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PROCESS SCREENING ANALYSIS OF ALTERNATIVE GAS TREATING AND SULFUR REMOVAL FOR GASIFICATION

Revised Final Report

December 2002

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Task Order No. 739656-00100
Task 2

Table of Contents

PAGE NO.

Table of Contents
(continued)

Table of Contents
(continued)

List of Tables

TABLE NO. **PAGE NO.**

List of Figures

FIGURE NO. **PAGE NO.**

Glossary and Abbreviations

ACI	American Combustion, Inc.
AGE	acid gas enrichment
AGI	acid gas injection
AGR	acid gas removal
bar	SI unit of pressure (1 bar = 14.5 psi)
BFW	boiler feedwater
BSR	Beavon Stretford Reactor
Btu	British thermal units (1,055 joules)
°C	temperature, degrees Centigrade (Celsius)
CCT	Clean Coal Technology (DOE)
CFB	circulating fluidized-bed
CGCU	cold gas cleanup
CO	carbon monoxide
CO_2	carbon dioxide
COPE	Claus Oxygen-based Process Expansion
COS	carbonyl sulfide
d	day
DEA	diethanolamine
DGA	diglycolamine
DIPA	diisopropanol amine
DOE	U.S. Department of Energy
DSRP	Direct Sulfur Recovery Process
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
°F	temperature, degrees Fahrenheit (°F = 1.8 x °C + 32)
FEF	front end furnace
ft	feet
ft^2	square feet
g	gram
GE	General Electric Company
GT	gas turbine
GTI	Gas Technology Institute
HAPS	Hazardous Air Pollutants
HCN	hydrogen cyanide

(continued)

Hg	mercury
HGCU	hot gas cleanup
HP	high pressure (steam)
hr	hour
HRSG	heat recovery steam generator
HRU	heat recovery unit
HSS	heat stable salts
HTW	High-Temperature Winkler (gasification process)
IGCC	integrated gasification combined cycle
in^2	square inch
KBR	Kellogg Brown & Root
lb(s)	pound(s) (454 grams)
LLB	Lurgi Lentjes Babcock
LNG	liquefied natural gas
LP	low pressure (steam)
lt	long ton (2,240 pounds, 1,016 kg) (Note: A long ton is not a metric ton.)
LTS	low temperature separation
M	thousand
MDEA	methyldiethanolamine
MEA	monoethanolamine
min	minute
MM	million (1×10^6)
MMEA	methyl monoethanolamine
mt	metric ton (2,204.6 pounds, 1,000 kg)
MW	megawatt
MWh	megawatts per hour
Ncm^2	normal centimeters squared
Nm^3	normal meters cubed
NSPS	New Source Performance Standards
OAQPS	Office of Air Quality Planning & Standards (U.S. EPA)
Oxyburner	oxygen burner
OxyClaus	oxygen-blown Claus

Glossary and Abbreviations
(continued)

PCD	particulates control device
ppm	parts per million
ppmv	parts per million volume
ppmw	parts per million by weight
PSDF	Power Systems Development Facility
psi(a)	pounds per square inch (absolute)
R&D	research and development
Redox	reduction-oxidation
RTI	Research Triangle Institute
scf	standard cubic feet (1 atm, 60°F)
SCOT	Shell Claus Off-gas Treating
SCR	selective catalytic reduction
SGD	safeguard device
SHA	sterically hindered amines
SR	sulfur recovery
SRU	sulfur recovery unit
st	short ton (2,000 pounds, 907 kilograms)
SWPC	Siemens Westinghouse Power Corporation
SWS	sour water stripper
t	ton
TECO	Tampa Electric Company (Florida)
TGT	tail gas treating
UOP	Universal Oil Products
vol%	volume percent
WHB	waste heat boiler
wt%	weight percent
%	percent
@	at
µg	micrograms (10^{-6} grams)

1. SUMMARY

This report updates a 1987 SFA Pacific, Inc. report to the Electric Power Research Institute (EPRI) that dealt with acid gas treating and sulfur recovery for integrated gasification combined cycle (IGCC) power generation [1]. Not only are the emission regulations more stringent than those prevailing at the time of the first report, but there is now sufficient commercial experience in IGCC that points the way to the processes that will meet current and potential future regulations.

Using the SFA Pacific Gasification Database [2], together with a literature survey and limited contacts with licensors and plant operators, SFA Pacific identified the processes that are applicable to IGCC under the current and proposed U.S. emission standards and reviewed their performance characteristics. Mercury removal, acid gas cleanup, sulfur recovery, tail gas treating, and hot and warm gas cleanup processes were reviewed. In addition, CO_2 removal for potential sequestration and acid gas injection into saline aquifers and depleted gas/oil wells were addressed.

This report essentially concludes that the gas treating processes available in 1987 are still the commercial mainstays of the industry. However, in many cases their designs today and in the future would be different in some respects for different gasification processes and applications—and to meet the more stringent environmental regulations. The impact of the latter, of course, is usually increased capital and operating costs. Identifying the “best” process options for specific applications would require engineering and cost evaluations of the integrated system options, including process licensors’ evaluations. Such tasks are well beyond the scope of this review report.

Nevertheless, the gas treating processes—particularly the acid gas removal (AGR) process options—used with gasification processes since 1987 suggest industry preferences for certain processes. Those patterns, combined with general industry perceptions about the applicability of AGR processes in particular, provide some guidelines for the preliminary identification of options for various IGCC applications—and related performance, design, and optimization issues.

The summary of the other major findings and conclusions of this report follow.

Mercury Removal

Recent experience with mercury removal from synthesis gas is limited to the Tennessee Eastman gasification facility, where carbon beds remove 90-95% of the mercury from coal derived synthesis gas. However, there is much commercial experience with mercury removal in the natural gas industry. There, mercury is being removed to below detectable limits. Similar performance of the carbon beds can be expected in synthesis gas applications. The major remaining problem is the disposal of mercury-laden spent carbon. Mercury sulfide on the spent carbon is stable and currently the best option is to dispose of it at certified storage sites. Regeneration with mercury recovery is complex and expensive.

Acid Gas Removal (AGR)

Currently, the processes of choice in commercial IGCC facilities for the removal of acid gases are both the chemical solvent AGR processes based on aqueous methyldiethanolamine (MDEA) and the physical solvent-based Selexol process—which uses mixtures of dimethyl ethers of polyethylene glycol. In most of the IGCC applications now, with both of these AGR processes, the AGR units are preceded by carbonyl sulfide (COS) hydrolysis units to convert most of the COS to H_2S. This then enables the AGR units to accomplish deeper total sulfur removal and lower H_2S levels. Total sulfur ($COS+H_2S$) levels of <20 ppmv may be required if selective catalytic reduction (SCR) is to be used with IGCC—to prevent ammonium sulfate salt deposition and corrosion problems in the colder sections of the heat recovery steam generator (HRSG).

While physical solvent processes are capable of meeting the stringent sulfur cleanup required for SCR, the processes themselves are more expensive than the MDEA-based amine ones. With COS hydrolysis, MDEA-based solvents can also meet a 10-20 ppmv total sulfur level in the treated gas, albeit at the expense of increased solvent circulation rates and a decrease in H_2S selectivity. The use of MDEA-based solvents will require acid gas enrichment (AGE) to give a suitable feed for the Claus plant. Commercial MDEA formulations (with proprietary additives) have been developed, which offer enhanced selectivity for H_2S, and their use is widespread in the gas treating industry.

BASF Corporation has shown some success in tests of its newly formulated MDEA solvent that removes much of the COS while retaining a high degree of H_2S selectivity. However, the performance to date is not adequate for the elimination of the COS hydrolysis step. In fact, SFA Pacific believes that if SCR is to be used, COS hydrolysis will be necessary for any acid gas removal system, except possibly the Rectisol process.

Although the Selexol process by itself is more expensive than an MDEA AGR process, the total AGR, sulfur recovery (SR) process, and tailgas treating (TGT) process package—based on Selexol could be more cost effective than the package based on MDEA—especially if the syngas pressure is high and deep sulfur removal is required (i.e., to 10-20 ppmv). Deeper desulfirization can be accomplished by chilling the Selexol process. However, CO_2 co-absorption then also increases.

For future IGCC with CO_2 removal for sequestration, a two-stage Selexol process presently appears to be the preferred AGR process—as indicated by ongoing engineering studies at EPRI and various engineering firms with IGCC interests. In CO_2 removal applications, the Selexol process is chilled—thus facilitating deep H_2S removal as well as CO_2 removal.

The Rectisol physical solvent AGR process—based on low-temperature (refrigerated) methanol—is capable of deep total sulfur removal, but it is regarded as the most expensive AGR process. Therefore, its use is generally reserved for chemical synthesis gas applications in which very pure syngas is required. Its use in IGCCs with CO_2 removal has also been proposed.

Further studies of the main IGCC processes with various feedstocks and all of the potentially competitive AGR options are required to quantify the relative performance and cost benefits of the various options and elucidate the ranges of conditions and cases in which they are competitive. Related studies are underway at EPRI and various engineering organizations.

Sulfur Recovery

The Claus process remains the mainstay of sulfur recovery, and is likely to remain so in the future. The principal development over the past several years has been the use of oxygen-enriched Claus plants. While oxygen enrichment doesn't improve sulfur recovery to a significant extent, it does result in less tail gas and allows for more complete destruction of sour water stripper off-gases. The smaller tail gas flow allows for the more economical handling of the Claus tail gases, discussed further below.

Acid gas enrichment will be necessary to enable Claus plant sulfur recovery approaching 98%. For higher sulfur recovery a tail gas treating unit is necessary, as is the current practice in IGCC plants and elsewhere.

Tail Gas Treating

The principal current tail gas treating approach is to hydrogenate/hydrolyze the sulfur species in the tail gas and then scrub out the resulting H_2S in an acid gas removal absorber. This approach is capable of boosting total sulfur recovery to well over 99.9%.

In some IGCC plant designs Claus tail gas, after H_2S scrubbing, is compressed and routed to the combustion turbine. This tail gas handling eliminates the need for a tail gas incinerator and provides additional fuel and mass flow to the combustion turbine. H_2S can be scrubbed in a stand alone separate process, such as Shell Claus Off-gas Treating (SCOT), or could be routed to the acid gas removal unit upstream of the Claus plant.

Tail gas treating of this type will remain the dominant and a required step in order to meet the proposed regulations.

Hot and Warm Gas Cleanup

Various systems for dry removal of the particulates and sulfur components of syngas over the 500-1,100ºF temperature range have been tested at the pilot plant level and a small number have been installed in commercial-scale IGCC demonstration plants in the U.S. and Europe. However, both industry interest (which has always been limited) and government interest in hot gas cleanup (HGCU) have declined for several important reasons; namely:

- Process and equipment development challenges; e.g., attrition of the desulfurization sorbents; chloride stress corrosion issues; and the high cost and unproven status of gas turbine (GT) fuel control valves for syngas at temperatures above about 800ºF.
- Hot gas desulfurization has not been demonstrated. The hot desulfurization processes in the Tampa Electric and Piñon Pine IGCC demonstrations were never operated.
- The trend toward increasingly stringent air emissions standards, including mercury removal from fossil power plant stack gas and the potential for mandated CO_2 mitigation. Specifically, HGCU at this stage of its development does not remove ammonia or HCN, COS, mercury (Hg), or CO_2 from syngas. Ammonia and HCN are converted to NO_x and COS is converted to SO_2 in GTs. Very low levels of SO_2 are required to prevent ammonium bisulfate fouling of the low-temperature HRSG surfaces in IGCC, if SCR is required. Present indications are that efficient and economical Hg removal will require syngas at temperature levels of conventional cold gas cleanup (CGCU) and removal by activated carbon before the GT.
- The success of the demonstration and commercial O_2-blown coal, petroleum coke, and petroleum residual oil gasification projects for IGCC and chemical synthesis gas production with conventional CGCU—in the U.S. and Europe. And the number of commercial IGCC projects with CGCU has been proliferating worldwide.

At the same time, hot particulates control devices (candle filters) have been successfully demonstrated at least three of the IGCC and gasification demonstration projects. These barrier filters represent the only currently commercially applicable HGCU technology. Particulates removal is the only hot gas cleaning technology perceived to have a future.

The U.S. DOE's recent extensive gasification industry interviews found that currently there is not much incentive for gas cleanup operations above 700ºF. Prior engineering analyses have persuaded the industry that the efficiency improvements from operating above 800ºF are not worth the additional capital costs due to materials and the increased equipment sizes resulting from the larger volumetric flows. DOE also found industry concerns about the effectiveness of dry sorbent-based technologies and the efficiency of regeneration at lower temperatures. Nevertheless, the interviews indicated some interest in the possibility of dry cleanup processes that operate at temperatures closer to downstream requirements of GT fuel systems and catalytic synthesis processes; e.g., in the 300-700ºF range.

Recognizing many of the issues and limitations surrounding hot gas cleaning technologies and their applications, DOE's Gasification Technologies program has transitioned its gas cleaning component away from the development of high-temperature approaches to more moderate temperatures consistent with downstream applications.

The development of hot gas cleanup systems for deep cleaning of sulfur and nitrogen components from syngas appear to be long-term prospects, if at all achievable.

Acid Gas Injection

A novel way to dispense with sulfur recovery and tail gas treating is to inject the acid gas into saline aquifers and depleted gas/oil reservoirs. Acid gas injection (AGI) has now been widely practiced by the oil and gas industry for the past decade. This eliminates the need to upgrade or build ever more expensive sulfur recovery facilities as the environmental regulations tighten. AGI may be a good alternative for IGCC plants, particularly if CO_2 removal for sequestration is required in the future.

CO_2 Removal for Sequestration

Oxygen-blown IGCC plants with conventional cold gas cleanup are particularly suitable for nearly total CO_2 removal from synthesis gas, if CO_2 sequestration should be required. All that would be necessary is a CO shift reactor and an additional CO_2 scrubbing step. Thus, the H_2S would be removed by one AGR process (absorber and stripper) and the CO_2 would be removed by the second-stage AGR process (absorber and stripper). CO shift and CO_2 removal can be integrated into the acid gas removal system as is widely done commercially in the petrochemical industry. CO shift can be done upstream of the main acid gas absorber, using sulfur tolerant catalyst, or after H_2S removal. The first approach has the advantage that synthesis gas does not have to be cooled prior to shifting, and is particularly suitable to slurry fed gasifiers. The latter approach allows for simpler selective H_2S removal.

2. INTRODUCTION

Background

In 1987, SFA Pacific, Inc. analyzed, for the Electric Power Research Institute (EPRI), alternative gas treating and sulfur recovery processes for use in Integrated Gasification Combined Cycle (IGCC) electric power plant applications. The resulting EPRI report [1] identified the suitable state-of-the-art processes for use in IGCC under the then-prevailing emission standards. Since that time, the emissions standards have become much more stringent, and the knowledge base of IGCC technologies has advanced significantly. Because of these changes, an update of the previous effort has become desirable; this report is the resulting update.

For the 1987 report, EPRI specified the raw syngas composition, temperature, and pressure—as well as the H_2S and overall sulfur removal requirements, and other product gas characteristics. The focus of the 1987 analysis was on the New Source Performance Standards (NSPS) prevailing at that time, which essentially required 90% overall sulfur removal from bituminous coal-fired electric power plants. The analysis also limited fuel gas H_2S content to 4 ppmv. Two more cases were also addressed then. The first specified a more stringent overall sulfur removal of 95% for power plants. The other case considered that the gasification synthesis gas was to be fed to a once-through methanol synthesis process, limiting the total synthesis gas sulfur content to less than 0.1 ppmv (H_2S and COS combined). The 1987 report essentially centered on sulfur removal via acid gas scrubbing, sulfur recovery, and sulfur tail gas treating processes.

Current emissions standards have not only become more stringent in regard to the Criteria Pollutants (SO_2, NO_x, CO, and particulates), but now require virtually total removal of volatile and non-volatile trace elements and organic compounds that result from gasification of coal and hydrocarbons and the subsequent combustion of the resulting fuel gas. In addition, recent global pressures to limit CO_2 emissions have also focused attention on the abilities of the various gas treating processes to remove and isolate CO_2. The selection of suitable gas treating, sulfur recovery, and tail gas processes becomes critical and complex if all of these emissions goals are to be achieved with a suitable degree of success.

Report Objective

The objective of this report is to review the commercial gas treating and sulfur recovery processes that are suitable for IGCC applications and that can meet current and future more stringent emissions requirements. The performance characteristics, limitations, and other issues of the processes are addressed.

One of the ancillary goals was to identify suitable methods of removing mercury from gas streams to meet both emissions regulations and to prevent potential equipment failures both before and after gas combustion.

While this report was not intended to be a guide for choosing the best applicable process for a given situation, the patterns of commercial use of the various gas treating processes and general industry perceptions about the processes suggest some general guidelines for the preliminary selection of certain process for IGCC applications—particularly AGR processes. These guidelines are outlined in Section 6 – Acid Gas Removal Processes. However, it is emphasized that several process options may be applicable to any given project, the economics of which will depend on the type of gasification process, feedstock, emissions regulations, plant location, existing infrastructure and tie-ins to existing facilities, client preferences, etc. The choice between the processes for specific applications would require process licensors' evaluations—tasks that are well beyond the scope of this report. Therefore, the economics of gas cleanup are not addressed in this report, other than in qualitative terms; i.e., brief discussions of design and performance parameters that influence costs.

Anyone considering a specific project, gasification process, system configuration, and emissions standards is advised to contact the suppliers of the applicable processes covered in this report for the latest relevant technical and cost information and support.

Approach to the Task

The principal approach used in this task was to review the developments that have taken place in gasification, gas treating and sulfur recovery and to identify those gas treating and sulfur recovery processes that have the best potential for meeting current and future emissions goals. The SFA Pacific Gasification Database [2] was used in the preliminary stages of the project to identify the newer large commercial gasification projects, the feedstocks and specific gasification technologies employed, and the specific applications (i.e., IGCC, cogeneration, H_2 production, chemicals, etc.). Recently published papers and reports on these projects were then reviewed—and selected industry contacts were made—to identify the specific gas treating processes used, as well as those most often chosen to meet specific syngas specifications and/or emissions goals. These processes were then screened for their performance in meeting their design emissions goals. Any known process limitations were identified.

The solvents discussed in this report represent those that are preferred in the current commercial gasification designs. These are solvents with which the most experience has been accumulated in gasification applications or comparable gas treating applications.

The process review was extended beyond gasification applications, since some processes that have long been used in the natural gas industry would also be applicable in gasification. This is particularly true for the removal of mercury, which the natural gas industry has been addressing for several decades. The natural gas industry also has vast experience in natural gas treating, using processes that are common with gasification applications. That common experience has also been reviewed. The experience of the refining industry in meeting the ever-tightening regulations in tail gas treating and sulfur recovery, especially in the use of oxygen-blown Claus units, has also been tapped.

3. EMISSIONS REGULATIONS

The original 1987 gas treating and sulfur removal process study addressed the then-applicable U.S. Environmental Protection Agency (EPA) New Source Performance Standards (NSPS) as published in the Federal Register in 1979 and the design emissions bases as specified by EPRI, outlined in the Introduction section of this report. Since that time, the NSPS standard has been tightened as well as new list of controllable pollutants has been added. Even stricter standards are being considered that would be applicable to IGCC systems. A brief outline of the current and possible future emissions standards is given below. These current and possible standards are the bases for the assessment of the performance of the gas treating and sulfur removal processes considered in this report.

The NSPS regulations have been revised several times since the promulgation of the U.S. Clean Air Act Amendments of 1970. Each revision resulted in the tightening of emissions specifications, especially for particulates and NO_x. The current NSPS emissions limits for the criteria pollutants from fossil-fired utility and industrial bolilers are as follows:

• Particulates (PM_{10})	0.03 lb/MMBtu
• NO_x	0.15 lb/MMBtu (or 1.6 lb/MWh)
• SO_2	1.2 lb/MMBtu

Now EPA is expected to stringently regulate the emissions of mercury by 2007—and to further tighten the emissions of all the criteria pollutants. At least one of the advanced pulverized coal-fired power plant suppliers has recently announced emissions goals that are lower than the current standards, yet undoubtedly achievable; e.g.:

• Particulates (PM_{10})	0.006 lb/MMBtu
• NO_x	0.016 lb/MMBtu (or up to 99.5% reduction)
• SO_2	0.040 lb/MMBtu (or up to 99% reduction)

The goal of the U.S. DOE's *Vision 21* Program is to effectively remove all environmental concerns associated with the use of fossil fuels for producing electricity, transportation fuels, and high-value chemicals. *Vision 21* is supporting R&D and technology demonstrations. The program's environmental targets are:

- Atmospheric release of—
  - < 0.01 lb/MMBtu of both SO_2 and NO_x
  - < 0.005 lb/MMBtu PM
  - < one-half of emission rates for organic compounds listed in the "Utility Hazardous Air Pollutants (HAPS) Report"
  - < 1 lb/trillion Btu mercury
- 40-50% reduction of CO_2 emissions by efficiency improvement
  - 100% reduction with sequestration

Cleanup Process Implications

Sulfur Removal

The process implication of standards as low as the above emissions capabilities claims of vendors is that gas cleanup has to improve significantly over the performance currently achieved in the IGCC units. Currently, sulfur removal in IGCC units reaches about 97.5% for bituminous high-sulfur coals, well above the NSPS requirement of approximately 80% removal to achieve the maximum SO_2 specification of 1.2 lb/MMBtu of heat input. However, an SO_2 emissions standard of 0.04 lb/MMBtu would require better than a 99.5% sulfur removal level, which is achievable by some processes but at a high cost.

An additional complication for sulfur removal arises if the emissions standard proposed for NO_x will be much lower than the current 0.15 lb/MMBtu emissions standard. Achieving a level of 0.016 lb/MMBtu (approximately 6 ppmv) in the IGCC exhaust gas could require the use of SCR. The SO_3 that is formed from SO_2 by combustion and by further oxidation of SO_2 over the SCR catalyst leads to the formation of sulfuric acid (H_2SO_4). The sulfuric acid, in turn, can react with ammonia slip from the SCR unit to form ammonium sulfate and ammonium bisulfate salts. These salts are known to deposit in the low temperature sections of the heat recovery steam generator (HRSG) units, which would lead to equipment corrosion and fouling, and will require frequent unit shutdowns for cleaning. To prevent such salts from forming would require extremely low levels of sulfur in the flue gas, probably less than 3 ppmv total sulfur (equivalent to about 20 ppmv in the clean synthesis gas). This would require better than 99.8% sulfur removal from the gas. Again, this is a possible but very costly target.

Mercury Removal

Current experience at gasification plants shows that approximately 60% to 70% of the initial mercury in bituminous coal exits in the flue gas [3]. The level of mercury in the flue gases of these plants, based on the total heat input in the coal, is about 4 to 5 lb/trillion Btu. Since most of the mercury partitions into the gas phase, some type of a gas phase mercury removal process would have to be utilized. A conservative assumption would be that all mercury in coal partitions to the gas phase. Current experience at the Eastman Kingsport plant shows that approximately 90-95% of the mercury could be removed from gas by carbon beds.

The scope of this process review update is limited to sulfur and mercury removal from coal gases, and to the discussion of process performance as it relates to CO_2 in connection to the global warming issues. Control of NO_x, particulates, and other trace gas constituents are only discussed in relation to sulfur and mercury control, when applicable.

4. IGCC GAS PROCESSING OPTIONS

There are several possible gas scrubbing options for IGCC that can meet various emission specifications and processing goals. Typical current process layouts are based on minimal gas processing in order to meet current emission regulations. Future stricter regulations will require additional processing steps and improvements in the performance of the currently used processes. In addition, if CO_2 abatement will be required in the future, additional processing steps will be required. This section discusses the various gas processing options that are currently being utilized and that may be required in the future.

Current IGCC Gas Processing

There is now a broad base of experience in gas scrubbing and sulfur recovery processes – made available from the numerous gasification projects that have been carried out in the past or that are operating currently. This experience covers a spectrum of gasification processes and feedstocks; namely, coals, all types of petroleum residues, natural gas, various waste streams, and biomass.

Syngas Characteristics and Gas Cleaning

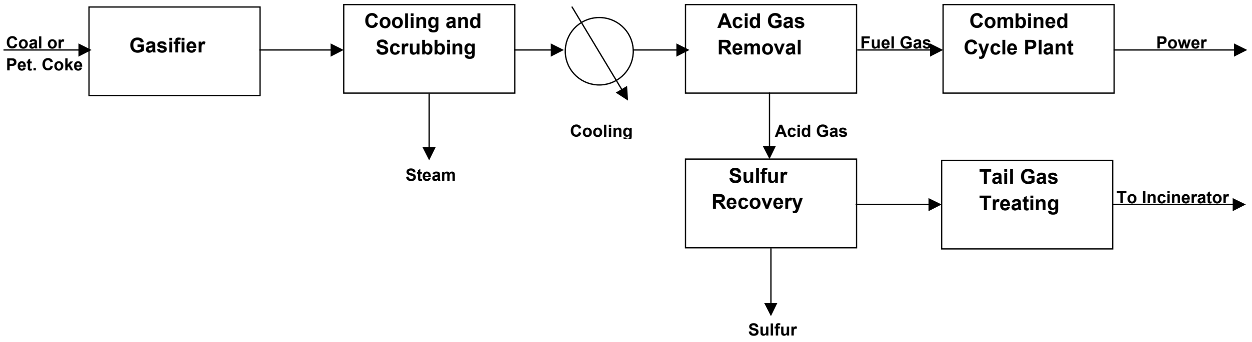
The raw syngases produced by the gasification of various feedstocks are similar in that the predominant gas components are hydrogen (H_2) and carbon monoxide (CO) (the desired combustible or reactive components for chemical synthesis), carbon dioxide (CO_2), water vapor (H_2O), and various impurities. However, the concentrations of these various components depend on the feedstock composition and the specific gasification process employed.

The primary feedstock impurities of concern are the sulfur and ash constituents. In gasification, the sulfur is converted mainly to H_2S and COS, a portion of the ash is entrained as particulates, and the mercury is vaporized. The entrained particulate matter also includes unburned carbon. Small amounts of HCN and NH_3, and traces of metal carbonyl compounds, are also produced.

Gas scrubbing addresses mainly particulate scrubbing, sulfur removal, and the removal of various chemical trace components from the gas. The required extents of removal of each of the impurities depend on the application; i.e., IGCC or chemical synthesis. For example, to prevent deactivation of methanol and Fischer-Tropsch synthesis catalysts, reduction of the total syngas sulfur content to <0.1 ppmv is required. This is a much more stringent requirement than that for IGCC, which is project-specific, but currently probably not more stringent than the 10-20 ppmv (0.04-0.08 lb/MMBtu) specification for SCR operation (discussed later).

Figure 4-1 shows a simplified process flow diagram of a generic IGCC power plant that meets current U.S. EPA emission regulations. The flow scheme is based on a pressurized, oxygen-blown entrained-flow gasifier, currently the most widely used type. Other gasifiers, particularly fixed bed types, may require additional steps to remove pyrolysis byproducts. The hot raw gasifier synthesis can be immediately cooled in a waste heat boiler to generate high pressure steam (the heat recovery mode of operation) or quenched with water, thereby adding steam directly to the syngas (the direct quench mode of operation). The cooled gas is then scrubbed to remove particulates, hydrogen chloride, hydrogen cyanide, and ammonia that may be present. Another option to water scrubbing for particulate removal is the use of ceramic candle filters or sintered metal filters. Both of these latter options have been used successfully in IGCC plants. The gas is then cooled to near ambient temperatures, and proceeds to an acid gas removal (AGR) unit, where the sulfur compounds and some carbon dioxide are removed. The scrubbed gas is then combusted in the gas turbine of the combined cycle power plant, while the removed acid gas from the AGR unit goes to a sulfur recovery (SR) unit, which recovers sulfur as a usable byproduct.

