APPENDIX E Engineering Evaluation of Hot-Gas Desulfurization with Sulfur Recovery, Topical Report, May 1998



May 1998

Engineering Evaluation of Hot-Gas Desulfurization with Sulfur Recovery

Topical Report

Work performed under Contract No. DE-AC21-94MC31258

for U.S. Department of Energy Federal Energy Technology Center 3610 Collins Ferry Road Morgantown, WV 26505

by S.K. Gangwal J.W. Portzer Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709

> and G.W. Roberts S.C. Kozup North Carolina State University Raleigh, NC 27695



This report was prepared by the Research Triangle Institute (RTI) as an account of work sponsored by the U.S. Department of Energy. RTI makes no warranty or representation, expressed or implied, with respect to the information contained in this report, or that the use of any apparatus, method or process disclosed in this report may not infringe privately owned rights. Furthermore, RTI assumes no liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

Engineering Evaluation of Hot-Gas Desulfurization with Sulfur Recovery

Topical Report

Work performed under Contract No. DE-AC21-94MC31258

for
U.S. Department of Energy
Federal Energy Technology Center
3610 Collins Ferry Road
Morgantown, WV 26505

by
S.K. Gangwal
J.W. Portzer
Research Triangle Institute
3040 Cornwallis Road
Research Triangle Park, NC 27709

and
G.W. Roberts
S.C. Kozup
Chemical Engineering Department
North Carolina State University
Raleigh, NC 27695

May 1998

ABSTRACT

Engineering evaluations and economic comparisons of two hot-gas desulfurization (HGD) processes with elemental sulfur recovery, being developed by Research Triangle Institute, are presented. In the first process, known as the Direct Sulfur Recovery Process (DSRP), the SO₂ tail gas from air regeneration of zinc-based HGD sorbent is catalytically reduced to elemental sulfur with high selectivity using a small slipstream of coal gas. DSRP is a highly efficient first-generation process, promising sulfur recoveries as high as 99% in a single reaction stage. In the second process, known as the Advanced Hot Gas Process (AHGP), the zinc-based HGD sorbent is modified with iron so that the iron portion of the sorbent can be regenerated using SO₂. This is followed by air regeneration to fully regenerate the sorbent and provide the required SO₂ for iron regeneration. This second-generation process uses less coal gas than DSRP. Commercial embodiments of both processes were developed. Process simulations with mass and energy balances were conducted using ASPEN Plus. Results show that AHGP is a more complex process to operate and may require more labor cost than the DSRP. Also capital costs for the AHGP are higher than those for the DSRP.

However, annual operating costs for the AHGP appear to be considerably less than those for the DSRP with a potential break-even point between the two processes after just 2 years of operation for an integrated gasification combined cycle (IGCC) power plant using 3 to 5 wt% sulfur coal. Thus, despite its complexity, the potential savings with the AHGP encourage further development and scaleup of this advanced process.

TABLE OF CONTENTS

	P	age
Abs	ract	. ii
Lis	of Figures	. iv
	of Tables	
Acl	nowledgments	v
Exe	utive Summary	1
	ntroduction	1
	Objective	
	Background	
	Sorbent Development	
	Reactor and Systems	
	Direct Sulfur Recovery Process	
	Advanced Hot-Gas Process	
	Approach	
	Results	
	Conclusions	
	References	

Appendix—Process Modeling of Hot-Gas Desulfurization

LIST OF FIGURES

Figure	Page
E-1	Advanced IGCC system
E-2	Schematic of Sierra hot-gas desulfurization system4
E-3	Hot-gas desulfurization with DSRP 5
E-4	Advanced hot-gas process
E-5	Schematic of AHGP desulfurization and regeneration reactors9
E-6	Comparison of key elements of DSRP and AHGP9
E-7	Annual costs as a function of sulfur feed
E-8	Cumulative HGD investment
	LIST OF TABLES
Table	Page
E-1 E-2	Simulation Cases Considered

ACKNOWLEDGMENTS

This research was sponsored by the Federal Energy Technology Center of the U.S. Department of Energy. Valuable guidance and suggestions provided by the Contracting Officer's Representative, Mr. Thomas P. Dorchak, are sincerely acknowledged.

EXECUTIVE SUMMARY

INTRODUCTION

Hot-gas desulfurization (HGD) of coal gas in integrated gasification combined cycle (IGCC) power systems has received a great deal of attention over the past two decades due to the potential for high thermal efficiency (up to 47%) and low environmental impact of these advanced power systems. In an advanced IGCC system, coal is gasified at elevated pressures, typically 20 to 30 atm, to produce a low-volume fuel gas which is desulfurized prior to burning in a combustion turbine to produce electricity. Higher efficiency and lower cost are achieved by efficient air and steam integration, and modular designs of the gasification, hot-gas cleanup, and turbine subsystems (Figure E-1). Hot gas cleanup primarily involves removal of particulates and sulfur—mostly hydrogen sulfide (H₂S) and some carbonyl sulfide (COS). H₂S and COS can be efficiently removed to less than 20 ppmv at 350 to 650 °C using zinc-based metal oxide sorbents that can be regenerated for multicycle operation.

Air regeneration of these sorbents results in a dilute sulfur dioxide (SO₂)-containing tail gas that needs to be disposed. Options include conversion of the SO₂ to calcium sulfate using lime (or limestone) for landfilling or conversion to saleable products such as sulfuric acid or elemental sulfur. Elemental sulfur, an essential industrial commodity, is an attractive option because it is the lowest volume product and can be readily stored, disposed, transported, and/or sold.

