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H₂S-Removal Processes for Low-Btu Coal Gas

M. S. Edwards

OAK RIDGE NATIONAL LABORATORY
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H₂S-REMOVAL PROCESSES FOR LOW-BTU COAL GAS

M. S. Edwards

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for the
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PREFACE

This report on H₂S-removal processes for low-Btu gas derived from coal is part of a series of Oak Ridge National Laboratory reports on the evaluation of fossil energy technology. Other reports in this series are as follows:

1. W. C. Ulrich, M. S. Edwards, and R. Salmon, Process Designs and Economic Evaluations for the Linked Vertical Well In Situ Coal Gasification Process, ORNL-5341, to be published.
2. W. C. Ulrich, Evaluation of In Situ Coal Gasification Processes on a Regional Basis, ORNL-5279 (December 1977).
3. R. Salmon et al., Engineering Evaluations of Coal Conversion Processes: Part 1. Hydrocarbonization and Synthoil - Information Base, Process Selection, and Preliminary Evaluation of Alternatives, ORNL/TM-5034 (August 1977).
4. J. M. Holmes et al., Hydrocarbonization Process Evaluation Report: Vol. I - Conceptual Design and Cost Estimate of a Commercial-Scale Facility, ORNL-5212; Vol. II - Evaluation of Process Feasibility, ORNL-5213 (July 1977).
5. R. Salmon, M. S. Edwards, and W. C. Ulrich, Evaluation of the Synthoil Process: Vol. I - Process Design and Economic Evaluation of a 100,000-Barrel/Stream Day Facility, ORNL-5209; Vol. II - Status of Development, ORNL-5210; Vol. III - Unit Block Flow Diagrams for a 100,000-Barrel/Stream Day Facility, ORNL-5211 (June 1977).
6. R. Salmon, PRP - A Discounted Cash Flow Program for Calculating the Production Cost (Product Price) of the Product from a Process Plant, ORNL-5251 (March 1977).

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H₂S-REMOVAL PROCESSES FOR LOW-BTU COAL GAS

M. S. Edwards

ABSTRACT

Process descriptions are provided for seven methods of removing H₂S from a low-Btu coal-derived gas. The processes include MDEA, Benfield, Selexol, Sulfinol, Stretford, MERC Iron Oxide, and Molecular Sieve. Each of these processes was selected as representing a particular category of gas treating (e.g., physical solvent systems). The open literature contains over 50 processes for H₂S removal, of which 35 were briefly characterized in the literature survey. Using a technical evaluation of these 35 processes, 21 were eliminated as unsuitable for the required application. The remaining 14 processes represent six categories of gas treating. A seventh category, low-temperature solid sorption, was subsequently added. The processes were qualitatively compared within their respective categories to select a representative process in each of the seven categories.

1. INTRODUCTION

This report presents the results of a review and evaluation of methods for removing sulfurous compounds, principally H₂S, from coal-derived low-Btu gas streams. Low-Btu gas is generally produced in air-blown gasifiers and has a higher heating value (HHV) in the range 100 to 250 Btu per standard cubic foot. This work has been performed for the Fossil Energy Office of Program Planning and Analysis (OPPA) of the Energy Research and Development Administration (now the Department of Energy). The work reported is one of a number of evaluations at Oak Ridge National Laboratory that are related to the technical and economic aspects of converting coal to clean energy. This effort specifically supports evaluations of converting coal to low-Btu gas for power generation (steam raising, direct-fired heating, and electricity production).

This review and evaluation is based solely on information in the open literature; therefore, it is not possible to include many technical details about most of the processes described in this report. Similarly, it has not been possible to develop consistent designs and cost estimates for each

process. The intent of this report is to provide background material for the understanding of processes for removing H_2S from low-Btu coal-derived gas. The information in this report, by itself, is not sufficient as a basis for selecting an H_2S -removal process, nor is it intended to be.

The principal objectives of this study are:

1. to identify available processes for removing sulfurous gases (principally H_2S) from low-Btu coal-derived gas,
2. to evaluate such processes within specified categories and to determine within each category an appropriate process for further description, and
3. to describe the operation and economics of the selected processes.

The amount of H_2S removal required is a basic assumption in this report. At this time, federal standards do not define the allowable SO_2 emissions from combustion of low-Btu coal-derived gas in power plants; however, standards do exist for power generation by direct combustion of coal.¹

Although the current federal limits specifically refer to the generation of electricity by the direct combustion of coal in large steam plants, low-Btu gasification of coal (followed by combustion, steam production, and electricity generation) operates with the same feed material and yields the same product. These standards, therefore, should give some indication of the maximum allowable levels that might be expected for low-Btu gas. Direct translation of these standards for SO_2 allows about 1000 ppmv H_2S equivalent in 150 Btu/scf fuel gas expected from a typical low-Btu coal gasifier. Figure 1.1 shows the relationship between the H_2S content and higher heating value (HHV) of the fuel gas and the amount of SO_2 emitted per million Btu.

1.1 Reference

1. Title 40 Code of Federal Regulations, Part 60, Sects. 42 to 44, Dec. 23, 1971.

Fig. 1.1. Effect of fuel-gas H_2S content and higher heating value on SO_2 emissions. The dotted line indicates the current federal standard of $1.2 \text{ lb SO}_2 \text{ per } 10^6 \text{ Btu}$ and shows the allowable H_2S content for gases of various heating values at that level of SO_2 emission.

2. SUMMARY

Over 50 processes capable of removing H_2S from gas streams are described in the open literature. The range of treating conditions exhibited by these processes is extreme, including temperatures from below $-70^{\circ}F$ ($-57^{\circ}C$) to above $1500^{\circ}F$ ($815^{\circ}C$) and pressures from vacuum to above 1000 psia (6.9 MPa). As a result of the literature survey reported in Sect. 3, 35 processes have been selected as potentially useful in low-Btu gas treating. A technical evaluation has reduced the number of processes to those 14 deemed most suitable. Subsequently, the processes within each category of H_2S removal (amine systems, physical solvent systems, etc.) have been compared to determine an appropriate representative process for each category. Section 4 describes the methods and criteria used in the selection of the specific processes. The selected processes are described in Sect. 5. The descriptions include much of the available open-literature information and are intended to assist in final selection of the most appropriate gas-cleanup process for specific low-Btu coal-gas applications.

2.1 Evaluation Criteria

Technical evaluation of the 35 processes identified in Sect. 3 has resulted in the elimination of 21 processes. Examples of the criteria used include:

1. Chemical compatibility of treating systems with the selected low-Btu gas to be treated. In the amine systems, for example, primary amines combine with COS and CS_2 in the fuel gas and are not regenerated in the stripper. Because relatively large purge streams would be required to maintain solution activity as a result of these reactions [especially with monoethanolamine (MEA)], primary amines have not been considered further for coal-derived low-Btu gas cleanup. (Some high-temperature reclamation is possible, but this adds to capital and operating costs.)

2. Stability of the treating solutions under normal operating conditions. Solution stability is generally excellent in the systems listed in Sect. 3. Triethanolamine (TEA) has been eliminated, in the literature survey, because of its poor stability, along with low H_2S capacity and reactivity, in comparison with other amines.

3. Degree of solution toxicity. The use of toxic chemicals in treating solutions is a major concern. Processes that use highly toxic solutions or additives such as arsenic or cyanide (e.g., Vetrocoke CO₂, Vetrocoke H₂S, and Fischer) are considered undesirable and have been eliminated from the selection process. (Competing processes exist which do not pose such environmental risks.)

Other criteria considered include desired purity of the fuel gas, selectivity for H₂S over CO₂, pressure and temperature of operation, process complexity, commercial experience, especially on coal-derived gases, and availability of design and/or cost information.

2.2 Final Selection

The 14 processes remaining after the technical evaluation comprise six basic categories. However, there are insufficient data in the literature to assess the applicability of molecular sieves. Consequently, a seventh category, low-temperature solid sorption, has been added.

The procedure described has yielded a total of 15 processes in seven categories (Table 2.1). The remaining processes have been assessed to determine a single representative process within each category (Sect. 4.2). Because this selection procedure is qualitative, the selected processes (Sect. 4.2) should not be considered the most suitable in a particular category for all applications. In several cases, the specific process has been selected because of better data availability, rather than a conclusion of better operability or economic advantage. Often there were not sufficient comparable data on competing processes for such a conclusion to be drawn.

With the foregoing caveats in mind, the processes shown in Table 2.2 have been finally selected as representatives of their respective categories. Descriptions of these processes are presented in Sect. 5. Final selection of the most suitable process for removing H₂S from a low-Btu coal gas will depend on the specific application and will normally require vendor-supplied design and cost information.

Table 2.1. Processes remaining after technical evaluation

Category	Process
Low-temperature chemical absorption using amines	DEA DIPA MDEA
Low-temperature chemical absorption using alkali salts	Alkazid "DIK" Benfield Catacarb
Low-temperature physical solvent absorption	Rectisol Selexol
Low-temperature mixed chemical/ physical absorption	Sulfinol
Low-temperature absorption- oxidation system	Stretford Takahax
High-temperature H ₂ S removal	Battelle Molten Salt Conoco Dolomite MERC iron oxide/fly ash
Low-temperature solid sorption	Molecular sieve

Table 2.2. Processes selected for description

Category	Process
Amine	MDEA
Alkali salt	Benfield
Physical solvent	Selexol
Mixed solvents	Sulfinol
Absorption/oxidation	Stretford
High-temperature	MERC iron oxide
Low-temperature solid sorption	Molecular sieve

3. LITERATURE SURVEY

The initial review of the literature has revealed more than 50 processes and concepts for the removal of H_2S from various gas streams.¹⁻⁵ To aid in the selection of processes deserving further study, the area of fuel gas treating has been divided into several categories: (1) low-temperature absorption with regeneration of H_2S , (2) low-temperature absorption followed by oxidation of H_2S , and (3) high-temperature H_2S removal. Preliminary screening of the available literature has eliminated some possibilities at this point. Low-temperature solid sorption of H_2S (iron sponge, molecular sieve, activated carbon, etc.) is not considered economically competitive with low-temperature liquid absorption, except for final or trace impurity removal.⁶⁻⁸ Low-Btu gas streams do not require extreme purity. Current federal emissions limitations on sulfur from coal (Sect. 1) are much less stringent than the level of <1 ppmv H_2S required to protect methanation catalysts in high-Btu gasification processes. Low-temperature solid sorption, therefore, is not further considered in the literature survey. [Some questions regarding the range of application of molecular sieves remain in the technical literature. Accurately assessing any possible economic and technical advantages of molecular sieves versus low-temperature liquid systems is outside the scope of this survey, but Union Carbide Corporation, Linde Division has provided a brief economic evaluation to tentatively define the limits of applicability for molecular sieves on low-Btu gas (Sect. 5.6).]

A multitude of solvents can be used to perform low-temperature liquid absorption of H_2S (and CO_2 in most cases). Preliminary screening has deleted several systems from further study. Nonregenerative caustic scrubbing (e.g., NaOH solution) is used only for final or trace impurity removal and has been excluded because the chemical usage and operating expense is extreme when compared to regenerative systems. Ammonia solution scrubbing (used in coke-oven gas treating at low pressures) has been excluded because reported H_2S removal efficiency is low ($<90\%$) and the release of compounds other than ammonium sulfate as an end product is very costly in steam and chemical consumption.⁹ The more desirable regeneration components (anhydrous ammonia and hydrogen sulfide) can

be produced but only with more elaborate and expensive treatment. The use of water alone to remove gas impurities has also been excluded. Aqueous additives greatly increase the efficiency of gas scrubbing and have supplanted the commercial applications of water washing.¹⁰

3.1 Literature Survey Results

Solvents for low-temperature absorption, with regeneration of H_2S , can be divided into three commercial categories: (1) chemical absorption with amines, (2) chemical absorption with alkali salts, and (3) physical solvent sorption. A fourth category consists of commercialized combinations of physical and chemical solvents. In these categories, the selection has been restricted to processes that have been commercialized or at least demonstrated on a pilot scale by a commercial interest. These categories cover the vast majority of commercial processes for treating natural gas, refinery gas, and coal-derived gas. A general schematic of these processes is shown in Fig. 3.1. Table 3.1 lists the applicable amine systems. Table 3.2 lists alkali salt systems for H_2S removal; one exception is the Giammarco Vetrocoke CO_2 process that is designed to remove only CO_2 after the companion process (Vetrocoke H_2S) has removed H_2S . The remaining category, physical absorption, is displayed in Table 3.3. The last two processes listed in Table 3.3 (Sulfinol and Amisol) are actually combinations of physical and chemical (amine) solvents.

Low-temperature absorption of H_2S , followed by oxidation to sulfur or SO_2 , offers more than 25 candidates. These have been screened according to two criteria: (1) exclusion of processes specifically directed to cleanup of sulfur plant tail gas, and (2) desirability of high purity sulfur as the end product. The number of representative processes has thereby been reduced to five (Table 3.4). A general schematic of these processes is shown in Fig. 3.2.

High-temperature H_2S removal processes are still in the developmental or conceptual stage for applications above $800^\circ F$ ($425^\circ C$). Although some pilot- and commercial-scale tests have been performed below this temperature, expensive heat recovery systems are required to enhance efficiency, and tar/oil condensation presents plugging and wastewater treatment problems.

Fig. 3.1. General schematic diagram typical of amines, alkali salts, and physical absorption processes.

Table 3.1. Low-temperature chemical absorption — Amines

Principal absorbent	Process name	Typical absorber temperature (°F)	Absorber pressure (psi)	Reboiler steam (lb/gal solution)	Components removed			H ₂ S/CO ₂ selectivity	Relative solvent cost and process complexity	Commercial status	Notes
					H ₂ S	Organic sulfur	CO ₂				
MEA	Sulfiban monoethanolamine	80-110	Atm — 1000; not highly sensitive	0.8-1.5; nominally 1.0-1.2 lb/gal	Yes, down to 1 ppm level	COS, CS ₂ , modicum mercaptan	Yes, down to ppm level	Not selective	Low-cost solvent, medium complexity	Commercial — used on N.G. and refinery gases (excluding COS)	Redistillation unit required at 250 to 300°F to limit losses; COS and CS ₂ react irreversibly; highly reactive, high vapor pressure; heat exchange normally required; corrosion and foaming can occur.
DEA	Diethanolamine	100-130	Atm — 1000; not highly sensitive	Similar to MEA	Yes, down to 4 ppmv	COS, CS ₂ absorbed reversibly (some mercaptans)	Yes, down to ppm level	Not selective	Slightly higher solvent cost than MEA but less complex	Commercial — used on gases which contain COS	Minor solvent degradation — treated by carbon adsorption and/or filtra- tion; higher absorber temperature requires less heat exchange; corrosion less than in MEA; foaming can occur; low solvent vaporization losses.
DEA	Societe National des Petrols d'Aquitaine SNPA-DEA	90-120	500-1100; high acid- gas pressure desirable (<50 psi)	0.9-1.1	Yes, down to 4 ppmv	Some COS removed	Yes, <1%	Not selective	High-pressure absorption may require inter- mediate flashing	Commercial — developed for high- pressure natural gas treatment	Process operates at high DEA concen- tration (~30 wt % vs normal 10 to 25%), yielding lower solution circulation rates, lower utility consumption, higher corrosion.
MDEA	Methyldiethanolamine	80-120	Not highly pressure sensitive	Somewhat lower than MEA/DEA	Yes, down to 4 ppmv (but not selectively)	Mercaptans not removed	Yes, normally 25-75% removal	Partially selective	Much higher solvent cost than MEA	Commercial — limited applica- tions to date	Partial selectivity decreases as degree of H ₂ S removal increases; corrosion and foaming occur; redistillation required; lower circulation and steam rates than MEA/DEA.
DIPA	Shell ADIP di-isopropanolamine	90-130	Not highly sensitive	0.7-0.8	Yes, <10 ppmv	Partial removal of COS (some mercaptans)	Yes, normally 30-90% removal	Partially selective	Much higher solvent cost than MEA	Commercial — used for refinery gases which include COS	Lower steam consumption than MEA/DEA; noncorrosive operation; typically treats refinery gases with H ₂ S/CO ₂ ratios of 10:1 to H ₂ S levels <100 ppmv; no redistillation required.
DGA	Fluor Econamine diglycolamine	90-130	Not highly sensitive	~1.5	Yes, <4 ppmv	COS, CS ₂ degrades solution	Yes, below that normally provided by MEA	Not selective	Higher solvent cost than DIPA, as complex as MEA	Commercial	Solution concentration of 65 wt % DGA or higher reduces circulation rate (up to 40% less than MEA), thus reducing equipment sizes and utilities; corrosion can occur; redistillation required (370°F) to regenerate degradation compounds.

Table 3.2. Low-temperature chemical absorption - alkali salts

Principal absorbent	Process name	Typical absorber temperature (°F)	Absorber pressure (psi)	Reboiler steam (lb/gal)	Components removed			H ₂ S/CO ₂ selectivity	Relative solvent cost and process complexity	Commercial status	Notes
					H ₂ S	Organic sulfur	CO ₂				
Na ₂ CO ₃	Seaboard sodium carbonate	Ambient	Low	No	Yes, 85-95% removal	Unknown	Yes	Partially selective	Low-cost solvent; simple operation	First commercial regenerative process on coke oven gases (now obsolete)	Air regeneration precludes economic sulfur recovery; high circulation rates; HCN degrades solution.
Na ₂ CO ₃	Vacuum carbonate sodium carbonate	Ambient	Low	Below 0.6	Yes, nominal 90%	Unknown	Yes, nominal 10%	Partially selective	Low-cost solvent; simple operation	Outgrowth of Seaboard - used for coke oven gas (now obsolete)	Vacuum distillation reduces steam consumption to 1/6 that at atmospheric pressure; typical coke-oven gas impurities (e.g., HCN) can be handled; nominal +90% HCN removed; very high H ₂ S removal increases CO ₂ removal.
K ₂ CO ₃	Hot Pot potassium carbonate	Amb-240	100-1000	~0.5	Yes, to 4 ppmv (CO ₂ must be present also)	COS hydrolyzed to CO ₂ + H ₂ S and removed	Yes, to 1.5% - single stage, <0.8% - two stage	Can be selective	Low-cost solvent; simple operation for bulk CO ₂	Commercial for CO ₂ /CO ₂ + H ₂ S high-pressure bulk removal	Developed for bulk CO ₂ removal at relatively high CO ₂ partial pressures; no rich/lean solution heat exchange required; staging and cooling required for high purity; corrosion occurs.
K ₂ CO ₃	Benfield and HiPure potassium carbonate plus amine additives, and other activators	Amb-280; nominally 230	100-2000	<0.3 up to 1.0, highly process dependent	Yes, to 4 ppmv Benfield, <1 ppm HiPure	Can remove 100% COS, 75% CS ₂ , 70-80% mercaptans	Yes, to 500 ppmv Benfield, <50 ppmv HiPure	Selectivity increases complexity and/or residual impurities	Staged operation and cooling for high purity	Commercial high acid-gas pressure; bulk removal favored	Complex operation (split stream, two-stage, etc.) required for high-purity product; corrosion occurs; HiPure is two-stage with two separate solution circuits.
K ₂ CO ₃	Catacarb potassium carbonate plus amine and other activators	Amb-280; nominal bulk temp 230	Nominally 100-1000	<0.3 up to 1.0, process dependent	Yes, <4 ppmv	COS, CS ₂	Yes, <0.05%	Selectivity increases complexity and/or residual impurities	Staged operation and cooling for high purity	Commercial high acid-gas pressure; bulk removal favored	Corrosion reduced; solution capacity increased by additives; two stages and cooling required for high-purity product; selectivity typically reduces H ₂ S removal ability.
K ₂ CO ₃	Ciammarco Vetrocoke CO ₂ potassium carbonate plus arsenic trioxide (AsO ₃)	120-220	200-1000	Below 0.5	Removed in Vetrocoke H ₂ S process (Table 3.4)	Minor amounts only	Yes, to 0.05%	Designed for CO ₂ removal after H ₂ S is removed	Simple operation	Commercial - used to remove CO ₂ after separate H ₂ S removal	Nonvolatile solution; corrosion inhibited by additive; air can be used to strip rich solution; arsenite solution is toxic.
K ₃ PO ₄	Tripotassium phosphate	90-150	Atm-1000; nominally at 400	1.0	Yes, typically <400 ppmv	Nonreactive with COS	Yes	Partially selective	High complexity required for high-purity product	Displaced by amine systems	Absorbent is nonvolatile, insoluble in hydrocarbons, nonreactive with COS; can be more economic than MEA where CO ₂ /H ₂ S ratio >4:1 because of selectivity; high degree of H ₂ S removal not demonstrated.
K + weak organic acid	Alkazid "M" potassium salt of methyl-amino-propionic acid	70-100	Atm-1000	0.1-0.2	Yes, to 5 ppmv	Unknown	Yes	Not selective	As complex as amine systems	Commercial overseas	Very low solvent vapor pressure; low pressure absorption yields residual H ₂ S >50 ppmv; very low steam consumption; reported noncorrosive.
K + weak organic acid	Alkazid DIK potassium salt of dimethylaminoacetic acid	70-100	Atm-1000	0.1-0.2	Yes, to 5 ppmv (but non-selective)	No	Yes	Less selective than K ₃ PO ₄ (tripotassium phosphate)	As complex as amine systems	Commercial overseas	Some degradation by HCN; very low solvent vapor pressure; high selectivity and/or low pressure yield residual H ₂ S >50 ppmv; more selective for H ₂ S than MDEA; low steam consumption.
NaOH + phenol	Alkazid "S"	a	a	a	Yes	No	Yes	Not selective	a	Not commercial	Developed for gases containing many impurities (e.g., NH ₃ , HCN, CS ₂ , etc.); not commercialized.
NaOH + phenol	Sodium phenolate	a	a	High	Yes, ~90%	a	Yes	Partially selective	a	Obsolete (displaced by other processes)	Corrosion occurs; high H ₂ S capacity; high steam consumption.

^a Limited or no commercial data.

Table 3.3. Low-temperature physical absorption

Principal absorbent	Process name	Typical absorber temperature (°F)	Absorber pressure (psi)	Regeneration heat	Components removed			H ₂ S/CO ₂ selectivity	Relative solvent cost and process complexity	Commercial status	Notes
					H ₂ S	Organic sulfur	CO ₂				
Physical Absorption											
MeOH	Lurgi Rectisol methanol	Down to -100, normally -40 to -70	300-2000	Very low	Yes, down to 0.02 ppmv	Yes, COS <0.1 ppmv	Yes, down to 1 ppmv, normally to 0.1%	Can be selective in staged operation	Low solvent cost but extremely complex process	Commercial — on coal and oil gasification processes	High solvent vaporization losses; requires external cooling; absorbs heavy hydrocarbons, oils, water; no corrosion; requires N ₂ for CO ₂ stripper; yields rich H ₂ S Claus feed.
NMP	Lurgi Purisol N-methyl--2-pyrrolidone	80-105	~1000	Minor amount for solvent drying	Yes, <4 ppmv attainable	Yes, but process not designed for such	Yes, <0.1%	More selective than MeOH	Selectivity or high purity require high complexity	Commercial — high acid-gas pressure, bulk removal favored	Low solvent vapor losses; yields H ₂ S-rich off-gas; noncorrosive, nonfoaming, absorbs heavy hydrocarbons, water; requires N ₂ or air for residual CO ₂ stripping.
DMPEG	Allied Chemical Selexol dimethylether polyethylene glycol	20-100	300-1000	Very low	Yes, <1 ppmv	Yes, <1 ppmv	Yes, normally to 1%	Can be selective, with stages and recycle	High solvent cost, moderate complexity for bulk removal	Commercial — designed for high acid-gas pressures, bulk removal	Noncorrosive, nonfoaming, low solvent vapor losses; absorbs heavy hydrocarbons, water, NH ₃ , HCN; uses air for final stripping; multistage flashing required to minimize fuel losses, maximize selectivity.
PC	Fluor Solvent propylene carbonate	20-80	400-2000	Very low	Yes, <4 ppmv	Yes	Yes, <1%	Can be selective (multistage)	Flash regeneration when only bulk removal required	Commercial — designed for high acid-gas pressures, bulk removal	Stable, noncorrosive, low solvent vapor losses; absorbs heavy hydrocarbons, water; becomes more complex for high purity product; external refrigeration may be needed.
MCA	Union Oil Solvent methylcyanoacetate	20-60	500-1000	Very low	Yes, <4 ppmv	Yes	Yes, <0.1%	Can be selective	High solvent cost	Pilot plant	More effective than PC for acid gas removal while minimizing hydrocarbon losses; steam stripping may be required for high purity; higher vapor losses expected.
TBP	Estasolvan tri-n-butyl phosphate	Ambient	~1000	Low	Yes, <4 ppmv	Yes, COS <4 ppmv RSH <25 ppmv	Yes, but normally minimized	Designed for selective operation	High complexity to minimize hydrocarbon losses	Pilot plant testing overseas, for natural gas plants	Multistage flashing required to minimize hydrocarbon losses; no vapor pressure losses, low viscosity, nonfoaming; high quality Claus plant feed.
Physical/Chemical Absorption											
Sulfolane	Shell Sulfinol tetrahydrothiophene dioxide plus di-isopropanolamine	110	Atm-1000; higher pressures favored	0.5-1.0 lb/gal	Yes, <4 ppmv	COS, mercaptans, total sulfur <16 ppmv	Yes, 50 ppmv possible, normal 0.3%	Not very selective	High solvent cost, high complexity	Commercial — high acid-gas pressure favored	Physical/chemical absorption; high solubility of hydrocarbons requires intermediate flash; very stable solution, low corrosion; high acid-gas loading yields lower circulating rates than MEA.
MEOH + MEA or DEA	Lurgi Amisol methanol plus monoethanolamine or diethanolamine	95	Higher pressures favored (440 psia operation reported)	Low	Yes, 0.1 ppmv	Yes, COS to 0.1 ppmv	Yes, below 5 ppmv possible	Not operated selectively	Low solvent cost, less complex than Rectisol	Commercial — for gas from partial oxidation of oil	High solubility for hydrocarbons; low corrosion; loss of CO, H ₂ about 0.2 to 0.35% unless staged flashing and recycle used.

Table 3.4. Low-temperature absorption — oxidation^a

Absorbent and reactants	Process name	Typical absorber temperature (°F)	Absorber pressure (psi)	Components removed			H ₂ S/CO ₂ selectivity	Commercial status	Notes
				H ₂ S	Organic sulfur	Others			
Na ₂ CO ₃ + ADA	Stretford ADA/Vanadate sodium carbonate plus anthraquinone disulfonic acid and sodium vanadate	70-110	Atm-300	Yes, <1 ppmv	Light mercaptan removed but COS/CS ₂ not affected	HCN — essentially complete removal	Completely selective but CO ₂ decreases absorber efficiency	Commercial — designed for H ₂ S removal from coal gas	Maximum sulfur removal rate commercialized below 100 TPD; design data to 1000 psi operation; solution degraded by HCN; product sulfur >99% pure; waste blowdown must be treated; control of pH required.
Na ₂ CO ₃ + NSA	Takahax sodium carbonate plus naphthoquinone sulfonic acid	Ambient	Atmospheric	Yes	Unknown	HCN	Selective	Commercial — designed for H ₂ S removal from coke-oven gas	Compared to Stretford: lower residence time required for reactions; sulfur product requires filtration instead of flotation; noncorrosive solution; purge liquid contains no metal contaminants.
Na ₂ CO ₃ + Fe(OH) ₃	Burkheiser sodium carbonate plus iron oxide suspension	Ambient	Atmospheric	Yes	Unknown	HCN	Selective	Commercialized — becoming obsolete	Impurities recycled to gasifier; only end products sulfur and ammonia; complex flowsheet required.
Na ₂ CO ₃ + AsO ₃	Giammarco — Vetrocoke H ₂ S sodium (or potassium) carbonate plus arsenic trioxide	Amb-300	Atmospheric	Yes, <0.5 ppmv	Unknown	HCN	Selective	Commercial	Noncorrosive, long residence time for conversions; sulfur product contains arsenic without additional treatment; CO ₂ stream required for pH control; arsenic highly toxic.
K ₄ Fe(CN) ₆ + KHCO ₃	Fischer alkaline aqueous solution of potassium ferri/ferro cyanide	Ambient	Atmospheric	Yes	Unknown	HCN, also used as a reactant	Selective	Commercialized — becoming obsolete	Solution regenerated by electrolysis; good quality sulfur product; toxic cyanic compounds used; rapid reaction rates.

^aProcesses directed specifically to sulfur plant tail-gas cleanup are excluded. Ability to produce high-quality sulfur deemed necessary. Only currently available commercial processes are listed, although other possible processes have been reviewed.

Fig. 3.2. General schematic diagram typical of absorption-oxidation processes.

Four examples of the more advanced concepts for high-temperature H_2S removal are included in Table 3.5, along with an example of a commercialized process designed to operate at somewhat lower temperature.

Tables 3.1 through 3.5 contain most of the information on which the selections of high- and low-temperature candidate processes are based.

3.2 General Descriptions of Gas Cleanup Processes

Brief generic descriptions of the six basic process categories (Tables 3.1 through 3.5) point out some of the technical considerations used in the selection of candidates. Of major concern is the identification of technical points which permit some processes to be retained for further investigation.

3.2.1 Amine systems

Amine gas treating systems have been available in the commercial market for over 40 years. The current major use of amines, principally monoethanolamine (MEA) and diethanolamine (DEA), is for natural gas--acid gas removal.

Primary amines have one carbon group attached to nitrogen:^{1,2}

Secondary amines contain two carbon groups attached to nitrogen:

Table 3.5. High-temperature H₂S absorption/adsorption

Reactant	Process name	Operating temperature (°F)	Operating pressure (psi)	Components removed			Commercial status	Notes
				H ₂ S	Organic sulfur	Others		
CaCO ₃	Battelle Molten Salt solution of calcium carbonate in eutectic melt of alkali metal salts or carbonates	1200-1700	Atmospheric	Yes, 95% removal	Possibly COS	Particulates scrubbed out	Laboratory tests	Can contribute to alkali metal carryover in product gas; continuous operation not demonstrated; corrosive system; NH ₃ not expected to be removed.
Fe ₂ O ₃ + fly ash	Morgantown Energy Research Center fly ash--iron oxide sorbent (U. of Ky. -- coal ash only)	1000-1500, to 1700 with silica--iron-oxide sorbent	Atmospheric	Yes, 90-95% removal typical	COS	a	Pilot studies	Air regeneration of sorbent yields dilute SO ₂ off-gas; regeneration is highly exothermic; tars do not foul sorbent (above 1000°F); attrition will occur in moving-bed system.
Molten metal	IGT Meissner Process	900		Yes, >98% removal	COS	a	Laboratory tests	Proprietary; electrolytic regeneration proposed.
MgO · CaCO ₃	Dolomite acceptor (Conoco, CCNY)	1500-1700	200-250 typical	Yes, >95% removal possible	COS	Some CO ₂	Laboratory tests	Half-calcined dolomite required; steam and CO ₂ required for regeneration; attrition will occur; alkali release from dolomite can occur; heating and cooling cycles required.
FeO	Appleby-Frodingham hot ferric oxide	600-750	Normally low	Yes, 98% removal by two stages, >99% in four stages	COS	a	Commercialized for coke oven gas (obsolete)	Sulfur recovered as sulfuric acid; good heat recovery, low labor costs; massive attrition, plugging and erosion of piping; regeneration temperature (up to 1500°F) requires heat input.

^aNot available.

diisopropanolamine (DIPA).

Tertiary amines have three carbon groups attached to nitrogen:

triethanolamine (TEA),

methyldiethanolamine (MDEA).

Amine systems operate via chemical combination with acid gases (H_2S , CO_2 , COS , etc.) in an absorber, followed by cleavage of the chemical bond in a separate regenerator (generally by thermal action provided in a reboiler or by direct steam stripping). The primary amine, MEA, forms compounds with COS and CS_2 which do not thermally decompose. DGA also forms refractory compounds with COS and CS_2 which are not recovered in the regenerator, although some reclamation can be achieved with high-temperature techniques.^{11,12} Selectivity of amines for the removal of H_2S over CO_2 increases with the addition of carbon groups to the nitrogen atom; primary amines are the least selective, and tertiary amines are the

most selective. Amine reactivity with H_2S decreases with the increase in the number of carbon chains attached to the nitrogen.

3.2.2 Alkali salt systems

The commercial application of alkali salt solutions for the removal of acid gases predates amine systems by several decades. Salts proposed for acid-gas removal include sodium and potassium carbonate, phosphate, phenolate and borate, as well as potassium salts of weak organic acids (e.g., Alkazid "M" process).¹³ However, the commercial importance of alkali salt systems has generally been associated with the bulk removal of CO_2 by carbonate solutions. Recent improvements through additions of activators to carbonate systems (e.g., Catacarb, Benfield, etc.) have significantly extended the range of economic applicability of alkali salt processes. Such modern carbonate systems are generally operated at higher acid-gas partial pressures and absorber temperatures (above 200°F), and they require less regeneration heat than conventional amine systems. The carbonate also hydrolyzes COS to a significant extent. Although technically capable of treating gases to very low residual acid-gas levels, modern carbonate systems require additional cooling and heating, as well as staged operations.

