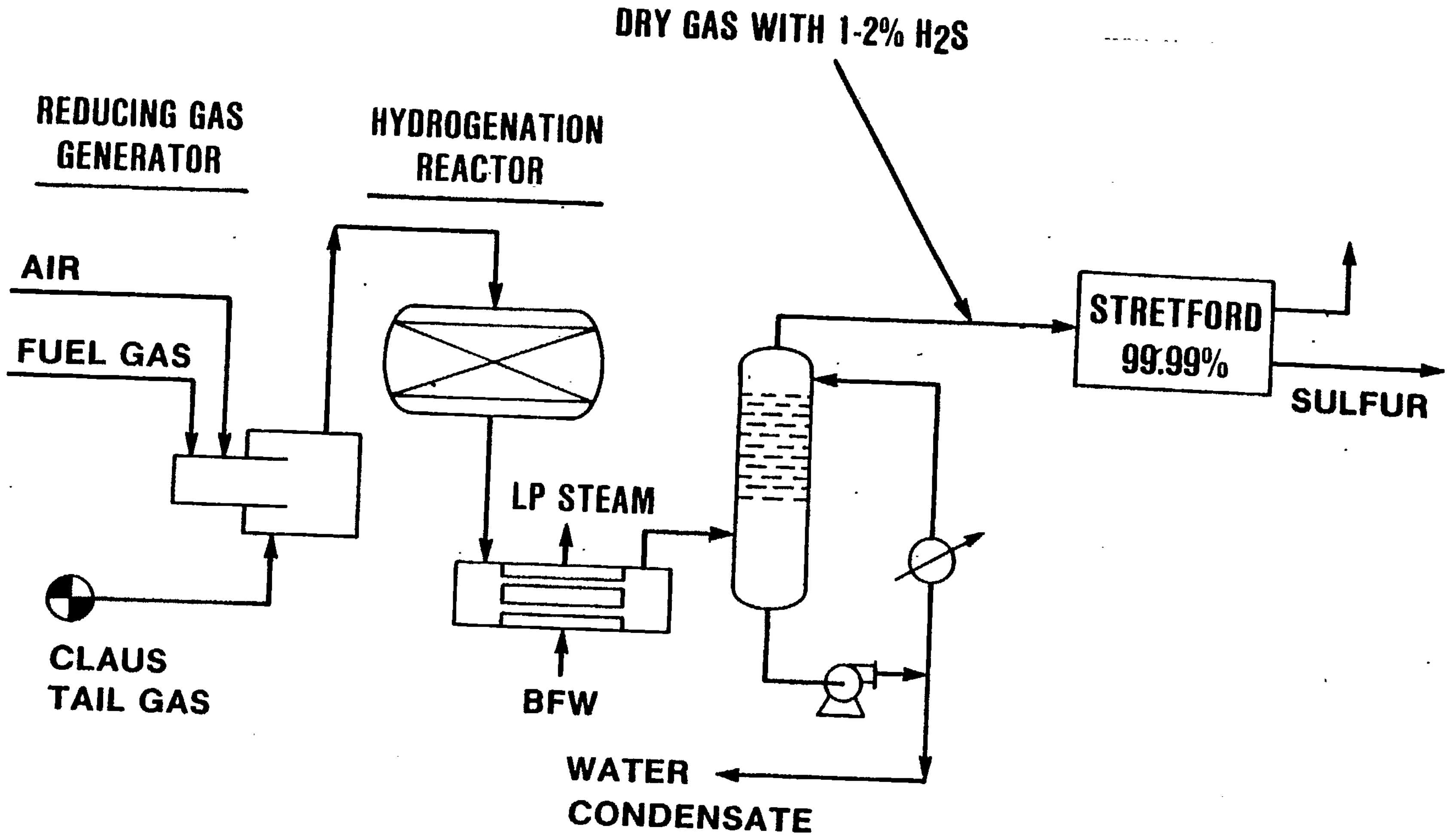

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FIG. 4-5 BEAVON SULFUR RECOVERY PROCESS (BSRP)

5.0 COMMERCIAL ECONOMICS DATA

Two cases of typical commercial designs and economics data provided by R. M. Parsons Co. are shown in Table 5-1.

6.0 ADVANTAGES & DISADVANTAGES

Advantages

- Can process feed gas containing a wide range of H_2S concentration.
- Removes H_2S from acid gas streams with low H_2S content.

Disadvantages

- Reagent consumption is high.
- Potential operational problems with sulfur flotation.
- Minor impurities in the feed gas often cause undesirable side reactions.
- Many units have not performed up to design specifications.
- Quality of the sulfur produced is poor.

7.0 COMMERCIAL INSTALLATIONS

A list of commercial installations is shown in Table 7-1. This list does not include approximately 50 commercial installations in United Kingdom,, which are no longer in operation due to conversion to natural gas. The largest plant constructed to date removed 77 STPD per day of sulfur from a gas flow of 190 MM SCFD.

Nearly all of the installations referred to in Table 7-1 for Claus Tail Gas and Refinery Gas used the BSRP process while the ones for coke-oven gases and low-Btu gases used the Holmes-Stretford Process. Although the Cleanair Process has been extensively piloted and three commercial units have been built, no successful commercial operation has been reported, yet.