Figure 4-1
Simplified Flow Diagram of IGCC Meeting Current U.S. EPA Regulations



Source: SFA Pacific, Inc.

Conventional solvent based AGR units, both of amine and physical solvent types, and conventional Claus SR units – with their associated tail gas treating (TGT) units, are easily capable of meeting the fairly stringent current U.S. EPA emissions regulations. In a few circumstances, where local more stringent regulations apply, or in U.S. EPA designated non-attainment areas, further sulfur removal may be required. Carbonyl sulfide (COS), which is usually present at a several hundred ppmv level in syngas from coal and petroleum residues is difficult to remove quantitatively in AGR units. Therefore, further sulfur removal may be accomplished by the addition of a COS hydrolysis unit (before the AGR), which catalytically converts COS to H_2S, which can then be easily scrubbed out in the AGR unit.

High sulfur coal IGCC plants that use COS hydrolysis, together with conventional AGR and SR units, have been able to achieve nearly 98% sulfur recovery, equivalent to sulfur emissions of about 0.10 lb/MMBtu of coal input [4]. By also using TGT units, even higher sulfur recoveries, up to 99.8%, can be achieved.

High levels of sulfur recovery have been reported in the Sarlux IGCC plant in Italy, which gasifies a high-sulfur petroleum residue. There, an oxygen-blown Claus (OxyClaus) unit, licensed by Lurgi, is used. The tail gas from this sulfur recovery unit, after passing through a hydrolysis unit, is compressed and fed back to the main Selexol acid gas absorber. Thus, the only sulfur leaving the plant is that which leaves the AGR unit in the cleaned up syngas (fuel gas), which is combusted in the gas turbine. The overall sulfur recovery of the plant, designed for 95%, has reached as high as 99.8% in tests.

AGR Processes Employed Commercially with Gasification

As indicated in the Introduction of this report, the SFA Pacific Gasification Database [2] was used in the preliminary stages of this project to identify the newer, large commercial gasification projects, the specific gasification technologies employed, and the specific applications (i.e., IGCC, cogeneration, H_2 production, chemical synthesis, etc.). The Database was also used – along with recently published papers and reports on these projects, plus selected industry contacts – to identify the specific gas treating processes used, as well as those most often chosen to meet specific syngas specifications and/or emissions goals.

The results of this review are represented in Table 4-1, which provides a partial listing of gasification installations from the SFA Pacific Gasification Database showing the year of start up, feedstock, acid gas removal (AGR) process employed, and application. The major demonstration and commercial IGCC and/or cogeneration (cogen) projects are included (indicated as such in the table and highlighted by shading), as well as many projects producing or co-producing hydrogen, ammonia, Fischer-Tropsch liquids (hydrocarbons), and chemicals (C in the table). The Agip (2004 start up), PIEMSA (2006), and Total Fina (2006) projects are still in planning. Additional gasification projects that are known to be in planning are not included in Table 4-1 since data on the sulfur removal and sulfur recovery processes selected or proposed for those projects are not yet available. Of course not all projects in planning actually get built.

The Gasification Database and current publications show that both amine-based and physical solvent-based AGR processes are widely employed. Specifically, Table 4-1 shows the following patterns:

- MDEA (methyl diethanolamine) based AGR has been the predominant process for IGCC applications up to the late 1990s, and it continues to be selected for new projects. Ten of the projects in Table 4-1, including eight IGCC/cogeneration projects, employ MDEA.
- The Selexol process (based on mixed dimethyl ethers of polyethelene glycol as the physical solvent) has emerged as a competitor to MDEA. Selexol has now been used in or specified for five gasification projects. The first Selexol process applications since the SCE Cool Water IGCC demonstration in the 1980s have materialized just within the past several years. Keep in mind that the selection and design of the AGR and sulfur recovery (SR) process have to be completed by the time plant construction begins and that power plant construction then typically takes about three years.

Table 4-1
Partial Listing of Gasification Installations by Acid Gas Removal (AGR) Process and Year of Startup

~~Chemical (Amine) and Physical Solvents Employed in the AGR Processes Listed~~

Adip - aqueous di-isopropanol amine or MDEA
MDEA - aqueous methyldiethanolamine
Rectisol - methanol
Selexol - dimethyl ether of polyethylene glycol
Sulfinol - mixture of aqueous amine (e.g., Dipa) and the physical solvent Sulfolane (tetra-hydrothiophene dioxide)
Sulfinol-M - mixture of aqueous MDEA and Sulfolane

Plant Owner	Country	Start up	Feedstock	Gasification Process	AGR Process	Application [a]
Sasol Chemical Ind. (Pty.) Ltd./Sasol Ltd.	South Africa	1955	subbit. coal	Lurgi Dry Ash	Rectisol	FT liquids
Mitsubishi Petrochemicals	Japan	1961	Bunker C oil	Shell	Adip	C
Lucky Goldstar Chemical Ltd.	South Korea	1969	Bunker C oil	Shell	Sulfinol	ammonia
Sasol Chemical Ind. (Pty.) Ltd./Sasol Ltd.	South Africa	1977	subbit. coal	Lurgi Dry Ash	Rectisol	FT liquids
Hydro Agri Brunsbüttel	Germany	1978	heavy vac. residue	Shell	Rectisol	ammonia
Sasol Chemical Ind (Pty.) Ltd./Sasol Ltd.	South Africa	1982	subbit. coal	Lurgi Dry Ash	Rectisol	FT liquids
Gujarat National Fertilizer Co.	India	1982	refinery residue	Texaco	Rectisol	ammonia
Eastman Chemical Co.	United States	1983	coal	Texaco	Rectisol	methanol, & other C
Dakota Gasification Co.	United States	1984	lignite & ref. residue	Lurgi Dry Ash	Rectisol	synthetic natural gas (methane)
SCE Cool Water	United States	1984	bituminous coal	Texaco	Selexol	IGCC
Quimigal Adubos	Portugal	1984	vacuum residue	Shell	Rectisol	ammonia
Mitteldeutsche Erdöl-Raffinerie GmbH	Germany	1985	visbreaker residue	Shell	Rectisol	methanol
Rheinbraun	Germany	1986	brown coal	HTW	Rectisol	methanol
SAR GmbH	Germany	1986	vacuum residue	Texaco	Sulfinol	H2 & oxochemicals
LGTI	United States	1987	subbit. coal	E-GAS	MDEA	IGCC/Cogen
China Nat'l Tech. Import Co. (CNTIC)	China	1987	anthracite	Lurgi Dry Ash	Rectisol	ammonia
BP Chemicals, Ltd.	United Kingdom	1989	natural gas	Texaco	MDEA	acetyls
NUON (formerly Demkolec BV)	Netherlands	1994	coal	Shell	Sulfinol-M	IGCC
Global Energy, Inc.	United States	1995	coal, pet coke	E-GAS	MDEA [b]	IGCC
Dalian Chemical Industrial Corp.	China	1995	visbreaker residue	Texaco	Rectisol	ammonia
Frontier Oil & Refining Co. (Texaco Inc.)	United States	1996	pet coke	Texaco	MDEA	Cogen
Tampa Electric Co.	United States	1996	bit. coal	Texaco	MDEA [b]	IGCC
Schwarze Pump	Germany	1996	municipal waste	GSP/Noell	Rectisol	IGCC & methanol
Inner Mongolia Fertilizer Co.	China	1996	vacuum residue	Shell	Rectisol	ammonia
Juijiang Petrochemical Co.	China	1996	vacuum residue	Shell	Rectisol	ammonia
Sokolovska Uhelna, A.S.	Czech Republic	1996	coal	Lurgi Dry Ash	Rectisol	IGCC/Cogen
Elcogas SA	Spain	1997	coal & pet coke	PRENFLO	MDEA [b]	IGCC
Shell Nederland Raffinaderij BV	Netherlands	1997	visbreaker residue	Shell	Rectisol	IGCC/Cogen, H_2
Unspecified owner	Germany	1997	visbreaker residue	Texaco	Sulfinol	methanol
Sierra Pacific Power Co.	United States	1998	coal	KRW	Limestone/ZnO [c]	IGCC
Lanzhou Chemical Industrial Co.	China	1998	vacuum residue	Shell	Rectisol	ammonia
ISAB Energy	Italy	2000	heavy oil	Texaco	MDEA [b]	IGCC, H_2
Motiva Delaware Refinery	United States	2000	pet coke	Texaco	MDEA	IGCC/Cogen
Henan	China	2000	anthracite	Lurgi Dry Ash	Rectisol	ammonia
EPZ	Netherlands	2000	demolition wood	Lurgi CFB	Scrubber	fuel gas
Farmland Industries, Inc.	United States	2000	pet coke	Texaco	Selexol	ammonia
ExxonMobil Baytown Syngas Project	United States	2001	deasphalter bottom	Texaco	Rectisol	H_2, CO
api Energia S.p.A.	Italy	2001	visbreaker residue	Texaco	Selexol [b]	IGCC, H_2
SARLUX srl	Italy	2001	visbreaker residue	Texaco	Selexol [b]	IGCC/Cogen
ExxonMobil	Singapore	2001	residual oil	Texaco	FLEXSORB [d]	IGCC/Cogen
Shin Nihon Sekiyu (Nippon Pet. Ref. Co.)	Japan	2004	vacuum residue	Texaco	ADIP [b]	IGCC
AgipPetroli/EniPower	Italy	2004 [e]	visbreaker residue	Shell	Amine [b]	IGCC, H_2
PIEMSA	Spain	2006 [e]	visbreaker tar	Texaco	MDEA [b]	IGCC, H_2
Total Fina Elf/Texaco	France	2006 [e]	refinery residues	Texaco	Selexol	H_2

[a] FT liquids = Fischer-Tropsch hydrocarbons, C = chemicals, IGCC = Integrated Gasification Combined Cycle , Cogen = Combustion Turbine Cogeneration

[b] COS hydrolysis precedes the acid gas removal process in this plant.

[c] Commissioning of this demonstration plant was unsuccessful and the project was terminated. Consequently, both the KRW gasification process and the limestone/ZnO hot gas cleanup process remain unproven.

[d] Version not disclosed—indicated only as "generic FLEXSORB."

[e] In planning/engineering/development.

Source: SFA Pacific Coal Gasification Database

- The Sulfinol Process, which is based on a mixture of chemical solvents (aqueous amines) and the physical solvent Sulfolane (tetra-hydrothiophene dioxide) has been used in five of the projects since 1969, including two IGCC plants (one which is just in start up now) and three chemical synthesis applications.
- The Rectisol process (based on refrigerated methanol as the physical solvent) continues to be the predominant process used when very pure syngas is required for chemical synthesis.
- Nearly all of the IGCC plants commissioned after 1994 employ COS hydrolysis before the AGR process, except where the Rectisol process is used. This step is necessary to facilitate low total sulfur removal in the MDEA and Selexol processes. The Rectisol process can remove both H_2S and COS to very low levels.

The foregoing AGR processes also were the predominant processes reviewed in the 1987 Gas Treating Report. Thus it is clear that the predominant AGR processes employed commercially then are still the mainstays of the growing gasification market.

Note that the AGR processes compared in Tables 3-5 and 3-6 of the 1987 Gas Treating Report were based on syngas clean up without COS hydrolysis before the AGR units (as per EPRI's specifications). Thus, while relatively deep H_2S removal (down to <4 ppmv) was achieved in the various licensor supplied designs, the COS content of the syngas remained very high. Those results would be unacceptable for most IGCC applications now. There was only one exception—the Rectisol process applied to low sulfur syngas, in which case the COS was reduced to 25 ppmv. Therefore, those tabular comparisons should not be used to assess the AGR process options for today's market and environmental standards.

Overall, in all types of AGR applications worldwide (natural gas, refinery gases, synthesis gas, etc.) hundreds of MDEA-based AGR units have been installed, more than 55 Selexol plants have been installed, over 200 Sulfinol units have been licensed, and more than 100 Rectisol units are in operation or under construction worldwide [66].

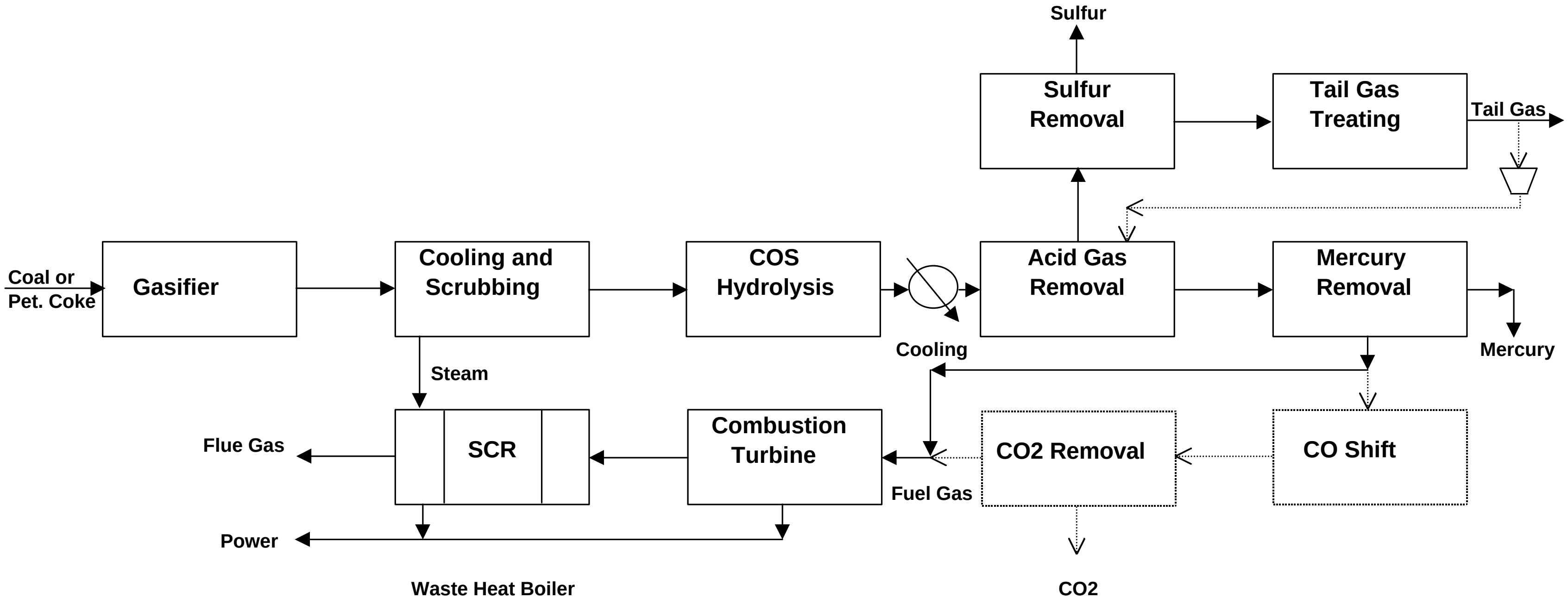
The increased experience with these processes in IGCC and other gasification projects over the past 10-15 years has enabled improved designs and performance, reduced risk, and greater confidence in their application.

These and other selected similar AGR processes and their characteristics are discussed further in Section 6. Considerations in the selection of AGR processes for IGCC applications are also discussed there.

Future IGCC Processes

Future IGCC process schemes will have to take into account much stricter emission regulations for SO_2, NO_x, and particulates. They will also have to address the removal of various trace components, particularly mercury, which up to now has not been considered to any great extent. In addition, the potential for CO_2 recovery for sequestration may have to be addressed in the future. Figure 4-2 shows an example IGCC plant flow scheme that includes processing steps that consider all of these issues.

Figure 4-2
Simplified Flow Diagram of IGCC for Potential Future Emission Regulations



Source: SFA Pacific, Inc.

COS hydrolysis is no longer an option, but is a required step in order to meet the anticipated very strict sulfur emissions regulations. A mercury removal step is needed, either before or after the AGR unit, depending principally on the operating temperature of the AGR process.

Current NO_x control methods for combustion turbines (CTs) may not be sufficient to meet the anticipated future single digit NO_x limits; i.e., limits of 9 ppmv (@15% O_2, dry). The lean premixed dry low-NO_x combustors used with natural gas are not applicable to firing hydrogen-containing syngas, due to the high flame speeds of H_2. With syngas, diffusion combustors must be used – and steam-injection and/or dilution with N_2 are used to reduce the flame temperature and control NO_x formation. If the efforts of GE (and the other CT vendors) to develop a <9 ppmv NO_x capability for their syngas-fired CTs are not successful, SCR would have to be used for post-combustion control of NO_x to the desired low level. The SCR unit would be placed in the heat recovery steam generator (HRSG). However, the use of SCR will call for extremely low sulfur content – probably <20 ppmv and possibly as low as 10 ppmv – in the CT exhaust gas to prevent ammonium bisulfate fouling of the colder heat transfer (boiler feedwater heater and evaporator) tubes in the HRSG [64].

The performance of the SR and the TGT units will also be critical to meet the proposed standards. The H_2S that is scrubbed out in a typical TGT unit is usually recycled back to the Claus plant, while the off-gas from the scrubber, which contains H_2S and COS, is usually incinerated and vented to the atmosphere. The sulfur content of the TGT unit off-gas is typically about 250 ppmv. Although AGR processes, using COS hydrolysis up-stream, can lower TGT off-gas sulfur content to below 50 ppmv, future regulations may require even better performance. Another way of handling the problem would be to recycle all of the SR unit tail gas back to the main AGR unit absorber, as discussed in Section 7 under the OxyClaus process.

If CO_2 removal becomes mandatory, then the CO in the synthesis gas will have to be shifted with steam to CO_2 and H_2, followed by partial or complete CO_2 removal. The placement of both the CO shift reactor and the bulk CO_2 removal units may be optional, depending on the gasification process, shift catalyst, and process economics. The shift reactor could immediately following gasification and water scrubbing of the raw syngas, if sufficient steam is available in the gas and a sulfur-tolerant shift catalyst is used. Bulk CO_2 removal could also be integrated into the overall AGR process by staging selective absorption for H_2S first, followed by bulk CO_2 removal.

Given the depth of scrubbing that the synthesis gas undergoes in the IGCC flow scheme, it is unlikely that other trace components, other than mercury, will present any problems. It is expected that ammonia, HCN, HCl, and all of the particulates will be scrubbed out by water before reaching the COS hydrolysis or the AGR steps. Any remaining metal carbonyls will be scrubbed out by the carbon beds that are used for mercury removal.

As stated in the Section 2 – Introduction, the principal objective of this work is to assess the performance of currently available AGR, SR, and mercury removal processes that might meet the proposed stringent regulations.

5. MERCURY REMOVAL

Future regulations propose to limit mercury air emissions from gasification off gases to levels that are barely detectable by current analytical methods. Prior concerns with mercury have been associated principally with metallurgical failures during gas processing. Mercury forms amalgams with aluminum and other metals and its control became paramount when heat exchanger failures in 1973 at an Algerian liquefied natural gas (LNG) plant were attributed to this phenomenon. Earlier, mercury amalgam formation was also blamed for equipment failures at the natural gas fields at Groningen, in The Netherlands. The natural gas industry spurred development of the mercury removal methods in the early 1970s. The gasification industry addressed this issue for the first time with the startup of the Eastman Chemical's coal-to-chemicals facility at Kingsport, Tennessee in 1983.

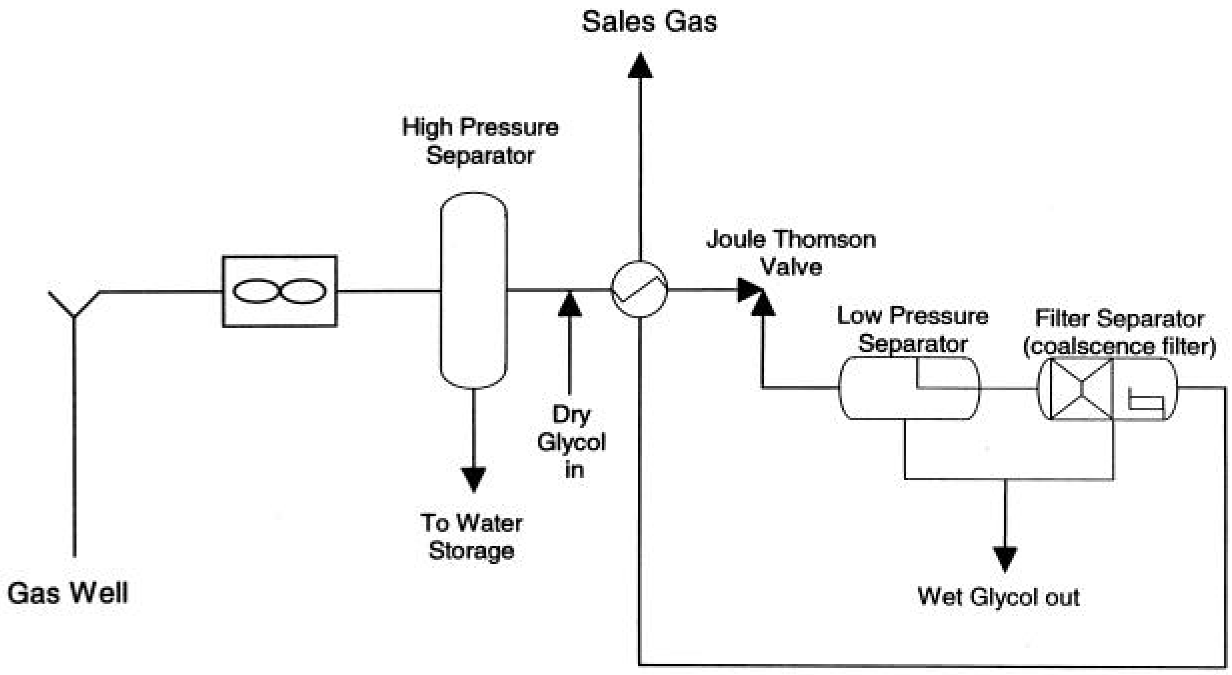
Little design data were available for mercury removal prior to the early 1970s. The caustic/chlorine industry had to remove mercury from the hydrogen gas prior to that time, and some data existed for mercury removal from air. Condensation of mercury by the low temperature separation process was used in these cases. This process is described briefly below. Two mercury adsorption systems have also been developed, one based on activated carbon and the other on zeolite adsorbents. The carbon system is non-regenerable, while the zeolite system is regenerable. These two systems are also discussed below.

Low Temperature Separation

The first experience with mercury removal from natural gas, using the low temperature separation (LTS) process, was at the aforementioned Groningen fields in 1972 [5]. The process is shown schematically in Figure 5-1. Natural gas from the field is precooled and the water is condensed out. Dry glycol is then injected to further dry the gas to prevent water condensation in the pipeline. After heat exchange, for additional precooling, the gas is expanded through a Joule Thomson valve. The wet glycol, now containing the condensed mercury, is then separated from the natural gas. The gas leaves this separation process containing about 1-15 $\mu g/Nm^3$ of mercury, depending on the temperature of the process [6]. Although this level of mercury may be acceptable in the natural gas, it would be unacceptable in LNG or in IGCC fuel gas—an order of magnitude better removal would be required. For example, the two early Indonesian LNG plants, Arun and Badak, use activated carbon adsorption beds to remove mercury from natural gas before the liquefaction cycle. The Eastman coal-to-chemicals plant is also equipped with activated carbon adsorption beds.

Operating the LTS process at very low temperatures would improve mercury separation significantly. However, further treatment of the water/mercury condensed phase is required. The LTS process, in applications where virtually total removal of mercury is necessary, is not a very economic nor a practical method and has been superseded by adsorption.

Figure 5-1
Low Temperature Mercury Separation Process



Source: Reference 6

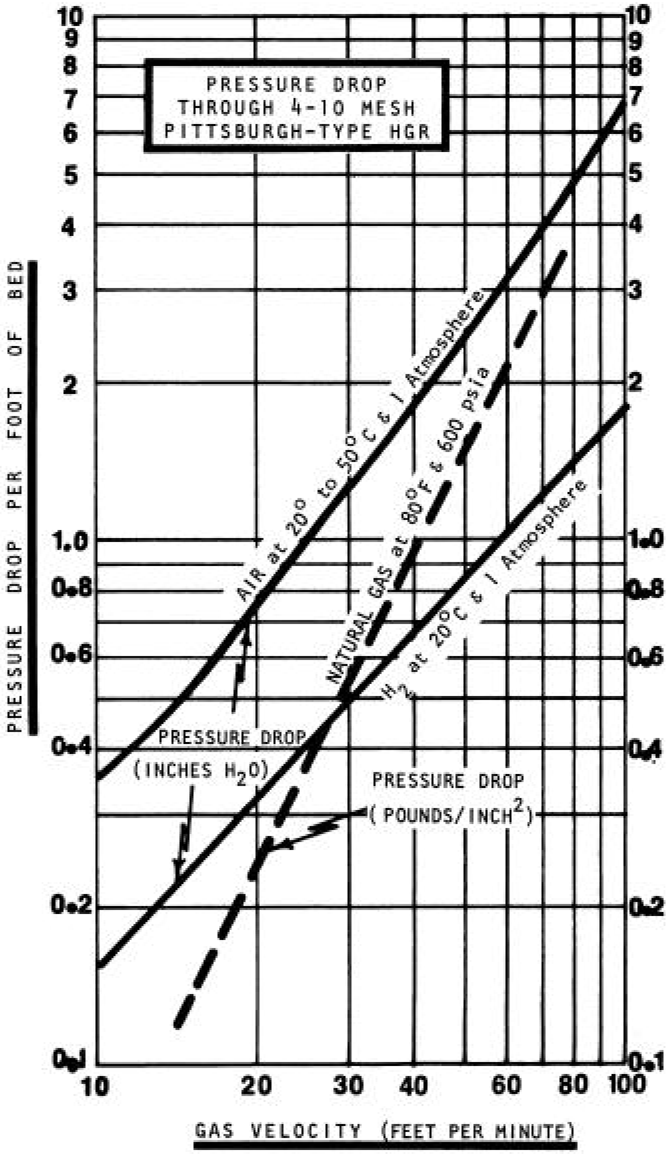
Activated Carbon

One of the principal suppliers and developers of activated carbon adsorbents for mercury removal, as well as for other gas components, is Calgon Carbon Corporation in Pittsburgh, Pennsylvania. The Calgon Type-HGR carbon has been used for low-pressure drop adsorption of mercury from natural gas since the early 1970s. Another activated carbon manufacturer is Norit, perhaps the biggest one in the world. There are many other activated carbon suppliers worldwide. The carbon is impregnated with sulfur at a concentration of about 10-15 wt%. The mercury reacts with sulfur as the gas goes through the sulfur bed to form HgS. After the sulfur on the carbon is exhausted, the spent adsorbent is shipped to a hazardous chemicals disposal site. HgS is a very stable compound and its long-term storage presents no problems. The spent carbon can also be incinerated and the mercury recovered from the incinerator gas via cooling and condensation.