3.2.3 Physical absorption systems

Physical absorbents remove gases according to gas solubility in the absorbent; therefore, physical absorption processes are sensitive to operating temperature and pressure (typically operating at subambient temperature and high acid-gas partial pressure). When bulk removal and/or selectivity for H_2S are desired in a high-pressure system, physical absorption can offer substantial savings over chemical systems, in heat and power consumption. Although H_2S , CO_2 , and minor components (e.g., HCN, CS_2 , etc.) are more soluble than fuel gases (e.g., H_2 , CO, and CH_4), physical solvents do absorb hydrocarbons, especially the heavier species and aromatics. Unless a complex regeneration scheme is used (e.g., multistage flashing and recycle streams), hydrocarbon losses can be excessive. If present in the regenerated, rich- H_2S stream and if fed to a Claus sulfur recovery plant, hydrocarbons and trace impurities lead

to operational difficulties and/or increased capital expense.¹⁴ If high purity is not required in the treated gas, physical absorption systems operating at high pressure can be regenerated with simple pressure flashing.

3.2.4 Mixed solvent systems

Two systems which offer a combination of physical and chemical absorbents have been publicized.¹⁵ The Shell Sulfinol process (Table 3.3) combines a physical solvent sulfolane with the secondary amine, DIPA. The Amisol process, recently announced by Lurgi, uses a mixture of methanol and either DEA or MEA. The Amisol process has only recently been operated commercially, and limited data are available.

Combining physical and chemical solvents increases the flexibility of treating conditions. Because of the added chemical solvent, Sulfinol can treat lower-pressure streams to higher purities than can a pure physical solvent. Conversely, Sulfinol can absorb more acid gas per gallon of solvent (i.e., higher acid-gas loading) at high pressure than can a pure amine system because of the presence of the physical solvent. This dual nature is also apparent in the disadvantages; Sulfinol requires higher utility consumption than a pure physical solvent and results in higher hydrocarbon losses than a pure amine system.

3.2.5 Absorption-oxidation systems

The processes delineated in Tables 3.1 through 3.3 all produce a regeneration stream of acid gas requiring further treatment to convert H_2S to sulfur. Table 3.4 lists processes which convert the H_2S to sulfur while in solution. These processes can combine H_2S removal from fuel gases with direct sulfur recovery, thereby avoiding the requirement for additional acid-gas processing. Typical operating conditions are ambient temperature and atmospheric pressure, although higher pressure absorption is feasible. Air oxidation is generally used to regenerate the solution and release sulfur. Low rates of sulfur production per train are currently the rule; for example, the maximum single-train size reported in the United States for the Stretford process is approximately 30 tons of sulfur per day. By comparison, high-temperature Claus plants for recovering

sulfur from H_2S can have single-train capacities above 500 tons of sulfur per day. The low-temperature absorption/oxidation processes are completely selective for H_2S over CO_2 ; they also typically react with other minor impurities, such as HCN . Very low levels of H_2S (<1 ppmv) are achievable if necessary, but COS is not affected by these processes.

3.2.6 High-temperature systems

Several processes are also under development to remove H_2S from fuel gases at high temperatures. This would avoid the thermal penalty of cooling the fuel gas before introduction into a low-temperature gas cleanup process. The following processes (Table 3.5) represent the major areas of current interest and development in hot-gas cleanup: iron oxide sorption, solid dolomite reactants, and molten salt (or metal) systems. The Appleby-Frodingham fluidized iron oxide system (Table 3.5) has been commercialized at a temperature somewhat lower than that which is desired by current hot-gas system developers.

Iron oxide sorption has been tested extensively and successfully. A major problem with this process is the regeneration off-gas, where air regeneration yields a dilute SO_2 stream. Because sulfur is presumably to be recovered in solid form, costly treating of the off-gas would be required. Sulfuric acid production would be a less expensive conversion option, but it is highly dependent on local market conditions, and long-term acid storage would be prohibitively expensive.

Calcined and half-calcined dolomites provide two major advantages over iron oxide: (1) regeneration (with steam and CO_2) releases H_2S which is easier to convert to solid sulfur than SO_2 , and (2) the recommended operating temperature is higher. Problems identified with the dolomite systems include: (1) particle attrition in fluidized systems, (2) decline of sorption capacity with cycling, (3) low H_2S content in the off-gas, and (4) the need for steam and CO_2 for regeneration. Limestone has also been investigated (by Air Products and Chemicals, Inc.) but is not recommended for high-temperature H_2S removal from fuel gases because of poor limestone regenerability, rapid coke deposition, and high energy consumption.

The molten salt process, as envisioned by Battelle's Pacific Northwest Laboratories, has the advantage of removing particulates, as well as H_2S . The best method of removing the particulates from the molten salt is still undetermined. Regeneration of the solution with CO_2 releases H_2S ; however, the pilot plant has not yet been operated in continuous absorption-regeneration cycles. Materials of construction suitable for operation above $1400^\circ F$ have not been identified.

3.3 Examination of Potential Low-Btu Fuel Gas Compositions and Conditions

A range of gas compositions and conditions are found in the literature. Representative gas compositions from a number of fluid- and entrained-bed, air-blown gasifiers are listed in Table 3.6.

It is useful for further screening to develop a representative example of the product gas to which some of the previously discussed gas cleanup processes may be applied. An example composition suitable for use in evaluating high- and low-temperature gas cleaning has been developed from the data in Table 3.6, along with likely values for the gasifier exit gas temperature and pressure. This example product-gas stream is given in Table 3.7. Although hypothetical, the example product gas reflects what could easily be produced in many air-blown gasifiers, given the heterogeneity of feed coals and processing conditions.

Other contaminants not specified in Table 3.7 are expected to be present (e.g., alkali metals, HCN , CS_2 , and particulates). A recent report by Westinghouse, for example, projected amounts of some of these for a U-Gas gasifier, assuming Illinois No. 6 feed coal:¹⁶

<u>Compound</u>	<u>Possible Level</u>
HCl	110 ppm
KCl	2.1-21 ppm
NaCl	0.8-8.0 ppm
Particulates (at gasifier exit)	$>4000 \text{ lb}/10^6 \text{ scf}$
Particulates remaining (after 2 stages of cyclone)	$(\sim 50 \text{ lb}/10^6 \text{ scf})$

Table 3.6. Representative gas composition (mole %): fluid- and entrained-bed, air-blown gasifiers

Component	Entrained-bed			Fluidized-bed					
	Babcock and Wilcox	Combustion Engineering	Foster- Wheeler	Bituminous Coal Research		PERC Synthane	IGT U-Gas		
	(Ref. a)	(Ref. a)	(Ref. a)	(Ref. a)	(Ref. b)	(Ref. a)	(Ref. a)	(Ref. c)	(Ref. d)
CO	23.3	22.1	29.3	25.7	16.7	10.1	19.6	21.8	20
CO ₂	4.6	7.0	3.3	5.2	8.8	17.9	9.9	6.0	10
H ₂	8.4	17.0	14.5	23.4	12.0	21.5	17.5	13.9	14
H ₂ S	0.2	0.6	0.7	0.2	0.5	0.7	0.7	0.7	NR
COS	NR ^e	NR	NR	NR	0.1	NR	NR	0.03	NR
N ₂	63.5	53.3	48.7	45.5	47.7	43.5	48.9	49.1	51
CH ₄	NR	0.03	3.5	NR	3.1	5.6	3.4	3.0	5
NH ₃	NR	NR	NR	NR	0.4	NR	NR	0.02	NR
H ₂ O	Dry basis	Dry	Dry	Dry	10.7	Dry	Dry	5.5	Dry
Coal	Pittsburgh No. 8	Kentucky Bituminous	Illinois No. 6	Eastern	Illinois No. 6	Illinois No. 6	Bituminous	Illinois	NR
T _{exit}	1800°F	1600°F	<1800°F	<1200°F	1800°F	1400°F	>1550°F	1730°F	NR
P _{exit}	0-300 psig	Atmospheric	350 psig	<235 psig	500 psia	1000 psia	50-350 psig	350 psig	300 psia

^a Handbook of Gasifiers and Gas Treating Systems, FE-1772-11, Dravo Corp. for the Energy Research and Development Admin., Washington, D.C., February 1976.

^b F. L. Robson and A. J. Giramonti, "The Environmental Impact of Coal-Based Advanced Power Generating Systems," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, May 1974, St. Louis, Missouri, PB 238 304, October 1974.

^c J. G. Patel, K. B. Burnham, and J. W. Loeding, "The IGT Low-Btu Process - Design and Economics," presented at the Symposium on Comparative Economics for Synfuels Processing, ACS Centennial Meeting, New York, Apr. 4-6, 1976.

^d Bcoz-Allen & Hamilton, Inc., Evaluation of Techniques to Remove and Recover Sulfur Present in Fuel Gases Produced in Heavy Fossil Fuel Conversion Plants, 9075-015, for the Environmental Protection Agency, Washington, D.C., January 1975.

^e Not reported.

Table 3.7. Example product gas^{a,b}

Component	Concentration (mole %)
CO	20.00
CO ₂	8.00
H ₂	13.95
H ₂ S	0.70
COS	0.05
N ₂	48.00
CH ₄	3.00
NH ₃	0.30
H ₂ O	<u>6.00</u>
	100.00

^aReflects a hypothetical fluid- or entrained-bed, air-blown gasifier.

^bParameters used: coal, Illinois No. 6; T_{exit} , 1700°F; P_{exit} , 250 psia; heating value (HHV), 150 Btu/scf.

Workers at the Pittsburgh Energy Research Center have measured several other compounds that are present in small concentrations:¹⁷

<u>Compound</u>	<u>Level</u>
CS ₂	10 ppm
HCN	20 ppb
C ₄ H ₄ S	31 ppm
CH ₃ SH	60 ppm

Many other minor and trace compounds were detected in the gas produced from Illinois No. 6 coal in a fluidized-bed gasifier.

Fluidized-bed gasification produces some light oils, whereas entrained-bed systems are generally considered to minimize such production. In either case, condensable tar production is considered to be negligible because of high gasification temperatures. Minimizing tar production is, in fact, a perceived advantage of entrained- and fluidized-bed gasifiers over fixed-bed gasifiers. The nominal heating value of the product gas (Table 3.7) is about 150 Btu/scf (HHV). The sulfur content of the low-Btu gas will have a significant impact on the economics of gas treating, but variations in sulfur content do not appear to substantially change the decisions concerning the selections of low- and high-temperature gas cleanup processes (Sect. 4).

3.4 References

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4. GAS CLEANUP PROCESS SELECTION

The task of selecting the proper process for gas purification in a specific application has been divided into several stages or levels of effort. The first level is described in the literature search (Sect. 3); this preliminary screening has reduced consideration to 35 possibilities, out of more than 50 originally reviewed. The next level of screening has deleted processes deemed unsuitable because of technical or environmental constraints. Some examples of this level of screening are presented in the summary of results (Sect. 2). A more detailed treatment is presented later in this section, indicating the processes removed from further consideration and furnishing the criteria used for their elimination. This second level of review has reduced the gas cleanup possibilities to 14. The third level of screening has compared the remaining 14 processes to determine which process in a particular category (e.g., physical absorption) is best suited for the desired application, both technically and economically. This stage has reduced consideration to six processes, one in each category. Given specific gasifier data and operating specifications, one of these remaining processes could be selected, on the basis of preliminary costing, as the most suitable cleanup system. Complete capital and operating costs must then be estimated for the selected system. This fourth stage is outside the scope of this report on gas cleanup processes; however, the descriptions of specific processes in Sect. 5 provide considerable open literature design and cost information which should assist in final process selection, given a specific low-Btu coal gas application.

4.1 Technical Evaluation

Of the 35 processes identified in Tables 3.1 through 3.5, 21 processes have been removed from further consideration for a variety of technical or environmental reasons. Availability of information in the open literature is also a concern. Table 4.1 lists the criteria used in this procedure. In cases where justification for one of these points is not obvious, the rationale is further discussed in this section, as appropriate. Three

Table 4.1. Rating criteria for gas cleanup processes

Priority	Rating criteria
High	<p>Capability of removing H_2S to below 100 ppmv</p> <p>Regeneration of either salable sulfur directly or suitable Claus plant feed (minimum 10 mole % H_2S, over 20 mole % desired)</p> <p>Previous commercial application, especially on same or similar gas streams</p> <p>No irreversible reactions (or very minor) with expected gas constituents such as COS, CS_2, HCN</p> <p>Availability of sufficient data for economic evaluation</p>
Medium	<p>Selectivity for H_2S over CO_2 and hydrocarbons</p> <p>Minimum heat exchange</p> <p>Minimum toxicity of process solution</p>
Low	<p>Removal of COS, CS_2, and organic sulfur compounds</p> <p>Proven operation at low to medium pressures (up to 500 psia) and/or low acid-gas partial pressures (below 20 psi)</p> <p>Minimum utility requirements, especially of high-temperature, high-quality steam and electricity</p> <p>Minimum process complexity</p>

general classes of criteria are used; the most important or highest priority criteria must be satisfied for successful process operation. Next in importance are those criteria with significant economic or environmental impacts on a process. Of low priority are those points which offer qualitative advantages that, although not crucial, do allow more efficient operation or lower costs. When two processes rate approximately equal with regard to the other criteria, the low-priority criteria aid in the final selection of a candidate process. The goal of minimizing overall cost of gas treating is implicit in the criteria listed.

4.1.1 Amine systems

Starting with chemical absorption systems which regenerate H_2S , several amine solvents can be disqualified. Primary amines (MEA and DGA) degenerate irreversibly when reacted with COS and CS_2 present in the low-Btu fuel gas. (Some reclamation of DGA is possible, but this requires high-temperature distillation.^{1,2}) A lack of selectivity for H_2S over CO_2 adds to the mismatch of the primary amines to low-Btu fuel gas treating where CO_2 removal is not required. The high-purity levels achievable even at low absorber pressure are not significant for fuel gases because there is no compelling process need for high-purity gas, as there is in high-Btu gasification.

In a high-Btu gasification process, catalyst sensitivity to sulfur imposes purity levels for H_2S of about one part per million by volume (ppmv).³ For low-Btu fuel gas, restriction of H_2S content is based on environmental concerns; meeting the current federal specifications for sulfur emissions translates to about 1000 ppmv H_2S (equivalent) in the fuel gas (Sect. 1). This results from applying the sulfur emissions limit from large, new coal-fired power plants (1.2 lb SO_2 per million Btu heat input) to a fuel gas at about 150 Btu/scf. Actual SO_2 emission restrictions on low-Btu gas have not yet been nationally established; however, it appears prudent to design systems that have emissions that are lower than the currently allowable SO_2 emissions in case future regulations are more stringent. In this evaluation, the proposed level for SO_2 emissions from H_2S is an order of magnitude more stringent than the currently allowed limits; H_2S is limited to 100 ppmv in the low-Btu

fuel gas (150 Btu/scf). In addition, of course, other sulfur-containing gases such as COS or CS₂ will form SO₂ when combusted. The level of such gases is estimated to be sufficiently low (typically 500 ppmv COS, or less, and much lower for other sulfurous gases), so that even quantitative conversion to SO₂ will not exceed federal stationary source standards. This assumes no removal of COS during cleanup; SO₂ emissions will be lower for those gas cleanup processes capable of some degree of COS removal (e.g., Benfield and Selexol). The <100-ppmv specification on H₂S is easily met by other amine systems; hence, the ability of primary amines to reach very low levels of H₂S is not beneficial in the case of low-Btu gas.

The SNPA-DEA process is screened out because it was developed to enhance DEA's ability to remove H₂S to very low levels. As noted previously, this is not of any particular advantage for low-Btu gas treating. It was commercialized to treat high-pressure natural gas to pipeline specifications (typically less than 4 ppmv H₂S).⁴⁻⁶ Such extensive treating is not expected to be required for low-Btu fuel gas.

Three amine systems remain for further evaluation: DEA, DIPA, and MDEA.

4.1.2 Alkali salt systems

Most of the alkali salt systems can be screened out at this point. The Seaboard process uses air regeneration of the rich solution; the regenerated H₂S is then not suitable for feed to a sulfur recovery plant. The sulfur-containing stream cannot be vented to the atmosphere because of environmental regulations; therefore, processes such as this are not considered further. The Vacuum Carbonate system, although capable of regenerating a suitable H₂S feed for a sulfur plant, has not been used to remove H₂S to the desired 100-ppmv level. This process has been supplanted by systems that oxidize H₂S to sulfur in the liquid phase.⁷

Uncatalyzed hot potassium carbonate has also been supplanted by more efficient systems. Originally commercialized for bulk CO₂ removal, the process has been displaced by catalyzed versions (e.g., Benfield and Catacarb) for application to H₂S and CO₂ removal. The catalyzed systems decrease the required circulation rate and thereby reduce steam consumption by increasing solution activity.

The Giammarco Vetrocoke CO₂ process is another catalyzed carbonate system, but the catalyst of general use in this process is arsenic trioxide. Because of toxicity concerns, the process was dropped in favor of nontoxic competitors.

Tripotassium phosphate also suffers in comparison with activated carbonate systems. Steam consumption is higher with this process, and H₂S is not removed to as low a concentration. Typical applications of tripotassium phosphate have removed H₂S to about 400 ppmv, well above the level specified in this evaluation. In addition, the system does not affect COS which passes through the absorber.

Similarly, Alkazid "S" (sodium phenolate) has been eliminated because of high steam consumption, poor H₂S removal ability, negligible effect on COS, and lack of commercial experience. Even though it is commercial, can treat H₂S to low levels, and has a low steam consumption, Alkazid "M" has also been eliminated. There are three main concerns with the process: (1) it is not selective for H₂S (as are the catalyzed carbonate systems), (2) it is complex, and (3) its low operating temperature provides no advantage over amine systems. The requirement for heat exchange imposed by the low absorption temperature places this process at an economic and efficiency disadvantage when compared with the activated carbonate systems.

Three processes remain for further consideration: Alkazid "DIK," Benfield, and Catacarb.

4.1.3 Physical absorption systems

Within the area of low-temperature physical absorption, the Union Oil process using methylcyanoacetate and the Estasolvan process with tri-N-butyl phosphate have not been developed to the commercial status associated with competing physical absorption systems. Because so little data are available on these systems and because available data refer to treatment of natural gas and not coal gases, no further evaluation has been pursued.

Of the remaining physical solvent processes listed in the literature search, the Purisol and Fluor Solvent processes also do not appear to be applicable to low-Btu gas cleanup. Lurgi's Purisol process was developed specifically for high partial pressure acid-gas removal at ambient

temperature. The solvent has a relatively small absorption power at the low-to-medium pressures expected in low-Btu gasification.⁸ The Fluor Solvent process was also designed for high acid-gas partial pressures (above 75 psi) and is not considered by the Fluor Corporation to be competitive at low-to-medium pressures (below 800 psig).^{9,10}

The Rectisol and Selexol processes remain for further consideration.

4.1.4 Mixed solvent systems

The Lurgi Amisol process was developed to achieve high-purity removal of both H_2S and CO_2 . The process is not operated selectively, and only limited information is available; therefore, the Amisol process is disqualified, leaving Sulfinol as the sole process in the mixed solvent category.

4.1.5 Absorption-oxidation systems

In the area of low-temperature absorption followed by liquid phase oxidation of H_2S to sulfur, two of the listed processes pose safety hazards. Both the Giammarco Vetrocoke H_2S process, using arsenic trioxide, and the Fischer process, with cyanic compounds, have been deleted in favor of alternatives with less toxic solutions.

The Burkheiser process is not considered in more detail because it is much more complex than the alternate processes (Stretford or Takahax). The present status of the Burkheiser process is also less favorable than alternatives; the general process type (iron oxide suspension in alkaline solutions) has been supplanted by other processes.¹¹

Two processes remain for further evaluation: Stretford and Takahax.

4.1.6 High-temperature systems

For high-temperature removal of H_2S , two of the listed systems have been eliminated. The IGT Meissner process is proprietary, and insufficient information is available to permit an assessment of applicability. The Appleby-Frodingham process of fluidized iron oxide was plagued with problems of massive sorbent attrition, plugging, and erosion of piping. Although these problems appear to be amenable to solution with present technology, the process was also operated below the desired level for high-temperature

H₂S removal.¹² The relatively low temperature (about 700 to 750°F) would require significantly more fuel gas cooling than competing concepts operated above 1000°F. Fixed-bed operations (e.g., the MERC process) are less troubled by sorbent attrition and have fewer operational problems.

Three concepts remain for further consideration: Battelle Molten Salt, Conoco Dolomite, and MERC Iron Oxide--Fly Ash.

4.2 Selection of Specific H₂S-Removal Processes

The third and final level of screening involves intracategorical comparisons to determine, where possible, the optimum process in each category for desulfurization of low-Btu fuel gas at low-to-moderate pressures. The 14 processes reviewed are listed by category in Table 4.2.

For this third stage, the screening criteria discussed in Sect. 4.1 are still valid, but the differences are minor and provide less guidance for the selection of one process over another within the same category. Because those processes selected in each category will be described in more detail in Sect. 5, the availability of design and economic data is the controlling consideration. To supplement open literature information, the process vendors (or developers) of the systems listed in Table 4.2 have been contacted for process and economic data. The only exception to this is the DEA process, for which a wealth of design and cost data are available in the open literature.

4.2.1 Amine systems

The amine systems listed in Table 4.2 (DEA, MDEA, and DIPA) have been subjected to several pertinent criteria: (1) the ability to regenerate a suitable Claus plant feed, (2) previous commercial application, (3) compatibility with fuel gas constituents (e.g., COS, CS₂, etc.), and (4) availability of data. Such high-priority concerns are the major considerations in the selection of a candidate amine system. All three amine systems are capable of removing H₂S to levels below 100 ppm. Additional purity is not considered a requirement here. Selectivity for H₂S removal over CO₂, which releases an acid gas with an H₂S concentration above the minimum required to assure an adequate Claus sulfur

Table 4.2. Processes remaining after technical evaluation

General process	Specific process	Vendor
Low-temperature chemical absorption — amines	DEA	Numerous vendors
	DIPA	Shell Development Co. — ADIP process
	MDEA	Dow Chemical Co.
Low-temperature chemical absorption — alkali salts	Alkazid "DIK"	Davy Powergas, Inc.
	Benfield	Benfield Corp.
	Catacarb	A. G. Eickmeyer & Assoc.
Low-temperature physical absorption	Rectisol	American Lurgi Corp.
	Selexol	Allied Chemical Corp.
Low-temperature chemical/physical absorption	Sulfinol	Shell Development Co.
Low-temperature absorption/oxidation	Stretford	Peabody Process Systems, Inc.
	Takahax	Ford, Bacon & Davis Texas, Inc.
High-temperature H ₂ S removal	Battelle	Battelle Pacific
	Molten Salt	Northwest Lab.
	Conoco Dolomite	Conoco Coal Development Co.
	MERC Iron Oxide/ Fly Ash	Morgantown Energy Research Center

plant feed, is considered an asset. Higher H_2S concentration in the sulfur plant feed results in lower capital and operating costs and enhanced sulfur recovery in a Claus plant. Of course, if such selectivity requires higher costs in the gas treating system (e.g., higher solution circulation rates and more expensive solutions), the overall costs must be examined to determine if any advantage remains.

Both MDEA and DIPA exhibit higher selectivity for H_2S than does DEA.^{13,14} According to the data of Pearce and Brownlie (Dow Chemical Company),¹³ MDEA or DEA would yield a Claus plant feed with more than 10% H_2S from a fuel gas with a CO_2 content of 8 vol % and an H_2S content of 0.7 vol %; however, the regenerated acid gas from an MDEA system is expected to be above 25% H_2S , whereas less than 20% H_2S is expected from a DEA system. In the Shell ADIP process using DIPA on the same fuel gas, low-pressure absorption (approximately atmospheric) will yield an acid gas with 40 to 50 vol % H_2S . The data on the ADIP process are primarily based upon low-pressure applications, and reliable estimates of H_2S selectivity are not yet available at higher pressures (e.g., ≥ 150 psi). Although the H_2S selectivity of DIPA decreases with increasing pressure, it is felt that the H_2S content of the regenerated acid gas will still be above 20% at fuel-gas pressures around 100 to 200 psi.¹⁴

MDEA appears to be somewhat more expensive in solvent cost but lower in steam consumption than DEA or DIPA; however, published data on directly comparable applications are insufficient to accurately assess these points. Similarly, the published data do not allow an accurate comparison of required solution circulation rates for the three amines; all have been used in commercial installations, with DEA the most commonly used and MDEA the least commonly used of the three. Little processing information has been published on the ADIP process; however, the same is true for the use of MDEA. Under these circumstances, a technically defensible choice is not possible. The data available on MDEA are more suitable for process design and economic studies than those available on DIPA. Because both MDEA and DIPA offer advantages over DEA and the data for MDEA are more suited for process design, the MDEA process has been chosen. This selection is presented with the caution that direct economic comparisons for specific

gas treating cases are required to accurately predict the most favorable amine process.

4.2.2 Alkali salt systems

In the category of chemical absorption with alkali salts (Alkazid "DIK," Benfield, and Catacarb), the selection of a single process is also difficult. The Alkazid process is deleted because (1) data have not been reported for coal-derived gas; (2) the process is not in operation in the United States; (3) it operates at relatively low temperatures (about 100 to 130°F); and (4) design data are lacking. The choice between the Benfield and Catacarb processes is difficult to make. Numerous publications and published quotes are available for the Benfield process. The Catacarb process has fewer sources and a more limited information base from which to derive further design or economic data. In addition, a comparison of vendor quotes obtained for both Benfield and Catacarb in several specific applications show no particular capital or operating cost advantage for either process.^{15,16} Hence, the availability of information on the Benfield system, especially with regard to its operation on a coal-derived gas, makes it a reasonable choice as the representative process in the category of alkali salts.

4.2.3 Physical absorption systems

In this category, the choice has been simplified by vendor-supplied information. American Lurgi Corporation indicates that their licensed Rectisol process is not suitable for the conditions expected in low-Btu gasification.¹⁷ Rectisol has higher operating and capital costs than hot potassium carbonate systems under the study conditions of minimal purity requirements, relatively low pressures (i.e., ≤ 500 psig), and thermal penalty for the removal of hydrocarbons in solution.¹⁷ Under these conditions, selectivity of the Rectisol process for H₂S is comparable to that achievable by a hot carbonate system. Selexol, however, has been promoted for similar applications. Its ability to achieve a high degree of selectivity for H₂S removal, even at low pressures, is sufficient to retain the Selexol process as the candidate physical absorption process.

4.2.4 Mixed solvent systems

Only one process, Sulfinol, remains in the category of low-temperature chemical and physical absorption; therefore, Sulfinol is considered the candidate process for this category.

4.2.5 Absorption-oxidation systems

In choosing between the Stretford and the Takahax processes, availability of cost and design information is again the major concern. The data published on the Takahax process are insufficient to permit design or cost estimates; therefore, the Stretford process is selected as the candidate process in low-temperature absorption/oxidation. Without any cost information on Takahax, it is not possible to compare the Takahax process economics with those of the Stretford process or with other fuel gas treating alternatives (e.g., amine removal of acid gases with Claus-plant conversion of H_2S to sulfur).

4.2.6 High-temperature systems

The remaining processes listed in Table 4.2 in the category high-temperature H_2S removal have not been commercialized, but all three (iron oxide, dolomite, and molten salt) have undergone varying degrees of laboratory development. Previous reviews of hot-gas purification by Battelle Columbus Laboratories and Stone and Webster Engineering Corporation agree that the fixed-bed iron oxide system under development at the Morgantown Energy Research Center is the most advanced possibility of the three.^{18,19} These reviewers do not imply that iron oxide systems have the most promise economically, but they do imply that such systems are closer to commercial application. This seems reasonable since a fluid-bed iron oxide process (the Appleby-Frodingham process) was operated commercially for a time, although with technical problems and at a lower temperature (around 750°F) than currently desired.²⁰ The potential for early development has led others to include fixed-bed iron oxide systems in conceptual evaluations and is considered sufficient for the inclusion of iron oxide in this review.^{19,21}

The remaining two systems under consideration are essentially based on the reaction of H_2S with calcium carbonate at temperatures above 1200°F . The Conoco fluid-bed process utilizes half-calcined dolomite ($\text{CaCO}_3 \cdot \text{MgO}$) and regenerates the stone with CO_2 and steam to release a dilute H_2S stream (less than 3%).²² Potential problems include:

1. Regenerated H_2S concentration is too low for feeding to a Claus sulfur plant.
2. Carbon buildup, if present, cannot be removed by combustion.
3. Regeneration of the stone is slow.
4. The H_2S removal activity declines with cycling.
5. Attrition is caused by fluid-bed operation and recycling.

The Battelle-Northwest process uses dissolved CaCO_3 in a melt of molten alkali-metal carbonates above 1000°F . This avoids several problems inherent in the fluid-bed dolomite process but introduces certain other concerns.

The molten salt system offers the possibility of solids removal, concurrent with H_2S removal. Unfortunately, the published data on the Battelle-Northwest process are not sufficiently complete to assess the continuous solids removal ability. Partial solution of some coal-ash compounds in the molten salt has led to a concern that the salt will be degraded with regard to H_2S removal ability or corrosion problems. The removal of undissolved solids contained in the molten salt has also not been demonstrated. R. H. Moore (Battelle-Northwest) indicates that a pilot-scale test of the molten salt process was to be initiated in late 1977.²³ The potential for the molten salt process is judged greater than for the Conoco fluid-bed process because of the possibility of concurrent solids removal. However, the unresolved problems are also greater at this time for the molten salt process. Considering, as an example, the requirement for alonized (aluminum-coated) surfaces in the molten salt process for corrosion protection, mercury carryover from coals with significant mercury content could produce severe corrosion levels if brought into contact with such surfaces.²⁴⁻²⁶ In addition, the aluminum diffusion layer is protective only up to 1380°F .²⁷ Pitting corrosion has been

observed above this temperature; hence, at design temperatures of 1600 to 1700°F, corrosion considerations are unresolved. Testing to date of the Battelle-Northwest process is insufficient to preclude these concerns; therefore, the Conoco fluid-bed dolomite process is selected as the representative CaCO_3 process for high-temperature H_2S removal.

Comparing the fluid-bed dolomite process with the fixed-bed iron oxide process, pertinent points are as follows:

1. The dolomite process regenerates H_2S rather than SO_2 , as the iron oxide process does, thus a simpler route to solid-sulfur recovery is available.
2. The low H_2S content regenerated in the Conoco process requires a more expensive liquid-phase sulfur recovery system.
3. Design absorption temperature for the Conoco half-calcined dolomite process is above 1600°F, whereas the iron oxide process using fly-ash support is limited to about 1500°F.
4. A switch to silica-based sorbents should permit extension of the iron oxide process to above 1600°F.
5. Fixed-bed operation leads to complex switching between several beds of iron oxide for absorption/regeneration cycles.
6. Fluid-bed operation of dolomite produces attrited fines.
7. Iron oxide can be reliably regenerated without loss of activity whereas dolomite activity declines significantly during the initial cycles.

The most important advantages for the dolomite system over the iron oxide system are regeneration of H_2S and an operating temperature above 1600°F. However, the Conoco dolomite system does not yield an H_2S -rich off-gas suitable for Claus plant sulfur recovery. Furthermore, a silica-based iron oxide sorbent is predicted to be operable above 1600°F. Therefore, the advantages of the iron oxide system outweigh the advantages of the dolomite. With the more durable silica-based sorbent, the iron oxide process may also be amenable to moving-bed technology; (fluid-bed operations seem doubtful without development of even stronger supports).

Operation in a moving-bed system would permit regeneration with oxygen-enriched air by allowing better heat-release control, yielding a higher SO_2 concentration than fixed-bed operation. This is preferable for feed to various SO_2 -to-sulfur reduction processes. The combination of present ability to remove H_2S up to 1500°F with a fly ash-based sorbent with excellent regenerability, along with the indicated advance in absorption temperature and the possibility of moving-bed operation with a silica-based sorbent, makes the iron oxide system under development at the Morgantown Energy Research Center the most suitable of the high-temperature H_2S removal processes for further description.

4.3 Addition of Molecular Sieves

Review of the available literature indicates that the data for molecular sieves, representing the category of low-temperature solid sorption, are insufficient to rule out their use for gas cleanup. Some of the literature indicates that this process is not suitable for bulk H_2S removal from low-Btu gases, but data supporting this conclusion are not presented. It has been accordingly decided to add molecular sieves to the list of processes that are to be described in detail. This results in a total of seven categories, each represented by one process.