TABLE 5-1 TYPICAL DESIGN DATA FOR STRETFORD SULFUR RECOVERY SYSTEM

Plant Data	Case 1	Case 2
• Feed gas		
- Composition, mol %		
H_2S	1.7	.9
CO_2	98.3	99.1
Total:	100.0	100.0
- Flow rate, MMSCFD	295	546
- Assumed temperature, deg F	100	100
- Assumed pressure, psig	3-5	3-5
- Sulfur in feed, LT/D	189	185
• Stretford Unit		
- No. of absorbers	6	8
- No. of venturi/mixers	12	16
- No. of Stretford trains	3	4
• Utilities required (both cases identical)		
- 50 psig steam, lb/hr	24,900	24,900
- Process water, GPM	124	124
- Cooling water, GPM (11 deg F rise)	6,520	6,520
• Utilities produced		
- Steam condensate, lb/hr	24,900	24,900
• Cost of chemicals, $/day	13,500	13,500
• No. of operators/shift	3	3
• Maintenance cost, % of plant value	4	4
• Total installed cost, mm $	47	57
- Boundary limits plant		
- Clear and level site		
- U.S. Gulf Coast costs		
- Excludes chemicals, catalysts, spare parts, escalation beyond 4 Qtr '83, contingency, offsite facilities, utilities, start-up services, license and royalty fees		

Source: Ref 7

TABLE 7-1 LIST OF STRETFORD PLANTS OPERATING OR UNDER CONSTRUCTION

PRESSURE LESS THAN 1 BAR

Claus Tail Gas	37
Coke Oven Gases	25
Regeneration Off-Gas	
Rectisol	1
Amine	2
Selexol	1
Benfield	1
Low Btu Gases	
Coal	4
Petroleum Coke	1
Miscellaneous	
Geothermal Vent Gas	9
Coal Liquefaction (Misc. Vent Gas)	1
Reformer Gas	4
Natural Gas	2
Refinery Gas	2
Oilfield Gas	1
Ore Roasting	1

PRESSURE 1 - 6 BAR

Natural Gas	3
S.N.G. (Desulphiding)	3
Refinery Gas	2
Reformer Gas	1

PRESSURE 6 - 15 BAR

Natural Gas	1
S.N.G. (Desulphiding)	1

PRESSURE 15 - 20 BAR

Coal Gasification	1

PRESSURE GREATER THAN 20 BAR

Natural Gas	2

Source: Ref. 1

8.0 REFERENCES

1. **Wilson, B. M., and R. D. Newell, "H_2S Removal by the Stretford Process - Further Development by the British Gas Corporation"**, paper presented at the National AIChE Meeting, Atlanta, March 11-14, 1984.

2. **Clute, A. E., "Sulfur Recovery from Low Hydrogen Sulfide Content Gases"**, Chemical Engineering Progress, 78 (10), October 1982, pp 61-65.

3. **Parekh, R. D., "Handbook of Gasifiers and Gas Treatment Systems"**, pp3A.59, September 1982, WD-TR-82/008-010.

4. **Smith C. R. and B. Mills, "Cost Effective Improvements to the Holmes-Stretford Process,"** Chem. engrs. Symposium Series No. 57, Salford (1979).

5. **"Gas Processing Handbook"**, Hydrocarbon Processing, April 1979, p. 135.

6. **Goar, B. G. and James, J. A., "Tail Gas Cleanup Process - A Review"**, paper presented at the 1983 Gas Conditioning Conference.

STATUS SUMMARY

UNISULF SULFUR RECOVERY

1.0 GENERAL INFORMATION

Developer:	Union Oil Co. of California, Union Science & Technology Division, Brea, CA 92621; and The Ralph M. Parsons Co., (BSR/Unisulf) Pasadena, CA 91124
Licensor:	Same as above
Type:	A homogenous catalytic process in which H_2S is absorbed and oxidized to elemental sulfur by a proprietary solution.
Conditions:	The process is operated at atmospheric pressure with solution temperatures between 90 to 120°F. It can recover over 99.9% of the sulfur from gas streams containing a wide range of H_2S.
Applications:	The process has been applied to Rectisol off-gas and oil shale retort off-gas. A modified version, BSR/Unisulf can be used to treat Claus plant tail gas.
Status:	The process was developed at Union Oil's Science and Technology Division at Brea, California. The first commercial test of the Unisulf solution was made at SASOL I in late 1981. At present, a unit has been installed at Union Oil's oil shale facility in Colorado and another is under construction (BSR/Unisulf) for Claus tailgas cleanup.

2.0 PROCESS CHEMISTRY

Typical components of the Unisulf solution are:
- Sodium Carbonate and Bicarbonate,
- Vanadium Complex,
- Thiocyanate ions,
- Carboxylate complexing agent,
- A water-soluble aromatic compound and water.

The Unisulf process uses the vanadium ion as a catalyst reagent to promote the overall reaction

$$H_2S + 1/2\ O_2 \longrightarrow H_2O + S$$

In the absorber H_2S is absorbed in solution and ionized. The sulfide ions are oxidized by the vanadium ions:

$$2V^{+5} + H_2S + 2OH^- \longrightarrow 2V^{+4} + 2H_2O + S$$

In the oxidizer, the reduced vanadium ions are oxidized by the oxygen in the sparged air stream:

$$2V^{+4} + H_2S + 1/2O_2 \longrightarrow 2V^{+5} + 2OH^-$$

Side reactions that form thiosulfate and sulfate salts do not occur.

A BSR (Beavon) reactor is sometimes installed upstream of the Unisulf asbsorber to convert sulfur compounds other than H_2S to H_2S via the following reactions:

$$SO_2 + 3H_2 \longrightarrow H_2S + 2H_2O$$

$$S_x + xH_2 \longrightarrow xH_2S$$

$$COS + H_2O \longrightarrow CO_2 + H_2S$$

$$CS_2 + 2H_2O \longrightarrow 2H_2S + CO_2$$

3.0 PROCESS DESCRIPTION

A simplified process flow scheme is shown in Figure 3-1. Acid gas is fed to a venturi scrubber and absorber operating in series. The absorber serves as a reaction vessel to oxidize the absorbed H_2S to particles of elemental sulfur. After a short residence time in the absorber, the slurry is transferred to an oxidizing vessel into which air is sparged to oxidize the reduced vanadium ions from V^{+4} to V^{+5}. Simultaneously, the sulfur particles adhere to the air bubbles and float to the surface of the aqueous solution by froth flotation. The sulfur froth overflows through a weir into a receiving froth tank, forming a slurry which is later mechanically separated from the mother liquor by either filtering or by centrifuging. The filtrate is pumped to a balance tank which also receives the regenerated solution from the oxidizer. The balance tank serves as an inventory vessel for the regenerated solution, which is recycled back to the absorber and venturi scrubber. The sulfur filter cake can be used as it is, or it can be slurried with fresh water and sent to an autoclave to produce en sulfur. Except for the autoclave, the entire process operates at ambient temperature (70 to 120°F).