Research Triangle Institute (RTI), with U.S. Department of Energy (DOE) sponsorship, is pursuing the development of two processes for elemental sulfur production in conjunction with

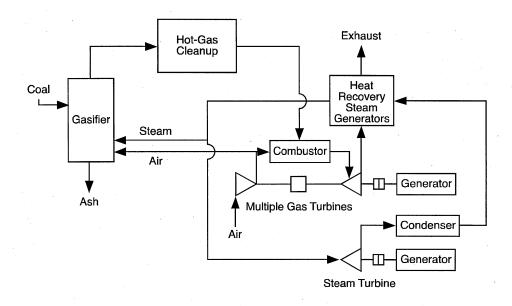


Figure E-1. Advanced IGCC system.

hot-gas desulfurization. The first process, called the Direct Sulfur Recovery Process (DSRP), involves the selective catalytic reduction of the SO₂ tail gas to sulfur using a small slipstream of the coal gas. DSRP is a highly efficient process that can recover up to 99% of SO₂ as elemental sulfur in a single catalytic reactor. However, for every mole of sulfur produced two moles of hydrogen (H₂) and/or carbon monoxide (CO) are consumed in DSRP and this represents an energy penalty for the IGCC plant. DSRP is currently in an advanced state of development.

A second-generation process being pursued by RTI involves the use of a modified zinc-based sorbent (containing zinc and iron). This sorbent can be regenerated using SO₂ and O₂ to directly produce sulfur. This process, called the Advanced Hot-Gas Process (AHGP), is expected to use much less coal gas than DSRP. DSRP is currently at the pilot-plant scale development stage, whereas AHGP has been demonstrated at small bench-scale. Both DSRP and AHGP are scheduled for slipstream testing at DOE's Power Systems Development Facility (PSDF), Wilsonville, Alabama, in 1999.

OBJECTIVE

The objective of this report is to develop process simulations with mass and heat balances for the DSRP and AHGP and to provide a **preliminary** economic comparison of the two processes in conjunction with an IGCC power plant employing HGD. The process simulation and economic evaluation were carried out by RTI's subcontractor, North Carolina State University (NCSU). NCSU's report of this work in its entirety is attached as an appendix. Background, brief process description, and important results and conclusions are provided below as a stand-alone executive summary.

BACKGROUND

Sorbent Development

Research on HGD methods for coal gas in IGCC systems has concentrated on the use of regenerable metal oxide sorbents (Gangwal, 1991, 1996; Gangwal et al., 1993, 1995; Harrison, 1995; Jalan, 1985; Thambimuthu, 1993). This research and development effort has been spearheaded by DOE's Federal Energy Technology Center (FETC) and its predecessor agencies since 1975.

The HGD process using a regenerable metal oxide (MO) sorbent is typically carried out in a two-reactor system consisting of a desulfurizer and an air regenerator

$$MO + H_2S \rightarrow MS + H_2O$$
 (desulfurizer)
 $MS + (3/2) O_2 \rightarrow MO + SO_2$ (regenerator).

The main requirement of the metal oxide sorbent is that it should selectively react with H_2S and COS in a reducing fuel gas at desired conditions (2 to 3 Mpa, 350 to 750 °C). The thermodynamics of the reaction should be favorable enough to achieve the desired level of H_2S and COS removal (as much as 99% or more). The metal oxide should be stable in the reducing gas environment, i.e., reduction of MO to M should be slow or thermodynamically unfavorable since

it leads to loss of valuable fuel gas and could also lead to volatile metal evaporation and decrepitation of sorbent structure.

The principle requirement during air regeneration is that the sorbent should predominantly revert back to its oxide rather than to sulfate $(MO + SO_2 + 1/2 O_2 \rightarrow MSO_4)$. Air regeneration is highly exothermic and requires tight temperature control using large quantities of diluent (N_2) or other means to prevent sorbent sintering and sulfate formation.

The bulk of research on regenerable sorbents has been on zinc-based sorbents because sorbents based on zinc oxide appear to have the fewest technical problems among all sorbents. Zinc oxide (ZnO) has highly attractive thermodynamics for $\rm H_2S$ adsorption and can reduce the $\rm H_2S$ to partsper-million levels over a very wide temperature range. Iron oxide appears to be the most popular sorbent for use at around 400 °C.

A combined ZnO-iron oxide (Fe₂O₃) sorbent, namely, zinc ferrite (ZnFe₂O₄) was developed by Grindley and Steinfeld (1981) to combine the advantages of ZnO and Fe₂O₃. A temperature range of 550 to 750 °C received the major research emphasis in the United States during the 1980s and early 1990s. Because of zinc oxide's potential for reduction (ZnO + $H_2 \rightarrow Zn + H_2O$) at >600 °C followed by evaporation, a zinc oxide-titanium oxide sorbent, namely zinc titanate sorbent, was developed and tested at high temperature and high pressure (HTHP) (Gangwal et al., 1988). Zinc titanate is currently one of the leading sorbents.

During recent years, research emphasis has shifted toward lower temperatures (350 to 550 °C) based on a study in the Netherlands (NOVEM, 1991). According to this study, the thermal efficiency of an 800-MWe IGCC plant increased from 42.75% using cold-gas cleanup to 45.14% using HGD at 350 °C and to 45.46% using HGD at 600 °C. The small efficiency increase from 350 to 600 °C suggested that temperature severity of HGD could be significantly reduced without much loss of efficiency.