4.4 References

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5. DESCRIPTIONS OF SPECIFIC H₂S-REMOVAL PROCESSES

The processes selected (Sect. 4) for description and possible application to low-Btu gas streams are shown in Table 5.1. This section describes these processes and provides information to assist in determining the most applicable process for a given set of operating conditions and gas stream compositions. Also discussed is an evaluation (provided by Union Carbide Corporation, Linde Division) of molecular sieve applications. The following descriptions and economics are based on nonproprietary sources and reflect the author's interpretation of occasionally conflicting claims. No endorsements or guarantees are implied by the technical descriptions, and cost data are considered conceptual rather than definitive. Each vendor or developer listed (Table 5.1) has been given the opportunity to review the section on his process for errors of commission or omission, and pertinent corrections have been incorporated in the descriptions.

Specific processes are described in the order shown by Table 5.1. Each process description is divided into four general areas. First, background information involving process history, reported applications, and general process advantages and some disadvantages is provided. The process description (e.g., flowsheet) for preferred applications is then presented, along with a discussion of various alternatives available for other applications. Process data are then presented, including pertinent chemical and physical properties (where available), reactions involved, and the process chemistry in general. The final area discussed includes the process operation and economics, including published quotes of utility and capital cost requirements, particularly for applications to coal-derived gases that have been evaluated.

Table 5.1. Specific gas cleanup processes

Processes	Vendor/developer
Low-temperature processes	
Chemical absorption	
Amine — methyldiethanolamine (MDEA)	Dow Chemical Co.
Alkali — potassium carbonate/additives (Benfield)	The Benfield Corp.
Absorption/oxidation — sodium carbonate/additives (Stretford)	Peabody Engineered Systems (for the Holmes-Stretford process)
Physical absorption	
Mixed — sulfolane/di-isopropanol amine (Sulfinol)	Shell Development Co.
Dimethylether polyethylene glycol (Selexol)	Allied Chemical Corp.
Solid sorption	
Molecular sieves	Union Carbide Corp.
High-temperature process	
Iron oxide--fly-ash (or silica) sorbent	Morgantown Energy Research Center

5.1 The MDEA Process

5.1.1 Background

The use of MDEA for removal of acid gases has received attention from several organizations over the past thirty years; however, commercial application of MDEA has been quite limited to date.¹ Pilot plant work and commercial-scale testing has been performed on MDEA by the Fluor Corporation since the late 1940s.¹⁻³ Dow Chemical Corporation has also investigated acid gas absorption by MDEA in pilot plant studies.⁴ Graff Engineering Corporation offers the Trencor process, which utilizes MDEA for the selective removal of H_2S from fuel- and tail-gas streams.⁵ In addition, BASF (Badische Anilin-und Soda-Fabrik) has patented a version of the MDEA process which reportedly will remove carbonyl sulfide.⁶

Four units are believed to be currently operating in the United States: two treat refinery off-gas to increase the H_2S content in the gas fed to Claus plants; a Trencor-M installation treats a sulfur recovery plant tail gas; and a recent conversion from DEA to MDEA performed by Dow Chemical Corporation treats a natural gas to reduce H_2S concentration to below pipeline specification.⁷ These plants take advantage of MDEA's selectivity for H_2S removal in the presence of CO_2 and produce a regenerated acid gas much richer in H_2S than that which is achievable with conventional amine (MEA or DEA) treating.^{1,4} This is the principal advantage cited for MDEA over MEA and DEA. In addition, lower utility consumptions are possible because CO_2 absorption is minimized and MDEA has lower heats of reaction than MEA or DEA.⁴ A major disadvantage for MDEA is the higher solvent cost which is two to three times that for conventional amines.¹

5.1.2 Process description

The application of MDEA to a fuel gas for removal of acid gases results in a flowsheet similar to that found in conventional amine treating plants (Fig. 5.1). If economics dictates, air cooling may be specified instead of water cooling. The treating solution generally contains 30 to 50 wt % MDEA in water. Tray columns may be used for the absorber and regenerator, although use of packed columns does not appear to be precluded for technical reasons. An early commercial test by Fluor of the MDEA process

ORNL DWG 77-1440

Fig. 5.1. Typical flowsheet for MDEA process.

provides some data on the required number of absorber trays. The general conclusion offered by Miller and Kohl is that the use of 20 absorber trays would allow maximum H₂S removal, while use of only 12 trays would permit maximum selectivity for H₂S over CO₂. Use of 8 absorber trays resulted in lower CO₂ removal, but over 10% of the feed H₂S was not absorbed under test conditions. In each case, 16 trays were used in the regenerator, with rich solution fed to the fourth tray from the top of the regenerator.³

Gas to be treated is fed to the bottom of the absorber; lean MDEA solution is pumped to the top of the absorber. The solution absorbs most of the H₂S and some CO₂ while flowing downward through the absorber and countercurrent to the gas stream. Rich solution at the bottom of the absorber is preheated by countercurrent heat exchange with the regenerator bottoms stream. Preheated rich solution enters the regenerator and the acid gas is stripped from solution by a combination of reduced pressure, elevated temperature, and stripping steam rising from the reboiler. Regenerator pressure is generally below 10 psig, with a reboiler temperature of about 240°F. Regenerator overhead is partially condensed to remove most of the steam carryover. Condensate is refluxed to the top of the regenerator. Remaining water vapor goes to sulfur recovery with evolved acid gases.

A sidestream of regenerator bottoms is sent to a reclaimer, where a portion of the degraded solution is recovered by high-temperature distillation at 250 to 300°F.¹ Unreclaimed amine sludge is sent to disposal. Lean solution from the bottom of the regenerator is cooled by heat exchange with rich solution and then pumped to absorber pressure. Additional cooling is required to reduce the lean solution temperature to the desired operating level, generally 80 to 125°F.⁴

5.1.3 Process data

Methyldiethanolamine has the chemical structure

Physical properties for MDEA are shown in Table 5.2, along with MEA and DEA for comparison.^{8,9} MDEA reacts chemically with H_2S , CO_2 , HCN , and organic sulfides. The reactions with H_2S and CO_2 can be represented as⁴

Reactions between MDEA and HCN or organic acids form thermally stable compounds which lead to solution degradation and amine losses.^{1,3,4}

Carbon dioxide must first react with water to form the ionized species that reacts with MDEA. This indirect reaction is believed responsible for MDEA's partial selectivity for H_2S in the presence of CO_2 . An amine's effectiveness in absorbing acid gas is primarily due to its alkalinity. Kohl and Riesenfeld provide a measure of amine alkalinity by determining solution pH while neutralizing the solutions with CO_2 ; their values for MDEA, MEA, and DEA are shown in Fig. 5.2.⁸

Selectivities for H_2S over CO_2 , acid-gas capacities, and heats of reaction for MDEA, MEA, and DEA are shown in Table 5.3.⁴ Solutions tested for selectivity and acid-gas capacity are 1.3 N (gram equivalents per liter solution). Numerous pilot- and commercial-scale data are available on MDEA performance.²⁻⁵ Pilot plant data on natural gas, reported by Frazier and Kohl, cover a wide range of absorption pressures and H_2S -to- CO_2 feed-gas ratios (resulting data listed in Table 5.4).² The 4-in.-diam absorber used in the pilot tests was 12 ft in length and was packed with 3/8-in. porcelain rings. Several tests were run at different absorber lengths (Table 5.4).

A more narrow range of tests reported by Miller and Kohl deals with treating sour gas in a refinery on a commercial scale. The concentration of H_2S in the feed gas ranged from 5 to 6 vol %, while CO_2 content was only 1 to 2 vol %. Because a high feed-gas H_2S content decreases MDEA selectivity, this plant did not provide optimum conditions for high selectivity.^{3,4} Absorber pressure was maintained at 150 psig, and regeneration occurred in a 16-tray column at 10 to 15 psig. A lean aqueous solution of 20 wt % MDEA was fed to the absorber at three points during the tests, such that either 8, 12, or 20 trays were utilized. The amount of acid gas unabsorbed is

Table 5.2. Amine physical properties

Property	MDEA	MEA	DEA
Molecular weight	119.17	61.09	105.14
Density, lb/gal	8.67 at 68°F	8.47 at 68°F	9.09 at 86°F
Boiling point, °F			
at 14.7 psia	447.1	338.7	515.1 ^a
at 0.97 psia	327	212	369
at 0.19 psia	262	156	302
Vapor pressure, psia			
at 68°F	<0.0002	0.004	<0.0002
Freezing point, °F	-5.8	50.5	82.4
Flash point, °F (Cleveland open cup)	260	200	280
Solubility in water,			
% by wt at 68°F	Complete	Complete	96.4
Viscosity, cP	101 at 68°F	24.1 at 68°F	380 at 86°F
Heat of vaporization, Btu/lb	223 at 14.7 psia	355 at 14.7 psia	288 at 0.44 psia
Approximate cost, \$/lb	0.90 ^b	0.38 ^c	0.39 ^{b,c}

^aDEA decomposes at this temperature.

^bUnion Carbide Corp. quote for bulk quantities (May 3, 1977).

^cChemical Marketing Reporter quote for bulk quantities (Aug. 15, 1977).

Fig. 5.2. Amine solution alkalinity upon addition of CO₂.

Table 5.3. Acid-gas selectivity, capacity, and heats of reaction for various amines

Compound	Selectivity ^a	Capacity (mole gas/mole amine)		Heat evolved by reaction (Btu/lb)	
		H ₂ S	CO ₂	H ₂ S	CO ₂
MDEA	3.85	0.10	0.12	450	577
MEA	0.89	0.07	0.50	650	820
DEA	2.27	0.09	0.32	493	650

$$^a \text{Selectivity} = \frac{(\text{mole \% H}_2\text{S})_{\text{feed gas}} - (\text{mole \% H}_2\text{S})_{\text{treated gas}}}{(\text{mole \% H}_2\text{S})_{\text{feed gas}}} \div \frac{(\text{mole \% CO}_2)_{\text{feed gas}} - (\text{mole \% CO}_2)_{\text{treated gas}}}{(\text{mole \% CO}_2)_{\text{feed gas}}}$$

Table 5.4. Pilot plant results with aqueous MDEA solution

Run No.	Absorber pressure (psia)	Gas/liquid rates (scf feed gas/gal solution)	MDEA in solution (wt %)	Feed gas		Treated gas		Selectivity ^a	Acid gas absorbed mole gas/mole MDEA (scf/gal)
				vol % CO ₂	vol % H ₂ S	Vol % CO ₂	ppmv H ₂ S		
1	57	17.9	35	4.1	0.42	1.72	17.6 ^b	1.72	0.06 (0.5)
2	58	17.1	35	23.9	0.82	14.6	32.0 ^b	2.56	0.17 (1.6)
3	65	17.6	37	35.5	0.34	25.5	0.8 ^c	3.55	0.23 (2.3)
4 ^d	65	17.1	35	48.1	0.41	41.3	16.0 ^b	7.05	0.23 (2.1)
5	60	22.4	32	25.4	5.0	19.6	9.3 ^c	4.38	0.30 (2.5)
6	215	19.6	30	7.5	3.2	2.15	28.8 ^b	1.40	0.32 (2.5)
7	595	87.5	35	8.0	0.70	3.47	4.0 ^b	1.77	0.51 (4.8)
8 ^e	760	24.3	11	11.1	2.3	1.61	7.2 ^b	1.17	0.96 (2.8)
9 ^e	760	47.2	13	14.1	2.5	8.8	320 ^b	2.63	0.97 (3.3)

^aDefined in Table 5.3.

^bDetermined by continuous I₂ titration. Includes compounds other than H₂S, up to the equivalent of 4 ppmv H₂S.

^cDetermined by cadmium sulfide precipitation.

^dOne-half absorber length used.

^eThree-fourths absorber length used.

shown in Fig. 5.3 as a function of the solution acid-gas loading and the number of trays used. Although the data points are scattered, certain trends are apparent. Use of 20 absorber trays results in minimum solution circulation and maximum gas purity, whereas use of 12 trays increases selectivity for H_2S over CO_2 . The use of 8 trays permits minimum CO_2 absorption, but the amine solution acid-gas loading is lowered and gas purity is reduced.³ For a given operation, therefore, a balance must be made between the interrelated parameters of circulation rate, number of trays, desired gas purity, and selectivity for H_2S .

The lean solution generally was fed to the absorber at a temperature between 90 to 100°F; the maximum range was 84 to 109°F. Selectivity for H_2S was generally increased at lower temperatures, whereas higher temperatures rapidly reduced solution acid-gas capacity.³

Regeneration performance also has been reported by Miller and Kohl. Operation of the regenerator at solution concentrations ranging from 14 to 20 wt % MDEA, solution loadings from 0.43 to 0.75 moles acid gas per mole MDEA, and CO_2 -to- H_2S mole ratios from 0.03 to 0.19 produced data on the H_2S content remaining in the lean MDEA as a function of the reflux ratio. Figure 5.4 shows the relationship between residual H_2S in lean solution and the ratio of reflux to acid gas in the regenerator.³ Very effective stripping of the MDEA solution can be provided at a reflux ratio of about 1 mole of water refluxed to the regenerator per mole of acid gas stripped. In these commercial-scale tests, a reflux ratio of 1 represents approximately 2 lb of reboiler steam required per pound of acid gas. This value is comparable to steam consumption in typical DEA units but it is somewhat lower than that generally used in MEA treating.³

Pearce and Brownlie (Dow Corporation) have published curves for MDEA selectivity as a function of feed CO_2 -to- H_2S ratio, number of trays, and H_2S partial pressure. Figure 5.5 gives MDEA selectivity when 8 absorber trays are used, and Fig. 5.6 reflects the use of 12 trays.⁴

Fig. 5.3. Effect of solution loading and number of trays on acid-gas absorption.

Fig. 5.4. Regenerator performance.

Fig. 5.5, MDEA selectivity using eight absorber trays. Selectivity is defined in Table 5.3.

Fig. 5.6. MDEA selectivity using 12 absorber trays. Selectivity is defined in Table 5.3.

5.1.4 Process operation and economics

Most of the parameters involved in operation of the MDEA process have been discussed in the course of reviewing available process data. Some additional information is available to aid in assessing MDEA process operations.

A comparison of two cases of MDEA with MEA treating provides insight into energy requirements for the MDEA process. The first case reported by Pearce and Brownlie specifies H_2S removal to below 50 ppm; the second case assumes a less stringent H_2S -removal requirement to below 1000 ppm.⁴ The comparison in Table 5.5 is made with inhibited 30 wt % MEA solution at maximum acid-gas loading.

Table 5.5. Operation of MDEA compared with MEA^a

Property	Case 1		Case 2	
	MDEA	MEA	MDEA	MEA
Solution circulation, gpm	545	742	255	732
Reboiler duty, 10^6 Btu/hr	28	46	13	45
Required H_2S in treated gas, ppm	<50	<50	<1000	<1000
Delivered H_2S in treated gas, ppm	<50	<5	<1000	<10

^aBase conditions: 6925 moles/hr feed gas; temperature = 105°F;
pressure = 75 psia; 43 moles/hr feed H_2S = 0.62 vol %;
696 moles/hr feed CO_2 = 10.05 vol %.

Maximum energy savings will result from operation at maximum MDEA concentration (about 50 wt %) and maximum acid-gas loading. Corrosion inhibitors are required under these conditions to prevent excessive corrosion rates on the order of 26 mils/year (0.026 in./year).⁴ A 20-week, commercial-scale test with about 20 wt % MDEA solution showed only minor equipment corrosion in the reboiler and on the lean solution side of the rich/lean solution heat exchanger. The maximum corrosion rate was 7.0 mils/year (0.0070 in./year) in the reboiler, which was considered no more serious than that which is typical of DEA and MEA treating systems. In general, MDEA systems appear to be no more corrosive than MEA or DEA systems, and carbon steel construction should be suitable.³

Few capital or operating cost estimates are available for MDEA plants. Graff Engineering Corporation has made some estimates on the use of their Trencor-M (MDEA) process to treat coal-derived gases.^{5,10} Crow and Baumann report capital cost and utilities for treating the entire acid gas stream produced in a 12,000-tons/day coal gasification plant, including sulfur recovery. Based on a coal which would yield the equivalent of 120 tons/day elemental sulfur, when gasified, and an H₂S concentration of 60% in the Claus plant feed gas, the capital cost with Gulf Coast conditions was about \$6.4 million at the time of the report and about \$9 million in the first quarter of 1977. Utilities for this MDEA application were reported as:⁵

Electricity	1155 kW
Fuel gas (high-Btu coal gas)	755 x 10 ³ scfd
Hydrogen (low-Btu coal gas)	1350 x 10 ³ scfd
Boiler water makeup	7 gpm

The plant was essentially air cooled, with an excess of 72,000 lb/hr of 50 psi steam generated in adjacent plant operations such as ammonia gas combustion.⁵

In response to a request from A. W. Lemmon et al. (Battelle-Columbus Laboratories), an additional estimate was made by Graff Engineering Corporation for a coal-gas application. The information supplied to Graff Engineering is listed in Table 5.6, along with the vendor response.¹⁰ Capital cost is escalated to the first quarter of 1977 and includes the required Claus plant for conversion of H_2S to elemental sulfur, at 25% of the total cost. The low-Btu coal gas specified by Graff Engineering is to be desulfurized to 300 ppm H_2S . The Claus plant feed gas is estimated to contain 45% H_2S on a dry basis. Capital cost is indicated to scale with the 0.65 power of the size. The design plant would remove H_2S from the low-Btu coal gas and from the tail gas of the Claus plant, following reductive incineration with fuel gas to convert residual SO_2 to H_2S . A filter is specified on the lean solution for removing any solid impurities.¹⁰

Estimation of capital and operating costs for MDEA systems can be performed on the basis of information reviewed in Sect. 5.1.3. Conventional amine plant design (MEA or DEA) is suitable, with allowance for MDEA selectivity for H_2S shown in Figs. 5.3, 5.5, and 5.6, and solution loadings shown in Table 5.4 and Fig. 5.3.

Table 5.6. Selective removal of H₂S from a low-Btu gas

Component	Feed gas composition		Condition		MDEA plant characteristics (Graff Engineering - Trencor)	
	lb-mole/hr ^a	vol % ^b				
H ₂	2,008.7	18.51	Temperature	1100 to 1200°F	Steam	26,500 lb/hr
CO	1,906.2	17.57	Pressure	300 psig	Fuel	1.25 x 10 ⁶ Btu/hr
CO ₂	973.6	8.97	Sulfur (H ₂ S)	2,133 lb/hr	Hydrogen	25 lb/hr
CH ₄	276.7	2.55	Dust	572 lb/hr	Power	250 kW
C ₂ H ₆	25.6	0.24	Tar	991 lb/hr	Chemicals	35 lb/day MDEA 20 lb/day Na ₂ CO ₃
N ₂	4,991.0	46.00	HHV	150 Btu/scf	Capital cost ^c	\$4.1 million
H ₂ S	66.6	0.61				
H ₂ O	602.2	5.55				
	10,850.6	100.00				

^aTotal lb/hr feed gas = 258,433.

^bAverage molecular weight feed gas = 23.82.

^cCapital cost includes Claus plant at 25% of the total.

5.1.5 References

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5.2 The Benfield Process

5.2.1 Background

The Benfield process had its origins in work performed at the United States Bureau of Mines in the early 1950s. H. E. Benson, J. H. Field, and co-workers were attempting to develop an economic method of removing high-concentration CO_2 from coal synthesis gas, as part of the government program on Fischer-Tropsch conversion of synthesis gas (syngas) to liquid fuels. To meet this need, the use of potassium carbonate at high absorption temperatures (about 230°F) was piloted at the Bureau of Mines in 1950 and 1951.¹ These studies were later extended to investigate removal of sulfurous gases.

Private research conducted by The Benfield Corporation on laboratory-, pilot-, and semicommercial-scale processes has resulted in patentable innovations to the Bureau of Mines hot potassium carbonate process;² improvements such as solution additives accelerate the rate of acid-gas absorption, and thereby decrease solution circulation rates, tower sizes, and thermal losses.^{3,4}

Advantages cited for the hot carbonate process include: (1) use of a nonvolatile, low-cost, chemically stable solution, (2) low solubility of fuel gas components, especially when compared to physical solvents, and (3) high-temperature operation (up to 280°F).⁴ In its preferred applications, hot carbonate requires much less reboiler heat than amine systems because of the high absorption temperature, which minimizes heating of the rich solution to regeneration temperature; heat interchange from absorber to stripper is also reduced or eliminated.⁵ These process advantages translate to capital and operating cost savings.⁶

Over 400 installations using Benfield-designed systems were operating or under construction by 1975.⁴ Dravo reports that almost half of these systems employ activated solutions or other Benfield innovations, while ten were designed for the Benfield HiPure process. The HiPure process is a recent development that extends the capability of activated hot potassium carbonate for removing H_2S to below 1 ppm and for removing CO_2 to below 10 ppm.⁷

Benfield systems have been applied to natural gases and to gases derived from partial oxidation of petroleum and coal.⁴ Significantly, a Benfield system has been successfully operated on raw gas from coal produced in a Lurgi gasifier in Westfield, Scotland. In over thirteen years of operation, the system has demonstrated no significant corrosion or foaming, nor have contaminants in the gas stream been harmfully reactive with the solution.⁴ A Benfield system has been installed in the Synthane pilot plant at Bruceton, Pennsylvania, for the removal of H_2S and CO_2 after water-gas shift is performed on the medium-Btu syngas. This system has not yet been integrated with the gasifier because shakedown is not complete in the upstream units.⁸

5.2.2 Process description

The Benfield process exhibits a simple configuration (Fig. 5.7) when designed for bulk acid-gas removal (i.e., removal of large amounts of acid gas without high purity requirements).⁹ The absorber and regenerator operate isothermally (typically near $230^\circ F$), thus eliminating the heat exchange between rich and lean solution streams that is required by amine systems. The towers may employ packing or trays, although typical applications favor the use of packing. Packing is preferred because it allows higher liquid-to-gas ratios (particularly in the absorber), minimizes possible corrosion and foaming problems, and permits low pressure drops.¹⁰ Proprietary packings such as Koch plastic Flexisaddles and Flexirings, Mass Transfer's plastic Cascade Mini-Rings, and metal and plastic Ballast Rings from Glitsch are suitable for use in hot carbonate systems.¹¹⁻¹⁴ P. A. Ruziska (Exxon Chemical) has published his company's experience with various packing materials in activated carbonate systems that remove only CO_2 .¹⁵ He presents an assessment of the technical problems to be considered when selecting a packing material.

Gas that requires cleanup is introduced to the base of the absorber and contacted in a countercurrent manner by the downflowing carbonate solution.³ Because regeneration of the rich solution is performed at low pressure (generally less than 10 psig), the rich solution from the bottom of the absorber requires pressure letdown. Hydraulic power recovery turbines are used when absorber pressures and/or circulation rates are

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Fig. 5.7. Illustration of Benfield single-stage design.

sufficiently high. The rich solution is then introduced to the top of the regenerator.¹ The solution is regenerated while passing downward, counter-current to rising steam and released gases.³ Acid gases are evolved by a combination of reduced pressure and stripping steam (generated in a process gas- or steam-heated solution reboiler).⁴ The overhead vapor of the regenerator undergoes partial condensation to remove much of the steam carryover. This condensate is refluxed to the top of the regenerator. If the hydrogen sulfide content exceeds emission limits, remaining water vapor and evolved acid gases are sent to a sulfur recovery plant. The Claus, dry-bed catalytic sulfur recovery process can be used if the H_2S concentration is above 15 mole %, although the process efficiency and economy is considerably enhanced with an H_2S concentration of 60 to 70 mole % or greater.¹⁶⁻²⁰ For regenerated acid gases with low concentrations of H_2S , sulfur recovery is typically performed by liquid phase oxidation processes (e.g., Giammarco-Vetrocoke H_2S , Stretford, Takahax, etc.).²¹

Various modifications and additions to the single-stage design (Fig. 5.7) are employed to increase acid-gas removal, to minimize capital and operating costs, or to satisfy specific process objectives (e.g., selective removal of H_2S).⁹ To remove additional acid gas, a cooled split-stream absorber can be designed. The bulk of the hot regenerated solution is introduced to an intermediate point of the absorber (Fig. 5.8).²² A portion of the regenerated solution (typically one-fourth to one-third) is cooled to between 160 and 200°F and injected at the top of the absorber.^{3,23} The acid-gas equilibrium pressure over the cooled solution is lowered, thus permitting further acid-gas absorption and increased fuel gas purity.³

Higher purities can be obtained with a two-stage design (Fig. 5.9).²² In this design, the carbonate stream to be cooled undergoes additional stripping in an added bottom regenerator stage.³ The more thorough regeneration reduces acid-gas back pressure in the lean solution, thereby enhancing acid-gas absorption. A further innovation, employing a side-stream withdrawal on the absorber as well as the stripper, uses two essentially independent circulating solutions in series to obtain high purity.²⁴ The Benfield HiPure process is capable of reducing H_2S to <1 ppm and CO_2 to <10 ppm. Advantages of this type of system for removing

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Fig. 5.8. Illustration of Benfield split-stream design.

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Fig. 5.9. Illustration of Benfield two-stage design.

acid gases to very low levels are described by H. Thirkell, as well as by H. E. Benson and R. W. Parrish.^{24,25} Because such levels are not specified for low-Btu fuel gas treating, this application of the HiPure process is not discussed; however, the HiPure configuration shown in Fig. 5.10 can also be used for selectively removing H₂S while minimizing CO₂ removal. Removing 90 to 98% of H₂S is possible while removing only 10 to 40% of CO₂.⁹

The choice between these various flow schemes mainly depends on the desired purity of treated gas.⁹ Additional considerations include availability of low-level heat, the value of adding capital expenses for obtaining lower operating expenses, and the desire for selective removal of various constituents. A general guide is provided in Fig. 5.11 which considers only operating pressure and desired final CO₂ content. Because H₂S is more soluble and more rapidly absorbed than CO₂, its concentration is invariably reduced to a greater extent.³

5.2.3 Process data

Many of the compounds commonly found in coal-derived gases react in the Benfield aqueous solution of 25 to 35% potassium carbonate and activators. The extents and rates of absorption vary considerably. The principal acid-gas constituents (CO₂ and H₂S) are readily absorbed through reactions represented by the following expressions, although the actual chemistry is somewhat modified by solution additives:¹

Hydrogen sulfide is more soluble than CO₂ and may be absorbed 50 times faster than CO₂, under selected operating conditions.⁹ Because potassium bicarbonate (KHCO₃) is formed in either reaction, H₂S and CO₂ equilibrium pressures over a solution are interdependent.⁵ When both components are present, this factor affects process design.

Fig. 5.10. Illustration of Benfield HiPure process.

Fig. 5.11. General guide to selecting Benfield process configuration.

When only H_2S is present in the fuel gas, eventual deactivation of the solution is caused by the buildup of unregenerable K_2S in the following series of reactions:²⁶

Because some CO_2 is lost from the system with each absorption-regeneration cycle, all the potassium eventually undergoes reaction (7); however, if some CO_2 is present (at least a CO_2 -to- H_2S mole ratio of 1:10), then permanent deactivation is avoided.¹ When the CO_2 -to- H_2S ratio is above 1:6, negligible capacity loss occurs. In the processes for low-Btu coal gasification being considered in this evaluation, the CO_2 -to- H_2S ratio is always greater than this minimum. Ratios of CO_2 to H_2S are typically 5:1 or 10:1. (Refer to Sect. 3, the literature survey, for example gas compositions.)

Coal-derived gases also typically contain organic sulfur compounds, hydrogen cyanide, ammonia, and various other impurities which are affected by the activated potassium carbonate solution.

Two compounds, carbonyl sulfide (COS) and carbon disulfide (CS_2), are not directly absorbed; they are first hydrolyzed in solution:³

The COS produced in reaction (10) must then undergo an additional hydrolysis before absorption, as in reaction (9). The hydrolysis reactions can proceed to completion, but the rates are slower than for CO_2 absorption alone. Relative capacities and rates are shown in Table 5.7.⁹

The rate of hydrolysis is only slightly dependent on extent of solution conversion to KHCO_3 or KHS , but it is highly dependent on temperature, doubling for each 50°F increase in solution temperature.³ Hydrolysis is catalyzed by the Benfield activators; the reaction rates are about 70%

Table 5.7. Relative absorption capacity and rate,
Benfield activated solution at 230°F^{a,b}

Component	Relative molar capacity	Relative molar rate
CO ₂	1	1
H ₂ S	1.41	3.6
COS	Hydrolyzes	0.36
CS ₂	Hydrolyzes	0.10
CH ₃ SH	0.03	1.2
NH ₃	0.10	3.5
HCN	c	c
SO ₂	c	c

^aCapacities measured to an equilibrium partial pressure of 2 psi; rates measured at a solution loading equivalent to an equilibrium partial pressure of 2 psi.

^bR. W. Parrish and H. B. Neilson, "Synthesis Gas Purification Including Removal of Trace Contaminants by the Benfield Process," presented at the 167th National Meeting of the ACS, Div. of Ind. and Eng. Chem., Los Angeles, Mar. 31-Apr. 5, 1974.

^cApproximately the same removal efficiencies as H₂S.

greater than in unactivated hot carbonate systems, and they are orders of magnitude faster than in water.^{3,4} Because the hydrolysis rate is dependent on temperature and because the overall rate of hydrolysis is slow relative to CO₂ removal, maximum COS and CS₂ removal entails higher absorber temperatures (around 250°F) and longer gas residence times. Increased capital costs (e.g., a taller absorber) are somewhat offset because the higher operating temperature permits a reduction in reboiler heat requirements.⁹

Commercial Benfield processes have achieved 75 to 99% COS removal. The design modification described in the preceding paragraph ensures COS removal to the 1 ppm level.⁹ Because of the additional stage of hydrolysis required, CS₂ removal is typically no better than 70 to 80%. Fortunately, the initial CS₂ concentration in the coal-derived gases under consideration represents only a trace of the total sulfur. Data reported by the Institute of Gas Technology for a suspension-type gasifier show CS₂ concentrations at only 5 to 10% of the concentration of COS, the latter being less than 10% of the H₂S concentration.²⁷ These low levels are expected from the thermodynamics of the gas phase equilibria for gasifiers operating at elevated temperatures. Lower temperature gasifiers produce more organic sulfur, along with substantial amounts of tar and oil.²⁸ However, such gasifiers are not under consideration in this evaluation for second generation applications.

Other sulfurous gases are also absorbed. Mercaptans are slightly acidic and directly react with potassium carbonate to form mercaptides:³

where R represents the attached hydrocarbon group (e.g., R represents CH₃ in methyl mercaptan CH₃SH).

Methyl mercaptans are rapidly absorbed, but to a limited extent (Table 5.7). The acidity decreases with increasing size of the hydrocarbon group, resulting in decreasing solubility for larger mercaptans. At least 70% removal of mercaptans is expected; complete removal of 4 ppm mercaptans has been reported at the Westfield, Scotland, Lurgi plant.⁹

Thiophene (C_4H_4S) is not predicted to be chemically active in a Benfield solution,³ and this has been verified by laboratory testing. However, a thiophene removal of 85% has been reported in the Westfield Lurgi unit.¹ This result is not explained in the literature, and the Benfield process is not guaranteed for thiophene removal.⁷

Ammonia (NH_3) is absorbed in the activated carbonate solution in a manner analogous to methyl mercaptan; that is, the rate of absorption is high, while the solution capacity is low.⁹

Sulfur dioxide (SO_2) and hydrogen cyanide (HCN) are strongly acidic. Only small amounts are expected and much of that will be removed in aqueous condensation and washing prior to encountering an acid-gas removal system. Any remaining SO_2 or HCN will be readily absorbed by activated potassium carbonate solution:⁹

Removal efficiencies are expected to be of the same order of magnitude as for H_2S .⁹ The potential for further reactions leads to undesirable compounds, such as sulfates, thiosulfates, and thiocyanates; however, the solution analysis (Table 5.8) taken after two years of operation in treating a Lurgi gasifier product indicates limited accumulation of such compounds.⁹

Activated carbonate solution is chemically stable with respect to heavier hydrocarbons (C_5^+). Reactions with olefinic, paraffinic, and cyclic liquid hydrocarbons have not been observed in natural gas treating plants. However, condensation of such compounds can initiate foaming in the solution, as can particulates.^{3,9} This can be avoided through (1) adequate gas disengaging prior to absorption, (2) solution filtration, (3) water and/or oil washing of the gas prior to absorption, and (4) maintaining absorber temperature above the hydrocarbon condensation point.