Activated Carbon Bed Design Principles

Simple design principles apply to calculating the quantity of carbon required for mercury removal [5]. The first is the consideration of pressure drop. Since the density of Type-HGR carbon is about 37 lbs/ft^3, the allowable pressure drop in a vertical bed should not exceed 37 lbs/ft^2 (0.26 lbs/in^2). Exceeding that pressure drop would cause the particles to lift in an upflow bed, or potentially crush and cause attrition of the solid particles. Referring to Figure 5-2, which shows the reported pressure drops through Type-HGR carbon for various gases, at the assumed pressure drop of about 0.26 lbs/in^2 the allowable gas velocity is about 20 ft/min for high pressure natural gas. Assuming that the synthesis gas molecular weight is about 20, its allowable velocity, extrapolated from that of the natural gas, is about 16 ft/min. At this permitted gas velocity, for synthesis gas flow equivalent to a 250 MW IGCC plant, the carbon bed diameter would be about 15 feet and its length about 8 feet. This would require approximately 50,000 pounds of activated carbon.

Figure 5-2
Pressure Drop through 4-10 Mesh Pittsburgh-Type HGR Carbon



Source: Reference 5

For the carbon bed size calculated above, and assuming that only 5 percent of the sulfur will actively pick up the mercury, the carbon bed will load up with nearly 2,000 pounds of mercury. Assuming a synthesis gas mercury loading equivalent to that of the Polk County IGCC plant (approx. 0.01 lbs/hr), the carbon bed should last well over 20 years. To reach the proposed emission regulations (0.20 lbs Hg per Trillion Btu heat input or 99% removal, at operator's discretion) would require approximately 95% removal of mercury from the gas. The carbon beds in the Eastman Chemical plant achieve 90-95% mercury removal. The 99% level of mercury removal from synthesis gas has not been tested yet. However, there is commercial experience in nearly total mercury removal from natural gas. Calgon has supplied activated carbon to a Texas pipeline company that achieves well over 99.99% mercury removal from high-pressure natural gas [7]. In that case, the mercury in the inlet gas is about $50 \mu g/Nm^3$ and the mercury in the outlet gas is $0.001 \mu g/Nm^3$ (below detectable limits). The inlet mercury concentration of this natural gas case is similar to what one would expect in the synthesis gas from gasification of bituminous coal. There is little reason not to expect that carbon beds could remove mercury from synthesis gas to below detectable levels. However, if carbon beds are designed for mercury removal, attention has to be paid also to any other trace components that can be adsorbed by carbon. The mercury carrying capacity of activated carbon can be significantly compromised by the presence of other trace compounds.

The principle problem with activated carbon is that it is non-regenerable, and requires disposal at a hazardous chemicals site, unless one wishes to recover mercury by combustion. In this case, a complex and expensive cooling/condensation method would be used, followed by trim gas phase carbon beds for residual mercury removal, and flue gas scrubbing for the resulting SO_2.

Metal Carbonyls. Activated carbon can remove other trace components from synthesis gas. Iron and nickel carbonyls ($Fe(CO)_5$, $Ni(CO)_4$) are both undesirable trace components in synthesis gases. Metal carbonyls are often present in synthesis gas that is made from petroleum residues. Nickel carbonyls are damaging to combustion turbines but can be removed from synthesis gas by activated carbon. Nickel deposits are periodically found on the gas turbine combustors at the ISAB IGCC project in Italy. It is postulated that the nickel comes from nickel carbonyls in the synthesis gas produced from petroleum pitch [23]. Nickel carbonyl problems are being solved with a carbon bed at the AGIP refinery in Italy, where iron and nickel carbonyls are removed from synthesis gas produced from visbreaker tar [24].

Metal carbonyls can also be absorbed by low-temperature solvents such as used by the Rectisol process. These metal compounds, if not removed, wind up in the Claus plant feed, and are burned to FeS and NiS and are then deposited on the Claus catalyst. Both of these outcomes are undesirable.

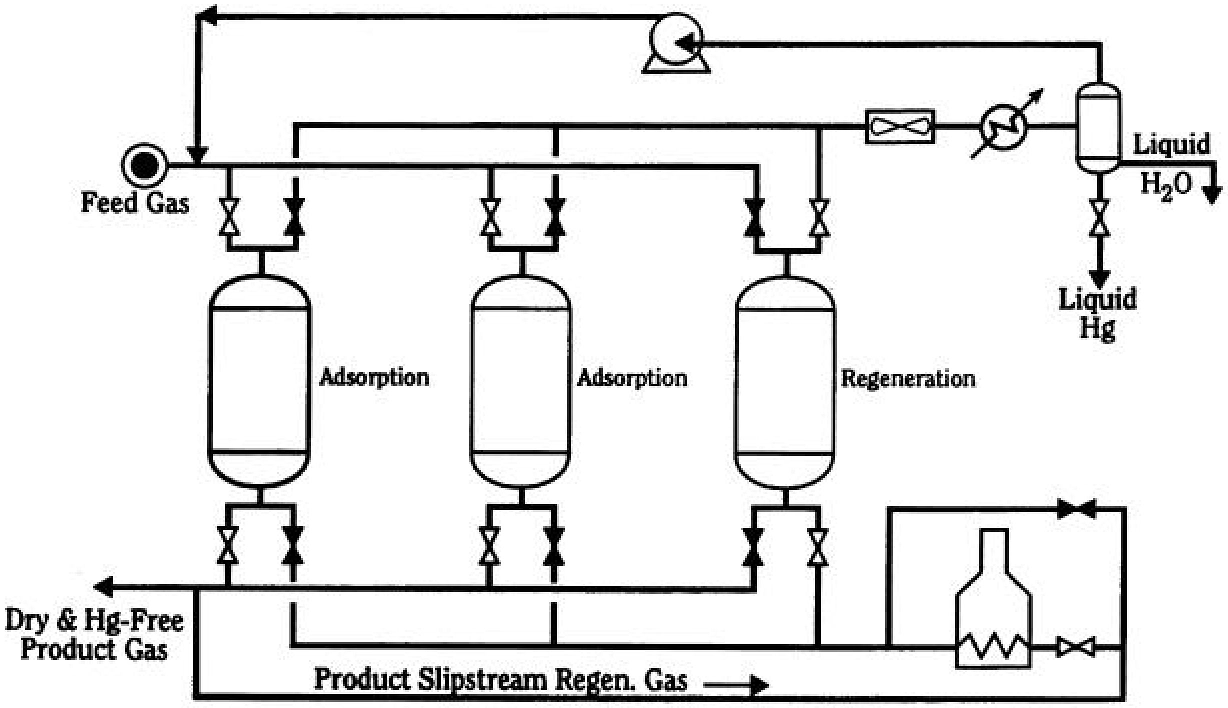
Zeolites

Zeolite adsorbents (Molecular Sieves) have been used by the natural gas industry primarily for drying. In the early 1970s, when the mercury problem surfaced, UOP began work on a zeolite adsorbent that would remove mercury from natural gas. The result was the development of a

Type 13X molecular sieve, loaded with about 0.5 wt% sulfur, that would remove mercury to very low levels. This work was followed by the development of a better molecular sieve product in the 1980s dubbed HgSIV [8]. HgSIV is a type X or Y zeolite with an outside coating of elemental silver. HgSIV both dries and removes mercury from the gas, it is also regenerable. The fact that HgSIV can be regenerated allows for small adsorbent bed sizes and its limited capacity for mercury is not a big detriment.

HgSIV is capable of removing mercury from natural gas to below detectable level ($<0.01 \mu g/Nm^3$). A number of commercial units (over 20), based on the HgSIV adsorbent, have been installed in natural gas service [9]. Several different process configurations can be used. One of these is shown in Figure 5-3. In this scheme, a portion of the cleaned gas is used to regenerate one of the spent beds. After cooling, the regeneration gas is compressed back into the feed gas. About 6% of the feed gas is used for regeneration. Typically, the regeneration offgas mercury content will be similar to that of the feed gas. Salable mercury can be recovered from the condensed liquid streams from the regeneration offgas.

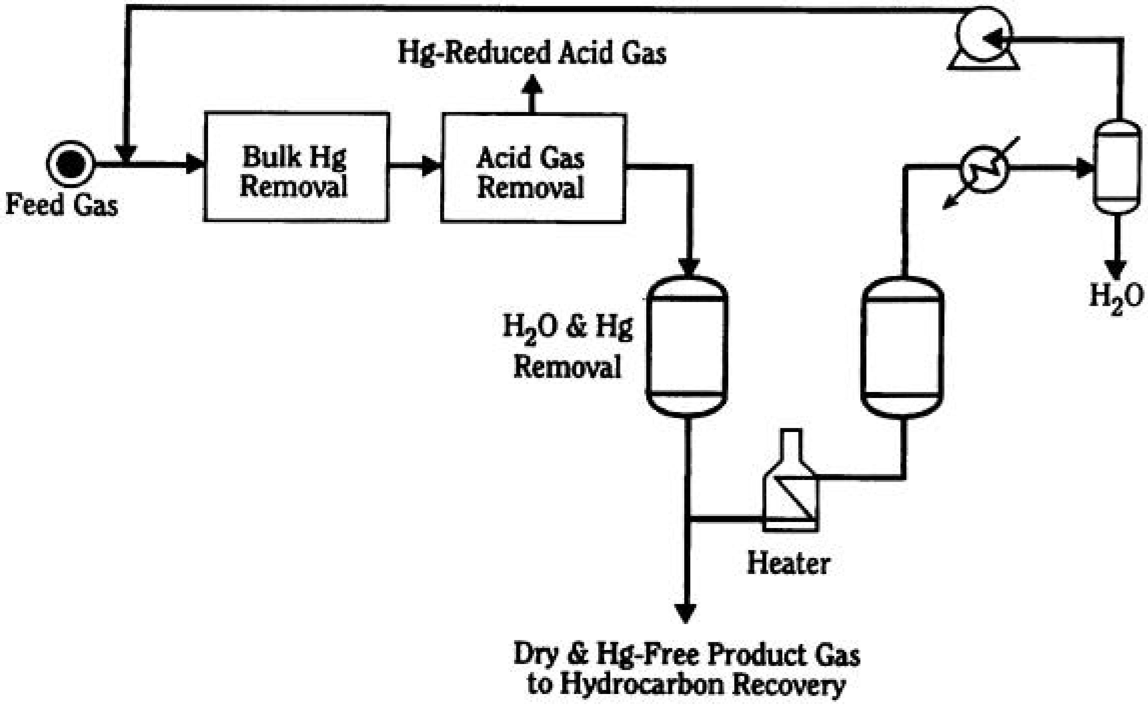
Figure 5-3
HgSIV Mercury Removal and Recovery System



Source: Reference 8

Other process schemes are possible. A bulk non-regenerable mercury removal unit could be used upstream of the acid gas removal unit. In this case, a carbon bed could be used to remove the bulk of the mercury, while a regenerable zeolite trim bed is downstream of the AGR unit to remove the balance of the mercury. The regeneration gas from the zeolite unit could then be recycled back to the bulk mercury removal unit. Such a scheme is depicted in Figure 5-4.

Figure 5-4
Integrated Carbon/Zeolite Hg-Removal System



Source: Reference 8

In another scheme, the spent regeneration gas could be sent to a non-regenerable mercury unit. The cleaned regeneration gas could then be compressed and combined with the clean synthesis gas, or could it be used for fuel or other purposes. In this case, nitrogen could be used for regeneration, which can then be vented to the atmosphere after mercury removal. The advantage of such a scheme is that the regeneration gas flow is much lower than that of the synthesis gas. Thus, much smaller beds will be required for its cleanup, and the disposal of the spent bed will be less of a problem. An activated carbon bed, with higher loading capability than the zeolite, can be used for this purpose.

The principle disadvantage of the zeolite adsorbent is its low carrying capacity for mercury. These molecular sieves were developed for simultaneous dehydration and mercury removal from natural gas, and consequently only a small portion of the material is dedicated to mercury removal. Additional development work will be required to produce material with higher loadings. The other disadvantage of the material, if it is to be used for bulk removal and disposal without regeneration, is its high cost. Zeolites are more expensive than activated carbon. Finally, there is no commercial experience with the use of zeolites to remove mercury from coal gasification gases.

Other Methods

Several other methods to remove mercury have been investigated over the years. Among these was the use of selenium on activated carbon [6]. However, selenium's high toxicity causes potential disposal problems for the spent carbon. Sorption by chromic acid on silica gel has also been tried, but found to result in very low mercury loadings. Silver on activated carbon has also been tried [5]. This results in excellent loadings and high removal potential. However, silver's high cost precludes its use in non-regenerative mode. No commercial silver-loaded carbon has yet been developed that could be regenerated.

In the short term, activated carbon and zeolites are the only practical systems for mercury removal from gasification synthesis gases. Activated carbon has the current advantage because of its commercial track record.

6. ACID GAS REMOVAL PROCESSES

There are numerous commercial acid gas removal (AGR) processes available to treat a variety of gas streams. These range from throwaway regenerable adsorbent-type to regenerable solvent-type processes. The solvent-type processes are the primary ones of interest for acid gas removal from synthesis gases. The solvent-type processes can be subdivided into three generic types:

- Chemical solvent
- Physical solvent
- Mixed chemical/physical

There are many commercial installations of each type, treating a variety of natural and synthesis gases. For synthesis gas treating, the principal chemical-type solvents of primary interest are aqueous amines, MDEA (methyl diethanol amine) being the current favorite. Amine-based solvents have been preferred by the natural gas industry over the physical solvents. The physical solvents co-absorb hydrocarbons to a much greater extent than the amines, causing loss of valuable hydrocarbons. However, since synthesis gas does not contain appreciable quantities of hydrocarbons, physical solvents are also used for synthesis gas clean up.

The currently favored physical solvents are methanol and dimethyl ether of polyethylene glycol, as represented by the Rectisol and the Selexol processes, respectively. The mixed chemical/physical processes usually employ mixtures of an amine and a physical solvent in an effort to capture the best characteristics of each solvent. The best known example of the mixed/chemical solvent process is Sulfinol, a mixture of sulfolane (tetrahydrothiophene dioxide) and an aqueous solution of an amine, either DIPA (diisopropanol amine) or MDEA.

The principal challenge of the AGR processes is to remove the sulfur compounds from the synthesis gas to as low a level as possible, consistent with the prevailing emission regulations, and as economically as possible. As SO_x emissions regulations become more stringent in the future, very high percentages of sulfur removal will be required. For example, to meet a SO_x limit of 0.04 lb/MMBtu, better than 99.3% sulfur removal from the syngas will be required in the case of IGCC based on Illinois No. 6 coal containing 3.0% sulfur. To meet DOE's *Vision 21* Program SO_2 target of 0.01 lb/MMBtu, better than 99.83% sulfur removal would be required. The total sulfur content of the treated synthesis gas has to be less than about 80 ppmv in order to achieve the 0.04 lb/MMBtu limit. This would not be a problem if only H_2S were present, since H_2S is easily removed by most AGR processes down to very low levels. However, the presence of COS in synthesis gas complicates the task, since its solubility is much lower than that of H_2S in both types of solvents—making it more difficult to remove.

For the sulfur recovery unit (SRU), usually based on the Claus process, to operate properly, it requires an H_2S-rich acid gas feed, meaning that H_2S has to be removed preferentially to CO_2 in the AGR. Thus, the AGR process has to show some level of selectivity for H_2S over CO_2. On the other hand, if CO_2 sequestration becomes desirable, then the AGR process should also have the capability for bulk removal of CO_2. Although these two goals seem unreconcilable at first glance, the task can usually be accomplished by staging acid gas absorption into separate tasks. For CO_2 capture, the capability of the process to achieve these two tasks in an efficient manner becomes very important.

The capabilities of the various solvent-based AGR processes to remove H_2S, CO_2, and COS are discussed below. Particular issues addressed are relative performance and cost factors, COS absorption, and the retention of H_2S/CO_2 selectivity while also removing CO_2.

Amine Processes

Amine processes are based on the removal of an acid gas by virtue of a loose chemical bond between the acid gas component and the amine. Three main types of amines are used commercially,

- Primary amine, usually MEA (monoethanolamine)
- Secondary amine, usually DEA (diethanol amine)
- Tertiary amine, usually MDEA (methyl diethanol amine)

The primary amines form the most stable bond with the acid gas, followed by the secondary amines. The least stable bond is formed by the tertiary amine. Although MEA has been extensively used by the natural gas industry in the past, because of its corrosivity it has, in large part, been supplanted by the less corrosive DEA. Both of these solvents are also degraded by COS, with DEA showing less degradation than MEA. The latter forms a non-regenerable degradation compound with COS. Thus, unless COS is removed or hydrolized to H_2S ahead of the amine scrubber, neither one of these two amines would be suitable for synthesis gas.

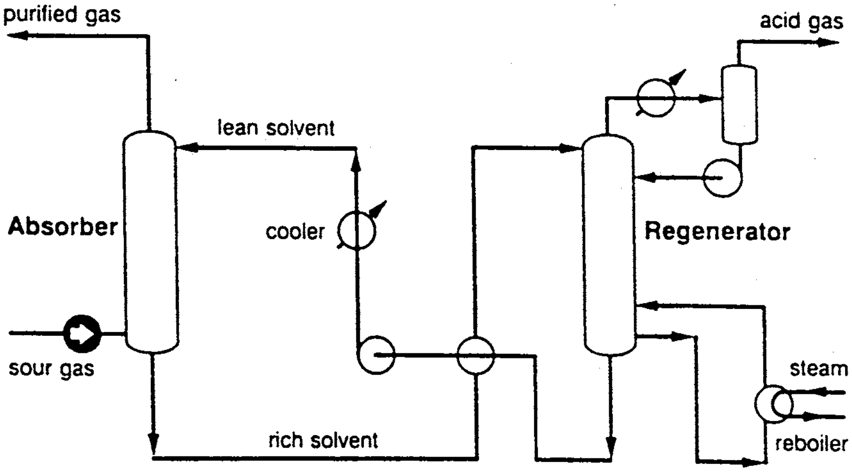
MDEA has become popular with the natural gas industry because it has a high H_2S/CO_2 selectivity, is very stable against degradation and is the least corrosive of the amines. Overall, there are hundreds of MDEA units worldwide in various applications. It is being used for synthesis gas treating in IGCCs at several commercial and demonstration sites. Its capabilities are discussed after the process flowsheet and design discussion below.

ExxonMobil has developed a proprietary sterically hindered amine process (FLEXSORB SE) that is selective towards H_2S. This process is discussed following MDEA. The FLEXSORB SE PLUS process (with an added physical solvent) is discussed in the section on mixed amine/physical solvent processes.

Flowsheet and Process Design

A simplified process flow scheme, representing a typical amine chemical solvent AGR process, is shown in Figure 6-1. Gas to be treated is introduced into the bottom of a trayed or packed tower and is contacted countercurrently with lean, regenerated solvent. Treated gas, now free of the acid gases, exits at the top of the tower. The rich solvent, now loaded with the acid gases, is sent from the bottom of the absorption tower for regeneration in a stripping tower. A reboiler supplies the heat to the regenerator to dissociate the chemically-bound acid gases from the solvent. Like the absorber, the stripping tower can be designed with either trays or packing. The stripped acid gases leave the top of the stripper and are vented to the atmosphere when only CO_2 is present, or are routed to a sulfur recovery plant when H_2S or other sulfur compounds are present. The lean, regenerated solvent is then pumped backed to the absorption tower via a lean/rich solvent heat exchanger and a lean solvent cooler.

Figure 6-1
Typical Amine Acid Gas Removal Process



Source: Comprimo

Additional equipment (not shown in Figure 6-1) may also be needed. For example, filter elements and solvent reclaimers may be needed to remove solvent degradation products, corrosion byproducts, and feedgas contaminants—all of which may otherwise accumulate in the process.

There are many variations of the process flow scheme shown in Figure 6-1. These variations depend on the solvent used, the composition, pressure, and temperature of the feed gas, and the treating requirements. Flash vessels for the rich solvent may be needed between the absorber and the regenerator—for example, when CO_2 is to be preferentially flashed from the solvent if it contains high ratios of CO_2 to H_2S. Flashing out CO_2 before the stripper enriches the H_2S content in the acid gas leaving the regenerator, which is fed to the sulfur recovery (SR) plant. The performance of the SR plant is improved by increasing the H_2S content of the H_2S-rich feedgas.

Performance and Cost Factors. These factors are qualitatively illustrated by the following general comparison of amine-based AGR with physical solvent-based AGR processes for sulfur removal applications. Physical solvent-based processes are discussed further later, after the amine processes.

- H_2S reaction rates with all aqueous amines are nearly "instantaneous"—enabling shorter gas-liquid contact times and smaller absorber column designs; i.e., a smaller number of trays or stages, and shorter and possibly smaller diameter columns. However, the rates of CO_2 reactions with various aqueous amines is much slower—and widely variable among the amines. The relative reaction rates of MEA, DIPA, and MDEA with CO_2 are as follows: 2,348 for MEA, 162 for DIPA, and 2 for MDEA [11]. The slowness of MDEA's reaction with CO_2 accounts for its popularity for use in H_2S selective service.
- The solvent loading (dissolution) rates in organic physical solvent systems are slower—such that approaching the high equilibrium solubilities enabled by physical solvents requires long contact times and the use of many trays or stages; i.e., taller and possibly larger diameter columns. However, as pressure increases, the physical solvent mass transfer rates and loadings improve—allowing a decrease in solvent circulation rates.
- The heat transfer coefficients of aqueous amine solutions are higher than those of organic physical solvents—so that less heat exchanger (coolers, reboilers) surface area is required with amine solutions.
- Amine-based AGR systems tend to have lower electric power requirements but higher stripping steam requirements than physical solvent-based AGR processes such as Selexol. The electric power requirements for pumping (solvent circulation), flash gas recompression, and refrigeration (if used—with physical solvents) and the heat requirements for solvent regeneration and are the major factors affecting the operating costs for AGR. The auxiliary electric power load of the AGR is subtracted from the IGGC plant's power output.
  - The heats of reaction between amines and acid gases are appreciable, whereas there are no significant heats of reaction or solution with physical solvents. Hence the higher stripper steam requirements of the amine-based AGR systems. The lower heats of solution in physical solvent systems facilitate both absorption (less cooling) and solvent regeneration (less heat required). Nevertheless, generally some low-pressure steam is available in IGCC plants, which can be applied to the AGR stripping needs without significant thermal efficiency penalty to the overall IGCC process.
  - Refrigeration is not normally used with the current Selexol physical solvent AGR processes when only H_2S removal is required, but is used in a 2-stage system when CO_2 removal is also required. The Rectisol physical solvent AGR process, based on methanol, is refrigerated for all applications to enhance solubilities and minimize solvent losses.
- COS hydrolysis upstream of the AGR is required for total sulfur removal to low levels—with both amine-based AGR processes and the Selexol Process. With refrigeration of the physical solvent processes, low total sulfur removal is achievable without prior COS hydrolysis.
- The primary material of construction for the MDEA, Selexol [67], and Rectisol processes is carbon steel. Some of the components in the Rectisol process require stainless steel,

which is much more expensive than carbon steel. Approximately 5% of the material in a Rectisol plant is stainless steel [70].

- With amine-based AGR, a second-stage acid gas enrichment (AGE) unit may be required to remove some of the CO_2 from the acid gas before it is fed to the SR unit. Physical solvent AGR processes produce a more concentrated H_2S acid gas feed to the SR unit—enabling better SR performance and a smaller SR plant and tail gas treating (TGT) plant. Alternatively, the tail gas (after hydrogenation) may be recycled to the AGR—eliminating the separate TGT plant. Therefore, the selection of the optimal AGR process for an IGCC application should be based on the integrated performance and costs of the entire COS hydrolysis, AGR, SR, TGT package—and its impact on the overall IGCC system performance and costs.

Generic Amine Processes. There is a growing availability of generic gas treating process know how and design tools, such as commercial process simulation packages, especially for amine-based AGR systems—including MDEA. However, the quality, reliability, etc. of the physical and chemical property data will vary among the packages, so that a diligent evaluation by the potential user is recommended before committing to and depending on a package. The principal advantage of a generic design is the avoidance of a licensing fee and the flexibility and the economic advantage it gives the plant owner in being able to buy solvents, related process chemicals, and other services (e.g., process consulting). The main disadvantage is the potential lack of technical support if the plant does not perform as designed. Obviously, experienced process licensors will be able to offer the most know how based on actual operating data. Physical and chemical property data and process performance data (mass transfer, kinetics, etc.) for proprietary MDEA formulations must be purchased from the solvent or process developers or licensors.

MDEA

H_2S/CO_2 Selectivity. MDEA became popular with the natural gas industry because of its high selectivity for H_2S over CO_2. This high selectivity allows for a reduced solvent circulation rate, as well as a richer H_2S feed to the sulfur recovery unit. MDEA's reaction with H_2S is almost instantaneous. However, its CO_2 reaction kinetics is much slower. MDEA, like other tertiary amines, forms bicarbonates on reacting with CO_2. Primary and secondary amines form carbamates with CO_2. The bicarbonate reaction is much slower than the carbamate one, and is postulated to be limited by the slow CO_2 hydration reaction with the amine [10]. The reaction rate of MDEA with CO_2 is about 2,300 times slower than that of CO_2 with MEA [11].

The natural gas industry began reporting the first successful use of MDEA for selectively removing H_2S in a test at a Marathon Oil Co. plant, utilizing generic MDEA. In that test, CO_2 removal was limited to about 30% while removing 99.0% of the H_2S in the feed gas. The treated gas had approximately 220 ppmv of the H_2S left in it, but was followed by a more complete removal with DEA to meet pipeline specifications. However, the solvent also was found to contain approximately 4% DEA—DEA enhances CO_2 pickup and led to the speculation that there would have been much better selectivity had the DEA not been there [12].

Some of the generic MDEA designs in IGCC plants that opted for a very high degree of CO_2 slip have been unable to achieve better than about 100 ppmv of H_2S in the treated gas. The Polk IGCC facility, for example, leaves 100-200 ppmv of H_2S in the treated gas while removing about 10-15% of the CO_2 from the feed gas to the MDEA absorber.

Commercial MDEA formulations (i.e., with proprietary additives) have been developed which are claimed to offer a much enhanced selectivity for H_2S than is the case for generic MDEA. UCARSOL is the trade name for a series of formulated amine solvents originally developed by Union Carbide and offered by UOP as a licensed package. More than 500 units of the version, called the Amine Guard FS Process have been installed worldwide, mostly treating natural gas, ammonia syngas, and hydrogen streams [66].

A test in a commercial natural gas sweetening plant of a UCARSOL MDEA solvent carried out in the early 1980s, CO_2 coabsorption was limited to less than 30%, while leaving less than 4 ppmv of H_2S in the treated gas. The feed gas in that test contained 0.55-0.78% H_2S and approximately 12% CO_2 [13].

Other developers of formulated MDEA solvents include BASF (discussed below under COS Removal and CO_2 Removal), Dow Chemical, and Shell. Dow Chemical, which acquired Union Carbide in an early 2001 merger—and also owns UOP, independently developed a series of formulated amines covered by the trade name Gas/Spec. Following the merger with Union Carbide, Dow sold its North American Gas/Spec business and its Global Ethanolamines (EOA) business to the British chemical company INEOS plc in 2001. Shell now offers the ADIP-X process, based on aqueous MDEA with an additive.