The Unisulf Process can remove only H_2S but not the other sulfur compounds such as COS, CS_2, and SO_2. For feeds containing these other sulfur compounds, such as the Claus plant tail gas, a variation of this process called the BSR/Unisulf Process can be used. A flowsheet for this process is shown in Figure 3-2. The acid gas is heated to reaction temperature by mixing with the hot combustion products from a patented reducing gas generator. The resulting gas contains hydrogen and carbon monoxide as reagents for hydrogenation. The hot mixture next passes through a bed of BSR cobalt molybdate catalyst where all sulfur compounds (COS, CS_2, SO_2) are converted to H_2S. The hydrogenated gas stream is first cooled in a steam generator and then by direct contact condenser to near ambient temperature. The condensed water is separated and the cooled gas is sent to the venturi scrubber in the Unisulf Process.

4.0 COMMERCIAL ECONOMICS DATA (Ref. 2)

Based on a Unisulf plant having a sulfur recovery capacity of 5 LTPD, the investment cost is approximately $4 million and the utilities cost is approximately $400/day.

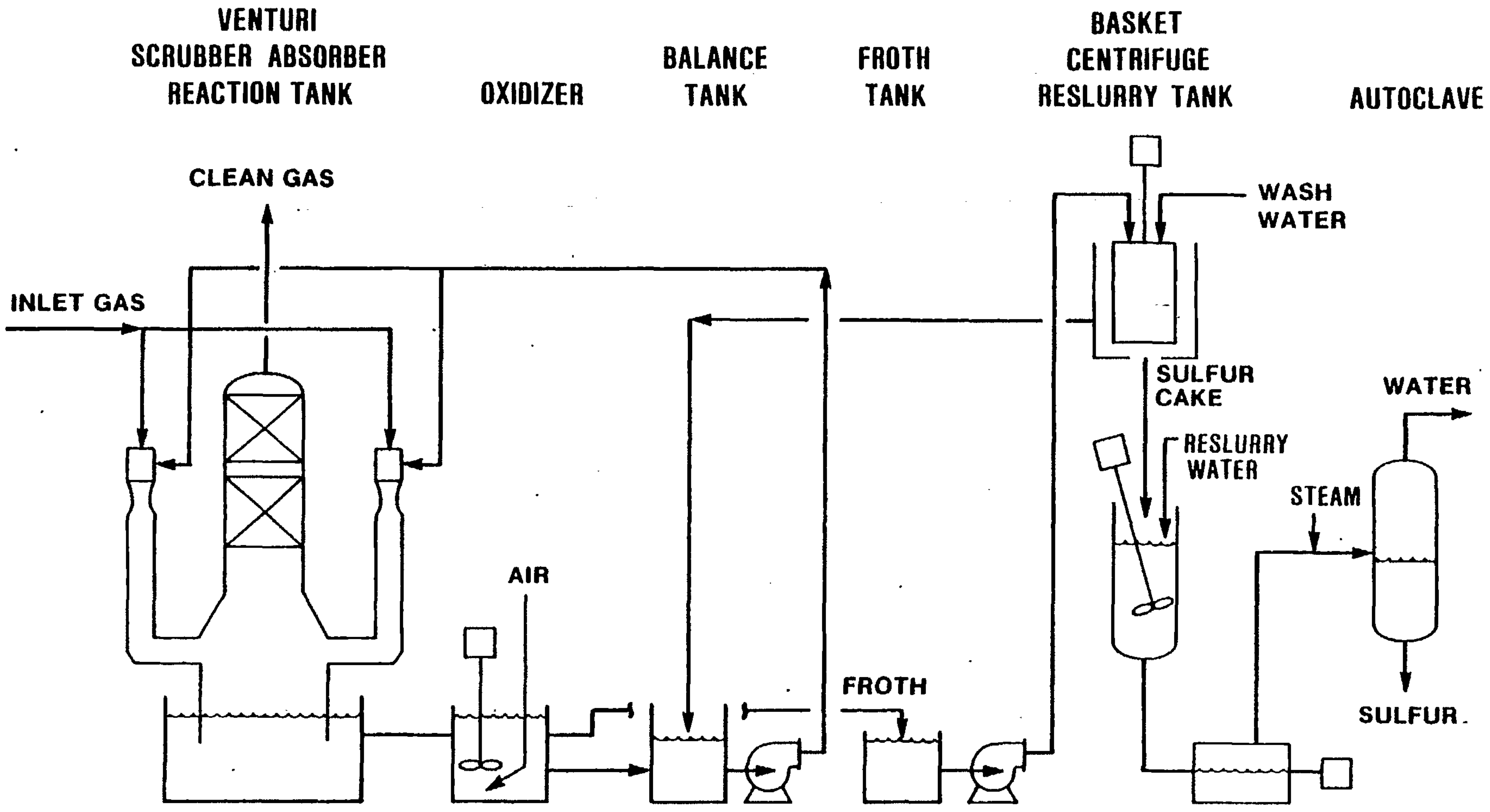

FIG. 3-1 **Unisulf Process.**

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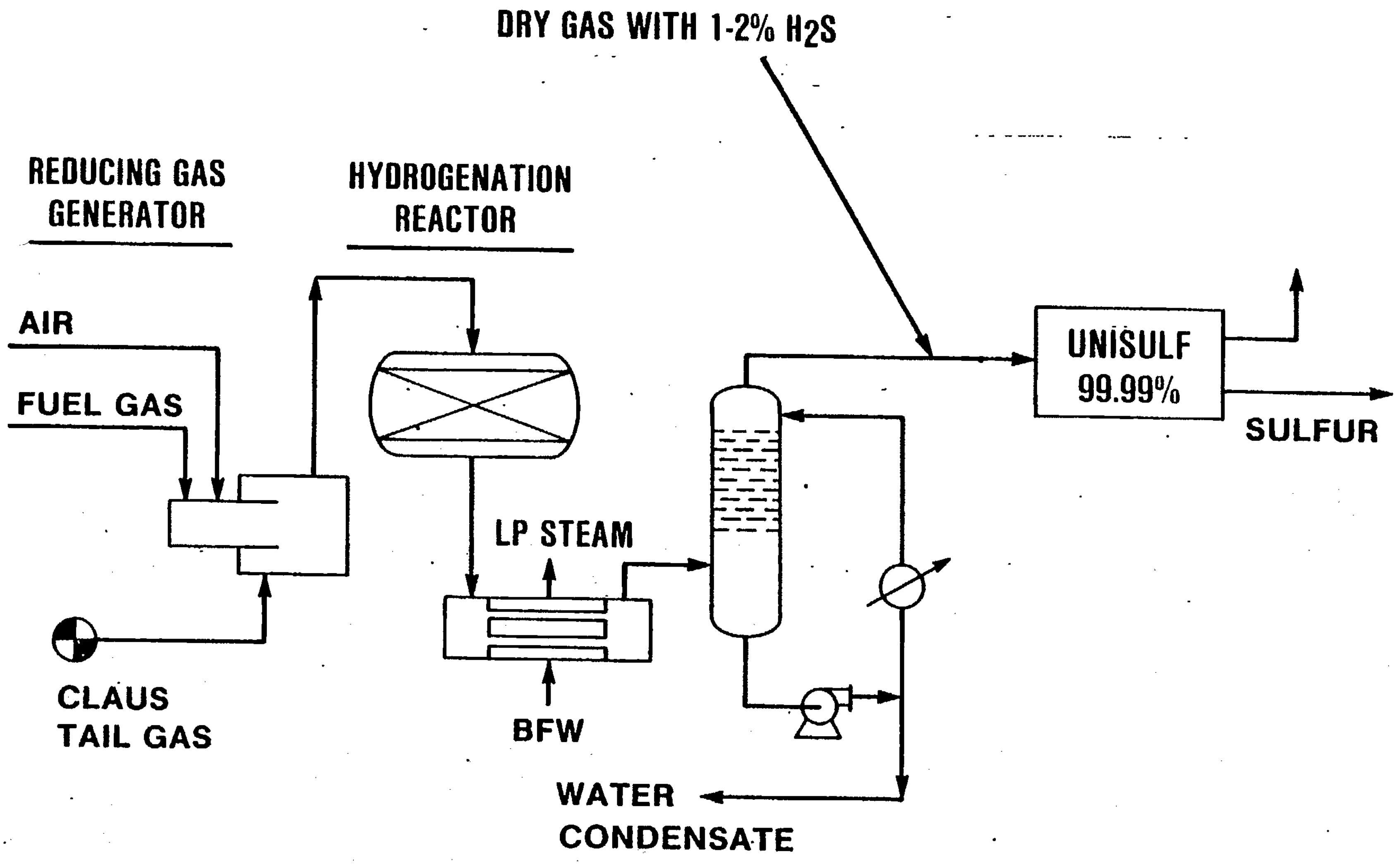

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FIG. 3-2 BSR UNISULF PROCESS

5.0 ADVANTAGES & DISADVANTAGES

Advantages

--Essentially complete removal of H_2S from acid gas streams with low H_2S content.

--Acid gas containing trace amounts of olefins and aromatics can be tolerated (only for Unisulf, not BSR/Unisulf.)

--No byproducts, such as thiosulfates, are formed. So, purging of the Unisulf solution is not required.

Disadvantages

--Potential operational problems with sulfur flotation.

6.0 COMMERCIAL INSTALLATIONS