The other constituents of low-Btu coal gases are essentially unaffected by the activated potassium carbonate solution. The solubility of these compounds (H_2 , CH_4 , CO , N_2) in the Benfield solution is much less than in

water.³ They are not reactive in the solution, with the possible exception of carbon monoxide. At high temperature and low concentration of KHCO_3 and KHS , CO can react with K_2CO_3 to form potassium formate (KCOOH).³ Table 5.8 cites a small amount that was produced in the Westfield unit; this is avoided by lowering the absorption temperature. In cases in which a high temperature is required for maximum COS and CS_2 removal, special techniques and process configurations are needed to avoid the production of potassium formate.³

Essentially no basic data have been published on the Benfield HiPure or activated hot potassium carbonate systems. Much data on unactivated hot carbonate systems have been produced by the original developers at the Bureau of Mines, among others.

Compilations of some of these data in concise tables and charts are available in the literature.²⁹⁻³¹ Because the modified kinetics of activated systems are not reflected in these sources, reported mass transfer rates and other kinetically related information cannot be directly applied to the Benfield activated carbonate systems. For example, data reported by Shrier and Danckwerts on amine-activated potassium carbonate solutions show absorption rates of CO_2 (at 18°C and 1 atm) enhanced by 25% when only 0.1 M (gram mole solute per liter of solution) DEA is added.³² Tests adding about 0.1 M 2-ethylaminoethanol (EAE) have demonstrated absorption rates of CO_2 (at 25°C and 0.1 atm) in the activated solution that were about five times greater than in unactivated carbonate solution.³² Although similar data for the Benfield activated carbonate systems are not available for the conditions of this evaluation (coal-derived, low-Btu gas cleanup at temperatures of $\geq 230^\circ\text{F}$), reaction rates are similarly expected to be enhanced over those in unactivated hot carbonate. This lack of data prevents the accurate design of an activated carbonate system; however, curves have been provided by The Benfield Corporation which allow preliminary estimates of capital costs and utility requirements for Benfield plants.³ These curves are discussed in Sect. 5.2.4.

Table 5.8. Benfield solution analysis^{a,b}

Compound	Weight (%)
Potassium carbonate (K_2CO_3)	22.0
Potassium bicarbonate ($KHCO_3$)	9.8
Potassium formate ($KCOOH$)	2.1
Potassium bisulfide (K_2S)	0.15
Thiosulfate, as sulfur ($S_2O_3^{2-}$)	0.02
Sulfate, as sulfur (SO_4^{2-})	0.02
Thiocyanate (CNS^-)	trace
Suspended solids	15 to 800 ppm

^aTaken after two years of operation at the Westfield, Scotland, Lurgi plant.

^bR. W. Parrish and H. B. Neilson, "Synthesis Gas Purification Including Removal of Trace Contaminants by the Benfield Process," presented at the 167th National Meeting of the ACS, Div. of Ind. and Eng. Chem., Los Angeles, Mar. 31-Apr. 5, 1974.

5.2.4 Process operation and economics

Curves published in a 1974 paper by McCrea and Field (The Benfield Corporation) provide typical operating requirements and capital costs for Benfield HiPure or hot potassium carbonate processes. Costs and utility requirements from these curves are purported to be within about 25% of carefully determined values.³ Although these curves are presented on the basis of CO₂ removal only, McCrea and Field state that reasonable capital cost and utility estimates can be obtained by assuming that the total acid gas (CO₂ and H₂S) consists of CO₂ alone when the CO₂-to-H₂S ratio is greater than 8:1.³ This is typically the case with coal-derived gases, where the CO₂-to-H₂S ratio ranges from 5:1 to 10:1 and above.

Regenerator heat input is a major consumer of energy in a Benfield system. The amount of regenerator heat varies with the degree to which the rich solution at the base of the absorber is converted to KHCO₃, other factors being equal.³ This, in turn, is dependent on the inlet partial pressure of CO₂. Values at the upper limit of the cross-hatched region of Fig. 5.12 represent applications in which excess heat or low-cost fuel is available or in which capital costs are minimized by use of a simple process configuration.³ It is expected that coal conversion facilities will seek to minimize required regenerator heat by incurring a higher capital cost and/or more complex flow pattern; therefore, required heat input will more likely be at the lower limit of the region.

The other major consumer of energy in a Benfield system is the pump that is used to cycle lean solution from the regenerator to the absorber. Required energy is principally affected by the total feed-gas pressure and by the inlet CO₂ partial pressure that influences the amount of CO₂ removed by a given amount of solution (Fig. 5.13). The energy load represents net consumption, assuming that the rich high-pressure solution is let down through a hydraulic turbine to supply some power.³

Rough estimates of the capital costs for Benfield processes in January 1977 (Fig. 5.14) are about 15% higher than those given in McCrea and Fields' paper.³ These estimates reflect two opposing influences since 1974: (1) inflation causing cost increases, and (2) process improvements

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Fig. 5.12. Typical regeneration energy required by Benfield processes.

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Fig. 5.13. Typical pumping energy required by Benfield processes.

ORNL DWG 77-1189R

Fig. 5.14. Typical capital costs of Benfield processes.

allowing cost decreases.³³ The costs are on a battery-limits-installed basis, exclusive of capital charges for providing any required utilities.³ Figure 5.14 is not considered sufficiently accurate to show the effect of feed-gas pressure or to differentiate between process configurations.³ The figure also does not provide costs for a Benfield process that is operated to selectively absorb H_2S ; the values shown represent nonselective operation. Conceptual costs have been published for selective H_2S removal, but process variations preclude a curve similar to that of Fig. 5.14. Instead, specific applications are shown in Table 5.9, along with the process parameters that are furnished in the cited references.

Table 5.9. Specific applications of the Benfield process for selective H₂S removal

Reference	Absorber pressure (psia)	CO ₂ (%)		Sulfur (ppm)		Energy consumed (Btu/scf of feed gas)	Capital cost (\$/10 ³ scf of feed gas per day)	H ₂ S in regenerated off-gas (%)
		Inlet	Exit	Inlet	Exit			
3	415	11.00	8.71	5800	100	13.3	7.2 ^a	20
3	315	13.90	10.39	7600	540	7.8	5.8 ^a	17
3	130	7.47	5.28	8000	170	11.1	5.6 ^a	26
4	b	b	b	b	750	6	13.16 ^c	22.9
4	b	b	b	b	210	10	13.79 ^c	19.7
4	b	b	b	b	100	11	16.12 ^c	b
4	b	b	b	b	50	15	18.02 ^c	b
4	b	b	b	b	40	13	30.62 ^c	17.1
34	290	13.89 ^d	12.17 ^d	7800 ^d	1000 ^d	b	9.0 ^{a,d}	25.0 ^d
35	315	9.5 ^d	6.7 ^d	6500 ^d	1100 ^d	6.4	7.5 ^{a,d}	15 ^d
35	315	9.5 ^d	8.0 ^d	6500 ^d	1100 ^d	9.8	9.3 ^{a,d}	25 ^d

^aCost escalated 15%, mid-1974 to first quarter 1977.

^bNot available.

^cCost escalated 5%, fourth quarter 1975 to first quarter 1977.

^dCalculated on dry gas basis.

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5.3 The Stretford Process

5.3.1 Background

The original Stretford process was developed in England during the early 1960s to remove hydrogen sulfide from coal-derived fuel gas.^{1,2} W. C. Holmes and Company, Limited, was appointed a licensee by the North Western Gas Board (England).³ Holmes and Company (now Peabody Holmes, a subsidiary of Peabody International Corporation) introduced various innovations, including gas pretreatment, sulfur recovery, and waste-liquor treatment; hence, the process marketed by Peabody Process Systems is referred to as the Holmes-Stretford Process.^{1,3} Other firm market variations of the Stretford process [e.g., Woodall-Duckham (USA), Limited, and Black, Sivalls, and Bryson, Inc.].⁴ Where information is available, a distinction is made between the types of Stretford processes offered by the various vendors.

The Stretford process has been applied to coal-derived gases from coal gasification and coke production, refinery gases, natural gas, and syngas.^{2,4} Over 50 plants are operating worldwide, with plant gas capacities from 0.1×10^6 to 200×10^6 scfd.⁴ Sulfur removal rates range from 0.5 tons/day to 90 tons/day.⁴ The largest single-train Stretford plant has been reported to handle 30 tons/day of sulfur, although larger units have been planned or are under construction.⁴ Woodall-Duckham reported an 80 tons/day, single-train Stretford plant under construction in Japan.⁴ Peabody has a design available for a 90 tons/day, single-train unit.⁵ Peabody Holmes has built 17 Stretford units to treat coal-derived gas (Table 5.10).^{1,6}

Advantages of the Stretford process include (1) complete selectivity for the removal of H_2S in the presence of CO_2 , (2) operability at H_2S concentrations in the feed gas ranging from 0.03 to 95 vol %, (3) nil effect of absorber pressure on operation, (4) removal of H_2S to less than 1 ppm, and (5) direct production of salable sulfur.^{4,7,8}

Major disadvantages of the Stretford process involve (1) side reactions, generating sodium thiocyanate from hydrogen cyanide in the feed gas, sodium thiosulfate, and sodium sulfite, which require additional

Table 5.10. Holmes-Stretford plants by Peabody Holmes
for coal-derived gases

Installation site	Year installed	Gas rate (10 ⁶ scfd)	Sulfur rate (tons/day) ^a
Coke-oven gas ^b			
Zeebrugge, Belgium	1965	11.0	4.5
Hamilton, Canada	1966	28.0	6.2
Ebbw Vale, Wales	1967	2.9	0.5
Hartlepool, England	1968	2.6	0.78
Ravenscraig, Scotland	1969	4.5	1.10
Orgreave, England	1970	26.0	14.6
Smithywood, England	1970	9.0	4.1
Hamilton, Canada	1970	14.0	2.95
Parkgate, England	1971	5.0	2.8
Sicartsa, Mexico	1974 ^c	26.0	6.2
Redcar, England	1974 ^c	43.2	20.8
Coal-gas ^d			
Whitchurch, England	1958	0.25	0.21
Liverpool, England	1960	6.0	3.36
Bristol I, England	1960	9.0	3.76
Bristol II, England	1961	9.0	3.76
Producer-gas ^e			
Johannesburg, South Africa	1965	6.0	1.99
Coal liquefaction off-gas			
Cresap, West Virginia	1975	0.4	0.75

^a 1 ton = 2000 lb.

^b Typical dry gas composition: 54% H₂, 30% CH₄, 7% CO, 2.8% CO₂, 1.0% H₂S, 0.2% HCN, 5% N₂.

^c Reported under construction.

^d Dry gas composition similar to coke-oven gas.

^e Typical dry gas composition: 15% H₂, 1% CH₄, 30% CO, 3.2% CO₂, 0.8% H₂S, 50% N₂.

treatment and/or disposal, and (2) relatively high solution circulation rates resulting from the low H_2S loading permitted.^{2,4,9}

5.3.2 Process description

Two basic Stretford plant designs are used, depending on the desired handling of any HCN. Hydrogen cyanide reacts irreversibly with Stretford solution, forming sodium thiocyanate. If large amounts are expected in the feed gas, a separate column can be specified to remove 97% of the HCN before it reaches the Stretford absorber, thereby preventing excessive purge treatment requirements in the Stretford system.¹⁰ If the HCN content is low, or if capital cost savings are more desirable than operating cost savings, the cyanide wash column is not used; a Stretford process flowsheet for this option is provided in Fig. 5.15.⁴

The basic Stretford process consists of (1) an absorber, (2) at least one oxidizer, (3) a sulfur removal process (filtration or centrifugation), (4) a method for handling Stretford purge solution, and (5) associated pumps, air blowers, and makeup equipment. The specific flowsheet chosen depends on the application and the refinements offered by the process vendor; therefore, many variations are possible on the design shown in Fig. 5.15. For example, several approaches to the treatment of Stretford solution purge liquor have been examined. The stream can be combusted in an excess of air, so that the residue is then suitable for disposal.¹¹ Laboratory tests have shown that the selective removal of over 93% pure sodium thiocyanate from spent Stretford solution is another possible treating method.¹¹ The method shown in the flowsheet (Fig. 5.15) is reductive incineration. In the Woodall-Duckham approach, purge liquor is combusted with a carefully controlled deficiency of air.^{4,11} Most of the thiocyanate and thiosulfate salts are converted to H_2S and Na_2CO_3 . The H_2S off-gas is recycled to the absorber feed while regenerated carbonate, caustic, and vanadium is mixed with fresh anthraquinone disulfonic acid (ADA) and returned to the absorber.^{4,11} Similarly, the zero-discharge process developed by Peabody Holmes in 1973 uses reductive incineration to crack the Stretford purge solution and recover vanadium and sodium salts.¹ Such reductive incineration of the purge liquor may not be required when feed gas HCN content is low. When HCN content is below 50 ppm, the small

Fig. 5.15. Stretford process flowsheet without HCN absorber.

purge that is generated can be disposed of by quenching gasifier bottom ash or by adding to coal that is fed to a gasifier.⁴

Alternate methods of sulfur treatment also exist, depending on the sulfur quality desired, the total sulfur production, and the cost of utilities.⁷ Large sulfur production rates may favor the use of one or more stages of centrifugation followed by melting the wet sulfur cake to produce high-grade molten sulfur; an autoclave can be used for the melting step.^{2,7,12} Filtration may also be used to recover a sulfur cake that can be melted to produce high-grade sulfur.^{2,7,13} Low sulfur throughputs can favor the disposition of sulfur as a wet cake.⁷ A recent innovation by Peabody incorporates a small, high-throughput centrifuging filter that offers advantages of small size and improved operability.¹⁴

The number and location of other tanks for storage and surge also vary. Absorber and oxidizer configurations are flexible as well. In some cases venturis can be used for absorption and/or oxidation, thereby allowing more compact plants to be built.^{3,14} Other available flowsheets are furnished in Sect. 5.3.4 to illustrate the specific process variation for which costs are provided.

5.3.3 Process data

Stretford solution is an aqueous mixture of ADA, sodium vanadate (NaVO_3), and sodium carbonate (Na_2CO_3), with other additives (e.g., citric acid) used in some variations.^{2,4,8,9} The idealized reactions which serve to remove H_2S from a gas stream are represented by:^{2,4,8}

where $\text{ADA}(\text{H}_2)$ represents the reduced form of ADA. Reactions (13) through (17) generally involve the ionized forms of the reactants in aqueous solution.¹⁴ The sum of these reactions gives the overall H_2S removal reaction

In this sequence of reactions (1) hydrogen sulfide is absorbed by sodium carbonate; (2) the reaction product is oxidized to free elemental sulfur via reduction of vanadium from pentavalent to quadrivalent oxidation state; and (3) the reduced vanadium is oxidized by reduction of ADA. Air is blown through the solution in the oxidizer vessel to reoxidize the reduced ADA. The rate of H_2S absorption increases in more alkaline solutions (i.e., high pH). However, pH values above 9.5 are unfavorable for conversion to elemental sulfur, as shown in Eq. (14). The process is generally operated in the pH range 8.5 to 9.5.²

The rate of conversion of hydrosulfide to elemental sulfur [Eq. (14)] is a function of vanadate concentration and solution pH.² Reaction rate is shown in Fig. 5.16 as a function of vanadate concentration. This follows the reaction rate equation of Thompson and Nicklin:¹⁵

$$\underline{t} = 1/\underline{K}(\underline{a}-\underline{b}) \times \ln[\underline{b}(\underline{a}-\underline{x})/\underline{a}(\underline{b}-\underline{x})] , \quad (19)$$

where $\underline{t}$ = time in minutes for reaction of $\underline{x}$ moles per liter hydrosulfide,

$\underline{K}$ = reaction rate constant, $[(\text{mole/l})(\text{hr})]^{-1}$,

$\underline{a}$ = initial vanadium concentration, (mole/l),

$\underline{b}$ = initial hydrosulfide concentration, (mole/l),

$\underline{x}$ = hydrosulfide reacted, (mole/l).

The reaction rate constant in Eq. (19) is a function of solution pH; values for $\underline{K}$ are provided in Fig. 5.17.² Using common commercial values for solution pH and vanadate concentration, curves can be obtained for reaction time as a function of the percent hydrosulfide converted to sulfur for various initial hydrosulfide concentrations.² Curves for a vanadate concentration of 0.01 M and pH of about 8.5 (corresponding to a $\underline{K}$ of 6000 from Fig. 5.17) are shown in Fig. 5.18.²

ORNL DWG 77-1397 R

Fig. 5.16. Rate of conversion of hydrosulfide as a function of vanadate concentration.

ORNL DWG 77-1391R

Fig. 5.17. Effect of pH on hydrosulfide reaction rate constant.

Fig. 5.18. Reaction time for conversion of hydrosulfide to sulfur under typical conditions.

Two moles of sodium vanadate are required to oxidize each mole of sodium hydrosulfide to sulfur. To prevent unreacted sodium hydrosulfide from reaching the oxidizer, where the undesired side reaction to thiosulfate readily occurs, vanadate concentration is maintained at about 10% in excess of the stoichiometric requirement.^{8,9} Because the quadrivalent vanadium can form a complex vanadium-oxygen-sulfur precipitate, various additives have been used to maintain solubility of the vanadium.^{2,4,9} Citric acid has been found effective and chemically stable as a complexing agent and is specified in the Holmes-Stretford process.^{4,9}

Another reported solution additive is iron salts. Small amounts of iron salts (about 50 to 100 ppm), solubilized by chelation with about 2700 ppm ethylene diamine tetracetic acid (EDTA), appreciably increase the rate of ADA reoxidation.²

Several side reactions occur in the Stretford process which degrade the treating solution. When HCN is negligible in the feed gas, the major problem is formation of thiosulfate, represented by:

Any SO_2 present in the feed gas also degrades the solution, as shown by the following reaction:⁴

The compounds in Eqs. (20) and (21) build up in solution and reduce the ability of the system to remove H_2S ; therefore, a purge stream is required, either for further treatment to recover chemicals or for disposal. Formation of sodium thiosulfate [Eq. (20)] is a function of solution temperature, solution pH, and the amount of unreacted hydrosulfide carried to the oxidizers, and it can be controlled to below 1% of the sodium hydrosulfide by proper plant operation.^{2,10} The effects of solution temperature and pH on the relative amount of thiosulfate formed are shown in Fig. 5.19.

When cyanide is present in the feed gas in large quantities, a substantial increase in purge requirements results from the reaction of HCN to sodium thiocyanide:⁹

ORNL DWG 77-1396R

Fig. 5.19. Relative production of thiosulfate as a function of temperature and pH.

As an example, a gas containing 1000 ppmv HCN will increase the purge stream by more than a factor of ten over that required by thiosulfate formation.¹⁰ A high HCN content is typical of coke-oven gases, and a separate HCN removal column is recommended prior to the H₂S absorber. For a 50 x 10⁶ ft³/day coke-oven gas containing 10,000 ppmv H₂S and 1000 ppmv HCN, the effect of using a column for separate removal of HCN via the Holmes polysulfide process is shown in Table 5.11.^{3,10}

Table 5.11. Stretford solution degradation by HCN

Parameter	Without HCN pretreat		With Holmes polysulfide process for removing HCN	
	H ₂ S	HCN	H ₂ S	HCN
Component				
Concentration, ppmv	10,000	1000	10,000	30
Assumed degradation rate, %	1	100	1	100
Sulfur unregenerable, lb/day	450	4500	450	135
Purge volume, gal/day	6000		700	

The amount of HCN expected in gases produced by the gasification of coal is not quantitatively established. It is known to vary with gasifier temperature, gas residence time, and other parameters; however, several estimates of HCN contents have been sufficiently high to require effluent treating for recovery of Stretford chemicals via reductive incineration.^{4,9} Economic requirements for a separate HCN absorber have yet to be demonstrated.

The last major constituent of coal-gas streams that may introduce problems is CO₂. Carbon dioxide is absorbed into sodium carbonate solution to form sodium bicarbonate. Because the solution pH is lowered, the solution H₂S absorption efficiency is lowered. This can significantly increase the absorber height required to maintain the same effectiveness.^{2,9}

Very little of the organic sulfur compounds COS and CS₂ are removed by the Stretford process; however, most of the methyl mercaptan is removed.³ Ammonia will dissolve in solution but does not chemically degrade the solution. However, when large concentrations on the order of 300 ppmv NH₃ are present in the feed gas, precautions are required to prevent release of NH₃ to the atmosphere in the solution oxidizer.¹⁰

Tars and oils can also interfere with the proper operation of a Stretford plant; therefore, if large quantities are present, pretreatment (e.g., electrostatic detarrer and oil scrubbers) is recommended prior to the H₂S absorber.¹⁰

5.3.4 Process operation and economics

The Stretford process is generally operated with feed-gas temperature from ambient to 120°F. Absorber pressure can range from near atmospheric to very high values without affecting process operability.^{4,7} Carbon steel construction is suitable for the Stretford process; however, inert linings such as epoxy resins are required for oxidizers and sulfur slurry tanks. Use of stainless steel linings for solution and sulfur slurry pumps is also recommended.²

Several conceptual estimates of the required operating and capital costs have been published for the Stretford process, as applied to coal-derived gases. For this evaluation, the two basic direct applications to a process gas, rather than an off-gas from an amine plant, for example, are for treating coke-oven gas and low-Btu fuel gas from coal.

Design parameters which directly affect the economics for the Stretford process include (1) allowable hydrosulfide loading of the solution, which sets the circulation rate and pumping costs, etc., and (2) required residence times in the various plant operations, which affect equipment sizes. Hydrosulfide loadings in solution up to 1000 ppm are reported for coke-oven gases. This translates to required solution circulation rates of 120 gal/lb of sulfur, as a minimum. Examples cited by Ellwood, for coke-oven gas and manufactured gas, report rates of 130 gal/lb of sulfur and 175 gal/lb of sulfur respectively.⁸

A. L. Kohl and F. C. Riesenfeld report that a residence time of 10 to 20 min is required in the base of the absorber or in a separate holding tank to permit maximum conversion of hydrosulfide to sulfur prior to entering the oxidizer.² This value can be obtained from Fig. 5.18. Ellwood reports that a 5-min delay is required after the addition of oxygen in the oxidizer to permit final ADA reoxidation.⁸ To remove essentially all H_2S from 14×10^6 ft³/day of coke-oven gas that contains 4400 ppmv H_2S requires an absorber 97 ft in height and 12 ft in diameter. The column is packed with four layers of wooden grids, each about 12 ft in height. The bottom 24 ft of the absorber is used as the holding tank to allow final conversion of hydrosulfide to sulfur.²

Recent cost estimates for Stretford treating of a coke-oven gas are given by Massey and Dunlap.¹¹ Table 5.12 lists the costs provided for three cases: (1) treating 20×10^6 scfd, (2) treating 60×10^6 scfd of coke-oven gas containing 8000 ppmv H_2S and 1200 ppmv HCN without HCN or effluent treatment, and (3) treating 60×10^6 scfd of the same gas with reductive incineration of the solution purge stream.¹¹ The economics reflect the state of the art as of second quarter 1974.¹¹ Costs on a first quarter 1977 basis are likely to be 30 to 50% higher because of inflation.

Several estimates are also available for applications of the Stretford process to low- and medium-Btu gases generated in coal gasifiers. S. Vasan and H. P. Willett have reported costs for a Holmes-Stretford plant with reductive incineration of the solution purge stream for treating a low-Btu gas from high-sulfur (4%) coal.⁶ The feed gas contains about 7000 ppmv H_2S . Required utilities and capital cost are shown in Table 5.13.⁶

Wilputte Corporation has published capital costs for various Holmes-Stretford plants treating a low-pressure coal gas generated in air-blown gasifiers.¹⁶ Costs are provided for treating gas derived from 3% sulfur bituminous coal and 0.7% sulfur lignite, at atmospheric pressure. Again, a purge liquor treating unit is included for recycling vanadium and sodium salts.¹⁶ The capital costs for various gas throughputs are shown in Table 5.14. Escalation from the report date to first quarter 1977 is less than 5% and is not included. Wilputte does not provide separate utility requirements for the H_2S removal plants.

Table 5.12. Economics of Stretford process
treating coke-oven gas^a

Parameter	Without HCN or solution purge treatment		Reductive incineration of purge included
Capacity, 10 ⁶ scfd	20	60	60
Operating costs			
Power, \$0.014/kWhr	64.60	186.20	252.00
Cooling water, \$0.12/1000 gal	-	-	2.16
Steam, \$1.50/1000 lb	43.20	95.04	237.60
Labor			
Operator, \$7.00/hr	84.00	84.00	168.00
Chemist, \$6.00/hr	12.00	12.00	12.00
Maintenance at 3% fixed investment per year, \$/day	119.18	230.14	238.56
Chemical makeup, \$/day	<u>53.36</u>	<u>150.08</u>	<u>668.28</u>
Total, \$/day	376.34	757.46	1578.60
Capital costs			
Investment, \$10 ⁶	1.45	2.88	3.45
Amortized at 7% DCF over 20 years, \$/day	375	724	892
Total annualized costs			
\$/day	751.34	1481.46	2470.60
\$/10 ⁶ scfd	37.57	24.69	41.18

^aFeed gas contains 8000 ppmv H₂S and 1200 ppmv HCN.

Table 5.13. Operation and cost of a conceptual
Holmes-Stretford plant for treating low-Btu coal gas

Design basis

Low-Btu coal-derived gas, 100×10^6 scfd
 Feed gas H_2S content, 7000 ppmv
 8000 hr on-stream operation per annum
 30 tons/day sulfur produced (no sulfur credit assumed)

Utilities

Holmes-Stretford chemicals (organics at \$3.50/lb)	12 lb/hr
Power	2500 hp
Steam (100 psi for sulfur melting)	1800 lb/hr
Fuel (purge solution treating)	5×10^6 Btu/hr

Estimated capital cost

December 1974	\$4 million to 4.5 million
January 1977	\$4.6 million to 5.1 million

Table 5.14. Holmes-Stretford process capital costs
for varying coals and capacities^a

Number of gasifiers	Gas produced, 10^6 scfd		Capital cost, \$	
	Bituminous	Lignite	Bituminous	Lignite
1	7.2	4.25	940,000	660,000
2	14.4	8.50	1,200,000	770,000
4	28.8	17.00	1,750,000	940,000
6	43.2	25.50	2,300,000	1,200,000

^aDesign basis: 3% sulfur bituminous coal, 0.7% sulfur lignite,
and 165 Btu/scf gas heating value.

Dravo Corporation has developed typical utility requirements for treating a feed gas containing about 1% H_2S and 0.2% HCN with reductive incineration of the purge liquor; these are listed in Table 5.15, based on 1×10^6 scf of feed gas.^{4,9}

A Battelle-Columbus Laboratories report includes three vendor responses to a request for Stretford design and cost information; the responses vary in degree of completeness and accuracy.⁹ The application is for the removal of H_2S from a low-Btu gas produced in an air-blown coal gasifier at about 300 psig. The specifications provided the vendors and their responses are listed in Tables 5.16 and 5.17. Capital costs have been escalated about 15% to first quarter 1977 values. The capital cost provided by R. M. Parsons includes cleaning and cooling the gas prior to the Stretford absorber, which accounts for about 50% of the total plant cost.⁹ Consumption of ADA and citric acid (reported by Peabody Process Systems) is estimated to increase four to five times if reductive incineration of the purge liquor is specified; capital cost is also increased 10 to 15%.⁹ However, vanadium and sodium salt consumption would be essentially eliminated by such treatment.⁶ Battelle-Columbus has calculated power requirements for the R. M. Parsons and the Peabody estimates by assuming a circulation rate of 200 gal/lb of sulfur;⁶ this is in line with the permissible hydrosulfide loading in solution.⁸

D. A. Waitzman et al., (Tennessee Valley Authority) have reported capital and operating costs for two Stretford applications.¹³ Both systems are designed for removal of H_2S from low-Btu coal gases, one at 9 psig on gas from a Wellman-Galusha gasifier and the other at 270 psig on gas from a Lurgi gasifier.¹³ The conceptual flowsheet for these Stretford plants and the material balances and operating conditions are shown in Fig. 5.20. Utilities consumptions and economics are given in Table 5.18. Costs are reported by TVA in 1975 values and have been escalated 10% to first quarter 1977 values for Table 5.18. Costs allowed by TVA for contingencies, startup and modifications, and the purchase of power during the tie-in period will vary with the specific application; therefore, these costs are not included in the total capital cost (Table 5.18). Similarly, costs associated with interest during construction reflect a utility-type financing and are not included.

Table 5.15. Typical Stretford utility requirements^a

	Quantity
Chemical	
ADA	5 lb
Sodium vanadate	0.06 lb
Citric acid	10 lb
Power	19 kWhr
Steam, 50 psig	730 lb
Fuel gas, 50% H ₂	4 x 10 ⁶ Btu
Water	2,160 gal

^aUtility consumption per 10^b scf of feed gas.

Table 5.16. Stretford process treating
300 psig low-Btu coal gas

Component	Composition		Condition	
	lb-mole/hr ^a	Vol %		
H ₂	2,008.7	18.51	Temperature	1100-1200°F
CO	1,906.2	17.57	Pressure	300 psig
CO ₂	973.6	8.97	Sulfur (H ₂ S)	2133 lb/hr
CH ₄	276.7	2.55	Dust	572 lb/hr
C ₂ H ₆	25.6	0.24	Tar	991 lb/hr
N ₂	4,991.0	46.00	HHV	150 Btu/scf
H ₂ S	66.6	0.61		
H ₂ O	<u>602.2</u>	<u>5.55</u>		
	10,850.6	100.00		

^aMole wt = 23.82; lb/hr = 258,433.

Table 5.17. Stretford plant characteristics

Vendor	Utilities				Capital cost (\$10 ⁶)
	Chemicals	Power	Steam	Cooling water	
J. F. Pritchard	\$300/day	2800 kW	5900 lb/hr	750 gpm	6.6
R. M. Parsons	40 lb/day ADA 30 lb/day vanadium 5800 lb/day Na ₂ CO ₃	a	5000 lb/hr	850 gpm	5.9
Peabody Engineered Systems	20 lb/day ADA 16 lb/day vanadium 300 lb/day Na ₂ CO ₃ 60 lb/day citric acid	a	a	a	4.0-4.6 ^b

^aNot available.

^bReductive incineration of purge liquor adds 10 to 15% to the capital cost.

GASIFIER:	WELLMAN / GALUSHA				LURGI			
STREAM:	1. FEED	GAS	2. TREATED	GAS	1. FEED	GAS	2. TREATED	GAS
COMPOSITION	LB / HR	VOL %	LB / HR	VOL %	LB / HR	VOL %	LB / HR	VOL %
H ₂	21,000	14.06	21,000	13.70	32,600	23.73	32,600	23.88
N ₂	1,012,900	48.73	1,012,900	47.47	773,900	40.56	773,900	40.80
H ₂ O	74,600	5.58	119,300	8.70	4,200	0.33	6,000	0.50
CH ₄	27,900	2.35	27,900	2.29	54,000	4.94	54,000	4.97
CO	486,700	23.43	486,700	22.82	301,800	15.82	301,800	15.92
CO ₂	168,200	5.15	168,200	5.02	414,900	13.84	414,900	13.93
H ₂ S	17,600	0.70	30	0.001	18,000	0.78	20	0.001
TOTAL, LB/HR	1,808,900		1,836,000		1,599,400		1,583,200	
10 ⁶ SCFH	26.63		27.34		24.45		24.30	
PRESS., PSIG	9		4		270		260	
TEMP., °F	100		115		100		115	
SULFUR PRODUCTION:	16,550 LB / HR				16,980 LB / HR			

Fig. 5.20. Stretford plant flowsheet and material balances in TVA evaluation of low-Btu gas applications.

Table 5.18. Stretford plant utility requirements and economics
in TVA evaluation of low-Btu gas applications

Parameter	Wellman-Galusha	Lurgi
Utilities		
Chemicals, \$/hr	59.70	56.00
Power, kW	6260	15,161
Steam, lb/hr	38,000	36,000
Water, gpm	7,204	6,754
Labor		
Operators, man-hours/hr	1.5	1.5
Analysts, man-hours/hr	0.28	0.28
Capital investment, \$10 ⁶		
Direct capital (battery limits)	20.76	23.20
Engineering design and supervision	2.49	2.78
Field construction expense	2.70	3.02
Contractor fee	1.45	1.62
Chemicals initial charge	0.51	0.49
Royalty	<u>0.55</u>	<u>0.61</u>
	28.46 ^a	31.72 ^a

^aLess contingency, startup, modifications, and interest during construction.

S. Kimmel et al. (Fluor Engineers and Constructors, Inc.) have also published operating and cost data for Stretford processes applied to coal gasification at low pressure.¹² Gasification of Illinois No. 6 bituminous coal with about 4.3% sulfur is assumed in an atmospheric entrained-bed gasifier, such as one being developed by Combustion Engineering.¹² Both air- and oxygen-blown gasification evaluations are included. Air-blown gasification requires four parallel Stretford treating plants; oxygen-blown gasification requires three.¹² The flowsheet common to both operations is shown in Fig. 5.21. The material balances, operating conditions, and economics of these operations are listed in Table 5.19 for one required train from each case. Costs for each single train have been escalated 10% to first quarter 1977. The gases are treated to reduce sulfur content to the equivalent of 1.0 lb SO₂ per million Btu of coal that is fed to the gasifiers.¹² Design for essentially complete H₂S removal would increase the Stretford plant sizes by about 10%.¹² The plant sizes specified for each train are two to three times the current 30 tons/day of sulfur maximum, although they are within the conceivable design limits for single-train Stretford units.^{4,5}

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Fig. 5.21. Stretford flowsheet for low-pressure H_2S removal.