Reactor and Systems

A two-reactor configuration is necessary for HGD due to its cyclic nature. Early developments emphasized fixed beds. The highly exothermic regeneration led to a move away from fixed beds toward moving beds (Ayala et al., 1995; Cook et al., 1992) and fluidized beds (Gupta and Gangwal, 1992). Two DOE Clean Coal Technology IGCC demonstration plants, namely TECO and Sierra-Pacific, employing General Electric's (GE's) moving-bed HGD reactor system and M.W. Kellogg's transport reactor HGD system, respectively, are scheduled to begin operation this year. Fluidized-bed HGD systems are receiving a lot of emphasis due to several potential advantages over fixed- and moving-bed reactors, including excellent gas-solid contact, fast kinetics, pneumatic transport, ability to handle particles in gas, and ability to control the highly exothermic regeneration process. However, an attrition-resistant sorbent that can withstand stresses induced by fluidization, transport, chemical transformation, and rapid temperature swings must be developed.

Development of an iron-oxide sorbent-based fluidized-bed HGD reactor system has been carried out in Japan over the past several years (Sugitani, 1989). The process is now up to 200 tons of

coal per day. The sorbent is prepared by crushing raw Australian iron oxide which is inexpensive, but attrition is a big problem with this sorbent. Durable zinc titanate and other zinc-based sorbent development is ongoing for application at the Sierra-Pacific plant for Kellogg's transport reactor (Gupta et al., 1996, 1997; Jothimurugesan et al., 1997; Khare et al., 1996).

A schematic of Kellogg's transport reactor system at Sierra-Pacific is shown in Figure E-2. This technology represents a significant development in HGD because it allows regeneration with neat air. Neat air regeneration produces a more concentrated SO₂ tail-gas stream containing around 14 vol% SO₂.

The initial sorbent tested at Sierra-Pacific was Phillips Z-Sorb III. Its attrition resistance was not acceptable. Phillips is continuing efforts to improve their sorbent. Recently RTI and Intercat have provided a much more attrition-resistant zinc titanate sorbent, EX-SO3, to Sierra-Pacific for testing after qualifying it through a series of bench- and process development unit (PDU)-scale tests (Gupta et al., 1997). This sorbent has been circulated in the system and has demonstrated satisfactory attrition resistance. Chemical reactivity tests with the sorbent are to be conducted shortly after the Sierra coal gasifier is fully commissioned and begins smooth operation.

Direct Sulfur Recovery Process

The patented DSRP being developed by RTI is a highly attractive option for recovery of sulfur from regeneration tail gas. Using a slipstream of coal gas as a reducing agent, it efficiently

converts the SO₂ to elemental sulfur, an essential industrial commodity that is easily stored and transported. In the DSRP (Dorchak et al., 1991), the SO₂ tail gas is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the HTHP conditions of the tail gas and coal gas. Overall reactions involved are shown below:

$$2 H_2 + SO_2 \rightarrow (1/n) S_n + 2 H_2O$$

$$2 CO + SO_2 \rightarrow (1/n) S_n + 2 CO_2$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

$$H_2 + (1/n) S_n \rightarrow H_2S$$

$$2 H_2S + SO_2 \rightarrow (3/n) S_n + 2 H_2O$$

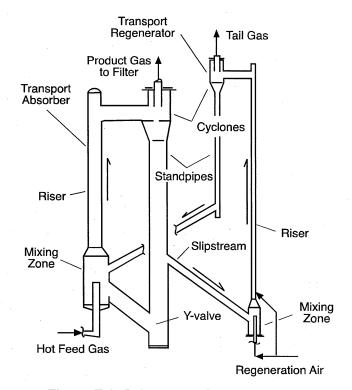


Figure E-2. Schematic of Sierra hot-gas desulfurization system.

RTI constructed and commissioned a mobile laboratory for DSRP demonstration with actual coal gas from the DOE-Morgantown coal gasifier. Slipstream testing using a 1-L fixed-bed of DSRP catalyst with actual coal gas (Portzer and Gangwal, 1995; Portzer et al., 1996) demonstrated that, with careful control of the stoichiometric ratio of the gas input, sulfur recovery of 96% to 98% can be consistently achieved in a single DSRP stage. The single-stage process, as it is proposed to be integrated with a metal oxide sorbent regenerator, is shown in Figure E-3. With the tail-gas recycle stream shown in the figure, there are no sulfur emissions from the DSRP. RTI also demonstrated the ruggedness of the DSRP catalyst by exposing it to coal gas for over 250 hours in a canister test.

The results show that, after a significant exposure time to actual coal gas, the DSRP catalyst continues to function in a highly efficient manner to convert SO₂ in a simulated regeneration tail gas to elemental sulfur. This demonstration of a rugged, single-stage catalytic process resulted in additional online experience and the assembling of more process engineering data. The development of the DSRP continues to look favorable as a feasible commercial process for the production of elemental sulfur from hot-gas desulfurizer regeneration tail gas.

Canisters of fixed-bed DSRP catalyst have been prepared for another exposure test with actual coal gas, this time at FETC's PSDF at Wilsonville, Alabama. Exposure is expected to take place sometime during FY 2000.

Additional development and testing of a fluidized-bed process is planned, capable of producing elemental sulfur from 14 vol% SO₂ at HTHP. These tests intend to demonstrate the use of DSRP in conjunction with the Kellogg transport regenerator producing 14 vol% SO₂. Due to the exothermic nature of the DSRP reactions, a fluidized-bed reactor is a preferred configuration at these high SO₂ concentrations. Two candidate attrition-resistant fluidizable DSRP catalysts have been prepared in cooperation with a catalyst manufacturer. A series of tests was conducted using these catalysts with up to 14 vol% SO₂ tail gas, at pressures from 1.0 to 2.0 Mpa, temperatures

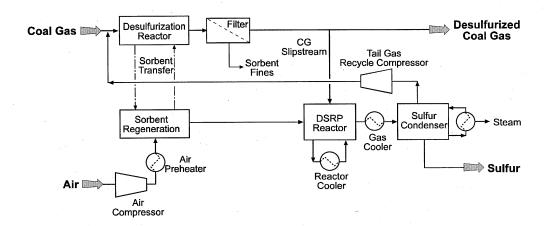


Figure E-3. Hot-gas desulfurization with DSRP.

from 500 to 600 °C, and space velocities from 3,000 to 6,000 stdcm³/cm³. Sulfur recoveries up to 98.5% were achieved during steady-state operation, and no attrition of the catalyst occurred in the fluidized-bed tests.