Unisulf solution has successfully been used to treat Rectisol off-gas to recover 26 LTPD sulfur. The unit was located at SASOL I and began operation in late 1981. A Unisulf unit has been installed at Union Oil's oil shale facility in Colorado to treat oil shale retort off-gas. A BSR/Unisulf unit is under construction for Claus tail gas cleanup.

7.0 REFERENCES

1. **Hass, R. H., Fenton, D. M., Gowdy, H. W., and Bingham, F. E., "SELECTOX and UNISULF: New Technologies for Sulfur Recovery"**, paper presented at the 1982 International Sulfur Conference, London, England, November 14-17, 1982.

2. **Gas Processing Handbook,"Unisulf"**, Hydrocarbon Processing, 63(4), pp 51, April 1984.

9.0 COMPARISON OF PERFORMANCE/DESIGN PARAMETERS

The GRI/Advisors Planning and Strategy (GAPS) Committee was established to develop a plan for guiding research in the areas of fossil fuel gasification and downstream gas processing. As part of the work, the committee has developed a procedure for evaluating sulfur recovery processes by setting up performance criteria to evaluate processes. This allows the identification of specific advantages and disadvantages of various processes and to establish research goals for process improvement and new process development. The "Musts" in Sulfur Removal technology are shown in Table 9-1. The technical criteria and standards developed for this technology appear in Table 9-2. A brief description and explanation of the same is provided where appropriate. Tables 9-3 and 9-4 summarize the performance of the six (Claus, Amoco Direct Oxidation, LO-CAT, Selectox, Stretford and Unisulf) processes. All the data in Tables 9-3 and 9-4 are extracted from the respective Status Summary reports and from the public sources. It should be noted that these data are based on current publicly available resources; as more data are developed or made available to the public by the licensors, this table could be updated. Footnotes at the end of the table are provided for additional clarification.