Table 5.19. Operation and economics of Stretford processes
for low-pressure H₂S removal

Parameter	Air case		Oxygen case	
	(lb-mole/hr)	(vol %)	(lb-mole/hr)	(vol %)
Feed gas composition				
CH ₄	0.2	0.00	12.7	0.05
H ₂	4,718.0	10.78	7,147.2	27.60
CO	9,350.3	21.37	15,083.7	58.26
CO ₂	2,138.5	4.89	581.9	2.25
H ₂ O	3,183.3	7.27	2,476.7	9.57
H ₂ S	226.0	0.52	300.8	1.16
COS	14.0	0.03	21.1	0.08
N ₂	24,131.2	55.14	266.9	1.03
NH ₃	0.4	0.00	0.3	0.00
	42,762.3		25,891.3	
Molecular weight	25.31		20.33	
Total, lb/hr	1,107,455		526,360	
Feed gas condition				
Pressure, psia	13.2		13.3	
Temperature, °F	109		110	
Treated gas conditions				
Pressure, psia	12.4		12.6	
Temperature, °F	110		110	
Sulfur produced, lb/hr	6433		8655	
Utilities reported				
Steam (240 psig), lb/hr	5395		7667	
Capital cost, \$10 ⁶	5.66		6.73	

5.3.5 References

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5.4 The Sulfinol Process

5.4.1 Background

The Sulfinol process was announced by the Shell Development Company in 1963. The first commercial application was in the Person oil field separator gas treating plant in Texas (1964), where it replaced the original monoethanolamine (MEA) treating solution.^{1,2} Over 100 additional Sulfinol plants have come onstream since the inception of the process.¹ About 110 Sulfinol units are currently reported operating worldwide, with about 80 of these operating in the United States and Canada. Five of these units are designed for selective removal of H_2S .³ E. J. Fisch et al. have provided a breakdown of the plants that are (1) operating, (2) under construction, or (3) under contract at the time of their paper, and they have listed the plants according to the type of gas being treated.¹ The breakdown of Sulfinol units is shown in Table 5.20.

The major advantages claimed for Sulfinol over conventional amine gas treating include:^{4,5}

1. lower solvent circulation rates;
2. reduced equipment sizes (thus lower plant cost);
3. lower solution heat capacity;
4. lower utility consumption;
5. lower solution degradation rates;
6. lower corrosion rates;
7. lower foaming tendency;
8. high efficiency removal of CO_2 , CS_2 , and mercaptans;
9. lower solvent vaporization losses;
10. lower heat exchange surface fouling; and
11. nonexpansion of the solution in freezing conditions.

Many of these properties are interrelated (e.g., lower circulation rates naturally lead to reduced equipment sizes and lower utility requirements).

Table 5.20. Sulfinol units, present and planned

Process	Units ^a
Hydrogen purification	
Steam reforming	29
Shell gasification (petroleum feedstock)	11
Coal gasification (Coalcon) ^{b,c}	1
Other gasification	4
Ethane treating	6
Natural-gas treating	
Dry gas	24
Wet gas ^{d,e}	15
LNG	1
Selective H ₂ S removal	5
Unclassified	<u>6</u>
	102

^aIn many cases there are several units at a given installation.

^bPlanned for Union Carbide Corp. Coalcon (coal conversion) demonstration plant (indefinite at present).

^cE. J. Fisch, Shell Oil Co., Houston, personal communication, Aug. 1, 1977.

^dWet natural gas contains significant amounts of C₃⁺ hydrocarbons (≥6% of total hydrocarbon content).

^eA. H. Younger, "Processes for Sour Natural Gas Treating," presented at Symposium on Sulphur Recovery from Hydrocarbon Feedstocks, Vancouver, British Columbia, Sept. 11, 1973.

Principal disadvantages stated for the Sulfinol process, as compared to amine systems, are:^{4,5}

1. absorption of heavy hydrocarbons (especially aromatics),
2. much higher solvent cost,
3. higher degree of plant housekeeping, and
4. a requisite royalty to the Shell Development Company.

Elaboration of the advantages and disadvantages of the Sulfinol process is provided in subsequent sections.

5.4.2 Process description

A Sulfinol process flowsheet typical of the Sulfinol process when treating a high-pressure gas is shown in Fig. 5.22. At high pressure, a significant amount of nonacid-gas components are physically dissolved in the Sulfinol solution that is passing countercurrent to the rising gas. This is principally evident with heavier hydrocarbons, but even light hydrocarbons like methane and ethane are absorbed to a small degree. The rich Sulfinol solution, after pressure letdown through a power recovery turbine, can be sent to a flash tank.⁶ Most of the dissolved fuel gas components are released at the lower pressure in the flash tank; these can be recompressed and recycled to the Sulfinol absorber or used as fuel gas in the plant.⁶ If the acid-gas content of the flash gas exceeds allowable limits for sulfurous gases, a small fuel gas scrubber can be incorporated into the process design. The flash gas can be treated to desired purity with a side stream of lean Sulfinol solution. The various options for handling flash gas are shown in Fig. 5.22.

The rich solution exiting the flash tank is preheated, before entering the top of the regenerator, by heat exchange with the lean solution that is exiting from the regenerator bottom. The rich Sulfinol solution is reduced to near atmospheric pressure (typically 5 to 10 psig) in the regenerator, and absorbed gases are stripped by a combination of the reduced pressure and ascending steam. Much of the water vapor in the overhead stream of the regenerator is condensed by the reflux condenser; reflux is returned to the top of the regenerator and remaining acid gases

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Fig. 5.22. Typical Sulfinol flowsheet for high-pressure absorption.

are sent to sulfur recovery. The bottoms stream of the regenerator is reboiled to strip residual acid gases. A small portion of the solution is sent to the reclaimer to recover a portion of the degraded amine constituent of Sulfinol solution. The net bottoms product of lean Sulfinol solution is first cooled by countercurrent heat exchange with the rich solution. After additional cooling, the lean solution is pumped to the top of the acid-gas absorber.

In Fig. 5.22 the lean solution cooler and the reflux condenser are shown as being water cooled. Air cooling can be substituted when minimal use of cooling water is desired.^{1,6} Although not shown in the flowsheet (Fig. 5.22), a cartridge filter rated at 2- to 4- μ m retention is typically employed to remove iron sulfide and other small particles that may accumulate in the solution.⁷ A side stream of about 5% of the solvent circulation is diverted through this filtering loop.⁷ A. H. Younger shows the side stream loop for filtration from the discharge side to the suction side of the lean solution pump.⁸ Required Sulfinol solution makeup can be added to the solution regenerator.⁹ Solution addition is required to make up mechanical and vapor losses, as well as minor unreclaimable degradation losses of the amine constituent of Sulfinol solution.⁷

When the Sulfinol process is used to treat gases at lower pressure and/or low hydrocarbon content, the intermediate flash step can be avoided. The concern here is not the loss of valuable fuel components but, rather, the hydrocarbon content of the regenerated acid gas. When the feed gas contains aromatic hydrocarbons at or above 0.3 mole %, the evolved acid gases will probably require treatment by charcoal adsorption before being processed in a Claus-type sulfur recovery plant.⁷ A charcoal adsorption unit will be required if the acid gas has a total hydrocarbon content of more than 2 mole % of the H_2S and/or a C_5^+ hydrocarbon content above 0.5 mole % of the H_2S .⁷ Such levels of hydrocarbons lead to carbon formation in conventional Claus plants, causing (1) Claus catalyst deactivation by carbon deposition, (2) increased pressure drops through the Claus plant, and (3) discoloration of the produced sulfur.^{10,11} When acid-gas absorption is at lower pressure, the utility of hydraulic power recovery turbines on the rich Sulfinol solution is diminished.

5.4.3 Process data

The Sulfinol solution contains three components in proportions that are varied to satisfy the specific, desired applications.¹² The physical solvent is sulfolane (tetrahydrothiophene dioxide).¹ When used in a Sulfinol plant that is treating sour natural gas, the concentration of sulfolane may range from 10 to 50% by weight.⁹ The chemical solvent is an alkanolamine (usually DIPA) at a concentration similar to that of sulfolane in treating natural gas.^{1,8} The remaining solution consists of water.

The limited data on physical properties of Sulfinol solution lists the heat capacity of Sulfinol solution at 150°F as 0.678 Btu/lb · °F, the viscosity at the same temperature as 4.6 cP, and the freezing point of the solution as about 28°F.⁴ Although specific vapor pressures are not disclosed, both sulfolane and DIPA are reported to have extremely low vapor pressures at normal absorber temperatures.^{2,4} Lean solution temperature is dependent on the specific application but typically ranges from 100 to 125°F.¹³ In one application treating a CO₂-rich gas, total vapor and degradation loss of DIPA was about 1 lb/10⁶ scf of gas; sulfolane mechanical and vapor loss in the same plant was about 0.6 lb/10⁶ scf.⁴ In a review of the first gas plant using Sulfinol treating, C. L. Dunn et al. report an overall solution loss of 0.5 lb/10⁶ scf of feed gas.²

In Fig. 5.23, the equilibrium solubilities of carbon dioxide and hydrogen sulfide in sulfolane and in Sulfinol solution are shown as a function of gas partial pressure; solubilities in 15 wt % MEA in water solution are shown for comparison.¹⁴⁻¹⁸ The curve for CO₂ in sulfolane is extrapolated from a value given by B. B. Woertz at one atmosphere, with the assumption that Henry's Law is applicable.¹⁶ For H₂S and CO₂ at low partial pressures, Sulfinol exhibits lower solvent loadings than MEA. At high acid-gas partial pressures, however, the presence of the physical solvent sulfolane allows much higher solvent loadings than are possible with MEA.

Physical property data on Sulfinol solution are scarce in the open literature (values reported by B. G. Goar previously presented in this

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Fig. 5.23. Acid-gas solubilities in various solvents.

section). However, data on the main constituents of the solution (sulfolane and DIPA) are more readily available. These data are recorded in Table 5.21 for sulfolane and DIPA, and they are shown in Figs. 5.24 through 5.26 for sulfolane only.^{15,19} Figure 5.24 shows the vapor pressure of sulfolane versus temperature, fitting the equation:¹⁵

$$\log_{10}P(\text{psia}) = 28.6443 - \frac{7831.26}{T(^{\circ}\text{F}) + 460} - 6.5633 \log_{10}[T(^{\circ}\text{F}) + 460] . \quad (23)$$

The viscosity and density of sulfolane, both as functions of temperature, are shown in Fig. 5.25.¹⁵ The addition of water lowers the values for both properties. Figure 5.26 demonstrates the lower melting points for sulfolane that result from the addition of water.¹⁵

The absorption of hydrocarbons in Sulfinol solution can produce operating problems and losses of valuable fuel constituents. Data on the first commercial Sulfinol operation (reported by C. L. Dunn et al.) are shown in Tables 5.22 and 5.23, which give the feed gas composition, operating data, and the disposition of hydrocarbons.² The plant treats oil field separator gas and so contains appreciable C_5^+ compounds and relatively low amounts of acid gas. A charcoal treater is required prior to the Claus sulfur plant to remove 90% of the C_5^+ hydrocarbons, for reasons discussed in Sect. 5.4.2.²

Data on the operation of two plants that treat synthesis gas have been reported by J. P. Klein. Such gas is frequently produced by partial oxidation of heavy fuel oil. Table 5.24 presents the operating data for these plants.²⁰ These data show that Sulfinol can remove well over 95% of COS under the conditions presented.

As the solubility curves in Fig. 5.23 demonstrate, the physical aspect of Sulfinol permits high acid-gas loadings at high acid-gas partial pressure. This produces much lower circulation rates than in chemical absorption processes.²¹ The absence of foaming tendency permits operation close to the equilibrium acid-gas content.²¹ Regeneration utility requirements are much lower for the Sulfinol system because (1) the circulation rates in such high-pressure applications are lower than those for chemical systems, (2) the heat capacity is only about 70% of aqueous MEA heat

Table 5.21. Physical properties of sulfolane and DIPA

Property	Sulfolane (tetrahydrothiophene dioxide)	DIPA (diisopropanolamine)
Chemical formula	$(\text{CH}_2)_4\text{SO}_2$	$[\text{CH}_3\text{CH}(\text{OH})\text{CH}_2]_2\text{NH}$
Molecular weight	120.17	133.19
Boiling point, °F at 14.7 psia	545	480
Freezing point, °F	82	108
Flash point, °F (Cleveland Open Cup)	350	260
Critical temperature, °R	1442	a
Critical pressure, psia	767.3	a
Heat of fusion, Btu/lb	4.9	a
Heat of vaporization, Btu/lb		
at 212°F	225	a
at 392°F	205	a
at 14.7 psia	a	184.5
Heat capacity, Btu/lb · °F		
at 86°F	0.31	a
at 212°F	0.35	a
at 392°F	0.40	a
Vapor pressure, psia at 68°F	(Fig. 5.24)	0.0002
Density, lb/gal	(Fig. 5.25)	
at 113°F		8.25
at 131°F		8.21
Viscosity, cP at 113°F	(Fig. 5.25)	198

^aNot available.

Fig. 5.24. Vapor pressure of sulfolane.

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Fig. 5.25. Viscosity and density of sulfolane. Sulfolane containing 3 wt % water (W) is depicted by dashed curves.

Fig. 5.26. Melting point of sulfolane-water mixture.

Table 5.22. Gas composition data from first Sulfinol plant^a

Species	Feed gas (mole %)	Amount of feed gas species removed by solution (%)	Acid gas (mole %)
C ₁ -C ₄	90.27	0.1	1.20
C ₅ ⁺	0.707	6	0.50
Aromatics (B, T, X)	0.023	95	0.20
Total hydrocarbons	91.00	0.16 ^b	1.90
CO ₂	6.90	>97 ^b	80.1
H ₂ S	1.60	>99 ^b	18.0
COS	(7 ppm)		
RSH	(19 ppm)	>95 ^b	
N ₂	0.50		

^aBecause of discrepancies between observed and calculated values, gas composition data are not in material balance.

^bValue not furnished in original data summary (estimated from other data provided).

Table 5.23. Physical parameters from first Sulfinol plant

	Value	
Operating parameter		
Absorber pressure	1000 psig	
Feed gas rate	32 x 10 ⁶ scfd	
Lean solvent cooler duty	7.5 Btu/scf feed gas	
Lean/rich exchanger duty	6.7 Btu/scf feed gas	
Regenerator reboiler	10.1 Btu/scf feed gas (1.1 lb steam per pound of acid gas)	
Example parameter	Case 1	Case 2
Solvent flow	315 gpm	335 gpm
Solvent loading of acid gas	6.0 scf/gal solution	5.7 scf/gal solution
H ₂ S in treated gas	10 ppmv	2 ppmv

Table 5.24. Operating data on two Sulfinol units

Property	Plant A		Plant B	
Feed rate, 10^6 scfd	13.0		4.2	
Absorber pressure, psia	588		485	
Absorber temperature, °F	104		120	
Number of trays	30		45	
	Feed gas	Treated gas	Feed gas	Treated gas
H ₂ S content	0.36 vol %	0.5 ppm	0.87 vol %	2 ppm
CO ₂ content	5.20 vol %	25 ppm	5.20 vol %	
COS content	125 ppm	0.3 ppm	155 ppm	5 ppm
50 psia steam consumption, lb steam/lb acid gas removed	1.9		1.5	
Electricity requirement, kWhr/ton acid gas removed	30		21	

capacity, and (3) the Sulfinol solution is more easily stripped than is a purely chemical solvent.²¹ Lower utilities requirements and circulation rates lead to reduced equipment sizes. This, in turn, leads to lower plant capital costs when compared to chemical systems.^{4,21}

Sulfinol solution is not degraded to any appreciable extent by COS or H₂S; however, CO₂ does react with DIPA to produce DIPA-Oxazolidone.⁴ The degradation product can be permitted to accumulate up to 10 wt % of the total DIPA in the Sulfinol solution without affecting plant operation.² Feed rates to the solvent reclaimer are estimated at 0.1 to 0.5 gpm per 1000 gpm of solvent circulation.^{2,4}

When treating gases that contain both H₂S and CO₂, the use of carbon steel throughout the Sulfinol plant is acceptable.²¹ Corrosion has not been a problem in such plants because the presence of H₂S inhibits corrosive effects of CO₂.²² Where H₂S concentration in the total acid-gas portion of the feed gas is close to 1 vol %, carbon steel construction is suitable; however, stainless steel will be required in critical areas of the plant when the H₂S concentration is substantially lower than 1 vol %.²² Avoidance of high velocities and turbulence and prevention of excessive tube wall temperatures are also recommended to prevent localized corrosion attacks.²² Applications of the Sulfinol process in coal-derived fuel gas treating facilities should generally be in the appropriate region for the use of carbon steel construction. In some coal-derived substitute natural gas (SNG) plant designs in which H₂S is removed prior to the CO shift reaction, stainless steel is required for a Sulfinol unit that removes CO₂ from the CO shift exit gas.

5.4.4 Process operation and economics

Several examples of the operation of Sulfinol units are provided in Tables 5.22 through 5.24. A comparison of Sulfinol operation with several amine treating systems is made in Table 5.25.⁴ The gas shown in case 3 of the table has the highest concentration of heavy hydrocarbons (C₅⁺ compounds); the resultant acid gas is still sufficiently low in hydrocarbons to allow normal Claus sulfur plant operation without further treatment.⁴

Table 5.25. Comparison of Sulfinol operation with various amine systems^{a,b}

	Case 1	Case 2	Case 3	Case 4	Case 5
Feed gas composition, mole %					
C ₁	87.90	71.5	63.01	25.8	80.94
C ₂	0.35	2.0	8.43	5.8	0.17
C ₃		1.7	3.71	3.2	0.05
C ₄		1.1	0.82	1.6	0.04
C ₅ ⁺		0.2	0.53 ^c		
N ₂	2.37	1.4	1.40	8.6	0.70
CO ₂	8.73	2.0	2.00	3.5	18.00
H ₂ S	<u>0.65</u>	<u>20.1</u>	<u>20.10</u>	<u>51.5</u>	<u>0.10</u>
	100.00	100.0	100.00	100.0	100.00
Trace sulfur compounds, ppmv					
COS	27.0	65.7	65.7	75.6	
RSH	23.7	17.0	17.0	35.0	
Treated gas CO ₂ content, mole %	<1.0	<1.0	<1.0	<1.0	2.0 for Sulfinol <1.0 for amines

Table 5.25. (continued)

	Case 1	Case 2	Case 3	Case 4	Case 5
Net solution pickup, scf acid gas/gal					
Sulfinol	4.39	8.78	8.57	16.14	5.24
MEA (15 wt % monoethanolamine aqueous solution)	3.00	3.00	3.00	3.00	3.00
DEA (25 wt % diethanolamine aqueous solution)	5.12	5.12	5.12	5.12	5.12
DGA (65 wt % diglycolamine aqueous solution)	5.10	5.10	5.10	5.10	5.10
Solution circulation rate, gpm at 110°F					
Sulfinol	1,483	1,748	1,790	2,366	2,167
MEA	2,170	5,115	5,115	12,730	4,190
DEA	1,272	2,997	2,997	7,460	2,455
DGA	1,277	3,010	3,010	7,490	2,465
Reboiler steam rate, lb steam/gal solution					
Sulfinol	0.78	1.06	1.17	1.10	0.77
MEA	1.10	1.10	1.10	1.10	1.10
DEA	1.15	1.15	1.15	1.15	1.15
DGA	1.20	1.20	1.20	1.20	1.20

Table 5.25. (continued)

	Case 1	Case 2	Case 3	Case 4	Case 5
Reboiler steam rate, lb steam/hr					
Sulfinol	69,740	111,440	125,960	156,000	99,600
MEA	143,200	337,590	337,59C	840,180	276,540
DEA	87,700	206,790	206,79C	514,740	169,400
DGA	91,950	216,720	216,72C	539,280	177,480

^aConstant comparative values:

Absorber pressure	1000 psia,
Feed gas temperature	110°F,
Dry feed gas flow	100 x 10 ⁶ scfd,
Treated gas H ₂ S	<4 ppmv,
Treated gas total sulfur	<15 ppmv.

^bAll results are based on the assumptions of single-stage absorption and rich/lean solution heat exchangers.

^cIncludes 0.02 mole % aromatics; regenerated acid gas will contain total hydrocarbons equal to 1.0 mole % of the H₂S; 20 mole % of these hydrocarbons will be C₅⁺ compounds.

B. G. Goar used circulation and steam rates determined by Shell's Sulfinol computer program, while amine circulation rates are based on net solution acid-gas pickup values common in the industry. Although amine solution loadings were held constant for all five cases, variations in actual practice will result from the varying H_2S -to- CO_2 ratios in the feed gases. Similarly, reboiler steam rates for the amine solutions are held constant, although varying H_2S -to- CO_2 ratios will change the actual requirements in practice.⁴ Fitzgerald and Richardson have provided empirical correlations for the effect of the H_2S -to- CO_2 ratio on MEA regenerator steam requirements.²³

Goar also provides circulation rates for Sulfinol in cases 1, 2, and 4 that show the effect of changing the absorber pressure (Table 5.26).⁴

Table 5.26. Sulfinol solution circulation rates,
gpm at 110°F

Absorber pressure (psia)	Case 1	Case 2	Case 4
100	2000	3300	6410
500	1540	1995	3230
1000	1483	1748	2366

The Sulfinol process has not yet been operated in the United States on gas derived from coal.⁷ However, Dravo Corporation has published conceptual design and economic information on the Sulfinol process for a commercial coal conversion facility; the Sulfinol process was selected for acid gas removal from a coal hydrocarbonization process gas.²⁴ Two parallel Sulfinol systems are required. The Sulfinol solution composition was selected by Shell Development Company and specified as 45 wt % DIPA, 40 wt % sulfolane, and 15 wt % water. The conceptual flowsheet is shown in Fig. 5.27, and the material balance and operating conditions are in Tables 5.27 and 5.28. The treated gas passes through the water wash

Fig. 5.27. Conceptual flowsheet for Sulfinol plant treating coal-derived gas.

Table 5.27. Material balance for Sulfinol plant
treating coal-derived gas

Gas composition	Feed gas (10 ³ lb/hr)	Treated gas (10 ³ lb/hr)	Acid gas (10 ³ lb/hr)
H ₂	203.59	203.59	
N ₂	32.71	32.71	
CO	215.44	215.44	
CO ₂	142.18	0.38	141.800
H ₂ O	6.74	7.66	2.010
H ₂ S	44.033	0.03	44.003
COS, CS ₂	0.85		0.85
CH ₄	393.60	393.60	
C ₂	176.87	176.87	
C ₃	79.93	79.93	
C ₄	27.31	27.31	
C ₅	3.53	3.53	
Light oil	0.39	0.39	
Heavy oil	0.03		
Phenolics	0.07		
Solids	0.24		
	1327.51	1141.44	188.663

Table 5.28. Operating conditions for Sulfinol plant
treating coal-derived gas

Condition	Magnitude		
	Feed gas	Treated gas	Acid gas
Pressure, psia	627	620	40 ^a
Temperature, °F	100	100	120
Lean solution circulation = 3,466,303 lb/hr (~6330 gpm)			
Solution makeup rate = 18,620 lb/hr ^b			
Makeup water rate = 2,933 lb/hr (~6 gpm)			
Sludge discharge = 18,960 lb/hr ^c			
Net solution pickup = 4.52 scf acid gas/gal solution			
Acid gas H ₂ S content = 28.5 vol %			

^aDravo reported 40 psia, but this value is inconsistent with the use of only 30 psig steam in the reboiler; a value of 20 psia is more in line with the specified reboiler steam.

^bSolution makeup is 50 wt % water.

^cSludge discharge consists of 9310 lb/hr water, 9310 lb/hr degradation products, and 340 lb/hr oil and solids.

column (Fig. 5.27) to recover any entrained Sulfinol solution.²⁴ Treated gas contains less than 50 ppm CO₂ and 0.5 ppm H₂S. Acid gas stripped from the Sulfinol solution is sent to a Claus plant for sulfur recovery.

The capital cost for the Sulfinol plant, consisting of two parallel units, was estimated in late 1975 at \$33.4 million; the cost in first quarter 1977 is about \$36.4 million. The Dravo Corporation added the first three months operating charges to the plant cost to obtain total capital required.²⁴ The total capital in first quarter 1977 is about \$39.21 million. A list of equipment costs for both units is given in Table 5.29. (Costs are for first quarter 1977.) For the Sulfinol plant the ratio of plant capital cost to purchased equipment cost is approximately 2.65.

Utility consumptions in the Dravo design are not provided for the Sulfinol plant; however, operating costs are listed.²⁴ A comparison of the direct annual operating costs, with the charges levied for the specific utilities, allows back calculation of some of the utilities requirements. The direct operating costs reported by the Dravo Corporation, in late 1975 dollars, are included in Table 5.30, along with estimated operating requirements based on the units' costs shown in the table. To calculate total annual cost for the Sulfinol plant, direct annual operating costs are added to indirect costs. Dravo includes 12.1% of the total capital for indirect costs.²⁴ This involves a charge of 12% of total capital investment, including three months of operating costs, as the annual costs of capital and 0.1% of total capital for general and administrative overhead.

Various costs have been published for Sulfinol solution. Dravo reports \$660/ton of solution, which is equivalent to about \$3/gal.²⁴ In 1970, C. D. Swaim gave an estimate of \$2.50/gal to \$2.90/gal for Sulfinol solution.²¹ R. S. Smith reported a relative cost per gallon of Sulfinol solution that is ten times higher than the cost of MEA solution.²⁵ The cost of solution must be considered when evaluating the Sulfinol process.

Table 5.29. Purchased equipment costs for Sulfinol
plant treating coal-derived gases

Equipment	Cost (\$10 ³)
Heat exchangers	
Lean solution coolers	1,155
Lean/rich exchangers	2,960
Regenerator reboilers	3,165
Reflux condensers	232
Superheaters	56
Vaporizers	<u>99</u>
	7,667
Columns	
Absorbers	2,391
Regenerators	379
Reclaimers	60
Water wash columns	<u>1,822</u>
	4,652
Tanks and drums	
Solution makeup tanks with agitators	7
Reflux drums	11
Flash tanks	<u>65</u>
	83
Pumps and compressors	
Solution booster pumps	746
Lean solution pumps	243
Reflux pumps	8
Makeup water pumps	59
Water circulation pumps	37
Solution makeup pumps	2
Flash gas recycle compressors	<u>218</u>
	1,313
Miscellaneous	
Solution filter	22
Total purchased equipment	<u>13,737</u>

Table 5.30. Operating costs for Sulfinol plant
treating coal-derived gas^a

Parameter	Annual cost	Operating requirement
Utilities		
Electricity, \$0.0184/kWhr	729,000	4,950 kW
Cooling water, \$0.15/10 ³ gal	1,566,000	21,750 gpm
Chemicals, \$660/ton	123,000	1,100 lb/day
Steam		
300 to 900 psig, \$2.50/10 ³ lb		
100 to 300 psig, \$1.90/10 ³ lb		
30 to 100 psig, \$1.80/10 ³ lb	5,165,000	~350,000 lb/hr
Labor		
Operating, \$50,000 per position	100,000	2 operators per shift
Maintenance, 2% capital	668,000	
Supervision, 15% operation and maintenance labor	115,000	
Administration and overhead, 60% total labor	530,000	
Supplies		
Operating, 30% operation labor	30,000	
Maintenance, 100% maintenance labor	668,000	
Taxes and insurance		
2.7% of capital	902,000	
Credit		
Condensate return, \$0.70/10 ³ gal	[241,000]	700 gpm

^aPlant assumed operating 8000 hr/year.

5.4.5 References

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5.5 The Selexol* Solvent Process

5.5.1 Background

The Selexol process for physical absorption of acid gases was developed in the early 1960s by Allied Chemical Corporation.¹ The first commercial installation of the process reported by Allied Chemical for the bulk removal of CO₂ from a synthesis gas was in 1965.^{2,3} Selective removal of sulfur compounds from natural gas was demonstrated in a commercial operation in 1969.³ Table 5.31 lists Selexol installations (in place or projected) as of June 1976.² The only Selexol system designed for selective sulfur removal from coal gases is in the BiGas pilot plant (completed in 1976). The Selexol unit in the coal gasification pilot plant had not been operated in an integrated mode with coal gases as of June 1977.⁴ Such integrated operation for H₂S and CO₂ removal was not expected before September of 1977; delay in Selexol plant operation has been a result of gasifier plant shakedown.

The Selexol process is claimed to have applicability in two areas: (1) the selective removal of sulfurous gases, and (2) the bulk removal of large quantities of acid gases.⁵ Successful examples of both areas are listed in Table 5.31. New and more difficult applications are anticipated in coal gasification plants that produce either substitute natural gas (SNG) or fuel gases with lower Btu content.⁶ The specific difficulties expected have somewhat different origins in these two types of coal gasification plants. Both types, though, introduce the uncertainty of coal-gas composition. Minor and trace components of coal gases are numerous, variable, and possibly troublesome due to interactions with scrubbing solutions or environmental impacts. The operability of gas cleanup processes on coal gas can only be reliably determined by actual experience on coal gasification streams, although potential problem areas can be identified by analogy with natural gas treating applications.

Low- or medium-Btu fuel gas treating adds other concerns. If the fuel gas is to be fired through gas turbines, CO₂ removal is not desirable. The mass of CO₂ at combustor pressure and temperature represents a source of kinetic energy from which a gas turbine can extract power. Hence, any CO₂

* Selexol is a registered trademark of Allied Chemical Corporation.

Table 5.31. Selexol installations^a

Owner and location	Contractor	Startup	Description
<u>Bulk CO₂ removal from synthesis gas</u>			
Allied Chemical Corp. Omaha, Neb.	Allied Chemical Corp.	1965	CO ₂ from 18% to 0.5%; 45 million scfd at 565 psia; air stripping, no steam required; carbon steel; original solvent- charge; reforming of natural gas.
Ammoriaque Synthetique et Derives S.A. (ASED) Willebroek, Belgium	Davy Powergas GmbH Cologne, West Germany	1975	CO ₂ from 33% to <1%; H ₂ S from 200 ppm to <4 ppm; HCN from 100 ppm to <10 ppm; 47 million scfd at 370 psia; partial oxidation of crude oil; replaced H ₂ O wash.
<u>Bulk CO₂ removal from natural gas</u>			
Coastal States Gas Producing Co. Six Shooter, Tex.	Fish engineering Houston, Tex.	1969	CO ₂ from 43% to <3.5%; H ₂ S from 5 ppm to <1 ppm; H ₂ O from satura- tion to <7 lb/million scf; 275 million scfd at 1000 psia; no stripping, no refrigeration.
Lone Star Gas Co. Ft. Stockton, Tex.	Olsen Engineering Davy Powergas, Inc. Houston, Tex.	1974	CO ₂ from 43% to <3.5%; H ₂ S from 30 ppm to 4 ppm; maintains H ₂ O at <7 lb/million scf; 50 million scfd at 1000 psia; no stripping, no refrigeration.
Lone Star Gas Co. Ft. Stockton, Tex.	Olsen Engineering Davy Powergas, Inc. Houston, Tex.	1975	Expansion to 100 million scfd.

Table 5.31. (continued)

Owner and location	Contractor	Startup	Description
<u>Selective sulfur removal from natural gas</u>			
Northern Natural Gas Co. Ft. Stockton, Tex.	Fish Engineering Houston, Tex.	1969	H ₂ S from 100 ppm to <4 ppm; CO ₂ from 18% to <2.5%; maintains H ₂ O at <7 lb/million scf; 130 million scfd at 1000 psia; inert-gas stripping, split flow.
Norddeutsche-Erdgas- Aufbereitungs-GmbH Mobil, Esso, Shell Sulingen, West Germany	Davy Powergas GmbH Cologne, West Germany	1970	H ₂ S from 4000 ppm to <2 ppm; CO ₂ from 7% to >5%; COS from 130 ppm to 70 ppm; maintains H ₂ O at <7 lb/million scf; 62 million scfd at 1000 psia; inert-gas stripping; replaced potassium carbonate.
Norddeutsche-Erdgas- Aufbereitungs-GmbH Mobil, Esso, Shell Sulingen, West Germany	Mobil Oil A.G. in Deutschland	1973	H ₂ S from 9.2% to <2 ppm; CO ₂ from 9.5% to 3%; COS from 130 ppm to 70 ppm; RSH from 100 ppm to <1 ppm; 30% H ₂ S to Claus plant; maintains H ₂ O at <7 lb/million scf; 62 million scfd at 1090 psia; inert-gas stripping; replaced Alkazid.
Norddeutsche-Erdgas- Aufbereitungs-GmbH Mobil, Esso, Shell Sulingen, West Germany	Mobil Oil A.G. in Deutschland	1975	Expansion to 67 million scfd.