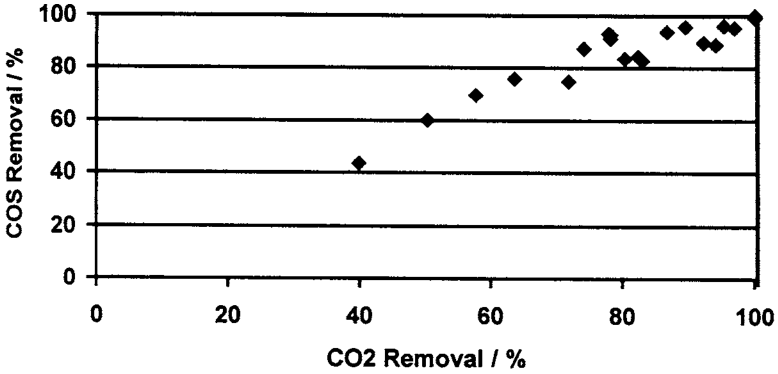
The overall advantages claimed for the formulated selective MDEA solvents are that the solvent circulation is reduced significantly and that fewer trays can be used in the absorption tower. The MDEA solvent content can be higher than that of other amines because it is less corrosive, reducing the circulation rates further. This leads to a much smaller and a less expensive plant. In addition, the acid gas from the regenerator is enriched in H_2S, and often allows the use of a conventional Claus SR process. The process layout is otherwise as simple as for any other amine, with the advantage that the solvent is usually more stable and a solvent reclaimer may not be needed.

COS Removal. MDEA does not combine with COS chemically. Only limited physical COS absorption takes place with MDEA. COS can be physically removed by MDEA only with very high solvent circulation rates, at which point the CO_2 is also removed quantitatively. For synthesis gases that contain appreciable quantities of COS, prior removal of the COS is usually required. A catalytic hydrolysis unit is usually employed ahead of the MDEA unit in these cases, as was done both at the Wabash River and Tampa Electric gasification plants.

A new formulated MDEA solvent was reported in 2000 that achieves a high degree of COS removal and retains appreciable selectivity for H_2S over CO_2. BASF Corporation ran a pilot plant and tested this new proprietary formulation in a commercial natural gas plant [14]. Figure 6-2 shows the result of the pilot plant runs. It shows the extent of COS removal as a function of CO_2 coabsorption. It shows that 80% of the COS can be removed while retaining a 40% CO_2

slip through the absorber. In the commercial plant test, nearly 99% of the COS was removed while keeping a high acid gas solvent loading (about 0.58 moles acid gas per mole amine). Such a high solvent loading implies a very low solvent circulation rate even for the best of amine designs. Of course, a relatively high CO_2 removal was also obtained in this test, over 90%.

Figure 6-2
COS vs. CO_2 Removal Using New aMDEA Formulation



Source: Reference 14

The new BASF formulation shows promise for using MDEA with synthesis gases for COS removal while maintaining a relatively high H_2S/CO_2 selectivity. H_2S can be virtually completely removed while the COS removal level can be targeted to meet the overall sulfur removal regulations. This strategy would limit CO_2 coabsorption and may preclude the need for a COS hydrolysis unit upstream of the amine unit. Such a formulated MDEA process is yet to be demonstrated.

CO_2 Removal. MDEA can also be formulated for high levels of CO_2 removal. For this task, various additives (activators) are used. The kinetics of the CO_2 reaction with MDEA is highly improved with such additives allowing for reasonable absorber sizes and solvent circulation rates. Among some of the additives that have been used are MEA (monoethanolamine), DEA (diethanolamine) and DGA (diglycolamine) [15]. BASF has used piperazine in its activated MDEA formulations. Piperazine, even at low levels (about 5%) enhances the rate of CO_2 absorption an order of magnitude over non-activated MDEA [16]. While such formulations are of interest in applications where deep CO_2 removal is required, in synthesis gases, the retention of a high H_2S/CO_2 selectivity is usually more important.

Activated amines are being used for the removal of CO_2 from synthesis gases in ammonia manufacture. The synthesis gas CO_2 partial pressure in ammonia plants is about 54 psi, a partial pressure high enough for consideration of a physical solvent. The treated synthesis gas CO_2 content in a typical ammonia plant is about 0.05 vol%. An activated MDEA solvent loading approaching 0.75 moles of CO_2/mole amine is typically achieved, resulting in a relatively low solvent circulation rate.

There are several activators that can be added to MDEA in various proportions to achieve a desired performance level. Formulations can be designed from high H_2S/CO_2 selectivity to virtually total H_2S and CO_2 removal. In many cases, the economics of an MDEA system can be competitive with a physical solvent even at high CO_2 partial pressures. At high CO_2 partial pressures and high solvent loadings, MDEA begins to act as a pseudo-physical solvent. The bulk of the CO_2 can be flashed off by pressure let-down, leading to low heat requirements in the solvent regenerator.

If both high H_2S/CO_2 selectivity and deep CO_2 removal are desired, then two different MDEA solvent formulations might be used, one for selective removal, followed by another one for the removal of the remaining CO_2. However, it is a nuisance to maintain two different solvent formulations, and some compromise may have to be reached between selectivity and CO_2 absorption.

For synthesis gas applications, where the CO_2/H_2S ratios are high (coal and petroleum residue gasifaction gases), current commercial MDEA solvents are not capable of producing an acid gas that is suitable for straight through Claus plants while providing deep sulfur removal. Under these conditions, the increased co-absorption of CO_2 makes the acid gas H_2S content too dilute. This is true even when a COS hydrolysis unit is used upstream of the MDEA absorber. An acid gas enrichment step would be needed to accomplish this. Such an approach was followed at Agip's Sannazzaro refinery [17].

Degradation of MDEA and Its Corrosivity. Early claims were that MDEA, unlike primary and secondary amines, do not degrade nor are corrosive, proved a little premature. MDEA does break down into various degradation products when subjected to high temperatures, which are typically found in the bottom of the solvent regenerator columns. Also, oxygen presence in the gas was found to be one cause of degradation of MDEA. The buildup of degradation products in the solvent changes the solvent characteristics and can lead to corrosion.

Corrosion problems have been experienced at a natural gas treating plant that uses a formulated MDEA solvent. This corrosion was attributed to the presence of 90-100 ppmv of oxygen in the natural gas being treated [18]. Such oxygen-caused degradation of MDEA and other amines has been known for some time [19]. The inlet gas stream at the plant contains 4% CO_2 and a small quantity of H_2S. The degradation products noticed in the solvent included acetate, formate, and oxalate, all known to be caused by the degradation of MDEA by oxygen. Other signs of oxygen degradation include the thiosulfate, when H_2S is present, as well as the presence of secondary amines, such as DEA and MMEA (methyl monoethanolamine), which also result from the degradation of MDEA.

Oxygen can also cause the formation of bicene [bis(2-hydroxyethyl)glycine] in MDEA-based solvents. Bicene is corrosive toward carbon steel. Other soluble metal species beside iron, such as chromium, are also found in amine solvents when treating gases with high concentrations of CO_2 [20]. Among several mechanisms proposed for bicene formation are the reactions of cyanide with formaldehyde, and the direct degradation of DEA with oxygen to bicene. The latter mechanism is probably the more important one since cyanides and formaldehyde are not present in natural gas, and are usually scrubbed out with water from synthesis gas, preventing them from reaching the amine unit. However, DEA may be present in MDEA-based solvents as an activator additive, a degradation product, or as an unintended solvent impurity in the original MDEA charge.

Degradation products include carboxylic acids that tend to form heat stable salts (HSS). Because MDEA is more difficult to recover by conventional distillation methods used for other, lower boiling amines, ion exchange methods are often used to reclaim MDEA. The HSS degradation products are removed by ion exchange resins and the reclaimed MDEA is returned to the process. The use of ion exchange solvent reclaiming is claimed to be more economic than periodic purging of the degraded high-cost solvent [21].

Degradation of MDEA and the resultant corrosion can be limited by the following means:

- Controlling solution temperatures in the solvent stripping tower, particularly in the reboiler
- Maintaining lower acid gas loadings of the solvent—lower than the theoretical equilibrium capacity
- Using a lower amine concentration
- Operating the solvent stripper at the lowest feasible pressure, thus keeping the boiling point of the solvent as low as possible
- Monitoring of the solvent for degradation products and providing a means for solvent reclaiming, when needed

In spite of the solvent degradation and performance limitations mentioned above, with proper operating procedures and solvent monitoring, MDEA-based AGR processes have been preferred over physical solvents for conventional IGCC applications until about the mid-1990s, as already discussed in Section 4 of this report. Recently, the Selexol physical solvent process has become more competitive with MDEA-based AGR.

Hindered Amines

ExxonMobil developed the FLEXSORB SE process, which is based on a family of proprietary sterically hindered amines (SHAs) in aqueous solutions or other physical solvents. The FLEXSORB SHAs are secondary amines that have a large hydrocarbon group attached to the nitrogen group. The large molecular structure hinders the CO_2 approach to the amine. The larger the structure the more difficult it becomes for the CO_2 to get close to the amine. They also appear to be unstable to the carbamate form of product and revert easily to the carbonate form found in the tertiary amines. Like tertiary amines, they are capable of a high degree of solvent loading—1 mole/mole, instead of 0.5 mole/mole typical of primary and secondary amines.

One version of the solvent, FLEXSORB SE Plus, is very selective towards H_2S and has been used in several plants for tail gas processing or lean acid gas enrichment (AGE). It is claimed that FLEXSORB SE Plus use in such services results in lower circulation rates than for other amines. Recently, Qatargas chose this process over activated MDEA for AGE of its lean acid gas feed to an existing Claus plant [26].

The first FLEXSORB SE process application to IGCC is in the ExxonMobil Singapore project. The version of the process used there has not been disclosed.

Physical Solvents

Two of the currently most-widely-used physical solvent processes for IGCC synthesis gases are Selexol and Rectisol. The Selexol process solvent is the dimethyl ether of polyethylene glycol, while the Rectisol solvent is methanol. Other physical solvent processes are also offered for license, but are less frequently used commercially. Since the operating principles of all physical solvent processes are similar, only the Selexol and Rectisol processes are individually discussed below.

The principal benefits of physical solvents are:

- High selectivity for H_2S and COS over CO_2
- High loadings at high acid gas partial pressures
- Solvent stability
- Low heat requirements because most of the solvent can be regenerated by a simple pressure letdown. (There is no significant heat of reaction or solution.)

The performance of a physical solvent can be easily predicted. The solubility of individual compounds follow Henry's law—the solubility of a compound in the solvent is directly proportional to its partial pressure in the gas phase—hence, the improvement in the performance of physical solvent AGR processes with increasing syngas pressure. The easily measured data for component solubility at several partial pressures and temperatures generally provides the necessary solubility curves.

Physical solvents are particularly applicable to synthesis gas applications. Unlike natural gases, where hydrocarbon coabsorption can be a problem for physical solvents, synthesis gases do not contain appreciable quantities of hydrocarbons. Physical solvent processes can be easily configured to take advantage of their high H_2S/CO_2 selectivity together with high levels of CO_2 recovery. This is usually accomplished by staging absorption for high H_2S removal, followed by CO_2 removal.

For physical solvents to be economically usable they must meet certain criteria. Among these criteria are the following:

- Very low vapor pressures—to prevent solvent losses
- High selectivity for acid gases vis-à-vis methane, hydrogen and carbon monoxide
- Low viscosity

- Heat stability
- Be non-corrosive to metals

Only a few solvents meet all these criteria. Among the ones that have been used commercially include N-methyl-2-pyrrolidone (Purisol process), tributylphosphate (Estasolvan process), propylene carbonate (Fluor Solvent process), methanol (Rectisol and IFPEXOL processes), polyethylene glycol dialkyl ethers (Selexol, Sepasolv MPE, and Genosorb processes). Methanol has a high vapor pressure and needs low temperatures (refrigeration) to prevent high solvent losses.

In recent IGCC projects, where physical solvents have been specified for acid gas removal, either the Selexol or the Rectisol processes have been chosen. At least twenty operating commercial gasification plants worldwide use either the Selexol or the Rectisol process for acid gas treating. These two processes are discussed below.

Selexol

The Selexol process was patented by Allied Chemical Corp. and has been used since the late 1960s. The process was sold to Norton in 1982 and then bought by Union Carbide in 1990 [22]. The Dow Chemical Co. acquired the gas processing expertise, including the Selexol process, from Union Carbide in 2001. The process is offered for license by several engineering companies—the most experienced of which with the process is probably UOP. There are more than 55 Selexol plants worldwide, treating natural and synthesis gases [66].

The Selexol process solvent is a mixture of dimethyl ethers of polyethylene glycol, and has the formulation $CH_3(CH_2CH_2O)_nCH_3$, where n is between 3 and 9. There are other process suppliers using the same solvent as the Selexol process. For example, Clariant GmbH, of Germany offers a family of dialkyl ethers of polyethylene glycol. The Clariant solvents, under the Genosorb name, include dimethyl ether- as well as dibutyl ether- of polyethylene glycols. The first-mentioned Clariant solvent is the same as that used in the Selexol process.

The Selexol solvent is chemically and thermally stable, and has a low vapor pressure that limits its losses to the treated gas. The solvent has a high solubility for CO_2, H_2S, and COS. It also has an appreciable selectivity for H_2S over CO_2. Table 6-1 shows the comparative and actual solubilities of various gases relative to methane at 25°C in the Selexol solvent.

Table 6-1
Solubilities of Gases in the Selexol Solvent

Component	Solubility Index [a]	Solubility, $Ncm^2/g.bar$, @25°C
H_2	0.2	0.03
CO	0.8	0.08
CH_4	1.0	0.2
CO_2	15	3.1

COS	35	7.0
H_2S	134	21
CH_3SH	340	68
C_6H_6	3,800	759
H_2O	11,000	2,200
HCN	38,000	6,600

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[a] K' CH_4/K' Component

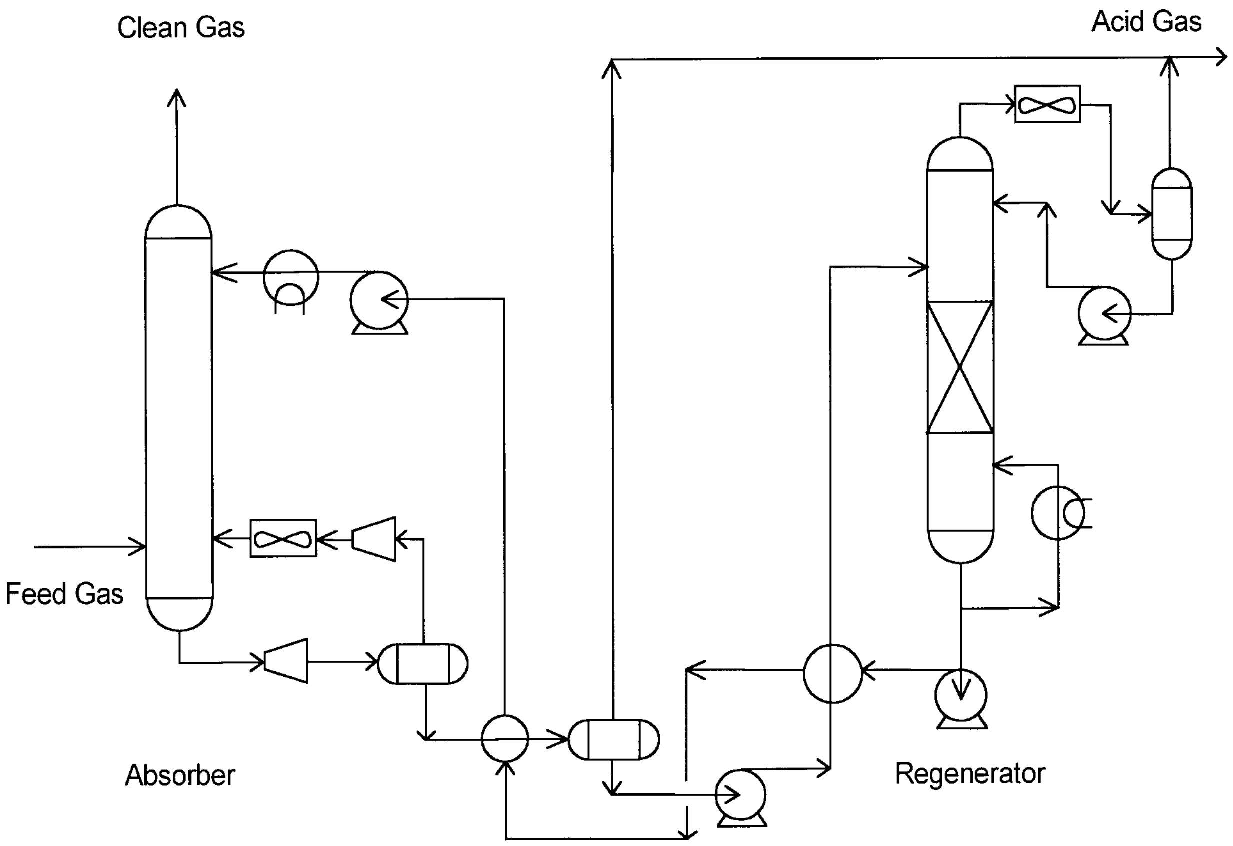
Sources: DOW, Clariant GmbH

The solubility and K value data in Table 6-1 are based on single component solubilities. It would be expected that these values should be approximately the same for non-polar components even in acid gas loaded solvents. In loaded solvents, the CO_2, H_2S, and other polar component interactions become significant. Therefore, the data in Table 6-1 should not be relied on for loaded solvents. The tables are useful, nevertheless, in explaining the selectivity between the various components. It should be noted that several physical solvent AGR process vendors claim that physical solubility properties of their solvents in some commercial software process simulation packages are inaccurate and could give results that are misleading [74].

The Selexol process can be configured in various ways, depending on the requirements for the level of H_2S/CO_2 selectivity, the depth of sulfur removal, the need for bulk CO_2 removal, and whether the gas needs to be dehydrated. Figure 6-3 shows a Selexol process layout for synthesis gas treating where a high level of both sulfur and CO_2 removal are required. The layout is similar to an amine unit, but with an extra low-pressure flash tank to reduce the load on the solvent regenerator. The offgas from the low-pressure flash is combined with the acid gas from the regenerator. This combined gas stream is then sent to a sulfur recovery unit. However, the H_2S content could be too low for use in a conventional Claus plant. A hydraulic power recovery unit may be used between the absorber and the first flash vessel, as shown in Figure 6-3. Hydraulic power recovery turbines are sometimes also used in amine systems.

The Selexol process can, however, be configured to give both a rich acid gas feed to the Claus unit as well as to provide for bulk CO_2 removal, as is done at the Farmland's gasification facility in Kansas. There, petroleum coke is gasified to produce ammonia. The synthesis gas undergoes a CO shift reaction before seeing the Selexol unit. Thus, the H_2S/CO_2 ratio is extremely low (0.6% H_2S and 41% CO_2). The first stage of the Selexol process layout at Farmland is selective absorption of H_2S. The acid gas from first stage absorption undergoes CO_2 stripping in a second

Figure 6-3
The Selexol Process



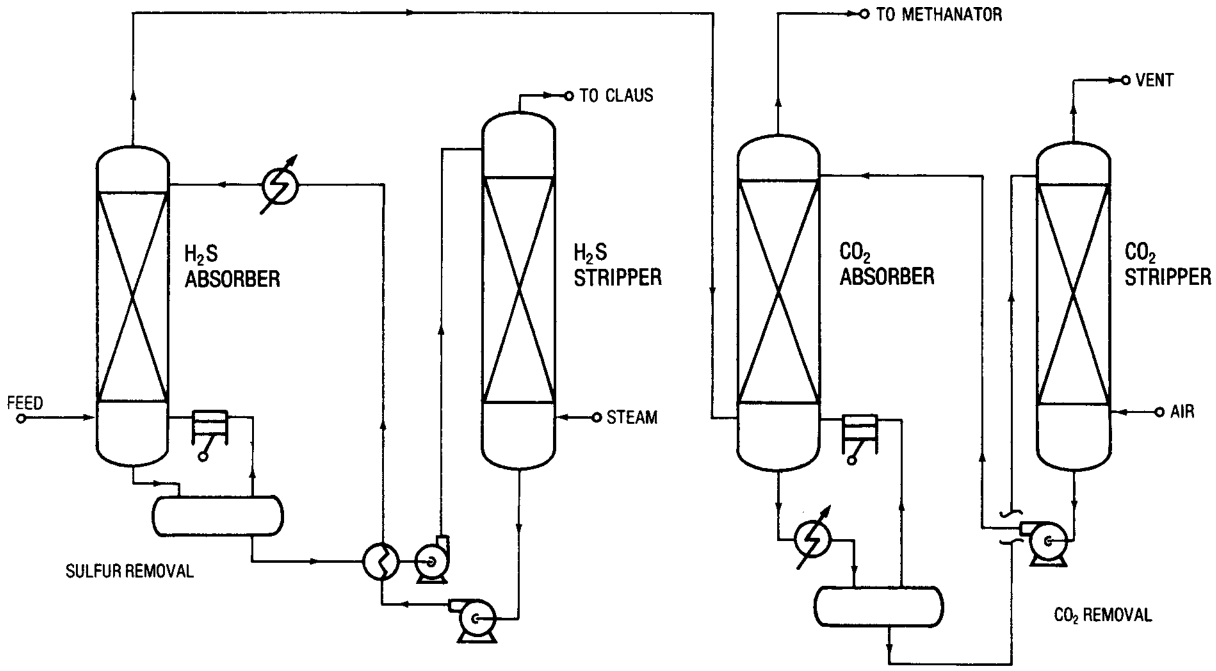
Source: SFA Pacific, Inc.

column using clean synthesis gas as the stripping medium. The resulting acid gas from the Selexol stripper has a 44% H_2S content, suitable for a Claus unit.

Where selective H_2S removal is required, together with deep CO_2 removal, two absorption and regeneration columns may be required—essentially a two-stage process. Such a process layout is illustrated in Figure 6-4 [23]. H_2S is selectively removed in the first column by a lean solvent that has been deeply stripped with steam, while CO_2 is removed, from the now H_2S-free gas, in the second absorber. The second-stage solvent can be regenerated with air or nitrogen if very deep CO_2 removal is required. If only bulk CO_2 removal is required, then the flashed gas, containing the bulk of the CO_2, can be vented and the second regenerator duty can be substantially lowered or be totally eliminated.

For selective removal of H_2S, without the need for bulk CO_2 removal, an absorber, a flash vessel and a steam stripper (regenerator) may be all that is required. The flashed gas is recompressed back into the absorption column, while the partially stripped solvent flows to the steam stripper.

Figure 6-4
Flow Diagram of Selexol Process for Acid Gas Removal from Coal-Derived Synthesis Gas



Source: Reference 23

For high levels of H_2S and COS removal, the Selexol process uses refrigeration to cool the lean solvent to 20-25°F. This allows for up to 99% of the COS to be removed, but at the expense of a high solvent circulation rate and appreciable CO_2 coabsorption. This also results in a low H_2S content of the acid gas going to sulfur recovery and high overall unit costs. A lower cost configuration, one that results in a high H_2S-content acid gas (low CO_2 coabsorption), allows much of the COS to bypass the absorber. The relatively poor selectivity between COS and CO_2 (about 2.3), as seen in Table 6-1, is the cause of this. A COS hydrolysis unit may be required if both a high H_2S-content acid gas and a high level of COS removal are to be achieved. However, the process can be configured to give both deep removal of sulfur compounds and selective H_2S over CO_2 removal if several absorption, flash, and regeneration stages are used. Such process configurations tend to be complex and costly. At the Sarlux IGCC plant in Italy, which gasifies petroleum pitch, the Selexol unit follows a COS hydrolysis step and gives an acid gas that is 50-80 vol% H_2S to the Claus plant. This acid gas composition is the result of an H_2S enrichment factor of about 2 to 3 through the Selexol unit. The H_2S content of the purified gas from the Selexol absorber at that plant is about 30 ppmv [24].

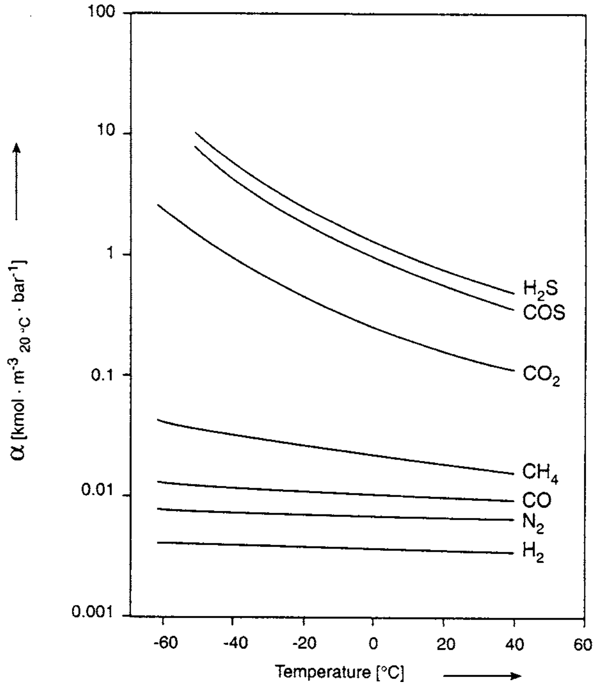
The Selexol solvent also effectively dehydrates the gas and removes any HCN that may be present.

Rectisol

The Rectisol process, developed by Lurgi GmbH, is the most widely used physical solvent gas treating process in the world. More than 100 Rectisol units are in operation or under construction worldwide. Its most prevalent application is for deep sulfur removal from synthesis gases that subsequently undergo catalytic conversion to such products as ammonia, hydrogen and Fischer Tropsch liquids.

The Rectisol process uses chilled methanol at a temperature of about -40°F to -80°F. Methanol's selectivity for H_2S over CO_2 at these temperatures is about 6/1 [23], a little lower than that of Selexol at its usual operating temperature. However, the solubilities of H_2S and COS in methanol, at typical process operating temperatures, are higher than in Selexol and allow for very deep sulfur removal (<0.1 ppmv H_2S plus COS). Rectisol's high selectivity for H_2S over CO_2, combined with the ability to remove COS, is the primary advantage of the process. Figure 6-5 shows the solubilities of various gas components in methanol. Chilled methanol also absorbs HCN, NH_3, and iron- and nickel-carbonyls. The solubilities of these trace components and other organic sulfur compounds are even higher than that of H_2S. Rectisol's complex scheme and the need to refrigerate the solvent are its main disadvantages, resulting in high capital and operating costs.