TABLE 9-1

'MUSTS' IN SULFUR RECOVERY TECHNOLOGY SELECTION

The sulfur recovery technology being considered must:

1. Be capable of processing the sulfur-bearing stream from either a selective or a non-selective acid gas removal unit which can desulfurize the gas from gasification of U.S. coals.
2. Recover at least 90 % of the sulfur from its feed gas in elemental or other marketable form.
3. Generate a tail gas stream which can be vented directly to the atmosphere or readily treated for such discharge by existing tail gas or flue gas treatment technology.
4. Require no exotic materials of construction.
5. Involve no solvent or process reagent regarded as highly toxic or highly carcinogenic.
6. Be developed such that the basic process concept is confirmed.

TABLE 9-2

TECHNICAL CRITERIA AND STANDARDS FOR SULFUR RECOVERY TECHNOLOGY

CRITERION	DESCRIPTION	STANDARD	EXPLANATION
1.0 ACID GAS PROCESSING CAPABILITY			
1.1 H2S - Low Range	0.5 to 5 vol % H2S	Full range	Process should operate as
1.2 H2S - Middle Range	5 to 25 vol % H2S	Full range	intended with wide range of feed
1.3 H2S - High Range	25 vol % H2S and greater	Full range	gas compositions, particularly in
1.4 COS and CS2		Up to 2 %	ranges of H2S content.
1.5 Mercaptans	Thio-compounds of light CnHm's	Up to 1 %	
1.6 NH3 and HCN		Up to 2 %	
1.7 Hydrocarbons		Up to 3 %	
2.0 SULFUR RECOVERY CAPABILITY			
2.1 H2S	Percent of feed gas constituents	90 %	For sulfur recovery unit only,
2.2 COS and CS2	converted to elemental sulfur.	90 %	not assuming a tandem unit for
2.3 Mercaptans		90 %	tail gas treating.
3.0 PROCESS EFFICIENCY			
3.1 Energy Consumption	MM Btu per Ton of Sulfur	1.7	Standard based on Claus process.
3.2 Energy Recovery	MM Btu per Ton of Sulfur	11.5	Standard based on Claus process.
3.3 Quality of Energy Recovered	Level of steam produced	500 psi sat'd	
4.0 BYPRODUCT PRODUCTION			
4.1 CO2 Recovery Efficiency		90 %	
4.2 Vent Gas CO2 Purity		> 99 %	For sale in EOR. H2S, O2, CH4, N2 and H2 are detrimental.
4.3 Other Byproducts	Value, $/ton of sulfur	$ 0.50/ton S	
5.0 COMPLEXITY OF PROCESS			
5.1 Reactor System, Type	Fixed-bed, liquid or solid, etc.	Solid fixed-bed	Simple system preferred, index < 1.0.
5.2 Major Process Steps	Number of reactors, towers, etc.	4	
5.3 Internal Recycles	Number: gas, liquid or solid	Zero	
5.4 Phase Separations	Number: gas/liquid, liquid/solid	3 gas/liquid	Standard based on Claus process.

TABLE 9-2
(continued)
TECHNICAL CRITERIA AND STANDARDS FOR SULFUR RECOVERY TECHNOLOGY

CRITERION	DESCRIPTION	STANDARD	EXPLANATION
6.0 REACTOR DESIGN CONSIDERATIONS			
6.1 Operating Temperature	Maximum, degr F	1100 degr F	Mild conditions preferred.
6.2 Operating Pressure	Maximum, psig	15 psig	Should match AGR discharge pressure, avoid compression.
6.3 Space Velocity	Throughput volume/volume of reagent or catalyst.	> 1000 /hr.	Higher SV means smaller reactor(s).
6.4 Approach to Equilibrium at Outlet		< 100 degr F	Maximum conversion preferred.
7.0 CATALYST/REAGENT PROPERTIES			
7.1 Active Constituents	General grouping	Non-noble	Less-expensive preferred.
7.2 Life/Cycle Time		> 2 years	
7.3 Regenerability		Regenerable	Disposable, short-life catalysts discouraged.
7.4 Safety in Handling	Catalyst/reagent should be non-corrosive and non-flammable.	High	Index vs. silica/alumina.
7.5 Spent Catalyst/Reagent Disposition	Special requirements or practices.	None	
7.6 Storage/Activation Requirements	Special requirements or practices.	None	
8.0 IMPACT ON SNG PLANT DESIGN			
8.1 Complexity	Index vs. Claus = 1.0	< 1.0 preferred	Impact on balance-of-plant.
8.2 Utilities & Reagents	Index vs. Claus = 1.0	< 1.0 preferred	Required by balance-of-plant.
8.3 Flexibility: Coal Types	Range of coal sulfur content.	All	
8.4 Flexibility: AGR Systems	Range of feed compositions accepted	All	
8.5 Flexibility: TGT/FGD	Range of compatibility.	All	
8.6 Design Viability	Number of extrapolations of key parameters for other areas.	None	Prefer that process does not call for unproven designs.
9.0 INTEGRABILITY			
9.1 Acid Gas Pretreatment	Extra steps required.	None	e.g., Compression, COS Hydrolysis.
9.2 Vent Gas Treatment	Extra steps required.	None	To achieve ventable effluent.
9.3 Sulfur Quality	Steps to upgrade to market quality.	None	