Table 5.31. (continued)

Owner and location	Contractor	Startup	Description
Wintershall AG Barnstorf, West Germany	Davy Powergas GmbH Cologne, West Germany	1970	H ₂ S from 7% to <1000 ppm; CO ₂ from 9% to 5%; maintains H ₂ O at <7 lb/million scf; 32 million scfd at 1000 psia; inert-gas stripping replaced propylene carbonate and glycol amine.
Wintershall AG Barnstorf, West Germany	Wintershall AG	1973	Expansion to 45 million scfd; 15 million scfd to <2 ppm H ₂ S.
Wintershall AG Ruetenbrock, West Germany	Comprimo b.v. Amsterdam	1976	H ₂ S from 60 ppm to <2 ppm; CO ₂ from 5% to 4%; maintains H ₂ O at <7 lb/million scf; 45 million scfd at 1000 psia; inert-gas stripping.
Wintershall AG Barnstorf, West Germany	Comprimo b.v. Amsterdam	1977	H ₂ S from 7% to <2 ppm; CO ₂ from 9% to 5%; COS from 118 ppm to 60 ppm; RSH from 100 ppm to <1 ppm; 68% H ₂ S to Claus plant; maintains H ₂ O at <7 lb/million scf; 45 million scfd at 1000 psia; steam stripping.
<u>Selective sulfur removal from synthesis gas</u>			
ERDA/AGA Bi-Gas pilot plant Homer City, Pa.	Stearns-Roger Denver, Colo.	1976	H ₂ S from 7000 ppm to <4 ppm; CO ₂ from 31% to <1%; 35% H ₂ S to Claus plant; <20 ppm H ₂ S to CO ₂ vent; 11 million scfd at 1500 psia maximum; steam stripping; gasification of coal to SNG.

^aAs of June 7, 1976.

removal in the gas cleanup step lowers the recoverable energy of the fuel gas. A second concern in fuel gas applications is the disposition of any CO_2 that is absorbed. The currently preferred method of sulfur recovery from regenerated acid gases is a Claus-type sulfur plant. Such plants operate most efficiently and economically at high H_2S -to- CO_2 ratios; therefore, if CO_2 is absorbed from the fuel gas and regenerated concurrently with H_2S regeneration, downstream sulfur recovery via Claus-plant technology is adversely affected. These concerns can be restated as gas cleanup process goals for minimizing both CO_2 removal from the fuel gas and CO_2 regeneration to the Claus-plant feed.

In plants producing SNG, the goals are different because removal of CO_2 from the coal gas is desired. The level to which H_2S must be removed is also different; SNG plants impose a requirement for H_2S removal to below 1 ppmv because of the sulfur-sensitive methanation reaction catalyst. Fuel gases require sulfur removal to meet less stringent SO_2 emission levels. Sulfur dioxide emission levels for coal-fuel gases are not yet nationally developed; however, various state agencies and tentative national goals indicate that required H_2S levels will be tens or hundreds of times higher than the levels required in SNG production. Product specifications for SNG typically limit CO_2 content to 1 vol % and below; hence, SNG production imposes the requirements for removal to low levels of both CO_2 and H_2S . Acid-gas removal is typically performed after the CO shift process in which the H_2 -to-CO ratio is adjusted by reacting CO and H_2O to produce H_2 and CO_2 . The CO_2 content of the shifted gas can be twenty times or more greater than the H_2S content. Even though both gases are removed, it is still desirable to regenerate a rich- H_2S stream so that Claus-plant technology can be employed for sulfur recovery. Selective absorption of H_2S , combined with excellent removal of H_2S , is required for the acid-gas removal process in this application.

5.5.2 Process description

Many variations of the Selexol process are possible, depending on the specific application sought. Conceptually, bulk removal of CO_2 is the simplest application. Single-stage absorption of CO_2 only is followed by regeneration of CO_2 by flashing to low pressure.⁶ Complications are

introduced when such a system is designed for high-efficiency power recovery and self-sufficient refrigeration.⁶ Additionally, some hydrocarbons are absorbed, as in all physical solvent systems. To prevent hydrocarbon release to the atmosphere and to minimize hydrocarbon product losses, an intermediate flash stage or stages may be required along with some recycling of hydrocarbon-rich flash gases. Figure 5.28 shows the complexity of a Selexol plant for bulk CO₂ removal considering the aforementioned factors. If thermal efficiency and energy losses were not considerations, the flow-sheet would be quite simple, so that only the absorber, low-pressure flash drum, Selexol pump, and inlet-gas cooler would remain; however, the more complex pattern is recommended in the present era of high energy costs.⁶

Two possible basic flowsheets result when sulfurous gases are to be removed, depending on the removal requirement for CO₂. Although not shown in the subsequent figures, hydraulic recovery turbines, turboexpanders, and self-sufficient refrigeration are still desirable features and require equipment and flow patterns similar to those shown in Fig. 5.28. The application of Selexol gas treating to a coal-derived fuel gas for principally removing H₂S produces the simplified flowsheet of Fig. 5.29. Removal of CO₂ is not desired in this case. Steam stripping is shown, but inert-gas or air stripping is preferable where the regenerated gas is suitable for venting to the atmosphere. In most types of selective H₂S removal, this will not be the case.

When both H₂S and CO₂ must be removed and a rich-H₂S regeneration stream is desired, a second set of absorbers and regenerators are added after the H₂S removal process. The basic flow pattern is represented in Fig. 5.30, although it is more complicated in practice. Essentially all H₂S and some of the organic sulfur compounds are absorbed in the first absorber, while CO₂ absorption is minimized. Regeneration in the first regenerator produces an off-gas that is rich in H₂S. The remaining CO₂ is absorbed to the specified level in the second absorber. Air stripping in the second regenerator yields a vent gas that is extremely low in sulfur compounds. Current designs generally specify ≤ 10 ppmv H₂S in the vent CO₂.

Fig. 5.28. Selexol bulk CO₂ removal.

Fig. 5.29. Selæxol selective H₂S removal, simplified.

ORNL DWG 77-1300 R

Fig. 5.30. Selexol selective H₂S and CO₂ removal, simplified.

5.5.3 Process data

The Allied Chemical Selexol process absorbs compounds according to physical solubility at absorber pressure and temperature. It is useful to examine both the physical properties of the Selexol solvent (dimethylether polyethylene glycol) and the varying solubilities of possible fuel gas constituents. Published properties of the Selexol solvent are shown in Table 5.32.⁶⁻⁸ The relative order of solubilities for various gas compounds in Selexol solvent is presented in Table 5.33.⁵ Absolute solubilities for compounds of greatest interest are shown in Fig. 5.31 as a function of the compounds' partial pressures.^{7,8} Temperatures lower than 70°F (Fig. 5.31) will increase gas solubility. By comparing the relative solubilities of gases shown in Table 5.33 to those shown in Fig. 5.31, rough estimates of the solubility curves for other compounds can be made. For example, ammonia will exhibit a curve intermediate to those of H₂S and COS.

The relative solubility of the Selexol solvent for water vapor is very high. If suitable regeneration of the solvent is provided (e.g., inert-gas stripping), the process can produce a dry product which meets natural gas pipeline dew point specifications.^{1,6} The removal of H₂O in fuel gases destined for combined-cycle turbine applications, however, is not an advantage. The Selexol process absorbs at low temperatures (typically 20 to 100°F), and only a small amount of water vapor remains in the gas phase at these temperatures. Hence, any additional removal of water vapor represents a very minor mass loss to the turbines.

A more serious concern relates to the solubilities of various hydrocarbons in the solvent. When heavier hydrocarbons are present (e.g., C₄ and above) major losses of heating value can occur. For low-Btu fuel gas applications, as opposed to SNG production, such losses represent a significant portion of the fuel gas heating value for gasifiers producing significant quantities of higher hydrocarbons (e.g., fixed-bed gasifiers). Hydrocarbons carried over to a Claus sulfur recovery plant necessitate advanced designs in the plant to prevent degradation of the catalyst or sulfur product. Minimizing higher hydrocarbon production by using higher temperature gasifiers, such as entrained-flow gasifiers, and utilizing

Table 5.32. Physical properties of the Selexol solvent

Property	Value
Freezing point, °F	-8 to -20
Flash point, °F	304
Vapor pressure at 77°F, mm Hg	0.0007
Density at 77°F, lb/gal	8.6
Specific heat, Btu/lb · °F	
at 41°F	0.49
at 121°F	0.51
Viscosity at 77°F, cP	5.8
Thermal conductivity at 77°F, Btu/hr · ft ² · °F/ft	0.11

Table 5.33. Order of relative solubility
in Selexol solvent^a

Component	
Highest solubility:	HCN
	H ₂ O
	C ₄ H ₄ S
	SO ₂
	C ₆ H ₆
	C ₇
	CS ₂
	CH ₃ SH
	C ₆
	H ₂ S
	NH ₃
	C ₅
	COS
	C ₄
	C ₃
	CO ₂
	C ₂
	C ₁
	CO
Lowest solubility:	H ₂

^aC_x are noncyclic C_xH_y compounds, y unspecified.

Fig. 5.31. Solubility of selected gases in Selexol solvent at 70°F.

effective multistage flashing techniques with some gas recycle can prevent significant heating value losses.⁵

Carbonyl sulfide is intermediate in solubility to H_2S and CO_2 . Where removal of COS is desired, the Selexol process selectivity for H_2S removal versus CO_2 removal is not used to full advantage. If COS removal is the limiting factor in sulfur removal, the task of producing a suitable Claus sulfur-plant feed gas is more difficult.⁶ Process designs have been developed for fuel gas applications which will absorb considerable portions of the COS while still producing Claus-plant feed (over 20 vol % of sulfurous gases).⁹

Selexol solvent is reported to be noncorrosive and inherently nonfoaming.¹⁰ Carbon steel construction is suitable throughout the process.⁸ Solvent degradation has not been recorded; thus no solvent reclaiming is required.¹ The combined effect of solution stability and extremely low solvent vapor pressure eliminates any solution makeup requirement, other than for leaks or other mechanical losses.¹ This is especially desirable in the Selexol process because the solvent is much more expensive than chemical solvents. The current cost of Selexol solvent is about \$8.50/gal.¹¹

In three natural gas treating applications, Selexol solvent proved capable of reducing H_2S content to below 4 ppmv.¹² The cases handled by the Selexol process include: (1) treating gas from 43% CO_2 and 16 ppmv H_2S to 3.5% CO_2 and 4 ppmv H_2S , (2) treating gas from 3.5% CO_2 and 128 ppmv H_2S to 3% CO_2 and 4 ppmv H_2S , and (3) treating gas from 18% CO_2 and 128 ppmv H_2S to 2.5% CO_2 and 4 ppmv H_2S . All three plants operate at 1000 psig and ambient to subambient absorption temperatures..

Similar data on coal gas treating plants are not yet available; however, Allied Chemical has published predicted results in several coal gas applications, including conversion of coal to SNG and low-Btu gas from coal plants. J. W. Sweny, of Allied Chemical, presents sample material balances for both possibilities (Table 5.34).⁶ Pressures, temperatures, and cost estimates are not supplied for the material balances shown. The SNG case is almost certainly at elevated pressure (400 psig or above), while both cases would typically operate at or below ambient temperature. A more detailed material balance is provided by Patel, Burnham, and Loeding

Table 5.34. Sample coal gas material balances

Component	Feed gas	H ₂ S off-gas	Treated gas	CO ₂ vent gas
<u>SNG case (vol %)</u>				
CO ₂	31	68	0.5	98
H ₂ S	0.7	32	<1 ppm	(5 ppm)
CH ₄	8		11	
H ₂	46		67	2
CO	15		22	
<u>Low-Btu gas case (vol %)</u>				
CO ₂	9.4	79	/	
H ₂ S	0.6	21	(153 ppm)	
COS	0.06			
CH ₄	4		4	
H ₂	15		15	
CO	20		21	
N ₂	51		53	
NH ₃	(85 ppm)	.	(12 ppm)	

for selective removal of H_2S from a low-Btu coal gas.¹³ Available data for this application is listed in Table 5.35. Further examples are explored in Sect. 5.5.4.

5.5.4 Process operation and economics

The Selexol process operates with low external heating and cooling requirements because of the low heats of physical absorption and a solvent specific heat that is half that of water.¹ Refrigeration required for subambient absorption temperatures can often be supplied internally by gas depressurization through turbine expanders (Fig. 5.28) and by heat interchange.^{1,7}

Purity levels achievable by the Selexol process are highly dependent on operating conditions. The process is capable of removing H_2S , COS, and mercaptan to below 1 ppm each.¹ Carbon dioxide removal can be varied from negligible to essentially complete. For example, removal of CO_2 to 40 ppm from a synthesis gas generated by partial oxidation of fuel oil has been commercially demonstrated in a plant that was installed in 1974.¹¹

Operating and capital costs for the Selexol system have been published for several specific gas applications. The three most probable process variations are (1) selective H_2S removal only, (2) selective removal of H_2S and CO_2 , and (3) nonselective removal of H_2S and CO_2 . The first two options have received the most attention for coal gas applications. The comparison in Table 5.36 of relative Selexol economics to those of MEA and potassium carbonate illustrates the third option that is applied to natural gas treating.⁷

Capital costs for the third option (nonselective removal of H_2S and CO_2) have been published for two coal-derived SNG plants, and capital costs have been published for the second option (selective removal of H_2S and CO_2) for four additional coal-derived SNG plants.¹⁴ Operating costs are not listed specifically for the Selexol process, but steam consumptions are available from the material and energy balances provided.¹⁵ Nonselective acid-gas removal is specified in the IGT Steam-Iron Hygas and the Conoco CO_2 Acceptor processes because the mole fraction of CO_2 is very low for both (about 15% of the mole fraction in the other four processes).

Table 5.35. Selective H₂S removal via Selexol process

	Feed gas		H ₂ S off-gas		Treated gas	
	(lb-mole/hr)	(vol %)	(lb-mole/hr)	(vol %)	(lb-mole/hr)	(vol %)
CO ₂	4,286	6.29	1,815	72.31	2,471	3.76
H ₂ S	491	0.72				
COS	24	0.04	502	20.00	13	0.02 (198 ppm)
CH ₄	2,126	3.12			2,126	3.24
H ₂	10,518	15.43			10,518	16.02
CO	15,525	22.78			15,525	23.65
N ₂	34,994	51.34			34,994	53.31
H ₂ O	193	0.28	193	7.69		
	68,157		2,510		65,647	
Temperature, °F	100		200		85	
Pressure, psia	335		20		330	
HHV, Btu/scf	160		129		161	
Capital investment (mid-1975 dollars), 15.9 million						
Capital investment (first quarter 1977 dollars), 17.5 million						

Table 5.36. Natural gas treating solvents — performance and relative economics^a

Parameter	20% aqueous MEA	Hot potassium carbonate	Selexol solvent
<u>Performance</u>			
Exit CO ₂	25 ppm	2 mole %	2 mole %
Exit H ₂ S	0.25 grain/100 scf	1 grain/100 scf	0.25 grain/100 scf
<u>Relative economics (% of MEA costs)</u>			
Plant capital cost	100	80	70
Direct annual operating costs			
Steam	100	70	10
Electricity	100	95	20
Cooling, process water	100	95	25
Total direct ^b	100	75	40
Indirect annual operating costs	100	80	75
Total annual operating costs	100	75	50

^aNatural gas treating solvents under the following conditions: plant capacity, 100×10^6 scfd; feed-gas pressure, 1000 psig; inlet CO₂, 30 mole %; and inlet H₂S, 20 grain/100 scf.

^bIncludes costs for losses, operating labor, and maintenance, along with steam, electric, and water costs.

Material balance, steam consumption, and capital costs information for nonselective acid-gas removal is shown in Tables 5.37, 5.38, and 5.39 respectively. Flows, energy consumptions, and costs are all one-half of the totals provided in the C. F. Braun and Company report. Although not stated, the acid-gas removal facilities are expected to consist of two parallel trains, compatible with the two-parallel-train approach adopted in the main process areas (e.g., gasification, CO shift, and methanation). Equipment nomenclature in the Selexol area is also consistent with the assumption of two parallel trains; hence, values given in Tables 5.37-5.39 are for a single Selexol plant. Costs have been escalated to first quarter 1977.

Material balance, steam consumption, and capital costs information for selective removal of H_2S and CO_2 in four other SNG plant designs are displayed in Tables 5.40, 5.41, and 5.42, respectively. Again, listed quantities are believed to be for one Selexol plant (i.e., one-half of the totals provided in the C. F. Braun and Company reports).^{14,15}

The Dravo Corporation has published typical utility requirements for the selective removal of H_2S and CO_2 from a 300 psig gas stream.¹ The feed gas contains about 0.5% H_2S and 35% CO_2 ; the treated gas has less than 0.1 ppm H_2S and 11% CO_2 . The estimated utility requirements per 10^6 scf of feed gas are: 3000 lb steam, 35,000 gal cooling water, and 900 kWhr electricity. Solvent loss is estimated to be about 0.5 lb/ 10^6 scf of feed gas.

Use of the Selexol process for selectively removing H_2S from coal-derived gases has also received attention. This application is desirable for low- and medium-Btu gases generated for power production, rather than for SNG manufacture. In this case it is necessary to remove sulfurous gases to meet restrictions on the emission of SO_2 from power plants, as discussed in Sect. 1. Carbon dioxide removal is not particularly desired. Two reports published in 1976 give capital cost estimates for the application of Selexol to selective removal of H_2S .^{13,16} Utilities consumptions are not specified by Patel, Burnham, and Loeding.¹³ The capital investment estimated for the Selexol plant is shown in Table 5.35. The Fluor report provides heating and cooling duties for the four examined applications that use the Selexol

Table 5.37. Nonselective acid-gas removal — material balance
Selsol absorption mode, single stage

	IGT Steam-Iron Hygas (vol %)		Conoco CO ₂ Acceptor (vol %)	
	Feed gas ^a	Treated gas	Feed gas	Treated gas
H ₂	50.03	53.60	64.36	64.64
CO	14.61	15.74	15.55	15.63
CO ₂	6.76	0.69	5.09	4.82
CH ₄	24.62	26.66	14.61	14.66
C ₂ H ₆	2.06	2.04		
N ₂	1.20	1.26	0.25	0.25
H ₂ S	0.23		0.03	
COS	0.007		(4 ppm)	
H ₂ O	0.15	0.003	0.11	0.005
C ₆ ⁺	0.34			
lb-mole/hr	30,253	28,252	39,217	39,026
lb/hr	405,285	311,300	405,400	398,960
Molecular weight	13.40	11.02	10.34	10.20
Temperature, °F	100	87	100	87
Pressure, psig	1,115	1,112	846	821

^aIncludes flash gas at 95°F, 75 psig; equal to 3 vol % of feed gas stream.

Table 5.38. Nonselective acid-gas removal — steam consumption

Equipment	IGT Steam-Iron Hygas	Conoco CO ₂ Acceptor
Reboiler	126,000 lb/hr, 150 psig saturated (108 x 10 ⁶ Btu/hr)	70,240 lb/hr, 200 psig, 410°F (59.8 x 10 ⁶ Btu/hr)
Pumps	Motor drive	33,180 lb/hr, 600 psig, 700°F (exhaust at 200 psig, 500°F)
Compressors	Motor drive	203,700 lb/hr, 600 psig, 700°F (exhaust at 200 psig, 500°F)

Table 5.39. Nonselective acid-gas removal — capital costs

	IGT Steam-Iron Hygas (\$)	Conoco CO ₂ Acceptor (\$)
Purchased equipment		
Columns	2,357,300	656,700
Reactors	490,600	495,000
Pressure vessels	507,100	59,400
Tanks	7,700	8,800
Exchangers	2,048,750	1,750,650
Pumps	602,800	258,500
Compressors and blowers	1,540,000	199,100
Refrigeration package	3,470,500	1,082,950
Cartridge filters	6,600	2,200
Miscellaneous	<u>573,650</u>	<u>216,700</u>
	11,605,000	4,730,000
Total installed cost	41.25 million	19.8 million

Table 5.40. Selective H₂S and CO₂ removal — material balance,
Selexol absorption mode, two stages

	IGT Steam-Oxygen Hygas (vol %)		BCR Bi-Gas (vol %)		ERDA-PERC Synthane (vol %)		Lurgi (vol %)	
	Feed gas	Treated gas	Feed gas	Treated gas	Feed gas	Treated gas	Feed gas ^a	Treated gas
H ₂	38.40	57.82	39.40	60.00	29.15	54.87	42.02	62.80
CO	11.23	16.87	12.31	18.70	7.40	13.86	11.58	17.31
CO ₂	33.17	0.80	34.50	1.09	46.50	1.52	34.44	2.79
CH ₄	15.52	23.03	13.33	19.95	14.56	26.73	10.63	15.88
C ₂ H ₆	1.21	1.47			1.79	2.65	0.51	0.77
N ₂			0.17	0.26	0.20	0.37	0.30	0.45
H ₂ S	0.24		0.20		0.29		0.26	
COS	0.005		0.008		0.003			
H ₂ O	0.08	0.007	0.08	0.003	0.10	0.007	0.26	0.005
C ₆ ⁺	0.15				0.001			
lb-mole/hr	45,779	30,390	51,986	34,112	52,154	27,688	55,164	36,914
lb/hr	993,300	315,520	1,128,230	348,000	1,243,300	300,340	1,176,420	377,990
Molecular weight	21.70	10.38	21.70	10.20	23.84	10.85	21.33	10.24
Temperature, °F	100	60	100	60	100	60	100	60
Pressure, psig	1,100	1,095	1,137	1,098	932	865	370	360
CO ₂ vent gas	632,350 lb/hr		737,600 lb/hr		792,200 lb/hr		774,000 lb/hr	

^aFeed-gas composition and condition estimated for Lurgi process.

Table 5.41. Selective H₂S and CO₂ removal — steam consumption

Equipment	IGT Steam-Oxygen Hygas	BCR Bi-Gas	ERDA-PERC Synthane	Lurgi
Heaters	4,600 lb/hr, 50 psig, 296°F steam (4.2 x 10 ⁶ Btu/hr)		6,200 lb/hr, 50 psig, 297°F steam (5.7 x 10 ⁶ Btu/hr)	7,250 lb/hr, 60 psig, saturated steam (6.6 x 10 ⁶ Btu/hr)
Reboilers	50,150 lb/hr, 150 psig, 365°F steam (43.0 x 10 ⁶ Btu/hr)	4,270 lb/hr, 50 psig, 311°F steam (3.9 x 10 ⁶ Btu/hr) 48,535 lb/hr, 150 psig, 365°F steam (41.6 x 10 ⁶ Btu/hr)	84,000 lb/hr, 150 psig, 365°F steam (72.0 x 10 ⁶ Btu/hr)	56,150 lb/hr, 150 psig, 450°F steam (50.9 x 10 ⁶ Btu/hr)
Air blowers	15,225 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg)	12,550 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg)	17,400 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg)	29,150 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg)
Pumps	20,800 lb/hr, 600 psig, 700°F steam (exhaust at 150 psig, 365°F steam) 41,190 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg)	95,190 lb/hr, 600 psig, 700°F steam (exhaust at 50 psig, 311°F steam)	150,930 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg)	25,000 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg)
Compressors	98,000 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg) 343,200 lb/hr, 1450 psig, 900°F steam (exhaust at 600 psig, 700°F steam)	58,800 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg) 41,015 lb/hr, 1000 psig, 900°F steam (91% exhaust at 6.5 in. Hg, 9% exhaust at 50 psig, 311°F steam) 364,760 lb/hr, 1450 psig, 900°F steam (exhaust at 600 psig, 700°F steam)	349,775 lb/hr, 150 psig, 365°F steam (exhaust at 50 psig, 297°F steam) 360,825 lb/hr, 1450 psig, 900°F steam (exhaust at 600 psig, 710°F steam) 78,340 lb/hr, 1450 psig, 900°F steam (exhaust at 6.5 in. Hg)	62,650 lb/hr, 600 psig, 700°F steam (exhaust at 6.5 in. Hg) 130,700 lb/hr, 1450 psig, 900°F steam (49% exhaust at 6.5 in. Hg, 51% exhaust at 150 psig, 450°F steam)
Miscellaneous	14,840 lb/hr, 150 psig, 365°F steam consumed in ejector			

Table 5.42. Selective H₂S and CO₂ removal — capital costs

	IGT Steam-Oxygen Hygas (\$)	BCR Bi-Gas (\$)	ERDA-PERC Synthane (\$)	Lurgi (\$)
Purchased equipment				
Columns	4,928,550	5,886,650	6,724,300	3,253,800
Reactors	550,000	539,000	429,000	352,000
Pressure vessels	859,100	1,176,450	1,793,000	1,871,650
Tanks	17,600	15,400	15,400	15,400
Exchangers, shell and tube	1,841,400	2,471,150	2,379,300	2,277,000
Exchangers, air coolers	892,100	705,650	1,228,150	948,200
Pumps	1,455,850	1,529,000	1,938,750	1,641,200
Compressors and blowers	3,305,600	3,267,000	3,450,700	3,315,400
Refrigeration package	3,267,000	3,267,000	3,379,200	3,267,000
Cartridge filters	31,350	8,250	29,700	30,800
Jet ejectors	15,500	12,650	13,200	13,750
Miscellaneous	<u>873,950</u>	<u>976,800</u>	<u>1,059,300</u>	<u>833,800</u>
	18,040,000	19,855,000	22,440,000	17,820,000
Total installed cost	59.4 million	62.7 million	69.85 million	64.35 million

process; however, power consumed in the process pumps is not specified.¹⁶ The gasification systems for which Selexol is specified are (1) Lurgi moving-bed gasification, and (2) Institute of Gas Technology fluidized-bed gasification (U-Gas), each in air blown and oxygen blown applications. The gasifiers are designed for operation at 340 psig. Four parallel trains of the Selexol process are used in each of the four gasification processes. Tables 5.43 and 5.44 show material balances, heating and cooling loads, and operating conditions reported by the Fluor Corporation for one of the four parallel trains. The capital costs, listed at the end of Table 5.44, represent one-fourth of the total costs reported by Fluor (escalated to first quarter 1977). The gas stream, labeled Flash gas, results from flashing the rich Selexol solution that exits from the absorber bottom. In Fig. 5.29 this gas stream is shown as being recycled to the absorber. In the designs by Fluor, the flash gas is not recycled; it is sent to the fuel-gas system for combustion. A small amount of makeup water is added to the regenerator reflux to compensate for water lost in the acid-gas stream. The makeup water requirement is listed in Table 5.44 as a utility requirement.

The removal requirement specified for H_2S , in the Fluor designs, is based on an emission limit for SO_2 of 1.0 lb per million Btu of coal charged to the plant.¹⁷ This translates to a removal of 85 to 95% of the inlet H_2S . Such removal efficiencies are easily achievable with the Selexol process while regenerating an acid gas with more than 15 vol % H_2S ; therefore, the acid gas can be treated in a Claus-type sulfur plant rather than in a more expensive liquid-phase sulfur plant. The sulfur removal criterion is conjectural because federal standards do not yet exist for power plants fired by coal-derived gases. Emission levels below that used in the Fluor report would increase the capital and operating expenses for a Selexol system.

A report by Lemmon, Hsieh, and Weller (Battelle-Columbus) provides a response from Allied Chemical Corporation for a Selexol selective H_2S removal process, listing capital cost and utilities requirements.⁹ The information provided Allied Chemical concerning the coal-derived gas composition and condition is shown in Table 5.45. Table 5.46 shows the

Table 5.43. Selective removal of H₂S — material balance

	Air-blown Lurgi gasifier material balance (vol %)				Oxygen-blown Lurgi gasifier material balance (vol %)				Air-blown IGT gasifier material balance (vol %)				Oxygen-blown IGT gasifier material balance (vol %)			
	Feed gas	H ₂ S off-gas	Treated gas	Flash gas	Feed gas	H ₂ S off-gas	Treated gas	Flash gas	Feed gas	H ₂ S off-gas	Treated gas	Flash gas	Feed gas	H ₂ S off-gas	Treated gas	Flash gas
H ₂	23.79	0.25	24.80	10.18	42.46	0.16	45.90	6.60	17.20	0.30	17.69	8.99	34.90	0.28	36.37	12.41
CO	16.55	0.67	17.19	13.40	15.21	0.25	16.35	5.73	20.07	1.30	20.58	18.40	41.10	1.39	42.71	28.92
CO ₂	13.45	73.54	10.74	45.99	31.02	73.05	27.06	78.31	9.45	65.57	7.89	30.75	14.86	61.75	12.68	44.51
CH ₄	3.95	0.77	4.05	6.54	8.69	0.59	9.29	4.43	3.38	1.04	3.44	5.68	6.67	1.11	6.85	9.08
C ₂ ^a	0.10	0.16	0.09	0.25	0.65	0.43	0.65	1.08								
N ₂	41.05	0.70	42.77	21.05	0.37		0.41	0.10	48.85	1.59	50.21	33.56	0.80	0.01	0.83	0.38
H ₂ S	0.72	15.95	0.09	1.76	1.19	17.64	0.07	2.81	0.67	22.11	0.09	1.86	1.27	27.26	0.18	3.79
COS	0.03	0.27	0.02	0.10	0.05	0.20	0.04	0.13	0.02	0.39	0.02	0.06	0.04	0.51	0.03	0.15
H ₂ O	0.36	7.69	0.23	0.73	0.36	7.68	0.23	0.81	0.36	7.70	0.08	0.67	0.36	7.69	0.35	0.76
lb-mole/hr	30,628.3	1,201.8	29,278.8	198.5	18,601.4	1,128.2	17,144.8	391.0	34,756.1	881.4	33,683.6	163.6	18,256.0	710.3	17,464.6	132.1
lb/hr	729,607	47,958	667,211	6,355	389,355	45,077	330,913	15,238	857,188	34,370	817,418	4,905	375,610	27,511	344,920	4,098
Molecular weight	23.82	39.9	22.79	32.02	20.93	39.93	19.30	38.97	24.66	39.00	24.27	29.98	20.57	38.73	19.75	31.02
Temperature, °F	100	120	103	b	100	120	103	b	100	120	102	b	100	120	103	b
Pressure, psig	248	7	243	65	242	7	237	65	255	7	250	65	255	7	250	65

^aValue for Lurgi gasification is sum of C₂H₄ and C₂H₆ components.^bNot available.

Table 5.44. Selective removal of H₂S — utilities and capital costs

	Air-blown Lurgi	Oxygen-blown Lurgi	Air-blown IGT	Oxygen-blown IGT
Utilities				
Regenerator heat load	90.4 x 10 ⁶ Btu/hr	62.7 x 10 ⁶ Btu/hr	74.0 x 10 ⁶ Btu/hr	46.0 x 10 ⁶ Btu/hr
Regenerator overhead condenser cooling load ^a	20.2 x 10 ⁶ Btu/hr	13.0 x 10 ⁶ Btu/hr	3.0 x 10 ⁶ Btu/hr ^b	10.0 x 10 ⁶ Btu/hr
Lean solution cooling load	62.3 x 10 ⁶ Btu/hr	55.1 x 10 ⁶ Btu/hr	70.0 x 10 ⁶ Btu/hr	39.0 x 10 ⁶ Btu/hr
Makeup water	1.5 gal/min	2.2 gal/min	4.0 gal/min	1.1 gal/min
Capital costs	\$11.2 million	\$8.5 million	\$10.0 million	\$6.9 million

^aAir cooling specified in Fluor report (ref. 16).

^bValue inconsistent with others reported; by comparison with other heating and cooling loads, the condenser cooling load is estimated to be between 15 x 10⁶ and 20 x 10⁶ Btu/hr.

Table 5.45. Selective removal of H₂S from a low-Btu gas

	Feed gas composition		Condition	
	(lb-mole/hr)	(vol %)	Parameter	Value
H ₂	2,008.7	18.51	Temperature	1100 to 1200°F
CO	1,906.2	17.57	Pressure	300 psig
CO ₂	973.6	8.97	Sulfur (H ₂ S)	2,133 lb/hr
CH ₄	276.7	2.55	Dust	572 lb/hr
C ₂ H ₆	25.6	0.24	Tar	991 lb/hr
N ₂	4,991.0	46.00	HHV	150 Btu/scf
H ₂ S	66.6	0.61		
H ₂ O	602.2	5.55		
	10,850.6	100.00		
1b/hr	258,433			
Molecular weight of gas	23.82			

Table 5.46. Sellexol plant characteristics

	Value
Utilities	
Regenerator heat load	17 x 10 ⁶ Btu/hr
Cooling load	11 x 10 ⁶ Btu/hr
Power	600 bhp
Chemicals	50 lb/day Sellexol solvent (dimethylether polyethylene glycol)
Capital cost	\$3.8 million

Allied Chemical Corporation response. The capital cost has been escalated to first quarter 1977. The vendor response reports the H_2S off-gas to be concentrated and therefore suitable for Claus-type sulfur recovery. The specific concentration of H_2S is not provided, although Battelle-Columbus opines a concentration of 20 to 30% H_2S in the Claus-plant feed.⁹ The level of H_2S removal required is not clearly stated in the Battelle-Columbus report, but discussion of the gas cleaning requirements invokes the federal limit of 1.2 lb SO_2 per million Btu of fuel. This is stated to be equivalent to about 1100 ppm H_2S in the treated fuel gas; hence, it is assumed that the Selexol process is designed to remove at least 85% of the H_2S in the feed gas.