Figure 6-5
Absorption Coefficient α of Various Gases in Methanol
(Partial Pressure: 1 bar)

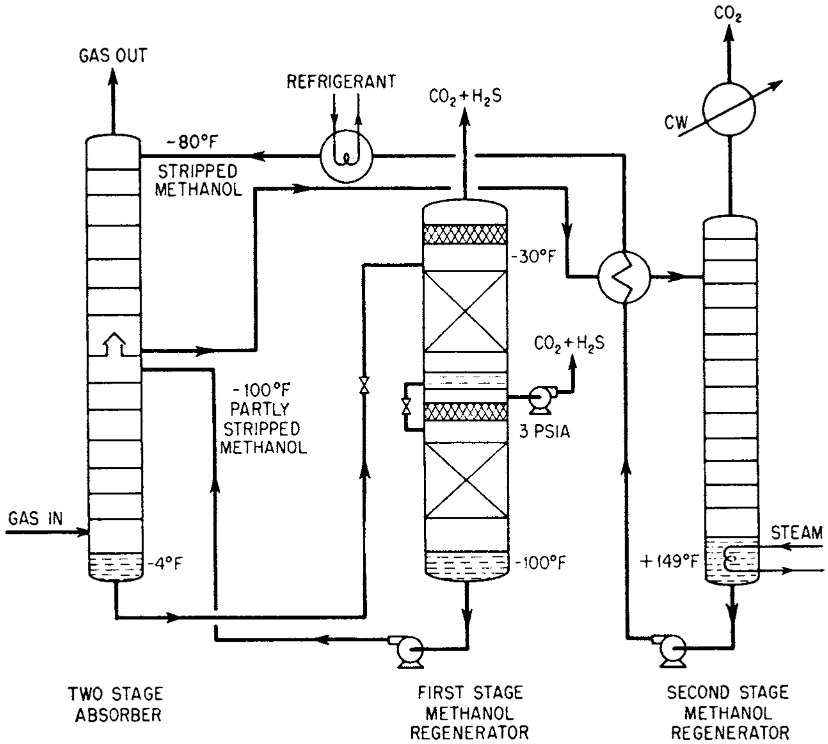


Source: Lurgi GmbH

As in the case of the solubility data presented in Table 6-1, the data in Figure 6-4 are based on single component solubilities and should not be applied to loaded solvents.

There are many possible process configurations for Rectisol, depending on process requirements. Different process layouts are used for selective H_2S removal, deep CO_2 removal, and for deep non-selective CO_2 and H_2S removal. An example flow scheme of a basic Rectisol process is shown in Figure 6-6. In this flow scheme, bulk removal of CO_2 and nearly all of the removal of H_2S and COS take place in the bottom section of the absorber. The methanol solvent contacting the feed gas in the first stage of the absorber is stripped in two stages of flashing via pressure reduction. The regenerated solvent is virtually free of sulfur compounds but contains some CO_2. The acid gas leaving the first stage solvent regenerator is suitable for a Claus plant. The second stage of absorption is designed for the removal of the remaining sulfur compounds and CO_2. The solvent from the bottom of the second stage of the absorber is stripped deeply in a steam-heated regenerator and is returned to the top of the absorption column after cooling and refrigeration.

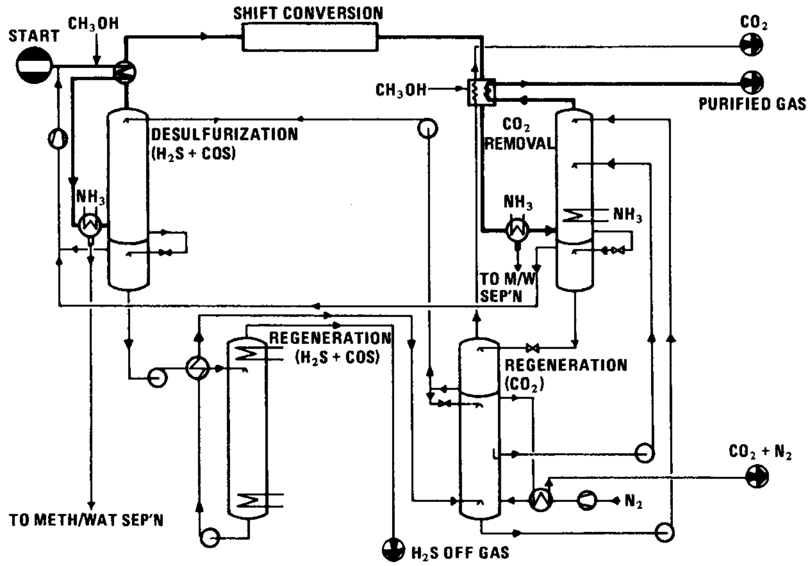
Figure 6-6
Rectisol Process Flow Diagram



Source: Reference 23

If all carbon is to be removed from synthesis gas, such as for example for hydrogen manufacture or for CO_2 sequestration, then another Rectisol layout could be used. In such a scheme, separate absorption and solvent regeneration steps would be used, with a shift conversion step between the two steps. Selective removal of the sulfur compounds would take place in the first stage, followed by the shift conversion step. Bulk CO_2 removal would take place in the second stage. An example of such a flow scheme is shown in Figure 6-7. The actual layouts of the process can vary considerably from those shown in the figures and specific designs can only be obtained from process licensors.

Figure 6-7
Flow Diagram of Rectisol Process for Selective Hydrogen Sulfide Removal, Followed by Carbon Dioxide Removal



Source: Reference 23

The Rectisol process is very flexible and can be configured to address the separation of synthesis gas into various components, depending on the final products that are desired from the gas. It is very suitable to complex schemes where a combination of products are needed, such as for example hydrogen, carbon monoxide, ammonia and methanol synthesis gases and fuel gas side streams.

Chilled methanol will remove many metallic trace components from the gas, including mercury. If mercury is present in the gas, then a carbon bed may be required ahead of the Rectisol unit to prevent the mercury from forming metal amalgams in the low temperature sections of the process.

Mixed Amine/Physical Solvent Processes

A number of processes use a mixture of amines and physical solvents to take advantage of the best characteristics of both types. A mixed solvent is generally a compromise between H_2S selectivity and the degree of the physical solubilities of the other sulfur compounds. Among the most numerous applications of such processes used commercially are Sulfinol (Shell) and FLEXSORB (ExxonMobil). These two processes are described below.

Sulfinol

The Sulfinol process, developed by Shell in the early 1960s, is a combination process that uses a mixture of amines and a physical solvent. The solvent consists of an aqueous amine and sulfolane. Sulfinol-D uses diisopropanolamine (DIPA), while Sulfinol-M uses MDEA. The mixed solvents allow for better solvent loadings at high acid gas partial pressures and higher solubility of COS and organic sulfur compounds than straight aqueous amines.

There are some 200 Sulfinol plants in operation worldwide [66], most of which use the Sulfinol-D solvent formulations. Sulfinol-D is primarily used in cases where selective removal of H_2S is not of primary concern, but where partial removal of organic sulfur compounds (mercaptans and CS_2) is desired, typically in natural gas and refinery applications. Sulfinol-D is also able to remove some COS via physical solubility in sulfolane and partial hydrolysis to H_2S induced by the secondary amine (DIPA). However, deep removal of COS by Sulfinol-D cannot be guaranteed. Unlike solvents that use other primary and secondary amines (MEA, DEA) Sulfinol-D is claimed not to be degraded by these sulfur compounds. Sulfinol-D has also been used for selective removal of H_2S in at least one natural gas plant which was designed for a moderate amount of CO_2 slip.

Sulfinol-M is used when a higher degree of H_2S selectivity is needed. H_2S selectivity in Sulfinol-M is controlled by the kinetics of the reaction of H_2S with MDEA as well as by the physical solubilities of H_2S and CO_2 in the solvent. The CO_2 partial pressure over the solvent is several times greater than that of H_2S at the same solvent loadings resulting in some degree of equilibrium selectivity [25]. The design for H_2S selectivity becomes more complex for a solvent that claims a high degree of physical solubility, when both the interaction of the kinetic and physical solubility factors have to be considered simultaneously. A high degree of physical solubility is enhanced by equilibrium loading at long residence time and the use of many trays in the absorber, while fast reaction kinetics facilitates the use of a smaller number of trays and shorter contact time. While there are benefits to be gained by higher solubilities of the sulfur compounds in a solvent such as Sulfinol-M, these benefits are best obtained with a high absorber tray count, which in turn compromises H_2S selectivity. Sulfinol-M is capable of virtually complete COS removal and a total treated gas sulfur specification of less than 40 ppmv.

For synthesis gas applications, where the ratio of CO_2 to H_2S is high (higher than about 5/1), the Sulfinol-M process without an additional enrichment step is unlikely to give an acid gas suitable for a straight through Claus plant. It is also likely to require an upstream COS hydrolysis unit if a very high degree of sulfur removal is needed (about 10-20 ppmv total sulfur in treated gas). Sulfinol-M process could be a better choice than a straight MDEA process under certain conditions. Specific performance parameters for the process, as for any other proprietary process, can only be obtained from the licensors.

FLEXSORB PS and Hybrid FLEXSORB SE

ExxonMobil offers two mixed hindered amine/physical solvent versions of the FLEXSORB Process, discusses earlier in this section under Amine Processes. It appears that they were developed as a competitive answer to the Sulfinol Process. The Hybrid FLEXSORB SE Process employs a solution of the FLEXSORB SE amine, water, and an unspecified physical solvent. Two plants are in operation. The FLEXSORB PS solvent consists of a different hindered amine, water, and a physical solvent. Five of these plants are believed to be operating [66]. In one Canadian natural gas plant, Sulfinol D solvent was replaced with FLEXSORB PS solvent to reduce the solvent circulation rate and reboiler duty. There are no known commercial applications of the FLEXSORB PS Process for the selective removal of H_2S.

General Perceptions of AGR Process Suitability for IGCC

The general industry perspective of AGR process for IGCC, reflected in the patterns indicated previously by Table 4-1 and also in ongoing EPRI-sponsored engineering and cost studies of IGCC [64,65,68,69], is summarized below.

- MDEA-based AGR is generally regarded as a low capital cost option for IGCC without CO_2 removal for sequestration—if the syngas pressure is low (e.g., less than 30 atm) and the SO_2 and NO_x emissions limits are not stringent (i.e., if SCR is not required and required the total sulfur level is only about 30-50 ppmv). The stripping steam requirements of MDEA are higher than those of Selexol. If MDEA is pushed to deep sulfur removal, the CO_2 absorption will also increase—thereby diluting the acid gas feed to the SR plant and also reducing the fuel gas mass flow to the gas turbines (slightly reducing the power output).
- At high syngas pressures, physical solvent-based AGR processes become increasingly attractive. For example, with the ChevronTexaco Gasification Process at 900-1,000 psi and the Selexol AGR Process are being used in the API IGCC project in Italy and are also being evaluated in some current EPRI engineering studies. Without refrigeration, total sulfur levels of about 10-15 ppmv can be achieved. Lower levels are achievable with refrigeration, albeit with additional CO_2 co-absorption [67].
- AGR process options should be evaluated on the basis of the performance and costs of the total AGR, SR, TGT package. For example, the Selexol Process can produce a more concentrated acid gas feed to the SR unit, thereby improving its performance and reducing its cost, and the size and cost of the TGT unit. Alternatively, the tail gas (after hydrogenation) may be recycled to the absorber—eliminating the separate TGT unit.
- The syngas composition also impacts the selection of AGR. For example, the dry-fed Shell coal/coke gasification process produces less CO_2 than the slurry-fed ChevronTexaco and Global E-Gas gasification processes, thereby reducing the CO_2 co-absorption issue for MDEA-based AGR with the Shell Process.

- The Rectisol Process is regarded as the most expensive of these three AGR processes for IGCC without CO_2 recovery—because of its complexity and refrigeration requirements. Lurgi appears to concur with this perception, acknowledging that Selexol is one of “the solvents of choice in conventional IGCC gas purification” [71].
- COS hydrolysis before the AGR process is important for achieving low total sulfur levels in the cleaned up syngas with both chemical solvent-based AGR and the Selexol Process.
- If a future capability of removing CO_2 for sequestration is desired, the Selexol Process is more readily adapted to CO_2 removal by the addition of a second stage, and it is probably a better choice than MDEA.
- Two-stage physical solvent-based AGR processes are preferred for IGCC with CO_2 removal for sequestration [64]. For example, in ongoing EPRI/DOE-co-sponsored engineering and cost studies of CO_2 removal from power plants for sequestration, a two-stage Selexol Process is employed with the IGCC plant. H_2S is removed in the first stage and CO_2 is removed in the second stage [68,69]. A similar configuration based on Selexol was employed in a recent Texaco/GE/Jacobs Engineering assessment of IGCC with CO_2 removal [72]. Fluor, an experienced gasification plant designer and constructor, also recently reported a study of IGCC with CO_2 removal based on the Selexol Process [73]. While Lurgi is promoting its Rectisol Process for IGCC with CO_2 removal, no economics have been published on this option [71].

No comparative engineering and economic evaluations specifically of AGR process options for gasification and IGCC applications are available. However, current EPRI site-specific studies of the ChevronTexaco, Global E-Gas, and Shell gasification-based IGCC processes with various fuels, and MDEA, Selexol, and/or Sulfinol AGR process options should add to the understanding of the suitability of the various AGR options for IGCC, and their overall impact on the IGCC system performance and costs. However, the form in which the results of these sponsor-private studies eventually may be published has not yet been determined [65].

AGR Process Selection

Although the general perceptions of AGR discussed above provide some preliminary guidance in the selection of AGR options for an IGCC project, overall the final selection of an AGR process is a complex task. Several AGR options exist and a number of parameters affect the process design and the capital and operating costs of each option. The options may include various MDEA formulations (available from different licensors), the Selexol Process, the Purisol Process (which Lurgi is promoting as an alternative to Selexol for conventional IGCC [71]), the FLEXSORB hindered amine and mixed solvent processes, the Sulfinol mixed solvent process, and the Rectisol Process as an alternative to Selexol for low emissions IGCC with CO_2 removal.

The gasification process selected and feedstock options for an IGCC project will determine the untreated syngas flow rate, composition, and pressure. These parameters and the clean syngas composition specifications and plant emissions limits set the boundaries into which the gas treating package (AGR, SR, and TGT) must be fit.

Thus, the gasification process significantly selected impacts the AGR system options and their designs. The highest coal and petroleum coke gasification pressures (up to about 1,000 psi (69 bar) currently, and potentially about 20-30% higher) are achievable with the fuel/water slurry-fed ChevronTexaco Gasification Process. As noted previously, high pressure tends to favor physical solvent-based AGR systems. The slurry-fed Global E-Gas Gasification Process presently employs a T-shaped vessel configuration that limits its pressure to a lower level than that of the straight cylindrical design of ChevronTexaco. However, Global is considering a cylindrical design for a higher pressure gasifier. The dry pulverized fuel-fed Shell Gasification Process may be limited to a pressure of 600 psi (41 bar). The Shell Process also produces less CO_2 than the slurry-fed processes, which tends to encourage using MDEA for non-CO_2 removal situations, as noted previously [64].

The parameters that must be considered in AGR selection and gas treating system design optimization include the:

- Untreated syngas flow rate and composition, pressure, and temperature
- Acid gas components in the syngas, their concentrations, the depth of H_2S and total sulfur removal required, and the selectivity desired. The overall plant SO_2 and NO_x emissions must be considered here. A requirement for SCR on the combustion turbine exhaust gas, may be the factor that sets the total sulfur allowable in the clean syngas fuel. Future more stringent air emissions limits may necessitate significant changes in some AGR process designs (compared with current designs).
- Any parallel use of the syngas in co-production of hydrogen and/or chemicals—and the corresponding process requirements (e.g., CO shift for H_2 production) and synthesis gas specifications (e.g., <0.1 ppmv total sulfur for methanol and Fischer-Tropsch synthesis gas)
- Extent of CO_2 removal that is acceptable if it is not removed for sequestration—or that is required in the case of removal for sequestration, and the flexibility and cost of adding an optimal CO_2 removal capability at a later date
- AGR utilities requirements (stripper steam and auxiliary electric power). These will not be finalized until the design is optimized. The heat requirements for solvent regeneration and the electrical needs for pumping (solvent recirculation) and refrigeration (if used, with physical solvents) are the major factors affecting the operating costs for AGR, as discussed earlier.
- Solvent losses (make-up costs)
- Impact of the composition of the concentrated (H_2S-rich) acid gas leaving the AGR process on the design and costs of the downstream SR and TGT processes. The integration with and impact of the AGR on the entire system must be evaluated. Some AGR designs may allow recycling the Claus plant tail gas (after it is hydrogenated), thereby eliminating the TGT process.
- Impact of potential tie-ins to existing facilities
- Process complexity and transient behavior (e.g., load-following capability)

- Process flexibility with regard to feedstock changes and potential future tightening of emissions limits
- Process train philosophy

Project planners and plant designers/constructors may conduct preliminary screenings of AGR process options using various techniques and tools, including commercial process simulators. In the case of generic amine processes, some planners/developers and engineering/construction firms may use related commercially available process simulators for the designs of their AGR plants. The trade-offs in going that route were discussed earlier in this section. For AGR based on proprietary MDEA formulations and physical solvents, the AGR process licensors should be relied on for definitive designs (including preferred configurations) and bids. As mentioned earlier in this report section, some physical solvent-based AGR process vendors claim that the solubility data in some commercial process simulation packages are not accurate and could produce misleading results. The system design and optimization tasks should involve the collaboration of the selected AGR vendor, or competing vendors. The AGR vendor's and plant constructor's respective track records supplying successful plants should also be major considerations. Customer preferences and biases, as well as the experience, preferences, biases, and affiliations (licensing, etc.) of plant designers/constructors may also influence the selection of the AGR process.

7. SULFUR RECOVERY PROCESSES

Currently, most of the world's sulfur is produced from the acid gases coming from gas treating. The Claus process remains the mainstay for sulfur recovery. Conventional three-stage Claus plants, with indirect reheat and feeds with a high H_2S content, can approach 98% sulfur recovery efficiency. However, since environmental regulations have become more strict, SR plants are required to recover sulfur with over 99.8% efficiency. To meet these stricter regulations, the Claus process underwent various modifications and add-ons.

The add-on modifications to the Claus plant can be considered as a separate operation from the Claus process, in which case it is often called a tail gas treating (TGT) process. Or it can be called a Claus process extension. In this report, the add-on process is considered a TGT process only when the sulfur compounds in the Claus tail gas undergo conversion to H_2S. TGT processes are covered in the next section of the report.

Other sulfur recovery processes can replace the Claus process where it is uneconomic or cannot meet the required specifications. Usually such processes are used in small-scale plants, or where the H_2S content of the acid gas is too low for a Claus plant or one of its modified versions.

This section covers the conventional Claus process and its various modifications and extensions, as well as some other lesser-utilized sulfur recovery processes, such those based on wet oxidation (Redox).

The Claus Process

The Claus process was invented in 1883. It originally was based on a direct catalytic reaction of H_2S and oxygen. It was modified in 1936 to its current configuration, which includes a furnace in front of the catalytic stages. The next major modification to the process, in the mid-1960s, was the replacement of bauxite catalyst with synthetically produced aluminum oxide.

The Claus process converts H_2S to elemental sulfur via the following reactions:

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

$$2H_2S + SO_2 = 2H_2O + 3S$$

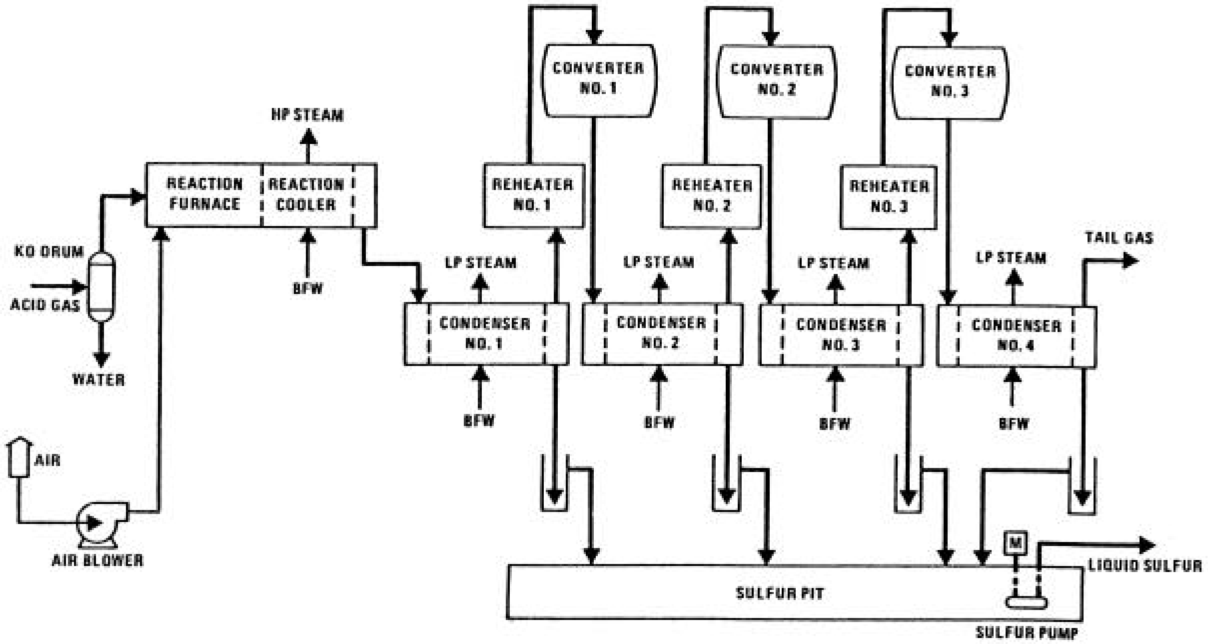
The second reaction, the Claus reaction, is equilibrium limited. The overall reaction is:

$$3H_2S + 3/2\ O_2 = 3H_2O + 3S$$

The sulfur in the vapor phase exists as S_2, S_6, and S_8 molecular species, with the S_2 predominating at higher temperatures, and S_8 predominating at lower temperatures.

A simplified process flow diagram of a typical three stage Claus plant is shown in Figure 7-1 [27]. One third of the H_2S is burned in the furnace with oxygen from the air to give sufficient SO_2 to react with the remaining H_2S. Since these reactions are highly exothermic, a waste heat boiler that recovers high pressure steam usually follows the furnace. Sulfur is condensed in a condenser that follows the high pressure steam recovery section. Low pressure steam is raised in the condenser. The tail gas from the first condenser then goes to several catalytic conversion stages, usually 2 to 3, where the remaining sulfur is recovered via the Claus reaction. Each catalytic stage consists of gas preheat, a catalytic reactor and a sulfur condenser. The liquid sulfur goes to the sulfur pit, while the tail gas proceeds to the incinerator or for further processing in a TGT unit.

Figure 7-1
Typical Three-Stage Claus Sulfur Plant



Source: Reference 27

Claus Plant Sulfur Recovery Efficiency

The Claus reaction is equilibrium limited and sulfur conversion is sensitive to the reaction temperature. The highest sulfur conversion in the thermal zone is limited to about 75% (typical furnace temperatures are in the range of 2,000-2,600°F (1,100-1,400°C)). As the temperature decreases, conversion increases dramatically. At 300°F (149°C), a temperature below the sulfur dew point, equilibrium conversion reaches well into the high 90% levels. Increased conversion at sulfur sub-dew temperatures is the reason for Claus process modifications discussed later in this section of the report.

In the thermal stage, some of the H_2S is converted to COS and CS_2. COS and CS_2 are partially converted to H_2S via hydrolysis in the catalytic stages as the temperature drops. The first catalytic stage usually operates at a higher temperature than subsequent stages to enhance this hydrolysis reaction and thus reduce the amounts of COS and CS_2 in the tail gas. Incomplete hydrolysis of the COS and CS_2 in the first stage results in reduced sulfur recovery efficiency.

The Claus plant furnace is often used for disposal of unwanted plant wastes such as sour water stripper off gases (with NH_3, HCN, and H_2S), hydrocarbons and other waste-laden gases. Most of these wastes can be combusted in the furnace to destruction. However, their combustion results in decreased sulfur recovery efficiency and a tail gas that may contain some unconverted waste materials. Heavy hydrocarbons and HCN may also cause sulfur to turn dark. NH_3 and HCN, if not completely destroyed, may form ammonium salts which plug the catalyst beds. NH_3 is the most prevalent component and is usually the hardest to destroy completely.

In actual operating Claus plants the concentrations of some sulfur species (e.g. COS and CS_2) appear to be higher than what one would calculate from equilibrium considerations. From these observations, it can be concluded that the Claus process is generally kinetically limited. Thus, most furnace designs have to address the three major parameters that affect reaction kinetics; temperature, residence time and mixing. To adequately destroy NH_3, a flame temperature above 2,280°F (1,250°C), and a residence time greater than 0.8 seconds are required in the furnace. Following these “rules of thumb,” and with good mixing in the furnace, the residual NH_3 content should be well below 150 ppmv [28].

Claus plant sulfur recovery efficiency depends on many factors, among which the most important are:

- H_2S concentration of the feed gas
- Number of catalytic stages
- Gas reheat method

Other lesser important factors that influence the recovery efficiency are:

- Water content of the feed gas
- Catalytic reactor and condenser temperatures
- Extent of COS and CS_2 hydrolysis in the first stage
- Sulfur entrainment in the plant tail gas

As mentioned before, a three-stage plant, using indirect heat, and that has H_2S-rich feed (about 70-80% H_2S) will approach a sulfur recovery efficiency of about 98%. Higher design efficiencies can be obtained with add-on units. However, the higher the upstream Claus plant efficiency the lower will be the load on the add-on unit, resulting in a lower investment. As the H_2S content of the feed gas is reduced sulfur recovery efficiency drops. The sulfur recovery efficiency of a three-stage Claus plant with indirect reheat will drop to about 96% when the H_2S content in the feed gas is about 50%.

In order to keep Claus plant recovery efficiencies approaching 94-96% for feed gases that contain about 20-50% H_2S a split-flow design is often used. In this version of the Claus plant, part of the feed gas is bypassed around the furnace to the first catalytic stage, while the rest of the gas is oxidized in the furnace to mostly SO_2. This results in a more stable temperature in the furnace.

Below about 15% H_2S content in the feed gas other means have to be used to maintain a stable temperature in the furnace, such as feed air preheating or oxygen enrichment. Such a lean H_2S feed gas results in low sulfur recovery efficiencies and high unit costs.

Large diluent streams in the feed to the Claus plant, such as N_2 from combustion, or a high CO_2 content in the feed gas, lead to higher cost Claus process and any add-on or tail gas units. One way to reduce diluent flows through the Claus plant and to obtain stable temperatures in the furnace for dilute H_2S streams is oxygen blown Claus, discussed below.

Oxygen-Blown Claus

Oxygen-blown Claus process was originally developed to increase capacity at existing conventional Claus plants and to increase flame temperatures of low H_2S content gases. The process has also been used to provide the capacity and operating flexibility for sulfur plants where the feed gas is variable in flow and composition such as often found in refineries. The application of the process has now been extended to grass roots installations, even for rich H_2S feed streams, to provide operating flexibility at lower costs than would be the case for conventional Claus units. At least four of the recently built gasification plants in Europe use oxygen enriched Claus units; Puertollano in Spain, and the three Italian plants, api Energia, ISAB, and SARLUX.

Oxygen enrichment results in higher temperatures in the front end furnace (FEF), potentially reaching temperatures as high as 2,900-3,000°F (1,600-1,650°C) as the enrichment moves beyond 40-70 vol% O_2 in the oxidant feed stream. A challenge for early process developers was finding a means to control high temperatures in the FEF. Although water vapor content of the gas stream has a tempering effect on the run-away temperatures, it is insufficient and high water content leads to other problems—excess water suppresses the Claus reaction. Two principal means have been used to achieve temperature control, recycle of cooled gas to the FEF (COPE process), and special burners that control the combustion process itself (OxyClaus process). Temperature control via staged combustion is also employed (SURE process).