Planning is underway to conduct a long-duration field test using a skid-mounted six-fold larger (based on reactor volume) (6X) DSRP unit with a slipstream of actual coal gas at PSDF. The mobile laboratory will be refitted at RTI as a control room for the 6X unit and will be moved along with the skid-mounted 6X unit to Wilsonville, Alabama, for the testing to be conducted in FY 2000. This larger unit will utilize a fluidized-bed reactor and will be designed for production of up to 22 times more sulfur than the 7.5-cm I.D. bench-scale unit used in the previous slipstream tests.

Advanced Hot-Gas Process

In the DSRP, for every mole of SO₂, 2 mol of reducing components are used, leading to a small but noticeable consumption of coal gas. Novel regeneration processes that could lead to elemental sulfur without use of coal gas or with limited use of coal gas are being developed (Gangwal et al., 1996; Harrison et al. 1996). KEMA's hot-gas cleanup process (Meijer et al., 1996) uses a proprietary fluidized-bed sorbent which can remove H₂S to below 20 ppmv and can be regenerated using SO₂, O₂ mixtures to directly produce elemental sulfur. Along similar lines, a second-generation process, known as the Advanced Hot-Gas Process (AHGP), is being developed by RTI to regenerate the desulfurization sorbent directly to elemental sulfur with minimal consumption of coal gas. In this process (Figure E-4), a zinc-iron sorbent is used and the regenerated by SO₂ in one stage to elemental sulfur. In the other stage, zinc sulfide and any remaining iron sulfide are regenerated by O₂ to provide the required SO₂. The sorbent is then returned to the desulfurizer.

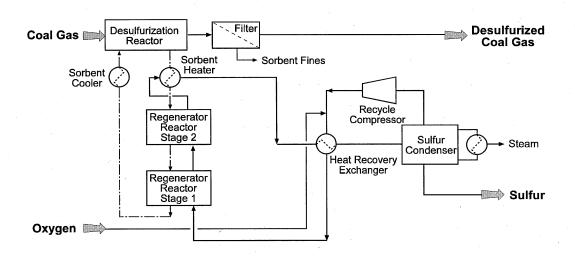


Figure E-4. Advanced hot-gas process.

The key chemical reactions of interest are as follows:

1. Sulfidation

$$\begin{aligned} \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{S} + \text{H}_2 &\rightarrow 2\text{FeS} + 3\text{H}_2\text{O} \\ \text{ZnO} + \text{H}_2\text{S} &\rightarrow \text{ZnS} + \text{H}_2\text{O} \end{aligned}$$

2. SO₂ regeneration

$$4\text{FeS} + 3\text{SO}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 7/2 \text{ S}_2$$

3. O_2 regeneration

$$2\text{FeS} + 7/2 \text{ O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2$$

 $2\text{nS} + 3/2 \text{ O}_2 \rightarrow \text{ZnO} + \text{SO}_2$.

The feasibility of SO₂ regeneration of combined zinc-iron sorbents was demonstrated using a thermogravimetric analyzer and high-pressure microreactor. Zinc sulfide shows essentially no SO₂ regeneration at temperatures of interest (500 to 600 °C), but zinc is needed to act as a polishing agent in the desulfurizer. A number of sorbents were prepared and tested at the bench scale over multiple cycles. Based on these tests, a highly attrition-resistant sorbent (R-5-58) was prepared and the process was demonstrated over 50 cycles in a 5.0-cm I.D. bench-scale reactor.

The results showed that R-5-58 removed $\rm H_2S$ down to 50 to 100 ppm levels with stable desulfurization activity over the duration. The surface area and pore volume of the sorbent did not change appreciably and the attrition index before and after the test was 3.6% and 1.2%, respectively. Sulfur balances were adequate and the $\rm SO_2$ regeneration step accounted for up to 70% of the total regeneration of the sorbent. This compares to a theoretical limit of approximately 80%, assuming complete regeneration by $\rm SO_2$ of the iron component.

The sorbent is being optimized further to increase its desulfurization efficiency. The goal is to develop a sorbent that can remove H_2S below 20 ppmv. Plans call for demonstrating the process at PSDF with a slipstream of actual coal gas in FY 1999 in conjunction with the DSRP field test at PDSF.

APPROACH

An engineering and economic evaluation of the DSRP (Figure E-3) and AHGP (Figure E-4) for large-scale IGCC plants was conducted using ASPEN PLUS[®] computer process simulation software by NCSU. The NCSU report is attached in its entirety as an appendix. Here we present a summary of the approach, key results, and conclusions.

Base case simulations of both processes assumed $0.85 \text{ mol}\% \text{ H}_2\text{S}$ in the coal-gas feed. Such an H_2S concentration in the coal gas would be produced by an oxygen-blown Texaco gasification using roughly a 3.6 wt% sulfur-containing coal. Both base cases generate 260 MWe from the clean coal gas. Simulations that deviate from the base cases use suffixes to denote the changes. Table E-1 displays the significance of the suffixes. In all cases a coal-gas feed pressure and

temperature of 275 psia and 482 °C, respectively, was used. However, H₂S concentration was varied from 0.25 to 2.5 mol% and power produced was varied from 110 to 540 MWe. Table E-2 shows the composition and flow rate of the raw coal gas feed to the base case HGD processes. The requirement of a higher amount of coal gas to produce the same 260 MW power by DSRP versus the AHGP is noteworthy. The DSRP was assumed to use the standard Sierra-Pacific dual transport reactor configuration shown in Figure E-2 for HGD. The DSRP reactor used for the 14% SO2 tail gas was a fast fluidized bed with an alumina-based catalyst. The AHGP reactor configuration on the other hand used a transport sulfider and a bubbling multistage fluidized-bed regenerator as shown in Figure E-5. The large bubbling reactor was required to provide a greater residence time for the slow SO₂ regeneration stage.