To assist in scaling the previously listed capital and operating costs to other applications, a parametric study of Selexol solvent treating costs, reported by R. V. Deraerschot, is valuable.³ Relative variations in capital and operating costs caused by changes in absorber pressure, temperature, and packing height are given in Table 5.47 for the case of selective H_2S and CO_2 removal from a gas produced by partial oxidation of oil.³ The capital component of relative treating cost is determined by amortization of capital cost over ten years, using straight line depreciation.

Table 5.47. Relative economics of Selexol

Parameter	Relative cost ratio		
	Capital	Operating	Treating
Pressure, psia			
250	1.27	1.08	1.16
500 ^a	1.00	1.00	1.00
1000	1.09	1.20	1.16
1500	1.35	1.39	1.37
Temperature, °F			
20 ^a	1.00	1.00	1.00
100	1.61	1.36	1.44
Packing height, ft			
100 ^a	1.00	1.00	1.00
150	0.80	0.46	0.56

^aBase case conditions.

5.5.5 References

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5.6 The Molecular Sieve Process

In Sect. 3, the consensus opinion found in the open literature appeared to relegate molecular sieve application to the removal of trace quantities of sulfur; however, the economics of molecular sieve processes for selectively removing bulk H_2S from low-Btu, coal-derived gas have not been well defined in the literature. It is appropriate, therefore, to include a description of molecular sieves, pointing out advantages and disadvantages. Costs for several coal-derived gas cleanup applications have been provided by a molecular sieve vendor (Union Carbide Corporation, Linde Division) and are discussed in Sect. 5.6.4 (process operation and economics).

5.6.1 Background

Naturally occurring molecular sieves belong to a mineral class known as zeolites. These hydrated silicates of aluminum, with various alkali metals, have a crystalline structure which can selectively adsorb and later release specific molecules.¹ Release of adsorbed water from heated zeolite and readsorption of water by cooled zeolite was noted 200 years ago, but it was not until the 1920s that the ability of molecular sieves to selectively adsorb other molecules was recorded. Several years later, x-ray diffraction tests disclosed the crystalline structure of zeolite.²

When the Linde Division began investigating various adsorbents in 1948, natural zeolite showed the most potential.² To overcome handicaps of mineral scarcity and natural chemical and physical variability, Linde Division pursued the possibility of synthesizing zeolite.² The program resulted in preparation of over 30 distinct synthetic zeolites by 1953, with commercial introduction in 1954.^{1,2} Since that time, extensive development of molecular sieves has resulted in a wide range of applications in the petroleum refining, chemical, natural gas, and atmospheric gas industries.³

The use of molecular sieves for desulfurizing various process streams is of principal interest in this evaluation. Dravo Corporation reports over 150 commercial desulfurization units installed worldwide, at gas

flow rates from 1×10^6 to 1000×10^6 scfd.⁴ Reported advantages of molecular sieve use for removal of H_2S include:^{3,5}

1. selective removal of H_2S in the presence of CO_2 ;
2. no corrosion, foaming, or wet chemical handling problems;
3. production of desired purity product immediately after startup, with infinite turn-down ratio;
4. little operator attention and low operating costs; and
5. regeneration of the spent bed, yielding an acid gas with an enriched H_2S content more suitable for further processing.

The use of molecular sieves also has several disadvantages:⁵⁻⁸

1. The adsorbent catalyzes the formation of COS from H_2S and CO_2 .
2. Regeneration requires heating of a substantial portion of treated gas to about 500 to 600°F.
3. Use of the regeneration gas may require additional processing because of the high H_2S content.
4. Substantial carry-over of oils or glycol decreases effective bed capacity and bed life.

5.6.2 Process description

The specific flowsheet for a molecular sieve desulfurization process is dependent on many design decisions, including the number of beds, the method of regeneration, the operating conditions, the desired gas purity, and the disposition of regeneration gas. The basic flowsheet which corresponds to the conceptual evaluations prepared by Linde Division for treating coal-derived gas is shown in Fig. 5.32.^{1,5,7-9} Gas flows are all in the vertical direction, which is typical of molecular sieve applications.¹⁰ The final disposition of regeneration gas is not addressed by the flowsheet in Fig. 5.32. Further discussion of this topic is deferred to Sect. 5.6.4 (process operation and economics).

Four primary methods exist for regenerating spent adsorbent.^{10,11} The process flowsheet in Fig. 5.32 shows a thermal swing cycle in which

Fig. 5.32. Molecular sieve H₂S removal process.

adsorbent capacity is significantly decreased by elevated temperature. Typically, a gas stream is used to directly heat the bed of regenerating adsorbent and to carry away desorbed gaseous species. A pressure swing cycle relies on reduced adsorbent capacity at lower pressures to desorb the significant compounds. The third possible method of regeneration depends on the removal of adsorbed compounds by absorption in a gaseous or liquid stream that is passed through the spent bed of adsorbent. The last method used commercially forces out adsorbed species by displacement with other compounds in a regeneration fluid.

The regeneration gas shown in Fig. 5.32 flows through a bed of adsorbent in the opposite direction of the feed gas. If regeneration is performed cocurrent to the direction of feed gas, some adsorbed compounds will be desorbed at the front of the bed, only to be resorbed in the relatively fresh adsorbent at the bed exit.¹⁰ These compounds must again be desorbed. With countercurrent heating, however, the unused section of the bed is not contacted by desorbed species. In addition, the bed is most active with lowest residual loading at the exit of the bed when returned to adsorbing duty. Cocurrent flow produces the opposite effect; that is, the lowest residual loading occurs at the entrance of the bed and a higher residual loading occurs at the bed exit. The lower exit loading, resulting from countercurrent regeneration, favors a higher degree of adsorbable compound removal in the subsequent adsorption step.¹⁰

Because a thermal swing cycle is used for regeneration, the regenerated bed requires cooling prior to its return to adsorption. Figure 5.32 shows the cooling gas flowing in the same direction as the feed gas. If the cooling gas contains no adsorbable component, then countercurrent cooling, with a separate gas stream for countercurrent regeneration, would provide the lowest bed exit residual loading.¹⁰ But the case under consideration uses a side-stream of product gas for both cooling and subsequent heating. In this system, cocurrent cooling (and countercurrent heating) results in a lower residual loading. This is the preferred mode of operation for many purification systems.¹⁰ Figure 5.33 shows the effects of flow directions in heating and cooling operations.¹⁰

Fig. 5.33. Options for direction of heating and cooling flows.

It is assumed that the cooling gas in option A (Fig. 5.33) contains no adsorbable compounds. Series cooling and heating with the same gas stream is not suitable for option A.

5.6.3 Process data

Molecular sieves are crystalline metal aluminosilicates with two basic structures in commercial use.^{2,11} Both contain tetrahedra formed by four oxygen atoms surrounding a silicon or aluminum atom. The silicon tetrahedron balances the excess oxygen charges with adjacent tetrahedra; however, an aluminum tetrahedron will still have a net negative charge after sharing oxygen with other tetrahedra because aluminum is trivalent while silicon is quadrivalent. Cations such as sodium, potassium, or calcium are added to balance the overall charge. Up to half of the crystalline structure can consist of alumina tetrahedra. The tetrahedra bond to form a truncated octahedron with a tetrahedron at each point.

When the octahedra bond to form a cubic array, the resulting molecular sieve is called type A.^{2,11} The second basic commercial structure, called type X, results from a tetrahedral (diamond-shaped) array of the octahedra. Chemical formulas for these types, where sodium is used to balance the charge, are shown below for the basic hydrated cell:²

The water of hydration is the maximum amount of water that fills the voids in the adsorbent structure. This loosely bound water is removed by moderate heating during preparation of the molecular sieve.

The dehydrated crystalline structures have specific uniform apertures which permit access to the internal cavities of molecular sieve crystals.^{2,11} The size of the apertures is controlled by varying the cation used for charge balancing or by changing the basic cell structure (e.g., type A or type X). The type 4A sieve, for example, has sodium cations which affect the pore size and produce a free aperture size of $3.5 \text{ \AA}$ ($3.5 \times 10^{-10} \text{ m}$). Molecules with effective diameters up to $4 \text{ \AA}$ can easily pass through this opening. Exchanging a large fraction of the sodium ions with potassium

ions will produce type 3A sieve with openings of about 3 Å. Analogously, exchange with calcium ions yields type 5A with approximately 5-Å openings. By going to the diamond-shaped structure of type X molecular sieves, the openings created by the crystalline structure are about 10 Å. By replacing some of the sodium ions in the 13X type, modest changes in the aperture size can be effected, similar to the variations in type A molecular sieves. Table 5.48 lists the basic types of molecular sieves marketed by Union Carbide Corporation.¹⁻³

Molecular sieves not only separate molecules by size, but also by preferential adsorption based on polarity. Molecules that can enter the pores are held more tightly when less volatile, more polar, or more unsaturated.² Compounds are held within the sieve structure by Van der Waals-type physical forces, following Langmuir's theory.¹¹ In this type of removal system, the amount of material adsorbed will show a rapid increase to its equilibrium value as its gas phase concentration is increased. Additional concentration increases cause no changes in adsorption equilibrium. This is demonstrated by the equilibrium capacity curves shown in Figs. 5.34 and 5.35 for various significant compounds.^{1,2,8,11} The capacity curves show that lower capacities are experienced by molecular sieves at elevated temperature. A change of 10°F in feed temperature, when operating near ambient temperatures, can cause a difference of as much as 20% in the required amount of molecular sieve.⁴

In a series of tests, Cines, Haskell, and Houser (Phillips Petroleum Company) have examined the removal of H₂S from natural gas.⁶ These experiments cover a range of feed temperatures, molecular sieve types, and H₂S concentrations (Table 5.49).⁶ The two gas compositions listed in the table reflect approximate gas composition before H₂S and CO₂ additions but after the O₂ in the gases has been reduced from 500 ppmv to below 2 ppmv by catalytic reaction with CO in 50% stoichiometric excess. Gas 2 was generated by addition of propane, butane, and pentane to gas 1; this was done to provide a natural gas enriched in natural gas liquids. No COS was detected in the feed gas. Regeneration occurred at 600 to 650°F and at process pressure. A countercurrent flow of inert gas stripped the bed while treated gas provided cocurrent cooling.

Table 5.48. Basic types of molecular sieves marketed by Union Carbide Corporation

Basic type	Nominal pore diameter (10^{-10} m)	Sieve form	Bulk density (lb/ft ³)	Maximum heat of adsorption (Btu/lb H ₂ O)	Equilibrium H ₂ O capacity (wt %) ^a	Applications
3A	3	Powder	30	1800	23.0	Dehydration of unsaturated hydrocarbon streams; drying polar liquids such as methanol and ethanol; adsorbs H ₂ O, NH ₃ , He (molecules with diameters less than 3 Å).
		1/16-in. pellets	44		20.0	
		1/8-in. pellets	44		20.0	
4A	4	Powder	30	1800	28.5	Static desiccant in refrigerant systems, other closed systems; drying saturated hydrocarbon streams; adsorbs H ₂ S, CO ₂ , SO ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₂ H ₅ OH (molecules less than 4 Å).
		1/16-in. pellets	45		22.0	
		1/8-in. pellets	45		22.0	
		8 x 12 mesh beads	45		22.0	
		4 x 8 mesh beads	45		22.0	
		14 x 30 mesh	44		22.0	
5A	5	Powder	30	1800	28.0	Separation of normal paraffins from branched-chain and cyclic hydrocarbons; adsorbs n-paraffins, n-olefins, n-C ₄ H ₉ OH (molecules less than 5 Å).
		1/16-in. pellets	43		21.5	
		1/8-in. pellets	43		21.5	
10X	8	Powder	30	1800	36.0	Separation of aromatic hydrocarbons; adsorbs isoparaffins and olefins, benzene (molecules with effective diameters less than 8 Å).
		1/16-in. pellets	36		28.0	
		1/8-in. pellets	36		28.0	
13X	10	Powder	30	1800	36.0	General gas drying; combined H ₂ O and CO ₂ removal; H ₂ S and especially mercaptan removal; adsorbs molecules with effective diameters less than 10 Å.
		1/16-in. pellets	38		28.5	
		1/8-in. pellets	38		28.5	
		8 x 12 mesh beads	42		28.5	
		4 x 8 mesh beads	42		28.5	
		14 x 30 mesh	38		28.5	

^a H₂O capacity: 1b H₂O per 100 lb activated adsorbent at 0.338 psia and 77°F.

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Fig. 5.34. Equilibrium molecular sieve capacity on type A sieve at 77°F vs pressure.

Fig. 5.35. H₂S equilibrium molecular sieve capacity on various molecular sieves at various temperatures.

Table 5.49. Test conditions for the removal
of H₂S from natural gas

Condition	Value
Parameter	
Pressure, psia	765
Temperature, °F	40-76
Linear velocity, ft/min	25
Feed gas compositions	
H ₂ S, ppmv	30-160
CO ₂ , vol %	1-3
C ₃ H ₈ and higher, vol %	1.3-4.7
Prior to H ₂ S and CO ₂ addition	<u>Gas 1 (vol %)</u> <u>Gas 2 (vol %)</u>
N ₂	1.5 1.5
CO ₂	0.4 0.4
CO	0.05 0.05
CH ₄	89.9 86.2
C ₂ H ₆	6.8 7.1
C ₃ H ₈	1.0 3.5
C ₄ H ₁₀	0.22 0.9
C ₅ H ₁₂	0.07 0.25
C ₆ H ₁₄₊	0.04 0.10

Cines and his co-workers explored the catalytic effect of five custom desulfurization grade molecular sieves on the reaction:⁶

Because the COS formed is not nearly adsorbed to the extent of H₂S, COS will appear in product-gas streams before H₂S breakthrough. Where a product-gas purity specification is based on allowable H₂S concentration, reaction (26) is advantageous because it reduces the total amount of H₂S that requires removal. This reaction will either reduce the amount of molecular sieve required or allow longer adsorption time for a fixed-bed size; however, specifications on product-gas purity related to total sulfur concentration are more difficult to meet as a result of reaction (26). Table 5.50 shows the results of tests when gas 1, at 2.2 vol % CO₂ and the specified H₂S feed concentrations, was treated until H₂S in the effluent reached 1 ppmv.⁶ At this point H₂S loading was determined. A wide range of catalytic activity is apparent. Type 4A and type 13X sieves were charge-balanced primarily by sodium cations and showed high conversion rates for H₂S to COS, especially the large pore-size, 13X type. Type 5A sieve, in which much of the sodium had been replaced by calcium, exhibited the lowest catalytic effect for reaction (26). Other custom-designed sieves can further reduce this conversion.

Table 5.50. Test results for H₂S removal with five molecular sieves^a

Molecular sieve number	Feed H ₂ S (ppmv)	Temperature (°F)	H ₂ S removal ^b (lb/100 lb sieve)		H ₂ S converted to COS (%)
			Total	Net adsorbed	
5A - I	40	76	0.16	0.15	5
5A - II	40	76	0.18	0.15	17
4A - I	33	60	0.93	0.42	55
4A - II	33	60	1.30	0.45	64
13X - I	33	60	1.07	0.13	88

^a Gas treated is gas 1 from Table 5.49, with 2.2 vol % CO₂.

^b Removal calculated when effluent H₂S reached 1 ppmv; total removal includes H₂S adsorbed and H₂S converted to COS.

The H_2S loadings reported in Table 5.50 are much lower than those shown at equilibrium in Fig. 5.35; at least two factors are cited for this:⁶

1. Tests were performed under dynamic conditions and equilibrium was not reached through the bed.
2. Other compounds competed with H_2S for adsorption, as a function of molecular sieve type.

Unpredictable effects on dynamic H_2S loadings were found to result from temperature variations and the addition of heavier hydrocarbons. Hence, experimental testing is recommended when commercial experience is not available for a particular application.⁶

The recommendation of actual testing, under conditions similar to those expected in a commercial system, is also voiced by Kunkel and Chobotuk (Amoco Production Company) who reviewed several problems in attaining design capability in treating natural gas.⁷ Some problems encountered and overcome include (1) valve leakage, (2) water contamination, (3) leakage through cracks in the refractory lining, and (4) flow maldistribution through the bed during high pressure operation (about 1200 psia). The flow maldistribution allowed bypassing of much of the bed, as well as rapid H_2S breakthrough. New inlet distributors were tried without success, but operation at lower pressure (about 465 psia) sufficiently improved flow distribution so that product-gas specifications could be met.⁷

5.6.4 Process operation and economics

The economics of molecular sieve H_2S removal can be highly affected by the disposition of the sour regeneration gas. Where the value of the gas is low and environmental limits on SO_2 are not exceeded, combustion of the regeneration gas as fuel within the treating facility is likely to be the lowest cost option. An exception is a system treating a small portion of a gas stream destined for further downstream processing. In this case, the regeneration gas can be reinjected into the mainstream of gas prior to such processing.⁷ This option is more prevalent in certain natural gas applications and is unlikely when treating a coal-derived,

low-Btu gas. For coal-gas applications, it is probable that the regeneration gas will require further processing. The net effect of molecular sieve treating, then, is to concentrate the H_2S in the regeneration gas.

Engineers and Fabricators Company (EFCO) has proposed a closed-cycle system for molecular sieve desulfurization in which the regeneration gas is treated to remove the bulk of the H_2S .⁸ In the EFCO process, the regeneration gas exiting the feed-exit exchanger (Fig. 5.32) is cooled, condensate is removed in a separator, and the gas is washed in an absorption tower to remove H_2S and COS . Removal of COS is required to prevent substantial buildup in the recycle system. Treated regeneration gas is recycled to the front of the molecular sieve plant. Sour wash solution is flashed to remove most of the absorbed acid gas and is then recycled to the top of the absorber. The flashed acid gas then requires treatment in a sulfur recovery plant (e.g., Claus, Stretford, etc.). This type of process is adaptable to treating coal-derived gas; however, the low-pressure systems expected for coal-derived, low-Btu gas (below 300 psia) will require a more extensive absorption system for the regeneration gas, and the treated regeneration gas would probably be blended back with the clean fuel gas or used elsewhere in the system for fuel, rather than being recycled to the molecular sieve adsorption beds.

Vendor quotes for molecular sieve plants that treat a number of low-Btu coal gases have been obtained from Union Carbide Corporation, Linde Division.⁵ Table 5.51 denotes the test cases provided Linde for their evaluation.¹² The design conditions include a maximum of 1000 ppmv sulfur compounds in the treated gas and a minimum of molecular sieve inventory and regeneration requirements. A summary of the vendor response is shown in Table 5.52.⁵ The flow pattern is similar to that shown in Fig. 5.32, where the regeneration gas is first used to cool a regenerated bed and then used for heating a second bed. Heating and cooling occur at about the same pressure as adsorption (about 240 psia); the cooling gas is at 90°F, while the heated gas is at 550°F. About the same quantity of H_2S is converted to COS in each case by the reaction shown in Eq. (26). For cases 3 and 4 in which feed H_2S is initially low, the percentage of conversion is much higher, although total sulfur in the treated gas is

Table 5.51. Test cases^a

Composition	Molecular weight	Case 1		Case 2		Case 3		Case 4	
		Mole %	lb/hr	Mole %	lb/hr	Mole %	lb/hr	Mole %	lb/hr
Component									
CC	28.01	21.28	596,053	21.28	29,803	21.43	563,285	21.43	28,154
CC ₂	44.01	8.51	374,525	8.51	18,726	8.57	353,936	8.57	17,696
F ₂	2.02	14.84	29,977	14.84	1,499	14.95	28,339	14.95	1,417
F ₂ S	34.08	0.74	25,219	0.74	1,261	0.11	3,518	0.11	176
COS	60.08	0.05	3,004	0.05	150	0.01	564	0.01	28
N ₂	28.01	51.07	1,430,471	51.07	71,524	51.42	1,351,568	51.42	67,578
CH ₄	16.04	3.19	51,168	3.19	2,558	3.21	48,317	3.21	2,416
F ₂ O	18.02	<u>0.32</u>	<u>5,766</u>	<u>0.32</u>	<u>288</u>	<u>0.30</u>	<u>5,073</u>	<u>0.30</u>	<u>254</u>
		100.00	2,516,183	100.00	125,809	100.00	2,354,600	100.00	117,729
Property									
10 ⁶ scfd		910.87		45.54		854.75		42.74	
Temperature, °F		90		90		90		90	
Pressure, psia		240		240		240		240	
Average molecular weight		25.16		25.16		25.09		25.09	

^a Case 1 — high sulfur, high flow rate; case 2 — high sulfur, low flow rate; case 3 — low sulfur, high flow rate; case 4 — low sulfur, low flow rate; remove H₂S to 100 ppmv; indicate level of removal of other components (e.g., H₂O, COS).

Table 5.52. H₂S removal from low-Btu coal
gas using molecular sieve adsorption

Parameter	Case 1	Case 2	Case 3	Case 4
Number of trains	6	1	4	1
Beds per train (adsorbing/heat and cool)	4/2	2/2	4/2	1/2
Cycle time, hr/bed (adsorbing/heat/cool)	4/1/1	4/2/2	4/1/1	4/4/4
Adsorbent, ft ³ /bed	2675	1470	1670	1335
Bed dimensions (diameter x height), ft	12.5 x 21.8	10 x 18.7	11.5 x 16.1	10 x 17
Gas flow per bed, 10 ⁶ scfd (adsorbing/series heat and cool)	38/65	22.75/20.5	53.5/48	42.7/10
Pressure drop, psi (adsorbing/heat/cool)	1/3/3	0.9/1.7/1.7	2.1/3.7/3.7	2.5/0.5/0.5
Product-gas composition, ppmv				
H ₂ O	<1	<1	<1	<1
H ₂ S	<10	<10	<10	<10
COS	<1000	<1000	<400	<600
Total H ₂ S removed, lb/100 lb sieve	3.84	4.17	1.27	1.27
Capital costs (uninstalled)	\$9.4 million	\$700,000	\$5.5 million	\$420,000

lower than for cases 1 and 2. The molecular sieve specified by Linde is type MZ 1116 (1/8-in. pellets). The sieve is a derivative of type A, in which calcium ions have been exchanged for a portion of the sodium ions, as in the manufacture of type 5A sieves, and post-treatment has been employed to produce a desulfurization-grade molecular sieve. Molecular sieves can be designed for much lower H_2S and COS levels than those shown in Table 5.52; however, the design specification only requests sulfur control to <1000 ppmv.

The dynamic H_2S loadings are given for total removal of H_2S . These values are much lower than equilibrium loadings because allowance is made for coadsorption of other compounds (principally H_2O) and because the beds are not operated to equilibrium.

To simplify installation, the beds have been sized to permit skid-mounted units.⁵ Use of field-erected vessels would reduce the required number of trains in cases 1 and 3, but would increase the time and complexity of installing these plants. The capital costs in Table 5.52 are for shop-manufactured equipment and include all vessels, piping, valves, heaters, controls, and the Linde molecular sieve required for each case.⁵ The vendor estimates that these costs are probably no more accurate than $\pm 20\%$. Not included in these costs are freight, site preparation, and erection costs (e.g., piping the skids up to adjacent processing systems). Such charges usually increase the total capital cost to twice the equipment cost for each system.⁵

The complete cost for the use of molecular sieves to desulfurize coal-derived fuel gas must include the expense of treating the regeneration gas. For such calculations, Table 5.53 lists the approximate conditions of the regeneration gases obtained in cases 1 through 4. The most important assumption used is that all of the adsorbed species are released to the heating gas during regeneration; this establishes the maximum load for further processing. Because major changes from the feed-gas composition are only expected for H_2S , COS , and H_2O , these are the only values listed. Other compounds should be present in approximately the same proportions as in the feed gas (Table 5.51).

Table 5.53. Approximate values for the sour regeneration gases

Parameter	Case 1	Case 2	Case 3	Case 4
Maximum temperature before heat recovery, °F	550	550	550	550
Total flow rate before regeneration, 10 ⁶ scfd	390	20.5	192	10
Approximate pressure, psia	230	233	227	233
Sour Regen gas composition				
H ₂ S, vol %	<1.57	<1.50	<0.35	<0.25
H ₂ O, vol %	<0.79	<0.75	<1.44	<1.47
COS, ppmv	<980	<980	<393	<590
Total flow rate after regeneration, 10 ⁶ scfd	399.42	20.97	195.50	10.17

A small amount of CO_2 is consumed in the conversion of H_2S to COS, but not enough to affect the purposes of this evaluation. The values shown for H_2S reflect an enrichment in H_2S concentration in the regeneration gases, as compared to that originally present in the feed gas. The use of molecular sieve treating has substantially reduced the sour-gas quantities while simultaneously increasing the H_2S contents. Thus, the load on a subsequent treating step such as physical solvent, amine, or hot potassium carbonate scrubbing is reduced from that which occurs when no molecular sieve system is used. The economic application of molecular sieves depends on the overall cost of such a combined system as compared to the cost of using only conventional liquid scrubbing. Operating costs, as well as capital costs, should be included in such an evaluation.

5.6.5 References

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5.7 The MERC High-Temperature Iron Oxide Process

5.7.1 Background

Original application of iron oxide to the removal of H_2S from coal-derived gases was at ambient temperatures, generally 100°F and below.¹ Such low-temperature applications have removed H_2S from coal gases since the middle of the nineteenth century. The Appleby-Frodingham Steel Company developed a regenerable process using pulverized iron oxide in a fluid-bed reactor to remove H_2S and organic sulfur compounds from coke-oven gases at elevated temperatures (around 700°F).² After pilot-plant development proved process feasibility in the 1950s, full-scale commercial plants were installed to treat coal-derived gases at the Exeter Works of the South Western Gas Board and in Scunthorpe, England. Operation demonstrated some technical problems, but none were believed insurmountable; however, economic concerns largely dictated the Exeter plant shutdown in 1965.² Operation at the Scunthorpe desulfurization plant has also been terminated.

Several years ago, experimental efforts on the removal of H_2S by fixed beds at high temperature were begun at Morgantown Energy Research Center of the Bureau of Mines (subsequently transferred to ERDA and then to the Department of Energy). Based on criteria of efficient H_2S removal above 1000°F , physical strength, regenerability, sorbent life, and economic feasibility, laboratory studies have led to the selection of iron oxide mixed with fly ash, in extruded pellets, as a promising sulfur-removal sorbent at high temperature.^{3,4} Subsequent studies have shown that silica is also a suitable supporting matrix for iron oxide and offers some advantages over fly ash.⁵ Testing of various mixtures of iron oxide and silica or fly-ash substrates has been successfully performed using actual hot, low-Btu fuel gas produced in a fixed-bed coal gasifier.^{5,6} Recent efforts have returned to laboratory-scale tests for gas characterization and contaminant removal.⁷

5.7.2 Process description

The MERC fixed-bed iron oxide process has not been commercially applied; therefore, proven flowsheets for the process are not yet available. Several organizations have performed conceptual evaluations of the MERC process in coal-derived fuel gas applications for the Electric Power Research Institute; these evaluations permit the assessment of process potential.^{8,9} (Discussion of the results of these reports is deferred to Sect. 5.7.4, process operation and economics.) The flowsheets proposed for the MERC process are similar and are shown, in a general fashion, in Fig. 5.36. Feed gas is shown entering at the top of the H₂S removal reactor and exiting at the bottom; the regeneration gas flows in the opposite direction. Reversal of these flows may be advisable to prevent particulate buildup at the top of the reactor.⁵

Of major concern to the MERC process is the manner of regeneration and the subsequent treatment of the regenerated SO₂ off-gas. The high exothermicity involved in the regeneration reaction imposes restrictions on the allowable methods for regeneration. Control of temperature excursions in the fixed-bed reactor is required to prevent sorbent and equipment damage; techniques employed include low air flowrates and dilution of air with nitrogen at higher flowrates.¹⁰ Air produces SO₂ concentrations in the off-gas of about 11 to 12%. Using a one-to-one ratio of air-to-nitrogen diluent allows higher flowrates without excess temperatures, but this cuts the off-gas SO₂ concentration in half.¹⁰

The SO₂ off-gas requires further treating, and several options have been proposed. When a market is available, the off-gas is suitable feed to a sulfuric acid plant. This was the approach pursued in the Appleby-Frodingham process.² Production of elemental sulfur is the other major option, and it requires a chemical reduction of the SO₂ in the off-gas. The TVA and Stone & Webster studies propose using the Allied Chemical Corporation's SO₂ reduction technology to reduce the off-gas SO₂ to elemental sulfur.^{8,9,11} This system requires a reducing gas for the reaction with SO₂; natural gas is used commercially.¹¹ TVA assumed use of such natural gas, while the Stone & Webster study relied on Allied Chemical's assessment that use of a coal-derived fuel gas would be

Fig. 5.36. Conceptual flowsheet for the MERC process.

feasible.^{8,9} Another possible process for reducing the SO_2 to elemental sulfur has been developed by the Foster-Wheeler Energy Corporation.^{12,13} Called the Resox* process, it relies on use of coal at high temperature, rather than a separate reducing gas, to reduce the SO_2 . Although concern has been voiced about the efficiency of SO_2 control at concentrations below 20 vol %, ⁹ the process is claimed operable down to 2 vol % inlet SO_2 .¹³ Possible methods exist to enrich the SO_2 content, if necessary, to ensure high efficiency (above 90%) SO_2 recovery as elemental sulfur.¹²

A potential improvement in the MERC process would be operation in a moving-bed continuous mode, rather than in the cyclic fixed-bed operation thus far demonstrated (Fig. 5.36).^{5,7,14} One major advantage for attempting moving- or fluidized-bed operation is the superior temperature control possible during regeneration.^{5,7} In addition, operation would be simplified by elimination of most of the manifolding and valves required for cyclic fixed-bed systems. The processing impediment to such operation is sorbent durability (e.g., minimal attrition and sorbent degradation required).¹⁴ This is especially difficult to achieve in a fluid-bed system; hence, extension of the MERC process to moving-bed operation is more compatible with sorbent strength. Figure 5.37 provides an example of the moving-bed process and illustrates the potential problems as well as the expected advantages.

Use of a cooled conveying system for the spent sorbent allows regeneration with high O_2 -content gas; thus the SO_2 off-gas can be produced at very high SO_2 concentrations, which simplifies downstream SO_2 processing. For the system shown in Fig. 5.37, mechanical concerns are paramount. Movement of a solid at process pressures (perhaps 200 to 300 psi) and at the temperatures likely for regeneration (1500 to 1700°F) will impose stringent and possibly unachievable requirements for mechanical conveying systems. The operating conditions may preclude such common conveying systems as screw or belt conveyors. Transport in dense phase by process gas or steam should be considered, as should maximum use of gravity transport. If the concept proves feasible, a moving-bed absorber would

* Resox is a registered trademark of the Foster-Wheeler Energy Corporation.

Fig. 5.37. Conceptual moving-bed iron oxide process.

also permit higher sulfur loading in the sorbent sent to regeneration. Constantly feeding fresh sorbent to the absorber prevents the H₂S breakthrough that would occur in a fixed bed operating at such high sulfur loadings. Maximum use of sorbent capacity for H₂S removal reduces the required amount of sorbent. Moving-bed operation offers several possible advantages, such as high SO₂ concentration in the off-gas and maximum sulfur loading of the sorbent. Two major questions must be resolved for its application: (1) the sorbent strength (e.g., resistance to attrition) and (2) the method of transporting the sorbent through a regeneration zone and back to the reactor.

5.7.3 Process data

A considerable amount of development effort has been devoted to producing a strong, dependable sorbent. At MERC and at Air Products and Chemicals, Inc. (under ERDA contract), numerous tests have been performed on various combinations of iron oxide on two supports (fly ash or silica).^{3,5,6,10,14-16} The results of these studies are reviewed herein to assess the potential of fixed-bed systems. Discussion of other approaches, such as moving-bed operation, has been presented in Sect. 5.7.2 and will not receive further attention.