It is safe to premix oxygen with air up to an oxygen level of about 28 vol%. Beyond that level, air and oxygen must be introduced separately. Proprietary burner designs have been developed by various companies for this purpose, mostly by oxygen suppliers.

Although oxygen enrichment has many benefits, its primary benefit for lean H_2S feeds is a stable furnace temperature. Sulfur recovery is not significantly enhanced by oxygen enrichment. A recent assessment of an oxygen enrichment option at the Qatargas refinery, which has a 14-18% H_2S feed, concluded that it would be more beneficial to install acid gas enrichment and add an air-blown extended Clausplant. Sulfur recovery, which at the Qatargas plant is about 95%, would have improved only marginally according to oxygen-blown Claus process licensors [26].

The COPE Process

The COPE (Claus Oxygen-based Process Expansion) process was developed by Air Products and Chemicals and Goar, Allison & Associates. In addition to these two companies, the process is also available from Technip USA. The basic feature of the process is the control of the FEF temperature by recycling cooled gas from the exit of the first sulfur condenser [29]. Gas recycle is only required when there is potential for the refractory to exceed a temperature of about 2,700°F. When gas recycle is not used, the process is known as COPE Phase I. The COPE Phase I process can increase the sulfur capacity of an air-blown Claus by about 50% for a rich acid gas feed [30]. The COPE Phase I process only needs a specially designed burner with separate feeding of air, oxygen, acid gas, recycle gas, and any fuel gas. The burner can handle up to 100 vol% oxygen.

The process has been used mainly to retrofit existing Claus plants at refineries to increase their capacity [31]. There are 19 Claus plants that use the COPE process. Six of these plants use the COPE Phase II version of the process (with gas recycle), the rest are equipped only with the proprietary COPE burner. All, except three plants, are retrofits of air-blown Claus facilities, mostly at refineries. Some of the revamped facilities doubled their sulfur handling capacities. One of the plants operates with 100% oxygen since 1985.

Only one IGCC facility, the Wabash River plant at Terre Haute, Indiana, uses the COPE process (Phase I). The tail gas from the COPE sulfur recovery unit is recycled back to the gasifier.

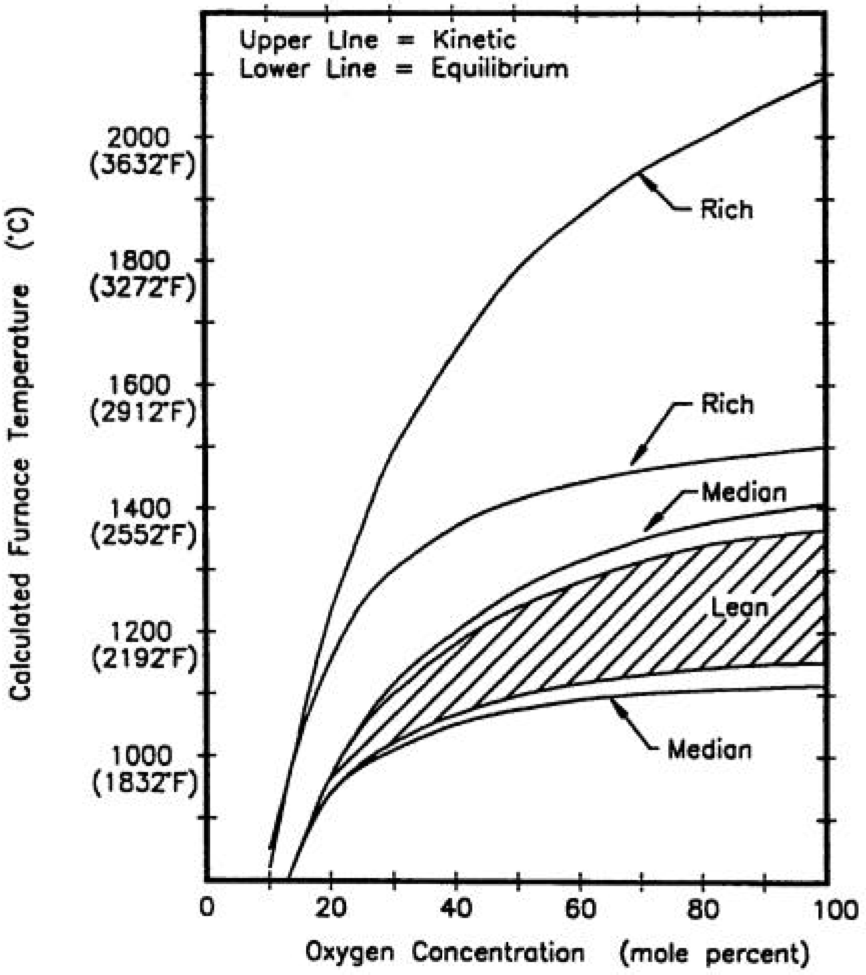
The licensors claim that the COPE process sulfur recovery can vary from 95-98% and that sulfur recovery can be improved by 0.5-1% over that of the conventional, air-blown Claus, depending on the H_2S concentration in the feed gas.

The OxyClaus Process

The Lurgi Oel Gas Chemie GmbH OxyClaus process is based on a proprietary burner that is claimed to control FEF temperatures to below the refractory limit even when 100% oxygen is used with rich H_2S streams. Beside the burner, no other cooling scheme is used in the OxyClaus FEF. The burner and the furnace are designed to reach thermal equilibrium instead of the kinetic equilibrium that is conventionally thought to prevail in a Claus furnace.

Figure 7-2 shows a plot of the theoretically calculated furnace temperatures reached using the kinetic models and the equilibrium models for the Claus reaction at various oxygen and H_2S concentrations [32]. It shows that the equilibrium model reaction temperatures are far below those of the kinetic model. Lurgi's experience shows that actual furnace temperatures reached

Figure 7-2
Reaction Furnace Temperature



Feed Cases for Figure 7-2			
Composition	Rich Feed	Median Feed	Lean Feed
(mole %)			
H_2S	90.00	50.00	20.00
CO_2	9.00	49.00	79.00
CH_4	0.75	0.75	0.75
C_2H_6	0.25	0.25	0.25
Total	100.00	100.00	100.00
Note: For the Lean Feed Case a 55% bypass was utilized.			

Source: Reference 32

with the OxyClaus commercial plants are closely duplicated by the equilibrium model calculations. It is postulated that that the high temperatures reached with oxygen combustion causes some decomposition of H_2S, CO_2 and H_2O via the following reactions:

$$H_2S \rightarrow H_2 + 0.5\ S$$

$$CO_2 \rightarrow CO + 0.5\ O_2$$

$$H_2O \rightarrow H_2 + 0.5\ O_2$$

These reactions are highly endothermic and cause a moderating influence on the exothermic Claus reaction. Water dissociation supplies additional oxygen for the formation of SO_2. It is also known that some of the H_2 and CO convert to H_2S and COS, as the gas cools in the waste heat boiler, via the following reactions:

$$H_2 + 0.5\ S_2 \rightarrow H_2S$$

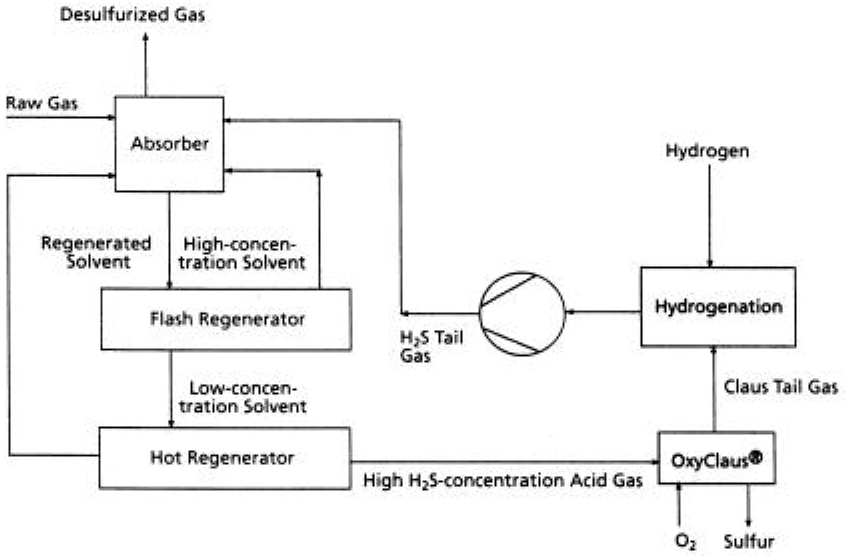
$$CO + 0.5\ S_2 \rightarrow COS$$

The COS and some of the unreacted H_2 and CO wind up in the Claus tail gas. The amount of H_2 in the tail gas is sufficient for the hydrogenation/hydrolysis step in the tail gas processing unit. This process step is discussed further in Section 8 – Tail Gas Treating.

The hydrogenated/hydrolyzed tail gas from the Claus plant, after compression, can be sent to the acid gas removal unit for H_2S cleanup. The CO and any remaining hydrogen in the tail gas can then be consumed in a combustion turbine after undergoing H_2S removal. A general scheme such as this is shown in Figure 7-3, where a tail gas from the OxyClaus unit is hydrogenated, and recompressed for treatment in a Lurgi Rectisol plant. Such a scheme is used at the SARLUX IGCC plant, using the Selexol process. There is little reason why other oxygen-blown Claus processes with an H_2S-rich acid gas could not avail themselves of such schemes as well.

Lurgi built approximately 22 sulfur recovery trains based on the OxyClaus process. Most of these were refinery Claus unit revamps. Two new OxyClaus plants are used at the SARLUX and the ISAB IGCC plants, and an older Claus plant, previously revamped at the AGIP Sannazaro refinery with the OxyClaus process, will be used for the IGCC facilty which is being engineered. None of the known OxyClaus plants operate on 100% oxygen. SARLUX operates with the highest oxygen concentration (70%) that Lurgi has used so far in a commercial plant.

Figure 7-3
Claus Plant/H_2S Removal in IGCC



Source: Lurgi Oel Gas Chemie GmbH

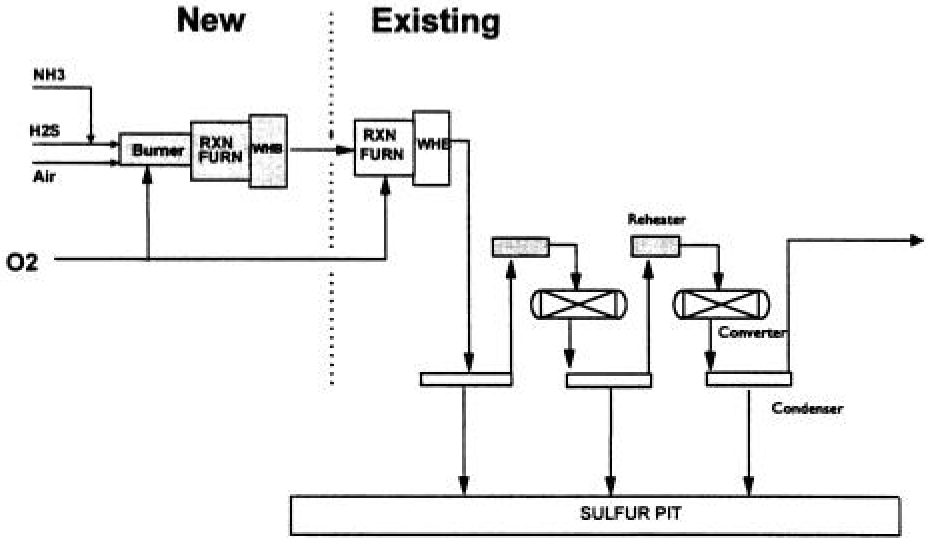
The SURE Process

The SURE oxygen-blown Claus process was developed by British Oxygen Corp. and Ralph M. Parsons Co. (now Parsons Corp.). The process is based on staged combustion. A portion of the oxygen and all of the air, together with all of the acid gas go to the first stage, while the rest of the oxygen is fed to the second combustion stage. The partially oxidized gases between the stages are cooled in a waste heat boiler. Only one burner is used (in the first stage)—the temperature of the gases going to the second stage is sufficiently high to autoignite with the rest of the oxygen. The process was initially developed to address Claus plant revamps. Figure 7-4 shows the version of the process used for a Claus plant revamp [33].

The two stage SURE process is only required for H_2S-rich acid gas applications. A proprietary SURE burner in a single stage furnace is all that is required for a lean H_2S feed, such as that at the Api Energia IGCC plant at the Falconara refinery, where 2 trains of a single stage SURE process are employed. The Api Energia IGCC SURE Claus plants operate with 100% oxygen. There were at least 8 such SURE burners operational in 1998 and 8 additional ones were in development projects, including the two needed for the Api Energia IGCC project.

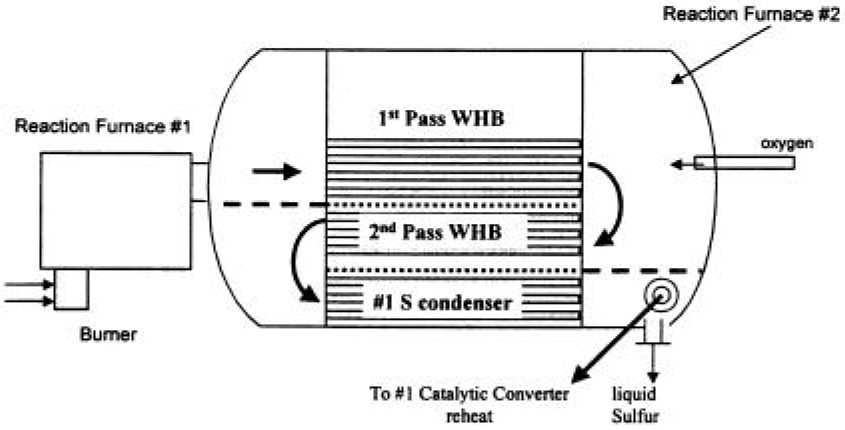
For H_2S-rich acid gases, a combination waste heat boiler (WHB) and second stage furnace have been developed by Siirtec Nigi and Parsons for the API Falconara refinery Claus plant revamp. These two functions were combined in one vessel and included the second stage oxygen lances. Figure 7-5 shows such a multi-pass WHB and second stage furnace.

Figure 7-4
Process Sketch of SURE Double Combustion Claus Process



Source: Reference 33

Figure 7-5
Sketch of Multi Pass Waste Heat Boiler with Integral #2 Reaction Furnace



Source: Reference 33

Other Oxygen-Blown Claus Process Services

Besides the COPE, SURE, and the Lurgi OxyClaus processes, several other oxygen suppliers offer their own versions of the oxygen-blown Claus processes. Among these are Air Liquide and Praxair.

Air Liquide, in partnership with Big Three Industrial and American Combustion, Inc. (ACI), offered the ClausPlus process in the past. Air Liquide had since purchased ACI and is now offering a proprietary oxygen burner (Oxyburner). This burner is being offered primarily as a means to destroy ammonia at refinery Claus plants. It is capable of handling 100% oxygen [34].

Praxair offers oxygen enrichment services for Claus plants. These consist of oxygen supply and control, and the evaluation of conversion options.

Extended Bed Claus Processes

There are two major extended bed Claus processes which improve Claus sulfur recovery by either adding, or replacing, the last Claus stage with a proprietary catalytic bed. Both of these processes can improve Claus sulfur recovery to over 99.5%. One process operates at above the sulfur dew point (SuperClaus), the other below the sulfur dew point (Sulfreen).

An extended bed process can be used without tail gas treating as long as the process tail gas sulfur regulations are within the sulfur recovery capabilities of the process. When sulfur recovery specifications reach 99.8+% then a tail gas treating process may be required, discussed in the next section of the report. In the extended bed processes, sulfur recoveries are limited by the presence of COS and/or CS_2 in the tail gas. Some of the extended bed processes offer modifications to their basic process to overcome this limitation. Usually, such modifications involve an additional hydrolysis step to convert all sulfur species to H_2S, followed by some form of recycle. However, such modified processes have not been used in IGCC projects, and are not discussed in this report. Extended bed Claus processes could be used to reduce the load on a tail gas treating process.

The SuperClaus Process

The SuperClaus process was developed by Comprimo, Gastec, and the University of Utrecht, in the Netherlands. The process is now owned by Stork Engineers & Contractors B.V. The process is based on the replacement or extension of the last stage of the Claus process by a catalytic bed that carries out a selective oxidation reaction. The first stages of the Claus reaction are carried out in the air deficient mode (high H_2S content). The gas that enters the selective oxidation reactor has a high H_2S content and very little SO_2. Some oxidant is bypassed around the Claus reactors to the selective catalytic stage that contains a silica/alumina catalyst. The following reaction takes place in that bed:

$$H_2S + \frac{1}{2} O_2 = S + H_2O$$

The reaction is not equilibrium limited as the Claus reaction, and most of the H_2S (over 85%) reacts to elemental sulfur. Because the reaction is not equilibrium limited, the catalyst is not sensitive to high H_2O content in the vapor and has little tendency to form undesirable compounds such as SO_2, COS, CS_2, and CO.

The process has been used successfully for about fifteen years in over two dozen commercial installations. Sulfur recoveries, for high H_2S content acid gas feeds (>50% H_2S), can vary from 98.3 to 98.8% for three catalytic stages (2 Claus plus 1 selective oxidation), to 98.9-99.2% for four stages (3 Claus plus 1 selective oxidation) [35].

The SuperClaus process can also be configured to give higher sulfur recoveries by inserting a hydrogenation reactor between the last Claus reactor and the selective oxidation reactor. This step converts any remaining SO_2 to H_2S and potentially raises sulfur recovery to about 99.5% for a rich H_2S acid gas feed. This version of the process is called "SuperClaus-99.5."

The principal problem with the selective oxidation processes is that an H_2S-rich acid gas stream is required together with an oxidant deficient furnace. Thus, as the acid gas stream gets leaner in H_2S, the sulfur recovery will drop appreciably and the lower combustion temperatures may lead to off-spec sulfur.

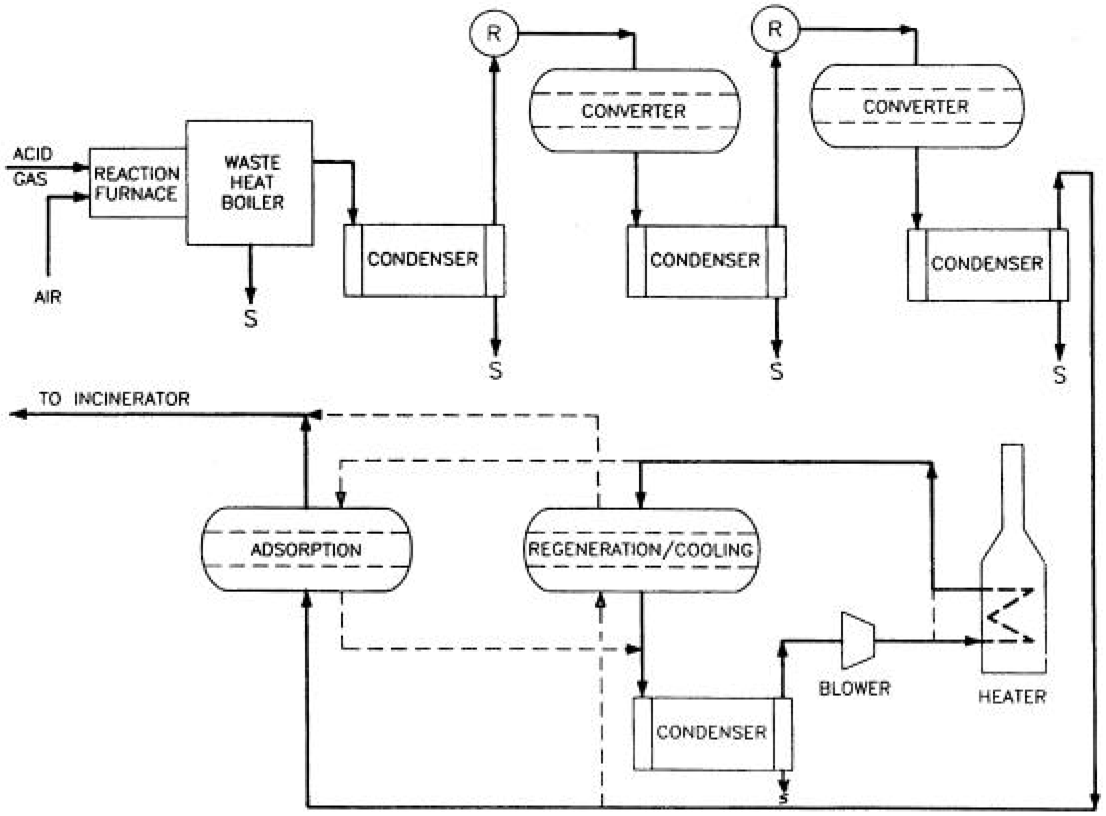
Extended Cold-Bed Claus Process

There are several processes that add a subdew reaction stage to a conventional Claus plant to increase its recovery. Among such processes are Sulfreen (offered by Lurgi and SNEA), CBA (offered by BP Amoco), and MCRC (offered by Delta Hudson). The Sulfreen process has the most installations and is the only one discussed here. The processes are similar, with the exception of how the regeneration gas stream is handled.

In the Sulfreen process, shown in Figure 7-6, the tail gas from the condenser of the last Claus reactor is sent directly, without reheat, to the subdew reactor. The last reactor operates below the sulfur dew point (270°F to 320°F) and adsorbs the sulfur on to the Claus catalyst. Sulfur recovery is enhanced by low temperature operation of the equilibrium limited Claus reaction. However, equilibrium is also limited by the presence of water. Typically, sulfur recoveries will vary from about 98.3% to 99.2%, depending on the number of adsorption stages and the H_2S content of the acid gas. There is a process variation that adds a hydrogenation reactor between the subdew adsorbers and the conventional last stage Claus reactor. This eliminates any excess COS and CS_2 that may be present, and could potentially raise sulfur recovery up to 99.8%, again depending on the richness of the acid gas and the number of reaction stages.

The beds are cycled between adsorption and regeneration. To remove the sulfur from the loaded beds, hot gas (500°F to 550°F) is passed over the bed. The hot regeneration gas then goes to a condenser for sulfur recovery.

Figure 7-6
The Sulfreen Process



Source: Reference 35

The principal differences between the processes lie in the way regeneration gas is handled. In the Sulfreen process, regeneration gas is self contained within the subdew portion of the process (recycled back from the condenser, through a heater, and back to the bed being regenerated). In the other two processes (CBA and MCRC), regeneration is integrated with the conventional Claus plant—the regeneration gas comes from the last stage Claus condenser.

About 50 commercial Sulfreen plants have been built. However, the cyclical nature of the plant operation and their sulfur recovery limitations may discourage their application in the future.

Other Sulfur Recovery Processes

Among the other important sulfur recovery processes are those based on catalytic oxidation and wet oxidation. Among the catalytic oxidation processes are the Selectox, BSR/Selectox, and the MODOP processes. The BSR/Selectox and the MODOP processes, are fed with the Claus tail gas and are usually considered tail gas processes. Wet oxidation processes include LO-CAT and

Sulferox. The three processes which will be briefly discussed below are Selectox, and the two wet oxidation processes (LO-CAT and Sulferox).

The Selectox Process

The Selectox process is based on replacing the Claus first stage thermal reactor (the furnace) with a catalytic oxidation step. A catalytic oxidation reactor can operate at much lower temperatures than the furnace and maintain a more stable flame temperature with lean H_2S feeds. The proprietary catalyst was developed by Unocal and Ralph M. Parsons Co. UOP now owns the rights to the Unocal technology.

Two versions of the process are offered by UOP. The first is a once through option, treating acid gases with up to 5% H_2S. In the once through mode, sulfur recoveries vary from 84 to 94% for H_2S concentrations in the feed gas of 2 to 5%, respectively. In the recycle version, that handles H_2S concentrations from 5 to 100%, gas is recycled from the Selectox reactor condenser to cool the reactor outlet temperature not to exceed 700°F. The temperature limit is set so that carbon steel can be used for the reactor vessel. A practical upper limit for H_2S concentration in the acid gas feed is about 50% for plants larger than about 50 lt/day. Higher concentrations lead to extremely large flows in the recycle loop [36].

Approximately 80% of the H_2S is converted to sulfur in the Selectox reactor. The reactions are of the typical Claus type—first H_2S is oxidized to SO_2 as the predominant reaction, then H_2S reacts with SO_2 to form elemental sulfur. The rest of the sulfur is recovered in conventional Claus stages. Up to 98% sulfur recovery efficiency can be achieved for a 50% H_2S acid gas feed to the recycle version of the Selectox process. Higher sulfur recoveries can only be had with tail gas treating, for which UOP offers the BSR/Selectox process. In this tail gas process, the gases are first hydrogenated to H_2S in the Beavon Stretford Reactor (BSR), then they proceed to another Selectox reactor stage. Sulfur recoveries up to 99.3% have been reported for BSR/Selectox.

About 16 Selectox plants have been built worldwide, ranging in size from about 0.5 to 30 lt/day of sulfur. It appears, from the installed plant inventory, that the process may not be economic for large sulfur plants, particularly for acid gases with a high H_2S content.

The process appears to be particularly applicable for acid gases with very lean H_2S feeds, but at relatively small scale. Reports have also surfaced that problems with catalyst deactivation, both Selectox and Claus, may be experienced when acid gases contain contaminants or gas flow upsets [37]. The absence of a Claus plant furnace allows some contaminants, such as various hydrocarbons, to react on the catalysts, causing hot spots. Thus, the process may not be as forgiving as conventional Claus.

Wet Oxidation (Redox) Processes—LO-CAT and SulFerox

The wet oxidation processes are based on reduction-oxidation (Redox) chemistry to oxidize the H_2S to elemental sulfur in an alkaline solution containing an oxygen carrier. Vanadium and iron are the two oxygen carriers that are used. The best example of a process using the vanadium carrier is Stretford. The most prominent examples of the processes using iron as a carrier are LO-CAT and SulFerox. LO-CAT was developed by ARI Technologies in the early 1970s and is now offered by U.S. Filter. The SulFerox process was developed by Shell Oil and Dow Chemical in the early 1980s. The Stretford process finds little use now because of the toxic nature of the vanadium solution. Thus, only the iron-based processes will be discussed below.

The optimum application for the wet oxidation processes is for low H_2S content acid gases and small plants, 1-20 lt/day of sulfur. Costs are too high for larger plants because of equipment size limitations and plant complexity. Even for small plants, the cost of sulfur recovery exceeds by far the selling price for recovered sulfur.

Both the LO-CAT and the SulFerox processes are essentially the same in principle. The description that follows is that for the LO-CAT process.