RESULTS

The preliminary process and economic evaluations conducted using ASPEN Plus are summarized. Figure E-6 compares key elements using a simple method in which each parameter for the DSRP-based process is arbitrarily assigned the value of 1.0. A range of values is produced for AHGP to cover

Table E-1. Simulation Cases Considered

Simulations	H₂S feed concentration (mol%)	MW produced
DSRP, AHGP (base cases)	0.85	260
DSRP-b, AHGP-b	2.50	260
DSRP-c, AHGP-c	0.25	260
DSRP-100, AHGP-100	0.85	110
DSRP-500, AHGP-500	0.85	540

Table E-2. Raw Gas Feed to Base Case Simulations

Component	DSRP (lb/h)	AHGP (lb/h)
H ₂ S	6,300	6,100
H ₂ O	70,500	69,000
H_2	11,800	11,500
CO	218,200	213,400
CO ₂	117,400	114,800
N_2	36,300	35,500
Total	460,500	450,300

the various cases being considered. The big advantage of the AHGP is clearly the reduced parasitic consumption of coal gas. The other operating cost elements are also lower for AHGP, because that process has a considerably lower compression power requirement. A desulfurization process based on the DSRP requires a large flow of compressed air to provide the oxygen necessary to regenerate the sulfided sorbent, and thus has a large compressor horsepower duty. By comparison, the AHGP uses oxygen only for a smaller, polishing regeneration and, by using pure oxygen, the compression duty is lowered further. The AHGP also has the SO₂ loop recycle compressor, but its duty is quite small compared to the DSRP air compressor.

[It should be noted that in the NCSU economic analysis (Appendix) the AHGP recycle compressor duty may be understated, as the calculation was based on a rough estimate for pressure drop, not a calculated value based on a piping design. By comparison, the duty for the DSRP air compressor is primarily a function of the head pressure of the system, which is well defined.]

The value of "capital cost of all equipment" for the AHGP is higher than for the DSRP-based process, as Figure E-5 shows. The higher equipment cost is primarily due to the higher cost of the AHGP reactor vessel(s). Although there are three separate reactor steps required with the DSRP-based process, the single AHGP multistage reactor vessel(s) is larger. The larger size is primarily due to the longer residence time required for the SO₂ regeneration. [It should be noted that the NCSU cost estimates (Appendix) do not include piping costs, so that the total plant capital costs will be higher than the installed equipment costs. However, since piping costs are often estimated as a direct function of the equipment cost numbers, the ratio of the installed equipment costs for the two processes shown in the figure will approximate the ratio of the total plant costs.]

Another advantage of the DSRP is that it is the easier, more understood, process to operate. This is because balancing the SO₂ production and consumption in the AHGP may be difficult.

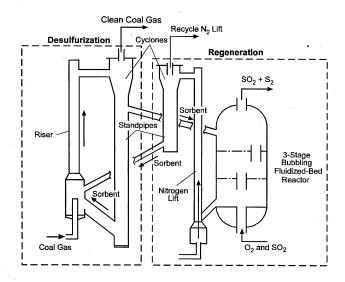


Figure E-5. Schematic of AHGP desulfurization and regeneration reactors.

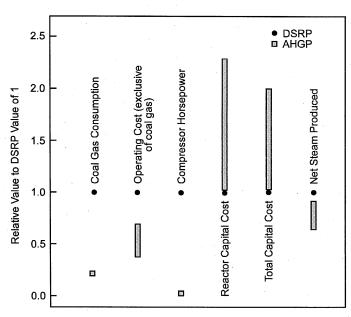


Figure E-6. Comparison of key elements of DSRP and AHGP.

Although the AHGP has a higher initial cost, indicated by its larger capital requirements, it has a significantly lower annual operating cost than DSRP. As shown in Figure E-7, the operating cost advantage of the AHGP increases as the sulfur to be recovered increases. The negative annual costs of AHGP at higher sulfur feed result from the sulfur credit with less consumption of coal gas. The operating cost difference is large enough to offset the installation cost of AHGP. As shown in Figure E-8, AHGP has a lower cumulative HGD investment after only 2 years of operation. Both Figures E-7 and E-8 are presented to illustrate only cost comparison of the two processes. Emphasis should not be placed on the accuracy of the absolute cost numbers presented in these figures.

CONCLUSIONS

ASPEN simulations of DSRP and AHGP revealed the complexity of both HGD processes. The AHGP appears to be the more difficult process to operate and may require more employees than

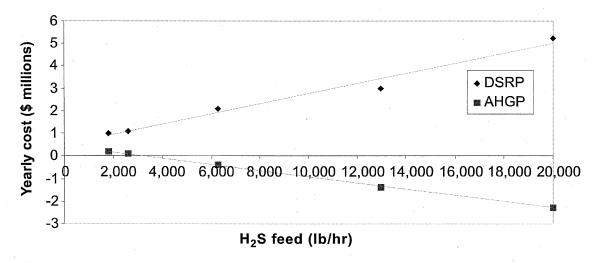


Figure E-7. Annual costs as a function of sulfur feed.