TABLE 9-2
(continued)
TECHNICAL CRITERIA AND STANDARDS FOR SULFUR RECOVERY TECHNOLOGY

CRITERION	DESCRIPTION	STANDARD	EXPLANATION
10.0 PROCESS TECHNIQUES			
10.1 Equipment Availability		Minimal Extrapolation	Use of equipment which is readily available or requires minimal extrapolation from proven range.
11.0 MATERIALS OF CONSTRUCTION			
11.1 Availability		Std'd Mat'ls	M/C available at reasonable cost.
11.2 Corrosion Resistance Required	Index vs. Claus = 1.0	< 1.0 preferred	Minimized required resistance.
12.0 CONTROLLABILITY			
12.1 Control System	Index vs. Claus = 1.0	< 1.0 preferred	Use existing control methods.
12.2 Turndown Capability	Fraction of normal rate which can be used without loss of efficiency.	50 %	
12.3 Response to Upset	Index vs. Claus = 1.0	> 1.0 preferred	Capability to maintain efficient sulfur removal when upset.
13.0 RELIABILITY			
13.1 Standby Requirements	Need for extra spares.	None	
13.2 Consequence of Failure		Minimum	Likelihood of damage to other units due to failure in sulfur recovery.
13.3 Maintenance Extent	Index vs. Claus = 1.0	< 1.0 preferred	
13.4 Overdesign Requirement	To accomodate variations in feed gas composition.	Minimum	
14.0 ENVIRONMENTAL CONSIDERATIONS			
14.1 Solid Effluents	Other than spent catalyst/reagent.	None	
14.2 Liquid Effluents	Other than spent catalyst/reagent.	None	
14.3 Gaseous Effluents	Other than CO2 vent stream.	None	

TABLE 9-3

PERFORMANCE OF SULFUR RECOVERY TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	CLAUS	DIRECT OXIDATION	LO-CAT
1.0 ACID GAS PROCESSING CAPABILITY				
1.1 H2S - Low Range	0.5 to 5 vol%	Unsuitable	> 2 % H2S	Full range
1.2 H2S - Middle Range	5 to 25 vol%	Unsuitable	< 15 % H2S	Low absorbent capacity
1.3 H2S - High Range	25 vol% and up	Full range	Unsuitable	Low absorbent capacity
1.4 COS and CS2	Thio-compounds	Affects Claus reaction	Affects Claus reaction	No interference
1.5 Mercaptans	of light CnHm's	Can lead to carbon deposition	Can lead to carbon deposition	Causes problems with sulfur flotation
1.6 NH3 and HCN		Special design req'd	Special design req'd	Sol'n degradation
1.7 Hydrocarbons		Carbon deposition and catalyst deactivation	Carbon deposition and catalyst deactivation	Causes foaming
2.0 SULFUR RECOVERY CAPABILITY				
2.1 H2S	% of feed gas	93 + % conversion	90 + % conversion	99 + % conversion
2.2 COS and CS2	constituents	> 90 % conversion	< 90 % conversion	None converted
2.3 Mercaptans	converted to S.	Portion converted	None converted	None converted
3.0 PROCESS EFFICIENCY				
3.1 Energy Consumption	MMBTU/Ton of S.	Index = 1.0	Index = 0.8	Index = 0.6
3.2 Energy Recovery	MMBTU/Ton of S.	Recovers steam	May recover heat	No energy recovery
3.3 Quality of Energy Recovered	Steam generated	Medium-pressure steam	Low-pressure steam	No energy recovery
4.0 BYPRODUCT PRODUCTION				
4.1 CO2 Recovery Efficiency		90 + % recovery of CO2	90 + % recovery of CO2	90 + % recovery of CO2
4.2 Vent Gas CO2 Purity		Dilution by nitrogen	No dilution	No dilution
4.3 Other Byproducts		No byproducts	No byproducts	No byproducts

TABLE 9-3(Cont'd)

PERFORMANCE OF SULFUR RECOVERY TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	CLAUS	DIRECT OXIDATION	LO-CAT
5.0 COMPLEXITY OF PROCESS				
5.1 Reactor System, Type	Solid fixed-bed	Index = 1.0	Index = 0.9	Index = 1.2
5.2 Major Process Steps	Reactors, towers	4 major steps	3 major steps	5 major steps
5.3 Internal Recycles		No recycles	No recycles	One recycle
5.4 Phase Separations		3 gas/liquid	1 gas/liquid	1 gas/liq, 1 liq/solid
6.0 REACTOR DESIGN CONSIDERATIONS				
6.1 Operating Temperature	deg F	2,400 degF maximum	1,000 degF maximum	Ambient
6.2 Operating Pressure		Compatible with AGR	Compatible with AGR	Compatible with AGR
6.3 Space Velocity	Gas SCFH/catalyst volume.	Index = 1.0	Index = 0.9	Index = 0.5
6.4 Approach to Equilibrium at Outlet		< 100 degr F	< 100 degr F	< 100 degr F
7.0 CATALYST/REAGENT PROPERTIES				
7.1 Active Constituents	Type	Alumina	Alumina	Iron complex
7.2 Life/Cycle Time		Acceptable	Acceptable	Loss to sulfur cake
7.3 Regenerability		Non-regenerable	Non-regenerable	Continuously regen'd
7.4 Safety in Handling		Index = 1.0	Index = 1.0	Index = 0.6
7.5 Spent Catalyst/Reagent Disposition		No treatment	No treatment	No treatment
7.6 Storage/Activation Requirements		No special req'ts	No special req'ts	Reagent storage & loading system
8.0 IMPACT ON SNG PLANT DESIGN				
8.1 Complexity		Index = 1.0	Index = 0.8	Index = 0.5
8.2 Utilities & Reagents		Index = 1.0	Index = 0.9	Index = 0.6
8.3 Flexibility: Coal Types		All types of coal	All types of coal	Low-sulfur only
8.4 Flexibility: AGR Systems		Selective required	Non-selective	Non-selective
8.5 Flexibility: TGT/FGD		Tail gas unit req'd	Tail gas unit req'd	Tail gas ventable
8.6 Design Viability	Extrapolation	No extrapolations	No extrapolations	No extrapolations