A chelating agent is used to carry the trivalent iron that oxidizes H_2S to elemental sulfur via the following simplified reaction:

$$H_2S + 2\ Fe^{+++} = S + 2\ Fe^{++} + 2H^+$$

The divalent iron is then regenerated back with oxygen via:

$$2\ Fe^{++} + 2\ H^+ + \frac{1}{2}\ O_2 = H_2O + 2\ Fe^{+++}$$

The overall reaction is:

$$H_2S + \frac{1}{2}\ O_2 = H_2O + S$$

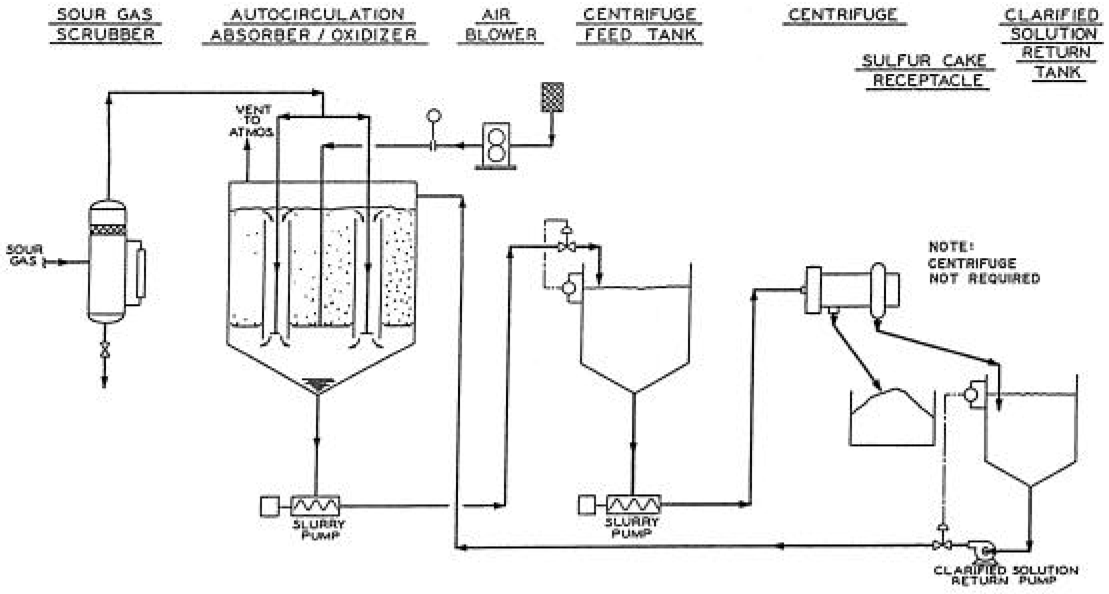
Figure 7-7 shows a simplified flow scheme for the LO-CAT process [38]. A single vessel is used for both H_2S absorption and oxidation, as well as for the reoxidation of the solvent. The solution from the reactor tank, which now contains about 10 wt% sulfur slurry, is filtered and the sulfur cake recovered. Recovered sulfur may be of poor quality, although purities as high as 99.9% are reported, and has no obvious market value. The sulfur cake is sometimes sent to landfills.

The SulFerox process differs from the LO-CAT in that the oxidation and the regeneration steps are carried out in separate vessels and sulfur is recovered from the filters, melted, and sent to sulfur storage. Also, the SulFerox process uses a higher concentration of iron chelates (about 2-4 wt% vs. 250-3,000 ppmw for the LO-CAT process). This higher solution loading allows for lower circulation rates and smaller equipment sizes. The quality of the SulFerox sulfur may also be poor—it's purity is usually >99.5% but does not meet Claus sulfur specs for color, being dark yellow.

Both processes are capable of up to 99+% sulfur recovery. However, using the processes for Claus tail gas treating requires hydrolysis of all SO_2 in the tail gas to H_2S because the SO_2 will react with the buffering base, KOH, and form K_2SO_4, which will consume the buffering solution and quickly saturate it [39].

There are about 100 LO-CAT and 20 SulFerox commercial operating plants worldwide. Recently, the two process suppliers merged their iron-chelate businesses in order to standardize the service and to jointly support reasearch and engineering in this type of process.

Figure 7-7
Simplified Flow Diagram of LO-CAT Autocirculation Process



Source: Reference 38

8. TAIL GAS TREATING

Tail gas treating involves the removal of the remaining sulfur compounds from gases remaining after sulfur recovery. Tail gas from a typical Claus process, whether a conventional Claus or one of the extended versions of the process, usually contains small but varying quantities of COS, CS_2, H_2S, SO_2, and elemental sulfur vapors. In addition, there may be H_2, CO, and CO_2 in the tail gas. In order to remove the rest of the sulfur compounds from the tail gas, all of the sulfur bearing species must first be converted to H_2S. Then, the resulting H_2S is absorbed into a solvent and the clean gas vented or recycled for further processing. This section discusses the currently most frequently used tail gas process—namely, catalytic hydrogenation/hydrolysis of the sulfur species to H_2S combined with the subsequent absorption of H_2S in a solvent.

Some of the extended Claus processes, already discussed in the Sulfur Recovery section of the report, are also offered as tail gas treating options. Usually such schemes involve placing a hydrolysis reactor between the last conventional Claus stage and the proprietary extended catalytic Claus stage of the given process. Such approaches have also been briefly mentioned in the Sulfur Recovery section. However, such processes have not been used up to now in commercial IGCC plants and are not discussed further.

Other sulfur recovery options, such as wet and catalytic oxidation, have also been used as tail gas treating options. These processes have already been discussed in the Sulfur Recovery section and will not be covered here because they would not be applicable to IGCC.

The clean gas resulting from the hydrolysis step can undergo further clean up in a dedicated absorption unit or be integrated with an upstream acid gas removal unit. The latter option is particularly suitable with physical absorption solvents, as has previously been discussed. The approach of treating the tail gas in a dedicated amine absorption unit and recycling the resulting acid gas to the Claus plant is the one used by the Shell Claus Off-gas Treating (SCOT) process, currently the most widely used tail gas treating option.

The hydrolysis process is also used separately from the tail gas treating process. This may be required when the acid gas removal process is incapable of removing sufficient quantity of the COS to meet the sulfur emissions regulations. In this case, the COS is hydrolyzed to H_2S before the acid gas removal step, as is done in several of the commercial IGCC plants.

The hydrogenation and hydrolysis steps, and the SCOT processes are discussed below.

Reduction of Sulfur Compounds via Hydrogenation and Hydrolysis

The reduction of COS, CS_2, SO_2, and sulfur vapor in Claus tail gas to H_2S is necessary when sulfur recovery of 99.9+% is required by regulations. Usually the sulfur recovery level is set by the allowable emissions of sulfur from the tail gas incinerator. In addition, the reduction of COS is done on raw synthesis gas when the downstream acid gas removal process is unable to remove

COS to a sufficient extent to meet sulfur emissions regulations from combustion of the cleaned fuel gas. These sulfur compounds are reduced to H_2S via hydrogenation or hydrolysis, at a raised temperature, over a catalytic bed.

Tail Gas Hydrogenation/Hydrolysis

The following description of the tail gas reduction/hydrolysis reactor is based on the one used in the SCOT process. Claus tail gas is reduced over a cobalt molybdate on alumina catalyst at a temperature of about 600°F (300°C). The reduction takes place mainly through the following reactions:

$$SO_2 + 3H_2 = 2H_2O + H_2S$$
$$S_8 + 8H_2 = 8H_2S$$
$$COS + H_2O = CO_2 + H_2S$$
$$CS_2 + 2H_2O = CO_2 + H_2S$$

When CO is also present in the tail gas then the following reactions could also take place:

$$SO_2 + 3CO = COS + 2CO_2$$
$$S_8 + 8CO = 8COS$$
$$H_2S + CO = COS + H_2$$
$$H_2O + CO = CO_2 + H_2$$

The last reaction (shift reaction) is very rapid, and the presence of CO does not seem to favor the first three reactions.

Elemental sulfur and SO_2 are reduced mainly via hydrogenation, while COS and CS_2 are mainly hydrolyzed to H_2S. Sulfur and SO_2 are virtually completely converted to H_2S when a stoichiometric excess of hydrogen is present (<10 ppmv SO_2). CS_2 is virtually completely hydrolyzed (to about 1 ppmv). COS conversion can reach over 98%, with the resulting tail gas containing about 10 ppmv COS [40].

The hydrogen can be supplied from an outside source, can already be in the Claus tail gas, or obtained by partial oxidation of the fuel gas in a furnace. The tail gas is preheated to the reactor temperature by an in-line burner that combusts fuel gas directly into the tail gas. The same burner can also be used to supply the needed hydrogen by partial combustion of the fuel gas. When oxygen enrichment is used in the Claus plant, there is often sufficient hydrogen in the tail gas to carry out the reduction without an outside hydrogen source. There is usually sufficient water vapor in the Claus tail gas for the hydrolysis reactions.

Raw Synthesis Gas Hydrolysis

A hydrolysis reactor is often used to convert the COS in the raw syngas to H_2S. The catalyst used in the reactor is of the activated alumina type. This catalyst does not activate the shift reaction, leaving the CO and other vapor constituents unconverted. The COS hydrolysis reaction over the catalyst is enhanced by low temperatures and high water concentrations. However, it is limited by the vapor dew point and must be carried out at a temperature high enough that water does not condense on the catalyst. Conversion of COS is highest at low temperatures, but will require a higher volume of catalyst. The operating temperature can be 300°F-500°F (150°C-260°C). At its normal operating temperature of about 475°F (245°C), COS conversion reaches chemical equilibrium, which usually corresponds to about 1-10 ppmv COS remaining in the converted gas [41].

The COS hydrolysis reactor is best placed right after the synthesis gas particulate scrubber, where the synthesis gas temperature is near that of the reactor operating temperature.

There is now ample commercial experience with this operation with synthesis gas and it should pose no design problems for engineering contractors or catalyst suppliers.

The SCOT Process

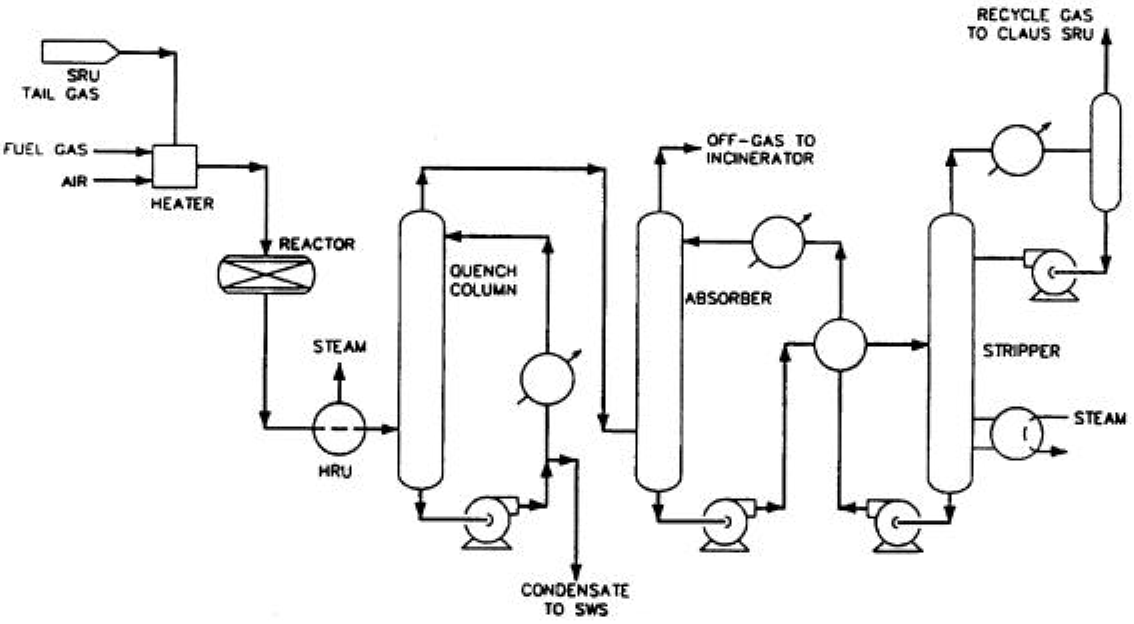
The SCOT (Shell Claus Off-gas Treating) process was developed by Shell in the early 1970s. Over 160 SCOT plants have been constructed worldwide since then. The process consists of a combination of a catalytic hydrogenation/hydrolysis step and an amine scrubbing unit. The hydrogenation/hydrolysis of the sulfur compounds in the tail gases from the Claus unit has already been covered above. This discussion will focus mainly on the options for amine scrubbing of the reduced gas from the hydrogenation/hydrolysis step.

The early SCOT units consisted of a hydrogenation/hydrolysis reactor and a conventional amine unit. Figure 8-1 shows a simplified schematic of a conventional early SCOT unit [42]. The Claus tail gas, after being reduced in the reactor, is cooled in a quench column and scrubbed by a Sulfinol solution. The clean tail gas goes to a Claus incinerator and the acid gas rich solution is regenerated in a stripping column. The treated tail gas can also be compressed and sent, with the clean fuel gas to the IGCC unit, avoiding the use of the incinerator as is done in the ISAB IGCC plant. The acid gas off the top of the stripper is recycled back to the Claus plant for further conversion of the H_2S. The treated tail gas in the early plants typically contained 300 ppmv of H_2S and about 10 ppmv of other sulfur compounds (COS + CS_2) [40].

The absorber is operated at near atmospheric pressure and the amine solvent is not highly loaded with acid gases. Because the solution is not highly loaded, unlike high pressure operation, there is no need for an intermediate flash vessel and the loaded solution goes directly to a stripper.

Early SCOT units used DIPA in the Sulfinol (Sulfinol-D) solution. MDEA-based Sulfinol (Sulfinol-M) was used later to enhance H_2S removal and to allow for selective rejection of CO_2 in the absorber. As environmental regulations tightened, the use of Sulfinol-M, together with a different plant configuration, allowed H_2S levels to be reduced to below 10 ppmv in the treated tail gas. Also, the solution circulation rate with Sulfinol-M was reduced because of lower CO_2 absorption.

Figure 8-1
The SCOT Process



Source: Reference 42

To achieve the lowest H_2S content in the treated gas, the Super-SCOT configuration was introduced. In this version, the loaded Sulfinol-M solution is regenerated in two stages. The partially stripped solvent goes to the middle of the absorber, while the fully stripped solvent goes to the top of the absorber. The solvent going to the top of the absorber is cooled below that used in the conventional SCOT process. Cooling water is required for top of the absorber solvent cooling, since air cooling would be insufficient. Super-SCOT can meet a 10 ppmv H_2S specification, but only with high stripping heat and solvent circulation penalties.

A later version of the SCOT process was introduced to address the high circulation and stripping duties of the Super-SCOT version. An MDEA-based Ucarsol 103 solvent is used in the L-S SCOT process version. An additive to this solvent improves stripping through equilibrium changes in the bottom of the stripper. Thus better stripping is achieved with the same steam rate, or less steam can be used for the same stripping requirements. This version can also achieve a 10 ppmv H_2S specification in the treated tail gas. Any unconverted COS is not absorbed in any of the SCOT process versions that use selective solvents. COS is partially removed if aqueous DIPA or Sulfinol-D are used as a solvents. Other solvents, such as Flexsorb, have also been used in SCOT units.

The SCOT process can be configured in various other ways. For example, it can be integrated with the upstream acid gas removal unit if the same solvent is used in both units. In this mode, a common stripper can be utilized. Another configuration has been used to cascade the upstream gas cleanup with the SCOT unit. An H_2S-lean acid gas from the upstream gas treating unit is sent to a SCOT process with two absorbers. In the first absorber, the H_2S lean acid gas is enriched, while the second absorber treats the Claus tail gas. A common stripper is used for both SCOT absorbers. In this latter configuration, different solvents could be used in both the upstream and the SCOT units. There are many other possible configurations for laying out the SCOT process.

Other licensors offer similar processes to SCOT, using their proprietary solvents and catalytic reduction reactors. However, the SCOT process remains by far the most widely used commercially.

9. HOT AND WARM GAS CLEANUP

The development of hot gas cleanup (HGCU) systems for acid gas and particulates removal from syngas has been pursued in the U.S., Europe, and Japan since the 1970s. Until about the mid-1990s, this work was primarily focused on syngas from air-blown gasification of coal. Air-blown gasification systems produce over twice the volume of syngas (due to the nitrogen dilution) that O_2-blown systems produce, and therefore incur more severe thermal, process efficiency, and capital cost penalties related to syngas cooling to comparable temperature levels. Conventional cold gas cleanup (CGCU) with air-blown systems is uneconomical. Hence, the success of air-blown gasification combined cycle power plants depends on the success of HGCU developments. However, HGCU is also applicable to syngas from O_2-blown gasification, so that O_2 gasification also would benefit from the successful development of competitive HGCU systems [43].

Drivers for HGCU

The drivers for HGCU in IGCC have been:

- The higher process efficiency achievable without syngas cooling and removal of water from the syngas.
- The elimination of sour water treating. (Sour water is produced when the syngas is cooled below the dew point of water.)
- The elimination of the “black mud” (troublesome ash-char-water mixture) produced in water-quenching or wet scrubbing of particulates from the syngas.
- Potential capital and operating cost savings related to the foregoing items.

Until the late 1990s, the focus of most HGCU programs was the removal of the sulfur, chloride, alkali, and particulates from syngas at temperatures close to the highest inlet temperature at which gas turbine (GT) fuel control and delivery systems could be designed. This level was set at about 1,000ºF by the requirement for very low alkali (potassium and sodium) content of the fuel gas to prevent alkali corrosion of hot GT components and the desire to avoid expensive materials and unreliable refractory-lined piping [44,45]. Below 1,000ºF the alkali vapor components are essentially completely condensed on particulates in the hot syngas, which are then filtered from the syngas by barrier filters [45]. However, this temperature requirement means that significant syngas cooling is still necessary, since commercial gasifiers produce raw syngas at 1,700-3,000ºF, depending on the gasifier design and the feedstock [46].

The removal of particulates from the hot gas by dry filtration avoids wet (water) scrubbing and the production of black mud—the unburned carbon-ash-water mixture produced when the raw syngas is quenched or wet scrubbed to remove the entrained particulates. Particulates recovered dry can be easily recycled to gasification to improve fuel utilization and process efficiency. Black mud is difficult to process and is not amenable to recovery of unburned carbon. It is therefore also a waste disposal problem.

Waning Interest in HGCU

Various HGCU systems have been tested at the pilot plant level and a small number have been installed in commercial-scale IGCC demonstration plants in the U.S. and Europe. However, both industry interest (which has always been limited) and government interest in HGCU have declined for several important reasons [45,47,48]; namely:

- Process and equipment development challenges in HGCU; e.g., excessive attrition of the solid desulfurization sorbents; chloride stress corrosion issues; and the high cost and unproven status of GT fuel control valves for syngas fuel at temperatures above about 800ºF.
- Hot gas desulfurization has not been demonstrated. The hot desulfurization processes installed as parts of the Tampa Electric and Piñon Pine IGCC demonstrations were never operated. The Piñon Pine gasifier itself did not achieve operability.
- The trend toward increasingly stringent air emissions standards, including mercury removal from fossil power plant stack gas and the potential for mandated CO_2 mitigation. Specifically, HGCU at this stage of its development does not remove ammonia or HCN, COS, mercury, CO_2, nor all of the H_2S from syngas. Ammonia and HCN are converted to NO_x and COS is converted to SO_2 in the GT. Very low levels of SO_2 are necessary to prevent ammonium bisulfate fouling of the low-temperature HRSG surfaces in IGCC cases in which SCR is required. Present indications are that efficient mercury removal will require syngas cooling to the temperature levels of CGCU.
- The success of the demonstration and commercial O_2-blown coal, petroleum coke, and petroleum residual oil gasification projects for IGCC and chemical synthesis gas production with conventional CGCU—in the U.S. and Europe. The number of commercial IGCC projects with CGCU has been proliferating worldwide [49].

At the same time, hot particulates control devices (candle filters) have been successfully demonstrated at least three of the IGCC and gasification demonstration projects (Berrenrath, Buggenum, Puertollano, and the switch at Wabash to metallic candles). These barrier filters represent the only currently commercially applicable HGCU technology. One conclusion of the U.S. Department of Energy's (DOE's) recent extensive gasification industry interviews is that removal of particulates is the only hot gas cleaning technology that is viewed to have a future [48]. Nevertheless, further performance and cost improvements in the technology are desirable. Breakage (fragility) is the most serious issue with ceramic filters.

The DOE gasification industry interviews also found that currently there is not much incentive for gas cleanup operations above 700ºF. Prior engineering analyses have persuaded the industry that the efficiency improvements from operating above 800ºF are not worth the additional capital costs due to materials and the increased equipment sizes resulting from the larger volumetric flows. The industry interviews also found concerns about the effectiveness of dry sorbent-based technologies and the efficiency of regeneration at lower temperatures. Nevertheless, the interviews indicated some interest in the possibility of dry cleanup processes that could operate at temperatures closer to downstream requirements; e.g., in the 300-700ºF range [48].

DOE has recognized many of the issues and limitations surrounding hot gas cleaning technologies and their applications. Consequently, DOE's Gasification Technologies program has transitioned its gas cleaning component away from the development of high-temperature approaches to more moderate temperatures consistent with downstream applications [48].

The commercial status of HGCU in IGCC is briefly reviewed here—focusing on the pertinent U.S. and European experience. Three long-running DOE R&D programs are also briefly mentioned. Overall, HGCU R&D in the U.S., Europe, and Asia appears to be continuing mainly at universities and both private and government research organizations, with government support.

Further Temperature Considerations

Mercury Removal

The prospect of stringent mercury emissions standards for coal-conversion plants seriously dampens the outlook for hot or warm gas cleanup. It is believed that mercury removal becomes more difficult as the syngas temperature increases. If it is necessary to cool the syngas for mercury removal, then the rationale for hot or warm gas desulfurization is gone unless related economic benefits can be demonstrated [45,47,48].

"Hot Gas" or "Warm Gas" Cleanup?

The term "hot gas" cleanup is actually a misnomer, because of the required syngas cooling to 1,000ºF for the removal of alkalis condensed on the particulate matter. Most of the cleanup systems that have been under development have maximum operating temperatures of about 900-1,100ºF [43]. So substantial syngas cooling is still required before gas cleanup—and "hot gas" cleanup is really "warm gas" cleanup. Even with partial cooling the syngas cooler is a significant capital cost item in IGCC.

GT Fuel Control Valves

Even further cooling to temperatures below about 700-800ºF is desireable, because of the expensive alloys and equipment sizes required for the GT combustor fuel control valves at higher syngas temperatures. GE prefers GT fuel temperatures under 300-400°F. Above 400ºF, the teflon sealing system in the flow control valves may melt, and metal seals are required, which are leakage prone. Valve size also must increase as temperature is increased. Above about 600ºF and up to 750ºF other materials must be used. Above 750ºF, higher-grade stainless steels and nickel-based super alloys must be used—culminating with Inconel at about 1,000ºF. GE is not certain that valves are available which would be suitable for elevated temperature syngas fueling of the large GTs (>125 MW) considered for large IGCC power plants [50]. The only GT fuel control valve designed and installed for 1,000ºF service is on the 70 MW GE Frame 7FA GT at the Piñon Pine IGCC. However, it appears that this fuel system will never be tested at the design conditions, since that IGCC demonstration has been terminated. Nevertheless, the GE Frame 6FA GT combined cycle portion of the plant is running well on natural gas [51].

Syngas Conversion to Synthetic Fuels

Catalytic synthesis gas conversion processes (e.g., methanol synthesis and Fischer-Tropsch synthesis) typically operate in the 400-650ºF temperature range and require contaminant-free syngas (no sulfur, trace metallic, or nitrogen constituents, except N_2). Some participants in DOE's gasification industry interviews indicated an interest in the potential for development of gas cleanup processes that operate at temperatures closer to the downstream requirements of synthesis processes than at the lower temperatures of conventional CGCU [47,48].

Particulates Removal Experience

Candle filters have been the focus of most efforts for final fine particulates removal with large syngas flows. These devices are porous ceramic or metal tubes mounted in bundles in tube sheets contained in a filter vessel. The syngas flows from the outside through the porous tube walls and flows out of the vessel through the insides of the tubes. Back pulsing the filtered gas dislodges the particulates from the outside walls and they are discharged from the bottom of the vessel. The issues with candle filters are the large number of candles required, first costs, difficult and labor-intensive field installation, blinding of pores by fine particulates, ash bridging between candles, flyash sticking to the candles, the requirement for off-line cleaning in some cases, breakage (fragility) of the ceramic candles, and candle life. Candle breakage without downstream wet scrubbing or other safeguards could result in catastrophic GT damage from the particulates.

Ceramic candle filters are or have been employed successfully in the gasification demonstrations in Europe. Most of the European demonstration plants have cyclones upstream, which remove most of the particulates before the syngas enters the filter vessels, thus greatly reducing the dust loadings on the candles. If breakage occurs, downstream water scrubbers remove the particulates and protect the plants' CGCU systems. All of those gasifiers are O_2-blown.

The 600 mt/d HTW lignite coal gasification demonstration plant (syngas to methanol) at Berrenrath, Germany concluded several years of successful operations late in 1997. The project reported 15,500 hours of apparently satisfactory operation with the filters up to the end of the demonstration program. The plant employed 450 candles supplied by Schumacher in an improved filter configuration jointly developed by Rheinbraun AG and Lurgi Lentjes Babcock (LLB) [52].

For the 250 MW coal-fired IGCC demonstration at Buggenum, The Netherlands (Shell Gasification Process), the last reported expected candle lifetime for the Buggenum plant's filters was 16,000 operating hours [53].

The 320 MW ELCOGAS coal- and coke-fired IGCC demonstration at Puertollano, Spain (Prenflo Gasification Process) employs similar filters (more than 2,000 candles), and appears to have resolved earlier candle failure problems. This plant does not have a cyclone ahead of the candle filters [54,55].

In the U.S., the 260 MW coal- and coke-fired IGCC demonstration at PSI Energy's Wabash River plant in Indiana (Global EGas Gasification Process) switched from ceramic to sintered metal candle filters in 1997, after two years of very costly experience with breakage of the fragile filters. During the first year of the plant's operation, 40% of its downtime was due to filter breakage, caused by bridging of the char between candles. The metallic high alloy filters also can be welded into the tube sheets, eliminating the difficulties of obtaining leakage-free seals at the tube sheets with the ceramic filters. The new filters have performed satisfactorily—running at 400 psi and 700-800ºF—although the pores gradually get plugged by the very fine char. The candles have to be removed every six months for cleaning, since on-line cleaning is not possible. Eventually the candles become irreversibly plugged and must be replaced.

Global is still testing ceramic candles in a syngas slipstream—and they are still breaking. The Wabash River plant does not have a cyclone ahead of the filter, so its syngas solids loading at the filter is about 10 times that of the syngas into the ceramic candle filters at the Buggenum plant. Global is proposing to install a cyclone in the slipstream for the ongoing candles testing, which is sponsored by DOE. Global also indicated that its next commercial plant would include a cyclone ahead of the filters. The company also recently re-evaluated the metallic candle filters versus wet scrubbing and concluded that they are better off to stay with dry particulates removal to avoid the black mud and water issues of wet scrubbing [56]. The Wabash River IGCC is a U.S. DOE Clean Coal Technology (CCT) Program demonstration project.

The 100 MW coal-fired Piñon Pine IGCC plant at Sierra Pacific's Tracy Station near Reno, Nevada (Kellogg Brown & Root (KBR) air-blown gasification with HGCU) also experienced ceramic candle breakage over the course of its many aborted start-up attempts. The filter system, provided by Westinghouse, appears to be similar to that used at the Berrenrath demonstration plant.

With HGCU systems the hot gas filter system must follow the desulfurization system. Excessive sorbent attrition can place an excessive load on the filters, causing breakage or plugging of the solids withdrawal line.