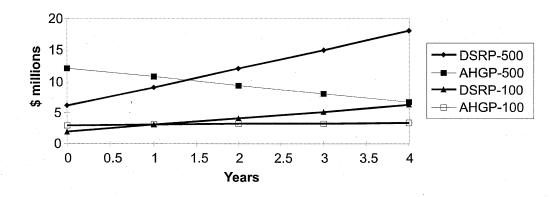


Figure E-8. Cumulative HGD investment.

the DSRP. Capital costs for the AHGP are higher than those for the DSRP—development of DSRP is also much closer to commercialization than AHGP. However, annual operating costs for the AHGP appear to be considerably less than those of the DSRP. Preliminary economic comparison shows that the total cost of implementing AHGP will be less than that of implementing DSRP after as little as 2 years of operation. Thus, despite its greater complexity, the potential savings with the AHGP encourage further development and scaleup of this advanced process.

REFERENCES

- Ayala, R.E., A.S. Feitelberg, and A.H. Furman. 1995. "Development of a High-Temperature Moving-Bed Coal Gas Desulfurization System." In *Proceedings of 12th Ann. Int. Pittsburgh Coal Conf.*, p. 1053, September 11-15, Pittsburgh.
- Cook, C.S., et al. 1992. "Integrated Operation of a Pressurized Fixed Bed Gasifier and Hot Gas Desulfurization System." In *Proceedings of 12th Annual Gasif. Gas Stream Cleanup Systems Contractor's Review Meeting*, Volume 1, DE93000228, p. 84.
- Dorchak, T.P., S.K. Gangwal, and W.J. McMichael. 1991. The Direct Sulfur Recovery Process. *Environmental Progress* 19(2):68.
- Gangwal, S.K. 1991. "Hot-Gas Desulfurization Sorbent Development for IGCC Systems." IChemE Symposium Series No. 123. Sheffield, UK, pp. 159-170.
- Gangwal, S.K. 1996. "Sulfur Removal from Gas Streams at High Temperature," 3rd International Symposium on Gas Cleaning at High Temperature. University of Karlsruhe, Karlsruhe, Germany, September.
- Gangwal, S.K., et al. 1988. "Bench-Scale Testing of Novel High-Temperature Desulfurization Sorbents." Report No. DOE/MC/23126-2662 (DE89000935).
- Gangwal, S.K., R. Gupta, and W.J. McMichael. 1993. "Sulfur Control Options for IGCC Systems." In *Proceedings of 17th Biennial Low-Rank Fuels Symposium*, University of North Dakota, Energy and Environmental Research Center, St. Louis, MO, May 10-13.
- Gangwal, S.K., R. Gupta, and W.J. McMichael. 1995. "Hot-Gas Cleanup-Sulfur Recovery-Technical, Environmental, and Economic Issues," *Heat Recovery Systems and CHP*. Vol. 15, No. 2, p. 205-214, Elsevier Science Limited.
- Grindley, T., and G. Steinfeld. 1981. "Development and Testing of Regenerable Hot Coal-Gas Desulfurization Sorbents." DOE/MC/16545-1125.
- Gupta, R., and S.K. Gangwal. 1992. "Enhanced Durability of Desulfurization Sorbents for Fluidized Bed Applications—Development and Testing of Zinc Titanate Sorbents." DOE/MC/25006-3271.

- Gupta, R., B.S. Turk, and S.K. Gangwal. 1996. "Bench-Scale Development of Fluid-Bed Spray Dried Sorbents." In *Proceedings of Advanced Coal-Fired Power Systems '96 Review Meeting*, Morgantown Energy Technology Center, Morgantown, WV, July.
- Gupta, R., B.S. Turk, and Albert A. Vierheilig. 1997. "Desulfurization Sorbents for Transport-Bed Applications." In *Proceedings of 1997 FETC Power Systems and Environmental Control Contractor's Meeting*, Pittsburgh, PA, July.
- Harrison, D.P. 1995. "Control of Gaseous Contaminants in IGCC Processes, An Overview," In *Proceedings of 12th Ann. Int. Pittsburgh Coal Conference*, p. 1047, September 11-15, Pittsburgh.
- Harrison, D.P., F.R. Groves, J.D. White, W. Huang, and A. Lopez-Oritz. 1996. "Advanced Sulfur Control Processing." In *Proceedings of Advanced Coal-Fired Power Systems '96 Review Meeting*, Morgantown Energy Technology Center, Morgantown, WV, July.
- Jalan, V. 1985. "High-Temperature Desulfurization of Coal Gases." In *Acid and Sour Gas Treating Processes*, Gulf Publishing Co., Houston, TX, Nov. 7.
- Jothimurugesan, K., S.K. Gangwal, R. Gupta, and B.S. Turk. 1997. "Advanced Hot-Gas Desulfurization Sorbents." In *Proceedings of 1997 FETC Power Systems and Environmental Control Contractor's Meeting*, Pittsburgh, PA, July.
- Khare, G.P., G.A. Delzer, G.J. Greenwood, and D.H. Kunbicek. 1996. "Phillips Sorbent Development for Tampa Electric and Sierra Pacific." In *Proceedings of Advanced Coal-Fired Power Systems '96 Review Meeting*, Morgantown Energy Technology Center, Morgantown, WV, July.
- Meijer, R., F.J.J.G. Janssen, G.L. Faring, and J.W. H. Hellendoorn. 1996. "KEMA's Hot Gas Cleanup Process." *In Proceedings of 3rd International Symposium on Gas Cleaning at High Temperature*. University of Karlsruhe, Karlsruhe, Germany, September.
- NOVEM. 1991. "System Study High Temperature Gas Cleaning at IGCC Systems." Netherlands Agency for Energy and the Environment.
- Portzer, J.W., and S.K. Gangwal. 1995. "Slipstream Testing of Hot Gas Desulfurization with Sulfur Recovery." In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, pp. 220-228. DOE/METC-95/1018, Vol. 1, NTIS/DE 95009732. Springfield, VA: National Technical Information Service.
- Portzer, J.W., B.S. Turk, and S.K. Gangwal. 1996. "Durability Testing of the Direct Sulfur Recovery Process." In *Proceedings of the Advanced Coal-Fired Power Systems Review Meeting July 16 B18, 1996.* (CD-ROM). U.S. Department of Energy. Morgantown, WV.
- Sugitani, T. 1989. Development of Hot-Gas Desulfurization Process. *Journal of the Fuel Society of Japan* 68(9):787.