TABLE 9-3(Cont'd)

PERFORMANCE OF SULFUR RECOVERY TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	CLAUS	DIRECT OXIDATION	LO-CAT
9.0 INTEGRABILITY				
9.1 Acid Gas Pretreatment	Type req'd	COS hydrolysis req'd	COS hydrolysis req'd	COS hydrolysis req'd
9.2 Vent Gas Treatment		Tail gas unit req'd	Tail gas unit req'd	Tail gas ventable
9.3 Sulfur Quality		Market quality	Market quality	Poor quality sulfur
10.0 PROCESS TECHNIQUES				
10.1 Equipment Availability	Extrapolation	Full scale equipment demonstrated	No extrapolations expected	No extrapolations expected
11.0 MATERIALS OF CONSTRUCTION				
11.1 Availability	Std'd Mat'ls	Standard materials	Standard materials	Standard materials
11.2 Corrosion Resistance Required		Index = 1.0	Index = 1.0	Index = 0.4
12.0 CONTROLLABILITY				
12.1 Control System		Index = 1.0	Index = 0.9	Index = 1.2
12.2 Turndown Capability	% of full rate	Wide turndown range	Wide turndown range	Wide turndown range
12.3 Response to Upset		Acceptable response	Acceptable response	Very responsive
13.0 RELIABILITY				
13.1 Standby Requirements	Spares	No idle spares	No idle spares	Idle spares req'd
13.2 Consequence of Failure	Risk involved	Minimum effect	Minimum effect	Minimum effect
13.3 Maintenance Extent		Index = 1.0	Index = 0.9	Index = 1.5
13.4 Overdesign Requirement	To accomodate variations in feed gas comp or rate.	Must add catalyst	Must add catalyst	Adjust circulation
14.0 ENVIRONMENTAL CONSIDERATIONS				
14.1 Solid Effluents	Extra steps	No solid effluents	No solid effluents	Poor quality sulfur
14.2 Liquid Effluents	Extra steps	No liquid effluents	No liquid effluents	No liquid effluents
14.3 Gaseous Effluents	Extra steps	No gaseous effluents	No gaseous effluents	Spent air str[illegible]

TABLE 9-4

PERFORMANCE OF SULFUR RECOVERY TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	SELECTOX	STRETFORD	UNISULF
1.0 ACID GAS PROCESSING CAPABILITY				
1.1 H2S - Low Range	0.5 to 5 vol%	> 1 % H2S	Full range	Full range
1.2 H2S - Middle Range	5 to 25 vol%	Full range	Low capacity	Low capacity
1.3 H2S - High Range	25 vol% and up	Low capacity	Low capacity	Low capacity
1.4 COS and CS2	Thio-compounds	Affects Claus reaction	No interference	No interference
1.5 Mercaptans	of light CnHm's	Can lead to carbon deposition	Causes problems with sulfur flotation	Causes problems with sulfur flotation
1.6 NH3 and HCN		Special design req'd	Sol'n degradation	Sol'n degradation
1.7 Hydrocarbons		Carbon deposition and catalyst deactivation	Causes foaming	Causes foaming
2.0 SULFUR RECOVERY CAPABILITY				
2.1 H2S	% of feed gas	96 + % conversion	99 + % conversion	99 + % conversion
2.2 COS and CS2	constituents	< 90 % conversion	None converted	None converted
2.3 Mercaptans	converted to S.	None converted	None converted	None converted
3.0 PROCESS EFFICIENCY				
3.1 Energy Consumption	MMBTU/Ton of S.	Index = 0.8	Index = 0.6	Index = 0.6
3.2 Energy Recovery	MMBTU/Ton of S.	May recover heat	No energy recovery	No energy recovery
3.3 Quality of Energy Recovered	Steam required	Low-pressure steam	No energy recovery	No energy recovery
4.0 BYPRODUCT PRODUCTION				
4.1 CO2 Recovery Efficiency		90 + % recovery of CO2	90 + % recovery of CO2	90 + % recovery of CO2
4.2 Vent Gas CO2 Content		Dilution by nitrogen	No dilution	No dilution
4.3 Other Byproducts		No byproducts	No byproducts	No byproducts

TABLE 9-4(Cont'd)