Hot Desulfurization Demonstrations

The only two large-scale "hot gas" desulfurization systems installed in the U.S.—both in DOE CCT IGCC demonstration projects—have never been demonstrated. Consequently, their ultimate commercial feasibility may never be known. Both systems were similarly based on the reaction of H_2S with zinc oxide-nickel oxide solid sorbents in an adsorption column—followed by regeneration of the sorbent by contact with air in a separate column. The regenerator off-gas contains SO_2, which must be converted to elemental sulfur or sulfuric acid in a final recovery operation. There are no large-scale hot or warm desulfurization demonstrations elsewhere.

As discussed earlier, the demise of the drivers for the development of these particular technologies probably now means that they are not worth pursuing as originally conceived for the demonstrations. The systems are briefly described further below.

The 260 MW coal-fired IGCC at Tampa Electric Company's (TECO's) Polk County Station in Florida (Texaco gasification process with a radiant syngas cooler, convective coolers, and water scrubbing) is equipped with both a 100% capacity CGCU system and a 10% capacity HGCU system—to be fed by a syngas slipstream. The plant is operating well with the CGCU system. The HGCU was based on a down-flow moving-bed H_2S adsorption process developed by GE. The design placed the absorber column on top of the down-flow regenerator column—in one tall column. The regenerated sorbent is transported back to the top of the column. The SO_2 was to be converted to sulfuric acid for sale. Some observers have noted that the physical size of the 10% capacity HGCU appears to be much larger than that of the 100% capacity CGCU section of the plant.

The HGCU demonstration was cancelled for the following reasons: (1) The fouling factors in the waste heat boiler (radiant syngas cooler) were not as severe as predicted. Consequently, heat recovery was more efficient and the syngas was cooled to about 700ºF—a much lower temperature than expected. A temperature of at least 900ºF is needed for the HGCU. (2) Cold flow attrition tests on the sorbent showed that sorbent attrition would be very high—leading to extremely high annual sorbent costs. (3) There were also concerns about the potential for chloride stress corrosion cracking with the materials used in the HGCU [57].

The Piñon Pine IGCC system in Nevada is designed with a KBR air-blown, fluidized-bed gasifier (operating at 1,800ºF) with limestone injection for partial in-situ H_2S capture (as CaS)—followed by final H_2S scrubbing from the syngas in an entrained-flow absorber. Unfortunately, numerous problems with solids transport (esp. flyash) in the gasifier system have prevented successful start up [51], and it appears that this DOE CCT Program demonstration project has been terminated.

The Piñon Pine flow scheme employs entrained-flow H_2S adsorption and regeneration columns—called transport reactors by KBR. The coal ash-char-CaO-CaS solids from the gasifier, the SO_2 from the regenerator, and additional limestone, are fed to a "sulfator"—a bubbling fluidized bed combustor in which most of the sulfur is converted to $CaSO_4$. Thus SO_2 emissions from this plant would come from both the GT exhaust gas and the sulfator. As in the TECO case, pre-startup testing indicated excessive sorbent attrition. As of the last start-up attempts (2000), a sulfur sorbent with satisfactory mechanical durability had not been identified [45].

It is instructive for future scale-up considerations to note that this 880 t/d gasifier design was a high-risk 40-fold scale-up from the successful 20-24 t/d pilot plant program in which the KBR gasifier was developed. Also, although the desulfurization transport reactor is patterned after proven catalytic reactors used in petroleum refining, the desulfurization system (including a qualified sorbent) itself was not previously demonstrated at an intermediate scale.

At the Berrenrath High-Temperature Winkler (HTW) gasification demonstration plant, Rheinbraun reportedly tested a technique called direct desulfurization or direct sulfur recovery. Apparently the addition (or presence) of a metal oxide catalyst into the gasifier or the syngas stream is required in this process, and an oxygen-containing gas is added to the syngas after the syngas cooler but before the candle filters at a temperature of about 400-520ºF. Rheinbraun claims that its tests at Berrenrath show that the H_2S is completely converted into elemental sulphur, while the COS is partly converted. The sulfur (solid particulates) and the dust are separated from the syngas by the filter. Ammonia is not removed in this process. This process has been proposed for testing with a slipstream at the planned 400 MW HTW IGCC plant at Vresova in the Czech Republic. DOE and DOE-sponsored researchers have also been investigating variations on this process [52,54].

HCl Removal

Nahcolite (naturally occurring sodium bicarbonate), Trona (naturally occurring sodium sesquicarbonate), synthetic sodium carbonate/bicarbonate mixtures, $Ca(OH)_2$, and other sorbents are effective for dry removal of HCl and HF from syngas. Sorbent requirements and performance depends on the gas conditions and the contaminant concentrations. Injection before the filter is necessary.

CO_2 Mitigation

There is no hot or warm gas cleanup process for CO_2 removal. However, it has been suggested that syngas shifted to H_2 and CO_2 could be separated with a hot gas membrane system into a pure H_2 stream and a CO_2 stream, which would contain all of the other gas contaminants, such as H_2S, COS, NH_3, etc. However, the H_2 would be produced at near-atmospheric pressure, requiring compression for use in IGCC or refinery processes [45,47,48]. The further processing of CO_2 that would be required would depend on the sequestering options available. Most likely, any hot gas membrane would require the prior removal of all particulate material and other trace components that may be corrosive or plug the membranes pores [45].

Continuing DOE and EPRI Warm Gas Cleanup Programs

Three long-running DOE-supported R&D programs on warm gas cleanup continue—at Siemens Westinghouse Power Corporation (SWPC), Research Triangle Institute (RTI), and the Power Systems Development Facility (PSDF)—operated by Southern Company Services at Wilsonville, Alabama. EPRI is also providing support for the PSDF program, along with the Southern Company.

SWPC's activities include: the assessment of barrier filter materials and filter performance, the development of a candle filter failure safeguard device (SGD), and R&D on a conceptual 4-stage process that the investigators are calling the "Ultra-Clean Process." While this process is targeting removal of H_2S, HCl, and particulates to sub-ppm levels, it does not remove NH_3, HCN, or mercury [58]. A 10 t/d fluidized bed gasification pilot plant is being constructed at the Gas Technology Institute (GTI) for testing the "Ultra-Clean Process." The filter R&D programs have concluded this year, while the "Ultra-Clean Process" R&D contract will run at least until mid-2004.

RTI is investigating a conceptual multi-step process that includes $H_2S/CO_2/H_2O$ removal by a solubility-selective polymer membrane, recovery of elemental sulfur by RTI's Direct Sulfur Recovery Process (DSRP), and removal of ammonia by zeolite molecular sieves. While the work is targeting very low emissions levels, rapidly decreasing membrane selectivity as temperature increases above 25ºC (77ºF) is a challenge. The other participants in this program are DuPont, Air Liquide, North Carolina State University, Prototech Company, SRI International, and Nexant [55].

The PSDF facilities include a 1.6 t/hr KBR transport reactor, SWPC particulates control devices, (PCDs – with candle filters), and a low-NO_x topping combustor with an Allison 501-KM gas turbine generator set (4 MW nominal). The transport reactor can be operated in the combustion mode or gasification mode. One of the PSDF's earlier anticipated uses was to have provided R&D support to the now defunct Piñon Pine IGCC demonstration. From DOE's perspective, the primary focus of the PSDF now is to demonstrate and evaluate the transport reactor and high-temperature, high-pressure PCDs for advanced power generation systems, such as GT combined cycles and fuel cells [55]. The transport reactor is also part of the research portfolio for DOE's *Vision 21* program, which includes evaluating the KBR reactor as a potential commercial gasifier and possibly using the facility for HGCU R&D [59]. Overall, the ambitious DOE/EPRI/Southern Company program for the PSDF through 2004 includes tests of both air- and O_2-blown KBR reactor gasification, hot gas filtration, ash removal, hot gas desulfurization, sulfur recovery, and trace element and mercury removal from syngas [60].

As a circulating entrained-flow reactor, the transport reactor offers the fuel flexibility characteristic of circulating fluidized-bed (CFB) systems. In addition, since it operates at higher solids circulation rates than conventional CFB reactors, it offers potential performance improvements relative to CFB reactors [55]—but not necessarily relative to the already commercially proven O_2-blown entrained-flow gasification processes.

Outlook

Continued improvements in hot particle filtration, which is commercially available technology, can be expected. Upstream cyclones are important components of a hot particle removal system—to minimize the load on the hot filters. Overall, hot gas filtration offers definite advantages to IGCC over water scrubbing.

The development of hot gas cleanup systems for deep cleaning of sulfur and nitrogen components from syngas appear to be long-term prospects. Large-scale demonstrations probably would not be achievable or practical before about 2010. Justification for such demonstrations could become difficult if commercial IGCC projects with CGCU continue to proliferate and operate well over the next several years.

The prospects of developing hot or warm gas cleanup processes for mercury and CO_2 removal presently are very challenging. Either, or both, the requirement for mercury recovery and/or CO_2 recovery from coal-fired power plants could become the Achilles' heel of dry gas cleanup—dictating the use of O_2-blown IGCC with CGCU.

10. ACID GAS INJECTION

Acid gas injection (AGI) is an alternative to sulfur recovery that is practiced widely in the natural gas and the petroleum industries. Essentially, it consists of compressing and injecting the acid gases from the gas processing units into depleted reservoirs or saline aquifers. It has previously been done on small acid gas streams that were too small for economic sulfur recovery. However, as the emission regulations have grown ever more stringent, it has become an economic alternative to the rising cost of sulfur recovery and tail gas treating. It is one way to eliminate all sulfur emissions, and in some cases, even to dispose of unwanted wastewater streams. Also, low sulfur prices make sulfur recovery less economic, and some operators have considered abandoning Claus sulfur recovery for AGI.

There were 22 AGI projects in Western Canada reported in 1999. Canada's first acid gas injection project was started in 1989. In terms of the amount of sulfur being injected, the Canadian projects vary from 1 to 465 t/d. There are also many operating projects in the United States. The biggest project under development in the United States is that of ExxonMobil at Labarge, Wyoming. In this project, about 63 MMscf/d of acid gas (65% H_2S and 35% CO_2) will be injected by 2003. The amount of sulfur that will be injected in this project is about 1,755 st/d.

These AGI projects, although intended primarily for sulfur disposal, are also CO_2 sequestration projects by default. The ExxonMobil project will also sequester about 1,300 st/d of CO_2, equivalent to approximately 24% of the CO_2 emitted from a 250 MW coal-fired IGCC facility.

There are three basic steps to AGI; compression, pipeline, and the injection well. There is some controversy as to whether the acid gas has to be dehydrated also. Some feel that dehydration reduces the potential for corrosion, due to water phase dropout at elevated pressures, and many projects have dehydration as a component.

The acid gas from the solvent regenerator of a gas treating plant is compressed from essentially atmospheric pressure to the wellhead injection pressure (700-2,000 psi) in several stages, usually four. Water will condense out in interstage coolers of the first three stages. The final stage outlet should have no condensed water present. Some projects have incorporated a glycol dehydrator either after the second or the third compression stage to make certain that no water will drop out after the final compression stage. All of the equipment up to the first stage compressor cylinder can be carbon steel. Interstage coolers and associated piping and scrubbers have to be of stainless steel. If a dehydrator is used, then all equipment downstream of the dehydrator can also be of carbon steel [61]. One engineering company (Gas Liquids Engineering, Ltd.) does not use dehydrators in its AGI designs, and has had no problems with water condensation in any of its projects [62].

For economic reasons, the pipeline from the gas processing facility to the wellhead is kept as short as possible, particularly if no dehydration is used because stainless steel is often specified in this case. If a glycol dehydrator is used, then some H_2S will be emitted from the glycol dehydrator vent. This H_2S stream will need to be incinerated before venting.

Marathon Oil has patented a process to inject acid gases together with wastewaters into a disposal wells. The acid gas comes as a liquid from the last stage compressor cooler, and is then carried with added wastewater through the wellhead choke with minimum flashing. Such a system does not use dehydrators. This system was first used at the Marathon plant in New Mexico in 1996 [63]. Consideration has to be given to materials of construction where water is likely to condense. Part of the pipeline and the wellhead, which handle corrosive wastewater, will need to be of stainless steel.

AGI offers an attractive alternative to sulfur recovery if suitable injection strata are available. The costs of drilling the well and building the compression facility can in some cases be less than other sulfur abatement options.

11. CO_2 REMOVAL FOR SEQUESTRATION

IGCC is exceptionally suitable for near total removal of CO_2 for subsequent sequestration, should that become necessary. Synthesis gas is CO shifted and the resulting CO_2 is removed by one of the acid gas removal (AGR) processes from the shifted hydrogen-rich fuel gas. CO_2 is then flashed and stripped out of the loaded solvent and is available for compression for subsequent sequestration. There are several process configurations for IGCC that could be used to remove nearly all of the CO_2. The process configurations depend on the placement of the CO shift step and the choice of the acid gas removal process. Figure 11-1 shows the processing options for handling acid gases in an IGCC plant. Essentially, the choice is whether the acid gases are removed from synthesis gas both before and after CO shift, or whether all of are removed after the shift step.

If CO_2 is to be sequestered, and well injection of H_2S together with CO_2 is allowed, as is commercially practiced (see the Acid Gas Injection section), then selective removal of H_2S is not necessary, since there is no need for sulfur recovery. This configuration is shown as Option 1 in Figure 11-1. If H_2S cannot be injected into the well with CO_2, then selective removal of H_2S will be necessary for the downstream sulfur plant. In either case, a physical solvent AGR process is the appropriate choice when sour gas CO shift is done.

Placement of the CO shift reactor ahead of the AGR has two advantages: (1) the gas isn't cooled after particulate removal and (2) the acid gas is removed in one step. This option may be particularly suitable for quench type gasifiers which have higher temperature, water-saturated raw synthesis gas after particulate removal. The shifted gas is then cooled and the acid gas scrubbed out. If sulfur recovery is necessary, then selective H_2S removal is necessary. CO_2 is then removed sequentially. An acid gas enrichment step may be necessary to increase the H_2S concentration to the sulfur recovery unit. Such configuration is shown as Option 2 in Figure 11-1. Because the CO_2 partial pressure is high, a physical solvent AGR process may be appropriate here. A physical solvent AGR process is even more appropriate for those gasifiers that produce more CO_2. A sulfur tolerant CO shift catalyst has to be used in this case.

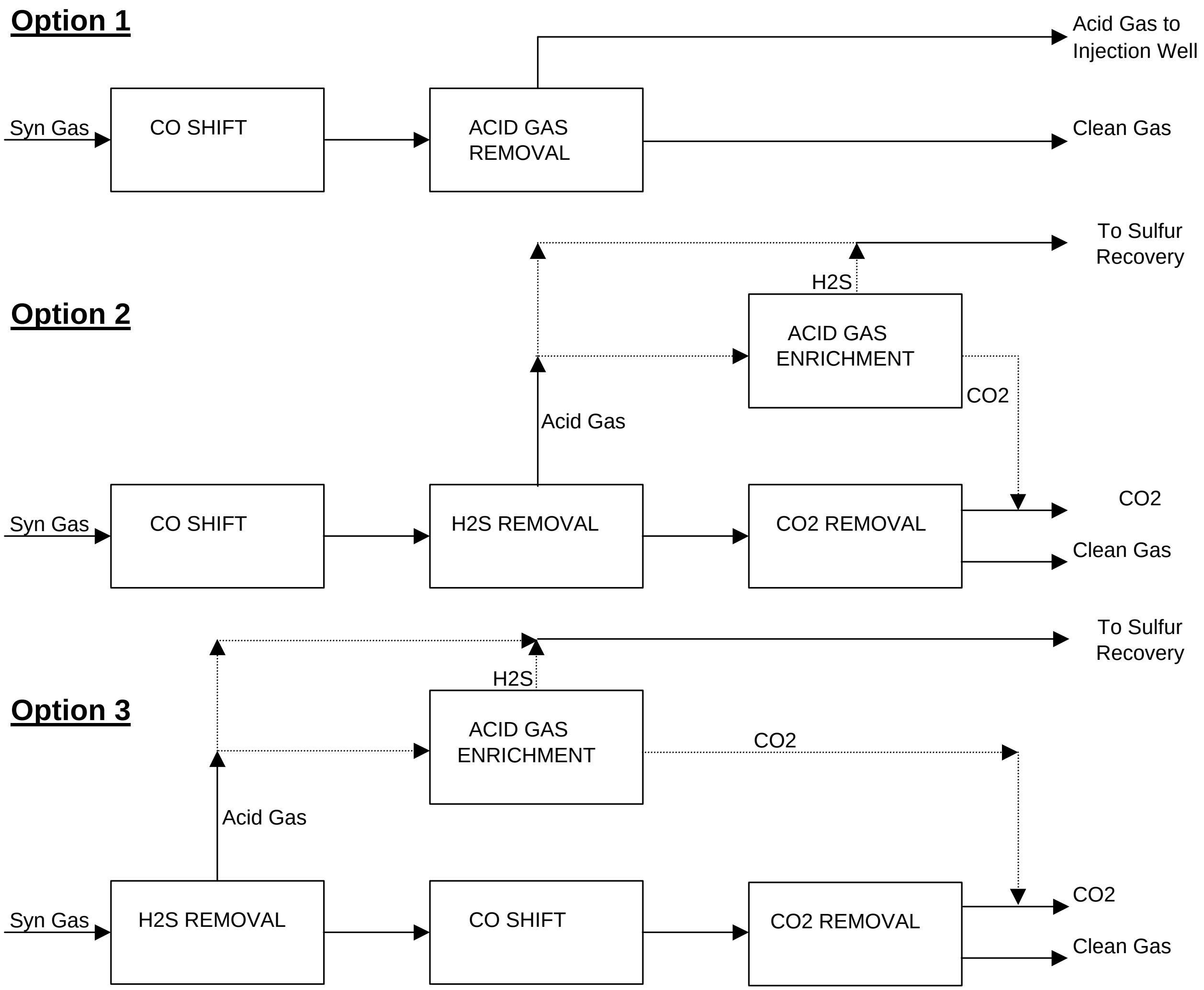
When selective removal of H_2S is required and the synthesis gas is cooler and contains less CO_2, then the CO shift reactor could be placed after H_2S is removed in the AGR unit. Gasifiers that are dry fed usually contain less CO_2 and, if a waste heat boiler is used with the gasifier, then the synthesis gas temperature may be lower than that of the quench-only gasifier. In this case, CO is shifted after H_2S removal, and the resulting CO_2 is removed in another absorber. Such a layout is shown as Option 3 in Figure 11-1, and is similar to that shown in Figure 6-6 (Acid Gas Removal section). Both amine and physical solvent processes could be considered in this case.

It is possible to use two separate AGR processes for H_2S and CO_2 removal to take advantage of the best characteristic of each. However, one process is simpler and is the preferred option. H_2S and CO_2 removal, although separate steps, are usually integrated in such a way that solvent absorption and regeneration are combined to use one column for each operation. Usually absorption takes place in two stages in the same column, with separate side feeds of partially and fully regenerated solvent. Solvent regeneration takes place via flashing and several stages of stripping in the regenerator column. Such integration is shown in Figures 6-5 and 6-6, which show the Lurgi Rectisol process schemes, can also be used for the amine processes.

CO_2 recovery is enhanced slightly when the acid gas enrichment step is included. However, this is costly and is only justified for improved operation of the sulfur recovery plant. CO shifting and CO_2 removal add substantial costs to IGCC and decrease plant efficiency.

Figure 11-1

CO_2 Separation Options for IGCC



Source: SFA Pacific, Inc.

12. CONCLUSIONS AND RECOMMENDATIONS

Conventional Cold Gas Cleanup

The currently available technologies for acid gas removal, sulfur recovery, and mercury and metal carbonyl removal are capable of meeting anticipated future more stringent regulations, but at a substantial economic penalty. The following are some of the conclusions and recommendations reached in this study.

- The gas treating processes available in 1987 are still the mainstays of industry today.
- Carbon beds are necessary for the removal of mercury and metal carbonyls. The technology is commercial, and can remove the compounds to below detectable limits. However, the regeneration of spent carbon with mercury on it is currently uneconomical—it is usually disposed of at a suitable storage site. Mercury laden carbon regeneration should be investigated further.
- Currently the main processes of choice in commercial IGCC facilities for the removal of acid gases are both the chemical solvent acid gas removal (AGR) processes based on methyldiethanolamine (MDEA) and the physical solvent-based Selexol process—which employs mixtures of dimethyl ethers of polyethelene glycol.
- Commercial MDEA formulations (with proprietary additives) have been developed, which offer enhanced selectivity for H_2S, and their use is widespread in the gas treating industry.
- BASF Corporation has shown some success in tests of its newly formulated MDEA solvent, which removes much of the COS while retaining a high degree of H_2S selectivity. However, the performance to date is not adequate for the elimination of the COS hydrolysis step. In fact, SFA Pacific believes that, if SCR is required, COS hydrolysis will be necessary for any acid gas removal system, except possibly the Rectisol physical solvent process (based on refrigerated methanol).
- COS hydrolysis is required for amine-based AGR processes and recommended for physical solvent-based AGR processes, if stringent emissions regulations are to be met. With COS hydrolysis and sufficient solvent circulation, any of the AGR processes considered in this report can meet a 20 ppmv level of total sulfur in the clean synthesis gas. This level of sulfur should be adequate to prevent deposits of ammonium sulfate salts in the HRSG of the IGCC if SCR should be required for post-combustion NO_x control with syngas-fired gas turbines.
- While physical solvent AGR processes are capable of meeting the stringent sulfur cleanup required for SCR, the processes themselves are more expensive than MDEA-based AGR processes. The H_2S dissolution and reaction rates are faster in aqueous amine systems—enabling shorter contact times and smaller absorber column designs; i.e., a smaller number of trays or stages, and shorter and possibly smaller diameter columns. The heat transfer coefficients of aqueous amine solutions are higher than those of organic

physical solvents—so that less heat exchanger (coolers, reboilers) surface area is required with amine solutions. However, amine-based AGR systems tend to have higher stripper steam requirements than physical solvent AGR systems. The electric power requirements for pumping (solvent recirculation) and refrigeration (if used – with physical solvents) and the heat requirements for solvent regeneration and are the major factors affecting the operating costs for AGR.

- Although the Selexol Process by itself is more expensive than an MDEA AGR process, the total AGR, sulfur recovery (SR) process, and tail gas treating (TGT) process package—based on Selexol in some cases could be more cost effective than the package based on MDEA—especially if the syngas pressure is high and deep sulfur removal is required (e.g., down to 10-20 ppmv). Deeper desulfurization can be accomplished by chilling the Selexol process. However, CO_2 co-absorption then also increases.
- The Rectisol Process—based on low-temperature (refrigerated) methanol—is capable of deep total sulfur removal, but its complexity and refrigeration make it the most expensive AGR Process. Therefore, its use is generally reserved for chemical synthesis gas applications in which very pure syngas (as low as <0.1 ppmv total sulfur) is required. The Rectisol process is the predominant commercial AGR process in these applications.
- Acid gas enrichment is desirable for high sulfur recovery in Claus plants. This can be accomplished in physical solvent AGR units internally by arranging various solvent flashes sequentially in such a way that partially and fully stripped solvent streams can be used to stage acid gas absorption. In amine-type processes, H_2S is enriched by separate low pressure, selective absorption of the acid gas from the primary solvent stripper. For mixed solvents, such as Sulfinol-M, a combination of the above methods can be used. The handling of flashed off gases could present some problems, since they will often contain sulfur compounds. They can ultimately be recycled for almost complete sulfur removal, but at additional complexity and cost.
- Some form of Claus tail gas treating (TGT) is required to reach 99.8+% sulfur recovery levels. This can be a combination of extended-bed Claus operation, followed by a hydrolysis step, or a conventional sequence of Claus and TGT. The simplest approach is acid gas enrichment for feed to the Claus plant, followed by TGT.
- TGT clean offgas, after additional absorption of the H_2S in the AGR unit, can be incinerated or compressed for combustion in the turbine. An oxygen blown Claus is advantageous in the latter case because of the much smaller gas stream that is seen by the compressor. Oxygen blown Claus provides additional sulfur throughput flexibility and provides for easier disposal of sour water off gases.
- For future IGCC with CO_2 removal for sequestration, a two-stage Selexol process presently appears to be the preferred AGR process—as indicated by ongoing engineering studies at EPRI and various engineering firms with IGCC interests. In CO_2 removal applications, the Selexol Process is chilled—thus facilitating deep H_2S removal as well as CO_2 removal. While the Rectisol process also has been proposed for use in IGCCs with CO_2 removal, this application does not appear to be the subject of any published cost studies.

- Further engineering and cost studies of the main IGCC processes with various feedstocks and all of the potentially competitive AGR options are required to quantify the relative performance and cost benefits of the various AGR options and elucidate the ranges of conditions and cases in which they are competitive. Related studies are underway at EPRI and various engineering organizations, which may be published later in some form. While information of this type exists within process licensor and engineering/construction organizations, it is generally proprietary. The FLEXSORB hindered amine processes, the Purisol physical solvent process, and the Sulfinol mixed amine/physical solvent process also should be evaluated.
- Acid gas injection (AGI) is now widely practiced by the oil and gas industry and should be investigated further for use with IGCC. It eliminates the need for sulfur recovery and TGT units by injecting acid gases from the AGR unit directly into a saline aquifer or a depleted gas or petroleum reservoir. It could prove more economical than trying to meet ever more stringent sulfur recovery regulations. It also provides a means for the sequestration of additional CO_2 should that be required in the future.
- Flexibility and operability of the AGR and SR systems are less compromised if they are not tightly integrated. In the AGR processes, for example, a separate enrichment train, rather than a tight integration of the enrichment section with the primary absorber and stripper, can improve the overall flexibility and operability of the system. The same could apply to the SR process when tail gas is recycled back to the primary absorber. It could be better to install a separate absorption stage. Although this approach may be more capital intensive, the overall economics of the IGCC system may be improved if the system availability is improved.
- This report provides information that IGCC project planners and developers can use to select AGR processes and gas treating process combinations and configurations for preliminary evaluations and screening studies. However, identifying the “best” process options for specific applications requires engineering and cost evaluations of the integrated system options—in which the inputs and evaluations of the specific process licensors are essential. The licensors should be contacted in the early stages of planning and project development to ensure that the most appropriate and best available information for the level of effort required is employed.

Hot and Warm Gas Cleanup

- Continued improvements in hot dry particle filtration, which is commercially available technology, can be expected. Further improvements are still needed to increase filter element life and to reduce filter installation, operating, and maintenance costs. Upstream cyclones are important components of a hot particle removal system—to minimize the load on the hot filters. Overall, hot gas filtration offers definite advantages to IGCC over water scrubbing. They include: avoiding black mud, recovering dry char for recycle to the gasifier, and improved process efficiency.

- The development of both hot and warm gas cleanup systems for deep cleaning of sulfur and nitrogen components from syngas appear to be long-term prospects, if at all achievable. Large-scale demonstrations probably would not be achievable or practical before about 2010. Justification for such demonstrations could become difficult if commercial IGCC projects with CGCU continue to proliferate and operate well over the next several years. Related scale-up issues must be realistically addressed.

- The prospects of developing hot or warm gas cleanup processes for mercury and CO_2 removal presently are very dim. Either, or both, the requirement for mercury recovery and/or CO_2 recovery from coal-fired power plants could become the Achilles' heel of dry gas cleanup—dictating the use of O_2-blown IGCC with CGCU.

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