The basic chemistry involved in the MERC process is sulfidation of iron oxide during absorption and reoxidation of the iron sulfide during regeneration. The proposed sequence of reactions representing this process begin with the fresh sorbent as Fe₂O₃. In the presence of hydrogen and temperatures above 650°F, the iron oxide is expected to be reduced to Fe₃O₄.⁵ Formation of further reduced species is also possible.⁷ The absorption reaction can then be represented as:⁷

Experimental measurement at MERC have not detected the formation of iron sulfides with S/Fe atom ratios higher than 1.1.⁷ Regeneration of the sulfided iron oxide can be represented by:⁷

A stoichiometric excess of oxygen then leads to further oxidation of the iron oxide to Fe_2O_3 .⁶ Basing the overall reactions on Fe_2O_3 , the absorption and regeneration steps can be represented by:

Other reactions may also occur in the process. For example, the water-gas shift reaction

is known to occur under absorber conditions.¹⁰ The reaction is catalyzed by the sorbent, and several runs have demonstrated that CO content is decreased and H_2 content is increased by several percent.¹⁰ Various parameters influence the impact of this reaction (i.e., temperature, inlet gas composition, and sorbent catalytic activity). These determine both the reaction equilibrium and the extent to which the reaction approaches equilibrium. For example, higher temperatures, although reducing the amount of CO shifted at equilibrium, increase the water-gas shift reaction rate, which allows a closer approach to theoretical completion.

A wide range of sorbent preparations and operating conditions have been reported.^{3,5,6,10,14-16} A summary of these highlights the preparations proven most successful in terms of H_2S removal capacity and crushing strength. Early tests showed that increasing the iron oxide concentration of fly ash, above the 15 wt % originally present, improved the sorption capacity.³ Above a total iron oxide content of 40 wt %, however, the sorbent had a fusion temperature within the range of normal operating conditions.³ Subsequent efforts (at MERC) used sorbents of 75 wt % fly ash and 25 wt % iron oxide, for effective total iron oxide contents below 40 wt %.^{5,6,10,14} Above 25 wt % added iron oxide, the prepared sorbents exhibited lower physical strengths and absorption capacities.⁵ Subsequent efforts have produced suitable sorbents at up to 42% iron oxide on fly ash.⁷ Silica-based sorbents, up to 45 wt % added iron oxide, did not experience degraded strengths or capacities.⁵

Although total iron oxide contents are not significantly different, the silica-supported iron oxide proved to have substantially greater sulfur capacity.⁵ This is probably caused by the bonding of fly ash--iron oxide in a matrix with silica and aluminum oxides, thereby reducing potential sulfur sorption sites.¹⁶ Various additives have also been tested for possible improvements in sorbent strength or sulfur capacity.¹⁰

Table 5.54 summarizes a number of sorbent tests at MERC, listing those sorbent preparations which resulted in high sorbent strength and sorption capacities.^{5,10,14} The H₂S capacities were calculated when the H₂S content in the gas exiting the absorber reached 0.64 vol % for the laboratory tests that used 2 vol % H₂S in the simulated producer gas feed.¹⁰ Effective capacity for a system specifying a much lower permissible H₂S breakthrough will be reduced from capacities listed in Table 5.54 that are closer to an equilibrium operation. The most favorable additives were laboratory-grade bentonite (a high-swelling clay material of 63% SiO₂ and 19% Al₂O₃) and sodium silicate solution (added as a technical-grade 40 to 42°Bé solution). Bentonite or sodium silicate were suitable additives for the fly-ash--supported sorbent, while only sodium silicate proved suitable for the silica-supported sorbent.⁵

The bed temperature for the tests in Table 5.54 was close to 1100°F. Sorption capacity declines at lower temperature. For example, tests with a producer gas at an average bed temperature of 1087°F gave an H₂S capacity of 10.43 wt % on a fly-ash--supported sorbent.⁷ Operation at 672°F, however, showed a reduced capacity of 7.60 wt %, while 616°F operation was still lower at 6.43 wt %.⁵ To prevent glass-like fusing of the fly ash, the maximum temperature recommended for long-term use of fly-ash--supported sorbents is 1500°F.^{5,10} Silica-supported sorbents have a higher fusion temperature that permits higher operating temperatures. Limited data indicate a likely temperature range of 1700 to 1800°F for long-term, silica-based sorbent operation.⁵ A silica--iron oxide sorbent was regenerated three times at 1750°F without apparent sulfur capacity loss or visible signs of damage.¹⁴ Long-term cycling tests of the silica--iron oxide sorbents have not been reported, but a fly-ash--iron oxide sorbent has been subjected to 30 cycles of absorption and regeneration.¹⁰ In

Table 5.54. Summary of high-potential H₂S sorbents tested by MERC

Sorbent	Additive	Crushing strength (lb/cm)	Surface area (m ² /g)	H ₂ S sorption capacity (wt %)
75% fly ash--25% iron oxide	0.5% bentonite	53.9 ± 13.9	1.073	11.90
	1.0% bentonite	53.2 ± 14.2	1.156	11.70
	1.5% bentonite	59.4 ± 7.3	1.503	10.50
	10 ml/lb sodium silicate	69.6 ± 35.8	a	10.40
55% silicate--45% iron oxide	None	75.5 ± 13.9	2.5	16.1
	6 ml/lb sodium silicate	68.0 ± 24.0	2.1	22.8

^aNot available.

treating a hot, simulated-producer gas containing tars and particulates, the sorbent showed little change in sulfur capacity, which remained about 10 to 12 wt % with no visible signs of damage.¹⁰

The sulfur capacities recorded in Table 5.54 generally were obtained on gas streams containing 8 to 12% steam.¹⁰ To examine the effect of higher steam concentrations, runs were made with steam contents of 15 to 20%. Along with increasing the extent of the water-gas shift reaction shown by reaction (31), excess steam also decreased the sulfur capacity of the sorbent. Two sets of comparison runs (at 1100°F and 1300°F) were reported.¹⁰ Both sets of data show approximately the same effect of increased steam content; that is, a 3% increase in steam content roughly correlates to a 1% decrease in sulfur capacity. The tests at 1100°F showed about 5% sulfur capacity decrease for a 15% steam increase.¹⁰ At 1300°F, a 28% decrease in sulfur capacity resulted from a 78% increase in steam content.¹⁰

Tests at Air Products and Chemicals, Inc. focused on initial sorbent capacity and strength; regenerability was not addressed in the work reported by E. L. Leuenberger.¹⁶ Specific details of the sorbent preparations were reported separately by D. M. Jenkins; variables included (1) iron oxide source (vendor), (2) amount of iron oxide added to the support, (3) use of fly ash or silica for support, (4) use of bentonite or kaolin as binder, and (5) conditions of the heat treatment applied to the raw, extruded pellet.¹⁵ The dynamic performance of the treated pellets was analyzed for sorption efficiency in 68 reported tests.¹⁶ The simulated, low-Btu gas used in the tests was free of tar and particulates and had a nominal composition as follows:¹⁶

<u>Component</u>	<u>Vol %</u>
N ₂	48.6
CO	20.5
H ₂	14.9
CO ₂	6.5
CH ₄	1.9
H ₂ S	0.6
H ₂ O	7.0

A fresh sorbent was used in each run; therefore, no data on regenerability and cycling ability were obtained. The value for sorption efficiency was defined by Air Products as the ratio of time the absorber is onstream (until a given percentage of H_2S breakthrough is achieved) and the time that would have been required had the bed perfectly absorbed H_2S (i.e., ultimate sulfur capacity throughout the bed prior to breakthrough).¹⁶ A more common measure of sorption efficiency is the ratio of average sulfur loading in the bed when a given percentage of H_2S breakthrough occurs to the equilibrium sulfur loading. In general, sorption efficiencies were determined when 10% of the feed H_2S content was present in the effluent.¹⁶

For the purpose of the Air Products and Chemicals, Inc. research objective (i.e., to develop a suitable fixed-bed absorbent from readily available and inexpensive materials), the defined sorption efficiency appears quite useful.¹⁶ For subsequent process design, however, values are required for effective sulfur capacity of the sorbent under specified conditions. For this reason, Table 5.55 provides results of six different iron oxide--fly-ash sorbents on the basis of ultimate and effective sulfur capacities. The range of values appears to be consistent with that reported in Table 5.54 for fly-ash--iron oxide sorbents. The effective sulfur capacities in Table 5.55 are lower than those in Table 5.54 because the former have been calculated at a lower H_2S breakthrough (10% of feed H_2S content).¹⁶ Values in Table 5.54 are the effective sulfur capacities at roughly 32% H_2S breakthrough and, therefore, are closer to ultimate sulfur capacity. Each of the sorbents shown in Table 5.55 contain 1.5% bentonite. Also, the addition of 2% hydroxypropylmethylcellulose (Methocel,^{*} type E, F, or K) in the wet sorbent mix was used to aid extrudability of the mix.¹⁵

Several other aspects of the efforts of Air Products and Chemicals, Inc. are pertinent to process design. Estimates are provided of the heat releases caused by the postulated reactions (previously discussed) represented by Eqs. (29) and (30). The estimated heat released by the absorption reaction [Eq. (29)] is 39,340 Btu per lb-mole of Fe_2O_3 reacted.¹⁶ If adiabatic conditions are assumed, temperature rise in the gas and solid,

* Methocel is a registered trademark of Dow Chemical Company.

Table 5.55: Fly-ash--iron oxide sorbents tested
by Air Products and Chemicals, Inc.

Sorbent code ^a	Iron oxide added ^b (wt %)	Ultimate sulfur capacity (wt %)	Effective sulfur capacity (wt %) ^c	Crushing strength (lb/cm)
705 x 9 - 2	25.5	10.84	6.50	54.3
705 x 10	24.9	11.23	5.95	37.2
705 x 11	28.7	13.92	9.74	64.6
705 x 13	31.7	10.33	6.71	36.0
705 x 14	26.0	10.17	5.09	35.0
705 x 15	27.3	8.71	3.66	44.0

^aAir Products and Chemicals, Inc. codes represent different suppliers of the iron oxide source added to fly ash.

^bIncludes impurities in the iron oxide.

^cCalculated at 10% H₂S breakthrough

during absorption, can be approximated as 20°F per 1% H₂S reacted in the gas and 100°F per 10% Fe₂O₃ reacted in the solid.¹⁶ Similar values for the regeneration reaction [Eq. (30)] are (1) 630,340 Btu of heat released per lb-mole Fe₂O₃ generated, (2) gas adiabatic temperature rise of 195°F per 1% O₂ reacted, and (3) solid adiabatic temperature rise of 1575°F per 10% Fe₂O₃ generated.¹⁶ These values for the regeneration reaction clearly show the magnitude of the temperature control problem in regeneration of fixed-sorbent beds. Effective heat transfer out of the fixed bed would significantly enhance the process development.

Laboratory-scale operations at MERC, using actual producer gas, demonstrated that particulates that were deposited during the absorption cycle were burned out during regeneration.⁶ E. L. Leuenberger provides estimates of expected heat release on the basis of the following reaction:¹⁶

The reaction is estimated to release 169,423 Btu per lb-mole of combusted carbon. The gas adiabatic temperature rise is estimated at 235°F per 1% O₂ consumed, while solid-phase temperature rise under adiabatic conditions is 565°F per 1% coke combusted.¹⁶ This will add to the problem of temperature control during regeneration. Bench-scale tests at higher particulate loadings exhibit bed plugging; this indicates at least some need for particulate removal prior to the bed.⁷

Experiments at Air Products have also been used to investigate the effect of varying design parameters (e.g., linear velocity, temperature, pressure, etc.) on the sorbent performance. These data are valuable for process design decisions. The tests used a single iron oxide supply containing 79.8% Fe₂O₃ and various impurities. This is the same source used in Table 5.55 for sorbent code 705 x 9 - 2. The design variables examined are:¹⁶

1. linear velocity,
2. gas hourly space velocity (volume of producer gas per volume of absorption bed per hour),
3. temperature,

4. producer-gas H_2S concentration,
5. sorbent pellet diameter,
6. type of sorbent support and additives,
7. sorbent iron oxide content, and
8. pressure of absorption.

Results are reported by Air Products and Chemicals, Inc. in terms of the effect on sorbent efficiency. For example, an increase in linear velocity from 1.2 ft/sec to 2.3 ft/sec [at a constant gas hourly space velocity (GHSV) of 3600] increased sorption efficiency, at 10% H_2S breakthrough, from 0.41 to 0.51.¹⁶ An increased linear velocity will also increase pressure drop through the bed; this must be balanced against the increased sorption efficiency.

Those runs that demonstrate the parameter variations are shown in Table 5.56.¹⁶ Many of the listed cases serve to illustrate more than one variation. Table 5.57 summarizes the effect on sorption efficiency caused by altering the previously discussed design parameters. Referring to the effects listed in Table 5.57, increasing superficial velocity at constant GHSV increases sorption efficiency, while increasing GHSV at constant linear velocity causes a decrease in efficiency. Increased temperature, up to 1200°F, increases efficiency; little change is produced above this level. At 900°F, running the bed on sulfur-free reducing gas (used to heat the bed to operating temperature) caused the sorbent to disintegrate, but this phenomenon was only observed in a very narrow temperature range.^{7,16} Sorbent disintegration has been partially avoided by using inert gas (N_2) to heat the bed prior to operation, but some particle degradation still occurred at 900°F.¹⁶ Operation at the other temperatures (Table 5.57) did not produce such sorbent degradation.¹⁶

Only a small effect on sorption efficiency is caused by doubling the H_2S content of the feed gas, and this may not be statistically significant.¹⁶ Such a conclusion is compatible with MERC's experience.¹⁰ Use of smaller diameter sorbent pellets improves efficiency about 5 to 10% at 20 psig. Varying the type of support or additive produces little

Table 5.56. Effect on sorption efficiency of varying design parameters

Case No.	Run number	Sorbent code	Iron oxide source added ^a (wt %)	Net iron oxide added (wt %)	Sorbent support	Additive	Porosity (% H ₂ O absorbed)	Crushing strength (lb/cm)	Bed volume (cm ³)	Linear velocity ^b (ft/sec)	Pressure (psig)	Bed Temp. (°F)	GHSV (ft ³ gas/ft ³ sorbent · hr)	% H ₂ S in feed	Sorption efficiency at 10% F ₂ S breakthrough
1	1718SG	705x9-2x1	25	21.0	Fly ash	Bentonite	16.1	54.3	500	0.6	20	1200	1700	0.6	0.59
2	1720SG	803x1-1x2	30	25.2	Fly ash	Bentonite	18.6	63.3	500	0.6	20	1200	1800	0.6	0.63
3	1722SG	801x1-1x3	15	12.6	Fly ash	Bentonite	19.7	45.8	500	0.6	20	1200	1800	0.6	0.62
4	1723SG	806x1-1x2	10	8.4	Fly ash	Bentonite	20.7	46.7	500	0.6	20	1200	1800	0.6	0.48
5	1724SG	705x12-1x3 ^c	25	21.0	Fly ash	Bentonite	17.6	64.3	500	0.6	20	1200	1800	0.6	0.63
6	1725SG	801x2-1x2 ^c	15	12.6	Fly ash	Bentonite	17.7	46.7	500	0.6	20	1200	1800	0.6	0.70
7	1726SG	705x9-2x4	25	21.0	Fly ash	Bentonite	16.13	77.0	500	0.6	20	1200	1800	0.6	0.63
8	1727SG	705x9-2x4	25	21.0	Fly ash	Bentonite	16.13	77.0	500	0.6	20	1200	1800	0.6	0.59
9	1728SG	705x9-2x4	25	21.0	Fly ash	Bentonite	16.13	77.0	500	0.6	20	1400	1800	0.6	0.58
10	1730SG	801x2-1x4 ^c	15	12.6	Fly ash	Bentonite	18.18	50.5	500	1.2	20	1200	1800	0.6	0.83
11	1731SG	705x9-2x4	25	21.0	Fly ash	Bentonite	16.13	77.0	500	0.6	150	1200	1700	0.6	0.69
12	1734SG	801x1-1x5	15	12.6	Fly ash	Bentonite	19.89	77.0	1000	1.2	20	1200	1800	0.6	0.75
13	1736SG	803x1-1x4	30	25.2	Fly ash	Bentonite	19.34	44.0	500	0.6	20	600	1800	0.6	0.00
14	1738SG	705x9-3x4	25	21.0	Fly ash	Bentonite	15.30	85.0	1000	1.2	20	1200	1700	0.6	0.66
15	1739SG	705x9-3x7	25	21.0	Fly ash	Bentonite	15.40	81.0	1000	2.3	20	1200	3400	0.6	0.51
16	1740SG	705x9-3x4	25	21.0	Fly ash	Bentonite	15.25	84.5	500	1.2	20	1200	3500	0.6	0.41
17	1741SG	705x9-3x6	25	21.0	Fly ash	Bentonite	15.10	98.5	1000	1.2	20	1200	1800	1.2	0.60
18	1746SG	812x1-1x5	60	50.4	Fly ash	Bentonite	12.40	46.7	500	0.6	20	1200	1800	0.6	0.51
19	1748SG	814x1-1x7	50	42.0	Fly ash	Bentonite	15.96	26.7	500	0.6	20	1200	1800	0.6	0.77
20	1752SG	814x4-2x6	50	42.0	Silica	Kaolin	17.70	55.4	500	0.6	20	1200	1800	0.6	0.68
21	1753SG	814x2-2x6	50	42.0	Fly ash	Kaolin	16.90	40.8	500	0.6	20	1200	1800	0.6	0.75
22	1754SG	814x3-1x6	50	42.0	Silica	Bentonite	17.50	63.8	500	0.6	20	1200	1800	0.6	0.72
23	1755SG	705x16-1x6	25	21.0	Silica	Bentonite	18.10	41.3	500	0.6	20	1200	1800	0.6	0.78
24	1756SG	814x1-1x7	50	42.0	Fly ash	Bentonite	15.96	26.7	500	0.6	20	1200	1800	0.6	0.71
25	1758SG	705x9-2x1	25	21.0	Fly ash	Bentonite	16.10	54.3	500	0.6	20	900	1800	0.6	0.42
26	1761SG	705x9-3x7	25	21.0	Fly ash	Bentonite	15.36	81.1	500	0.6	400	1200	1800	0.6	0.80
27	1762SG	814x1-1x12	50	42.0	Fly ash	Bentonite	15.34	33.5	500	0.6	400	1200	1800	0.6	0.76
28	1765SG	814x1-1x12	50	42.0	Fly ash	Bentonite	15.34	33.5	500	0.6	150	1200	1700	0.6	0.76
29	1766SG	814x3-3x2	50	42.0	Silica	Bentonite	16.93	50.5	500	0.6	400	1200	1800	0.6	0.79

^aIncludes impurities present in the iron oxide supply.^bSuperficial velocities corrected to 1200°F, 20 psig.^cPellet is 1/8-in. in diameter; others are 1/4-in.-diam pellets.

Table 5.57. Summary of effects on sorption efficiency caused by parameter variations

Parameter	Value	Case No. ^a	Sorption efficiency at 10% H ₂ S breakthrough
Linear velocity			
GHSV = 3600	1.2 ft/sec	16	0.41
	2.3 ft/sec	15	0.51
GHSV = 1800	0.6 ft/sec	1	0.59
	1.2 ft/sec	14	0.66
Gas hourly space velocity			
at linear velocity = 1.2 ft/sec	1800 ft ³ /ft ³ ·hr	14	0.66
	3600 ft ³ /ft ³ ·hr	16	0.41
Temperature	600°F	13	0.00
	900°F	25	0.42
	1200°F	8	0.59
	1400°F	9	0.58
Feed H ₂ S concentration	0.6 vol %	14	0.66
	1.2 vol %	17	0.60
Pellet diameter	1/8-in.	5	0.63
	1/4-in.	8	0.59
	1/8-in.	6	0.70
	1/4-in.	3	0.62
	1/8-in.	10	0.83
	1/4-in.	12	0.75
Sorbent composition ^b	Fly ash and bentonite	24	0.71
	Silica and bentonite	22	0.72
	Fly ash and kaolin	20	0.68
	Silica and kaolin	21	0.75
Iron oxide added to sorbent ^c			
Fly-ash support	8.4%	4	0.48
	12.6%	3	0.62
	21.0%	7	0.63
	25.2%	2	0.63
	42.0%	19	0.77
	50.4%	18	0.51
Silica support	21.0%	23	0.78
	42.0%	22	0.72
Absorber pressure			
Fly-ash support 21.0 wt % iron oxide	20 psig	8,1	0.59
	150 psig	11	0.69
	400 psig	26	0.80
Fly-ash support 42.0 wt % iron oxide	20 psig	24	0.71
	150 psig	28	0.76
	400 psig	27	0.76
Silica support 42.0 wt % iron oxide	20 psig	22	0.72
	400 psig	29	0.79

^aCase numbers refer to Table 5.56 listing.^bForty-two percent iron oxide added to all supports.^cNet iron oxide added excludes impurities in the iron oxide source.

change in sorption efficiency when the same amount of iron oxide is added; however, crushing strength of the sorbent is affected by composition (Table 5.56). Between 12 and 42%, the amount of iron oxide added to a fly-ash support produces only modest change in the efficiency, with 42% producing the highest efficiency. Again, however, sorbent strength can be decreased by high content of iron oxide. When a strong sorbent is produced at high iron oxide content (by proper heat treating), sorbent porosity generally suffers and sulfur capacity is reduced. Only a minor change in efficiency is found when iron oxide content of silica-supported sorbents is varied.

The effect of absorber pressure on sorption efficiency is most marked for the fly-ash sorbent at low iron oxide levels. Sorbents already at high efficiency at 20 psig (42% iron oxide--fly ash, 42% iron oxide--silica) show only small efficiency improvement at high pressure.

Because the results in Tables 5.56 and 5.57 do not include consideration of sorbent regenerability and cycling lifetime, they should be tempered by the findings at MERC. This is especially true for fly-ash--supported sorbents with iron oxide addition above 25 wt %. MERC experiments reported for such sorbents have shown problems in regeneration.³

5.7.4 Process operation and economics

The Tennessee Valley Authority has published a conceptual evaluation of low-Btu gasification systems which includes a hot-H₂S removal system based on MERC development efforts.⁸ The two cases reported are low-pressure gas treating (Wellman-Galusha gasification) and high-pressure gas treating (Lurgi technology). The designs of the hot-gas systems are based on the process assumptions listed in Table 5.58.⁸ The flow pattern specified is upflow for absorption and downflow for regeneration. Gas flow rate, condition, composition, and pertinent process economics for the Wellman-Galusha gasification process are shown in Tables 5.59 and 5.60. Tables 5.61 and 5.62 list the same information for iron oxide--fly-ash treating of a Lurgi-produced low-Btu gas. Costs are reported on a 1974 basis but have been escalated by 32% (Tables 5.60

Table 5.58. Hot-gas systems design process assumptions^a

Parameter	Value
Sorbent sulfur capacity	
at atmospheric pressure	5 wt %, maximum
at 300 psig	8 wt %, maximum
Sorbent	
composition	25% iron oxide/75% fly ash
bulk density	68.6 lb/ft ³
Treated gas H ₂ S content	0.10 vol %, maximum
Cycle time	
absorption	8 hr
regeneration	8 hr
Regeneration gas	98% O ₂ at 15 psig

^a Sulfur dioxide off-gas treating consists of reduction with natural gas, using Allied Chemical Corporation — technology, at 95% sulfur recovery.

Table 5.59. Hot H₂S removal at low pressure in a fixed-bed iron oxide--fly ash process

Component	Flow rate (lb/hr)	Composition (vol %)	Pressure (psig)	Temperature (°F)
Feed gas ^a			Atmospheric	1200
H ₂	19,300	13.76		
N ₂	927,900	47.69		
H ₂ O	95,400	7.62		
CH ₄	25,600	2.29		
CO	445,900	22.92		
CO ₂	154,100	5.04		
H ₂ S	<u>16,100</u>	0.68		
	1,684,300			
Exit H ₂ S		0.09		
Regenerating gas	20,000		15	95
O ₂ (98%), (+N)				
SO ₂ off-gas	26,600		10	1200
SO ₂ (97%), (+N)				

^a10⁶ scf/hr = 24.94.

Table 5.60. Hot H₂S removal economics at low pressure in
a fixed-bed iron oxide--fly ash process

	Value
Capital	
Equipment, including 28 iron oxide reactors, 14 ft diam x 24 ft beds	\$4,430,000
Installation, including piping, concrete, etc., but excluding land cost	\$2,520,500
Absorbent charge and loading	\$1,760,900
Ductwork	<u>\$6,076,900</u>
Capital for H ₂ S removal plant	\$14,788,300
Capital for sulfur recovery plant, including molten sulfur storage	\$4,517,000
Capital for O ₂ plant	\$5,895,100
Total direct capital for H ₂ S removal system	\$25,200,400
Indirect capital costs (engineering, construc- tion field expense, contractor fee)	\$7,536,000
Total capital investment for complete H ₂ S removal system	\$32,736,500
Operating	
Absorbent makeup	\$50/hr (onstream)
Sulfur plant catalyst makeup	\$2.50/hr
Operating labor (total system)	4 man-hour/hr
Sulfur plant natural gas usage	85.7 x 10 ⁶ Btu/hr
Sulfur plant steam usage	5 x 10 ⁶ Btu/hr
Sulfur plant heat generation	12 x 10 ⁶ Btu/hr
Electricity usage	4530 kW
H ₂ S removal plant	20 kWhr/hr
Sulfur recovery plant	369 kWhr/hr
O ₂ plant	4141 kWhr/hr
Sulfur production	12,500 lb/hr

Table 5.61. Hot H₂S removal at 300 psig in a fixed-bed iron oxide--fly ash process

Component	Flow rate (lb/hr)	Composition (vol %)	Pressure (psig)	Temperature (°F)
Feed gas ^a			300	1100
H ₂	33,600	20.80		
N ₂	796,800	35.56		
H ₂ O	182,100	12.63		
CH ₄	55,600	4.33		
CO	310,500	13.87		
CO ₂	427,000	12.13		
H ₂ S	<u>18,600</u>	0.68		
	1,824,200			
Treated gas ^{b,c}			280	1120
H ₂	36,500	22.62		
N ₂	796,800	35.56		
H ₂ O	164,300	11.40		
CH ₄	55,600	4.33		
CO	269,800	12.05		
CO ₂	491,100	13.95		
H ₂ S	<u>2,600</u>	0.09		
	1,816,700			
Regenerating gas	23,100		15	95
O ₂ (98%), (+N ₂)				
SO ₂ off-gas	30,600		10	1120
SO ₂ (97%), (+N ₂)				

^a10⁶ scf/hr = 28.72.^bWater-gas shift reaction assumed to proceed to equilibrium.^c10⁶ scf/hr = 28.71.

Table 5.62. Hot H₂S removal economics at 300 psig in a fixed-bed iron oxide--fly ash process

	Value
Capital	
Equipment, including 22 iron oxide reactors, 14 ft diam x 24 ft beds	\$6,689,800
Installation, including piping, concrete, etc., but excluding land cost	\$3,806,700
Absorbent charge and loading	\$1,440,100
Ductwork	<u>\$2,133,900</u>
Total capital for H ₂ S removal plant	\$14,070,500
Capital for sulfur recovery plant, including molten sulfur storage	\$4,910,300
Capital for O ₂ plant	\$6,520,800
Total direct capital for H ₂ S removal system	\$25,501,600
Indirect capital costs (engineering, construc- tion field expense, contractor fee)	\$7,727,600
Total capital investment for complete H ₂ S removal system	\$33,229,200
Operating	
Absorbent makeup	\$40/hr (onstream)
Sulfur plant catalyst makeup	\$2.85/hr
Operating labor (total system)	4 man-hour/hr
Sulfur plant natural gas usage	96.9 x 10 ⁶ Btu/hr
Sulfur plant steam usage	5.7 x 10 ⁶ Btu/hr
Sulfur plant heat generation	14 x 10 ⁶ Btu/hr
Electricity usage	5325 kW
H ₂ S removal plant	20 kWhr/hr
Sulfur recovery plant	425 kWhr/hr
O ₂ plant	4880 kWhr/hr
Sulfur production	14,400 lb/hr

and 5.62) to a first quarter 1977 base. The effect of the water-gas shift reaction is believed insignificant under near-atmospheric pressures, but the reaction is assumed to proceed to equilibrium in the 300 psig system.⁸ The treated gas composition is shown in Table 5.61 for the high-pressure case in order to demonstrate the assumed effect of the water-gas shift reaction. Such charges as contingencies, land, startup and modification allowances, working capital in general, or interest during construction have not been included in the total capital costs shown in these tables.

The major process uncertainty in the TVA study is the assumption of regeneration of spent sorbent using essentially pure oxygen. Unless some method of rapidly extracting heat from the regenerating bed is developed, very low O₂ flow rates would be required to control the bed temperature to below destructive levels. Such low O₂ flow rates may prove inconsistent with the assumed 8-hr regeneration, 8-hr absorption cycle.

A more recent report by Jones and Donohue (Stone & Webster Engineering Corporation) presents capital costs for five different gasification systems, assuming use of the MERC iron oxide--fly-ash concept.⁹ The five gasifiers considered for hot-gas cleanup are:⁹

1. air-blown, moving-bed Lurgi at 300 psia (type MAH),
2. oxygen-blown, moving-bed Lurgi at 300 psia (type MXH),
3. oxygen-blown, slagging British Gas Corporation gasifier at 300 psia (type MSH),
4. air-blown, entrained-bed Foster-Wheeler gasifier at 360 psia (type EAH), and
5. oxygen-blown, entrained-bed Foster-Wheeler gasifier at 360 psia (type EXH).

Tables 5.63 and 5.64 list the material balances and capital costs for the hot-gas purification system.⁹ The costs in Table 5.64 are escalated about 12% from the reported mid-1975 basis to first quarter 1977. The hot-gas purification costs are stated to include (1) the iron oxide plant, (2) the SO₂-recycle system, (3) the sulfur-recovery plant, and (4) high-temperature particulate-removal devices upstream and downstream of the iron oxide

Table 5.63. Material balances for five hot-gas purification applications^a

	Gasifier (vol %)				
	MAH	MXH	MSH	EAH	EXH
Composition					
H ₂	17.12	20.86	26.94	13.90	30.08
CO	11.91	7.47	54.36	28.17	34.79
CO ₂	9.68	15.24	1.81	3.40	12.62
H ₂ O	27.66	50.33	4.94	2.23	14.39
CH ₄	2.84	4.28	7.89	3.35	5.98
C ₂ H ₆	0.07	0.31	0.58	0.00	0.00
N ₂	29.55	0.18	0.38	47.81	0.44
NH ₃	0.36	0.40	0.94	0.42	0.63
H ₂ S	0.52	0.59	1.38	0.65	0.97
COS	0.02	0.03	0.06	0.07	0.10
Tar (mole wt = 125)	0.27	0.31	0.72	0.00	0.00
	100.00	100.00	100.00	100.00	100.00
Temperature, °F	1200	1200	1200	1400	1400
Pressure, psia	300	300	290	360	350

^aRegenerating gas, 98 vol % O₂ ~41,600 lb/hr;
 SO₂ off-gas, 97 vol % SO₂ ~55,300 lb/hr;
 sulfur recovery at 90% ~24,500 lb/hr.

Table 5.64. Capital costs for five hot-gas purification applications^a

Gasifier type	Capital cost (\$10 ⁶)
MAH	81.72
MXH	81.78
MSH	58.63
EAH	68.75
EXH	62.89

^aHot-gas purification system includes iron oxide H₂S removal, SO₂ recycle, sulfur recovery, and hot-gas particulate removal.

reactors.⁹ Approximate escalated costs for these last three plants in hot-gas purification are listed below.⁹

SO ₂ -recycle plant	\$11.2 million
Sulfur-recovery plant (Allied Chemical technology)	\$14.6 million
Particulate-removal devices	\$2.2 million

Comparing these costs to those in Table 5.64, the iron oxide plant alone accounts for 50 to 70% of the listed hot-gas purification system cost.

Among the process design parameters assumed by Jones and Donohue, the following are most pertinent:

1. Net sulfur pickup by regenerated sorbent has ranged from 5 to 10 wt % in MERC experiments. This study assumed 10 wt % a reasonable value for costing purposes.⁹
2. Absorption temperatures between 1000 and 1400°F were assumed suitable for the fly-ash--iron oxide sorbent.⁹
3. A major process assumption in the study is the method of sorbent regeneration.

Jones and Donohue propose using a recycled SO₂ stream to dilute the regeneration oxygen and control temperature in the sorbent bed.⁹

Although no credit is taken for any direct elemental sulfur production in the regeneration step, this method would produce a high-concentration SO₂ off-gas suitable for subsequent treating to recover sulfur. Experimental verification for this method is desirable.

The Stone & Webster Engineering Corporation study presumes that allowable SO₂ emissions from the plant are similar to direct coal-fired power plants (i.e., a maximum of 1.2 lb SO₂ per million Btu of coal feed). This level is not exceeded for the conceptual designs presented, given a 90% H₂S-removal efficiency from the coal gas in the iron oxide absorber and a 90% sulfur recovery from the SO₂ off-gas.

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