Thambimuthu, K.V. 1993. Gas Cleaning for Advanced Coal-Based Power Generation. Report by IEA Coal Research, IEACR/53, London, UK.

Appendix

Process Modeling of Hot-Gas Desulfurization

Steve C. Kozup George W. Roberts North Carolina State University

TABLE OF CONTENTS

			PA	GE	
EXECUTIVE SUMMARY					
I.	IN	TRO	DUCTION	. 2	
	1.	Bac	ckground	. 2	
	2.	Sul	fur Production	. 3	
Π.	BA	SIC	PROCESS DESCRIPTIONS	. 4	
	1.	Dir	rect Sulfur Recovery Process Sorbent Cycle	. 5	
	2.	Son	rbent Composition - DSRP	. 6	
	3.	Ad	vanced Hot Gas Process Sorbent Cycle	. 8	
	4.	Son	rbent Composition - AHGP	. 9	
Ш.	PH	YSI	CAL PROPERTIES	12	
	1.	Equ	uation of State	12	
		a.	Equation of State's Importance	12	
		b.	Selection	13	
	2.	Ele	emental Sulfur	15	
IV.	EQ	UIP	MENT	16	
	1.	DS	RP -Based Process Equipment	16	
		a.	Desulfurization and Regeneration Transport Reactors - DSRP	16	
		b.	DSRP Reactor - DSRP	19	
		c.	PRESAIR - DSRP	20	
		d.	RECYCOMP - DSRP	22	
		e.	High Pressure Condenser - DSRP	22	
		f.	VAPORIZR - DSRP	23	
		g.	PD-COOLR - DSRP	23	
		h.	AIR-HX - DSRP	24	
	2.	AF	HGP Equipment	25	
		a.	Desulfurization and Regeneration Reactors - AHGP	25	
		b.	LIFTCOMP - AHGP	28	
		c.	SO2-COMP - AHGP	28	
		d.	CON-COMP - AHGP	28	

		e. COND-EQ - AHGP	29
		f. DEMISTR - AHGP	29
		g. LP-COND - AHGP	29
		h. HEATX - AHGP	30
		i. N2-COOLR - AHGP	30
		j. RCYHEATR - AHGP	30
V.	PA	RAMETRIC STUDIES	31
	1.	H ₂ S Inlet Concentration	31
	2.	Power Generation	32
	3.	Pure Oxygen vs. Air Oxidation	32
		a. DSRP	32
		b. AHGP	33
VI.	ΑĽ	DDITIONAL PROCESS CONSIDERATIONS	35
	1.	Steam Generation	35
	2.	Material of Construction	36
	3.	Sulfur Storage	36
	4.	Process Operation	37
VII.	EC	ONOMIC ANALYSIS	38
	1.	Capital Expenditures	38
	2.	Yearly Operating Costs	39
		a. Electrical	42
		b. Cooling Water	43
		c. Oxygen	44
		d. Additional Employees	44
		e. Consumed Coal Gas	44
		f. Additional Yearly Expenditures	45
	3.	Economic Summary	45
VIII.	SU	MMARY	46
REFI	ERE	NCES	47
Appe	ndi	x A - Calculation of the SO ₂ Circulation Rate for AHGP	49
Appe	ndi	x B - Heat Transfer Coefficients	50
Appe	ndi	x C - Determination of Catalyst Velocity in DSRP Reactor	51
Anne	ndi	y D - Calculation of DSRP Catalyst Cycling Rate	5/

Appendix E - Process Flowsheets and Stream Summaries	. 56
Appendix F - Steam Generation Process Flowsheets	85
Appendix G - Calculation of Reactor Size	. 92
Appendix H - Sizing Reactors for the DSRP	94
Appendix I - Sizing Reactors for the AHGP	. 105
Appendix J - Power Generation Achievable from Clean Coal Gas	. 111
Appendix K - Calculation of Reactor Pressure Drops	. 113
Appendix L - Summary of the Process Pressure Drops	. 117
Appendix M - Summary of Major HGD Equipment	121
Appendix N - Summary of HGD Costs	124
Appendix O - Reaction Data Obtained from RTI	135

LIST OF TABLES

TAB	LE# PAGE
1.	Coal Gas Characteristics of Simulations
2.	Raw Coal Gas Feed to Base Case Simulations
3.	Heats of Reaction Calculated by RTI and ASPEN Model 6
4.	Equilibrium Conversion for FeS Oxidation by SO_2
5.	Al ₂ O ₃ Circulation Rate Effect on Regenerator Stage 1 Temperature
6.	Dew Point Temperatures for DSRP Product Distributions
7.	Coal Gas Fed to and Consumed by HGD for Various H2S Concentrations
8.	N ₂ Removal at Various N2 Concentrations, Condenser Temperatures and Pressures