PERFORMANCE OF SULFUR RECOVERY TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	SELECTOX	STRETFORD	UNISULF
5.0 COMPLEXITY OF PROCESS				
5.1 Reactor System, Type	Solid fixed-bed	Index = 0.9	Index = 1.3	Index = 1.2
5.2 Major Process Steps	Reactors, towers	3 major steps	6 major steps	6 major steps
5.3 Internal Recycles		One recycle	Two recycles	Two recycles
5.4 Phase Separations		1 gas/liquid	1 gas/liq, 1 liq/solid	1 gas/liq, 1 liq/solid
6.0 REACTOR DESIGN CONSIDERATIONS				
6.1 Operating Temperature	deg F	700 degF maximum	Ambient	Ambient
6.2 Operating Pressure		Compatible with AGR	Compatible with AGR	Compatible with AGR
6.3 Space Velocity	Gas SCFH/catalyst volume.	Index = 0.9	Index = 0.3	Index = 0.5
6.4 Approach to Equilibrium at Outlet		< 100 degr F	< 100 degr F	< 100 degr F
7.0 CATALYST/REAGENT PROPERTIES				
7.1 Active Constituents	Type	Non-noble	Vanadium complex	Vanadium complex
7.2 Life/Cycle Time		Acceptable	Loss to sulfur cake	Loss to sulfur cake
7.3 Regenerability		Non-regenerable	Continuously regen'd, some degradation	Continuously regen'd
7.4 Safety in Handling		Index = 1.0	Index = 0.8	Index = 0.8
7.5 Spent Catalyst/Reagent Disposition		No treatment	Treatment required	Treatment required
7.6 Storage/Activation Requirements		No special req'ts	Reagent storage & loading system	Reagent storage & loading system
8.0 IMPACT ON SNG PLANT DESIGN				
8.1 Complexity		Index = 0.8	Index = 0.6	Index = 0.5
8.2 Utilities & Reagents		Index = 0.9	Index = 0.7	Index = 0.6
8.3 Flexibility: Coal Types		All types of coal	All types of coal	All types of coal
8.4 Flexibility: AGR Systems		Non-selective	Non-selective	Non-selective
8.5 Flexibility: TGT/FGD		Tail gas unit req'd	Requires incineration	Tail gas ventable
8.6 Design Viability	Extrapolation	No extrapolations	No extrapolations	No extrapolations

TABLE 9-4(Cont'd)

PERFORMANCE OF SULFUR RECOVERY TECHNOLOGIES VS. CRITERIA

CRITERION	EXPLANATION	SELECTOX	STRETFORD	UNISULF
9.0 INTEGRABILITY				
9.1 Acid Gas Pretreatment	Type req'd	COS hydrolysis req'd	COS hydrolysis req'd	COS hydrolysis req'd
9.2 Vent Gas Treatment		Tail gas unit req'd	Incineration required	Tail gas ventable
9.3 Sulfur Quality		Market quality	Poor quality sulfur	Poor quality sulfur
10.0 PROCESS TECHNIQUES				
10.1 Equipment Availability	Extrapolation	No extrapolations expected	Full scale equipment demonstrated	No extrapolations expected
11.0 MATERIALS OF CONSTRUCTION				
11.1 Availability	Std'd Mat'ls	Standard materials	Standard materials	Standard materials
11.2 Corrosion Resistance Required		Index = 1.0	Index = 0.8	Index = 0.8
12.0 CONTROLLABILITY				
12.1 Control System		Index = 0.9	Index = 1.3	Index = 1.3
12.2 Turndown Capability	% of full rate	Wide turndown range	Turndown limited	Turndown limited
12.3 Response to Upset		Very responsive	Acceptable response	Acceptable response
13.0 RELIABILITY				
13.1 Standby Requirements	Spares	No idle spares	Idle spares req'd	Idle spares req'd
13.2 Consequence of Failure	Risk involved	Minimum effect	Minimum effect	Minimum effect
13.3 Maintenance Extent		Index = 0.9	Index = 1.5	Index = 1.5
13.4 Overdesign Requirement	To accomodate variations in feed gas comp	Must add catalyst	Adjust circulation	Adjust circulation
14.0 ENVIRONMENTAL CONSIDERATIONS				
14.1 Solid Effluents	Extra steps	No solid effluents	Poor quality sulfur	Poor quality sulfur
14.2 Liquid Effluents	Extra steps	No liquid effluents	No liquid effluents	No liquid effluents
14.3 Gaseous Effluents	Extra steps	No gaseous effluents	Spent air stream	Spent air stream

FOOTNOTES

CRITERIA	EXPLANATION
3.1	ENERGY CONSUMPTION - In general, the processes using liquid phase oxidation require less energy input than do the fixed-bed (gas-phase) processes.
3.2	ENERGY RECOVERY - The absorption processes typically operate at very low pressure and near ambient temperature, so opportunities for energy recovery are virtually nil. The Claus Process almost always recovers steam.
5.1	REACTOR SYSTEM AND TYPE - Fixed bed systems are simpler than the liquid phase oxidation systems. Stretford process has the complexity of sulfur froth flotation system.
6.3	SPACE VELOCITY - The liquid phase processes generally require larger reactors than do the fixed bed processes.
7.2	LIFE/CYCLE TIME FOR CATALYST - Stretford looses a portion of the absorbent solution in the purge stream and in the sulfur cake.
7.3	REGENERABILITY OF CATALYST - The liquid phase systems feature continual regeneration of the solution. The catalysts of the fixed bed processes cannot be regenerated.
7.4	SAFETY IN HANDLING - The fixed bed systems enjoy inherent safety due to their solid, non-corrosive and non-flammable catalysts. The solutions for Stretford and Unisulf are non-corrosive and non-flammable, while that of LO-CAT is slightly corrosive.
8.1	COMPLEXITY - The Claus process requires both a selective AGR system and a tail gas treatment unit, so is regarded as most complex. The Direct Oxidation and Selectox processes do not require selective AGR or tail gas treating. They do, however, involve added sulfur handling steps.
11.2	CORROSION RESISTANCE REQUIRED - The fixed bed processes do not require any special allowance for corrosion. Sections of the plant for Stretford and Unisulf systems must be plastic-coated to avoid corrosion due to sulfur deposition. The LO-CAT process requires stainless steel construction.

CRITERIA	EXPLANATION
12.1	CONTROL SYSTEMS - All of the processes can be operated with existing control methods. The liquid phase oxidation processes are judged as more difficult to control than solid fixed bed processes. LO-CAT has one less step than Stretford or Unisulf. The Claus process has control problems at the muffle furnace when the acid gas is lean in H_2S.
13.3	MAINTENANCE EXTENT - The liquid phase processes require considerable more maintenance of a routine nature than do the fixed bed processes. The muffle furnace of the Claus process requires maintenance beyond that required in the Direct Oxidation and Selectox processes.

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