LIST OF FIGURES

FIGU	JRE#	GE
1.	U.S. Sulfur Production	. 3
2.	DSRP - base Desulfurization	. 7
3.	AHGP Desulfurization	10
4.	RKS and PR Calculated SO ₂ Vapor Pressure Deviation From Tabulated Values	14
5.	Schematic of DSRP - Based HGD Process Desulfurization and Regeneration Reactors	18
6.	Schematic of AHGP Desulfurization and Regeneration Reactors	26
7.	Condenser for Removal of Nitrogen	34
8.	Schematic for HGD Steam Generation	35
9.	Distribution of Capital Costs	39
10.	Distribution of Yearly Expenditures	40
11.	Yearly Expenditures for Different Levels of Power Generation	40
12.	H ₂ S Concentration's Effect on HGD Yearly Operating Costs	41
13.	Power Generation's Effect on HGD Yearly Operating Costs	41
14.	Yearly Costs as a Function of Sulfur Feed	42
15	Cumulative HGD Investment	45

EXECUTIVE SUMMARY

This report summarizes the process simulation work and economic evaluations that were done under contract to Research Triangle Institute to aid in the design of hot gas desulfurization (HGD) processes. Two processes were evaluated for the removal of sulfur (as H₂S) from coal gas at high temperatures, that produce elemental sulfur as a byproduct. Complete mass and energy balances were accomplished for the Direct Sulfur Recovery Process (DSRP) -based process, for various feed conditions. The Advanced Hot Gas Desulfurization Process (AHGP) was also simulated for various feed conditions. ASPEN PLUS 9.3-1 was used for simulating the processes. The mass and energy balances were used in determining the equipment requirements. Equipment requirements were used for the estimation of capital costs and yearly operating costs.

The technical feasibility of the two processes was briefly evaluated. Operating the DSRP is less complicated than operating the AHGP. The AHGP contains a SO₂ loop that is balanced by reactions that consume and generate SO₂. The reaction that consumes SO₂ is equilibrium limited, and its equilibrium fractional conversion varies substantially over the range of possible reactor temperatures.

The economic evaluation shows that the AHGP has higher capital costs than the DSRP. However, the savings the AHGP provides with lower operating costs makes it the more attractive process. The economics in this report use two key assumptions: that there is a market credit for recovered elemental sulfur, and that the coal gas consumed by the HGD has an operating cost equal to the cost of the electricity that could have been generated from it. Using these and other assumptions, the analysis shows that, after only two years the AHGP should make up for its higher capital cost. After four years, AHGP could save millions over the DSRP (savings depend on plant size and the coal's sulfur concentration).

I. INTRODUCTION

1. Background

Integrated gasification combined cycle (IGCC) power plants gasify coal and then combust the coal gas to generate power. All new power plants are required to meet federal SO_X emission limitations, currently limited to 1.2 lbs per million BTU (Jaffee). Hot-gas desulfurization (HGD) removes sulfur from coal gas before combustion. HGD has the potential of reducing the cost of electricity (COE) in IGCC plants, compared to conventional liquid absorption desulfurization.

IGCC plants gasify coal using steam and either air or oxygen. The coal gas is then combusted and passes through a gas turbine, generating power. The hot exhaust gas from the turbine is then used to generate steam, which is used for additional power generation. Coal gas is produced at high temperatures and high pressures (HTHP), typically 450 to 800°C and 145 to 580 psia (Gangwal). HGD reduces the coal gas sulfur content before combustion while maintaining the coal gas at HTHP conditions. Currently, IGCC plants remove sulfur with liquid phase scrubbing. The scrubbing process cools the coal gas stream below 150°C. The temperature drop reduces thermal efficiency and limits the potential electricity cost reduction that is theoretically possible with IGCC power plants. IGCC power plants using liquid phase scrubbing have COE's equivalent to those of pulverized coal-based power plants (Gangwal). HGD would give IGCC power plants a competitive advantage. Implementing HGD will increase thermal efficiency, reduce the COE, and ensure SO₂ emissions are acceptable.

Another benefit of HGD is that the sulfur removed from the coal gas would be recovered as elemental sulfur, a valuable byproduct and easily stored material. This report describes work subcontracted to North Carolina State University (NCSU) from Research Triangle Institute (RTI). Two HGD processes that produce elemental sulfur were simulated using ASPEN PLUS 9.3-1. This work contributes to RTI efforts towards developing HGD technology. RTI research and development work includes sorbents development, characterization and a pilot-scale desulfurization testing.

Coal gas HGD and sulfur recovery could also be implemented in non-power producing applications. Although not the focus of this report, coal gas is used in methanation and Fischer-Tropsh synthesis. Methanation and Fisher-Tropsh catalysts require H₂S concentrations below 1 ppm (Cusumano) because H₂S and SO₂ poison catalysts with the formation of elemental sulfur.

2. Sulfur Production

The main purpose of the two desulfurization processes investigated is to remove sulfur from the coal gas prior to combustion, thereby reducing stack emissions. An advantage of these two processes is that elemental sulfur, which has commercial value, will be generated. Such "recovered sulfur" has been steadily replacing Frasch sulfur as a sulfur source (Figure 1). Frasch sulfur is obtained by drilling into sulfur deposits and injecting hot water, pushing molten sulfur to the surface.

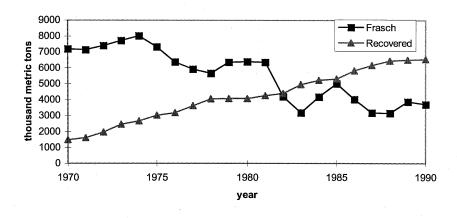


Figure 1: U.S. Sulfur Production

-Data from U.S. Geological Survey

Sulfur is used in both industrial and agricultural applications. In the U.S., the majority of sulfur is used for agricultural purposes (U.S. Geological).

Recovered sulfur can be sold for \$50 to \$150/ton (Caruanan). Since sulfur purification was not modeled, a \$50/ton credit was assigned to the recovered sulfur for the economic evaluation.